Supporting Information for

Synthesis and characterization of heterometallic complexes involving coinage metals and isoelectronic $Fe(CO)_5$, $[Mn(CO)_5]^-$ and $[Fe(CO)_4CN]^-$ ligands

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Theoretical methods

The geometry optimization followed by calculation of the vibrational frequencies were performed at the BP86-D3(BJ)/def2-SVP level.[1] Small-core effective core potentials were used for Ag and Au whereas all-electron basis sets were employed for the other metal atoms. All calculated complexes are minima on the potential energy surfaces as ensured by the absence of any imaginary frequency. All these calculations were carried out with Gaussian 16 program package.[2] The NBO analysis[3] were performed to evaluate the partial charge using NBO 6.0 program.[4]

The bonding situations were analyzed by means of an energy decomposition analysis (EDA)[5] together with the natural orbitals for chemical valence (NOCV)[6] method by using the ADF 2018.105 program package.[7] The EDA-NOCV calculations were carried out at the BP86-D3(BJ)/TZ2P-ZORA level[8] using the BP86-D3(BJ)/def2-SVP optimized geometries. In this analysis, the intrinsic interaction energy (ΔE_{int}) between two fragments can be divided into three energy components as follows:

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}} \qquad (1).$$

While the electrostatic ΔE_{elstat} term represents the quasiclassical electrostatic interaction between the unperturbed charge distributions of the prepared fragments, the Pauli repulsion ΔE_{Pauli} corresponds to the energy change associated with the transformation from the superposition of the unperturbed electron densities of the isolated fragments to the wavefunction, which properly obeys the Pauli principle through explicit antisymmetrization and renormalization of the production wavefunction. Since we included D3(BJ), it provides us with the dispersion interaction energy between two interacting fragments. The orbital term ΔE_{orb} is originated from the mixing of orbitals, charge transfer and polarization between the isolated fragments, which can be further decomposed into contributions from each irreducible representation of the point group of the interacting system as follows:

$$\Delta E_{orb} = \sum_{r} \Delta E_{r} \qquad (2)$$

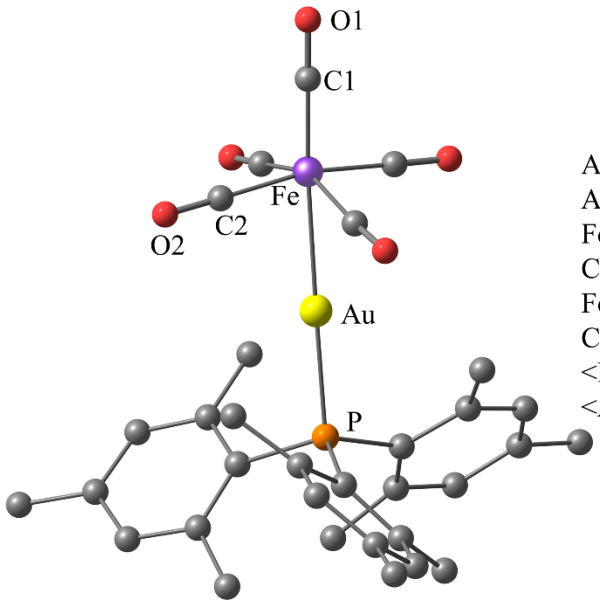
The combination of the EDA with NOCV enables the partition of the total orbital interactions into pairwise contributions of the orbital interactions which is very vital to get a complete picture of the bonding. The charge deformation $\Delta\rho_k(r)$, resulting from the mixing of the orbital pairs $\psi_k(r)$ and $\psi_{-k}(r)$ of the interacting fragments presents the amount and the shape of the charge flow due to the orbital interactions (Equation 3), and the associated energy term ΔE_{orb} provides with the size of stabilizing orbital energy originated from such interaction (Equation 4).

$$\Delta\rho_{orb}(r) = \sum_k \Delta\rho_k(r) = \sum_{k=1}^{N/2} \nu_k[-\psi_{-k}^2(r) + \psi_k^2(r)] \quad (3)$$

$$\Delta E_{orb} = \sum_k \Delta E_k^{orb} = \sum_{k=1}^{N/2} \nu_k[-F_{-k,-k}^{TS} + F_{k,k}^{TS}] \quad (4)$$

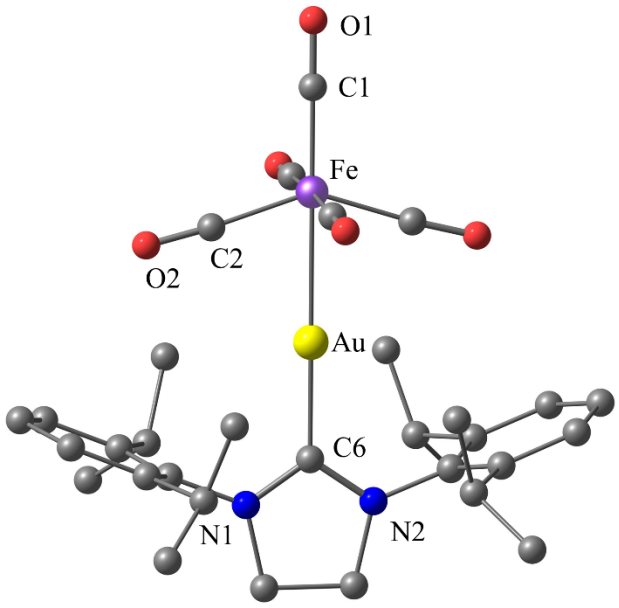
More details about the EDA-NOCV method and its application are given in recent reviews articles.[9]

Theoretical data



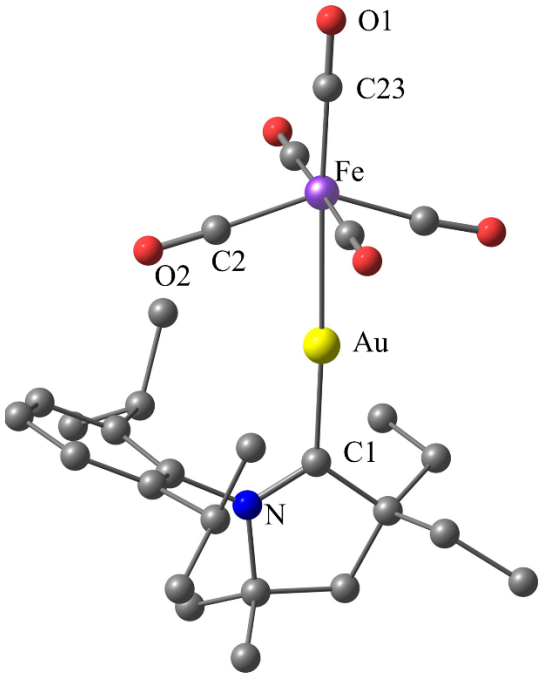
Au-P: 2.370 (2.322)
Au-Fe: 2.630 (2.567)
Fe-C1: 1.814 (1.854)
C1-O1: 1.151 (1.127)
Fe-C2: 1.828 (1.828)
C2-O2: 1.156 (1.130)
<P-Au-Fe: 177.5 (178.2)
<Au-Fe-C2: 70.2 (78.3)

(C_1, ^{1}A)
Complex 1^+



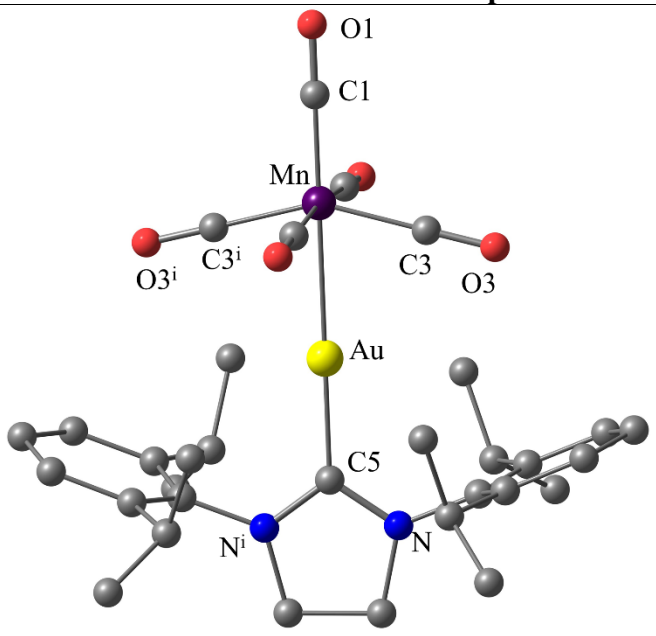
Au-C6: 2.019 (2.015)
Au-Fe: 2.595 (2.554)
Fe-C1: 1.812 (1.839)
C1-O1: 1.151 (1.123)
Fe-C2: 1.824 (1.821)
C2-O2: 1.155 (1.136)
C6-N1: 1.339 (1.319)
<C6-Au-Fe: 180.05 (178.0)
<Au-Fe-C2: 72.2 (76.0)

(C_{2v}, ^{1}A$_1$)
Complex 5^+



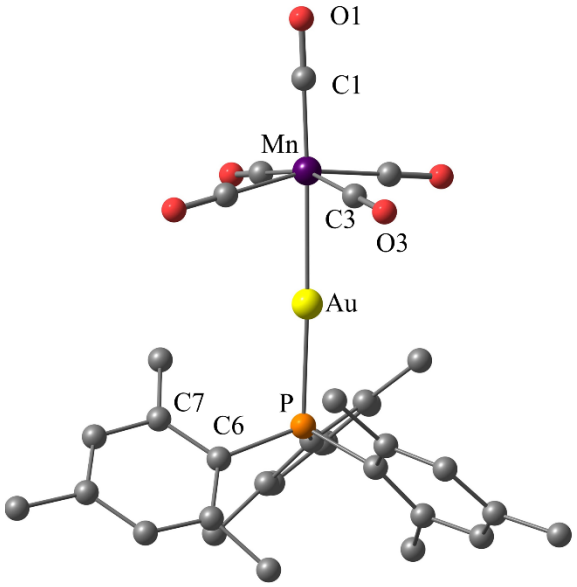
Au-C1: 2.022 (2.021)
Au-Fe: 2.630 (2.570)
Fe-C23: 1.812 (1.859)
C23-O1: 1.151 (1.123)
Fe-C2: 1.822 (1.831)
C2-O2: 1.154 (1.130)
C1-N: 1.310 (1.292)
<C1-Au-Fe: 177.5 (177.9)
<Au-Fe-C2: 74.6 (76.4)

(C_1, ^{1}A)
Complex 6$^+$



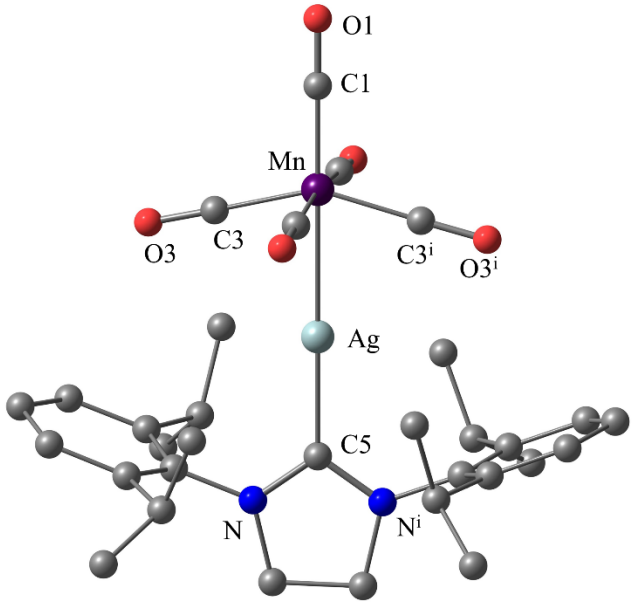
Au-C5: 2.027 (2.024)
Au-Mn: 2.587 (2.575)
Mn-C1: 1.806 (1.805)
C1-O1: 1.166 (1.147)
Mn-C3: 1.830 (1.835)
C3-O3: 1.167 (1.138)
C5-N: 1.346 (1.328)
<C5-Au-Mn: 180.0 (177.9)
<Au-Mn-C3: 76.4 (83.8)

(C_2, ^{1}A)
Complex 7



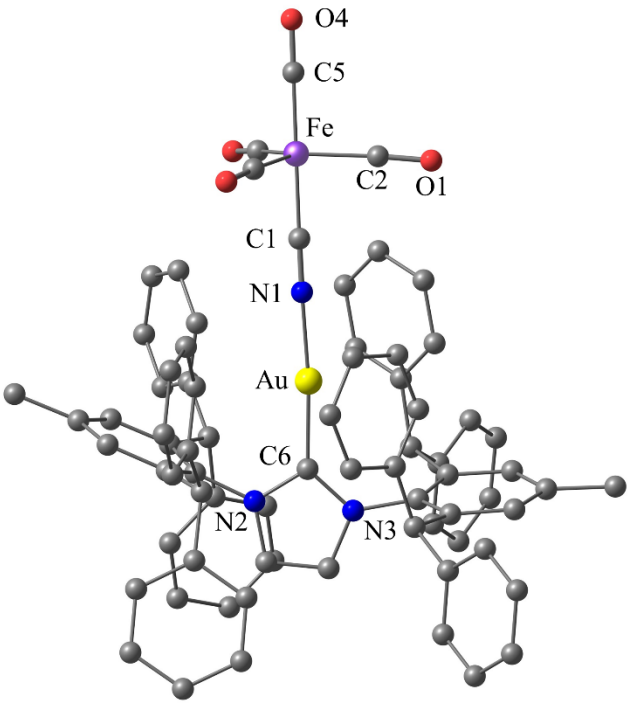
Au-P: 2.386 (2.324)
Au-Mn: 2.597 (2.575)
Mn-C1: 1.803 (1.822)
C1-O1: 1.165 (1.146)
Mn-C3: 1.835 (1.844)
C3-O3: 1.164 (1.145)
C6-P: 1.846 (1.833)
C6-C7: 1.432 (1.416)
<P-Au-Mn: 178.0 (174.5)
<Au-Mn-C3: 80.1 (74.8)

(C_1, ^{1}A)
Complex 8

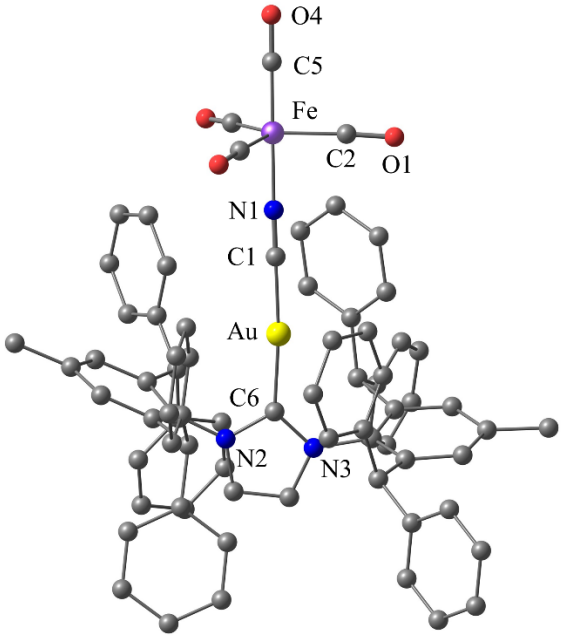


Ag-C5: 2.080 (2.113)
Ag-Mn: 2.561 (2.591)
Mn-C1: 1.804 (1.803)
C1-O1: 1.166 (1.144)
Mn-C3: 1.828 (1.832)
C3-O3: 1.169 (1.141)
C5-N: 1.344 (1.331)
<C5-Ag-Mn: 180.0 (179.1)
<Ag-Mn-C3: 75.7 (84.7)

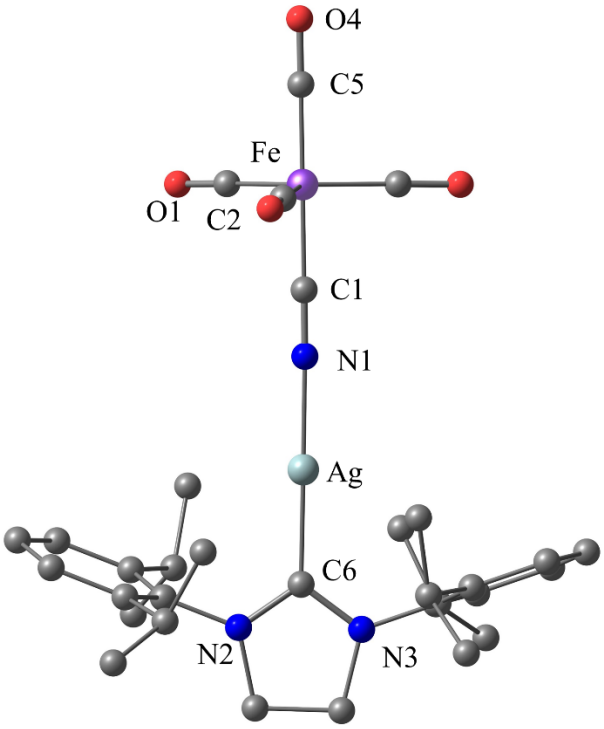
(C_2, ^{1}A)
Complex 9



(C_1, ^{1}A)
Complex 10; E_{rel}: 0.0 kcal/mol

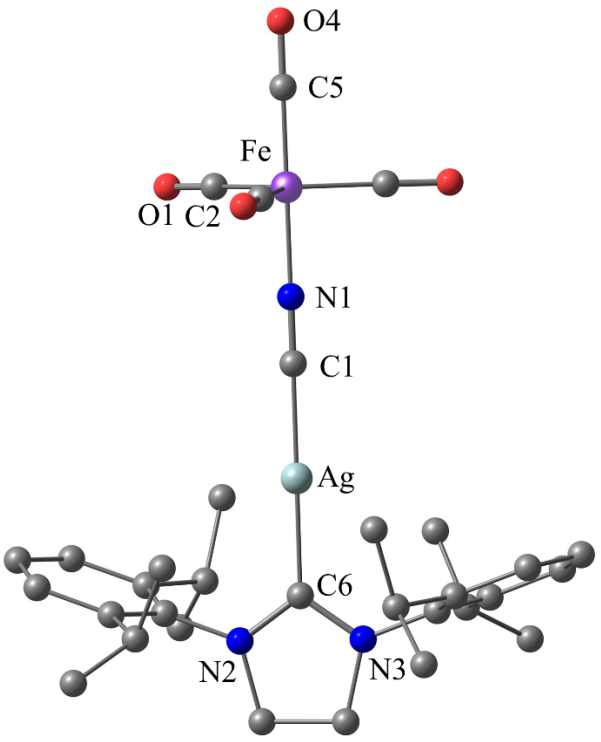


(C_1, ^{1}A)
Complex 10′; E_{rel}: 5.9 kcal/mol



Ag-C6: 2.038
Ag-N1: 2.014
N1-C1: 1.183
C1-Fe: 1.872
Fe-C5: 1.785
C5-O4: 1.164
Fe-C2: 1.789
C2-O1: 1.167
C6-N2: 1.347
C6-N3: 1.347
<C6-Ag-N1: 179.7
<Ag-N1-C1: 178.4
<N1-C1-Fe: 179.7
<C1-Fe-C2: 87.6

(C_1, ^{1}A)
Complex 11; E_{rel}: 0.0 kcal/mol



Ag-C6: 2.066
Ag-C1: 2.023
C1-N1: 1.176
N1-Fe: 1.928
Fe-C5: 1.759
C5-O4: 1.166
Fe-C2: 1.798
C2-O1: 1.166
C6-N2: 1.346
C6-N3: 1.346
<C6-Ag-C1: 179.8
<Ag-C1-N1: 179.7
<C1-N1-Fe: 179.9
<N1-Fe-C2: 88.7

E_{rel}: 9.5 kcal/mol

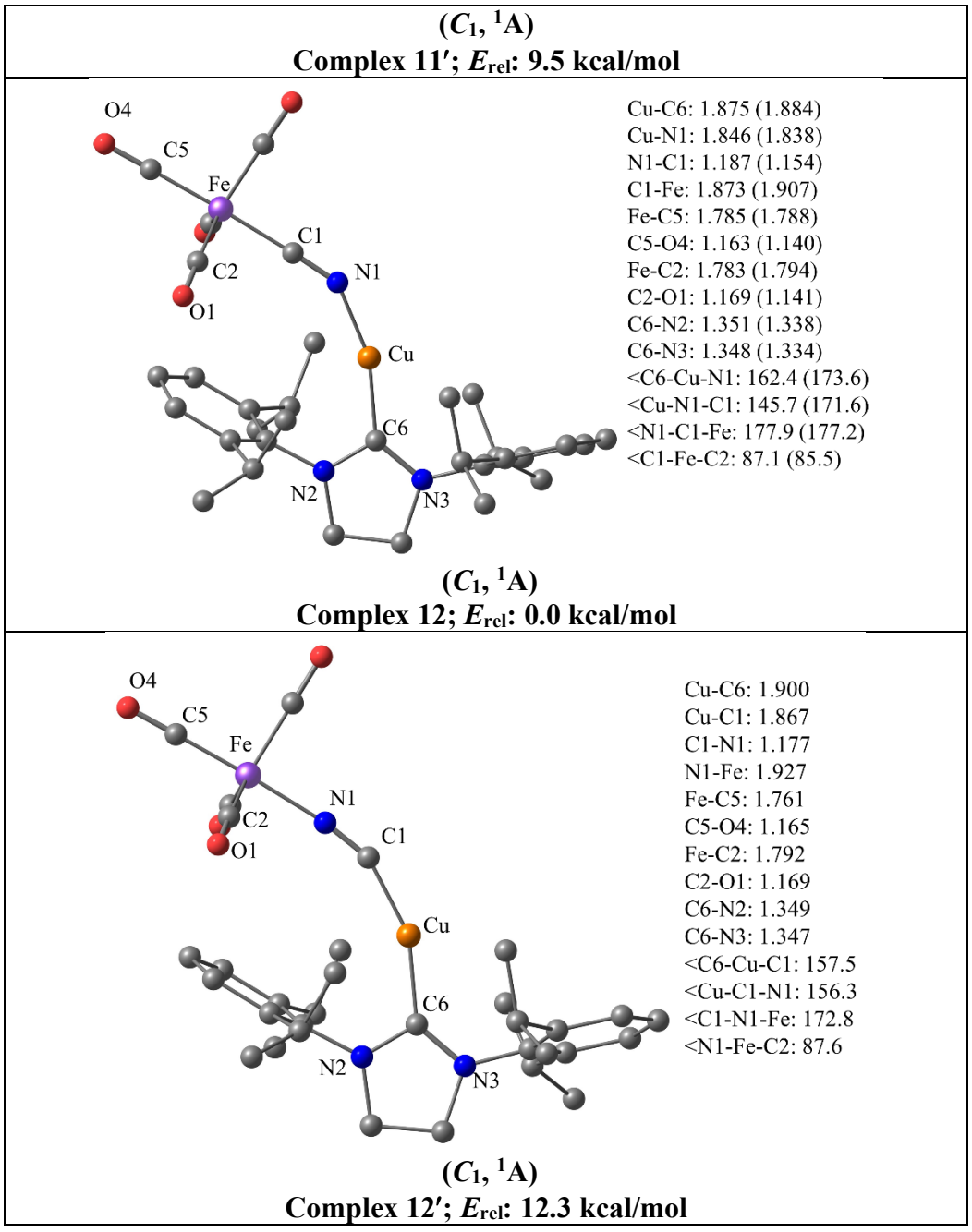
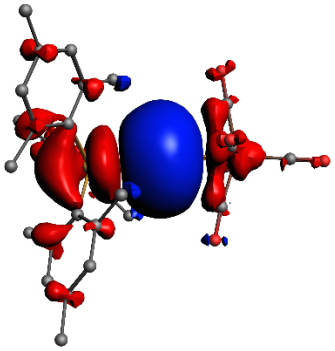
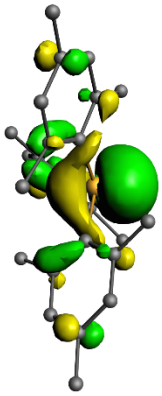
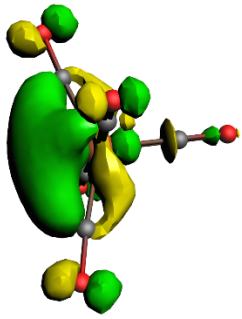
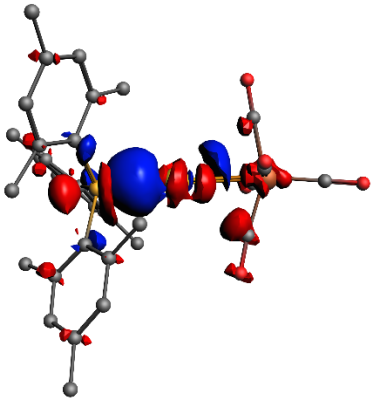
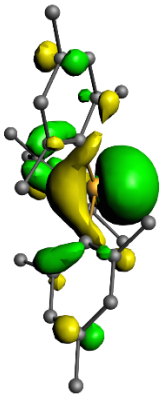
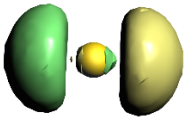
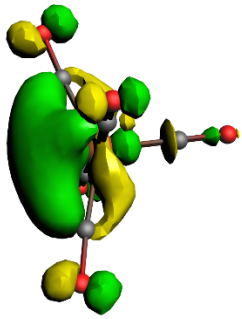


Figure S1. Optimized geometries of the studied complexes at the BP86-D3(BJ)/def2-SVP level. Bond lengths are given in Å, angles in degree. Experimental values are shown in parentheses.

$\Delta\rho$	[Mes_3P]	Au^+ (d^{10}, s^0)	[$Fe(CO)_5$]
 $\Delta\rho_{(1)}$ $\Delta E_{orb(1)} = -93.3$	 HOMO ($\nu_1 = -0.56$)	 LUMO ($\nu_1 = 1.15$)	 HOMO ($\nu_1 = -0.30$)
 $\Delta\rho_{(2)}$ $\Delta E_{orb(2)} = -18.2$	 HOMO ($\nu_2 = -0.14$)	 LUMO+1 ($\nu_2 = 0.20$)	 HOMO ($\nu_2 = -0.08$)

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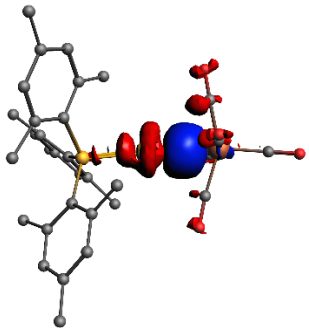
<td> 
$\Delta\rho_{(3)}$
$\Delta E_{orb(3)} = -9.9$</td>
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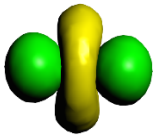
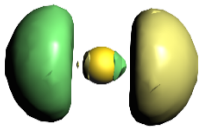
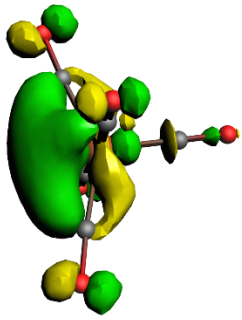
<td> 
HOMO ($\nu_3 = -0.05$)
 
LUMO+1 ($\nu_3 = 0.06$)</td>
<td> 
HOMO ($\nu_3 = -0.06$)</td>
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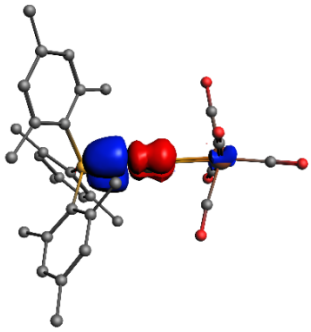
<td> 
$\Delta\rho_{(4)}$
$\Delta E_{orb(4)} = -6.4$</td>
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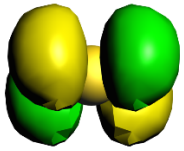
LUMO+1 ($\nu_4 = 0.01$)</td>
<td> 
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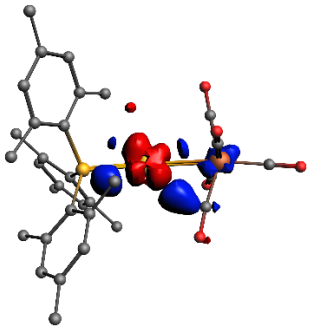
<td> 
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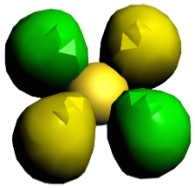
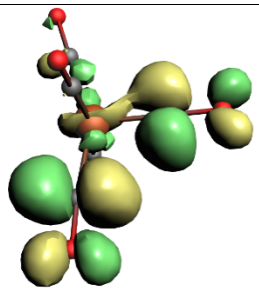
<td> 
HOMO″ ($\nu_5 = -0.05$)</td>
<td> 
LUMO+8 ($\nu_5 = 0.02$)</td>
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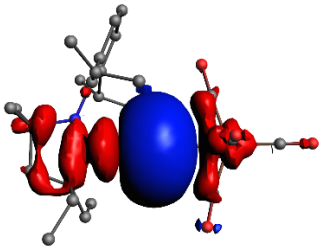
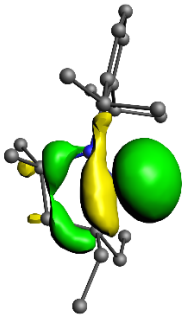
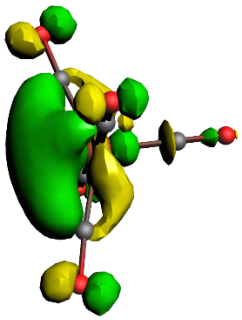
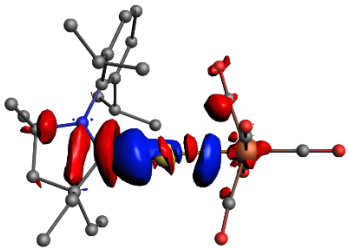
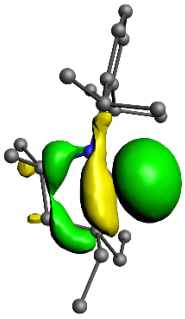
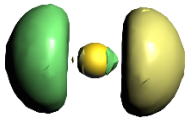
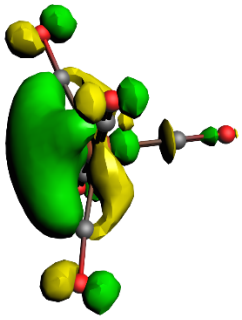
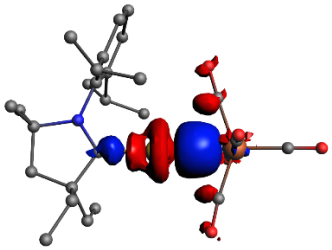
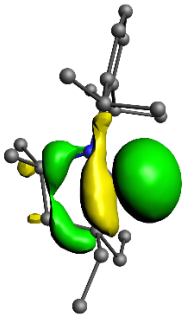
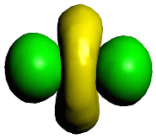
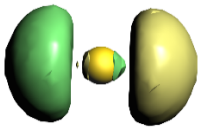
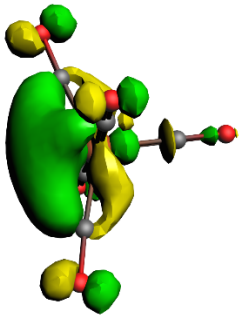
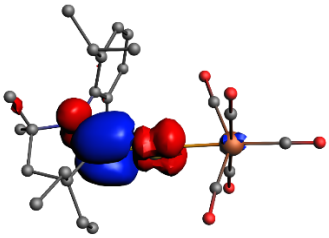
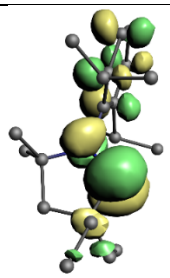
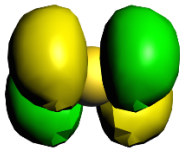
Figure S2. The shape of the deformation densities, $\Delta\rho_{(1)-(5)}$ which are associated with $\Delta E_{orb(1)-(5)}$, and the associated fragment orbitals for complex $\mathbf{1}^+$ at the BP86-D3(BJ)/TZ2P-ZORA//BP86-D3(BJ)/def2-SVP level. The isovalue is 0.0008 au. The eigenvalues $|\nu_n|$ give the size of the charge migration in e. The direction of the charge flow of the deformation densities is red→blue. Only the most important orbitals are shown.

