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SUPPORTING INFORMATION

Coinage metal complexes of multidentate Pacman phosphane ligands

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1 Experimental

General information. If not stated otherwise, all manipulations were carried out under oxygen- and moisture-free conditions in an inert argon atmosphere using standard Schlenk or drybox techniques. All glassware was heated three times *in vacuo* using a heat gun (650 °C) and cooled under argon atmosphere. Solvents were transferred using syringes, which were purged three times with argon prior to use. Solvents and reactants were either obtained from commercial sources or synthesized as detailed in Table S1.

Table S1: Origin and purification of solvents and reactants.

Substance	Origin	Purification
CH_2Cl_2	local trade	purified according to literature procedure[1] dried over P_4O_{10}, stored over CaH_2 freshly distilled and degassed (freeze-pump-thaw)
Et_2O	local trade	dried over Na/benzophenone freshly distilled prior to use
THF	Fisher Scientific, 99.5%	dried over Na/benzophenone freshly distilled prior to use
n-heptane	local trade	dried over Na/benzophenone/tetraglyme freshly distilled prior to use
AgOTf	J & K, 98 %	used as received
$CODPdCl_2$	old stock	-
CuOTf	old stock	-
$(i\text{Pr})_2NH$	Sigma Aldrich, 99 %	dried over Na freshly distilled prior to use
Me_2SAuCl	old stock	-
NEt_3	Sigma Aldrich, 99%	dried over Na freshly distilled prior to use
Pacman ligand	synthesized[2]	purified according to literature procedure[2]
PCl_3	Merck, for synthesis	dried over P_4O_{10} freshly distilled and degassed (freeze-pump-thaw)
$PhPCl_2$	old stock	-
CD_2Cl_2	euriso-top	dried over P_4O_{10} and CaH_2 freshly distilled prior to use

NMR spectra were recorded on Bruker spectrometers (AVANCE 250, AVANCE 300 or AVANCE 500) and were referenced internally to the deuterated solvent (^{13}C: CD_2Cl_2 δ_{ref} = 54.0 ppm), to protic impurities in the deuterated solvent (^{1}H: $CHDCl_2$ δ_{ref} = 5.32 ppm) or externally (^{31}P: 85% H_3PO_4 δ_{ref} = 0 ppm). All measurements were carried out at ambient temperature unless denoted otherwise. NMR signals were assigned using experimental data (e.g. chemical shifts, coupling constants, integrals where applicable, 2D NMR spectra)

IR spectra of crystalline samples were recorded on a Bruker Alpha II FT-IR spectrometer equipped with an ATR unit at ambient temperature under argon atmosphere. Relative intensities are reported according to the following intervals: very weak (vw, 0–10%), weak (w, 10–30%), medium (m, 30–60%), strong (s, 60–90%), very strong (vs, 90–100%).

Raman spectra of crystalline samples were recorded using a LabRAM HR 800 Horiba Jobin YVON Raman spectrometer equipped with an Olympus BX41 microscope with variable lenses. The samples were excited by an infrared laser (785 nm, 100 mW, air-cooled diode laser) or a red laser (633 nm, 17 mW, air-cooled HeNe laser). All measurements were carried out at ambient temperature unless stated otherwise.

Elemental analyses were obtained using an Elementar vario Micro cube CHNS analyser.

Melting points (uncorrected) were determined using a Stanford Research Systems EZ Melt at a heating rate of 20 °C/min. Decomposition processes were confirmed by DSC analyses.

DSC analyses were carried out at a heating rate of 5 °C/min using a Mettler-Toledo DSC 823e.

Mass spectra were recorded on an Advion Expression L benchtop mass spectrometer (*m/z* 10–2000) equipped with an Advion Expression CMS detector using sample solutions (APCI, ESI) or crystalline samples (APCI).

2 Structure elucidation

X-ray structure determination: X-ray quality crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. The samples were cooled to 123(2) K during measurement except sample **1**. **1** was measured at 203(2) K. The data were collected on a Bruker D8 Quest diffractometer or a Bruker Kappa Apex II diffractometer using Mo K_α radiation (λ = 0.71073 Å). The structures were solved by iterative methods (SHELXT)[3] and refined by full matrix least squares procedures (SHELXL).[4] Semi-empirical absorption corrections were applied (SADABS).[5] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

Table S2: Crystallographic details of the compounds **1** and **2**.

Compound	**1**	**2**
Chem. Formula	$C_{58}H_{58}N_8P_2{\cdot}4(C_4H_8O)$	$C_{58}H_{76}N_{10}P_2{\cdot}2(CH_2Cl_2)$
Formula weight [g/mol]	1217.47	1145.08
Colour	colourless	yellow
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	14.3958(8)	12.004(5)
b [Å]	14.8111(8)	14.462(6)
c [Å]	18.1114(10)	19.647(9)
α [°]	75.619(2)	75.746(19)
β [°]	89.545(2)	84.619(19)
γ [°]	65.078(2)	66.815(12)
V [Å^3]	3371.7(3)	3039(2)
Z	2	2
$\rho_{calcd.}$ [g/cm^3]	1.199	1.251
μ [mm^{-1}]	0.119	0.294
T [K]	203(2)	123(2)
Measured reflections	194764	23243
Independent reflections	19634	23243
Reflections with $I > 2\sigma(I)$	15606	14852
R_{int}	0.0407	0.0491
F(000)	1304	1216
$R_1(R[F^2>2\sigma(F^2)])$	0.0447	0.0688
w$R_2(F^2)$	0.1265	0.1714
GooF	1.089	1.024
No. of Parameters	621	817
CCDC #	2226460	2226461

Table S3: Crystallographic details of the compounds **[1Au][Cl]** and **[1Ag][OTf]**.

Compound	**[1Au][Cl]**	**[1Ag][OTf]**
Chem. Formula	$C_{58}H_{58}AuN_8P_2^+ \cdot Cl^- \cdot 3.825(CH_2Cl_2)$	$C_{58}H_{58}AgN_8P_2^+ \cdot CF_3O_3S^- \cdot 2(C_4H_8O)$
Formula weight [g/mol]	1486.50	1330.21
Colour	yellow	yellow
Crystal system	monoclinic	monoclinic
Space group	$P2_1/m$	Pc
a [Å]	14.2272(17)	20.6611(12)
b [Å]	13.2929(16)	19.3470(12)
c [Å]	17.217(2)	16.2836(11)
α [°]	90	90
β [°]	94.275(3)	104.971(2)
γ [°]	90	90
V [Å^3]	3247.1(7)	6288.1(7)
Z	2	4
$\rho_{calcd.}$ [g/cm^3]	1.520	1.405
μ [mm^{-1}]	2.716	0.471
T [K]	123(2)	123(2)
Measured reflections	16939	250644
Independent reflections	16939	44710
Reflections with $I > 2\sigma(I)$	14274	41005
R_{int}	0.0436	0.0419
$F(000)$	1497	2768
$R_1(R[F^2>2\sigma(F^2)])$	0.0378	0.0337
$wR_2(F^2)$	0.0834	0.0860
GooF	1.026	1.032
No. of Parameters	496	1648
CCDC #	2226462	2226466

Table S4: Crystallographic details of the compounds **[1Cu][OTf]** and **[2Au][$AuCl_2$]**.

Compound	**[1Cu][OTf]**	**[2Au][$AuCl_2$]**
Chem. Formula	$C_{58}H_{58}CuN_8P_2^+ \cdot CF_3O_3S^- \cdot C_4H_8O$	$C_{58}H_{76}Au_2N_{10}P_2^+ \cdot AuCl_2^- \cdot 2.39(C_4H_8O) \cdot 0.61(CH_2Cl_2)$
Formula weight [g/mol]	1213.77	1664.12
Colour	orange	yellow
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	19.9025(9)	16.7640(8)
b [Å]	19.0843(10)	14.1706(7)
c [Å]	15.6467(8)	29.9119(13)
α [°]	90	90
β [°]	102.216(2)	100.9550(10)
γ [°]	90	90
V [Å^3]	5808.4(5)	6976.3(6)
Z	4	4
$\rho_{calcd.}$ [g/cm^3]	1.388	1.584
μ [mm^{-1}]	0.533	4.422
T [K]	123(2)	123(2)
Measured reflections	131884	118200
Independent reflections	16923	22231
Reflections with $I > 2\sigma(I)$	12204	17962
R_{int}	0.1073	0.0629
$F(000)$	2536	3349
$R_1(R[F^2>2\sigma(F^2)])$	0.0451	0.0406
$wR_2(F^2)$	0.1164	0.0849
GooF	1.011	1.059
No. of Parameters	801	893
CCDC #	2226464	2226463

Table S5: Crystallographic details of the compounds **[2Ag·MeCN][OTf]** and **[2Cu·OTf]**.

Compound	**[2Ag·MeCN][OTf]**	**[2Cu·OTf]**
Chem. Formula	$C_{58}H_{76}AgN_{10}P_2{\cdot}CF_3O_3S^-{\cdot}6.253(C_2H_3N)$	$C_{59}H_{76}CuF_3N_{10}O_3P_2S{\cdot}2(C_4H_8O)$
Formula weight [g/mol]	1488.89	1332.04
Colour	colourless	orange
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a [Å]	15.7617(16)	15.1056(8)
b [Å]	26.139(3)	21.1586(11)
c [Å]	37.462(4)	21.5192(12)
α [°]	90	90
β [°]	99.706(3)	105.733(2)
γ [°]	90	90
V [Å^3]	15213(3)	6620.1(6)
Z	8	4
$\rho_{calcd.}$ [g/cm^3]	1.300	1.336
μ [mm^{-1}]	0.396	0.476
T [K]	123(2)	123(2)
Measured reflections	581353	229236
Independent reflections	29892	19305
Reflections with $I > 2\sigma(I)$	22294	13818
R_{int}	0.1135	0.0965
$F(000)$	6253	2824
$R_1(R[F^2>2\sigma(F^2)])$	0.0571	0.0495
$wR_2(F^2)$	0.1526	0.1313
GooF	1.072	1.012
No. of Parameters	1882	872
CCDC #	2226467	2226465

In the crystal, Pacman phosphane ligand **2** shows intermolecular interactions between the iminic nitrogen atoms N3 or N7, twisted outwards, and the pyrrolic hydrogen atoms H3 or H20 of other molecules of **2**, respectively (Figure S1). The interactions can be described by the parameters listed in Table S6.

In solution, no evidence of differently orientated iminic functions was observed. Only one signal for iminic protons is present in the ^{1}H NMR spectrum (Figure S4). This indicates that the twisting is only favoured in solid state due to the intermolecular interactions or that in solution a rotation faster than NMR time scale occurs.

Figure S1: Intermolecular interactions of **2** in the crystal. Ellipsoids are drawn at 50% probability at 123(2) K. Solvent and disorder of one N*i*Pr$_2$-group are omitted for clarity. Symmetry codes: (’): 1−x, 1−y, 1−z, (’’): 1−x, 1−y, z.

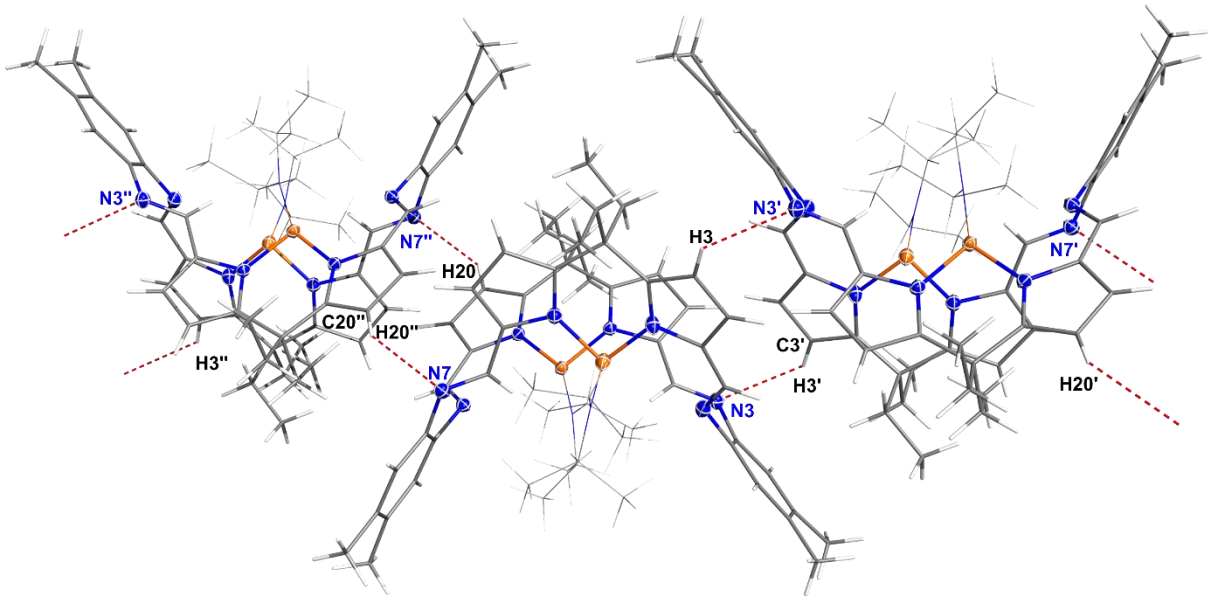
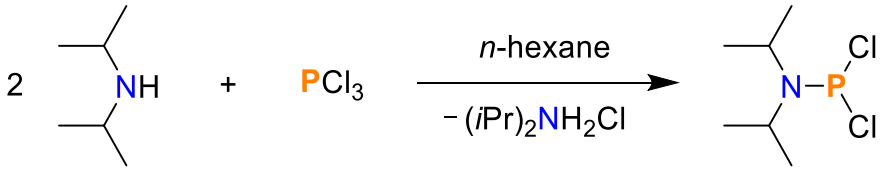


Table S6. Parameters of the intermolecular interactions of **2** (cf. Figure S1).

Parameter	N3, H3’, C3’	N7, H20’’, C20’’
d(H···N) [Å]	2.605(3)	2.627(3)
d(C-H···N) [Å]	3.399(4)	3.304(5)
α(C-H···N) [°]	141.3(2)	128.6(3)

3 Syntheses of starting materials

3.1 Dichloro-(di*iso*propylamino)-phosphine

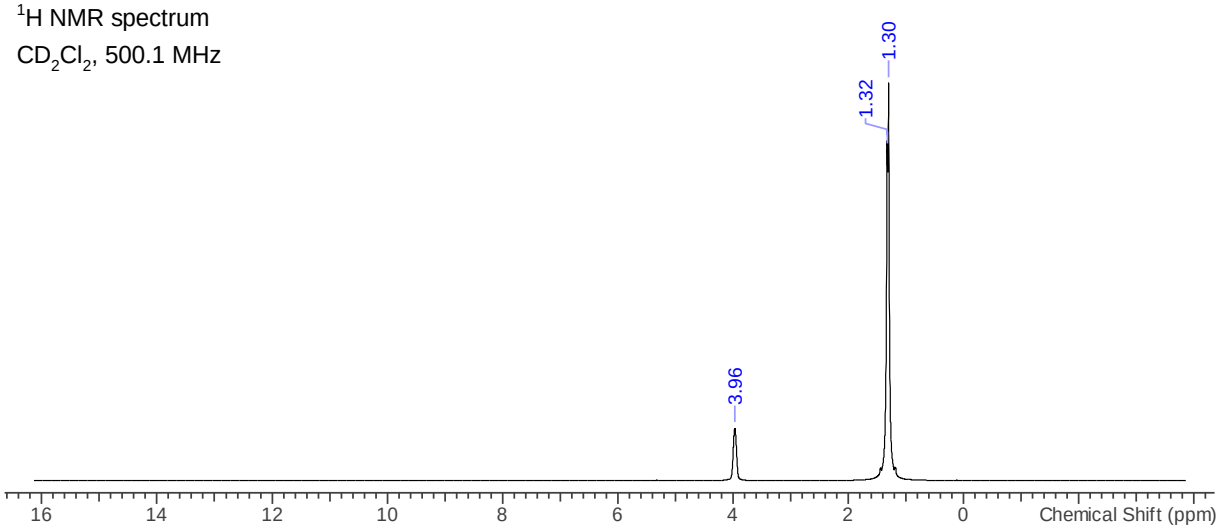


The synthesis is based on the procedure of R. I. PUGH.[6] A one litre flask equipped with an overhead stirrer, an overpressure valve and a dropping funnel is filled with a mixture of *n*-hexane (300 mL) and PCl_3 (36.68 g, 267.1 mmol). The dropping funnel is filled with $(iPr)_2NH$ (54.01 g, 533.7 mmol). The solution is cooled to 0 °C and the amine is added dropwise over a period of approximately 1 h. During this time, a colourless, voluminous precipitate is formed. The reaction solution is then heated to 40 °C and held at this temperature for 2 h. The solution is filtered off (pore 4) and the precipitate is washed three times via back-condensation of the solvent. The cloudy yellow extract is concentrated to a volume of approximately 60 mL and then filtered again (pore 4) giving a clear yellow liquid. The liquid is fractionally distilled at 0.66 mbar and an oil bath temperature of 85 °C. Bp: 62 °C. Yield: 35.06 g (173.5 mmol, 65.0%).

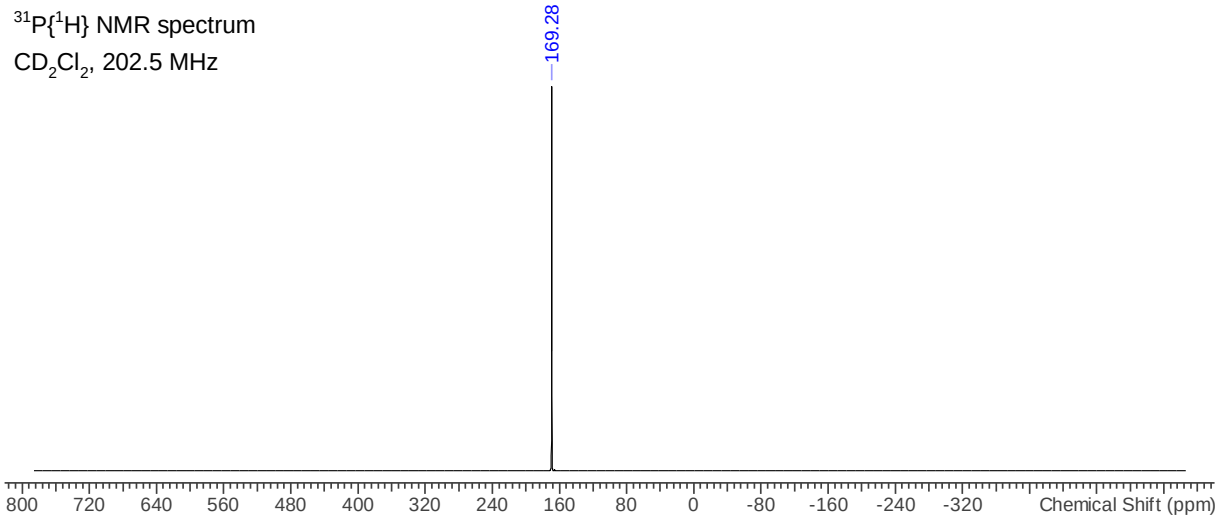
Bp. 62 °C (at 0.66 mbar). **$^{31}P\{^1H\}$ NMR** (CD_2Cl_2, 202.5 MHz): δ = 169.3 ppm (s). **^1H NMR** (CD_2Cl_2, 500.1 MHz): δ = 1.31 (d, $^3J(^1H,^1H)$ = 13.1 Hz ,12 H, CH_3), 3.96 (s, 2 H, CH).
No complete analysis was carried out, as the compound is already known from the literature.

Figure S2: NMR spectra of dichloro-(di*iso*propylamino)-phosphine.

^{1}H NMR spectrum
CD_2Cl_2, 500.1 MHz

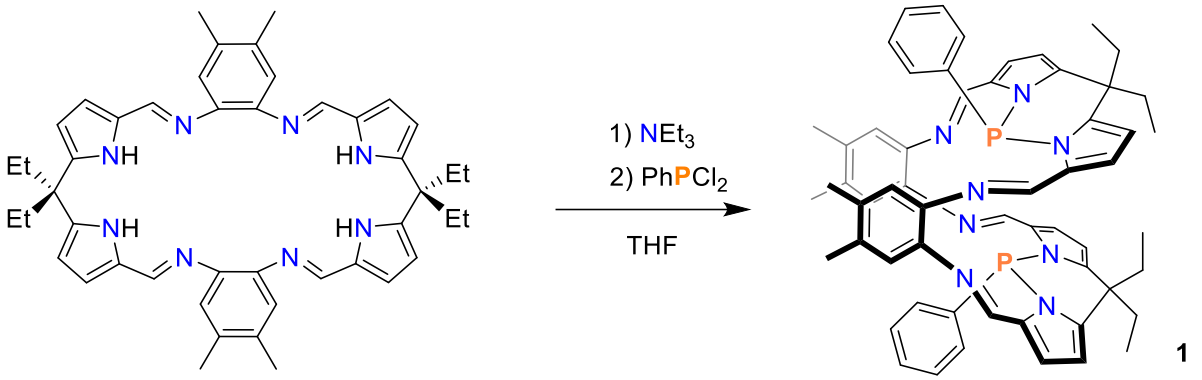


^{31}P{^{1}H} NMR spectrum
CD_2Cl_2, 202.5 MHz



4 Syntheses of compounds

4.1 Pacman phosphane ligand 1



The yellow Pacman ligand (5.27 g, 7.07 mmol) is dissolved in THF (100 mL) giving a dark orange-red solution. Triethylamine (8.0 mL, 58 mmol) is added at ambient temperature leading to a colour change to bright orange. The reaction solution is cooled to −80 °C and $PhPCl_2$ (2.0 mL, 15 mmol) is added dropwise. The reaction solution turns to a dark red-brown colour. The solution is kept at −80 °C for about 30 min and then slowly warmed up to ambient temperature overnight. During this time, a red precipitate is formed. The solvent is removed *in vacuo* (1×10^{-3} mbar) and the residue is dried for about 30 min at 50 °C. The solids are suspended in Et_2O (20 mL) and dried for another 3 h *in vacuo* (1×10^{-3} mbar) at 50 °C. Diethyl ether (150 ml) is added and the solution is degassed using the *freeze-pump-thaw* method. The raw product is extracted by sevenfold filtration and back-condensation of the diethyl ether. The extract is dried *in vacuo* (1×10^{-3} mbar) for 1 h at 50 °C. In addition to the desired *exo-exo*-isomer, an undesired *endo-exo*-isomer is also formed. To separate the *exo-exo*-isomer from the *endo-exo*-isomer, the orange powder is dissolved in THF (100 mL). The solution is concentrated *in vacuo* (1×10^{-3} mbar) and left to stand at 5 °C overnight for crystallization, resulting in the deposition of orange crystals of the *exo-exo*-isomer. The supernatant is removed via syringe at 0 °C and the orange crystals are washed at −80 °C with THF (2×5 mL). The crystals are dried *in vacuo* (1×10^{-3} mbar) for 5 h at 50 °C.

A second fraction can be isolated in the same manner. Approximately 1.35 equiv. of THF remain in the product. Yield: 2930 mg (2.85 mmol, 40.4%).

Mp. 284 °C (dec.). **EA** calc. (found) in %: C 74.16 (73.90), H 6.77 (6.60), N 10.88 (11.08). **^{31}P{^{1}H} NMR** (CD_2Cl_2, 202.5 MHz): δ = 68.1 ppm (s). **^{1}H NMR** (CD_2Cl_2, 500.1 MHz): δ = 7.63 (s, 4 H, iminic C*H*), 7.14 - 7.19 (m, 2 H, phenyl *para*-C*H*), 7.00 - 7.06 (m, 4 H, phenyl *meta*-C*H*), 6.93 - 6.98 (m, 4 H, phenyl *ortho*-C*H*), 6.70 (d, $^{3}J(^{1}H,^{1}H)$ = 3.7 Hz, 4 H, pyrrolic C*H*), 6.26 (d, $^{3}J(^{1}H,^{1}H)$ = 3.7 Hz, 4 H, pyrrolic C*H*), 5.85 (s, 4 H, aromatic C*H*), 3.65 - 3.71 (m, 5.6 H, THF), 2.17 (q, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, 4 H, *exo*-R-CH_2-CH_3), 2.11 (s, 12 H, Ar-CH_3), 1.80 - 1.84 (m, 5.6 H, THF), 1.77 (q, $^{3}J(^{1}H,^{1}H)$ = 7.4 Hz, 4 H, *endo*-R-CH_2-CH_3), 1.02 (t, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, 6 H, *exo*-R-CH_2-CH_3), 0.58 ppm (t, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, 6 H, *endo*-R-CH_2-CH_3). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 125.8 MHz): δ = 150.8 (s, iminic *C*H), 144.9 - 145.8 (m, phenyl *ipso*-*C*), 142.8 (s, pyrrolic *C*-C-Et), 142.4 (s, aromatic *C*), 134.6 (s, pyrrolic *C*), 133.3 (s, aromatic *C*-CH_3), 132.6 (m, phenyl *ortho*-*C*H), 128.7 (s, phenyl *para*-*C*H phenyl), 127.0 (s, phenyl *meta*-*C*H), 122.6 (s, aromatic *C*H), 120.7 (s, pyrrolic *C*H near imine), 108.5 (s, pyrrolic *C*H near Et-groups), 68.3 (s, THF), 44.5 (s, *C*-Et_2), 42.5 (s, *endo*-R-CH_2-CH_3), 32.1 (s, *exo*-R-CH_2-CH_3), 26.2 (s, THF), 19.3 (s, Ar-CH_3), 10.3 (s, *exo*-R-CH_2-CH_3), 9.7 ppm (s, *endo*-R-CH_2-CH_3). **^{15}N NMR** (CD_2Cl_2, 50.7 MHz): δ = −71.6 (s, iminic *N*), −216.3 ppm (d, $^{1}J(^{15}N,^{31}P)$ = 121 Hz, pyrrolic *N*). **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2964 (m), 2929 (m), 2917 (m), 2871 (m), 1622 (vs), 1540 (w), 1472 (s), 1453 (m), 1435 (m), 1408 (m), 1375 (m), 1354 (m), 1321 (m), 1288 (m), 1255 (s), 1204 (w), 1179 (m), 1130 (w), 1084 (vs), 1035 (s), 993 (m), 956 (m), 913 (w), 882 (s), 857 (m), 827 (m), 763 (vs), 742 (s), 715 (w), 693 (s), 651 (m), 633 (w), 608 (w), 592 (w), 563 (m), 538 (m), 517 (m), 497 (s), 482 (s), 443 (s), 425 (vs). **Raman** (633 nm, 20 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3120 (1), 3099 (1), 3051 (1), 2976 (1), 2936 (1), 2875 (1), 1909 (1), 1627 (10), 1593 (1), 1562 (3), 1491 (1), 1474 (2), 1394 (1), 1382 (1), 1325 (2), 1317 (1), 1277 (2), 1257 (2), 1182 (2), 1157 (1), 1097 (1), 1089 (1), 1035 (1), 1028 (1), 1002 (1), 997 (1), 959 (2), 928 (1), 914 (1), 887 (2), 874 (1), 865 (1), 850 (1), 822 (1), 739 (2), 690 (1), 619 (1), 598 (1), 532 (1), 520 (1), 516 (1), 509 (1), 484 (1), 473 (1), 454 (1), 415 (1), 398 (1), 375 (1), 358 (1), 348 (1), 326 (1), 312 (1),

296 (1), 284 (1), 236 (1), 135 (2), 98 (2). **MS** (APCI pos, THF, m/z): 929 $[M+H]^+$, 930 $[M+H]^+$, 946 $[M+H_2O]^+$.

Suitable crystals for single crystal X-ray crystallography were received as described above.

Figure S3: NMR, IR and Raman spectra of **1** (solvent signals indicated by asterisks).

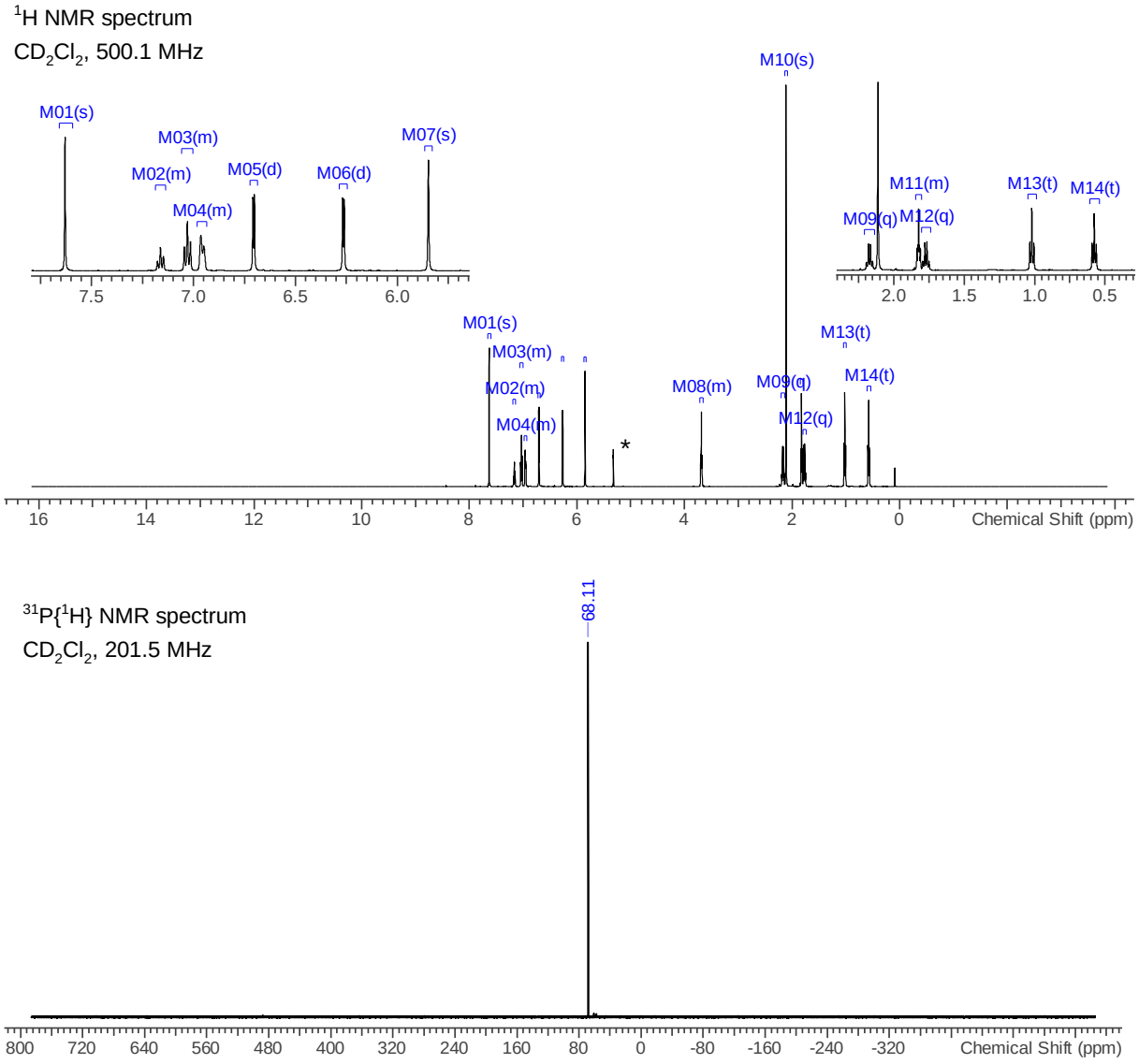
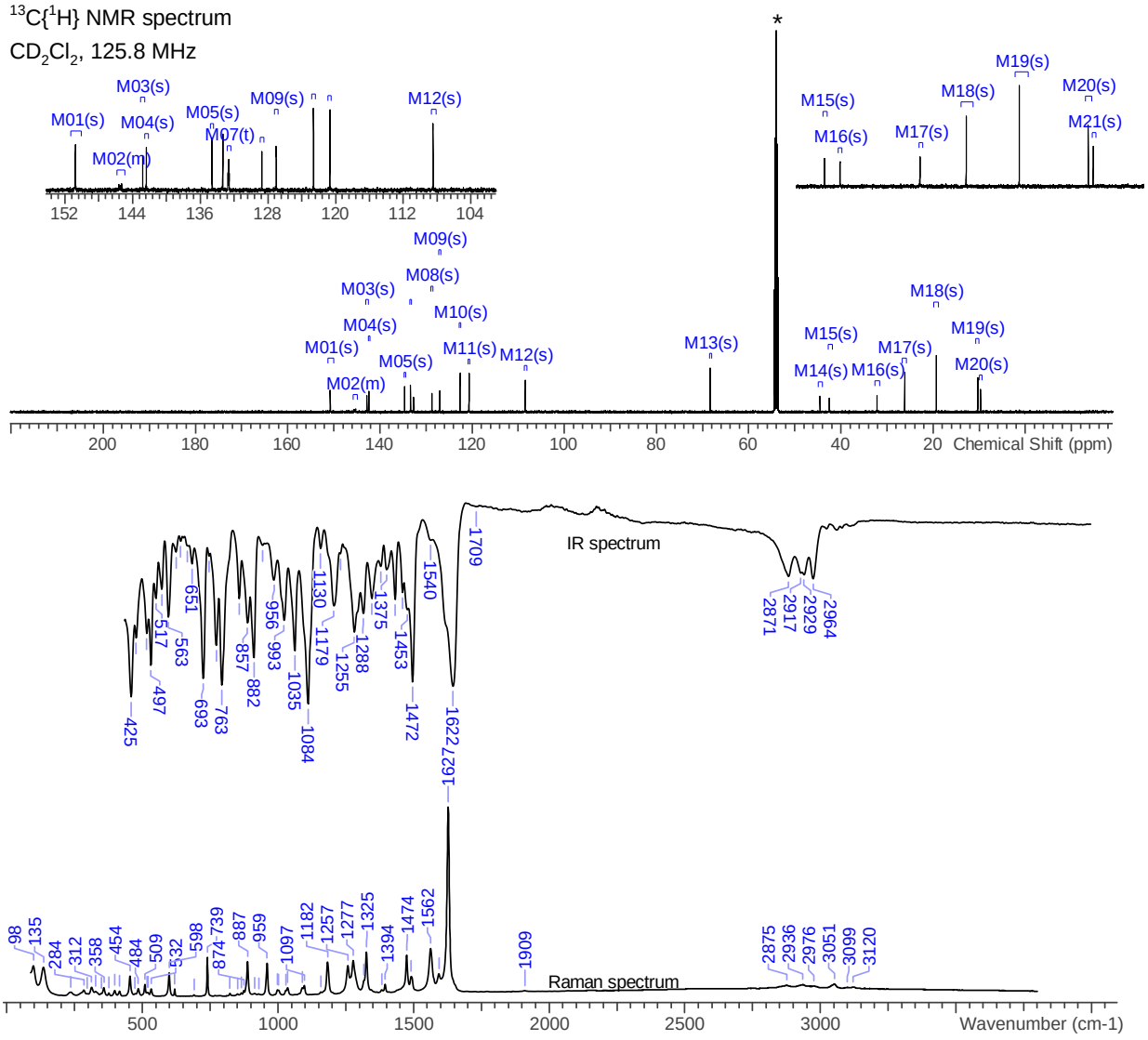
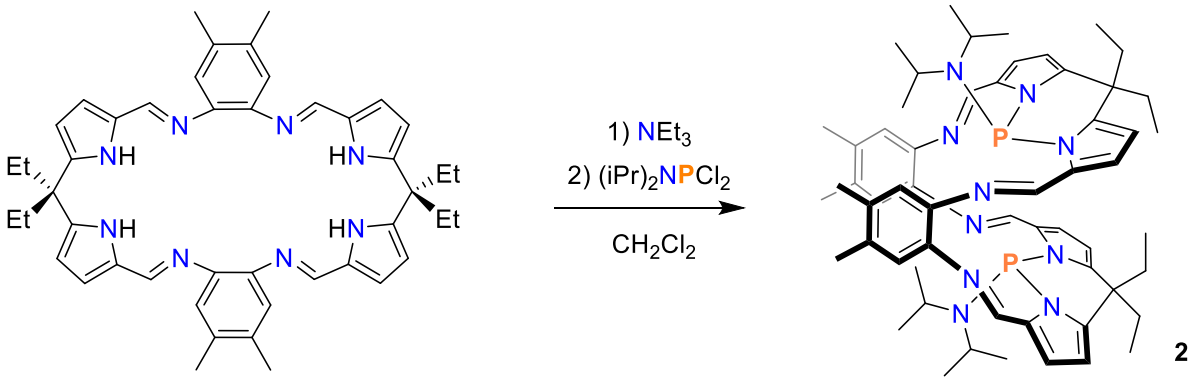


Figure S3 continued.