$\Delta\rho$	**[^{Et2}CAAC]**	**Au^+ (d^{10}, s^0)**	**[$Fe(CO)_5$]**

 $\Delta\rho_{(1)}$ $\Delta E_{orb(1)} = -89.4$	 HOMO ($\nu_1 = -0.47$)	 LUMO ($\nu_1 = 0.97$)	 HOMO ($\nu_1 = -0.29$)
 $\Delta\rho_{(2)}$ $\Delta E_{orb(2)} = -15.1$	 HOMO ($\nu_2 = -0.06$)	 LUMO+1 ($\nu_2 = 0.16$)	 HOMO ($\nu_2 = -0.10$)
 $\Delta\rho_{(3)}$ $\Delta E_{orb(3)} = -12.4$	 HOMO ($\nu_3 = 0.02$)	 HOMO ($\nu_3 = -0.07$)  LUMO+1 ($\nu_3 = 0.04$)	 HOMO ($\nu_3 = -0.04$)
 $\Delta\rho_{(4)}$ $\Delta E_{orb(4)} = -12.3$	 LUMO+2 ($\nu_4 = 0.05$)	 HOMO′ ($\nu_4 = -0.07$)	

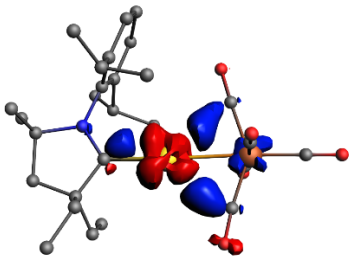
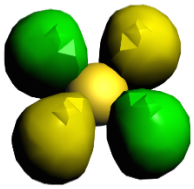
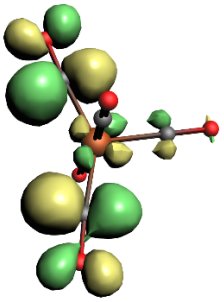
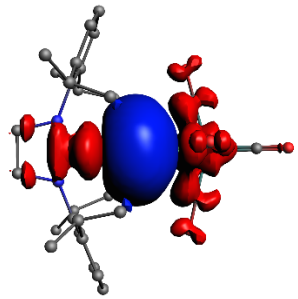
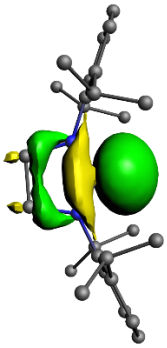
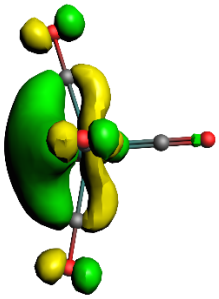
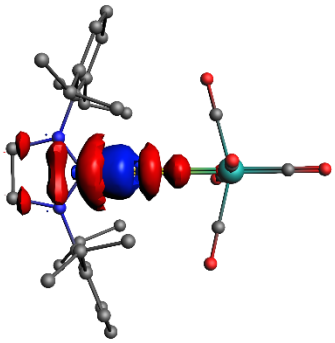
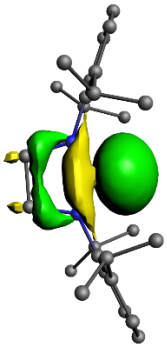
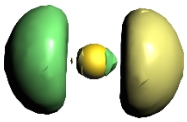
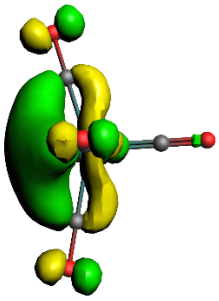
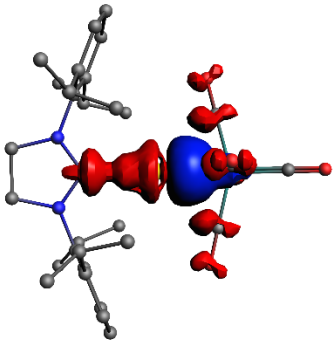
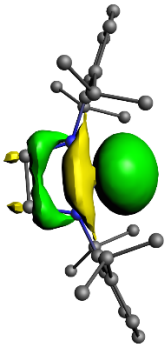
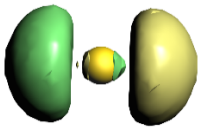
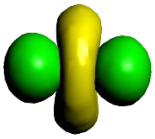
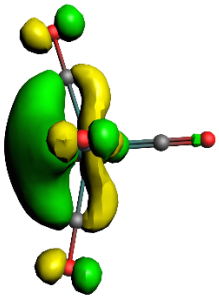
 $\Delta\rho_{(5)}$ $\Delta E_{orb(5)} = -8.6$		 HOMO″ ($\nu_5 = -0.05$)	 LUMO+8 ($\nu_5 = 0.04$)

Figure S3. The shape of the deformation densities, $\Delta\rho_{(1)-(5)}$ which are associated with $\Delta E_{orb(1)-(5)}$, and the associated fragment orbitals for complex $\mathbf{6}^+$ at the BP86-D3(BJ)/TZ2P-ZORA//BP86-D3(BJ)/def2-SVP level. The isovalue is 0.0008 au. The eigenvalues υ of the fragment orbitals give the size of the charge migration. The direction of the charge flow of the deformation densities is red→blue. Only the most important orbitals are shown.

$\Delta\rho$	[SIPr]	Au^{+} (d^{10}, s^{0})	$[Mn(CO)_5]^{-}$
 $\Delta\rho_{(1)}$ $\Delta E_{orb(1)}$ = -88.1	 HOMO (ν_1 = -0.32)	 LUMO (ν_1 = 1.02)	 HOMO (ν_1 = -0.49)
 $\Delta\rho_{(2)}$ $\Delta E_{orb(2)}$ = -14.3	 HOMO (ν_2 = -0.06)	 LUMO+1 (ν_2 = 0.09)	 HOMO (ν_2 = -0.01)
 $\Delta\rho_{(3)}$ $\Delta E_{orb(3)}$ = -15.3	 HOMO (ν_3 = -0.06)	 LUMO+1 (ν_3 = 0.17)  HOMO (ν_3 = -0.05)	 HOMO (ν_3 = -0.09)

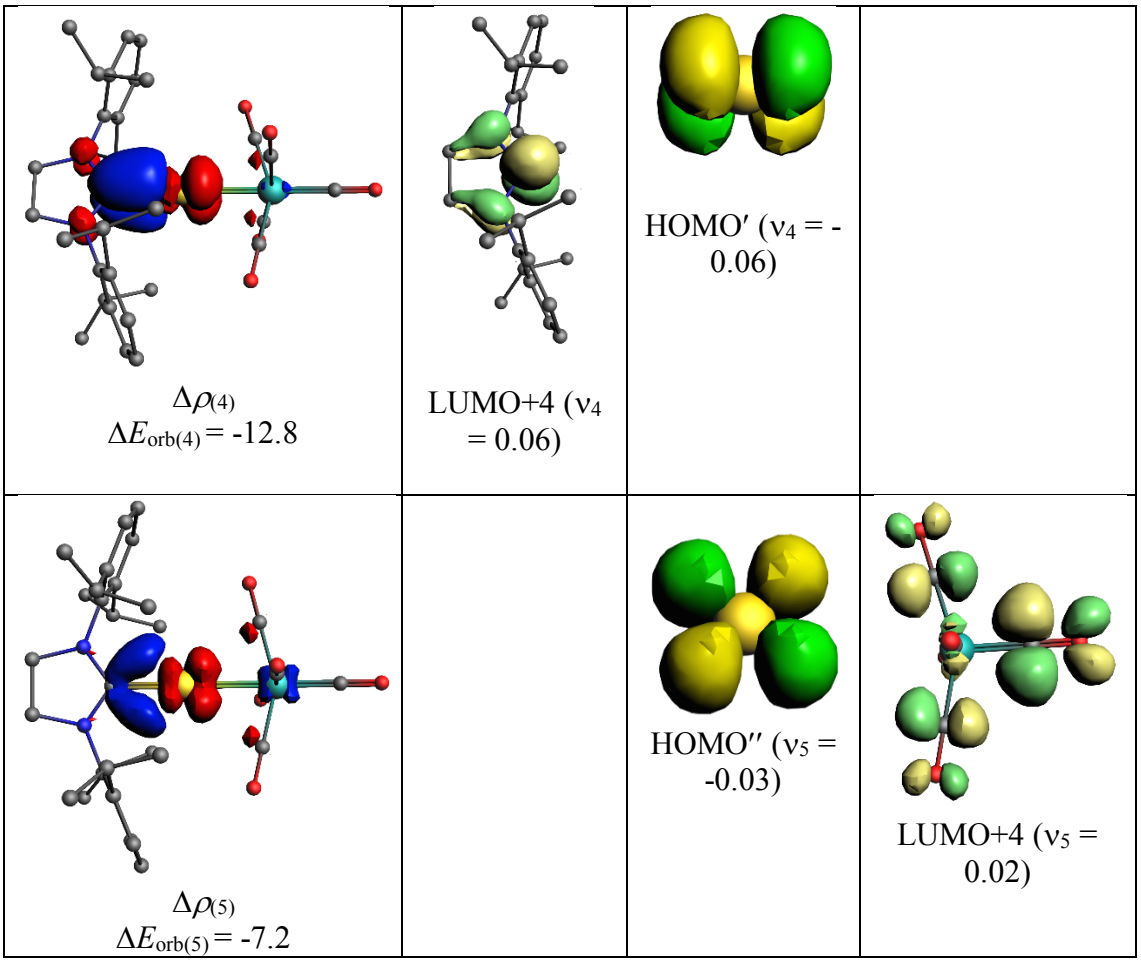
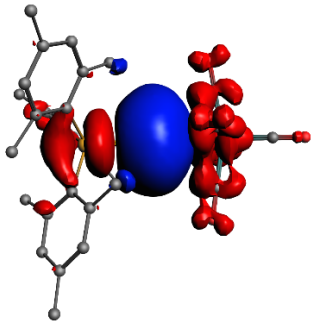
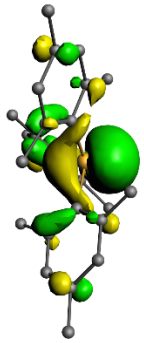
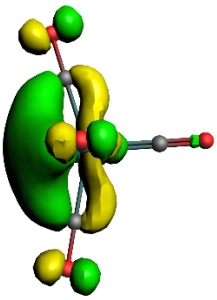
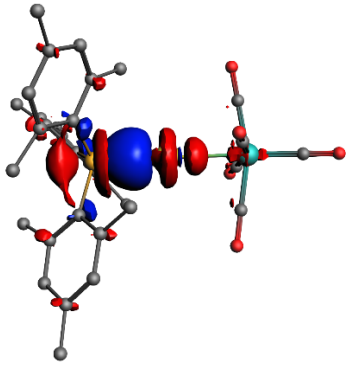
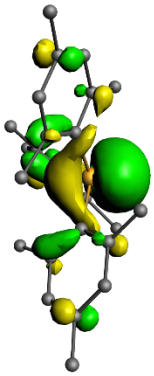
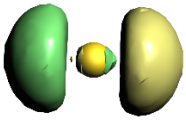
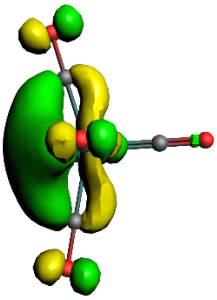
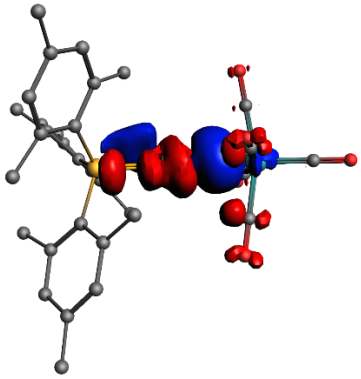
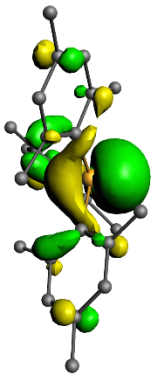
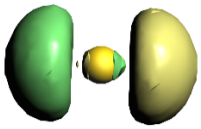
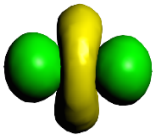
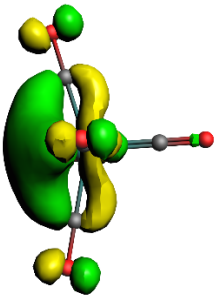


Figure S4. The shape of the deformation densities, $\Delta\rho_{(1)-(5)}$ which are associated with $\Delta E_{orb(1)-(5)}$, and the associated fragment orbitals for complex **7** at the BP86-D3(BJ)/TZ2P-ZORA//BP86-D3(BJ)/def2-SVP level. The isovalue is 0.0008 au. The eigenvalues υ of the fragment orbitals give the size of the charge migration. The direction of the charge flow of the deformation densities is red→blue. Only the most important orbitals are shown.

$\Delta\rho$	$[Mes_3P]$	Au^+ (d^{10}, s^0)	$[Mn(CO)_5]^-$
 $\Delta\rho_{(1)}$ $\Delta E_{orb(1)} = -90.6$	 HOMO ($\nu_1 = -0.30$)	 LUMO ($\nu_1 = 1.12$)	 HOMO ($\nu_1 = -0.56$)
 $\Delta\rho_{(2)}$ $\Delta E_{orb(2)} = -16.4$	 HOMO ($\nu_2 = -0.15$)	 LUMO+1 ($\nu_2 = 0.16$)	 HOMO ($\nu_2 = -0.03$)
 $\Delta\rho_{(3)}$ $\Delta E_{orb(3)} = -11.0$	 HOMO ($\nu_3 = -0.02$)	 LUMO+1 ($\nu_3 = 0.08$)  HOMO ($\nu_3 = -0.05$)	 HOMO ($\nu_3 = -0.06$)

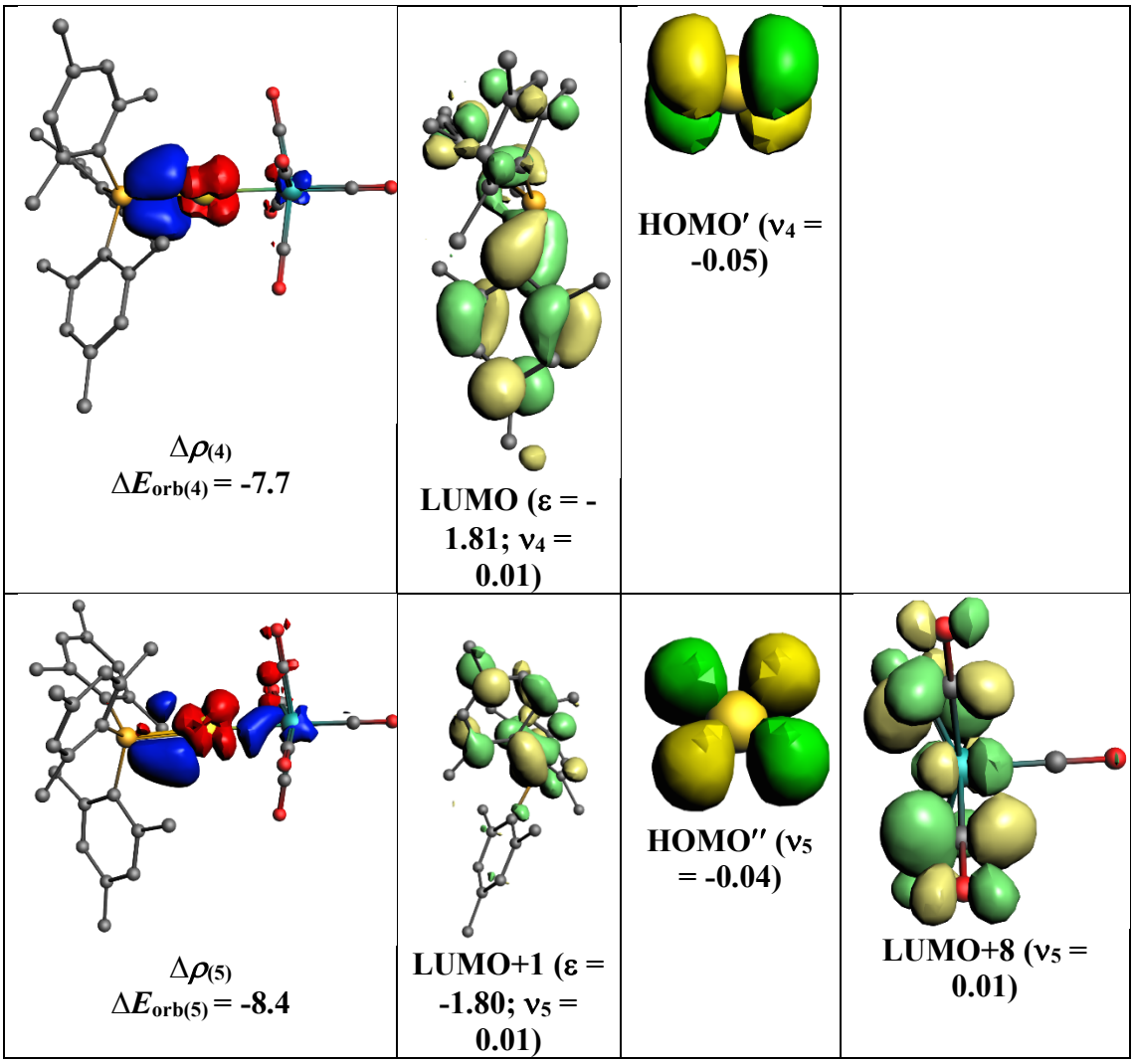
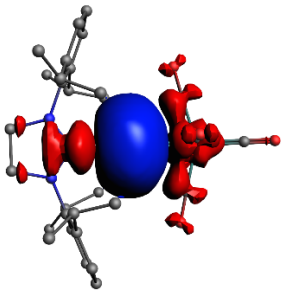
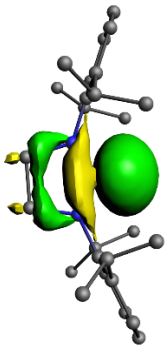
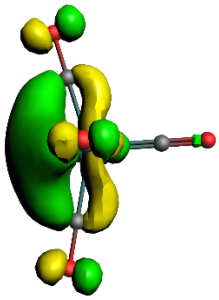
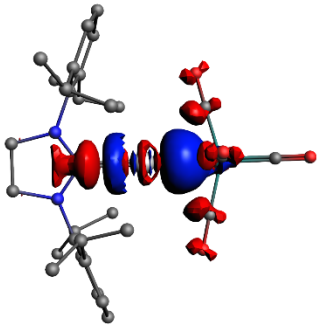
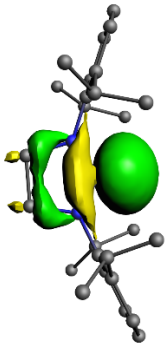
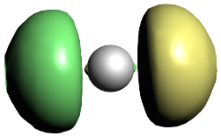
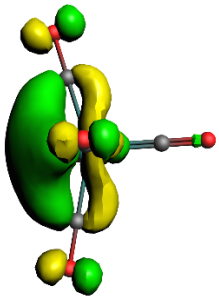
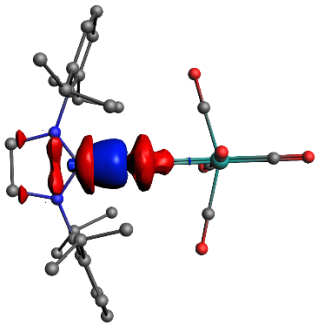
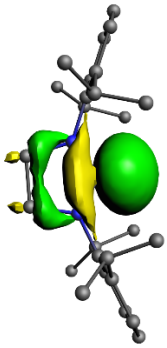
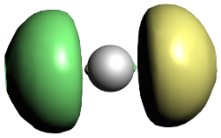
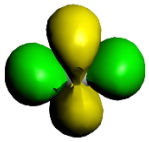


Figure S5. The shape of the deformation densities, $\Delta\rho_{(1)-(5)}$ which are associated with $\Delta E_{orb(1)-(5)}$, and the associated fragment orbitals for complex **8** at the BP86-D3(BJ)/TZ2P-ZORA//BP86-D3(BJ)/def2-SVP level. The isovalue is 0.0008 au. The eigenvalues υ of the fragment orbitals give the size of the charge migration. The direction of the charge flow of the deformation densities is red→blue. Only the most important orbitals are shown.

$\Delta\rho$	[SIPr]	Ag^{+} (d^{10}, s^{0})	$[Mn(CO)_5]^{-}$
 $\Delta\rho_{(1)}$ $\Delta E_{orb(1)}$ = -46.8	 HOMO (ν_1 = -0.18)	 LUMO (ν_1 = 0.65)	 HOMO (ν_1 = -0.35)
 $\Delta\rho_{(2)}$ $\Delta E_{orb(2)}$ = -12.7	 HOMO (ν_2 = -0.13)	 LUMO+1 (ν_2 = 0.22)	 HOMO (ν_2 = -0.09)
 $\Delta\rho_{(3)}$ $\Delta E_{orb(3)}$ = -9.5	 HOMO (ν_3 = -0.10)	 LUMO+1 (ν_3 = 0.04)  HOMO (ν_1 = -0.02)	

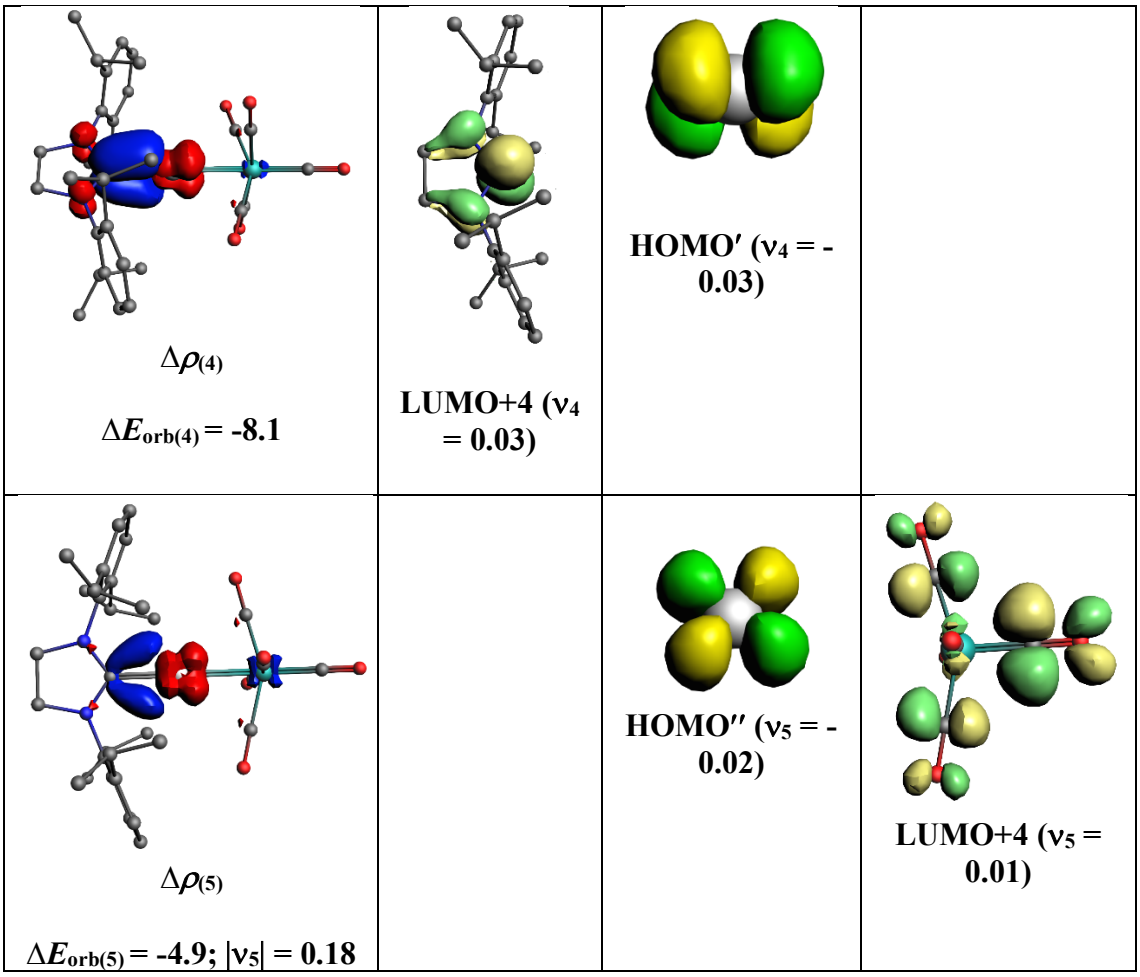
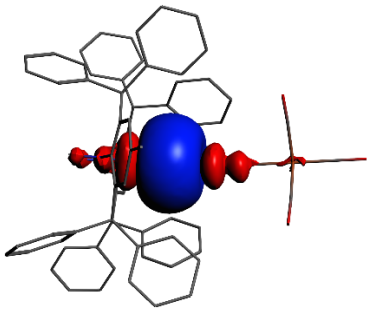
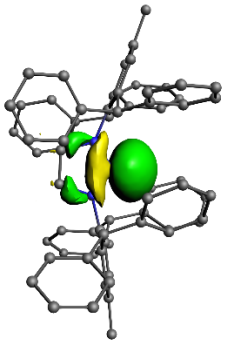
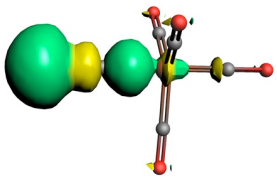
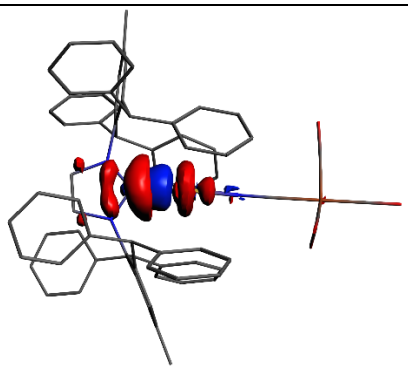
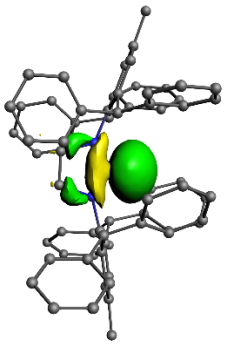
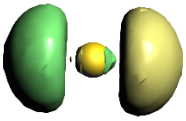
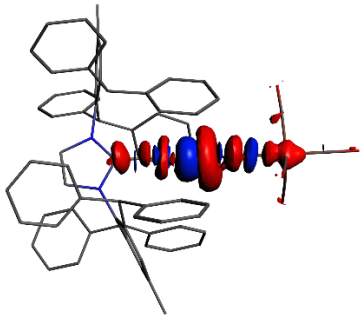
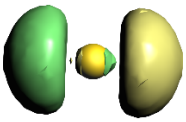
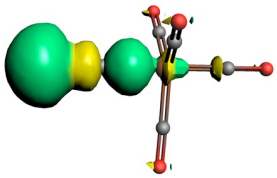


Figure S6. The shape of the deformation densities, $\Delta\rho_{(1)-(5)}$ which are associated with $\Delta E_{orb(1)-(5)}$, and the associated fragment orbitals for complex **9** at the BP86-D3(BJ)/TZ2P-ZORA//BP86-D3(BJ)/def2-SVP level. The isovalue is 0.0008 au. The eigenvalues υ of the fragment orbitals give the size of the charge migration. The direction of the charge flow of the deformation densities is red→blue. Only the most important orbitals are shown.

$\Delta\rho$	IPr	Au^+ (d^{10}, s^0)	$[Fe(CO)_4]CN^-$
 $\Delta\rho_{(1)}$ $\Delta E_{orb(1)}$ = **-94.9**	 HOMO (ν_1 = -0.38)	 **LUMO (ν_1 = 0.99)**	 **HOMO-4 (ν_1 = -0.21)**
 $\Delta\rho_{(2)}$ $\Delta E_{orb(2)}$ = **-18.3**	 HOMO (ν_2 = -0.04)	 **LUMO+1 (ν_2 = 0.06)**	
 $\Delta\rho_{(3)}$ $\Delta E_{orb(3)}$ = **-10.9**		 **LUMO+1 (ν_3 = 0.11)**	 **HOMO-4 (ν_3 = -0.05)**

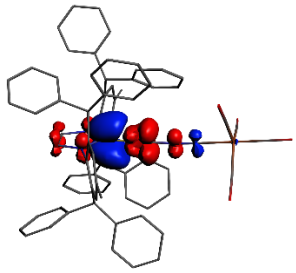
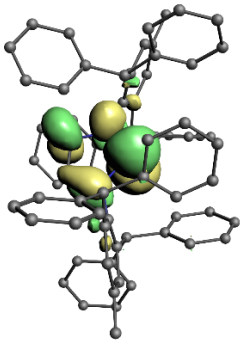
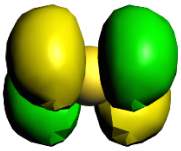
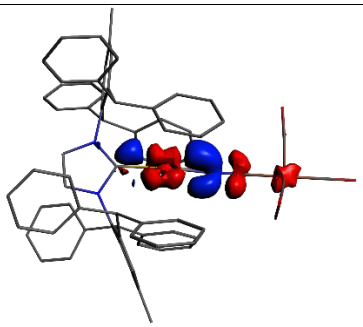
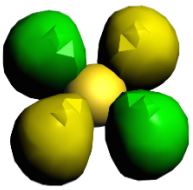
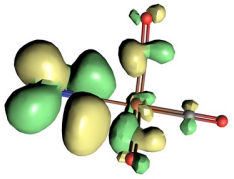
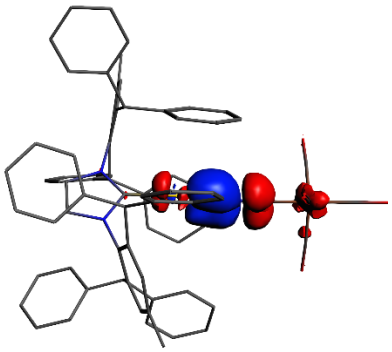
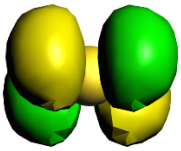
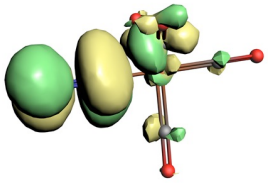
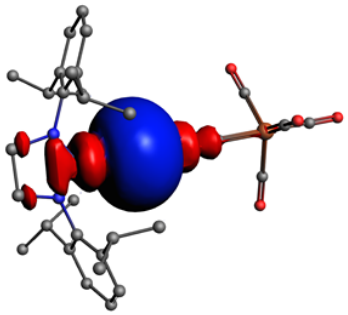
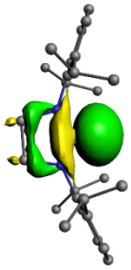
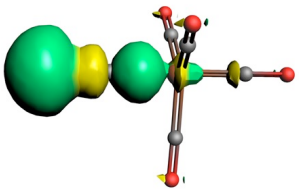
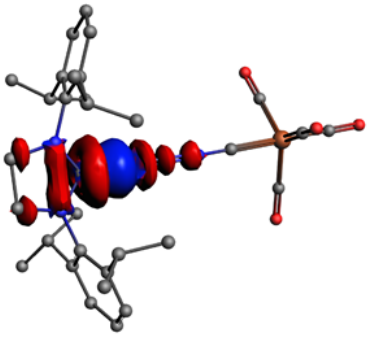
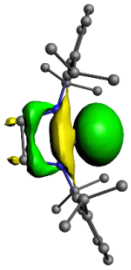
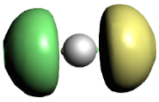
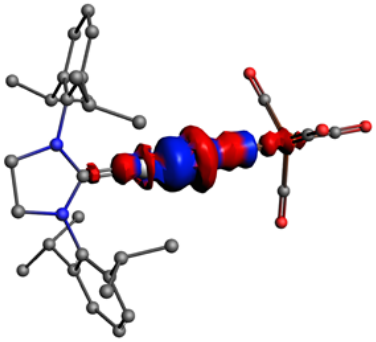
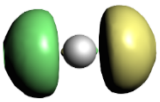
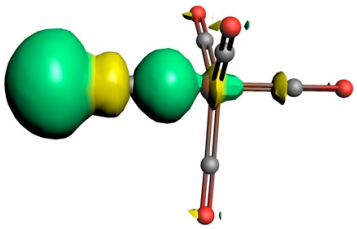
 $\Delta\rho_{(4)}$ $\Delta E_{orb(4)}$ = **-16.3**	 LUMO+21 (ν_4 = 0.06)	 **HOMO (ν_4 = -0.09)**	
 $\Delta\rho_{(5)}$ $\Delta E_{orb(5)}$ = **-11.1**		 HOMO′ (ν_5 = -0.06)	 **LUMO+10 (ε = 520; ν_5 = 0.03)**
 $\Delta\rho_{(6)}$ $\Delta E_{orb(6)}$ = **-9.2**		 **HOMO (ν_6 = -0.01)**	 **LUMO+11 (ν_6 = 0.02)**

Figure S7. The shape of the deformation densities, $\Delta\rho_{(1)-(6)}$ which are associated with $\Delta E_{orb(1)-(6)}$, and the associated fragment orbitals for complex **10** at the BP86-D3(BJ)/TZ2P-ZORA//BP86-D3(BJ)/def2-SVP level. The isovalue is 0.0008 au. The eigenvalues υ of the fragment orbitals give the size of the charge migration. The direction of the charge flow of the deformation densities is red→blue.