4.2 Pacman phosphane ligand 2



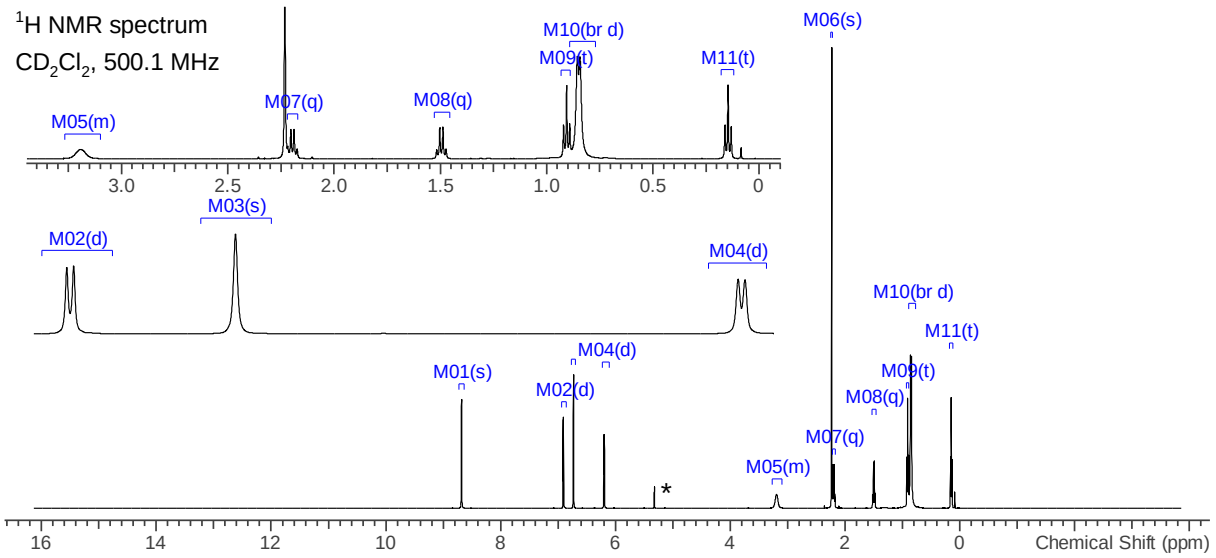
The yellow Pacman ligand (5.2 g, 7.3 mmol) is dissolved in dichloromethane (150 mL) giving a dark orange-red solution. Triethylamine (8.0 mL, 58 mmol) is added at ambient temperature leading to a colour change to bright orange. The reaction solution is cooled to −80 °C and (iPr)$_2$NPCl$_2$ (2.7 mL, 15 mmol) is added dropwise. It should be noted that the phosphane freezes very easily. Therefore, the cannula of the syringe should not be inserted too far into the cooled flask, to prevent the phosphane from clogging the syringe. The reaction solution turns to a dark red-brown colour. The solution is kept at −80 °C for about 30 min and then slowly warmed up to ambient temperature overnight. All volatiles are removed *in vacuo* (1×10^{-3} mbar) and the residue is dried for about 30 min at 50 °C. The yellow-brown solids are suspended in Et$_2$O (20 mL) and dried for another 3.5 h *in vacuo* (1×10^{-3} mbar) at 50 °C. The solids are transferred into a Soxhlet apparatus and a Schlenk flask is filled with Et$_2$O (150 mL). The flask is connected to the Soxhlet apparatus and the ether is heated to boiling via an oil bath. The solids are extracted for approximately 12 d. The extract is then dried *in vacuo* (1×10^{-3} mbar) for 2 h at 50 °C, yielding orange-brown solids. In addition to the desired *exo*-*exo*-isomer, an undesired *endo*-*exo*-isomer is also formed. To separate the *exo*-*exo*-isomer from the *endo*-*exo*-isomer, THF (100 mL) is added to wash the crude product. The dark red-brown solution containing the *endo*-*exo*-isomer is filtered off (pore 4) and the yellow residue containing the *exo*-*exo*-isomer is washed again with THF (10 mL). The solids are then dried *in vacuo* (1×10^{-3} mbar) at 50 °C for 2 h. The filtrate can be discarded. Yield: 3950 mg (4.05 mmol, 55.5%).

Mp. 310 °C (dec.). **EA** calc. (found) in %: C 71.43 (71.14), H 7.86 (7.60), N 14.36 (14.41). **^{31}P{^{1}H}-NMR** (CD_2Cl_2, 121.5 MHz): δ = 83.2 ppm (s). **^{1}H NMR** (CD_2Cl_2, 500.1 MHz): δ = 8.86 (s, 4 H, iminic C*H*), 6.91 (d, $^3J(^1H,^1H)$ = 3.7 Hz, 4 H, pyrrolic C*H*), 6.73 (s, 4 H, aromatic C*H*), 6.20 (d, $^3J(^1H,^1H)$ = 3.7 Hz, 4 H, pyrrolic C*H*), 3.10 - 3.27 (m, 4 H, *i*Pr-groups C*H*), 2.23 (s, 12 H, Ar-CH_3), 2.20 (q, $^3J(^1H,^1H)$ =7.3 Hz, 4 H, R-CH_2-CH$_3$), 1.49 (q, $^3J(^1H,^1H)$ =7.4 Hz, 4 H, R-CH_2-CH$_3$), 0.91 (t, $^3J(^1H,^1H)$ = 7.2 Hz, 6 H, R-CH$_2$-CH_3), 0.85 (br d, $^3J(^1H,^1H)$ =6.3 Hz, 24 H, *i*Pr-groups CH_3), 0.15 ppm (t, $^3J(^1H,^1H)$ = 7.3 Hz, 6 H, R-CH$_2$-

C*H*$_3$). **^{13}C{^{1}H}-NMR** (CD_2Cl_2, 125.8 MHz): δ = 153.3 (m, iminic *C*H), 142.8 (s, pyrrolic *C*-C-Et), 142.5 (s, aromatic *C*), 135.8 (m, pyrrolic *C*), 133.6 (s, aromatic *C*-CH_3), 123.6 (s, aromatic *C*H), 119.8 (s, pyrrolic *C*H near imine), 108.2 (s, pyrrolic *C*H near ethyl), 47.9 - 48.4 (m, *i*Pr-groups *C*H), 46.2 (s, R-*C*H_2-CH_3), 45.0 (s, C-Et_2), 32.8 (s, R-*C*H_2-CH_3), 23.8 (br s, *i*Pr-groups *C*H_3), 19.5 (s, aromatic *C*H_3), 9.8 (s, R-CH_2-*C*H_3), 9.4 ppm (s, R-CH_2-*C*H_3). **^{15}N-NMR** (CD_2Cl_2, 50.7 MHz): δ = −76.7 (s, iminic *N*), −215.9 (d, $^1J(^{15}N,^{31}P)$ = 142 Hz, pyrrolic *N*), −284.0 ppm (m, *i*Pr-groups *N*). **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2966 (m), 2925 (w), 2873 (w), 1622 (m), 1608 (s), 1544 (w), 1472 (s), 1402 (w), 1373 (m), 1340 (m), 1336 (m), 1299 (m), 1266 (m), 1243 (m), 1191 (m), 1175 (m), 1140 (w), 1123 (w), 1088 (s), 1024 (m), 979 (s), 952 (m), 880 (m), 855 (m), 818 (m), 791 (m), 771 (vs), 738 (w), 730 (m), 719 (w), 701 (m), 676 (m), 655 (w), 631 (m), 620 (m), 606 (w), 587 (w), 567 (m), 542 (m), 532 (m), 515 (s), 460 (m), 451 (m), 435 (s). **Raman** (784 nm, 20 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 1624 (8), 1607 (10), 1589 (7), 1550 (3), 1489 (4), 1474 (7), 1405 (3), 1382 (5), 1357 (2), 1335 (4), 1298 (4), 1258 (7), 1243 (5), 1203 (1), 1192 (1), 1177 (8), 1096 (2), 1077 (2), 1036 (3), 1024 (1), 976 (1), 963 (9), 951 (1), 890 (2), 882 (3), 873 (1), 865 (1), 852 (1), 816 (5), 796 (1), 782 (1), 740 (5), 731 (4), 707 (2), 677 (1), 649 (2), 631 (1), 621 (2), 587 (1), 558 (1), 541 (3), 526 (2), 517 (1), 494 (2), 479 (1), 462 (1), 440 (2), 432 (2), 408 (1), 384 (2), 372 (2), 350 (4), 331 (3), 286 (6), **MS** (APCI pos, THF, m/z): 975 $[M+H]^+$, 976 $[M+H]^+$, 977 $[M+H]^+$.

To obtain suitable crystals for single crystal X-ray crystallography, **2** is dissolved in dichloromethane. The solution is reduced *in vacuo* (1×10^{-3} mbar) until a yellow precipitate is formed. The precipitate is redissolved in heat and slowly cooled in a warm water bath for crystallisation.

Figure S4: NMR, IR and Raman spectra of **2** (solvent signals indicated by asterisks).



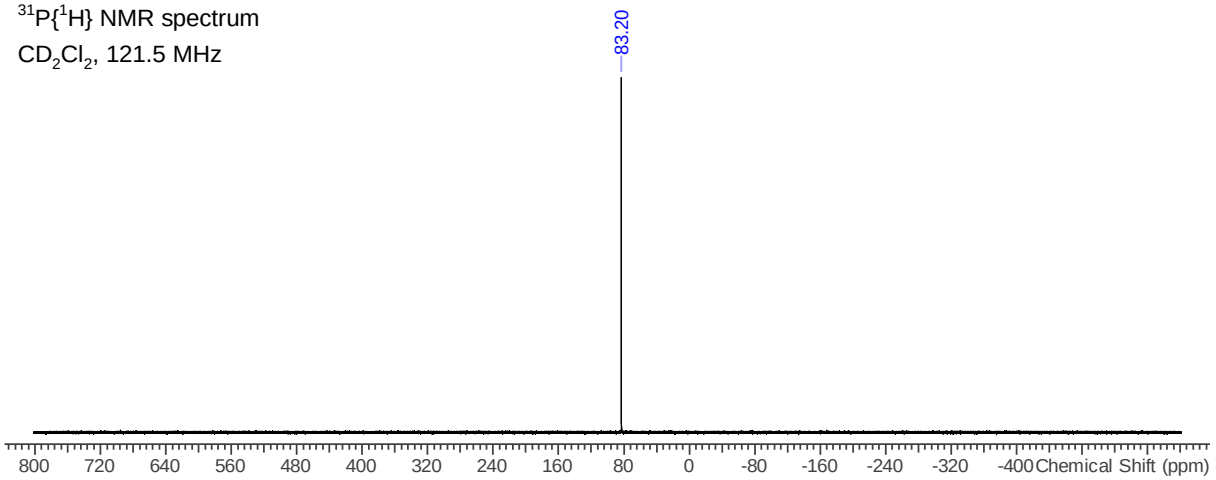
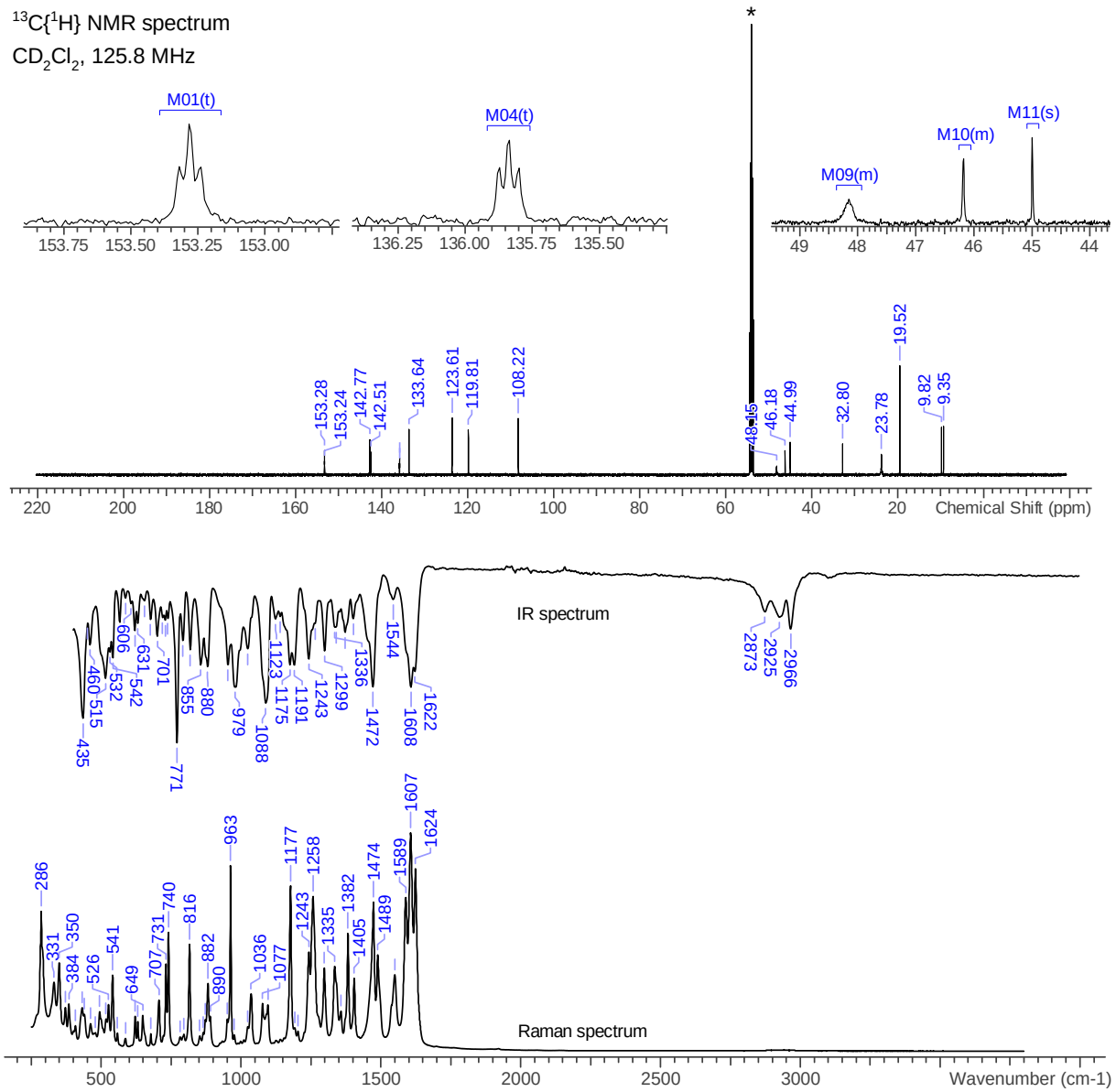
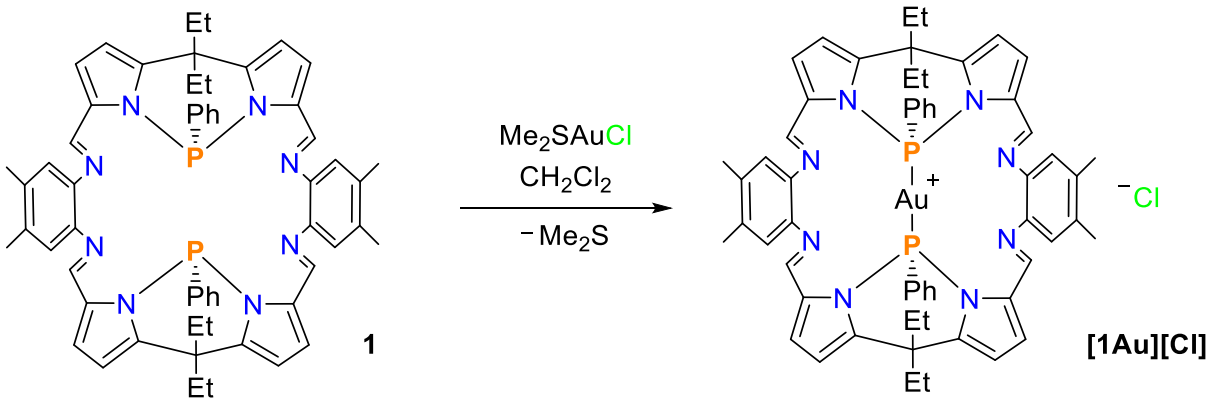


Figure S4 continued.



4.3 Pacman phosphane gold(I) complex [1Au][Cl]



A 25 mL Schlenk flask is filled with **1** (207 mg, 0.20 mmol) and colourless Me_2SAuCl (59.0 mg, 0.20 mmol). The solids are dissolved in dichloromethane (12 mL) giving an orange solution. The reaction mixture is stirred overnight. The solution is concentrated *in vacuo* (1×10^{-3} mbar) and left to stand at 5 °C overnight for crystallization, resulting in the deposition of yellow crystals. The supernatant is removed via a syringe and the yellow crystals are washed at −80 °C with dichloromethane (0.5 mL). The crystals are dried *in vacuo* (1×10^{-3} mbar) for 2 h at 50 °C. A second fraction can be isolated in the same manner. Yield: 205 mg (0.18 mmol, 88.0%).

Mp. 225 °C (dec.); **EA** calc. (found) in %: C 59.98 (59.14), H 5.03 (4.97), N 9.65 (9.51); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 202.5 MHz): δ = 85.5 ppm (s); **^{1}H NMR** (CD_2Cl_2, 500.13 MHz): δ = 7.67 (s, 4 H, iminic C*H*), 7.44 (t, $^{3}J(^{1}H,^{1}H)$ = 7.5 Hz, 2 H, phenyl *para*-C*H*), 7.20 (m, 4 H, phenyl *meta*-C*H*), 7.00 (q, *J* = 7.0 Hz, 4 H, phenyl *ortho*-C*H*), 6.92 (d, $^{3}J(^{1}H,^{1}H)$ = 3.8 Hz, 4 H, pyrrolic C*H* near imine), 6.48 (d, $^{3}J(^{1}H,^{1}H)$ = 3.8 Hz, 4 H, pyrrolic C*H* near Et-groups), 5.82 (s, 4 H, aromatic C*H*), 2.36 (q, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, 4H, *exo*-R-CH_2-CH$_3$), 2.14 (s, 12 H, Ar-CH_3), 1.89 (q, $^{3}J(^{1}H,^{1}H)$ = 7.5 Hz, 4 H, *endo*-R-CH_2-CH$_3$), 1.09 (t, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, 6 H, *exo*-R-CH$_2$-CH_3), 0.69 ppm (t, $^{3}J(^{1}H,^{1}H)$ = 7.5 Hz, 6 H, *endo*-R-CH$_2$-CH_3); **^{13}C{^{1}H} NMR** (CD_2Cl_2, 125.76 MHz): δ = 149.8 (s, iminic *C*H), 144.3 (s, pyrrolic *C*-C-Et), 140.3 (s, aromatic *C*), 137.6 (t, $J(^{13}C,^{31}P)$ = 39 Hz, phenyl *ipso*-*C*), 135.3 (s, aromatic *C*-CH$_3$), 134.8

(s, pyrrolic *C*), 132.6 (t, $J(^{13}C,^{31}P)$ = 8 Hz, phenyl *ortho*-*C*H), 132.2 (s, phenyl *para*-*C*H), 128.4 (t, $J(^{13}C,^{31}P)$ = 6 Hz, phenyl *meta*-*C*H), 124.2 (s, pyrrolic *C*H near imine), 122.2 (s, aromatic *C*H), 110.9 (s, pyrrolic *C*H near Et-groups), 45.1 (s, *C*-Et_2), 44.4 (s, *endo*-CH_2-CH_3), 31.5 (s, *exo*-CH_2-CH_3), 19.4 (s, Ar-CH_3), 10.4 (s, *endo*-CH_2-CH_3), 10.2 ppm (s *exo*-CH_2-CH_3); **^{15}N NMR** (50.68 MHz, CD_2Cl_2): δ = −67.5 (s, iminic *N*), −231.3 ppm (s, pyrrolic *N*); **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3059 (w), 3011 (w), 2962 (m), 2931 (m), 2919 (m), 2869 (m), 1624 (s), 1505 (w), 1476 (s), 1453 (m), 1437 (m), 1402 (m), 1377 (m), 1352 (m), 1317 (m), 1280 (m), 1253 (s), 1183 (m), 1134 (m), 1094 (s), 1035 (m), 993 (m), 975 (m), 882 (s), 862 (m), 824 (m), 783 (s), 767 (s), 738 (m), 703 (m), 690 (s), 645 (m), 637 (m), 596 (m), 571 (s), 544 (m), 536 (s), 505 (s), 472(vs), 443 (s), 420 (s); **Raman** (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3118 (1), 3056 (1), 3031 (1), 2978 (1), 2942 (1), 2917 (1), 2883 (1), 1624 (10), 1591 (2), 1562 (3), 1497 (2), 1475 (3), 1433 (1), 1391 (1), 1373 (1), 1340 (1), 1319 (3), 1276 (1), 1255 (4), 1180 (3), 1115 (1), 1098 (1), 1078 (1), 1037 (1), 1026 (1), 997 (2), 962 (2), 954 (2), 926 (1), 881 (2), 869 (1), 862 (1), 819 (1), 738 (3), 706 (1), 695 (1), 666 (1), 620 (3), 547 (1), 527 (1), 517 (1), 503 (1), 480 (2), 454 (1), 415 (1), 399 (1), 376 (1), 368 (1), 360 (1), 339 (1), 313 (1), 296 (1), 286 (1), 230 (1), 132 (4), 76 (4); **MS** (ESI, m/z, THF): 1125.1 $[M-Cl^-]^+$.

Suitable crystals for single crystal X-ray crystallography were received as described above.

Figure S5: NMR, IR and Raman spectra of **[1Au][Cl]** (solvent signals indicated by asterisks).

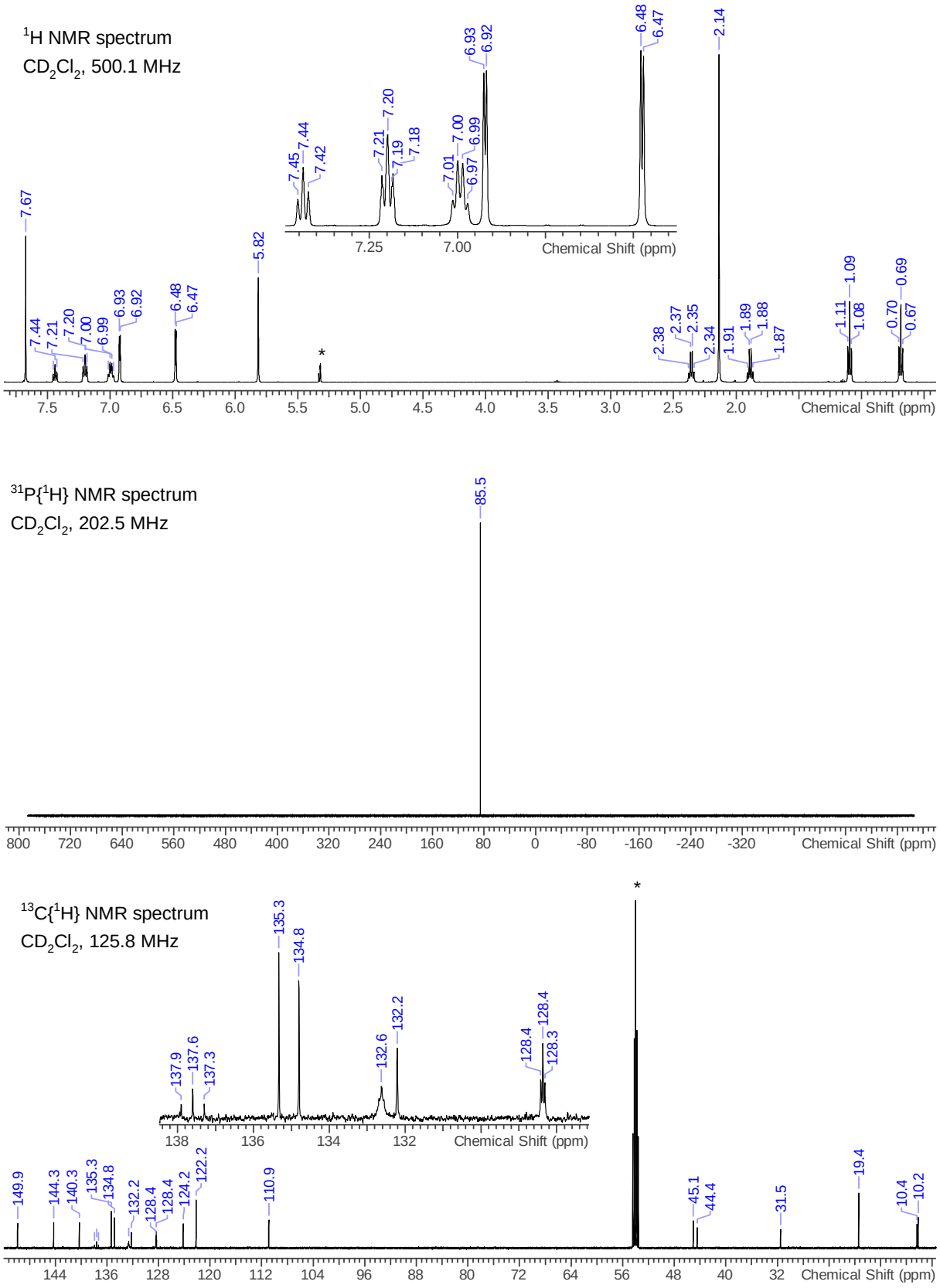
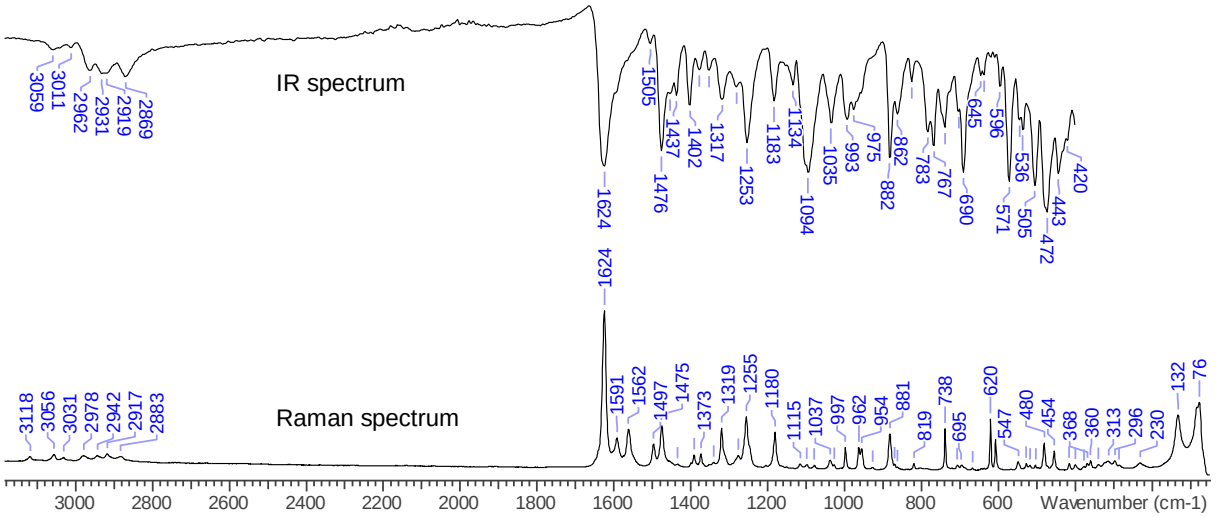
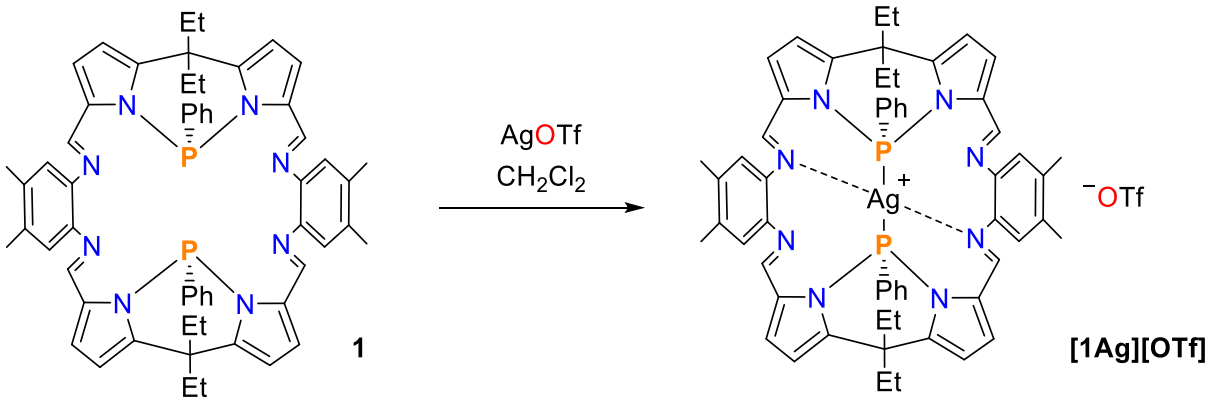


Figure S5 continued.



4.4 Pacman phosphane silver(I) complex [1Ag][OTf]



The reaction is carried out in the absence of light, as the AgOTf is light sensitive. A 25 mL Schlenk flask is filled with **1** (236 mg, 0.23 mmol) and colorless AgOTf (57.0 mg, 0.22 mmol). The solids are dissolved in dichloromethane (15 mL) giving a yellow solution. The reaction mixture is stirred for about 1 h during which the solution turns bright orange. THF (4 mL) is added to the solution, which is then concentrated *in vacuo* (1×10^{-3} mbar). The concentrated solution is left to stand in a water bath in the fridge at 5 °C overnight for crystallization, resulting in the deposition of colourless crystals. The crystals are too small to be measured by X-ray structure analysis. The crystals are therefore isolated by removing the supernatant via a syringe. The removed solution is treated as a second fraction analogous to the first. The isolated crystals of the first

fraction are washed with THF (2 mL) at −80 °C. The light yellow crystals are dried *in vacuo* (1×10^{-3} mbar) for 1 h at 50 °C and redissolved in THF (12 mL). The solution is then concentrated *in vacuo* (1×10^{-3} mbar) and left to stand in a warm water bath for crystallization. Suitable crystals for X-ray structure analysis can be obtained this way. Approximately 0.6 equiv. of THF remain in the product. Yield 216 mg (0.18 mmol, 80%).

Mp. 293 °C (dec.); **EA** calc. (incl. 0.6 equiv. THF) (found) in %: C 60.06 (60.00), H 5.32 (5.02), N 8.95 (9.50), S 2.56 (2.71); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 121.49 MHz): δ = 60.9 (d, $^{1}J(^{31}P,^{107}Ag)$ = 707 Hz, 2 P), 60.9 ppm (d, $^{1}J(^{31}P,^{109}Ag)$ = 822 Hz, 2 P); **^{1}H NMR** (CD_2Cl_2, 300.13 MHz): δ = 7.70 (m, 4 H, iminic C*H*), 7.43 (m, 2 H, phenyl *para*-C*H*), 7.22 (m, 4 H, phenyl *meta*-C*H*), 6.98 (m, 4 H, phenyl *ortho*-C*H*), 6.95 (d, $^{3}J(^{1}H,^{1}H)$ = 3.8 Hz, 4 H, pyrrolic C*H* near imine), 6.48 (d, $^{3}J(^{1}H,^{1}H)$ = 3.8 Hz, 4 H, pyrrolic C*H* near Et-groups), 5.91 (s, 4 H, aromatic C*H*), 3.68 (m, 2.5 H, THF), 2.39 (q, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, 4 H, *exo*-R-CH_2-CH_3), 2.15 (s, 12 H, Ar-CH_3), 1.89 (q, $^{3}J(^{1}H,^{1}H)$ = 7.6 Hz , 4 H, *endo*-R-CH_2-CH_3), 1.82 (m, 2.5 H, THF), 1.10 (t, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, 6 H, *exo*-R-CH_2-CH_3), 0.63 ppm (t, $^{3}J(^{1}H,^{1}H)$ = 7.6 Hz, 6H, *endo*-R-CH_2-CH_3); **^{13}C{^{1}H} NMR** (CD_2Cl_2, 125.76 MHz): δ = 152.2 (t, *J* = 3 Hz, iminic *C*H), 144.0 (s, pyrrolic *C*-C-Et), 140.7(s, aromatic *C*), 137.9 (m, phenyl *ipso*-*C*),135.8 (s, aromatic *C*-CH_3), 133.8 (s, pyrrolic *C*), 132.0 (s, phenyl *para*-*C*H), 131.9 (d, *J* = 9 Hz, phenyl *ortho*-*C*H), 128.6 (t, *J* = 5 Hz, phenyl *meta*-*C*H), 125.1 (s, pyrrolic *C*H near imine), 122.5 (s, aromatic *C*H), 110.8 (s, pyrrolic *C*H near Et-groups), 68.3 (s, THF), 45.3 (s, *C*-Et_2), 45.2 (s, *endo*-R-*C*H_2-CH_3), 32.6 (s, *exo*-R-*C*H_2-CH_3), 26.2 (s, THF), 19.4 (s, Ar-*C*H_3), 10.4 (s, *exo*-R-CH_2-*C*H_3), 10.1 ppm (s, *endo*-R-CH_2-*C*H_3); **^{15}N NMR** (50.68 MHz, CD_2Cl_2): δ = −80.6 (s, iminic *N*), −227.7 ppm (s, pyrrolic *N*); **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2962 (w), 2925 (w), 2871 (w), 1614 (s), 1595 (m), 1472 (s), 1437 (m), 1404 (m), 1377 (w), 1352 (w), 1321 (m), 1255 (vs), 1220 (m), 1183 (m), 1150 (m), 1140 (s), 1099 (s), 1029 (s), 993 (m), 985 (m), 961 (m), 884 (s), 862 (m), 829 (m), 785 (s), 746 (m), 690 (s), 635 (vs), 608 (m), 596 (m), 571 (s), 542 (m), 515 (s), 503 (s), 466 (s), 443 (m); **Raman** (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3115 (1), 3059 (1), 2980 (1), 2941 (1), 2919 (1), 2878 (1), 1625 (10), 1593 (5), 1565 (3), 1476 (3), 1408 (1), 1387 (1), 1371 (1), 1358 (1), 1345 (1), 1326 (3),

1299 (1), 1281 (1), 1259 (3), 1184 (1), 1115 (1), 1081 (1), 1047 (1), 1033 (1), 1001 (1), 964 (2), 890 (1), 807 (1), 790 (1), 741 (1), 719 (1), 650 (1), 620 (1), 609 (1), 579 (1), 544 (1), 507 (1), 470 (1), 458 (1), 420 (1), 363 (1), 343 (1), 300 (1), 206 (1), 188 (2), 131 (1), 82 (3); **MS** (ESI, m/z, THF): 1035.7 $[M-OTf^-]^+$.