$\Delta\rho$	[SIPr]	Ag^{+} (d^{10}, s^{0})	$[Fe(CO)_4]CN^{-}$
 $\Delta\rho_{(1)}$ $\Delta E_{orb(1)}$ = -49.6	 HOMO (ν_1 = -0.25)	 LUMO (ν_1 = 0.61)	 HOMO-4 (ν_1 = -0.14)
 $\Delta\rho_{(2)}$ $\Delta E_{orb(2)}$ = -12.8	 HOMO (ν_2 = -0.18)	 LUMO+1 (ν_2 = 0.13)	
 $\Delta\rho_{(3)}$ $\Delta E_{orb(3)}$ = -9.1		 LUMO+1 (ν_3 = 0.09)	 HOMO-4 (ν_3 = -0.09)

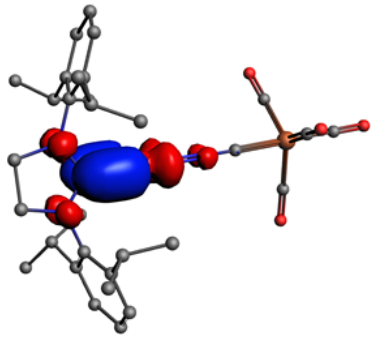
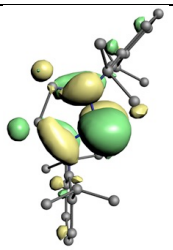
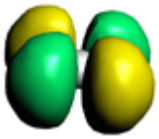
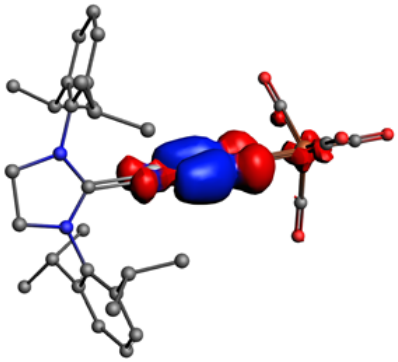
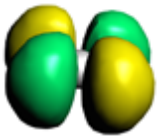
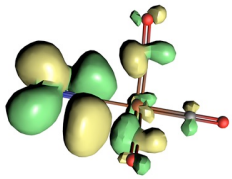
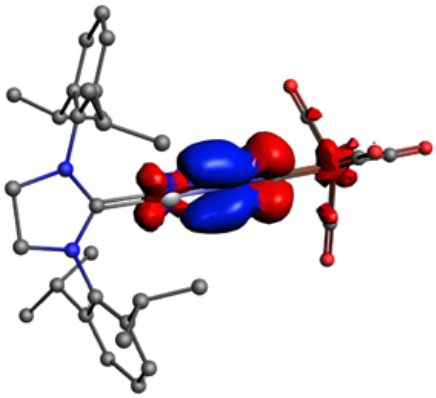
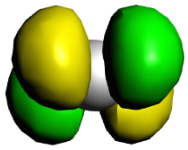
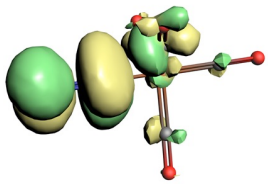
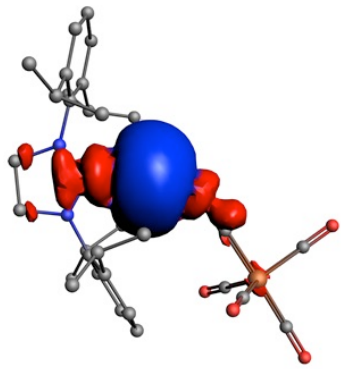
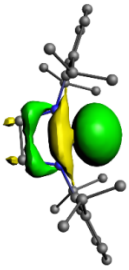
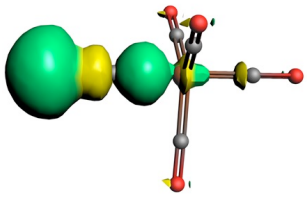
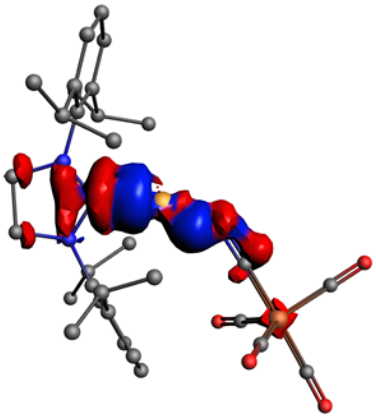
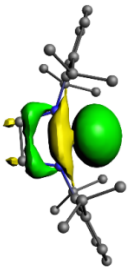
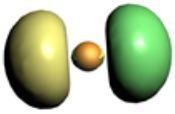
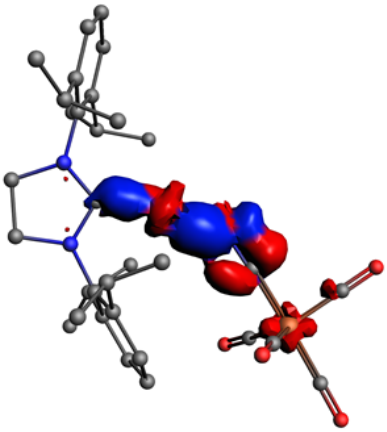
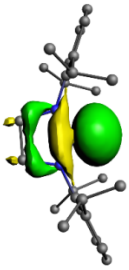
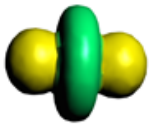
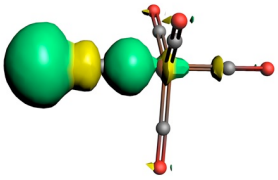
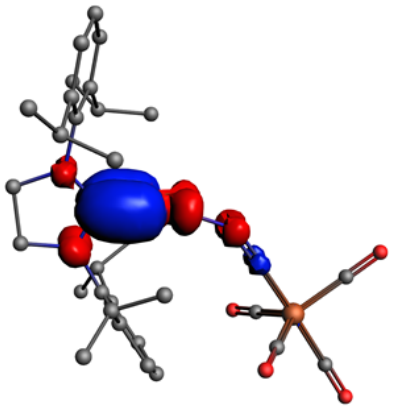
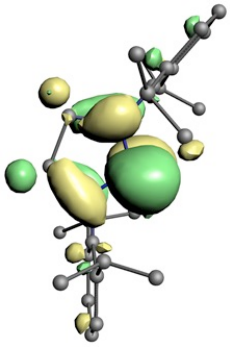
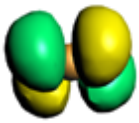
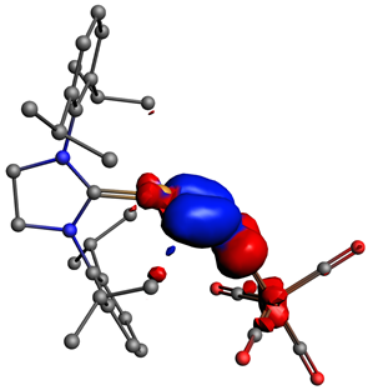
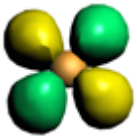
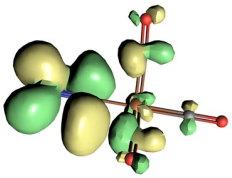
 $\Delta\rho_{(4)}$ $\Delta E_{orb(4)}$ = -9.6	 LUMO+4 (ν_4 = 0.03)	 HOMO (ν_4 = -0.03)	
 $\Delta\rho_{(5)}$ $\Delta E_{orb(5)}$ = -8.1		 HOMO (ν_5 = -0.01)	 LUMO+10 (ν_5 = 0.02)
 $\Delta\rho_{(6)}$ $\Delta E_{orb(6)}$ = -7.8		 HOMO′ (ν_6 = -0.01)	 LUMO+11 (ν_6 = 0.02)

Figure S8. The shape of the deformation densities, $\Delta\rho_{(1)-(6)}$ which are associated with $\Delta E_{orb(1)-(6)}$, and the associated fragment orbitals for complex **11** at the BP86-D3(BJ)/TZ2P-ZORA//BP86-D3(BJ)/def2-SVP level. The isovalue is 0.0008 au. The eigenvalues υ of the fragment orbitals give the size of the charge migration. The direction of the charge flow of the deformation densities is red→blue.

$\Delta\rho$	[SIPr]	Cu^{+} (d^{10}, s^{0})	$[Fe(CO)_4]CN^{-}$
 $\Delta\rho_{(1)}$ $\Delta E_{orb(1)} = -48.9$	 HOMO (ν_1 = -0.27)	 LUMO (ν_1 = 0.73)	 HOMO-4 (ν_1 = -0.14)
 $\Delta\rho_{(2)}$ $\Delta E_{orb(2)} = -15.5$	 HOMO (ν_2 = -0.24)	 LUMO+3 (ν_2 = 0.24)	
 $\Delta\rho_{(2)}$ $\Delta E_{orb(2)} = -16.9$; $\lvert\nu_2\rvert = 0.28$	 HOMO (ν_3 = -0.03)	 LUMO (ν_3 = 0.06)  HOMO (ν_3 = -0.03)	 HOMO-4 (ν_3 = -0.02)

 $\Delta\rho_{(4)}$ $\Delta E_{orb(4)} = -14.2$	 LUMO+4 (ν_4 = 0.05)	 HOMO′ (ν_4 = -0.07)	
 $\Delta\rho_{(5)}$ $\Delta E_{orb(5)} = -9.8$		 HOMO″ (ν_5 = -0.01)	 LUMO+11 (ν_5 = 0.02)

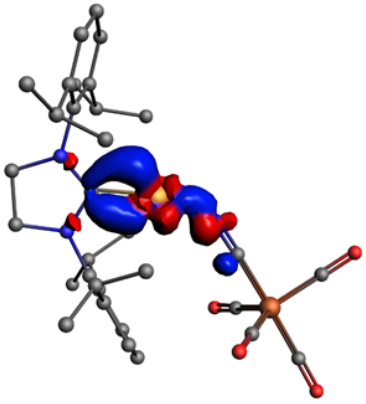
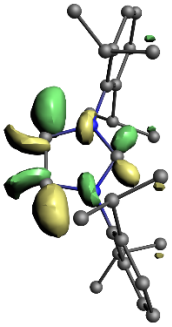
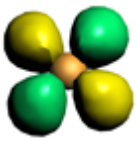
 $\Delta\rho_{(6)}$ $\Delta E_{orb(6)} = -7.8$	 LUMO+31 (ν_6 = 0.003)	 HOMO″ (ν_6 = -0.03)	

Figure S9. The shape of the deformation densities, $\Delta\rho_{(1)-(6)}$ which are associated with $\Delta E_{orb(1)-(6)}$, and the associated fragment orbitals for complex **12** at the BP86-D3(BJ)/TZ2P-ZORA//BP86-D3(BJ)/def2-SVP level. The isovalue is 0.0008 au. The eigenvalues υ of the fragment orbitals give the size of the charge migration. The direction of the charge flow of the deformation densities is red→blue.

Table S1. The C-O stretching frequencies (cm^{-1}) and the corresponding IR intensity (km/mol) at the BP86-D3(BJ)/def2-SVP level.

Molecule	$\tilde{\upsilon}_{CO}$	IR Intensity
Free CO	2150.5	60.5
$Fe(CO)_5$	2033.1	1043.3
	2033.1	1043.3
	2045.2	1236.0
	2051.0	0.0
	2129.2	0.0
1^+	2051.8	619.5
	2074.4	761.8
	2077.8	203.4
	2091.0	418.4
	2142.8	410.8
5^+	2050.8	687.9
	2068.8	192.1
	2077.6	745.7
	2089.7	421.4
	2144.7	217.3
6^+	2043.7	666.9
	2068.7	266.0
	2079.7	791.1
	2090.5	386.0
	2145.4	253.7
7	1973.5	967.5
	1985.8	1049.6
	1989.9	375.5
	2000.5	522.5
	2070.6	291.4

8	1989.4	1051.0
	1989.5	1051.4
	2002.2	770.0
	2005.4	0.6
	2074.3	553.1
9	1958.4	1023.1
	1976.1	212.7
	1976.6	1069.6
	1995.1	673.9
	20163.2	276.2
10	1973.6	869.9
	1976.9	911.7
	2007.4	519.8
	2060.4	958.8
	2184.7	414.8
11	1988.6	963.5
	1989.5	971.0
	2007.4	493.2
	2058.2	1036.3
	2156.0	481.5
12	1964.3	824.0
	1984.1	945.3
	2011.1	584.6
	2054.1	977.8
	2128.3	125.1

Table S2. EDA-NOCV results for complex **12** at the BP86-D3(BJ)/TZ2P-ZORA//BP86-D3(BJ)/def2-SVP level. Energy values are given in kcal/mol. Partial charges *q* using the NBO method.

Molecule		**12**
Fragments		**[SIPr] + $[NCFe(CO)_4]^-$ + Cu^+ (d^{10}, s^0)**
ΔE_{int}		-267.3
ΔE_{Pauli}		232.7
ΔE_{disp}		-27.0 (5.4%)
ΔE_{elstat}[a]		-338.1 (67.6%)
ΔE_{orb}[a]		-134.9 (27%)
$\Delta E_{orb(1)}$[b]	$[SIPr]\rightarrow Cu^+(s)\leftarrow[NCFe(CO)_4]^-$ (+,+) σ donation	-48.9 (36.2%)
$\Delta E_{orb(2)}$[b]	$[SIPr]\rightarrow Cu^+(p)$ σ donation	-15.5 (11.5%)
$\Delta E_{orb(3)}$[b]	$[SIPr]\rightarrow Cu^+(s)\leftarrow[NCFe(CO)_4]^-$ Cu^+ polarization	-16.9 (12.5%)
$\Delta E_{orb(4)}$[b]	$[SIPr]\leftarrow Cu^+(d)$ π backdonation	-14.2 (10.5%)
$\Delta E_{orb(5)}$[b]	$Cu^+(d)\rightarrow [NCFe(CO)_4]^-$ π backdonation	-9.8 (7.2%)
$\Delta E_{orb(6)}$[b]	$[SIPr]\leftarrow Cu^+(d)$ π backdonation	-7.8 (5.8%)
ΔE_{rest}[b]		-21.8 (16.2%)
$q[Fe(CO)_4]CN^-$		-0.80
q(Cu)		0.73
q(SIPr)		0.07

[a]The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$.
[b]The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}.

Table S3. The Cartesian coordinates of studied complexes at the BP86-D3(BJ)/def2-SVP level.

1^+

E = -3355.357502 au

1 1
Au 1.03473000 0.00880100 -0.07191200
P -1.33372500 0.00412100 0.01397200
O 6.60620500 -0.11466900 0.29989500
O 3.34055200 0.78865700 -2.89943700
O 3.36023500 -2.83584400 -0.90091400
O 2.74266400 -0.75365000 2.67738100
O 3.38368400 2.86235100 0.67700000
C 5.46444900 -0.07132200 0.16166400
C 3.45315700 0.48017700 -1.79413900
C 3.47088500 -1.73767500 -0.57224400
C 3.03572000 -0.45802100 1.59914100
C 3.48527600 1.75081800 0.39389800
C -1.78925400 0.10523200 1.79259100
C -1.10456100 1.07538900 2.59209800
C -1.33105300 1.09556700 3.97914800
H -0.80676100 1.85275400 4.58465100
C -2.21264100 0.20042800 4.61211500
C -2.92296000 -0.69452000 3.79387900
H -3.66756000 -1.36294700 4.25586500
C -2.75266000 -0.75922100 2.39649400
C -0.18531000 2.12926000 2.02032700
H -0.61234900 2.63672200 1.13189400
H 0.78528200 1.69105800 1.69224300
H 0.04425900 2.90018800 2.78012300
C -2.39560000 0.20965600 6.10802200
H -1.64194300 -0.44693500 6.59553800
H -3.39548000 -0.16629900 6.40139200
H -2.26368400 1.22559500 6.53051900
C -3.66657200 -1.69940900 1.64273400
H -4.08442400 -1.23805100 0.72791800
H -4.51475300 -1.99155600 2.29095100
H -3.15896500 -2.63028300 1.31929800
C -1.89092100 -1.57004800 -0.75371800
C -1.21945300 -2.76894600 -0.35391500
C -1.53192500 -3.97342700 -1.00783400

H -1.01720000 -4.89339000 -0.68596500 C -2.48698600 -4.04582200 -2.03823200 C -3.17993300 -2.86658100 -2.36194800 H -3.97879600 -2.90869900 -3.12005200 C -2.92475900 -1.62944100 -1.73749700 C -0.22527400 -2.82981800 0.78273100 H 0.75178100 -2.37811800 0.49526000 H -0.02695800 -3.88009200 1.06915100 H -0.56929100 -2.28557300 1.68520600 C -2.76431500 -5.34040100 -2.75835600 H -2.08459700 -5.45269800 -3.63138200 H -3.80168000 -5.38030900 -3.14515100 H -2.59931400 -6.21791700 -2.10215400 C -3.82729000 -0.47633200 -2.11603900 H -4.16980600 0.09785200 -1.23420900 H -4.72448900 -0.86236800 -2.63655400 H -3.33847200 0.25320200 -2.79255000 C -1.89945200 1.47264400 -0.93360200 C -1.29826700 1.69438700 -2.21405500 C -1.60772300 2.87298400 -2.91498900 H -1.14687400 3.03077600 -3.90366200 C -2.49550900 3.83969100 -2.40838200 C -3.12290100 3.56283800 -1.18141100 H -3.86989700 4.27368600 -0.79233600 C -2.86532600 2.39751100 -0.43224500 C -0.39318700 0.69318700 -2.89015200 H 0.56967600 0.56996800 -2.34003700 H -0.14373500 1.01840200 -3.91757600 H -0.84438800 -0.31865800 -2.94470900 C -2.77025600 5.11802000 -3.15801200 H -2.03372800 5.90126600 -2.87364700 H -3.77755800 5.51875500 -2.92989300 H -2.68780300 4.97616900 -4.25391000 C -3.69541200 2.19094600 0.81495100 H -4.07469400 1.15498500 0.90203400 H -4.56914500 2.87005200 0.79650400 H -3.13385400 2.39669300 1.74829900 Fe 3.66472000 -0.00356200 -0.05542900
5^{+}

E = -3126.494303 au

1 1
Au 0.00000000 0.00000000 0.48025500
Fe 0.00000000 0.00000000 3.07517800
O 0.00000000 0.00000000 6.03893700
O 0.00000000 2.85781400 2.23944200
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O 0.00000000 -2.85781400 2.23944200
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N 0.00000000 -1.10230900 -2.29828500
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C 0.00000000 1.73665100 2.51739700
C -1.81882700 0.00000000 3.00174500
C 0.00000000 -1.73665100 2.51739700
C 1.81882700 0.00000000 3.00174500
C 0.00000000 0.00000000 -1.53863900
C 0.00000000 0.77624500 -3.74544000
H 0.89708300 1.21325100 -4.23040900
H -0.89708300 1.21325100 -4.23040900
C 0.00000000 -0.77624500 -3.74544000
H -0.89708300 -1.21325100 -4.23040900
H 0.89708300 -1.21325100 -4.23040900
C 0.00000000 2.43930800 -1.76832800
C -1.24379100 3.06368400 -1.50092800
C -1.21639100 4.36766000 -0.96965100
H -2.16353400 4.88181800 -0.74556300
C 0.00000000 5.01619400 -0.71378300
H 0.00000000 6.03634800 -0.30008000
C 1.21639100 4.36766000 -0.96965100
H 2.16353400 4.88181800 -0.74556300
C 1.24379100 3.06368400 -1.50092800
C -2.56698300 2.33026700 -1.68842600
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H -3.89274200 4.06957600 -1.97050300
H -4.50873900 2.54923500 -2.67649700
H -3.17782900 3.44244200 -3.48741500

C 2.56698300 2.33026700 -1.68842600
H 2.35950800 1.39432300 -2.24968600
C 3.13053800 1.91637100 -0.31361100
H 3.35675100 2.80608200 0.30987300
H 4.06337700 1.32672300 -0.42331300
H 2.39396600 1.29506200 0.24029100
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H 3.17782900 3.44244200 -3.48741500
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H 4.50873900 -2.54923500 -2.67649700
H 3.17782900 -3.44244200 -3.48741500
C 3.13053800 -1.91637100 -0.31361100
H 2.39396600 -1.29506200 0.24029100
H 4.06337700 -1.32672300 -0.42331300
H 3.35675100 -2.80608200 0.30987300

6^+

E = -2879.532581 au

1 1
Au -0.60973000 0.54726700 -0.00683700
Fe -3.16045100 -0.09114800 0.04089900
O -6.06694700 -0.66726200 0.10363600
O -3.08930400 0.19451000 2.99648100
O -1.74186600 -2.69713400 0.26275200
O -3.11129200 -0.33299400 -2.91875700
O -2.93256500 2.86227500 -0.23273700
N 2.27986400 0.01925000 -0.04029800
C 1.36867100 0.96009600 -0.07855700
C 3.72668500 0.52821400 -0.10452000
C 3.49075300 2.02721300 -0.42708600
H 3.73369900 2.22046300 -1.48999800
H 4.15628400 2.67299400 0.17670300
C 1.98832200 2.33359000 -0.15685400
C 1.94836500 -1.38943200 0.08991300
C 1.76414200 -2.15094300 -1.09430900
C 1.48975100 -3.52430100 -0.94608200
H 1.34491300 -4.14281700 -1.84464800
C 1.38163600 -4.11072500 0.32125400
H 1.17438900 -5.18773200 0.41325400
C 1.50220000 -3.32063200 1.47096000
H 1.36748800 -3.78073500 2.46151100
C 1.77621200 -1.94099200 1.38701800
C 1.72534800 -1.52251400 -2.48439300
H 2.10590300 -0.48534700 -2.40442700
C 2.59571200 -2.26710200 -3.51118300
H 3.64443100 -2.36515100 -3.16664700
H 2.59993500 -1.72508400 -4.47869800
H 2.21168800 -3.28847400 -3.71088000
C 0.26216700 -1.41818200 -2.95990000
H -0.20648900 -2.41971400 -3.05280700
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H -0.33817300 -0.83060400 -2.23196900
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H 2.30966200 -2.63771200 4.13551900
H 2.68492200 -0.96572300 4.63542000
H 3.70937500 -1.78946000 3.41406600

C 0.30404000 -0.94297800 3.15739200
H -0.32458300 -0.47222300 2.37081800
H 0.25983600 -0.29952300 4.05966000
H -0.14657300 -1.92483500 3.41012500
C 4.50838900 -0.20433100 -1.19907300
H 4.54364100 -1.29614300 -1.01238300
H 5.55025500 0.17288900 -1.20199700
H 4.08265700 -0.02556300 -2.20406700
C 4.41410300 0.30602000 1.25034800
H 3.92178800 0.86559600 2.06825900
H 5.46062400 0.66234700 1.17858700
H 4.44108100 -0.76867400 1.51662900
C 1.32026200 3.16822100 -1.28107100
H 0.29362100 3.43490500 -0.94546000
H 1.87499500 4.12537400 -1.37017800
C 1.24939500 2.47579300 -2.64567900
H 2.25182000 2.18233700 -3.02138800
H 0.80310700 3.14757300 -3.40535600
H 0.62474300 1.55864600 -2.60562900
C 1.75074800 2.99693500 1.23935100
H 0.65776400 2.97681900 1.44594700
H 2.21626100 2.35290600 2.01701400
C 2.27799800 4.42840300 1.37000400
H 3.36211400 4.49622500 1.14261800
H 2.13650500 4.79249700 2.40719600
H 1.74646300 5.13133500 0.69854200
C -4.93767500 -0.44396000 0.07883500
C -3.10535200 0.08511800 1.85108400
C -2.26364000 -1.67113000 0.17653600
C -3.11840900 -0.23816700 -1.77194100
C -2.95011500 1.71022500 -0.12404500

7

E = -3013.984792 au

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Mn 0.00000000 0.00000000 3.09045500
O 0.00000000 0.00000000 6.06211800
O 2.96938700 -0.34608600 2.86237500
O 0.34069400 2.89441100 2.39313200

O -2.96938700 0.34608600 2.86237500
N -0.03013700 1.09675400 -2.30376300
C 0.00000000 0.00000000 4.89646700
C 1.81594600 -0.21255300 2.95185000
C 0.20669500 1.76651500 2.66043800
C -1.81594600 0.21255300 2.95185000
C 0.00000000 0.00000000 -1.52410800
C 0.05512100 0.77248300 -3.74525000
H 1.02177000 1.13680400 -4.15662100
H -0.76263400 1.27013300 -4.30549300
C 0.00000000 2.43525600 -1.78571700
C 1.24865000 3.01694400 -1.45588700
C 1.24212600 4.32534300 -0.93473600
H 2.19483900 4.80025600 -0.65350000
C 0.04042500 5.02050400 -0.74623400
H 0.05655000 6.03955700 -0.32949700
C -1.18440600 4.41419400 -1.05973200
H -2.12339400 4.95848000 -0.87621600
C -1.23061500 3.10760600 -1.58122200
C 2.55615500 2.24207400 -1.57269900
H 2.33049400 1.26820800 -2.05603100
C 3.11414800 1.92868500 -0.17059400
H 3.36118300 2.85858200 0.38222000
H 4.03382200 1.31218600 -0.23708100
H 2.36735000 1.36968500 0.43030600
C 3.58788200 2.97089100 -2.45295800
H 3.18399100 3.18177400 -3.46496600
H 4.50591200 2.35763100 -2.56713100
H 3.89183700 3.94051300 -2.00583800
C -2.56129400 2.39752300 -1.79929000
H -2.36163500 1.50078800 -2.42419700
C -3.10040300 1.89429100 -0.44405300
H -2.35400100 1.24847300 0.06493700
H -4.03329700 1.30844600 -0.57682200
H -3.31934400 2.74408200 0.23531100
C -3.59447400 3.26218500 -2.54056900
H -3.89911000 4.14429200 -1.93942700
H -4.51410200 2.67587200 -2.74536600
H -3.19813600 3.63406600 -3.50801200
O -0.34069400 -2.89441100 2.39313200
N 0.03013700 -1.09675400 -2.30376300
C -0.20669500 -1.76651500 2.66043800
C -0.05512100 -0.77248300 -3.74525000

H 0.76263400 -1.27013300 -4.30549300
H -1.02177000 -1.13680400 -4.15662100
C 0.00000000 -2.43525600 -1.78571700
C 1.23061500 -3.10760600 -1.58122200
C 1.18440600 -4.41419400 -1.05973200
H 2.12339400 -4.95848000 -0.87621600
C -0.04042500 -5.02050400 -0.74623400
H -0.05655000 -6.03955700 -0.32949700
C -1.24212600 -4.32534300 -0.93473600
H -2.19483900 -4.80025600 -0.65350000
C -1.24865000 -3.01694400 -1.45588700
C 2.56129400 -2.39752300 -1.79929000
H 2.36163500 -1.50078800 -2.42419700
C 3.10040300 -1.89429100 -0.44405300
H 3.31934400 -2.74408200 0.23531100
H 4.03329700 -1.30844600 -0.57682200
H 2.35400100 -1.24847300 0.06493700
C 3.59447400 -3.26218500 -2.54056900
H 3.19813600 -3.63406600 -3.50801200
H 4.51410200 -2.67587200 -2.74536600
H 3.89911000 -4.14429200 -1.93942700
C -2.55615500 -2.24207400 -1.57269900
H -2.33049400 -1.26820800 -2.05603100
C -3.11414800 -1.92868500 -0.17059400
H -2.36735000 -1.36968500 0.43030600
H -4.03382200 -1.31218600 -0.23708100
H -3.36118300 -2.85858200 0.38222000
C -3.58788200 -2.97089100 -2.45295800
H -3.89183700 -3.94051300 -2.00583800
H -4.50591200 -2.35763100 -2.56713100
H -3.18399100 -3.18177400 -3.46496600

8

E = -3242.852901 au

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Au -1.07941900 0.00139300 0.05682000
Mn -3.67600000 -0.00066000 0.03630600
P 1.30533800 0.00137000 -0.00821800
O -6.64147200 -0.00779900 -0.08937600
O -3.14481100 -1.90900200 -2.21604500

O -3.16690300 2.27131500 -1.85381500
O -3.33602100 1.90912800 2.32004400
O -3.31282900 -2.26720000 1.96298500
C -5.47761400 -0.00493100 -0.03891900
C -3.34875300 -1.16944500 -1.34017600
C -3.36326500 1.39042800 -1.11819600
C -3.46915200 1.16572200 1.43380000
C -3.45451300 -1.38552600 1.21571200
C 1.92823100 -0.76433900 1.55109700
C 1.29004800 -1.97739500 1.96612400
C 1.61083200 -2.52182100 3.22241300
H 1.11423600 -3.45773600 3.52721200
C 2.54050700 -1.92103900 4.08951300
C 3.20167200 -0.77008600 3.63138500
H 3.97932800 -0.31219000 4.26504500
C 2.93615400 -0.18282100 2.37702500
C 0.32052700 -2.74141000 1.09748600
H -0.63178200 -2.17899200 0.95898700
H 0.06944700 -3.71697000 1.55520400
H 0.71848100 -2.92461900 0.07846400
C 2.81783900 -2.49666700 5.45646000
H 2.05268800 -2.15649400 6.18845100
H 3.80711000 -2.17924400 5.84233300
H 2.78551400 -3.60517300 5.44710600
C 3.80592300 0.98881300 1.97874900
H 4.15437300 0.91402100 0.93095200
H 4.69852600 1.02972300 2.63312500
H 3.28450000 1.96363400 2.06085300
C 1.87603900 1.75039600 -0.15465700
C 1.25049200 2.70118700 0.71463300
C 1.52934300 4.06891400 0.54366200
H 1.04361100 4.78896800 1.22268700
C 2.40454000 4.54162200 -0.45002900
C 3.05589200 3.58536700 -1.24567400
H 3.79289300 3.92386200 -1.99278300
C 2.83137300 2.19930800 -1.11499100
C 0.33730500 2.30829100 1.85011700
H -0.62294900 1.88576300 1.47351700
H 0.09285700 3.18491700 2.47946400
H 0.77992500 1.52525300 2.49917500
C 2.63552100 6.01950200 -0.64803600
H 1.83469900 6.46043700 -1.28149400
H 3.60199100 6.21982200 -1.15215900

H 2.62369900 6.56765600 0.31593700
C 3.68769500 1.29035300 -1.96841700
H 4.08574600 0.43132500 -1.39533100
H 4.54796900 1.85944900 -2.37173400
H 3.13771900 0.85861100 -2.82863600
C 1.83451400 -0.98420700 -1.47692000
C 1.14320000 -0.72742800 -2.70460900
C 1.39417000 -1.55333400 -3.81457700
H 0.85662800 -1.34224900 -4.75367300
C 2.30383900 -2.62447800 -3.76759100
C 3.01869600 -2.81306600 -2.57399500
H 3.78252200 -3.60701900 -2.52784800
C 2.82451700 -2.01084200 -1.43045000
C 0.18580300 0.42467800 -2.89184300
H -0.75000400 0.27358300 -2.30592200
H -0.09660500 0.52996000 -3.95660500
H 0.60854600 1.39010200 -2.54647200
C 2.50448900 -3.53017600 -4.95757400
H 1.71169300 -4.30923300 -4.99582200
H 3.48019700 -4.05399000 -4.91476300
H 2.45097200 -2.96813800 -5.91217900
C 3.74658300 -2.26668700 -0.25897900
H 4.13478300 -1.32834100 0.18090800
H 4.61278700 -2.87121900 -0.59196500
H 3.25359300 -2.81439000 0.56924800

9

E = -3025.161378 au

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Ag 0.00000000 0.00000000 0.59369100
Mn 0.00000000 0.00000000 3.15515000
O 0.00000000 0.00000000 6.12484800
O 2.96875600 -0.32961400 2.90252700
O 0.31223600 2.89222600 2.43415200
O -2.96875600 0.32961400 2.90252700
N -0.03273400 1.09317000 -2.26854100
C 0.00000000 0.00000000 4.95875500
C 1.81382400 -0.20095400 3.00093300
C 0.19054400 1.76096700 2.70399600
C -1.81382400 0.20095400 3.00093300

C 0.00000000 0.00000000 -1.48654200
C 0.05973900 0.77115500 -3.71277500
H 1.03209600 1.13033300 -4.11523800
H -0.75020900 1.27540700 -4.27807500
C 0.00000000 2.43452300 -1.75778300
C 1.24752800 3.01362200 -1.41935800
C 1.24215600 4.32886100 -0.91470200
H 2.19399600 4.80179300 -0.62743200
C 0.04281000 5.03382400 -0.75161100
H 0.05986000 6.05845300 -0.34890600
C -1.18189800 4.43054600 -1.07249900
H -2.11934600 4.98327600 -0.90871600
C -1.22901400 3.11770600 -1.57735200
C 2.55197900 2.22984700 -1.50728800
H 2.33188600 1.25778300 -1.99674100
C 3.07220900 1.91405800 -0.09135700
H 3.30889500 2.84266700 0.46792500
H 3.98909500 1.29153200 -0.13161100
H 2.30810400 1.36165400 0.49402800
C 3.61124000 2.95082700 -2.36059900
H 3.23366100 3.16694500 -3.38154100
H 4.52574400 2.32891000 -2.45391200
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C -2.55842300 2.40639000 -1.79941100
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C -3.06550000 1.84766200 -0.45338500
H -2.30777600 1.18377500 0.01376300
H -3.99978200 1.26428100 -0.58687200
H -3.26864400 2.66884500 0.26461300
C -3.61611200 3.28687100 -2.48434200
H -3.92703000 4.13446900 -1.83854900
H -4.52888200 2.69486100 -2.70242000
H -3.24091500 3.70924800 -3.43929700
O -0.31223600 -2.89222600 2.43415200
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C -0.19054400 -1.76096700 2.70399600
C -0.05973900 -0.77115500 -3.71277500
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H -1.03209600 -1.13033300 -4.11523800
C 0.00000000 -2.43452300 -1.75778300
C 1.22901400 -3.11770600 -1.57735200
C 1.18189800 -4.43054600 -1.07249900
H 2.11934600 -4.98327600 -0.90871600

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C -1.24752800 -3.01362200 -1.41935800
C 2.55842300 -2.40639000 -1.79941100
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C 3.06550000 -1.84766200 -0.45338500
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H 3.99978200 -1.26428100 -0.58687200
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C -3.07220900 -1.91405800 -0.09135700
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C -3.61124000 -2.95082700 -2.36059900
H -3.91412700 -3.91650900 -1.90450200
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H -3.23366100 -3.16694500 -3.38154100

10

E = -4716.624869 au

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N -1.36070800 0.35699100 1.75145500
C -1.07921000 0.35493700 0.41147100
C -3.16239700 1.19500700 0.78368200
H -4.12444700 1.63082400 0.50127500
C -2.63260600 0.86261500 2.00338800
H -3.03169100 0.94571100 3.01707900
C -2.39091400 1.10263500 -1.58531200
C -1.89581900 2.28653200 -2.16706700
C -2.24243600 2.55718600 -3.50406700

H -1.87668000 3.48951100 -3.96247600
C -3.02461600 1.66472700 -4.26154200
C -3.42297100 0.44764400 -3.66761000
H -3.98536000 -0.29131000 -4.25935100
C -3.10739800 0.14248800 -2.33466200
C -0.89793000 3.16042100 -1.42143700
H -1.04220500 2.97059400 -0.33685500
C -1.17992300 4.64608900 -1.63118100
C -0.37445100 5.46183900 -2.44790400
H 0.51464000 5.02963700 -2.93199400
C -0.69318200 6.81920200 -2.63412500
H -0.05276700 7.44588500 -3.27463600
C -1.81745100 7.37661100 -2.00365000
H -2.06244300 8.44072900 -2.14611900
C -2.62808600 6.56733300 -1.18604000
H -3.51200600 6.99574500 -0.68712500
C -2.31043100 5.21317600 -1.00473700
H -2.94494500 4.57729200 -0.36584700
C 0.54629700 2.75349200 -1.74209200
C 1.58547400 3.21986000 -0.90763900
H 1.35005400 3.86818700 -0.04861700
C 2.92157700 2.87251400 -1.15870300
H 3.71110700 3.23635000 -0.48538000
C 3.24529500 2.04616900 -2.24839400
H 4.28849700 1.74784500 -2.43004700
C 2.22301900 1.57871600 -3.08721400
H 2.46634200 0.91296600 -3.92874100
C 0.88512700 1.92916600 -2.83541300
H 0.09430700 1.54074000 -3.49256400
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H -3.38771100 1.09333100 -6.32967000
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C -0.90055300 -4.14979400 -1.23052400
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C 0.13146200 -2.58685600 -2.77421400
H 0.98742200 -2.27541700 -3.39169200
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C 0.53190500 0.81354700 3.24279300
C 1.40852700 0.36067600 4.24028300
H 2.15699100 1.06040800 4.64276600
C 1.38717100 -0.97684400 4.69164200
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H 0.55299000 -2.95141800 4.33109900
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H 0.50051400 2.05272100 1.52965000
C 2.03506500 2.78439900 2.77340200
C 3.09260600 2.13914500 2.09400600
H 2.87549700 1.26185300 1.46232800
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H 5.21673200 2.09037400 1.66962500
C 4.68515700 3.73118100 3.01269600
H 5.71788400 4.10258600 3.10503400
C 3.63886400 4.37993600 3.68855800
H 3.84832200 5.26255300 4.31352200
C 2.31801600 3.90773400 3.57102200
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C -0.49303300 3.13386000 3.06465300
C -0.88390700 4.19884100 2.22611900
H -0.35458400 4.36592500 1.27533700
C -1.93463300 5.05433200 2.58957300
H -2.22093600 5.87589800 1.91489800
C -2.61336200 4.85869200 3.80610800
H -3.44122400 5.52604300 4.09272500
C -2.22246300 3.81085000 4.65666800

H -2.74152700 3.65557400 5.61586900
C -1.16810600 2.95634000 4.28832100
H -0.86912400 2.13053800 4.95288700
C 2.32880500 -1.42796800 5.78207000
H 3.35645700 -1.04803500 5.60776400
H 2.37436900 -2.53241600 5.85167800
H 2.00465200 -1.04016900 6.77224500
C -1.26582300 -2.45333600 2.30093200
H -1.39359700 -2.03352500 1.27925600
C -2.66299300 -2.55471900 2.89719200
C -2.86343200 -2.76913900 4.27651200
H -1.99128900 -2.86142700 4.94231700
C -4.16141700 -2.85573100 4.80604300
H -4.30045000 -3.02407300 5.88569500
C -5.28122500 -2.72476900 3.96471100
H -6.29816000 -2.79140200 4.38210100
C -5.09304700 -2.50636700 2.58942000
H -5.95925700 -2.40215700 1.91714000
C -3.79287400 -2.42105900 2.06613400
H -3.64518700 -2.24418300 0.99028400
C -0.54335100 -3.78034100 2.07420800
C 0.75035800 -3.74296000 1.50525500
H 1.21159300 -2.76987000 1.27057000
C 1.44152400 -4.92602800 1.21321500
H 2.44473700 -4.87395800 0.76229300
C 0.84050100 -6.17204000 1.47674700
H 1.37755600 -7.10481600 1.24362500
C -0.44819200 -6.21892000 2.03360500
H -0.92618800 -7.18997400 2.23869400
C -1.13720000 -5.02766200 2.33394200
H -2.14902800 -5.07008700 2.76518600
Fe 5.22734700 -1.68254600 -1.82625400
O 4.69162800 -4.33392200 -0.63942100
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11

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12

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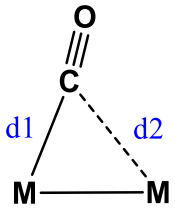
Table S4. Bridge asymmetry parameter α based on parameters from X-ray crystallographic data

Calculated α, bridge asymmetry parameter using observed distances (X-ray crystallographic), which is defined by Curtis and co-workers[10] as:

$$\alpha = \frac{d2 - d1}{d1}$$



where d1 and d2 are the shorter and longer M···CO distances, respectively. According to this system, carbonyls with $\alpha \geq 0.6$ are considered essentially terminal whereas $\alpha \leq 0.1$ are bridging carbonyls. Carbonyls with α values in-between these two cut-off points could be considered as semi-bridging carbonyls. Although this is not a definitive system of bridging ligand classification, the calculated α values for several compounds described in the manuscript are given below as added information.
Note however that the Fe-C-O and Mn-C-O angles of following complexes are near 180°, and show little to no effect due to CO bending towards the coinage metal ions.

Complex	Bridge asymmetry parameter α for four cis-CO groups			
$[Mes_3PAuFe(CO)_5][SbF_6]$ (**1**)	0.63	0.62	0.56	0.55
$[(IPr^*)AuFe(CO)_5][SbF_6]$ (**2**)	0.44	0.69	0.55	0.67
$[(SIPr)AuFe(CO)_5][SbF_6]$ (**5**)	0.46	0.66	0.51	0.66
$[(^{Et2}CAAC)Au(Fe(CO)_5)][SbF_6]$ (**6**)	0.52	0.58	0.57	0.66
$[(SIPr)AuMn(CO)_5]$ (**7**)	0.47	0.63	0.61	0.63
$[Mes_3PAuMn(CO)_5]$ (**8**)	0.50	0.65	0.49	0.69
$[(SIPr)AgMn(CO)_5]$ (**9**)	0.46	0.65	0.57	0.65

Figure S10. ^{1}H NMR spectrum of [(SIPr)Au-Fe$(CO)_5$][SbF_6] (**5**) (500.16 MHz) in CD_2Cl_2

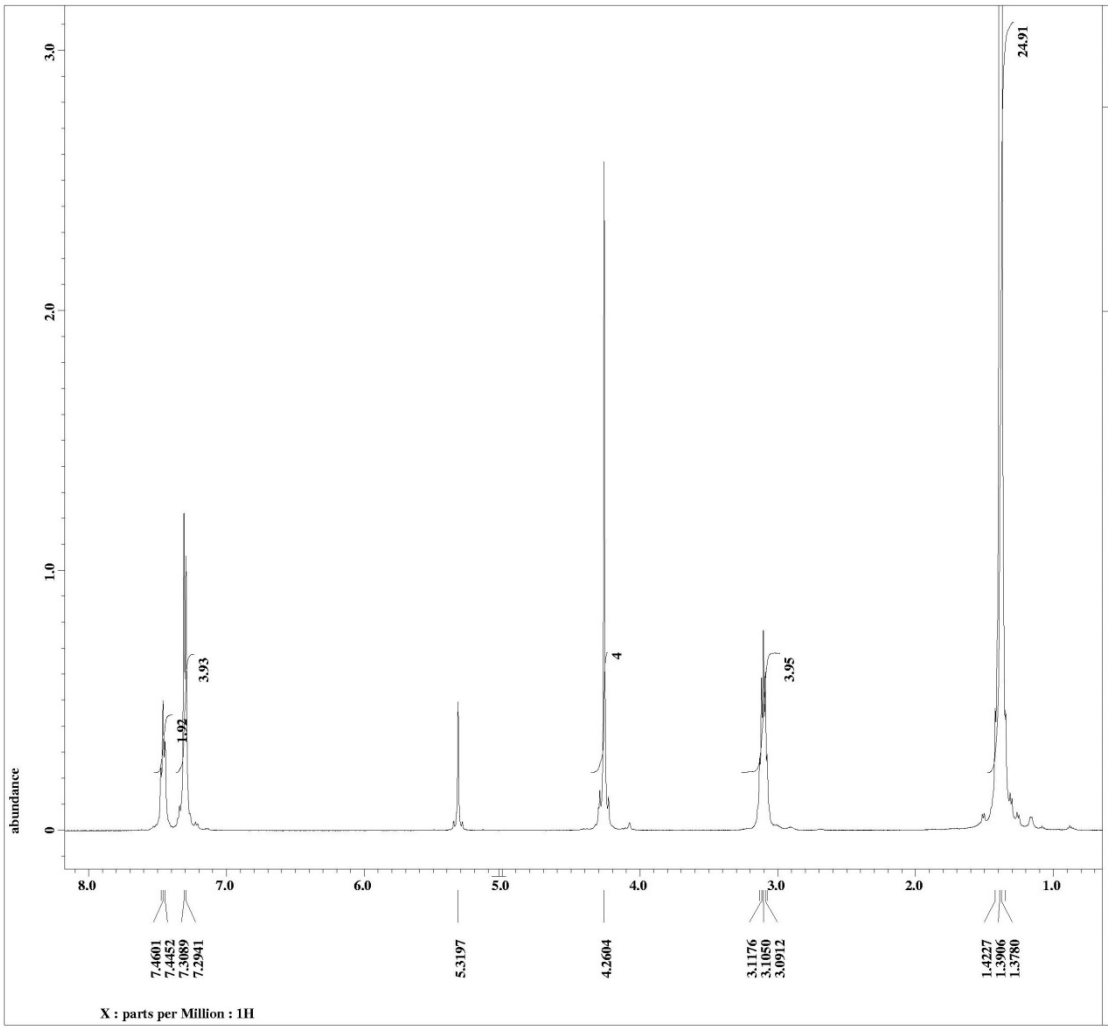


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of [(SIPr)Au-Fe(CO)$_5$][SbF$_6$] (**5**) (125.77 MHz) in CD_2Cl_2

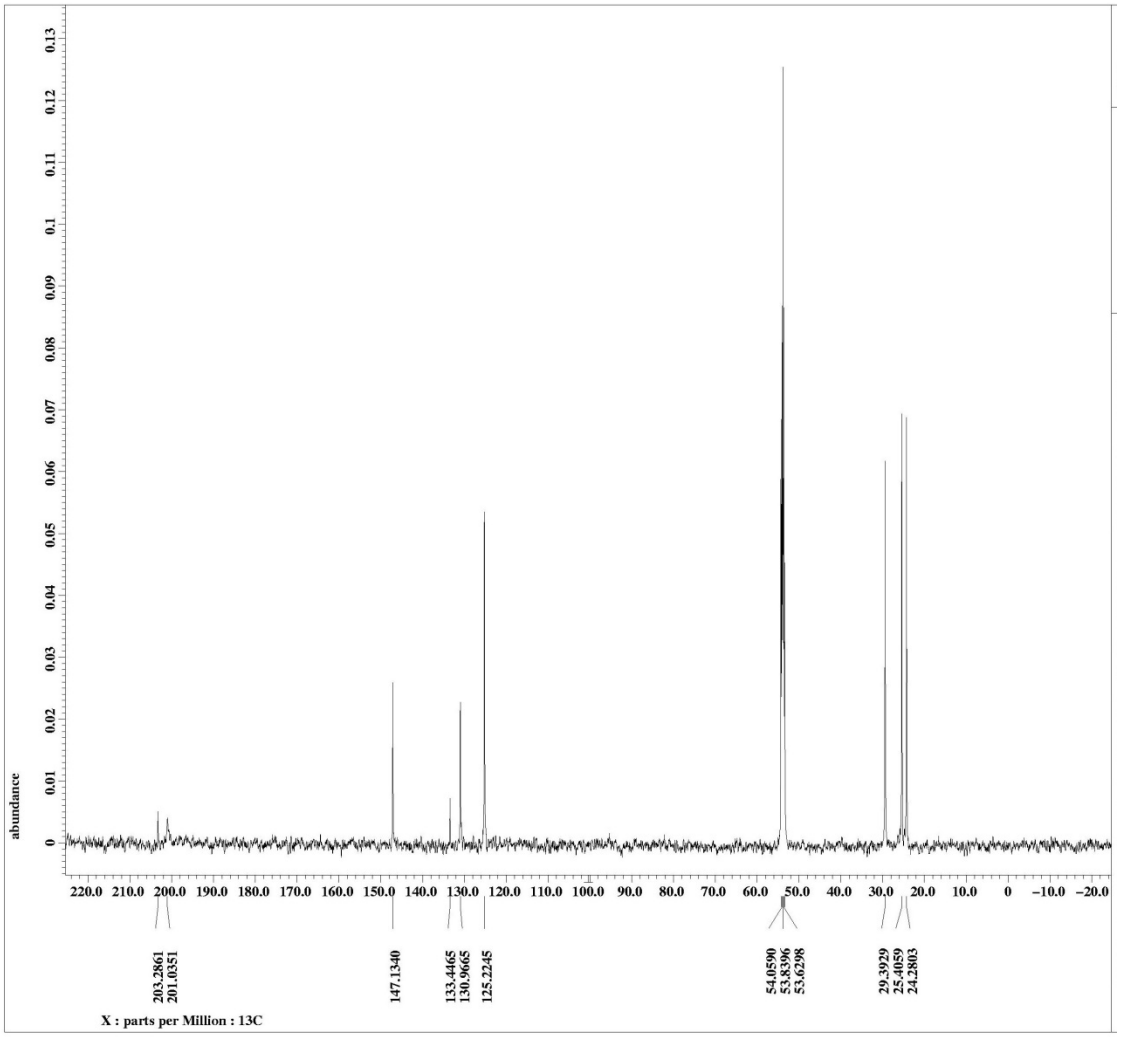


Figure S12. FT-IR spectrum (crystals on ATR, resolution, 2 cm^{-1}) of [(SIPr)Au-$Fe(CO)_5$][SbF_6] (**5**)

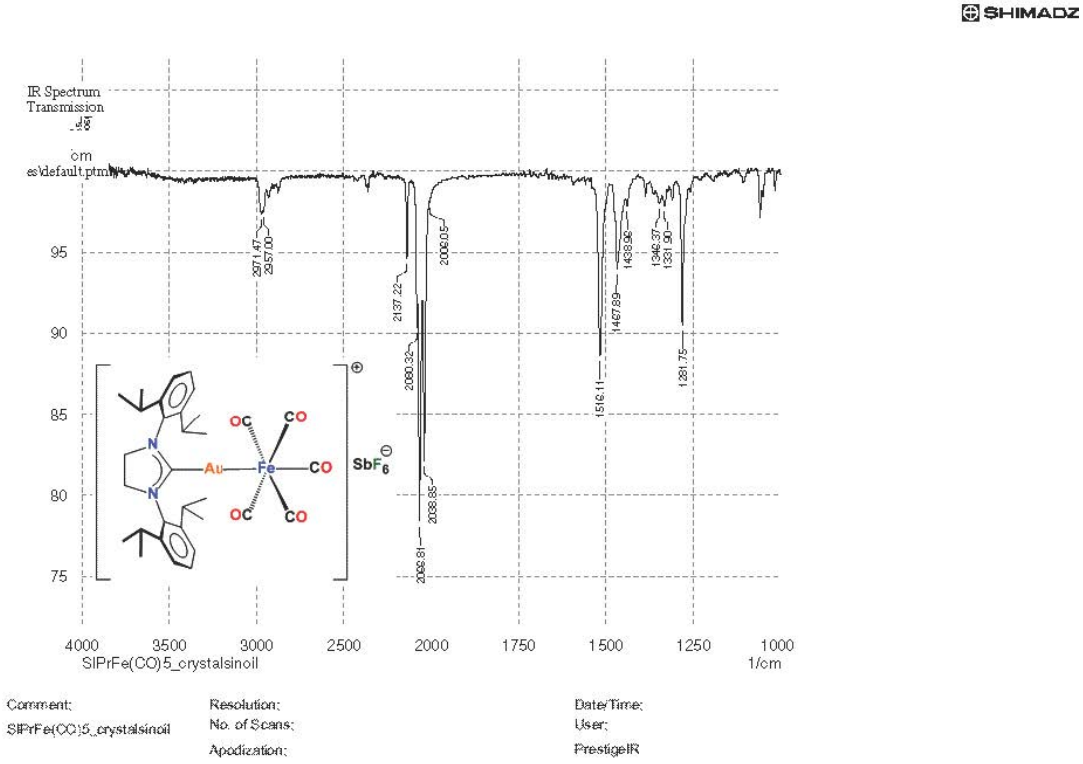


Figure S13. ^{1}H NMR spectrum of [(^{Et2}CAAC)Au-Fe(CO)$_5$][SbF$_6$] (**6**) (500.16 MHz) in CD_2Cl_2

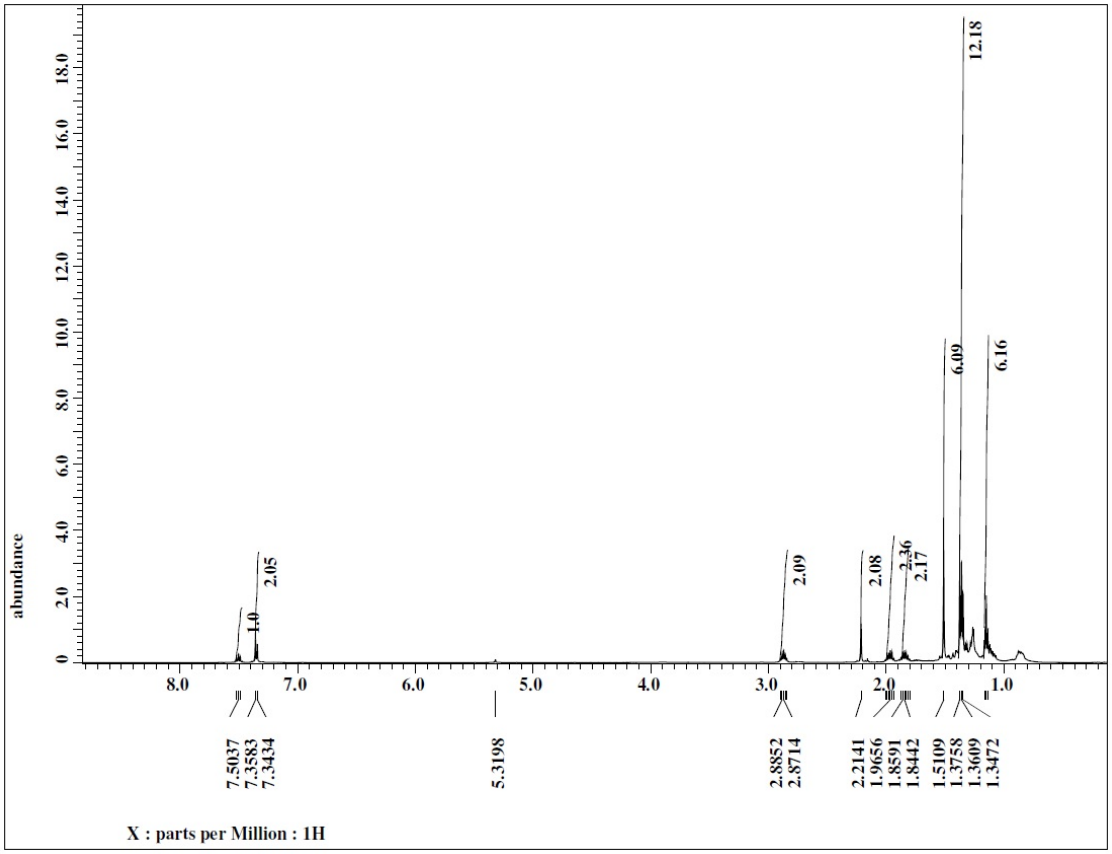


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of [(^{Et2}CAAC)Au-Fe(CO)$_5$][SbF_6] (**6**) (125.77 MHz) in CD_2Cl_2 and insert showing CO and carbene-C peaks.

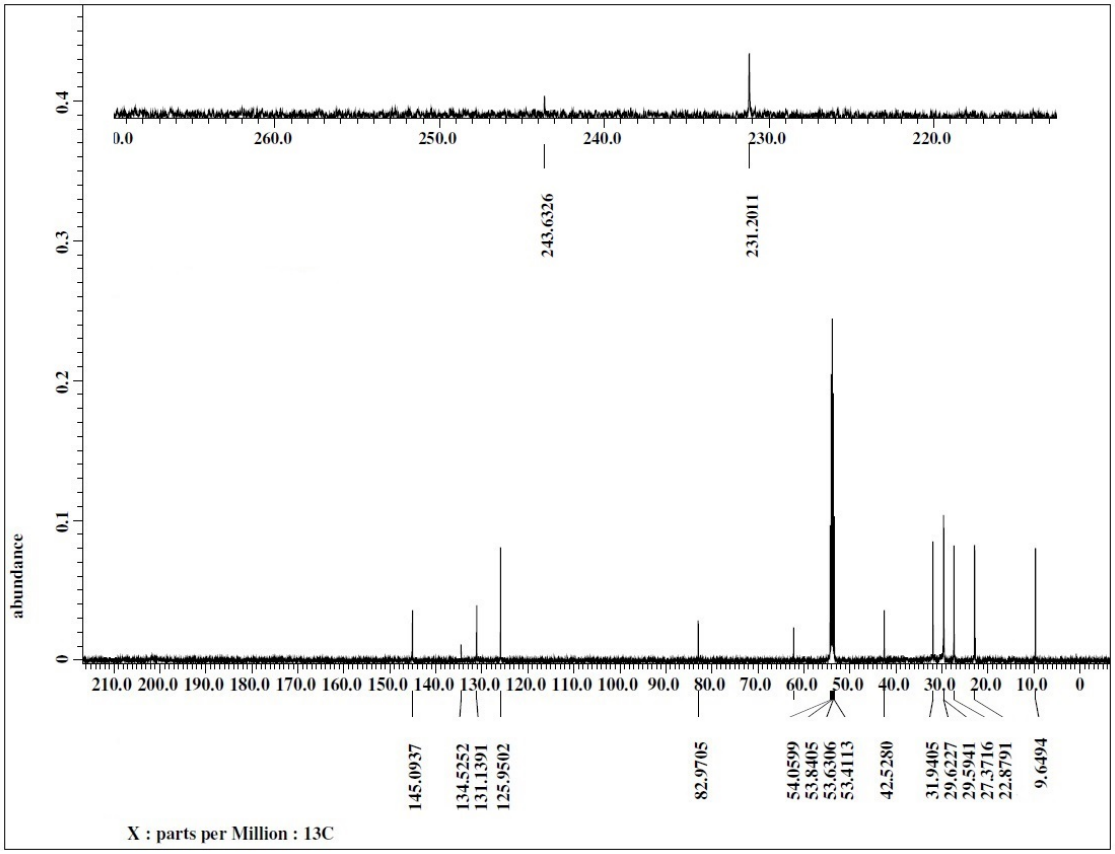


Figure S15. FT-IR spectrum (crystals on ATR, resolution, 2 cm^{-1}) of [(^{Et2}CAAC)Au-Fe(CO)$_5$][SbF$_6$] (**6**)

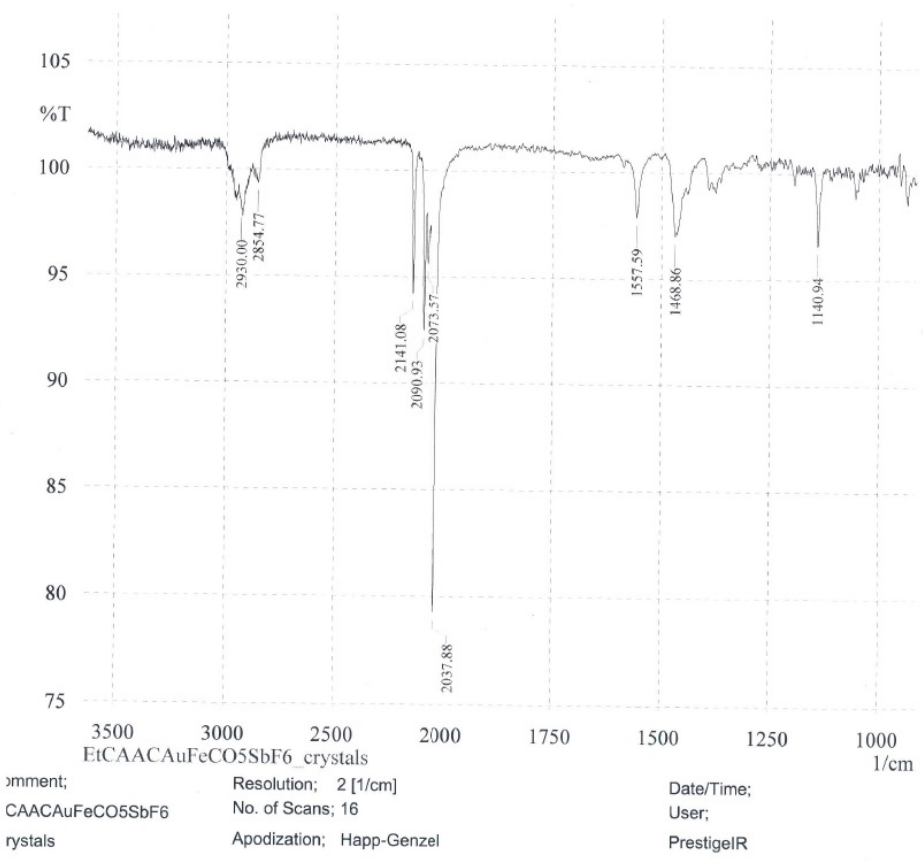


Figure S16. ^{1}H NMR spectrum of (SIPr)Au-Mn(CO)$_5$ (**7**) (500.16 MHz) in DMSO-d_6

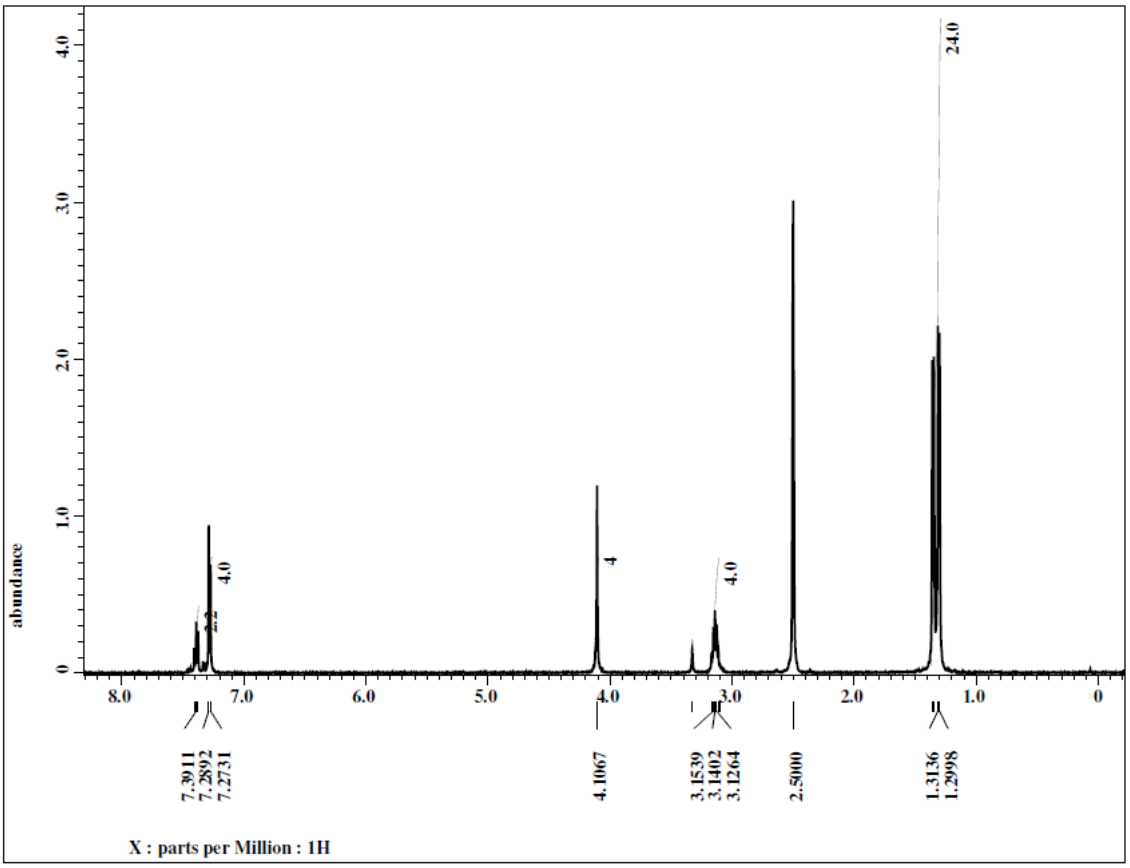


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of (SIPr)Au-Mn(CO)$_5$ (**7**) (125.77 MHz) in DMSO-*d*$_6$ and insert showing CO and carbene-C peaks.