Suitable crystals for single crystal X-ray crystallography were received as described above.

Figure S6: NMR, IR and Raman spectra of **[1Ag][OTf]** (solvent signals indicated by asterisks).

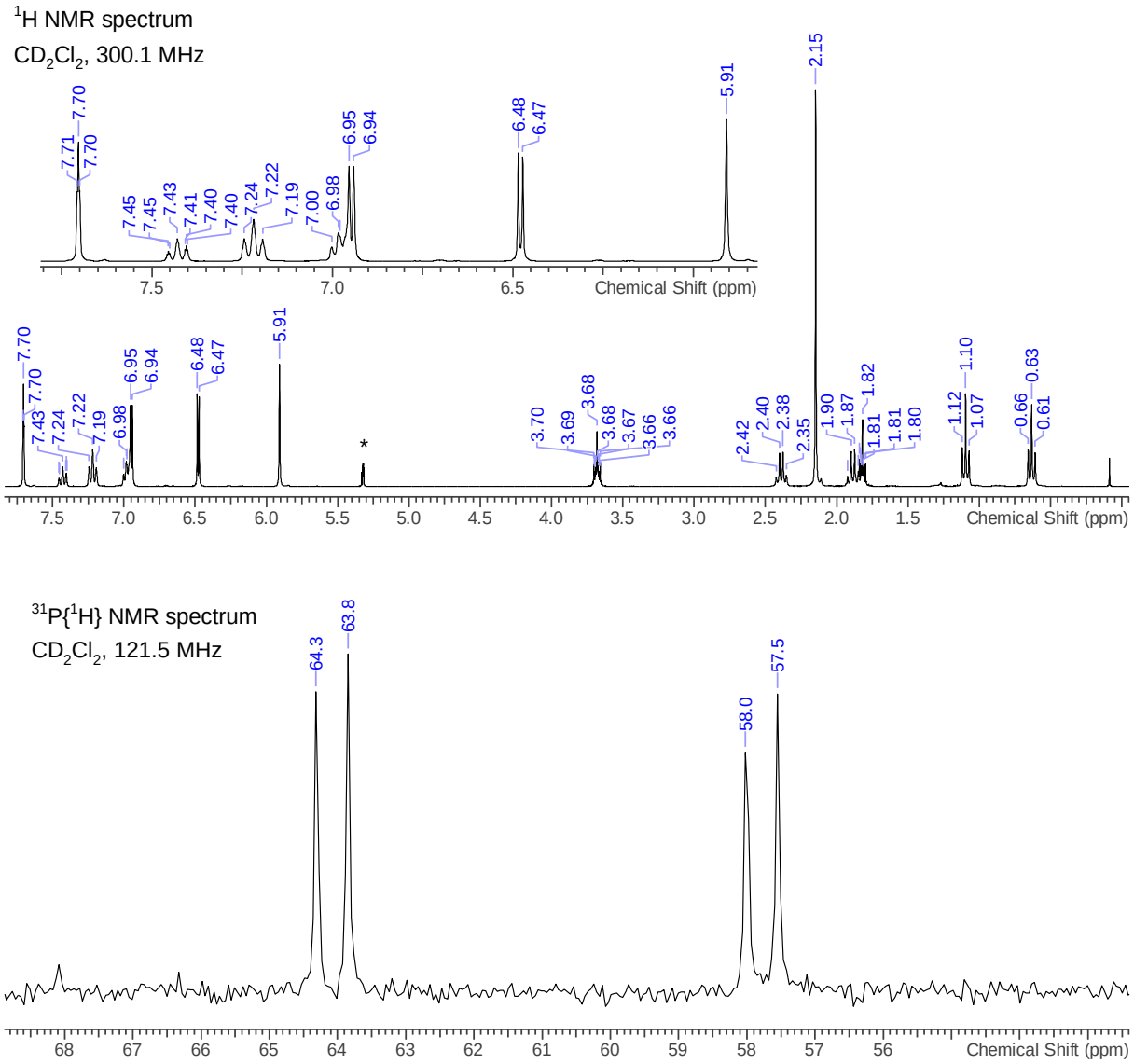
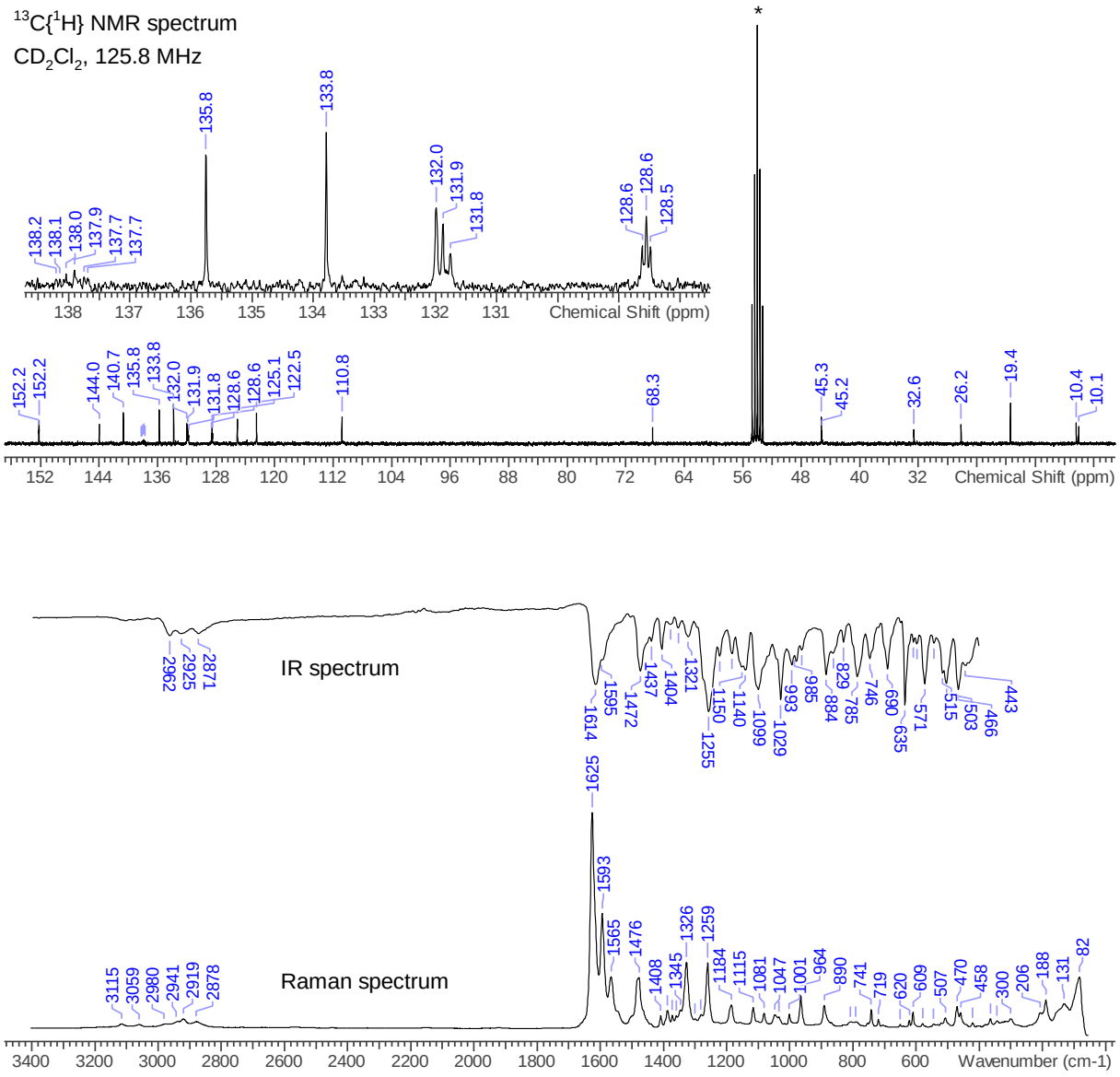
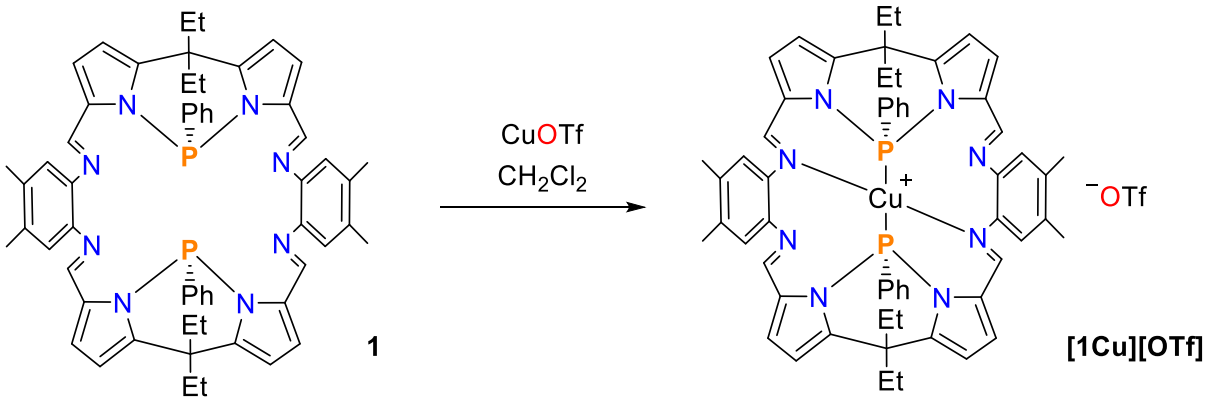


Figure S6: continued.



4.5 Pacman phosphane copper(I) complex [1Cu][OTf]



A 25 mL Schlenk flask is filled with **1** (208 mg, 0.20 mmol) and greyish

CuOTf · 0.5 toluene (51.8 mg, 0.20 mmol). The solids are dissolved in dichloromethane (10 mL) giving an orange solution. The solution is concentrated *in vacuo* (1×10^{-3} mbar) and THF (2 mL) is added dropwise to the solution. The solution is further concentrated *in vacuo* (1×10^{-3} mbar) and left to stand in warm a water bath in the fridge at 5 °C for crystallization, resulting in the deposition of orange crystals. The supernatant is removed via a syringe. The crystals are washed with dichloromethane (0.5 mL) at −80 °C and dried *in vacuo* (1×10^{-3} mbar) for 1.5 h at 50 °C. Approximately 0.5 equiv. of THF remain in the product. Yield: 179 mg (0.15 mmol, 75%).

Mp.: 263 °C (dec.); **EA** calc. (incl. 0.5 equiv THF) (found) in %: C 62.21 (61.63), H 5.31 (5.30), N 9.51 (9.22), S 2.70 (2.72); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 121.49 MHz): δ = 17.8 ppm (s); **^{1}H NMR** (CD_2Cl_2, 500.13 MHz): δ = 7.65 (s, 4 H, iminic C*H*), 7.30 (t, $^{3}J(^{1}H,^{1}H)$ = 7.5 Hz, 2 H, phenyl *para*-C*H*), 7.13 (t, $^{3}J(^{1}H,^{1}H)$ = 7.9 Hz, 4 H, phenyl *meta*-C*H*), 6.89 (d, $^{3}J(^{1}H,^{1}H)$ = 3.8 Hz, 4 H, pyrrolic C*H* near imine), 6.87 (m, 4 H, phenyl *ortho*-C*H*), 6.40 (d, $^{3}J(^{1}H,^{1}H)$ = 3.8 Hz, 4 H, pyrrolic C*H* near Et-groups), 6.33 (s, 4 H, aromatic C*H*), 3.68 (m, 2.1 H, THF), 2.32 (q, $^{3}J(^{1}H,^{1}H)$ = 7.3 Hz, 4 H, *exo*-R-CH_2-CH_3), 2.23 (s, 12 H, Ar-CH_3), 1.82 (m, 2.1 H, THF), 1.77 (q, $^{3}J(^{1}H,^{1}H)$ = 7.5 Hz, 4 H, *endo*-R-CH_2-CH_3), 1.08 (t, $^{3}J(^{1}H,^{1}H)$ = 7.3 Hz, 6 H, *exo*-R-CH_2-CH_3) 0.62 ppm (t, $^{3}J(^{1}H,^{1}H)$ = 7.5 Hz, 6 H, *endo*-R-CH_2-CH_3); **^{13}C{^{1}H} NMR** (CD_2Cl_2, 125.76 MHz): δ = 152.9 (s, iminic *C*H), 145.4 (s, pyrrolic *C*-C-Et_2), 141.3 (t, $^{1}J(^{13}C,\ ^{31}P)$ = 19 Hz, phenyl *ipso*-*C*), 140.4 (s, aromatic *C*), 136.7 (s, aromatic *C*-CH_3), 132.4 (s, pyrrolic *C*), 130.6 (s, phenyl *para*-*C*H), 128.8 (t, $^{2}J(^{13}C,\ ^{31}P)$ = 9 Hz, phenyl *ortho*-*C*H), 128.0 (t, $^{3}J(^{13}C,\ ^{31}P)$ = 5 Hz, phenyl *meta*-*C*H), 125.0 (s, pyrrolic *C*H near imine), 123.1 (s, aromatic *C*H), 111.3 (s, pyrrolic *C*H near Et-groups), 68.3 (s, THF), 44.9 (s, *C*-Et_2), 44.0 (s, *endo*-R-*C*H_2-CH_3), 31.0 (s, *exo*-R-*C*H_2-CH_3) 26.1 (s, THF), 19.7 (s, aromatic *C*H_3), 10.4 (s, *exo*-R-CH_2-*C*H_3), 10.0 ppm (s, *endo*-R-CH_2-*C*H_3); **^{15}N NMR** (50.68 MHz, CD_2Cl_2): δ = −107.2 (s, iminic *N*), −216.8 ppm (s, pyrrolic *N*); **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2970 (w), 2956 (w), 2925 (w), 2873 (w), 1618 (m), 1604 (m), 1585 (s), 1515 (w), 1470 (m), 1441 (w), 1410 (m), 1373 (w), 1356 (w), 1311 (m), 1278 (s), 1253 (vs), 1220 (m), 1179 (m), 1150 (m), 1134 (m), 1084 (s), 1062 (m), 1043 (m), 1029 (s), 998 (s), 973 (m), 942 (w),

892 (s), 868 (m), 855 (m), 839 (m), 802 (w), 783 (s), 748 (m), 740 (m), 721 (w), 695 (m), 635 (s), 600 (m), 579 (s), 569 (m), 550 (m), 534 (m), 515 (m), 491 (m), 470 (s), 458 (s), 425 (s); **Raman** (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3107 (1), 3059 (1), 2972 (1), 2962 (1), 2935 (1), 2922 (1), 2876 (1), 1620 (10), 1605 (8), 1588 (10), 1576 (5), 1519 (3), 1490 (2), 1472 (4), 1445 (1), 1413 (1), 1387 (3), 1370 (1), 1360 (3), 1346 (1), 1330 (2), 1314 (7), 1285 (3), 1260 (4), 1227 (1), 1180 (2), 1105 (2), 1084 (2), 1082 (2), 1047 (1), 1032 (1), 999 (2), 947 (1), 910 (1), 896 (1), 877 (1), 755 (1), 743 (2), 698 (1), 654 (1), 620 (1), 608 (1), 582 (1), 572 (1), 560 (1), 552 (1), 537 (1), 522 (1), 490 (1), 470 (3), 453 (4), 428 (1), 421 (1), 412 (1), 393 (1), 371 (1), 366 (1), 360 (1), 336 (1), 305 (1), 279 (1), 251 (1), 204 (2), 171 (1), 142 (3), 131 (4), 115 (4), 99 (4), 79 (5); **MS** (ESI, m/z, THF): 991.0 $[M-OTf^-]^+$.

Suitable crystals for single crystal X-ray crystallography were received as described above.

Figure S7: NMR, IR and Raman spectra of **[1Cu][OTf]** (solvent signals indicated by asterisks).