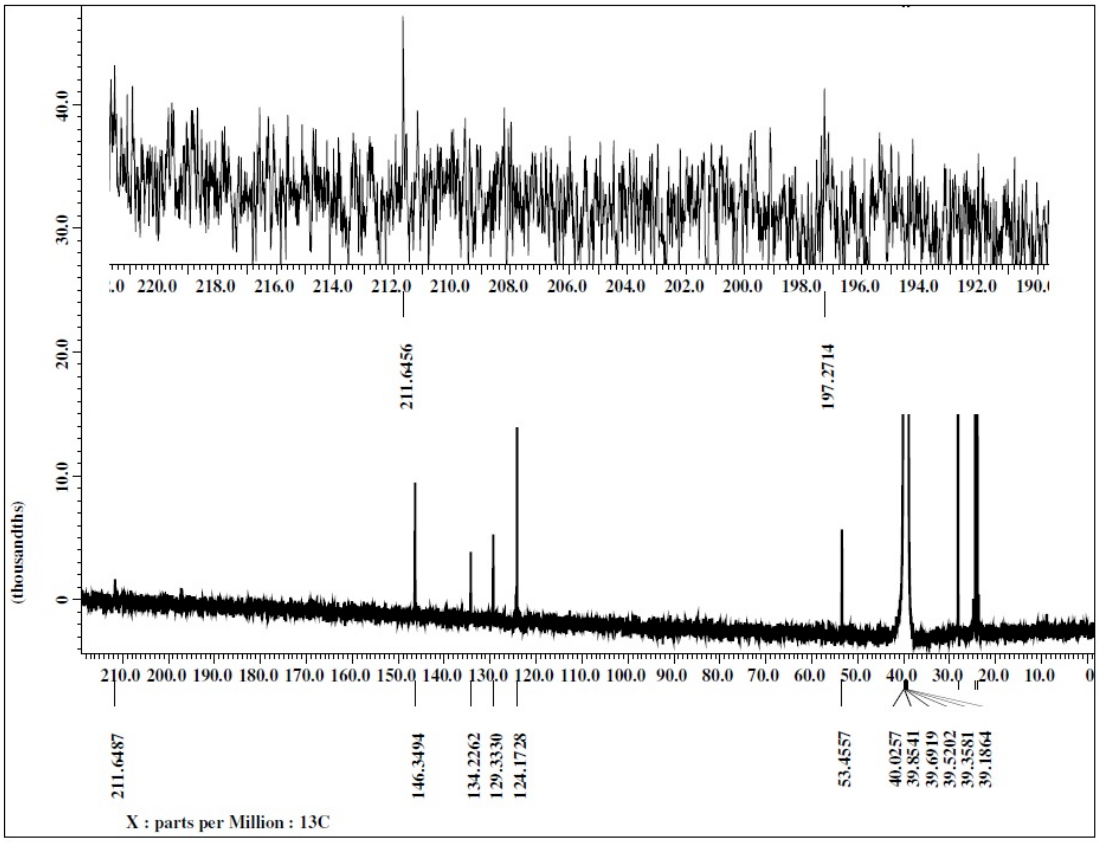


Figure S18. FT-IR spectrum (crystals on ATR, resolution, 2 cm^{-1}) of (SIPr)Au-$Mn(CO)_5$ (**7**)

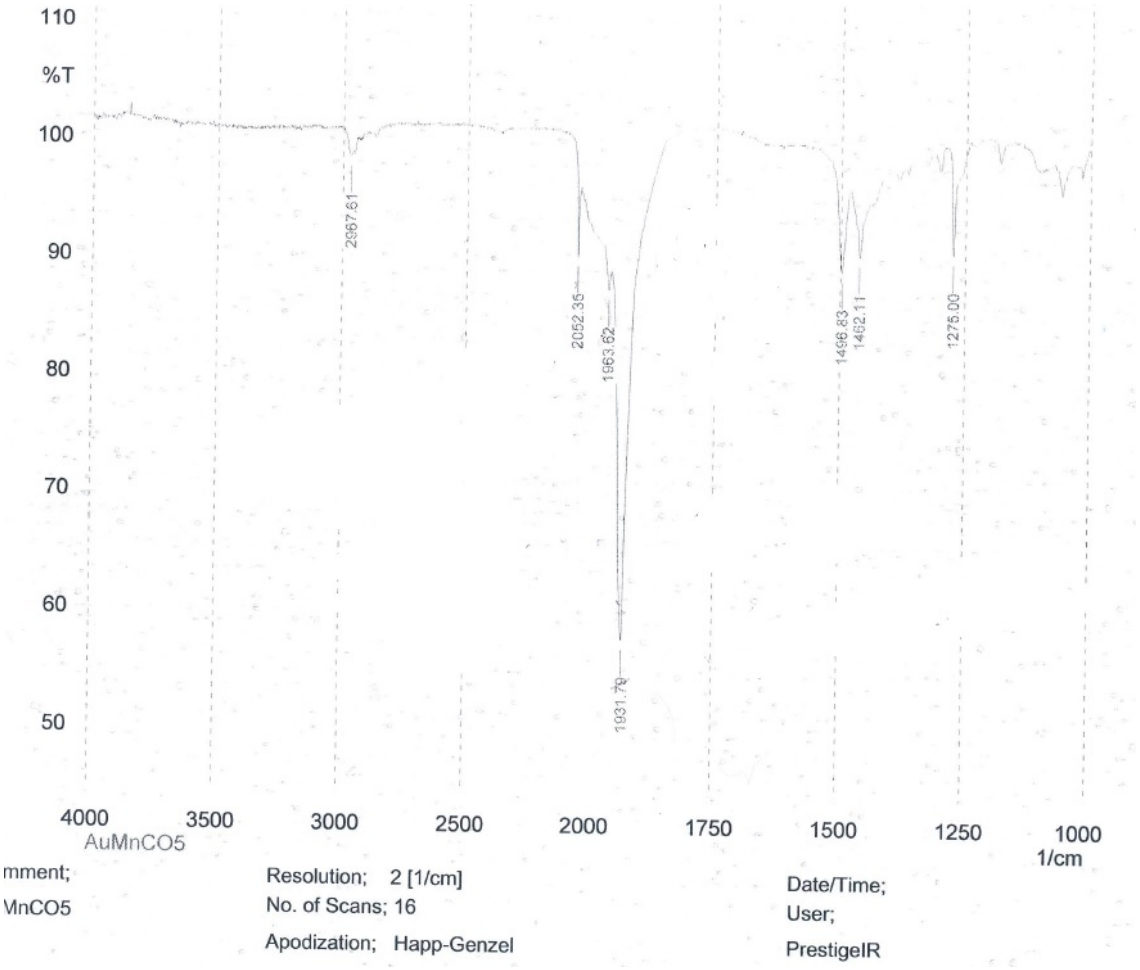


Figure S19. ^{1}H NMR spectrum of $Mes_3PAu\text{-}Mn(CO)_5$ (**8**) (500.16 MHz) in CD_2Cl_2

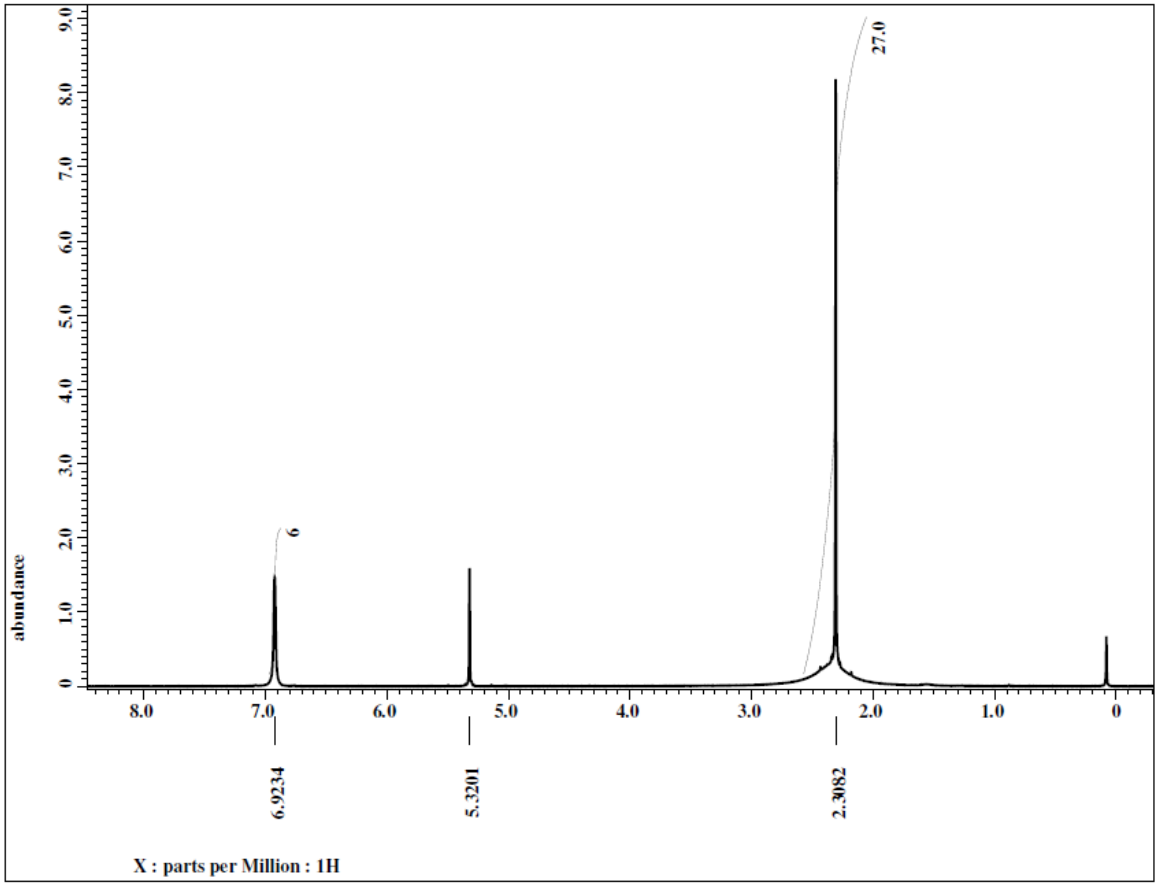


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of $Mes_3PAu\text{-}Mn(CO)_5$ (**8**) (125.77 MHz) in CD_2Cl_2

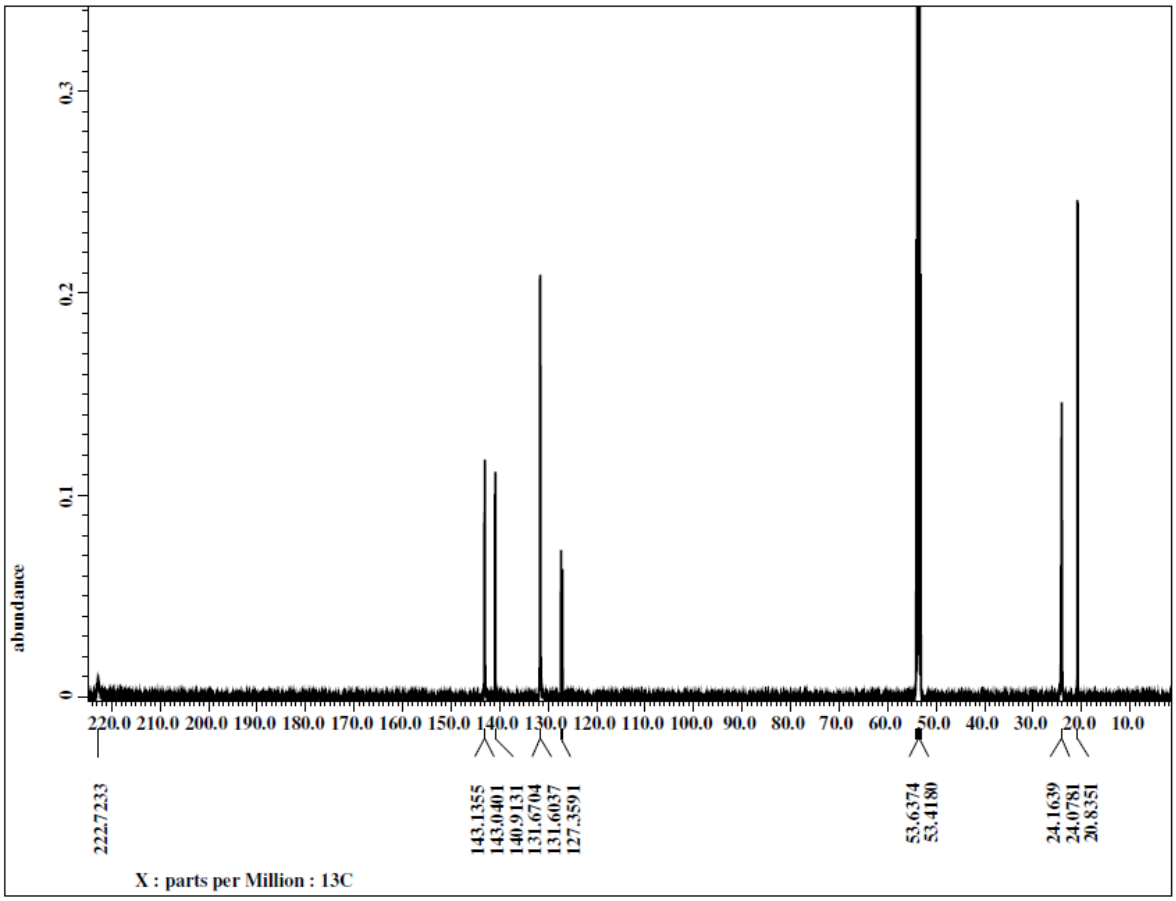


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum of $Mes_3PAu\text{-}Mn(CO)_5$ (**8**) (121.65 MHz) in CD_2Cl_2

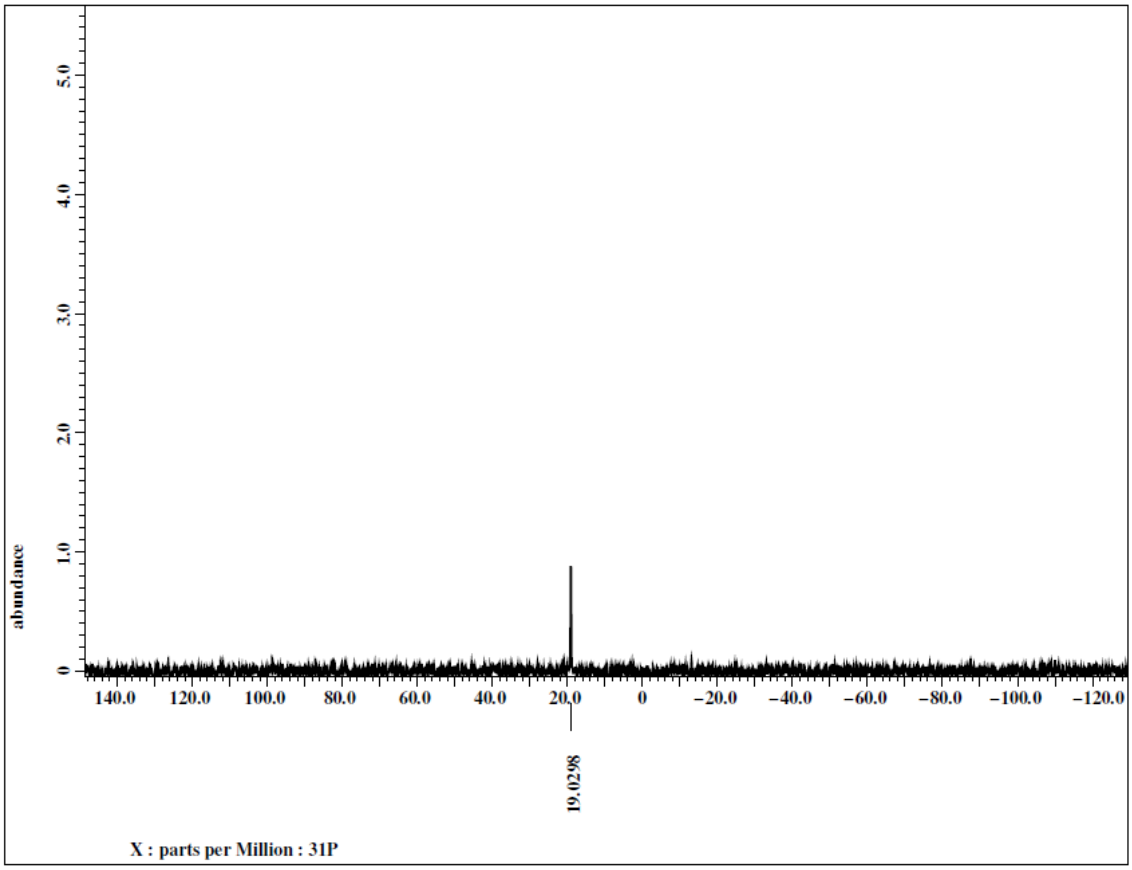


Figure S22. FT-IR spectrum (crystals on ATR, resolution, 2 cm^{-1}) of Mes_3PAu-$Mn(CO)_5$ (**8**)

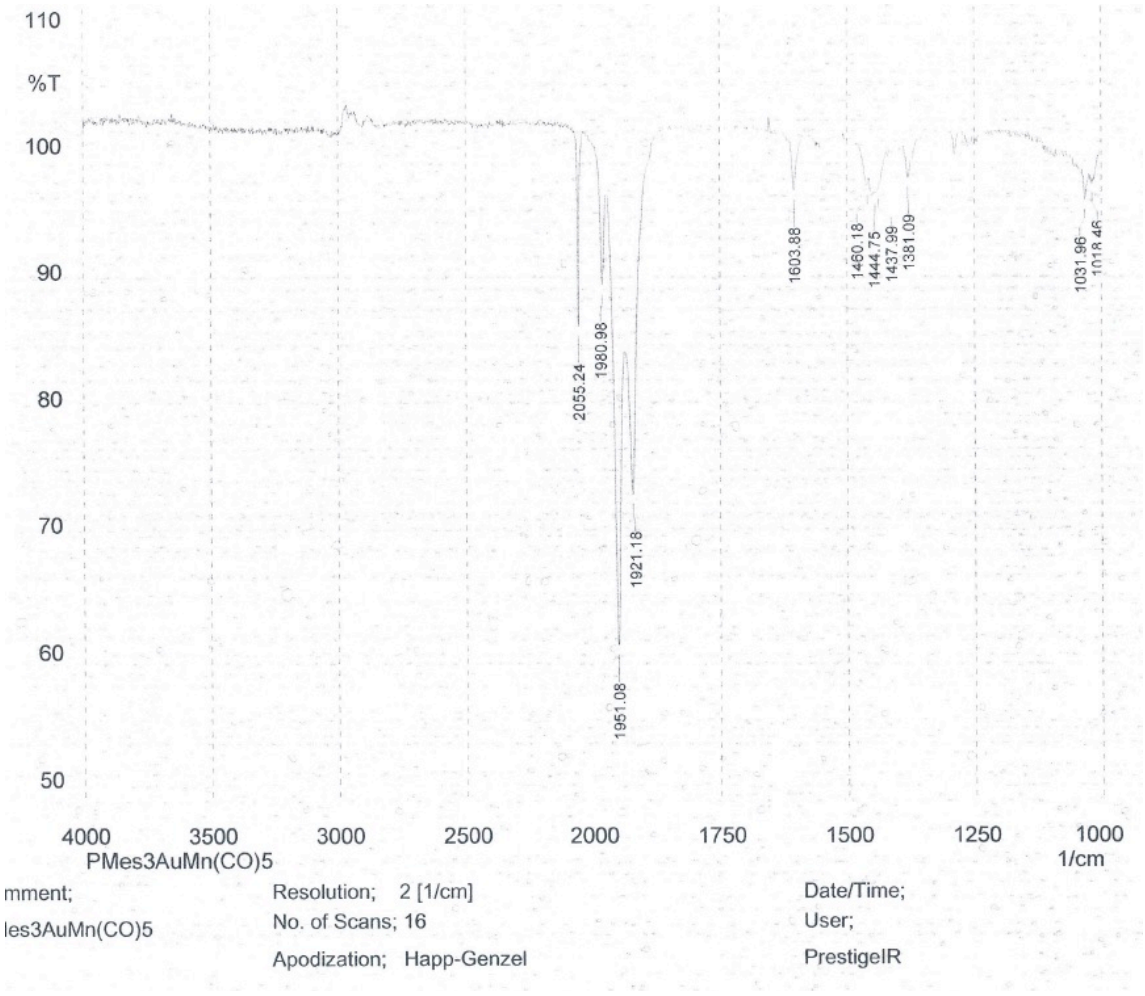


Figure S23. ^{1}H NMR spectrum of (SIPr)Ag-Mn(CO)$_5$ (**9**) (500.16 MHz) in CD_2Cl_2

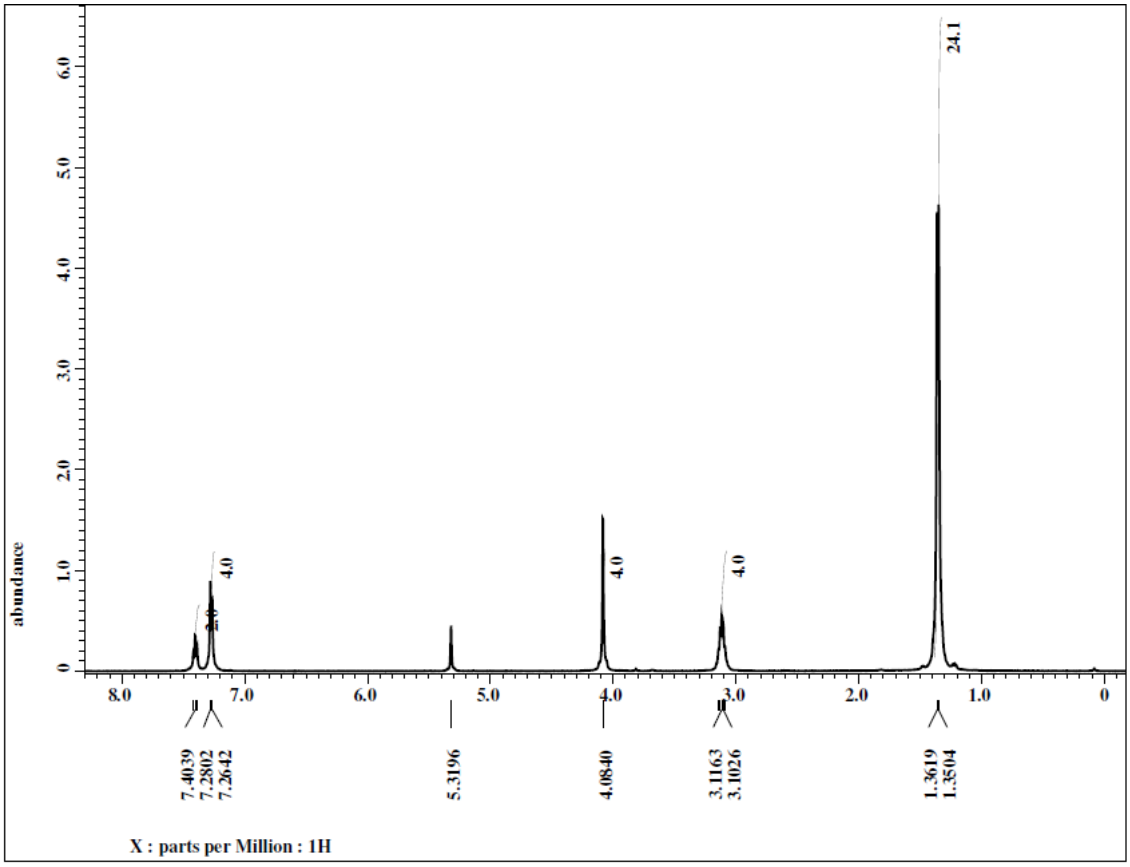


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of (SIPr)Ag-$Mn(CO)_5$ (**9**) (125.77 MHz) in CD_2Cl_2 and insert showing CO and carbene-C peaks.

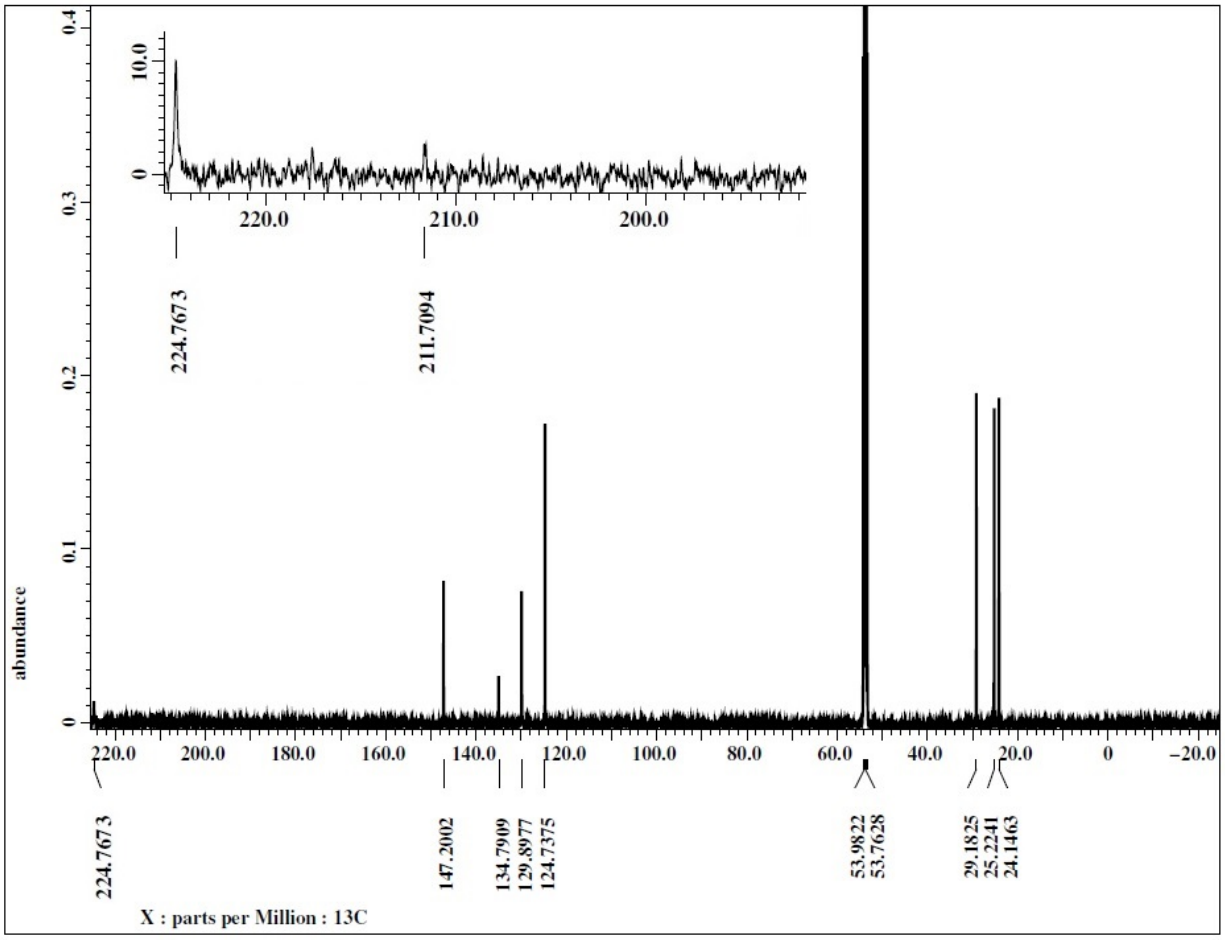


Figure S25. FT-IR spectrum (crystals on ATR, resolution, 2 cm^{-1}) of (SIPr)Ag-$Mn(CO)_5$ (**9**)

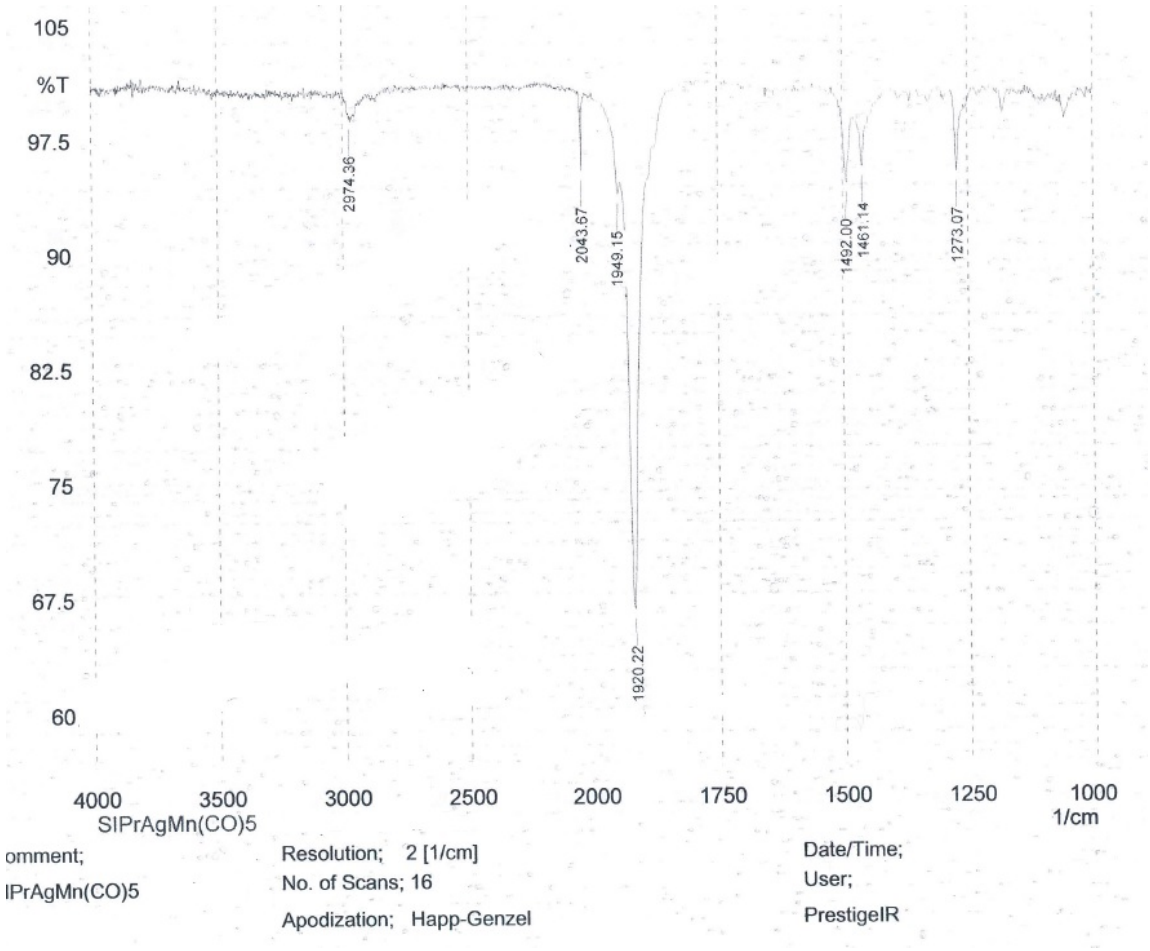


Figure S26. ^{1}H NMR spectrum of (IPr*)AuNCFe(CO)$_4$ (**10**) (500.16 MHz) in CD_2Cl_2

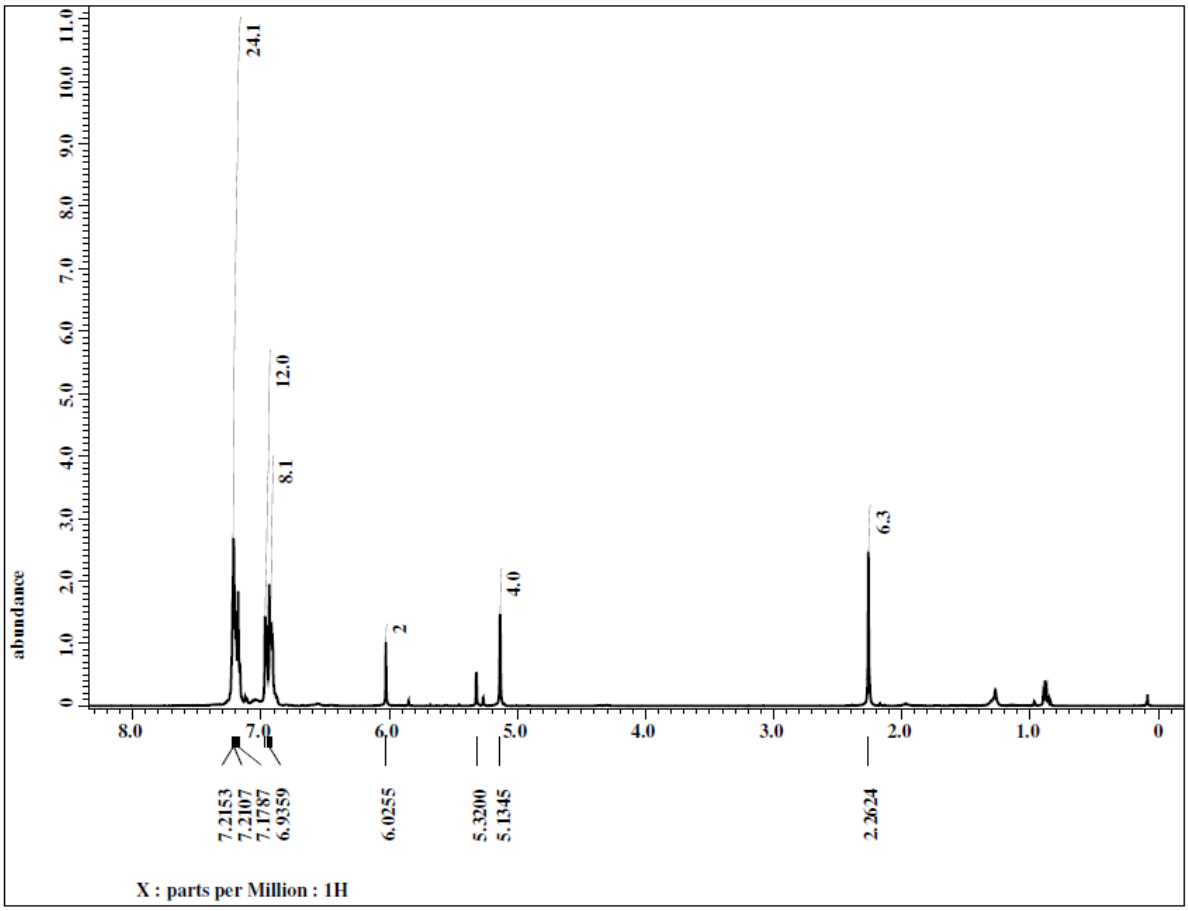


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of $(IPr^{*})AuNCFe(CO)_4$ (**10**) (125.77 MHz) in CD_2Cl_2 and insert showing CO and carbene-C peaks.