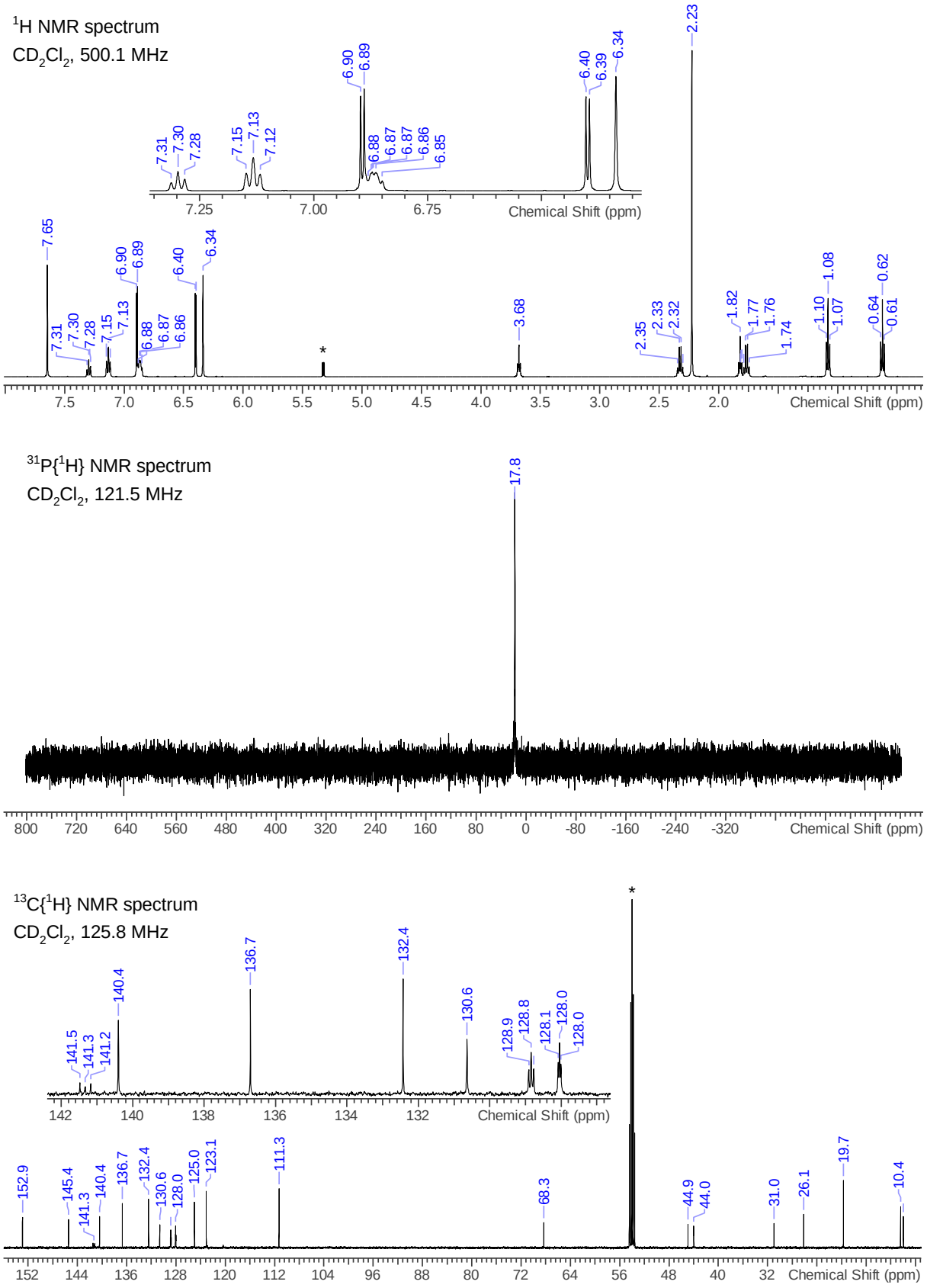
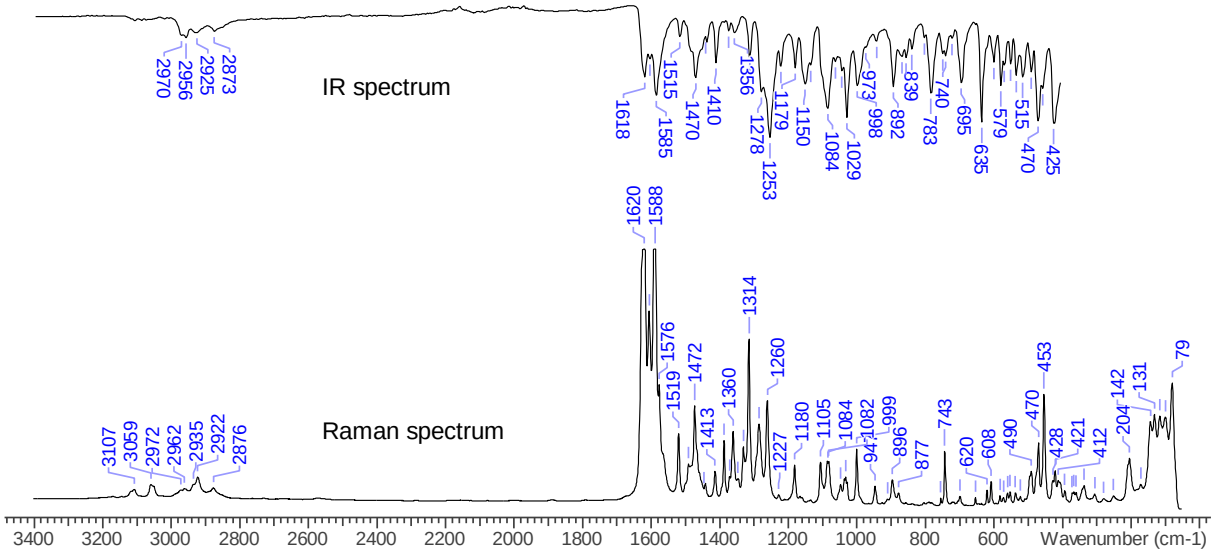
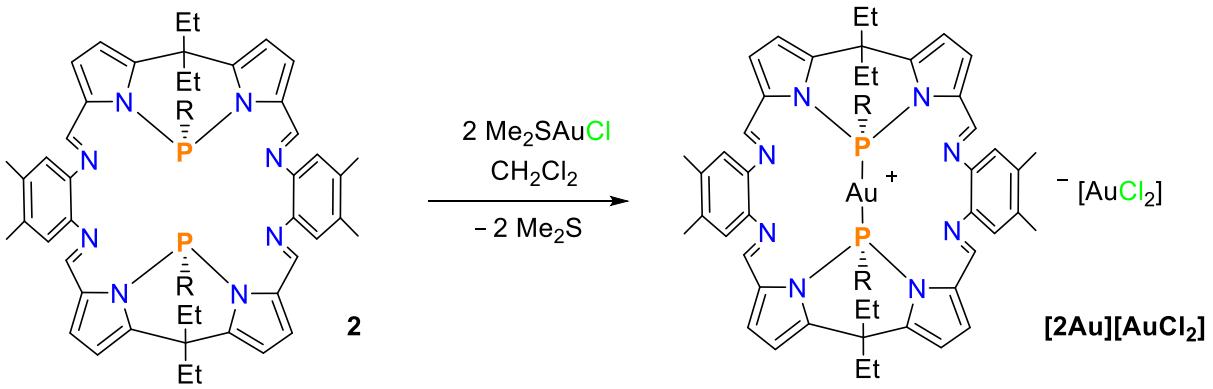


Figure S7: continued.



4.6 Pacman phosphane gold(I) complex [2Au][AuCl$_2$]



R = N(*i*Pr)$_2$

A 25 mL Schlenk flask is filled with **2** (195 mg, 0.20 mmol) and colorless Me$_2$SAuCl (118 mg, 0.40 mmol). The solids are dissolved in dichloromethane (12 mL) giving an orange solution. After stirring for 1 h at ambient temperature, the solvent is removed *in vacuo* (1×10^{-3} mbar) and the remaining yellow solids are redissolved in a mixture of dichloromethane (3 mL) and THF (3 mL). This solution is concentrated *in vacuo* (1×10^{-3} mbar) and is left to stand in a warm water bath in the fridge at 5 °C for crystallization, resulting in the deposition of yellow crystals. The supernatant is

removed via a syringe. The crystals are washed with dichloromethane (0.5 mL) at −80 °C and dried *in vacuo* (1×10^{-3} mbar) for 2 h at 50 °C.

The solution of the second fraction still contains **2** and is therefore dried *in vacuo* (1×10^{-3} mbar) and redissolved in THF whereas **2** remains as yellow precipitate. The solution is filtered off (pore 4) and the THF is removed from the filtrate in vacuo (1 × 10−3 mbar). The orange product is dried for 2 h at 50 °C. 198 mg (0.14 mmol, 68.8%).

Mp. 193 °C (dec.); **EA** calc. (found) in %: C 48.37 (47.88), H 5.32 (5.32), N 9.73 (9.78); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 121.49 MHz): δ = 95.1 ppm (s); **^{1}H NMR** (CD_2Cl_2, 500.13 MHz): δ = 8.57 (s, 4 H, iminic C*H*), 7.16 (d, $^{3}J(^{1}H,^{1}H)$ = 3.8 Hz, 4 H, pyrrolic C*H* near imine), 6.78 (s, 4 H, aromatic C*H*), 6.41 (d, $^{3}J(^{1}H,^{1}H)$ = 3.8 Hz, 4 H, pyrrolic C*H* near Et-groups), 4.39 (br s, 2 H, *i*Pr-groups C*H*), 3.07 (br s, 2 H, *i*Pr-groups C*H*), 2.27 (s, 12 H, Ar-CH_3), 2.24 (q, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, 4 H, *exo*-R-CH_2-CH_3), 1.67 (q, $^{3}J(^{1}H,^{1}H)$ = 7.3 Hz, 4 H, *endo*-R-CH_2-CH_3), 1.09 (br d, $^{3}J(^{1}H,^{1}H)$ = 4.0 Hz, 12 H, *i*Pr-groups CH_3), 0.89 (t, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, 6 H, *exo*-R-CH_2-CH_3), 0.80 (br d, $^{3}J(^{1}H,^{1}H)$ = 4.3 Hz, 12 H, *i*Pr-groups CH_3), 0.38 ppm (t, $^{3}J(^{1}H,^{1}H)$ = 7.3 Hz, 6 H, *endo*-R-CH_2-CH_3); **^{13}C{^{1}H} NMR** (CD_2Cl_2, 75.47 MHz): δ = 152.3 (s, iminic *C*H), 144.3 (s, pyrrolic *C*-C-Et), 142.1 (s, aromatic *C*), 135.6 (s, aromatic *C*-CH_3), 135.4 (t, $^{2}J(^{13}C,^{31}P)$ = 3 Hz, pyrrolic *C*), 124.7 (br s, pyrrolic *C*H near imine), 122.2 (s, aromatic *C*H), 111.1 (br s, pyrrolic *C*H near Et-groups), 49.0 (br s, *i*Pr-groups *C*H), 45.5 (s, *endo*-R-*C*H_2-CH_3), 45.1 (s, *C*-Et_2), 33.0 (s, *exo*-*C*H_2-CH_3), 24.9 (br s, *i*Pr-groups *C*H_3) 22.9 (br s, *i*Pr-groups *C*H_3), 19.7 (s, Ar-*C*H_3), 10.1 (s, *endo*-CH_2-*C*H_3), 9.9 ppm (s, *exo*-CH_2-*C*H_3); **^{15}N NMR** (50.68 MHz, CD_2Cl_2): δ = −72.3 (s, iminic *N*), −225.8 ppm (s, pyrrolic *N*); **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3098 (w), 2966 (m), 2929 (m), 2873 (m), 1622 (s), 1608 (s), 1546 (w), 1474 (s), 1402 (m), 1373 (m), 1334 (m), 1301 (m), 1241 (m), 1191 (s), 1175 (m), 1140 (m), 1090 (vs), 1024 (m), 998 (s), 977 (s), 954 (s), 880 (s), 855 (s), 818 (m), 791 (m), 771 (vs), 740 (m), 730 (m), 719 (m), 701 (m), 676 (m), 631 (m), 620 (m), 608 (m), 567 (m), 542 (s), 515 (s), 462 (s), 435 (vs); **Raman** (633 nm, 10 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3134 (1), 3119 (1), 3094 (1), 2974 (1), 2938 (1), 2920 (1), 2879 (1), 1623 (10), 1591 (4), 1561 (3), 1500 (2), 1479 (4), 1460 (1), 1390 (2), 1376 (2), 1350 (2), 1307 (1), 1282 (1), 1256 (4),

1235 (1), 1188 (2), 1144 (1), 1113 (1), 1080 (1), 1040 (1), 968 (1), 880 (1), 858 (1), 826 (1), 796 (1), 788 (1), 740 (1), 718 (1), 637 (1), 587 (1), 555 (1), 543 (1), 526 (1), 493 (1), 470 (1), 416 (1), 385 (1), 350 (1), 329 (1), 299 (1), 287 (1), 236 (1), 209 (1), 139 (1), 81 (3); **MS** (ESI, m/z, THF): 1172.0 $[M–[AuCl_2]^-]^+$.

Suitable crystals for single crystal X-ray crystallography were received as described above.

Figure S8: NMR, IR and Raman spectra of **[2Au][AuCl₂]** (solvent signals indicated by asterisks).

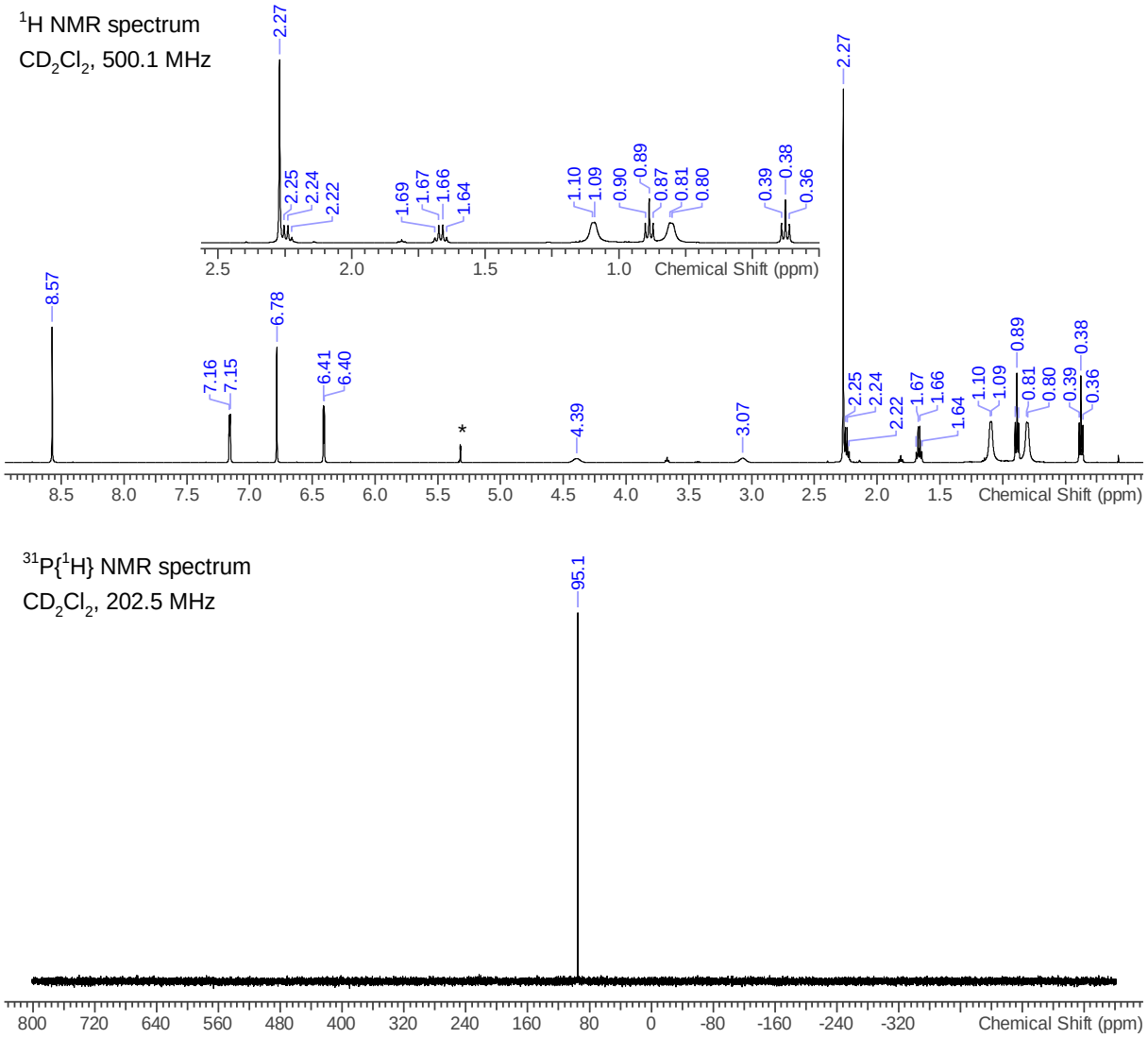
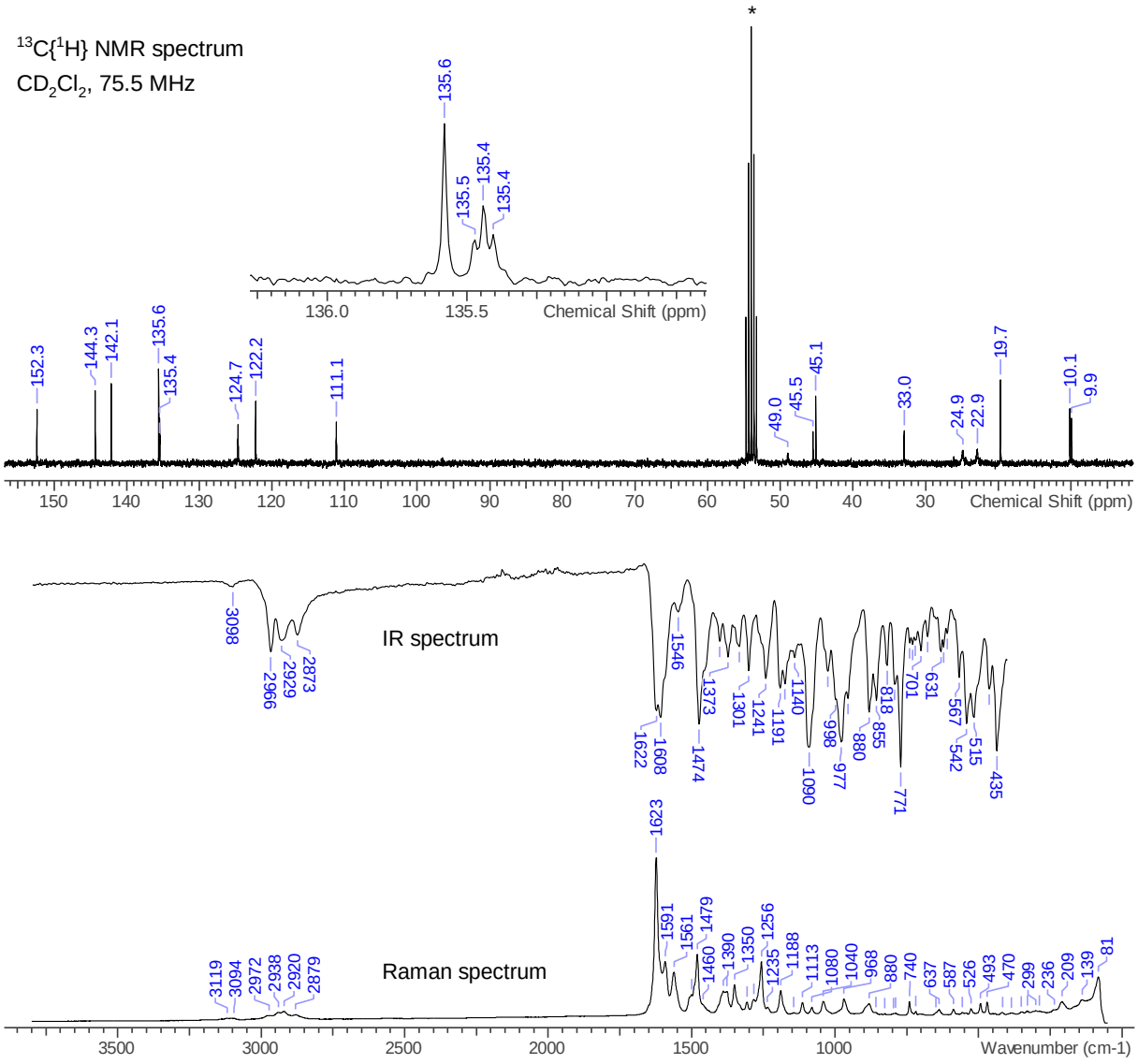
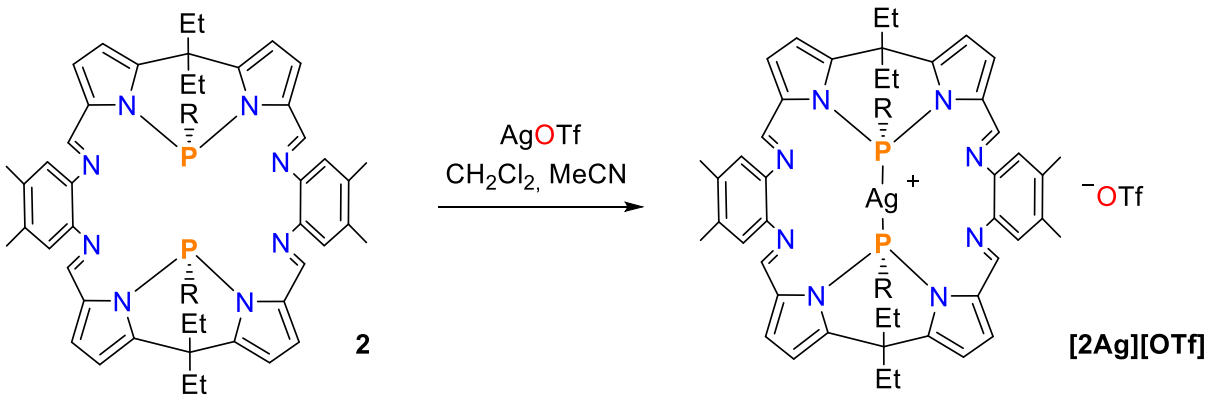


Figure S8 continued.



4.7 Pacman phosphane silver(I) complex [2Ag·MeCN][OTf]



R = N(*i*Pr)$_2$

The reaction is carried out in the absence of light, as the AgOTf is light sensitive. A 25 mL Schlenk flask is filled with **2** (204 mg, 0.21 mmol) and colourless AgOTf (53.3 mg, 0.21 mmol). The solids are dissolved in dichloromethane (10 mL) giving an orange-red solution. The reaction solution is stirred for approximately 2 h. Afterwards, the solution is concentrated *in vacuo* (1×10^{-3} mbar) to about half the volume. THF (2 mL) is added to the concentrated solution. The solution is further concentrated *in vacuo* (1×10^{-3} mbar) and is left to stand in a warm water bath in the fridge at 5 °C. resulting in the deposition of a yellow precipitate. The supernatant is removed via syringe and is treated as a second fraction analogous to the first. The remaining solids of the first fraction are washed with THF (0.5 mL) at –80 °C and dried *in vacuo* (1×10^{-3} mbar) for 2 h at 50 °C. Approximately 0.5 equiv. of THF remain in the product. Yield: 133 mg (0.11 mmol, 52%).

Mp. 254 °C (dec.); **EA** calc. (incl. 0.5 equiv. THF) (found) in %: C 57.77 (57.30), H 6.36 (6.20), N 11.04 (11.23), S 2.53 (2.35); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 202.46 MHz): δ = 75.4 (d, $^{1}J(^{31}P,^{107}Ag)$ = 670 Hz, 2 P), 75.4 ppm (d, $^{1}J(^{31}P,^{109}Ag)$ = 771 Hz, 2 P); **^{1}H NMR** (CD_2Cl_2, 300.13 MHz): δ = 8.01 (m, 4 H, iminic C*H*), 6.97 (d, $^{3}J(^{1}H,^{1}H)$ = 3.8 Hz, 4 H, pyrrolic C*H* near imine), 6.75 (s, 4 H, aromatic C*H*), 6.34 (d, $^{3}J(^{1}H,^{1}H)$ = 3.8 Hz, 4 H, pyrrolic C*H* near Et-groups), 3.68 (m, 2.1 H, THF), 2.28 (s, 12 H, Ar-CH_3), 2.24 (q, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, 4 H,

R-CH_2-CH_3), 1.82 (m, 2.1 H, THF), 1.54 (q, ^3J(^{1}H, ^{1}H) = 7.4 Hz, 4 H, R-CH_2-CH_3), 0.95 (br s, 24 H, *i*Pr-groups CH_3), 0.93 (t, ^3J(^{1}H, ^{1}H) = 7.2 Hz, 6 H, R-CH_2-CH_3), 0.42 ppm (t, ^3J(^{1}H, ^{1}H) = 7.4 Hz, 6 H, R-CH_2-CH_3) Due to broadening by dynamic effects the C*H* protons of the *iso*-propyl substituents were not observed; **^{13}C{^{1}H} NMR** (CD_2Cl_2, 125.76 MHz): δ = 153.6 (s, iminic *C*H), 144.4 (s, pyrrolic *C*-C-Et_2), 143.5 (s, aromatic *C*), 135.3 (s, aromatic *C*-CH_3), 134.7 (s, pyrrolic *C*), 127.6 (s, pyrrolic *C*H near imine), 121.0 (s, aromatic *C*H), 110.2 (s, pyrrolic *C*H), 68.3 (s, THF), 45.4 (s, R-*C*H_2-CH_3), 44.8 (s, *C*-Et_2), 30.8 (s, R-*C*H_2-CH_3), 26.1 (s, THF), 19.7 (s, Ar-*C*H_3), 9.7 (s, R-CH_2-*C*H_3), 9.6 ppm (s, R-CH_2-*C*H_3); **^{15}N NMR** (50.68 MHz, CD_2Cl_2): δ = −219.8 (s, pyrrolic *N*), −78.5 (s, iminic *N*); **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3110 (w), 2970 (m), 2933 (m), 2873 (m), 1622 (s), 1538 (w), 1474 (s), 1406 (m), 1371 (w), 1327 (w), 1301 (w), 1263 (vs), 1241 (s), 1222 (m), 1179 (s), 1146 (s), 1094 (s), 1066 (m), 1031 (vs), 991 (s), 981 (s), 882 (s), 857 (m), 829 (m), 787 (s), 752 (m), 740 (m), 684 (w), 658 (w), 635 (vs), 608 (m), 569 (s), 517 (s), 497 (m), 476 (m), 449 (s), 423 (m); **Raman** (633 nm, 10 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3122 (1), 3105 (1), 2980 (1), 2941 (1), 2923 (1), 2883 (1), 1630 (10), 1591 (6), 1567 (3), 1545 (2), 1499 (2), 1479 (4), 1409 (2), 1390 (2), 1357 (2), 1339 (3), 1303 (1), 1283 (2), 1260 (4), 1184 (2), 1143 (1), 1107 (2), 1078 (1), 1042 (2), 1031 (2), 992 (1), 962 (2), 887 (2), 828 (1), 807 (1), 795 (1), 742 (2), 719 (1), 699 (1), 612 (2), 573 (1), 545 (1), 500 (1), 479 (1), 465 (2), 415 (1), 394 (1), 371 (1), 347 (1), 309 (2), 209 (2), 172 (2), 137 (3), 79 (5); **MS** (ESI, m/z, THF): 1081.5 [M–OTf^-]$^+$.

To obtain suitable crystals for single crystal X-ray crystallography, **[2Ag·MeCN][OTf]** is dissolved in acetonitrile. The cloudy, red solution is filtered over silica gel (pore 4). The filtrate is reduced *in vacuo* (1×10^{-3} mbar) and left to stand in a water bath in the fridge at 5 °C overnight. yielding single crystals of the MeCN-adduct **[2Ag·MeCN][OTf]**.

Figure S9: NMR, IR and Raman spectra of **[2Ag·MeCN][OTf]** (solvent signals indicated by asterisks).

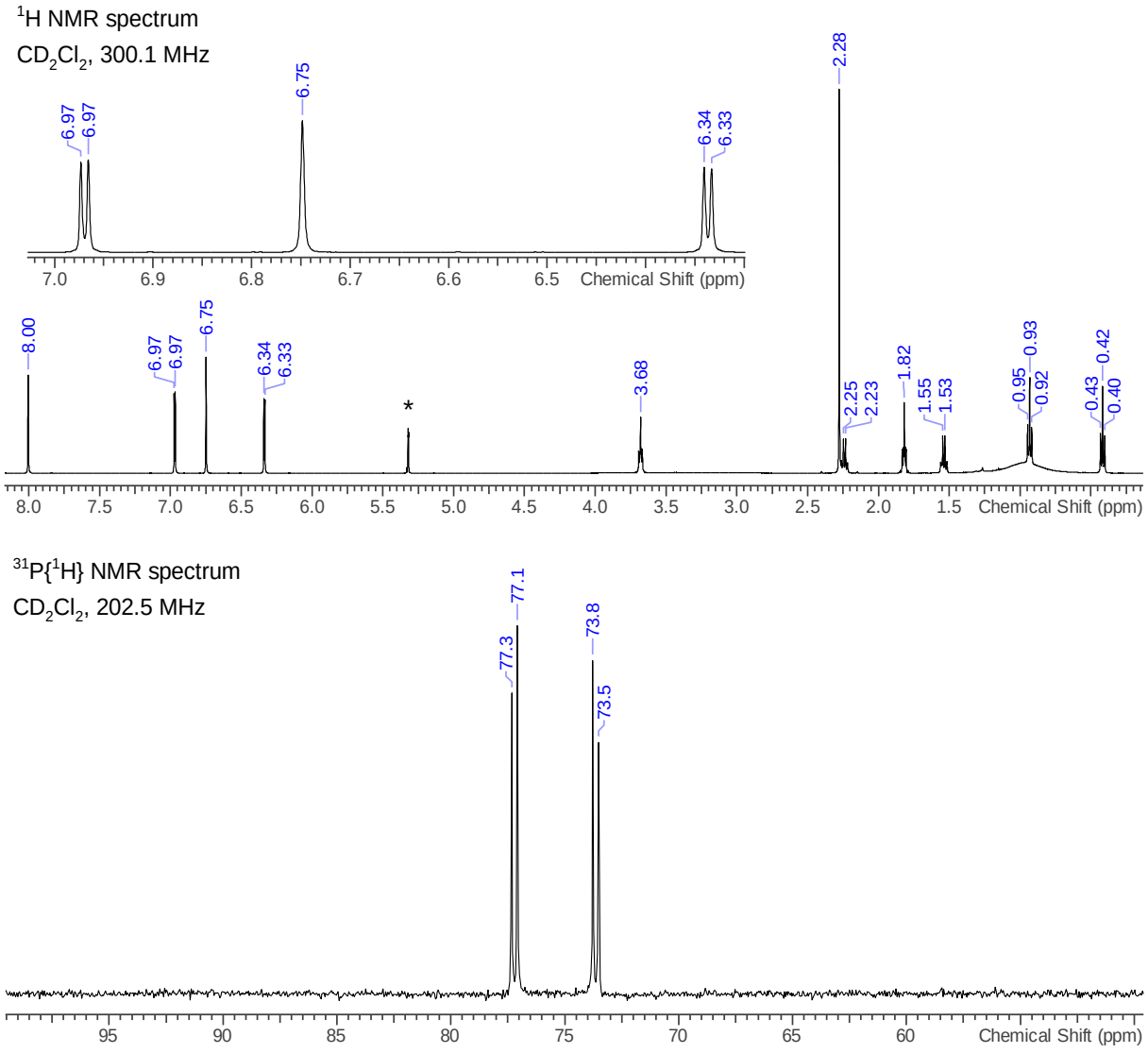
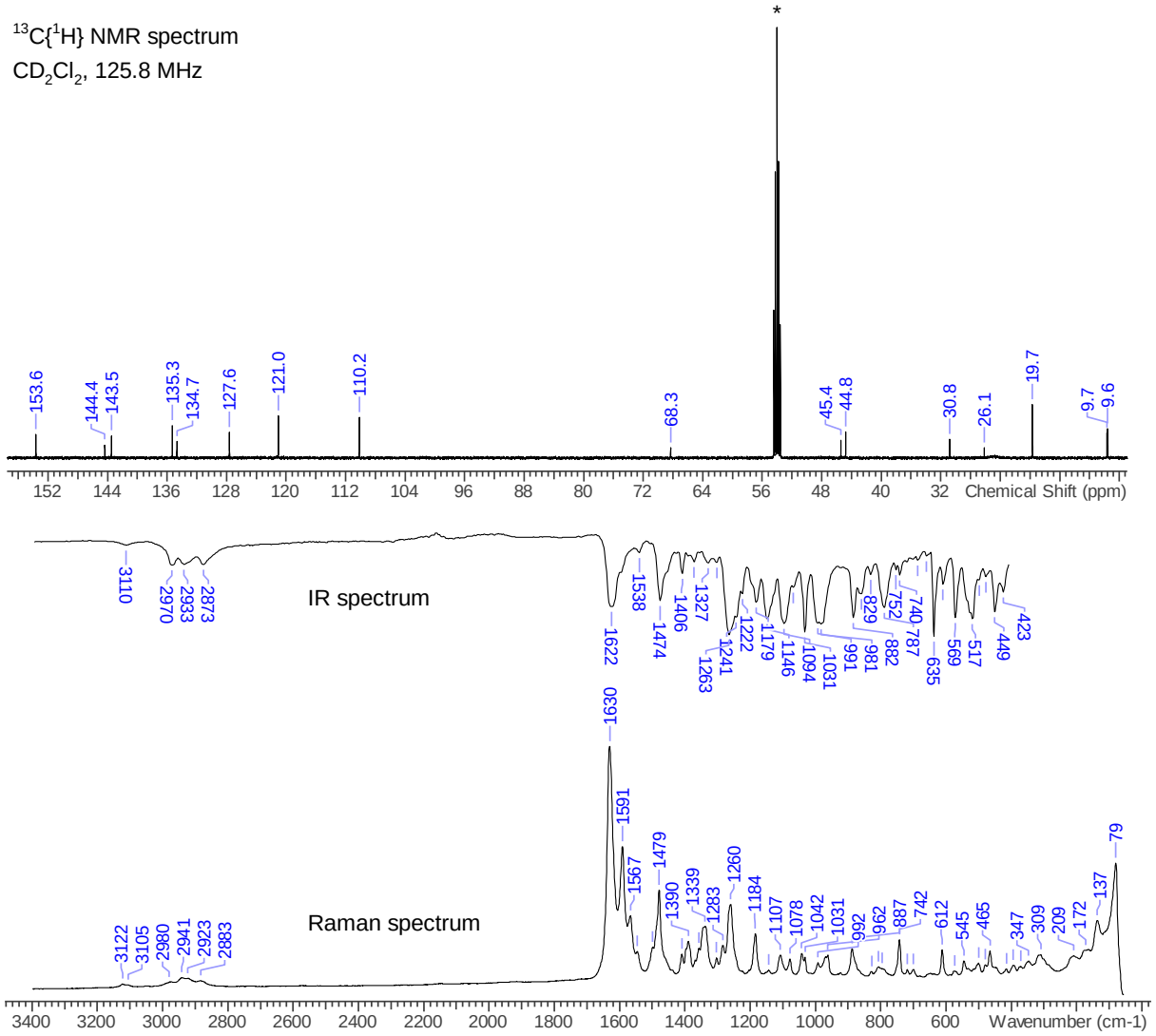
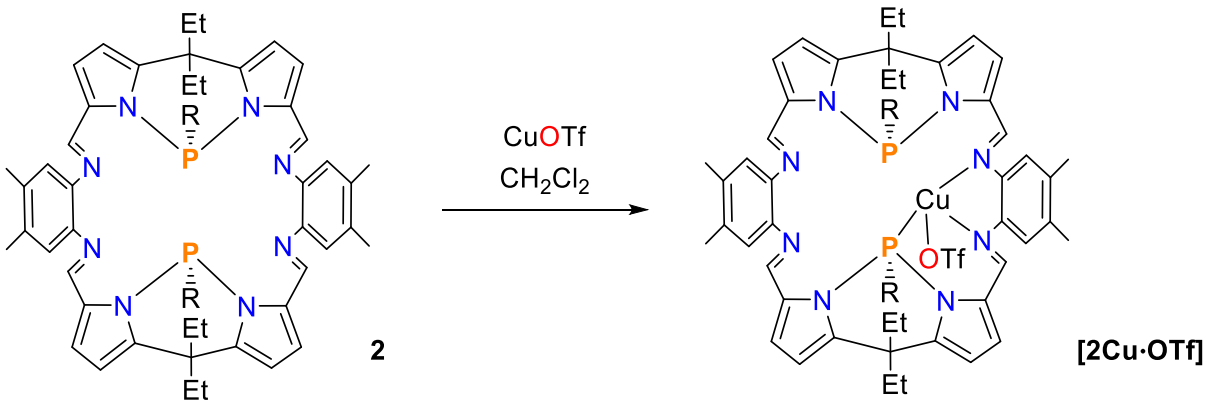


Figure S9 continued.