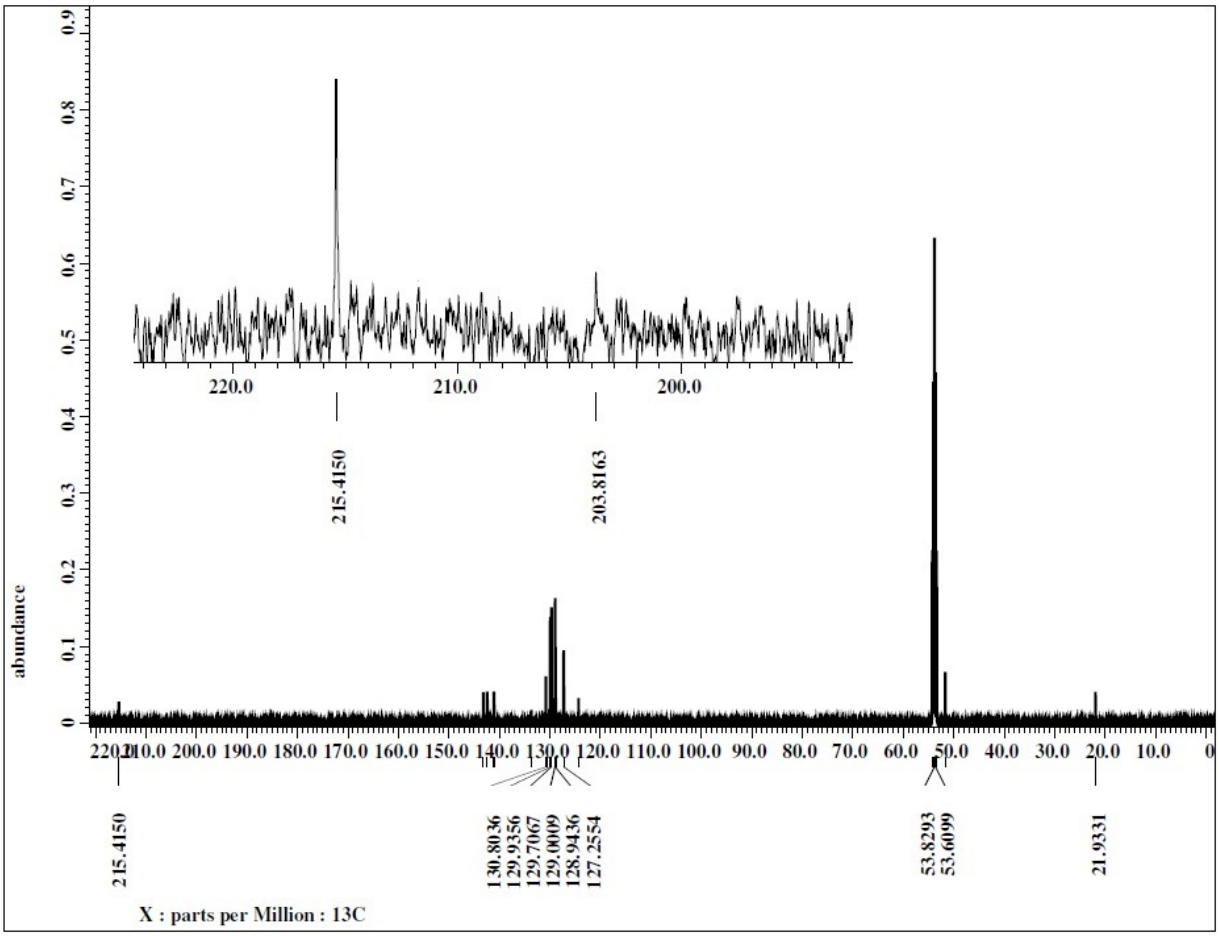


Figure S28. FT-IR spectrum (crystals on ATR, resolution, 2 cm^{-1}) of (IPr^*)AuNCFe(CO)$_4$ (**10**)

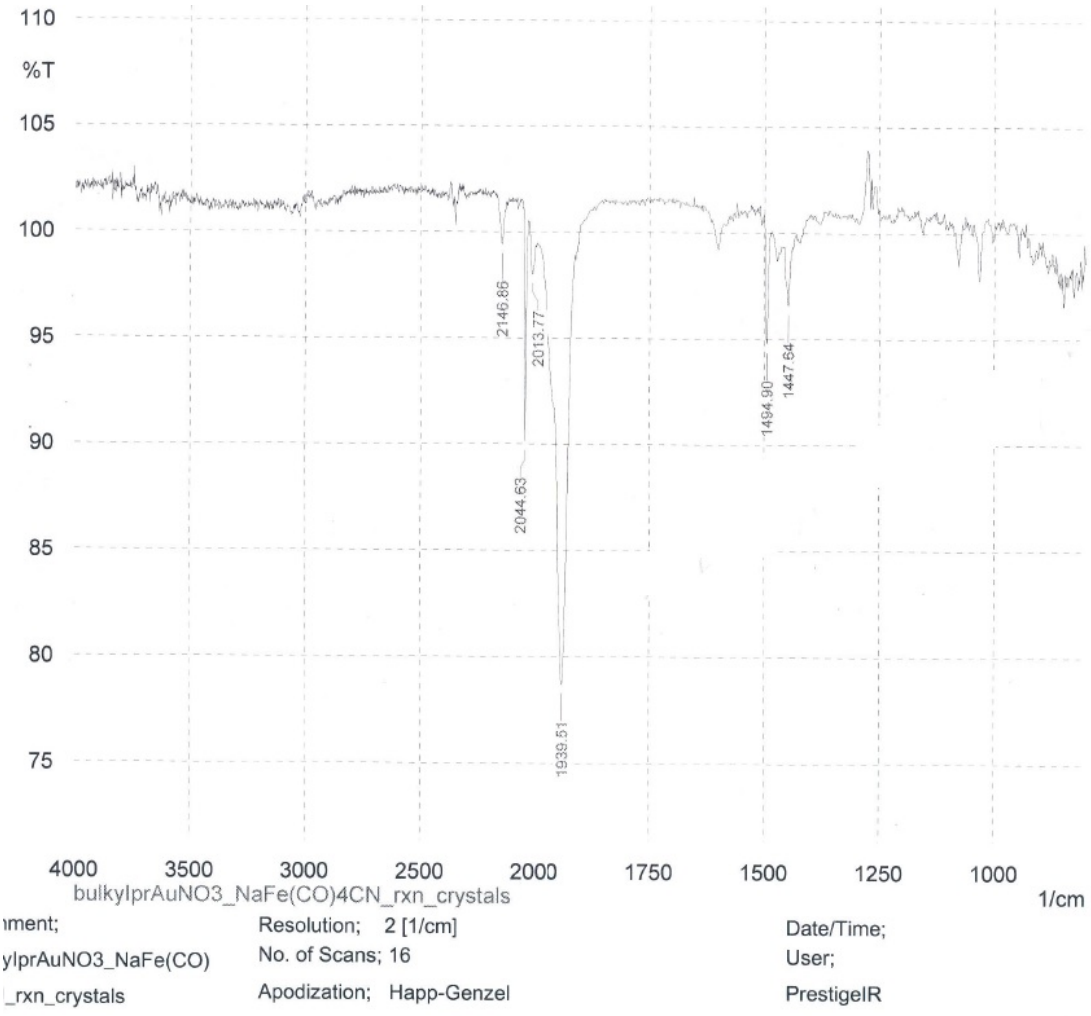


Figure S29. ^{1}H NMR spectrum of (SIPr)AgNCFe(CO)$_4$ (**11**) (500.16 MHz) in CD_2Cl_2

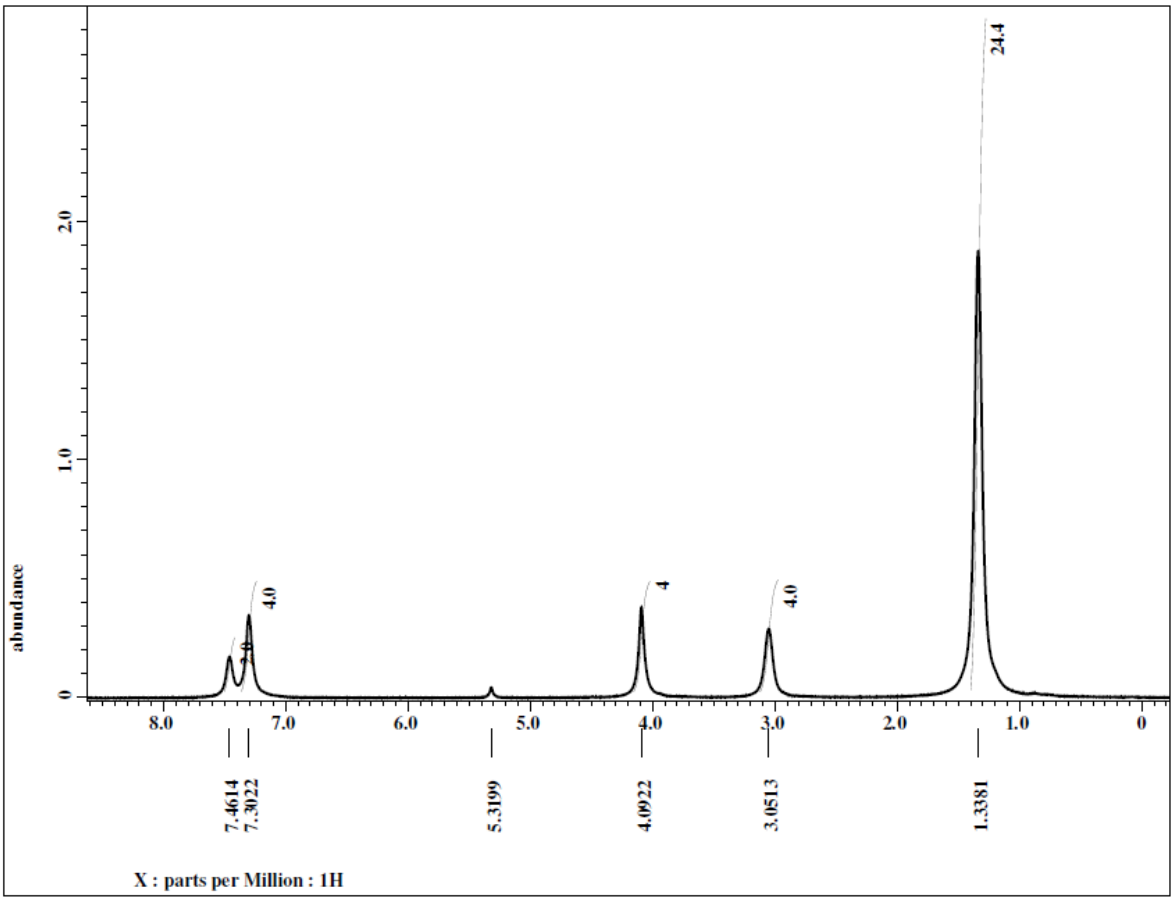


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of (SIPr)AgNCFe(CO)$_4$ (**11**) (125.77 MHz) in CD_2Cl_2 and insert showing CO and carbene-C peaks.

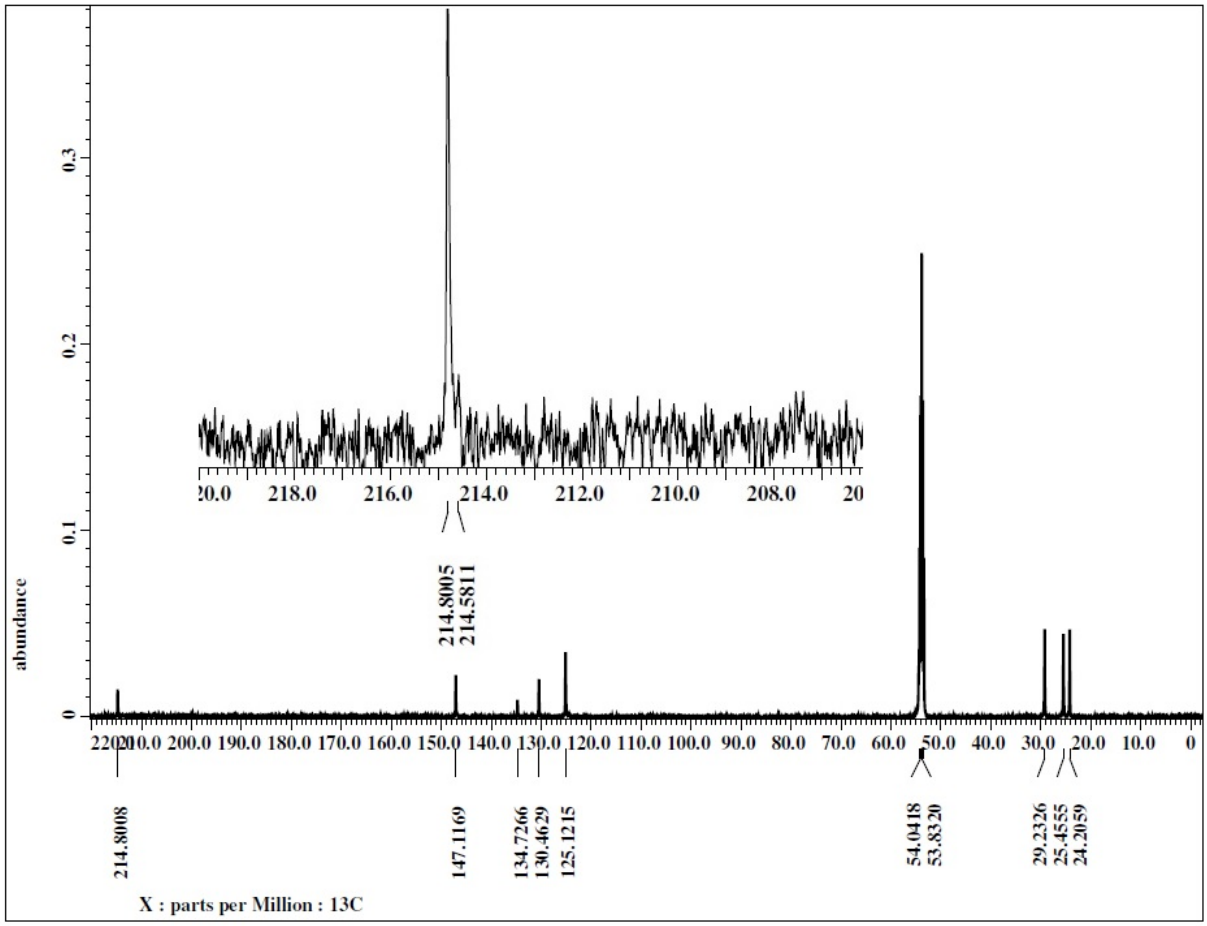


Figure S31. FT-IR spectrum (crystals on ATR, resolution, 2 cm^{-1}) of $(SIPr)AgNCFe(CO)_4$ (**11**)

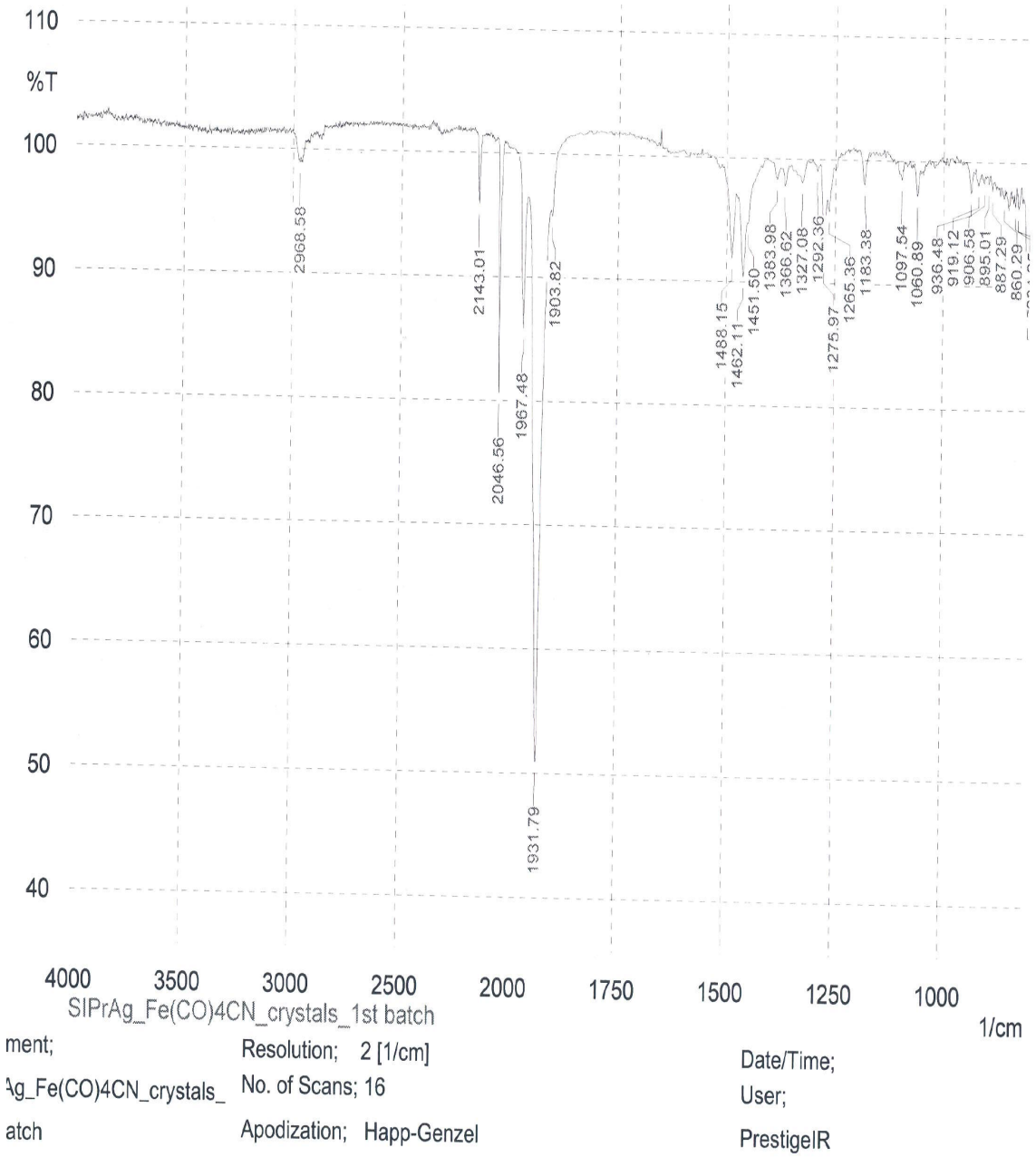


Figure S32. ^{1}H NMR spectrum of (SIPr)CuNCFe(CO)$_4$ (**12**) (500.16 MHz) in CD_2Cl_2

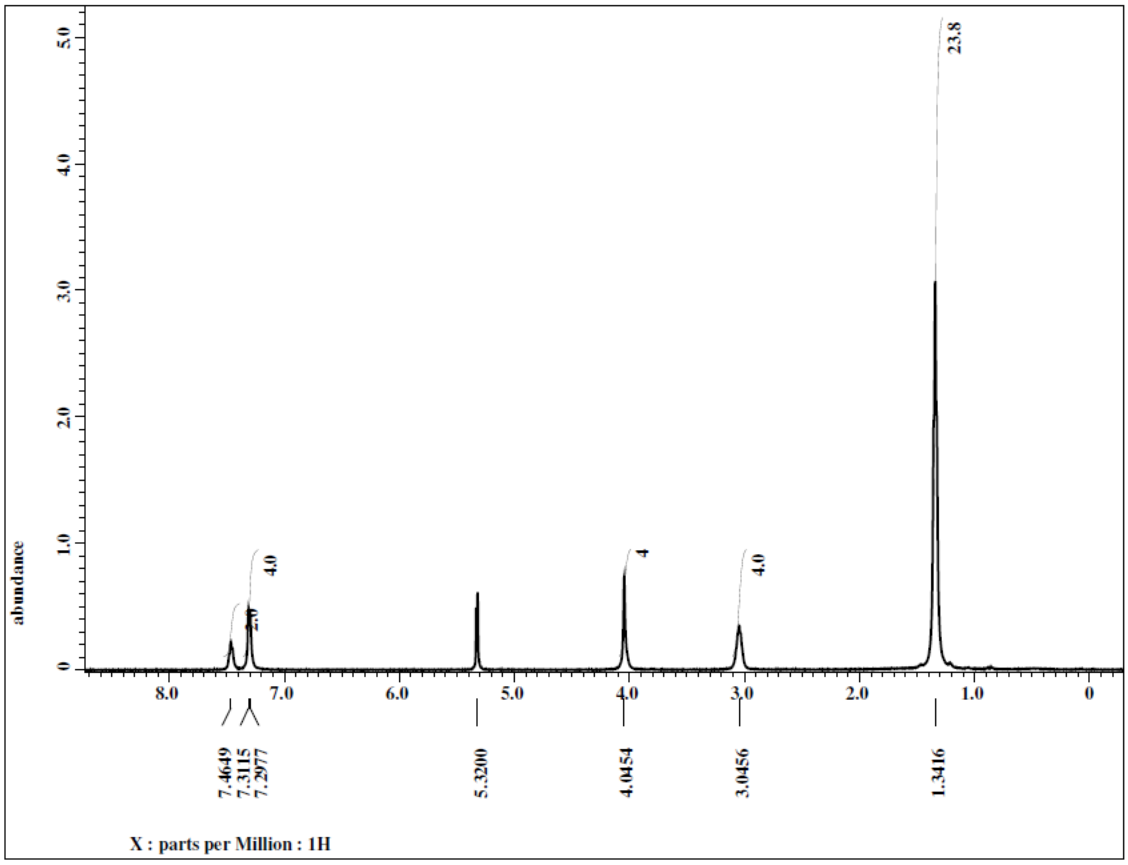


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of (SIPr)CuNCFe(CO)$_4$ (**12**) (125.77 MHz) in CD_2Cl_2 and insert showing CO and carbene-C peaks.

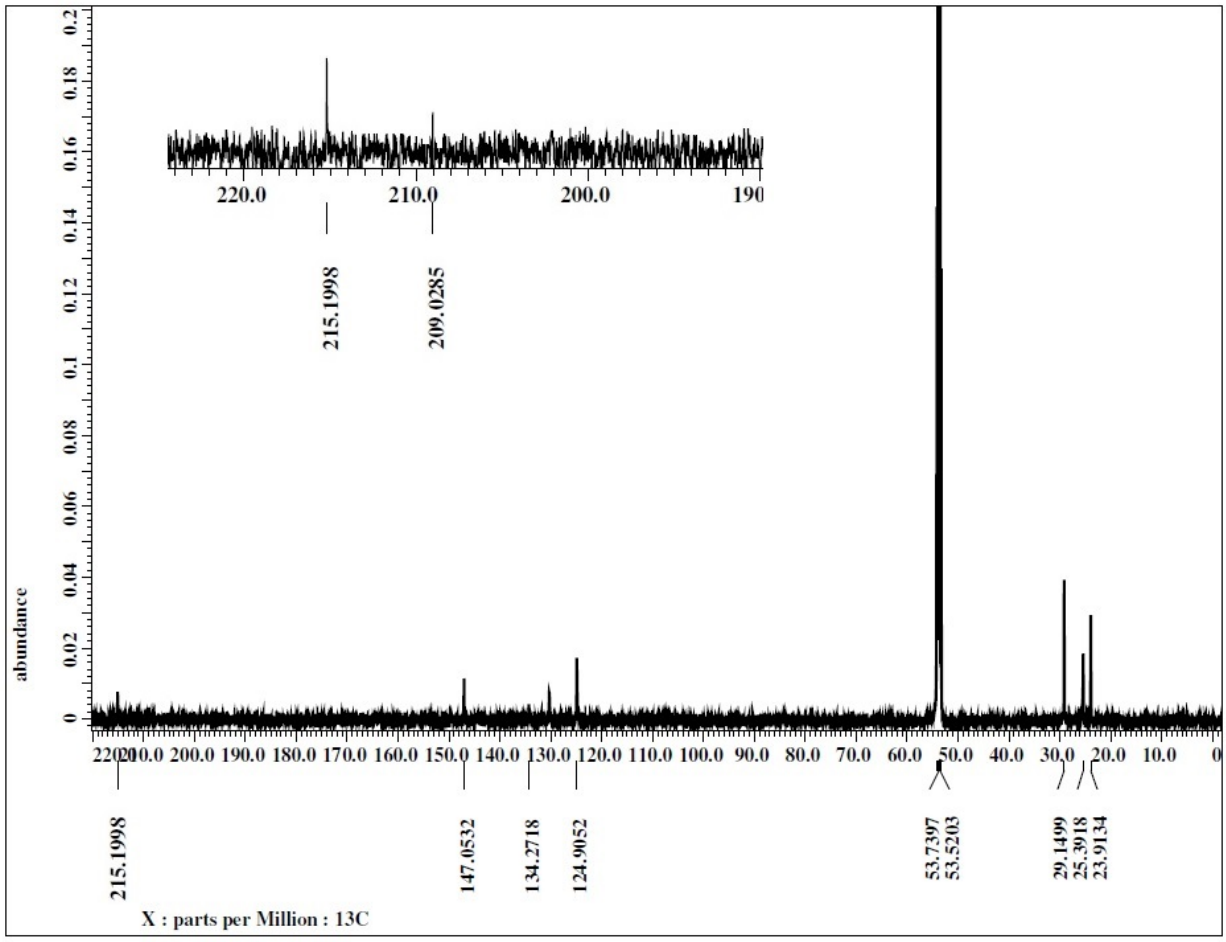


Figure S34. FT-IR spectrum (crystals on ATR, resolution, 2 cm^{-1}) of (SIPr)CuNCFe$(CO)_4$ (**12**)

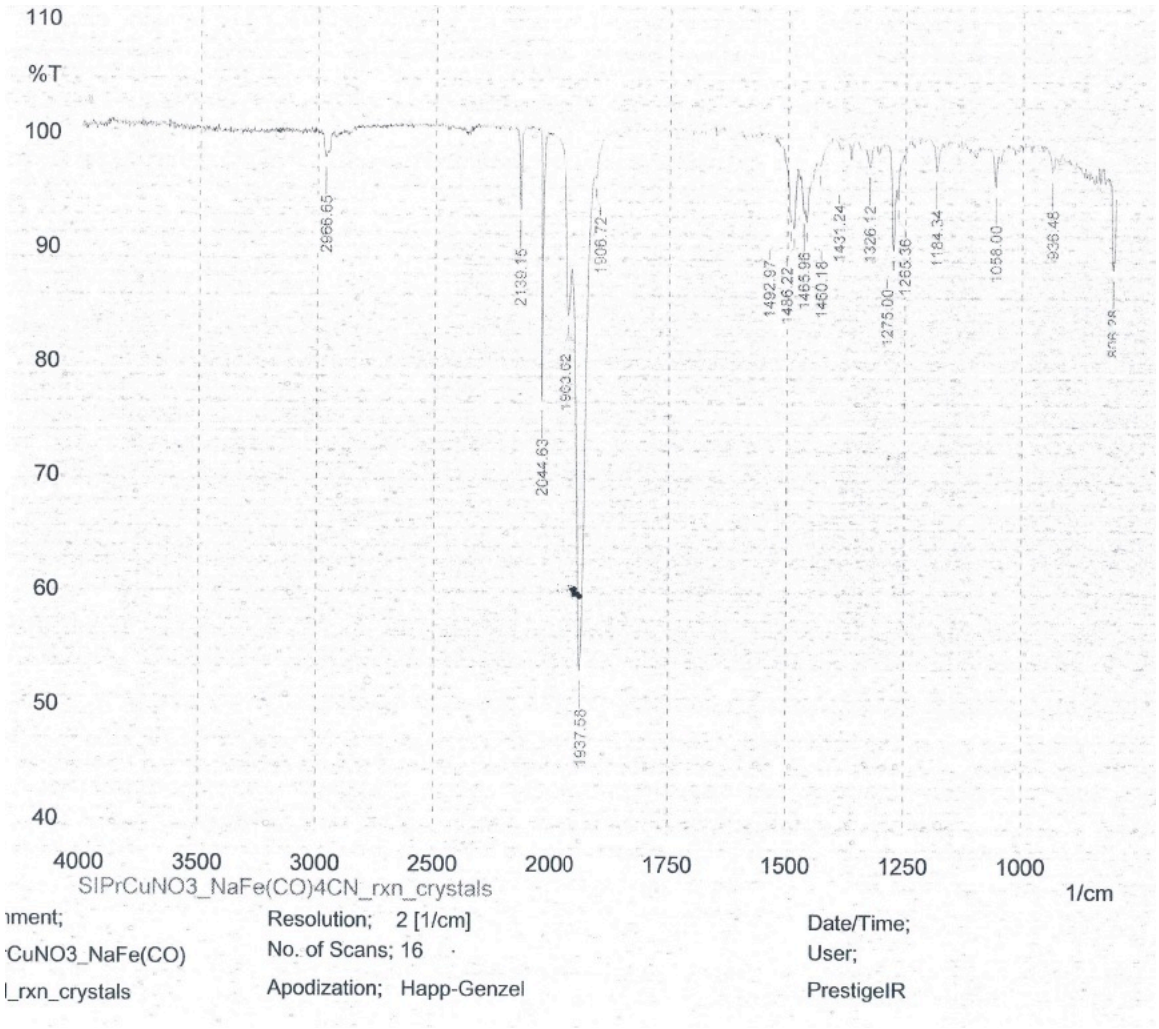


Figure S35. Molecular structure and atom numbering scheme for [(SIPr)Au-Fe(CO)$_5$][SbF$_6$] (**5**). Hydrogen atoms have been omitted for clarity.