4.8 Pacman phosphane copper(I) complex [2Cu·OTf]



R = N(*i*Pr)$_2$

A 25 mL Schlenk flask is filled with **2** (240 mg, 0.24 mmol) and greyish CuOTf · 0.5 toluene (63.0 mg, 0.24 mmol). The solids are dissolved in dichloromethane (10 mL), giving an orange-red solution. The solution is stirred for 2 h. Afterwards, the dichloromethane is removed *in vacuo* (1×10^{-3} mbar) and the remaining yellow-orange solids are dissolved in THF (5 mL). The solution is filtered over silica gel. Toluene (2 mL) is added dropwise to the filtrate. The solution is concentrated *in vacuo* (1×10^{-3} mbar) and is left to stand in a warm water bath in the fridge at 5 °C overnight, resulting in the deposition of orange crystals. The supernatant is removed via syringe and the remaining crystals are washed two times with THF (2×0.5 mL) at −80 °C. The crystals are dried *in vacuo* (1×10^{-3} mbar) for 3 h at 50 °C. Since the dried product still contains toluene the product is washed with THF three times (3×1 mL) and dried *in vacuo* (1×10^{-3} mbar) for 2 h at 60 °C each time. Approximately 0.75 equiv. of THF remain in the product. Yield: 224 mg (0.18 mmol, 75%).

Mp. 216 °C (dec.); **EA** calc. (incl. 0.75 equiv. THF) (found) in %: C 59.96 (59.57), H 6.66 (6.36), N 11.28 (11.43), S 2.58 (2.64); **^{31}P{^{1}H} NMR** (CD_2Cl_2, 121.49 MHz): δ = 69.0 ppm (s); **^{1}H NMR** (CD_2Cl_2, 300.13 MHz): δ = 8.34 (s, 4 H, iminic C*H*), 7.07 (d, $^{3}J(^{1}H,^{1}H)$ = 3.8 Hz, 4 H, pyrrolic C*H* near imine), 6.89 (s, 4 H, aromatic C*H*), 6.34 (d, $^{3}J(^{1}H,^{1}H)$ = 3.8 Hz, 4 H, pyrrolic C*H* near Et-groups), 3.45 - 3.78 (m, 3.1 THF) 2.29 (s, 12 H, Ar-CH_3), 2.21 (q,

$^3J(^1H,^1H)$ = 7.4 Hz, 4 H, R-C*H*$_2$-CH$_3$), 1.82 (m, 3.1THF), 1.52 (q, $^3J(^1H,^1H)$ = 7.5 Hz, 4 H, R-C*H*$_2$-CH$_3$), 0.94 (br s, 24 H, *i*Pr-groups C*H*$_3$), 0.88 (t, $^3J(^1H,^1H)$ = 7.4 Hz, 6 H, R-CH$_2$-C*H*$_3$), 0.42 ppm (t, $^3J(^1H,^1H)$ = 7.5 Hz, 6 H, R-CH$_2$-C*H*$_3$) Due to broadening by dynamic effects, the C*H* proton of the *iso*-propyl substituents were not observed; **^{13}C{^{1}H} NMR** (CD_2Cl_2, 125.76 MHz): δ = 154.2 (s, iminic *C*H), 145.3 (s, pyrrolic *C*-C-Et), 141.4 (s, aromatic *C*), 136.0 (s, aromatic *C*-CH$_3$), 134.8 (s, pyrrolic *C*), 125.7 (s, pyrrolic *C*H near imine), 122.8 (s, aromatic *C*H), 110.9 (s, pyrrolic *C*H near Et-groups), 68.3 (s, THF), 44.8 (s, *C*-Et$_2$), 44.5 (s, R-*C*H$_2$-CH$_3$), 31.2 (s, R-*C*H$_2$-CH$_3$), 26.1 (s, THF), 19.8 (s, Ar-*C*H$_3$), 9.7 (s, R-CH$_2$-*C*H$_3$), 9.6 ppm (s, R-CH$_2$-*C*H$_3$); **^{15}N NMR** (50.68 MHz, CD_2Cl_2): δ = −222.7 (s, pyrrolic *N*), −95.1 (s, iminic *N*); **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2966 (m), 2933 (w), 2875 (w), 1632 (m), 1608 (m), 1587 (m), 1529 (w), 1474 (m), 1406 (m), 1373 (w), 1327 (w), 1299 (w), 1259 (s), 1222 (m), 1193 (m), 1173 (m), 1146 (s), 1088 (s), 1029 (s), 983 (s), 880 (m), 853 (m), 829 (m), 779 (s), 752 (m), 740 (m), 723 (m), 695 (w), 678 (w), 635 (vs), 571 (s), 550 (m), 534 (s), 515 (s), 466 (s), 425 (s); **Raman** (633 nm, 5 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3125 (1), 2973 (1), 2939 (1), 2924 (1), 2882 (1), 1610 (10), 1584 (10), 1567 (6), 1520 (2), 1480 (4), 1404 (3), 1378 (2), 1358 (2), 1341 (3), 1326 (2), 1302 (2), 1288 (2), 1266 (4), 1237 (1), 1190 (3), 1183 (2), 1176 (2), 1152 (1), 1141 (1), 1104 (2), 1092 (1), 1082 (1), 1038 (1), 1027 (1), 971 (1), 956 (3), 896 (1), 875 (1), 868 (1), 835 (1), 820 (1), 796 (1), 757 (1), 743 (2), 732 (1), 728 (1), 647 (1), 639 (1), 630 (1), 609 (1), 594 (1), 583 (1), 575 (1), 565 (1), 552 (1), 536 (1), 523 (1), 499 (1), 461 (1), 437 (1), 395 (1), 381 (1), 363 (1), 348 (1), 317 (1), 245 (1), 211 (1), 175 (1), 149 (1), 96 (2); **MS** (ESI, m/z, THF): 1037.7 [M–OTf$^-$]$^+$.

Suitable crystals for single crystal X-ray crystallography were received as described above.

Figure S10: NMR, IR and Raman spectra of **[2Cu·OTf]** (solvent signals indicated by asterisks).

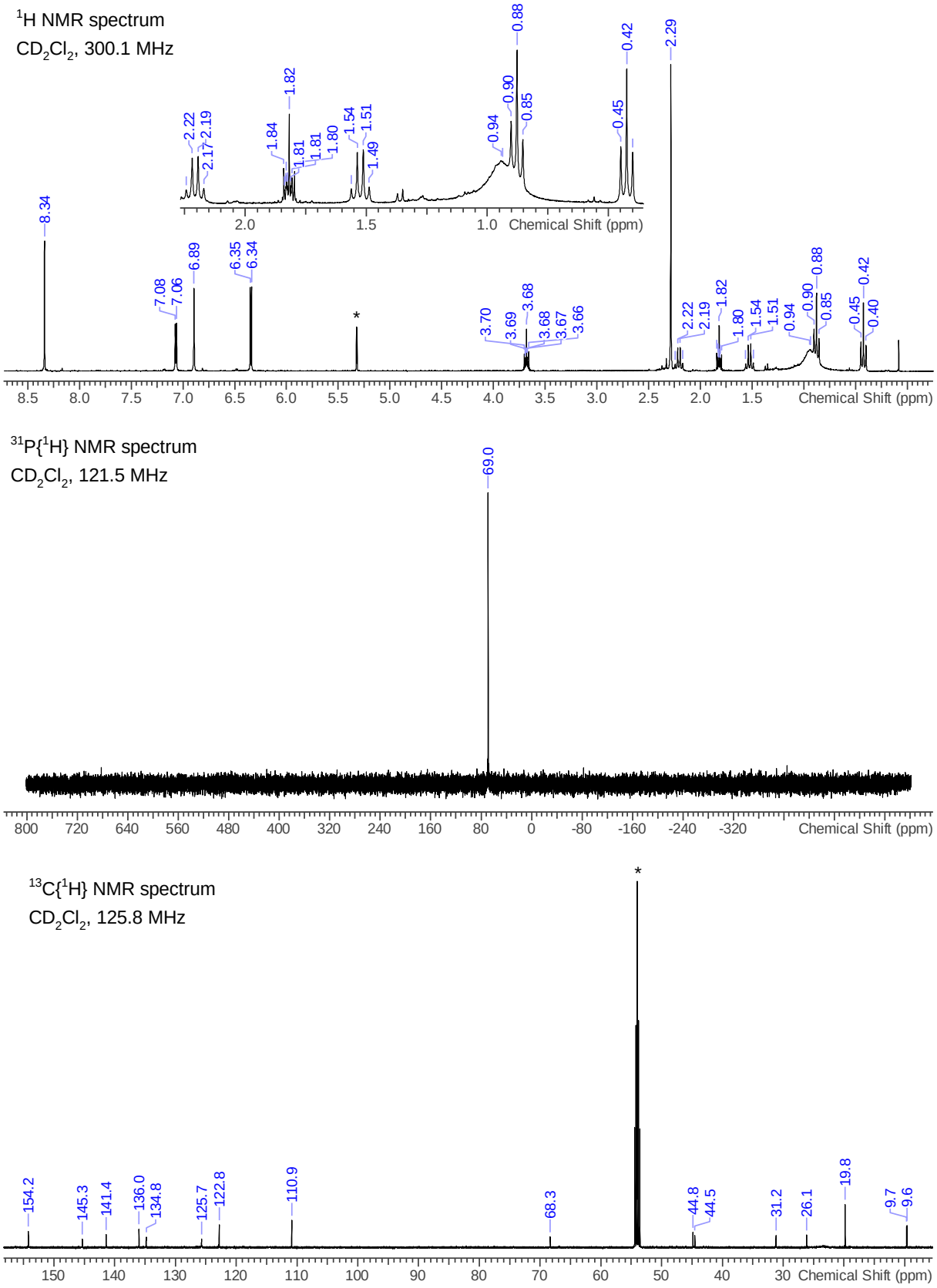
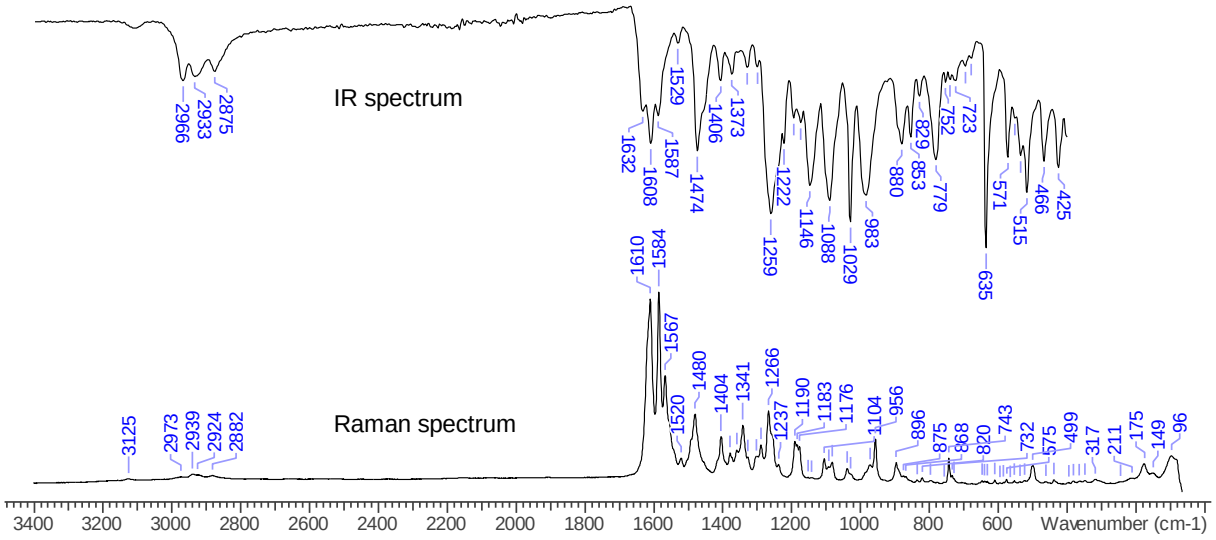


Figure S10 continued.



5 Computational details

5.1 General remarks

Computations were carried out using Gaussian09[7] and the standalone version of NBO 6.0.[8–11]

Structure optimizations employed the DFT functional PBE[12,13] in conjunction with Grimme's dispersion correction D3(BJ)[14,15] and the def2-TZVP basis set[16] (notation PBE-D3/def2TZVP). The resolution of identity (RI) approximation was employed, using the appropriate Coulomb fitting basis of the Weigend group.[17] All structures were fully optimized and confirmed as minima by frequency analyses.

Please note that all computations were carried out for single, isolated molecules in the gas phase (ideal gas approximation). There may well be significant differences between gas phase and condensed phase.

5.2 Summary of calculated data

Table S7. Summary of calculated data, including electronic energies and thermal corrections.

Compd.	PG	Opt. method	E_{tot}[a]	ΔG[b]
1	C_1	PBE-D3/def2TZVP	−3363.31797	0.9026
2	C_1		−3483.5301	1.1003
[1Au][Cl]	C_1		−3499.0214	0.9049
[1Ag][OTf]	C_1		−5003.5449	0.9095
[1Cu][OTf]	C_1		−3510.2376	0.9042
[2Au][$AuCl_2$]	C_1		−3619.2260	1.1042
[2Ag·MeCN][OTf]	C_1		−5120.3019	1.1194
[2Cu·OTf]	C_1		−3627.2091	1.1177

[a] Total SCF energy in a.u.; [b] thermal correction to Gibbs energy in a.u. (298 K unless stated otherwise).

5.3 Summary of NBO analyses

Table S8. Donor-acceptor energies E_{DA} for the interaction of N3 and P1 with the metals in **1Au**$^+$, **1Ag**$^+$ and **1Cu**$^+$.

Donor-acceptor	**1Au+**		**1Ag+**		**1Cu+**	
	E_{DA} [kJ mol^{-1}]	E_{DA} [kcal mol^{-1}]	E_{DA} [kJ mol^{-1}]	E_{DA} [kcal mol^{-1}]	E_{DA} [kJ mol^{-1}]	E_{DA} [kcal mol^{-1}]
N3-M1	21.67	5.18	37.53	8.97	118.87	28.41
P1-M1	781.74	186.84	296.02	70.75	238.91	57.10

Table S9. Donor-acceptor energies E_{DA} for the interaction of N7 and P1 with the metals in **2Au⁺**, **[2Ag·MeCN]⁺** and **[2Cu·OTf]**.

Donor-acceptor	**2Au+**		**[2Ag·MeCN]⁺**		**[2Cu·OTf]**	
	E_{DA} [kJ mol^{-1}]	E_{DA} [kcal mol^{-1}]	E_{DA} [kJ mol^{-1}]	E_{DA} [kcal mol^{-1}]	E_{DA} [kJ mol^{-1}]	E_{DA} [kcal mol^{-1}]
N7-M1	12.38	2.96	22.59	5.40	115.77	27.67
P1-M1	507.77	121.36	245.48	58.67	244.85	58.52
acetonitrile-M1	-	-	55.27	13.21	-	-
O1-M1	-	-	-	-	64.27	15.36

Table S10. Natural charges on P1 in **1** - **[2Cu·OTf]**.

Compound	natural charge on P1 [e]	Compound	natural charge on P1 [e]
1	1.22	**2**	1.36
1Au⁺	1.31	**2Au⁺**	1.50
1Ag⁺	1.19	**[2Ag·MeCN]⁺**	1.34
1Cu⁺	1.11	**[2Cu·OTf]**	1.28[a] 1.37[b]

[a] natural charge on P2 (coordinated to Cu); [b]natural charge on P1(not coordinated to Cu).

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