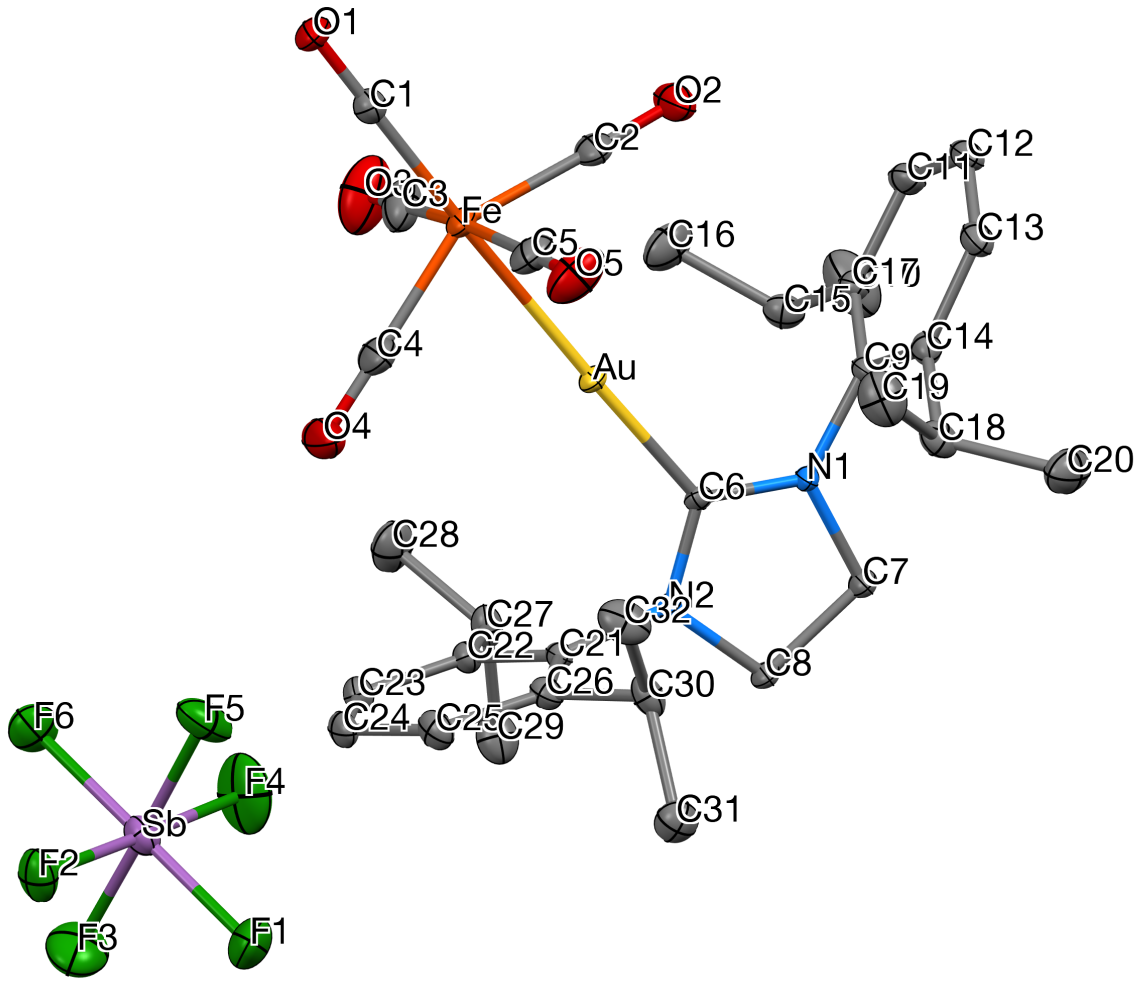


Table S5. Crystal data and structure refinement for [(SIPr)Au-Fe(CO)$_5$][SbF$_6$] (**5**)**.**

Identification code	RAD560
Empirical formula	$C_{32}H_{38}AuF_6FeN_2O_5Sb$
Formula weight	1019.21
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.4358(9)
b/Å	18.8623(14)
c/Å	15.7372(11)
α/°	90
β/°	89.999(2)

γ/°	90
Volume/Å^3	3691.4(5)
Z	4
ρ_{calc}g/cm^3	1.834
μ/mm^{-1}	5.148
F(000)	1976.0
Crystal size/mm^3	0.22 × 0.2 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.61 to 63.012
Index ranges	-18 ≤ h ≤ 18, -27 ≤ k ≤ 27, -23 ≤ l ≤ 23
Reflections collected	55176
Independent reflections	12278 [R_{int} = 0.0298, R_{sigma} = 0.0274]
Data/restraints/parameters	12278/0/442
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0173, wR_2 = 0.0392
Final R indexes [all data]	R_1 = 0.0182, wR_2 = 0.0394
Largest diff. peak/hole / e Å^{-3}	0.67/-1.82

Table S6. Bond Lengths for [(SIPr)Au-Fe(CO)$_5$][SbF$_6$] (**5**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au	Fe	2.5535(3)	C12	C13	1.384(3)
Au	C2	2.672(2)	C13	C14	1.391(3)
Au	C6	2.0147(16)	C14	C18	1.510(3)
Fe	C1	1.8386(18)	C15	C16	1.528(3)
Fe	C2	1.828(3)	C15	C17	1.523(3)
Fe	C3	1.830(3)	C18	C19	1.538(3)
Fe	C4	1.821(3)	C18	C20	1.533(3)
Fe	C5	1.830(2)	C21	C22	1.406(3)
O1	C1	1.122(2)	C21	C26	1.402(3)
O2	C2	1.136(3)	C22	C23	1.393(3)
O3	C3	1.126(3)	C22	C27	1.519(3)
O4	C4	1.136(3)	C23	C24	1.397(3)
O5	C5	1.126(3)	C24	C25	1.382(3)
N1	C6	1.319(2)	C25	C26	1.398(3)
N1	C7	1.479(2)	C26	C30	1.520(3)
N1	C9	1.428(2)	C27	C28	1.529(3)
N2	C6	1.322(2)	C27	C29	1.533(3)
N2	C8	1.473(2)	C30	C31	1.523(3)
N2	C21	1.430(2)	C30	C32	1.527(3)
C7	C8	1.539(3)	Sb	F1	1.8773(14)
C9	C10	1.408(3)	Sb	F2	1.8798(14)

C9	C14	1.402(3)	Sb	F3	1.8676(16)
C10	C11	1.389(3)	Sb	F4	1.8654(15)
C10	C15	1.514(3)	Sb	F5	1.8739(16)
C11	C12	1.392(3)	Sb	F6	1.8759(13)

Table S7. Bond Angles for [(SIPr)Au-Fe(CO)$_5$][SbF$_6$] (**5**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Fe	Au	C2	40.88(5)	C12	C13	C14	120.8(2)
C6	Au	Fe	177.97(5)	C9	C14	C18	122.38(18)
C6	Au	C2	137.36(7)	C13	C14	C9	117.5(2)
C1	Fe	Au	178.30(7)	C13	C14	C18	120.10(19)
C2	Fe	Au	73.06(7)	C10	C15	C16	110.92(18)
C2	Fe	C1	105.27(10)	C10	C15	C17	112.04(19)
C2	Fe	C3	88.65(11)	C17	C15	C16	111.0(2)
C2	Fe	C5	89.75(11)	C14	C18	C19	111.2(2)
C3	Fe	Au	86.19(8)	C14	C18	C20	110.33(19)
C3	Fe	C1	93.54(10)	C20	C18	C19	111.67(19)
C3	Fe	C5	172.58(10)	C22	C21	N2	118.96(17)
C4	Fe	Au	76.01(8)	C26	C21	N2	118.42(18)
C4	Fe	C1	105.66(10)	C26	C21	C22	122.54(18)
C4	Fe	C2	149.06(10)	C21	C22	C27	120.98(18)
C4	Fe	C3	88.54(13)	C23	C22	C21	117.78(18)
C4	Fe	C5	89.11(13)	C23	C22	C27	121.16(18)
C5	Fe	Au	86.42(6)	C22	C23	C24	120.5(2)
C5	Fe	C1	93.87(8)	C25	C24	C23	120.7(2)
C6	N1	C7	112.32(15)	C24	C25	C26	120.82(19)
C6	N1	C9	123.99(16)	C21	C26	C30	122.07(18)
C9	N1	C7	123.69(15)	C25	C26	C21	117.64(19)
C6	N2	C8	112.19(15)	C25	C26	C30	120.28(18)
C6	N2	C21	122.66(16)	C22	C27	C28	112.79(18)
C21	N2	C8	124.65(16)	C22	C27	C29	109.32(18)
O1	C1	Fe	177.45(17)	C28	C27	C29	111.19(19)
Fe	C2	Au	66.07(7)	C26	C30	C31	109.65(18)
O2	C2	Au	115.05(18)	C26	C30	C32	111.9(2)
O2	C2	Fe	178.6(2)	C31	C30	C32	111.67(18)
O3	C3	Fe	179.7(3)	F1	Sb	F2	89.75(7)
O4	C4	Fe	179.4(3)	F3	Sb	F1	90.93(9)
O5	C5	Fe	179.4(2)	F3	Sb	F2	90.65(8)
N1	C6	Au	124.80(13)	F3	Sb	F5	178.81(9)

N1	C6	N2	110.65(14)	F3	Sb	F6	89.32(8)
N2	C6	Au	124.54(14)	F4	Sb	F1	90.91(10)
N1	C7	C8	102.13(16)	F4	Sb	F2	179.01(10)
N2	C8	C7	102.62(16)	F4	Sb	F3	90.08(8)
C10	C9	N1	118.90(18)	F4	Sb	F5	90.75(9)
C14	C9	N1	118.15(18)	F4	Sb	F6	89.71(9)
C14	C9	C10	122.93(18)	F5	Sb	F1	89.91(8)
C9	C10	C15	121.16(18)	F5	Sb	F2	88.52(7)
C11	C10	C9	117.21(19)	F5	Sb	F6	89.83(7)
C11	C10	C15	121.61(19)	F6	Sb	F1	179.34(7)
C10	C11	C12	120.9(2)	F6	Sb	F2	89.63(7)
C13	C12	C11	120.6(2)				

Figure S36. Molecular structure and atom numbering scheme for [(^{Et2}CAAC)AuFe(CO)$_5$)][SbF$_6$] (**6**). Hydrogen atoms have been omitted for clarity.

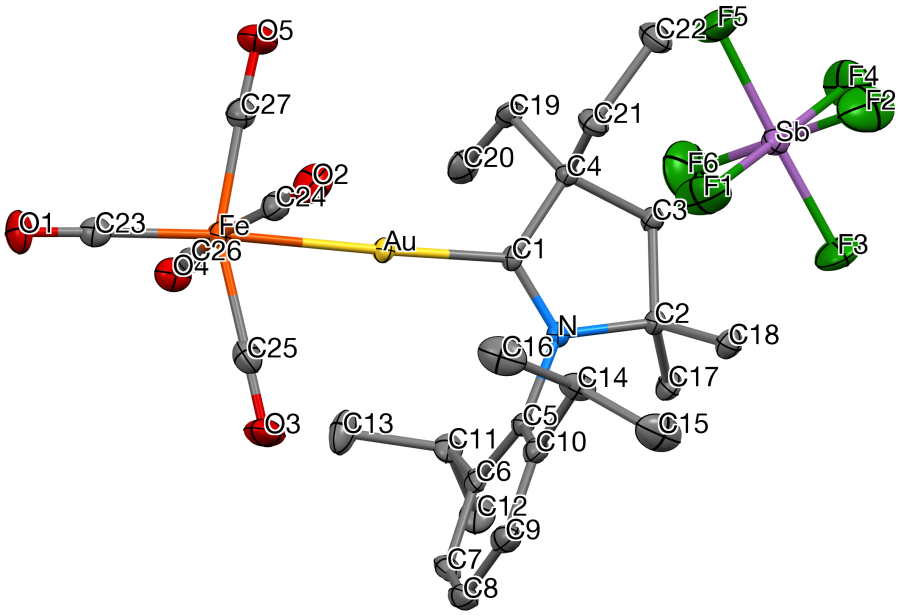


Table S8. Crystal data and structure refinement for [(^{Et2}CAAC)AuFe(CO)$_5$)][SbF$_6$] (**6**).

Identification code	RAD736
Empirical formula	$C_{27}H_{35}AuF_6FeNO_5Sb$
Formula weight	942.12
Temperature/K	100.01
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.2376(9)
b/Å	15.3986(10)
c/Å	14.8972(9)
α/°	90
β/°	98.783(2)
γ/°	90
Volume/Å^3	3227.8(4)
Z	4
ρ_{calc}g/cm^3	1.939
μ/mm^{-1}	5.878
F(000)	1816.0
Crystal size/mm^3	0.11 × 0.11 × 0.1

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.79 to 61.128
Index ranges	$-20 \le h \le 20$, $-22 \le k \le 22$, $-21 \le l \le 21$
Reflections collected	81911
Independent reflections	9890 [R_{int} = 0.0914, R_{sigma} = 0.0546]
Data/restraints/parameters	9890/0/387
Goodness-of-fit on F^2	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0358, wR_2 = 0.0534
Final R indexes [all data]	R_1 = 0.0626, wR_2 = 0.0594
Largest diff. peak/hole / e $Å^{-3}$	0.86/-1.29

Table S9. Bond Lengths for [(^{Et2}CAAC)AuFe(CO)$_5$)][SbF$_6$] (**6**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au	Fe	2.5696(5)	C4	C21	1.549(5)
Au	C1	2.020(3)	C5	C6	1.399(5)
Fe	C23	1.859(4)	C5	C10	1.406(5)
Fe	C24	1.838(4)	C6	C7	1.397(5)
Fe	C25	1.831(4)	C6	C11	1.514(5)
Fe	C26	1.815(4)	C7	C8	1.372(6)
Fe	C27	1.835(4)	C8	C9	1.384(6)
O1	C23	1.123(4)	C9	C10	1.393(5)
O2	C24	1.126(5)	C10	C14	1.528(5)
O3	C25	1.129(5)	C11	C12	1.532(5)
O4	C26	1.130(4)	C11	C13	1.536(5)
O5	C27	1.132(5)	C14	C15	1.528(6)
N	C1	1.293(4)	C14	C16	1.532(6)
N	C2	1.535(4)	C19	C20	1.520(5)
N	C5	1.458(4)	C21	C22	1.530(5)
C1	C4	1.498(5)	Sb	F1	1.862(3)
C2	C3	1.534(5)	Sb	F2	1.867(3)
C2	C17	1.523(5)	Sb	F3	1.870(3)
C2	C18	1.534(5)	Sb	F4	1.866(3)
C3	C4	1.555(5)	Sb	F5	1.882(3)
C4	C19	1.530(5)	Sb	F6	1.852(3)

Table S10. Bond Angles for [(^{Et2}CAAC)AuFe(CO)$_5$)][SbF$_6$] (**6**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Au	Fe	177.85(10)	C5	C6	C11	123.6(3)
C23	Fe	Au	173.46(12)	C7	C6	C5	117.1(3)

C24	Fe	Au	86.03(12)	C7	C6	C11	119.1(3)
C24	Fe	C23	99.99(17)	C8	C7	C6	121.2(4)
C25	Fe	Au	76.40(13)	C7	C8	C9	120.6(4)
C25	Fe	C23	101.02(17)	C8	C9	C10	121.0(4)
C25	Fe	C24	88.93(17)	C5	C10	C14	123.8(3)
C25	Fe	C27	156.09(18)	C9	C10	C5	117.1(3)
C26	Fe	Au	80.07(12)	C9	C10	C14	119.0(3)
C26	Fe	C23	94.01(17)	C6	C11	C12	113.4(3)
C26	Fe	C24	165.87(17)	C6	C11	C13	109.4(3)
C26	Fe	C25	90.28(17)	C12	C11	C13	110.0(3)
C26	Fe	C27	88.75(17)	C10	C14	C16	110.2(3)
C27	Fe	Au	79.90(12)	C15	C14	C10	112.0(3)
C27	Fe	C23	102.88(17)	C15	C14	C16	110.6(3)
C27	Fe	C24	86.29(18)	C20	C19	C4	114.2(3)
C1	N	C2	114.4(3)	C22	C21	C4	114.9(3)
C1	N	C5	123.0(3)	O1	C23	Fe	175.5(3)
C5	N	C2	122.5(3)	O2	C24	Fe	175.5(4)
N	C1	Au	124.2(3)	O3	C25	Fe	178.7(4)
N	C1	C4	112.0(3)	O4	C26	Fe	179.0(4)
C4	C1	Au	123.7(2)	O5	C27	Fe	177.8(4)
C3	C2	N	101.0(3)	F1	Sb	F2	90.25(16)
C3	C2	C18	112.7(3)	F1	Sb	F3	90.36(13)
C17	C2	N	111.3(3)	F1	Sb	F4	179.56(14)
C17	C2	C3	112.5(3)	F1	Sb	F5	90.39(12)
C17	C2	C18	109.4(3)	F2	Sb	F3	88.94(14)
C18	C2	N	109.6(3)	F2	Sb	F5	89.36(14)
C2	C3	C4	107.4(3)	F3	Sb	F5	178.14(13)
C1	C4	C3	103.1(3)	F4	Sb	F2	89.70(16)
C1	C4	C19	111.0(3)	F4	Sb	F3	90.07(13)
C1	C4	C21	105.7(3)	F4	Sb	F5	89.17(13)
C19	C4	C3	112.7(3)	F6	Sb	F1	90.00(16)
C19	C4	C21	111.6(3)	F6	Sb	F2	179.70(17)
C21	C4	C3	112.2(3)	F6	Sb	F3	90.88(15)
C6	C5	N	118.9(3)	F6	Sb	F4	90.06(16)
C6	C5	C10	122.8(3)	F6	Sb	F5	90.82(15)
C10	C5	N	118.3(3)				

Figure S37. Molecular structure and atom numbering scheme for [(SIPr)AuMn(CO)$_5$] (**7**)•THF**.** Hydrogen atoms have been omitted for clarity.

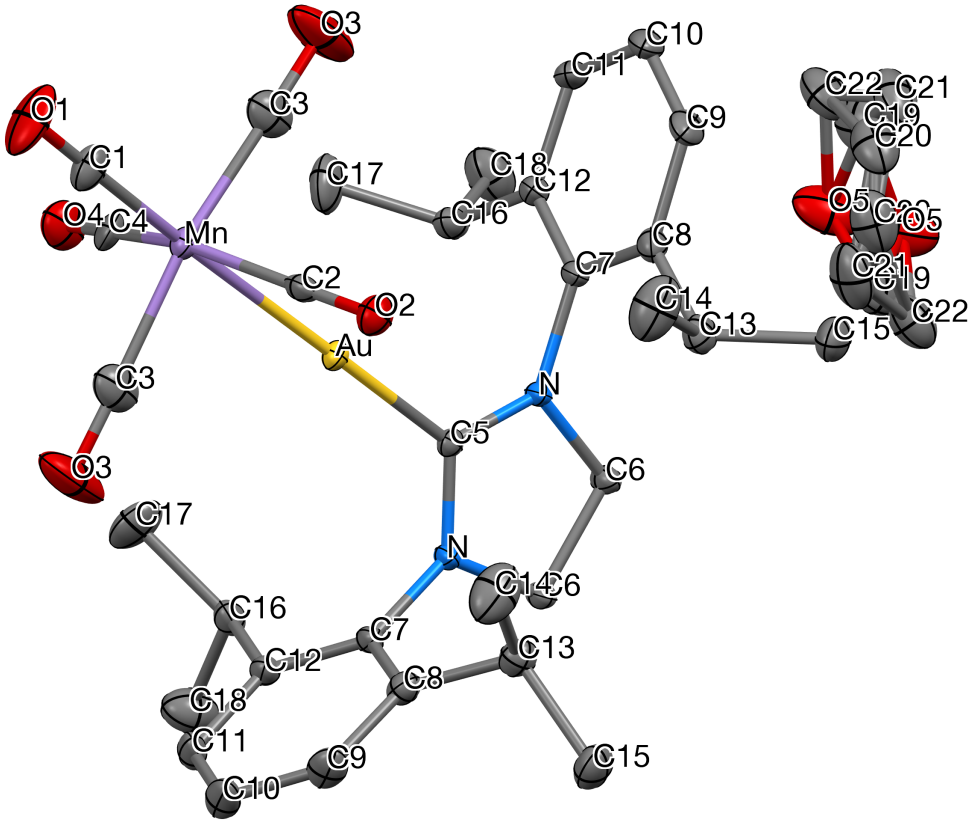


Table S11. Crystal data and structure refinement [(SIPr)AuMn(CO)$_5$] (**7**)•THF**.**

Identification code	RAD568
Empirical formula	$C_{36}H_{46}AuMnN_2O_6$
Formula weight	854.65
Temperature/K	100.01
Crystal system	orthorhombic
Space group	Pbcm
a/Å	8.6463(5)
b/Å	19.4473(12)
c/Å	21.4257(13)
α/°	90
β/°	90
γ/°	90

Volume/Å^3	3602.7(4)
Z	4
ρ_{calc}g/cm^3	1.576
μ/mm^{-1}	4.463
F(000)	1712.0
Crystal size/mm^3	0.18 × 0.14 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.056 to 56.556
Index ranges	-11 ≤ h ≤ 11, -25 ≤ k ≤ 25, -28 ≤ l ≤ 28
Reflections collected	41145
Independent reflections	4588 [R_{int} = 0.0457, R_{sigma} = 0.0244]
Data/restraints/parameters	4588/0/248
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0196, wR_2 = 0.0375
Final R indexes [all data]	R_1 = 0.0248, wR_2 = 0.0388
Largest diff. peak/hole / e Å^{-3}	0.58/-0.91

Table S12. Bond Lengths for [(SIPr)AuMn(CO)$_5$] (**7**)•THF**.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au	Mn	2.5754(4)	C7	C12	1.399(3)
Au	C2	2.688(3)	C8	C9	1.396(3)
Au	C5	2.025(3)	C8	C13	1.515(3)
Mn	C1	1.805(3)	C9	C10	1.380(3)
Mn	C2	1.829(3)	C10	C11	1.380(3)
Mn	C3	1.834(2)	C11	C12	1.394(3)
Mn	C3^1	1.834(2)	C12	C16	1.513(3)
Mn	C4	1.833(3)	C13	C14	1.527(3)
O1	C1	1.147(4)	C13	C15	1.527(3)
O2	C2	1.151(4)	C16	C17	1.522(3)
O3	C3	1.139(3)	C16	C18	1.518(3)
O4	C4	1.142(4)	O5	C19	1.415(11)
N	C5	1.328(2)	O5	C22	1.438(11)
N	C6	1.474(2)	C19	C20	1.503(13)
N	C7	1.439(2)	C20	C21	1.508(11)
C6	C6^1	1.535(4)	C21	C22	1.496(13)
C7	C8	1.397(3)			

^{1}+X,+Y,3/2-Z

Table S13. Bond Angles for [(SIPr)AuMn(CO)$_5$] (**7**)•THF.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Mn	Au	C2	40.60(7)	N^1	C5	Au	125.30(11)
C5	Au	Mn	177.90(7)	N	C5	Au	125.30(12)
C5	Au	C2	141.51(10)	N^1	C5	N	109.4(2)
C1	Mn	Au	173.24(10)	N	C6	C6^1	102.38(9)
C1	Mn	C2	100.21(14)	C8	C7	N	118.53(17)
C1	Mn	C3	96.40(9)	C8	C7	C12	122.56(18)
C1	Mn	C3^1	96.40(9)	C12	C7	N	118.90(17)
C1	Mn	C4	104.69(13)	C7	C8	C13	123.17(18)
C2	Mn	Au	73.02(9)	C9	C8	C7	117.60(19)
C2	Mn	C3	90.04(7)	C9	C8	C13	119.23(19)
C2	Mn	C3^1	90.04(7)	C10	C9	C8	120.7(2)
C2	Mn	C4	155.10(13)	C11	C10	C9	120.7(2)
C3^1	Mn	Au	83.79(9)	C10	C11	C12	120.7(2)
C3	Mn	Au	83.79(9)	C7	C12	C16	122.02(18)
C3^1	Mn	C3	166.98(17)	C11	C12	C7	117.66(19)
C4	Mn	Au	82.07(9)	C11	C12	C16	120.31(19)
C4	Mn	C3^1	87.22(7)	C8	C13	C14	110.68(19)
C4	Mn	C3	87.22(7)	C8	C13	C15	111.68(19)
C5	N	C6	112.94(16)	C14	C13	C15	110.57(19)
C5	N	C7	124.79(17)	C12	C16	C17	110.89(19)
C7	N	C6	121.90(15)	C12	C16	C18	112.20(19)
O1	C1	Mn	178.6(3)	C18	C16	C17	110.8(2)
Mn	C2	Au	66.38(9)	C19	O5	C22	109.4(4)
O2	C2	Au	115.2(2)	O5	C19	C20	106.1(7)
O2	C2	Mn	178.4(3)	C19	C20	C21	102.1(8)
O3	C3	Mn	178.1(2)	C22	C21	C20	101.7(7)
O4	C4	Mn	179.1(3)	O5	C22	C21	106.0(7)

^{1}+X,+Y,3/2-Z

Figure S38. Molecular structure and atom numbering scheme for [$Mes_3PAuMn(CO)_5$] (**8**). Hydrogen atoms have been omitted for clarity.

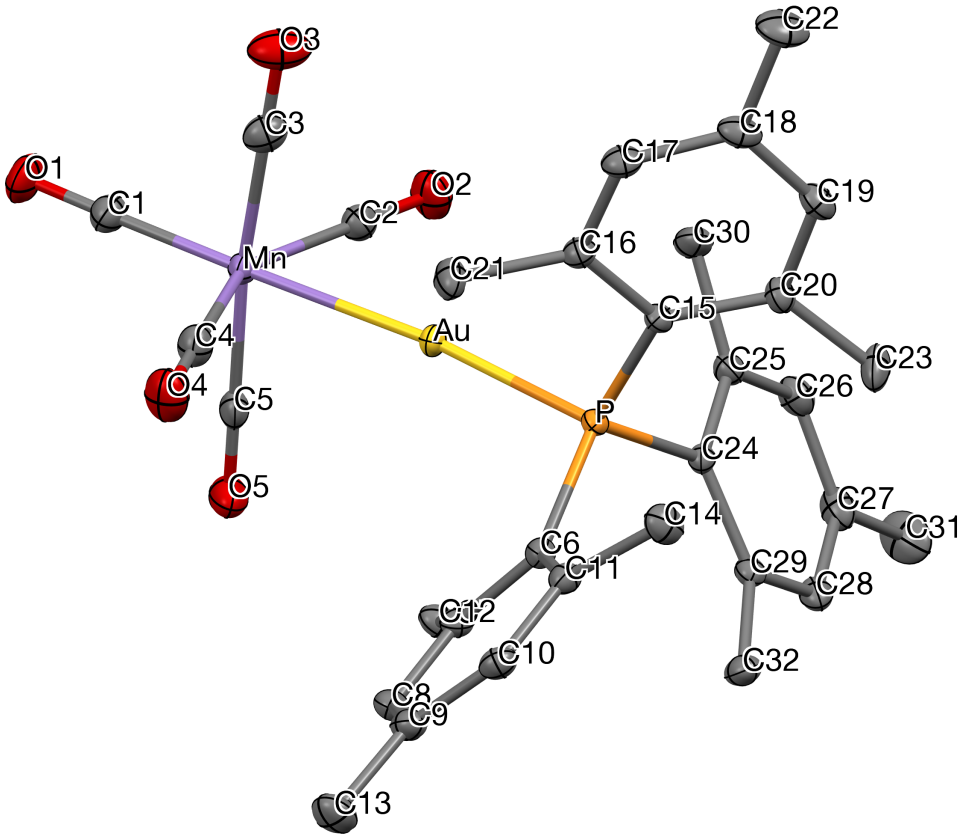


Table S14. Crystal data and structure refinement for [$Mes_3PAuMn(CO)_5$] (**8**).

Identification code	RAD575
Empirical formula	$C_{32}H_{33}AuMnO_5P$
Formula weight	780.46
Temperature/K	99.94
Crystal system	triclinic
Space group	P-1
a/Å	10.8061(8)
b/Å	11.9033(9)
c/Å	13.6638(10)
α/°	82.628(2)
β/°	78.028(2)
γ/°	64.197(2)

Volume/Å^3	1546.5(2)
Z	2
ρ_{calc}g/cm^3	1.676
μ/mm^{-1}	5.235
F(000)	768.0
Crystal size/mm^3	0.14 × 0.09 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.102 to 61.016
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -19 ≤ l ≤ 19
Reflections collected	21831
Independent reflections	9373 [R_{int} = 0.0175, R_{sigma} = 0.0241]
Data/restraints/parameters	9373/0/370
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0177, wR_2 = 0.0433
Final R indexes [all data]	R_1 = 0.0191, wR_2 = 0.0438
Largest diff. peak/hole / e Å^{-3}	0.78/-1.56

Table S15. Bond Lengths for [$Mes_3PAuMn(CO)_5$] (**8**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au	Mn	2.5746(3)	C9	C13	1.509(2)
Au	P	2.3238(4)	C10	C11	1.393(2)
Mn	C1	1.8215(18)	C11	C14	1.515(2)
Mn	C2	1.8251(18)	C15	C16	1.418(2)
Mn	C3	1.8408(19)	C15	C20	1.413(2)
Mn	C4	1.8436(18)	C16	C17	1.395(2)
Mn	C5	1.8443(19)	C16	C21	1.506(2)
P	C6	1.8409(16)	C17	C18	1.385(2)
P	C15	1.8336(16)	C18	C19	1.388(3)
P	C24	1.8325(16)	C18	C22	1.504(2)
O1	C1	1.146(2)	C19	C20	1.397(2)
O2	C2	1.147(2)	C20	C23	1.509(2)
O3	C3	1.140(2)	C24	C25	1.416(2)
O4	C4	1.145(2)	C24	C29	1.414(2)
O5	C5	1.142(2)	C25	C26	1.393(2)
C6	C7	1.417(2)	C25	C30	1.511(2)
C6	C11	1.415(2)	C26	C27	1.387(3)
C7	C8	1.391(2)	C27	C28	1.382(3)
C7	C12	1.510(2)	C27	C31	1.507(3)
C8	C9	1.387(2)	C28	C29	1.400(2)
C9	C10	1.388(2)	C29	C32	1.504(2)

Table S16. Bond Angles for [$Mes_3PAuMn(CO)_5$] (**8**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P	Au	Mn	174.496(11)	C8	C9	C13	120.48(16)
C1	Mn	Au	178.72(6)	C10	C9	C13	121.87(16)
C1	Mn	C2	104.78(8)	C9	C10	C11	122.71(15)
C1	Mn	C3	93.43(8)	C6	C11	C14	124.75(15)
C1	Mn	C4	105.36(8)	C10	C11	C6	118.89(15)
C1	Mn	C5	92.79(8)	C10	C11	C14	116.29(15)
C2	Mn	Au	75.10(6)	C16	C15	P	116.78(12)
C2	Mn	C3	89.63(8)	C20	C15	P	123.99(12)
C2	Mn	C4	149.83(8)	C20	C15	C16	119.11(14)
C2	Mn	C5	88.92(8)	C15	C16	C21	124.00(14)
C3	Mn	Au	85.30(6)	C17	C16	C15	119.12(15)
C3	Mn	C4	89.81(8)	C17	C16	C21	116.82(15)
C3	Mn	C5	173.78(8)	C18	C17	C16	122.22(16)
C4	Mn	Au	74.79(6)	C17	C18	C19	117.92(15)
C4	Mn	C5	88.41(8)	C17	C18	C22	121.16(17)
C5	Mn	Au	88.48(5)	C19	C18	C22	120.91(17)
C6	P	Au	105.86(5)	C18	C19	C20	122.38(16)
C15	P	Au	110.78(5)	C15	C20	C23	124.95(15)
C15	P	C6	110.08(7)	C19	C20	C15	118.91(15)
C24	P	Au	107.20(5)	C19	C20	C23	116.09(15)
C24	P	C6	112.54(7)	C25	C24	P	116.78(11)
C24	P	C15	110.26(7)	C29	C24	P	123.83(12)
O1	C1	Mn	178.65(18)	C29	C24	C25	119.21(14)
O2	C2	Mn	179.04(16)	C24	C25	C30	123.77(15)
O3	C3	Mn	179.34(18)	C26	C25	C24	119.40(15)
O4	C4	Mn	178.97(18)	C26	C25	C30	116.78(15)
O5	C5	Mn	179.75(19)	C27	C26	C25	121.96(16)
C7	C6	P	116.71(12)	C26	C27	C31	121.08(18)
C11	C6	P	124.03(12)	C28	C27	C26	117.96(15)
C11	C6	C7	118.72(14)	C28	C27	C31	120.95(17)
C6	C7	C12	124.28(14)	C27	C28	C29	122.76(16)
C8	C7	C6	119.48(15)	C24	C29	C32	125.01(14)
C8	C7	C12	116.05(14)	C28	C29	C24	118.45(15)
C9	C8	C7	122.14(15)	C28	C29	C32	116.45(14)
C8	C9	C10	117.62(15)				

Figure S39. Molecular structure and atom numbering scheme for [(SIPr)AgMn(CO)$_5$] (**9**)•THF. Hydrogen atoms have been omitted for clarity.

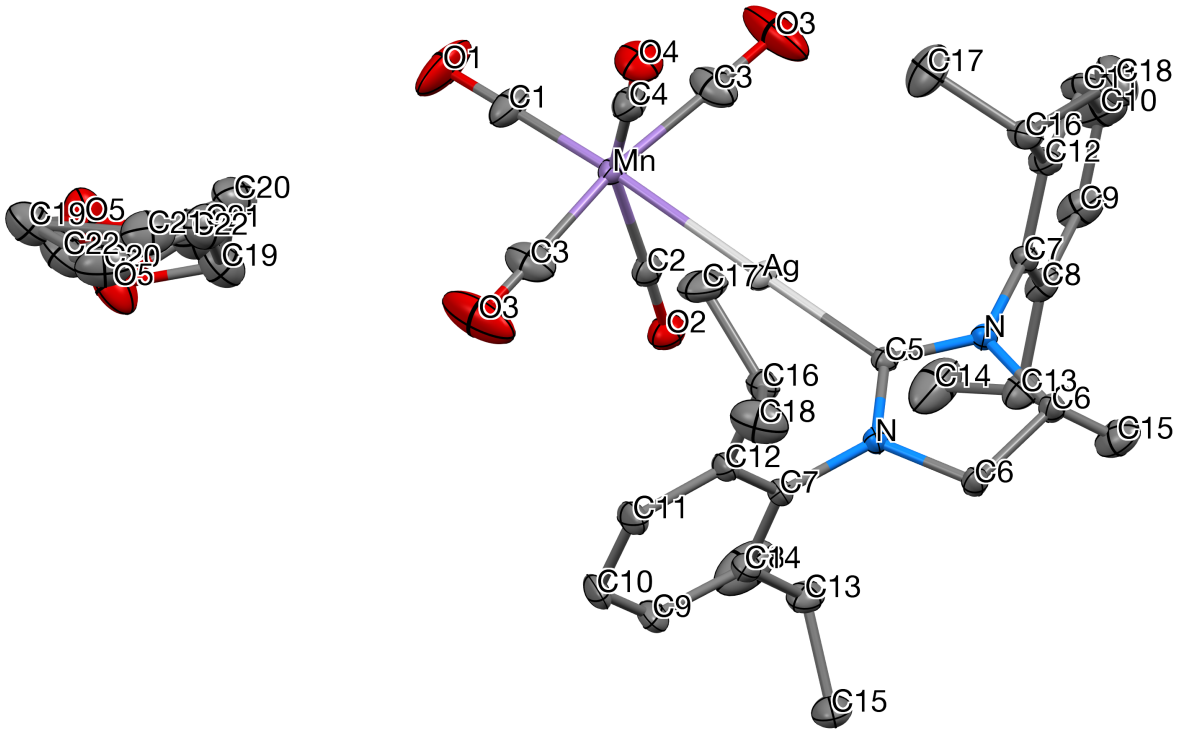


Table S17. Crystal data and structure refinement for [(SIPr)AgMn(CO)$_5$] (**9**)•THF.

Identification code	RAD569
Empirical formula	$C_{36}H_{46}AgMnN_2O_6$
Formula weight	765.56
Temperature/K	100.0
Crystal system	orthorhombic
Space group	Pbcm
a/Å	8.6971(6)
b/Å	19.4845(13)
c/Å	21.3902(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3624.8(4)
Z	4
ρ_{calc}g/cm^3	1.403
μ/mm^{-1}	0.933

F(000)	1584.0
Crystal size/mm^3	0.18 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.038 to 63.01
Index ranges	-12 ≤ h ≤ 12, -28 ≤ k ≤ 28, -31 ≤ l ≤ 31
Reflections collected	51706
Independent reflections	6180 [R_{int} = 0.0296, R_{sigma} = 0.0168]
Data/restraints/parameters	6180/66/248
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0239, wR_2 = 0.0590
Final R indexes [all data]	R_1 = 0.0284, wR_2 = 0.0613
Largest diff. peak/hole / e Å^{-3}	0.48/-0.73

Table S18. Bond Lengths for [(SIPr)AgMn(CO)$_5$] (**9**)•THF**.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ag	Mn	2.5905(3)	C7	C12	1.4010(15)
Ag	C2	2.6789(17)	C8	C9	1.3981(17)
Ag	C5	2.1133(15)	C8	C13	1.5147(18)
Mn	C1	1.8038(19)	C9	C10	1.380(2)
Mn	C2	1.8300(17)	C10	C11	1.384(2)
Mn	C3[1]	1.8318(15)	C11	C12	1.3950(16)
Mn	C3	1.8318(15)	C12	C16	1.5169(17)
Mn	C4	1.8360(18)	C13	C14	1.530(2)
O1	C1	1.144(2)	C13	C15	1.5285(18)
O2	C2	1.151(2)	C16	C17	1.5237(18)
O3	C3	1.1407(19)	C16	C18	1.522(2)
O4	C4	1.145(2)	O5	C19	1.432(5)
N	C5	1.3307(12)	O5	C22	1.431(5)
N	C6	1.4773(13)	C19	C20	1.510(5)
N	C7	1.4376(13)	C20	C21	1.506(6)
C6	C6[1]	1.534(2)	C21	C22	1.509(5)
C7	C8	1.4033(15)			

[1]+X,+Y,3/2-Z

Table S19. Bond Angles for [(SIPr)AgMn(CO)$_5$] (**9**)•THF

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Mn	Ag	C2	40.60(4)	N[1]	C5	Ag	125.59(6)
C5	Ag	Mn	179.03(4)	N	C5	Ag	125.59(6)
C5	Ag	C2	140.37(5)	N[1]	C5	N	108.76(13)

C1	Mn	Ag	173.56(6)	N	C6	C6[1]	102.30(5)
C1	Mn	C2	101.26(8)	C8	C7	N	118.74(10)
C1	Mn	C3[1]	95.44(6)	C12	C7	N	118.94(10)
C1	Mn	C3	95.45(6)	C12	C7	C8	122.32(10)
C1	Mn	C4	106.97(8)	C7	C8	C13	122.89(10)
C2	Mn	Ag	72.30(5)	C9	C8	C7	117.68(11)
C2	Mn	C3[1]	90.31(4)	C9	C8	C13	119.43(11)
C2	Mn	C3	90.30(4)	C10	C9	C8	120.89(12)
C2	Mn	C4	151.77(8)	C9	C10	C11	120.43(12)
C3	Mn	Ag	84.74(6)	C10	C11	C12	121.01(13)
C3[1]	Mn	Ag	84.75(6)	C7	C12	C16	121.85(10)
C3	Mn	C3[1]	168.76(11)	C11	C12	C7	117.67(11)
C3	Mn	C4	87.08(5)	C11	C12	C16	120.47(11)
C3[1]	Mn	C4	87.08(5)	C8	C13	C14	110.46(12)
C4	Mn	Ag	79.47(6)	C8	C13	C15	111.59(12)
C5	N	C6	113.31(9)	C15	C13	C14	110.42(12)
C5	N	C7	124.35(9)	C12	C16	C17	110.58(11)
C7	N	C6	121.97(8)	C12	C16	C18	112.27(11)
O1	C1	Mn	178.83(18)	C18	C16	C17	111.22(12)
Mn	C2	Ag	67.11(5)	C22	O5	C19	109.7(3)
O2	C2	Ag	115.18(12)	O5	C19	C20	105.5(3)
O2	C2	Mn	177.71(15)	C21	C20	C19	102.3(3)
O3	C3	Mn	178.49(14)	C20	C21	C22	102.0(3)
O4	C4	Mn	179.23(16)	O5	C22	C21	106.1(3)

[1]+X,+Y,3/2-Z

Figure S40. Molecular structure and atom numbering scheme for [(SIPr)CuNCFe(CO)$_4$] (**12**)•CH_2Cl_2**.** Hydrogen atoms have been omitted for clarity.

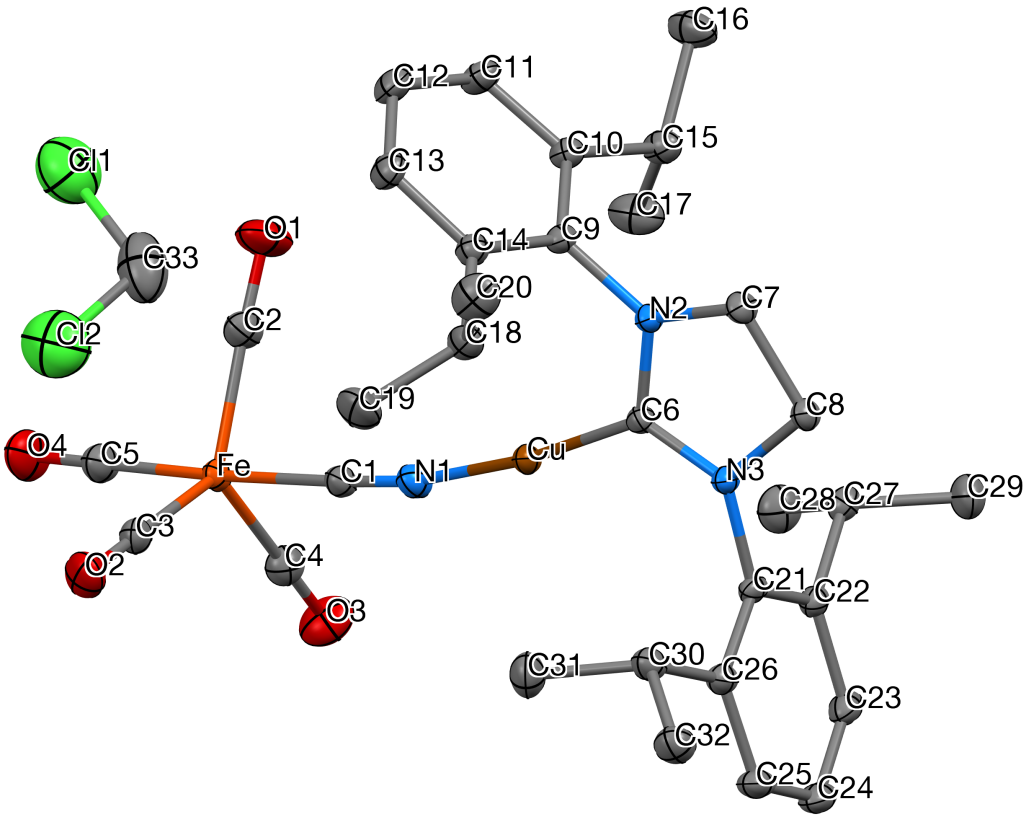


Table S20. Crystal data and structure refinement for [(SIPr)CuNCFe(CO)$_4$] (**12**)•CH_2Cl_2**.**

Identification code	RAD605
Empirical formula	$C_{33}H_{40}Cl_2CuFeN_3O_4$
Formula weight	732.97
Temperature/K	99.99
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.1739(7)
b/Å	18.4203(11)
c/Å	18.3635(11)
α/°	90
β/°	106.685(2)
γ/°	90
Volume/Å^3	3620.6(4)
Z	4
ρ_{calc}g/cm^3	1.345
μ/mm^{-1}	1.173
F(000)	1520.0

Crystal size/mm^3	0.48 × 0.26 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.406 to 61.016
Index ranges	-15 ≤ h ≤ 15, -26 ≤ k ≤ 26, -26 ≤ l ≤ 26
Reflections collected	50316
Independent reflections	11033 [R_{int} = 0.0229, R_{sigma} = 0.0196]
Data/restraints/parameters	11033/0/405
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0324, wR_2 = 0.0856
Final R indexes [all data]	R_1 = 0.0366, wR_2 = 0.0885
Largest diff. peak/hole / e Å^{-3}	0.84/-1.21

Table S21. Bond Lengths for [(SIPr)CuNCFe(CO)$_4$] (**12**)•CH_2Cl_2

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu	N1	1.8378(12)	C11	C12	1.387(2)
Cu	C6	1.8834(12)	C12	C13	1.385(2)
Fe	C1	1.9073(13)	C13	C14	1.3983(18)
Fe	C2	1.7945(15)	C14	C18	1.5184(19)
Fe	C3	1.8007(15)	C15	C16	1.528(2)
Fe	C4	1.8003(15)	C15	C17	1.528(2)
Fe	C5	1.7880(15)	C18	C19	1.531(2)
O1	C2	1.1408(19)	C18	C20	1.531(2)
O2	C3	1.1454(18)	C21	C22	1.4008(18)
O3	C4	1.139(2)	C21	C26	1.4054(18)
O4	C5	1.1401(19)	C22	C23	1.3976(18)
N1	C1	1.1535(18)	C22	C27	1.5178(19)
N2	C6	1.3377(15)	C23	C24	1.387(2)
N2	C7	1.4806(16)	C24	C25	1.383(2)
N2	C9	1.4399(16)	C25	C26	1.3963(18)
N3	C6	1.3335(15)	C26	C30	1.519(2)
N3	C8	1.4791(16)	C27	C28	1.529(2)
N3	C21	1.4362(15)	C27	C29	1.527(2)
C7	C8	1.5334(18)	C30	C31	1.535(2)
C9	C10	1.4054(17)	C30	C32	1.528(2)
C9	C14	1.4032(18)	Cl1	C33	1.766(3)
C10	C11	1.3933(18)	Cl2	C33	1.759(3)
C10	C15	1.5175(19)			

Table S22. Bond Angles for [(SIPr)CuNCFe(CO)$_4$] (**12**)•CH_2Cl_2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Cu	C6	173.56(5)	C11	C10	C15	121.62(12)
C2	Fe	C1	85.48(6)	C12	C11	C10	120.97(13)
C2	Fe	C3	122.06(7)	C13	C12	C11	120.51(13)
C2	Fe	C4	119.16(7)	C12	C13	C14	120.80(13)
C3	Fe	C1	88.03(6)	C9	C14	C18	122.65(12)
C4	Fe	C1	90.68(6)	C13	C14	C9	117.63(12)
C4	Fe	C3	118.42(7)	C13	C14	C18	119.72(12)
C5	Fe	C1	177.55(6)	C10	C15	C16	113.32(12)
C5	Fe	C2	92.12(7)	C10	C15	C17	110.56(13)
C5	Fe	C3	92.82(7)	C16	C15	C17	109.62(13)
C5	Fe	C4	90.93(7)	C14	C18	C19	111.11(13)
C1	N1	Cu	171.57(12)	C14	C18	C20	110.90(12)
C6	N2	C7	112.74(10)	C19	C18	C20	111.12(14)
C6	N2	C9	122.96(10)	C22	C21	N3	118.71(11)
C9	N2	C7	121.82(10)	C22	C21	C26	122.86(12)
C6	N3	C8	112.70(10)	C26	C21	N3	118.36(12)
C6	N3	C21	125.56(10)	C21	C22	C27	122.37(11)
C21	N3	C8	120.48(10)	C23	C22	C21	117.50(12)
N1	C1	Fe	177.26(13)	C23	C22	C27	120.11(12)
O1	C2	Fe	177.73(15)	C24	C23	C22	120.82(13)
O2	C3	Fe	179.18(13)	C25	C24	C23	120.43(13)
O3	C4	Fe	178.19(14)	C24	C25	C26	121.19(13)
O4	C5	Fe	179.14(16)	C21	C26	C30	121.56(11)
N2	C6	Cu	122.15(9)	C25	C26	C21	117.18(13)
N3	C6	Cu	129.16(9)	C25	C26	C30	121.18(12)
N3	C6	N2	108.64(11)	C22	C27	C28	110.46(12)
N2	C7	C8	101.66(10)	C22	C27	C29	112.00(12)
N3	C8	C7	102.02(10)	C29	C27	C28	110.98(13)
C10	C9	N2	118.70(11)	C26	C30	C31	109.37(12)
C14	C9	N2	118.80(11)	C26	C30	C32	113.54(12)
C14	C9	C10	122.50(12)	C32	C30	C31	110.05(12)
C9	C10	C15	120.75(12)	Cl2	C33	Cl1	111.91(14)
C11	C10	C9	117.59(12)				

Figure S41. Molecular structure of **[(SIPr)H][Fe(CO)$_4$CN]•THF**.

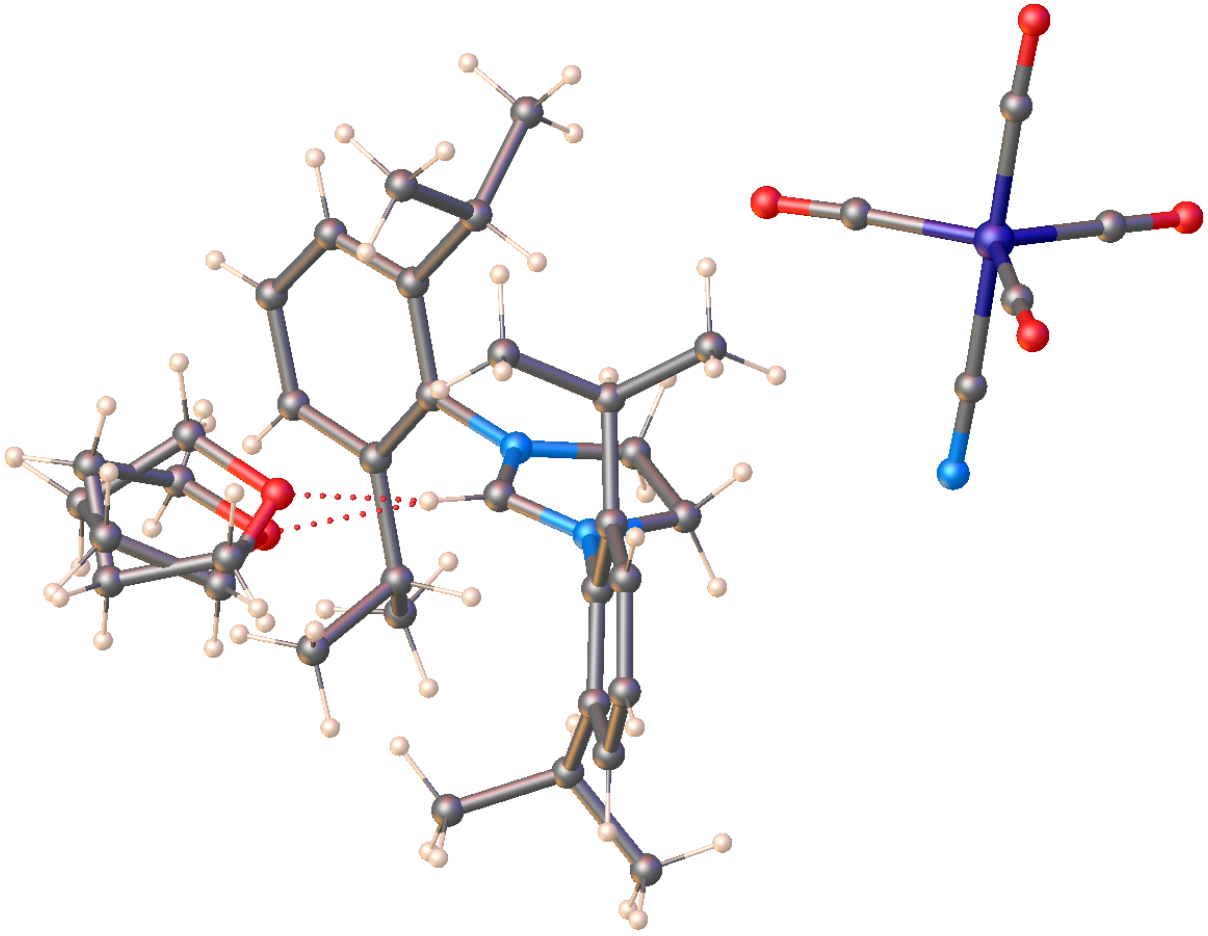


Figure S42. Molecular structure and atom numbering scheme for **[(SIPr)H][Fe(CO)$_4$CN]•THF.** Hydrogen atoms have been omitted for clarity.

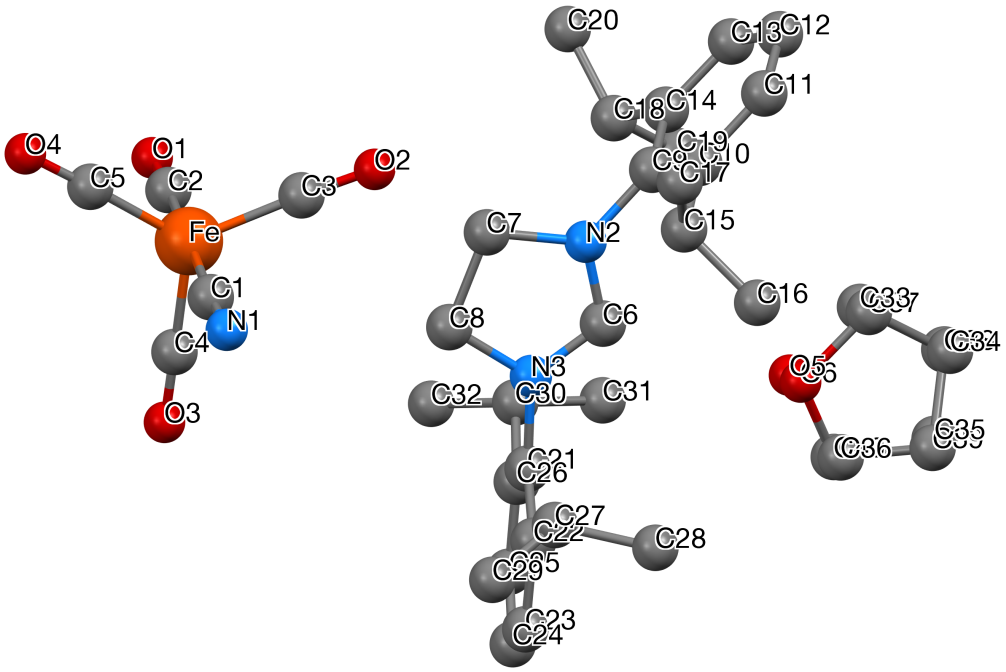


Table S23. Crystal data and structure refinement for [(SIPr)H][Fe(CO)$_4$CN]•THF.

Identification code	RAD598
Empirical formula	$C_{36}H_{47}FeN_3O_5$
Formula weight	657.61
Temperature/K	200.01
Crystal system	triclinic
Space group	P-1
a/Å	9.9687(5)
b/Å	13.3064(6)
c/Å	14.7378(7)
α/°	91.383(2)
β/°	100.116(2)
γ/°	105.058(2)
Volume/Å^3	1853.45(15)
Z	2
ρ_{calc}g/cm^3	1.178
μ/mm^{-1}	0.448

F(000)	700.0
Crystal size/mm^3	0.4 × 0.16 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.002 to 56.562
Index ranges	-13 ≤ h ≤ 13, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19
Reflections collected	22318
Independent reflections	9185 [R_{int} = 0.0245, R_{sigma} = 0.0317]
Data/restraints/parameters	9185/76/460
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0510, wR_2 = 0.1419
Final R indexes [all data]	R_1 = 0.0666, wR_2 = 0.1526
Largest diff. peak/hole / e Å^{-3}	0.68/-0.39

Table S24. Bond Lengths for [(SIPr)H][Fe(CO)$_4$CN]•THF.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe	C1	1.932(2)	C14	C18	1.522(3)
Fe	C4	1.771(2)	C14	C13	1.388(3)
Fe	C3	1.785(3)	C10	C15	1.516(3)
Fe	C5	1.780(3)	C10	C11	1.394(3)
Fe	C2	1.770(2)	C24	C25	1.373(3)
N3	C6	1.303(2)	C27	C29	1.525(3)
N3	C21	1.442(2)	C27	C28	1.525(4)
N3	C8	1.477(2)	C18	C20	1.517(4)
N2	C6	1.306(2)	C18	C19	1.511(4)
N2	C7	1.480(2)	C15	C17	1.515(4)
N2	C9	1.440(2)	C15	C16	1.512(5)
N1	C1	1.155(3)	C11	C12	1.370(4)
C7	C8	1.528(3)	C13	C12	1.375(4)
C21	C22	1.396(3)	C32	C30	1.507(4)
C21	C26	1.394(3)	C31	C30	1.515(5)
O3	C4	1.140(3)	O6	C40	1.436(2)
C9	C14	1.396(3)	O6	C37	1.435(2)
C9	C10	1.393(3)	C39	C40	1.535(2)
O2	C3	1.144(3)	C39	C38	1.533(2)
C22	C23	1.392(3)	C37	C38	1.534(2)
C22	C27	1.518(3)	O5	C36	1.440(2)
C26	C25	1.391(3)	O5	C33	1.432(2)
C26	C30	1.518(3)	C36	C35	1.534(2)
O1	C2	1.152(3)	C35	C34	1.532(2)
O4	C5	1.142(3)	C33	C34	1.532(2)
C23	C24	1.374(3)			

Table S25. Bond Angles for [(SIPr)H][Fe(CO)$_4$CN]•THF.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	Fe	C1	88.83(10)	C9	C10	C15	122.62(18)
C4	Fe	C3	119.35(13)	C9	C10	C11	116.6(2)
C4	Fe	C5	117.39(13)	C11	C10	C15	120.69(19)
C3	Fe	C1	85.26(10)	C25	C24	C23	120.4(2)
C5	Fe	C1	88.92(10)	C22	C27	C29	112.31(19)
C5	Fe	C3	122.75(13)	C22	C27	C28	109.0(2)
C2	Fe	C1	179.73(11)	C29	C27	C28	111.3(2)
C2	Fe	C4	90.98(12)	O3	C4	Fe	178.4(2)
C2	Fe	C3	95.01(13)	C20	C18	C14	112.0(2)
C2	Fe	C5	91.00(13)	C19	C18	C14	110.4(2)
C6	N3	C21	126.73(15)	C19	C18	C20	110.7(3)
C6	N3	C8	110.30(14)	C17	C15	C10	112.5(2)
C21	N3	C8	122.97(14)	C16	C15	C10	111.0(2)
C6	N2	C7	110.30(14)	C16	C15	C17	110.2(2)
C6	N2	C9	124.98(15)	C24	C25	C26	121.34(19)
C9	N2	C7	124.69(15)	O2	C3	Fe	176.6(2)
N3	C6	N2	113.70(15)	C12	C11	C10	121.2(2)
N1	C1	Fe	177.75(17)	O4	C5	Fe	177.7(3)
N2	C7	C8	102.67(14)	O1	C2	Fe	177.7(3)
C22	C21	N3	118.45(15)	C12	C13	C14	120.8(2)
C26	C21	N3	118.44(17)	C11	C12	C13	120.8(2)
C26	C21	C22	123.09(17)	C32	C30	C26	112.1(2)
C14	C9	N2	118.27(16)	C32	C30	C31	112.1(3)
C10	C9	N2	118.41(17)	C31	C30	C26	110.6(3)
C10	C9	C14	123.32(17)	N3	C8	C7	102.98(14)
C21	C22	C27	121.93(17)	C37	O6	C40	110.6(5)
C23	C22	C21	117.12(17)	C38	C39	C40	94.4(3)
C23	C22	C27	120.79(18)	O6	C40	C39	94.1(5)
C21	C26	C30	122.27(18)	O6	C37	C38	101.3(4)
C25	C26	C21	116.95(19)	C39	C38	C37	93.2(3)
C25	C26	C30	120.77(18)	C33	O5	C36	102.0(6)
C24	C23	C22	121.0(2)	O5	C36	C35	103.8(5)
C9	C14	C18	122.57(18)	C34	C35	C36	93.7(3)
C13	C14	C9	117.17(19)	O5	C33	C34	109.0(6)
C13	C14	C18	120.26(19)	C33	C34	C35	93.9(3)

Figure S43. Molecular structure and atom numbering scheme for **(IPr*)AuNCFe(CO)$_4$.** Hydrogen atoms have been omitted for clarity. *These are poorly diffracting crystals with low data quality. The molecular structure has been included only to show the atom connectivity.*

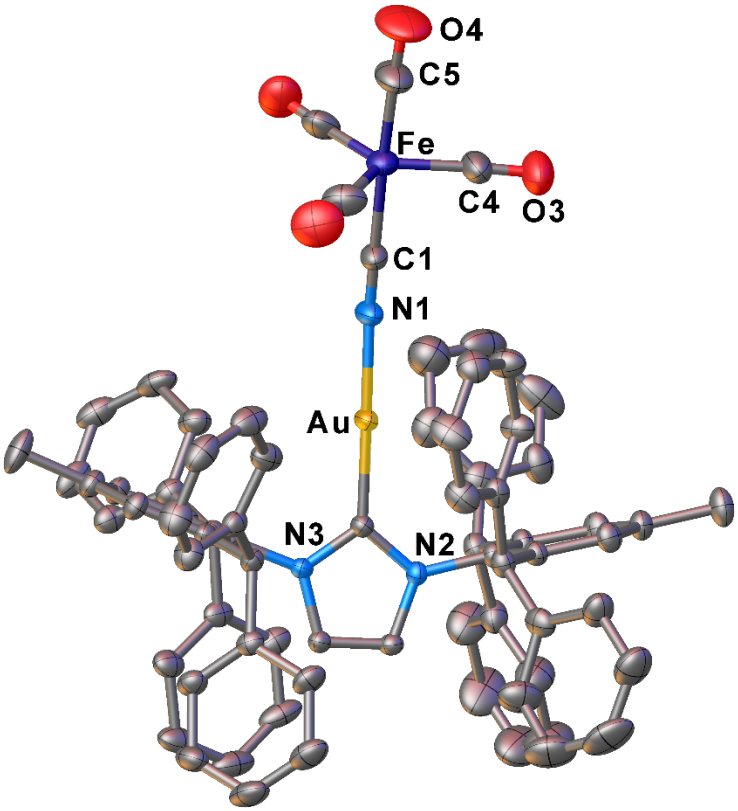


Table S26. Crystal data and structure refinement for (IPr*)AuNCFe(CO)$_4$

Identification code	RAD650
Empirical formula	$C_{74}H_{56}AuFeN_3O_4$
Formula weight	1304.03
Temperature/K	299.07
Crystal system	orthorhombic
Space group	Pbcn
a/Å	35.042(3)
b/Å	17.2901(14)
c/Å	24.913(2)
α/°	90

β/°	90
γ/°	90
Volume/Å^3	15094(2)
Z	8
ρ_{calc}g/cm^3	1.148
μ/mm^{-1}	2.176
F(000)	5264.0
Crystal size/mm^3	0.25 × 0.17 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.464 to 52.746
Index ranges	-43 ≤ h ≤ 43, -21 ≤ k ≤ 21, -31 ≤ l ≤ 31
Reflections collected	144906
Independent reflections	15415 [R_{int} = 0.1087, R_{sigma} = 0.0539]
Data/restraints/parameters	15415/0/750
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0751, wR_2 = 0.2053
Final R indexes [all data]	R_1 = 0.1304, wR_2 = 0.2526
Largest diff. peak/hole / e Å^{-3}	5.99/-1.90

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