Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information for:

Unveiling the stereoelectronic properties of a triphenylene-based tris-N-heterocyclic carbene

Sergio Gonell, Roberto G. Alabau, Macarena Poyatos and Eduardo Peris

General methods. The imidazolium-based salt **3**[1] and the metal complexes $[RhCl(COD)]_2$,[2] $[RhCl(CO)_2]_2$,[3] and $[RhCl(BimNtBu_2)(COD)]$[4] (BimN*t*Bu = 1,3-di(*tert*-butyl)-benzimidazolylidene) were synthesized as previously reported. All operations were carried out by using standard Schlenk techniques under nitrogen atmosphere unless otherwise stated. Anhydrous solvents were dried using a solvent purification system (SPS M BRAUN) or purchased from Aldrich and degassed prior to use by purging with nitrogen and kept over molecular sieves. All other reagents were used as received from commercial suppliers. NMR spectra were recorded on a Varian Innova 300 and 500 MHz, using $CDCl_3$ as solvent. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas. Exact mass analysis was realized using Q-TOF premier mass spectrometer with electrospray source (Waters, Manchester, UK) operating at a resolution of ca. 16 000 (fwhm). Elemental analyses were carried out on a EuroEA3000 Eurovector Analyzer. Infrared spectra (FTIR) were obtained on a BrukerEQUINOX 55 spectrometer with a spectra window of 4000 - 600cm^{-1}.

1. Synthesis and characterization of the metal complexes

1.1. Synthesis of complex 4

KHMDS (0.5 M in toluene, 0.85 mL, 0.425 mmol, 3.15 equiv.) was added dropwise to a suspension of **3** (128.2 mg, 0.135 mmol) in THF (10 mL) at 0ºC. After stirring at that temperature for 10 minutes, a solution of $[RhCl(COD)]_2$ (100 mg, 0.203 mmol) in THF (5 mL) was added *via* oven dried cannula. The resulting mixture was stirred for 10 minutes at 0ºC and for 2 hours at 50ºC. After this time, the volatile components were removed under vacuum. The crude solid was dissolved in CH_2Cl_2 and purified by column chromatography. Flash chromatography using mixtures of CH_2Cl_2/acetone (from 95:5 to 7:3) afforded the separation of a yellow band that contained compound **4**. Compound **4** was obtained as a yellow solid after precipitation in a mixture of dichloromethane/hexanes. Yield: 81.4 mg (42 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74 (s, 6H, CH_{arom}), 5.10 (brs, 6H, CH_{COD}), 3.08 (brs, 6H, CH_{COD}), 2.58 (s, 54H, C(CH_3)$_3$), 2.50 (brs, 12H, C$H_{2\ COD}$), 1.78-1.86 (m, 12H, C$H_{2\ COD}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.9 (d, $^1J_{Rh\text{-}C}$ = 49.1 Hz, Rh-$C_{carbene}$), 135.5 ($C_{q\ arom}$), 124.0 ($C_{q\ arom}$), 107.8 (CH_{arom}), 94.4 (d, $^1J_{Rh\text{-}C}$ = 15.8 Hz, Rh-CH_{COD}), 67.9 (d, $^1J_{Rh\text{-}C}$ = 15.8 Hz, Rh-CH_{COD}), 60.9 (*C*(CH$_3$)$_3$), 32.6 (C(*C*H$_3$)$_3$), 32.4 (*C*H$_2$-COD), 28.8 (*C*H$_2$-COD). Electrospray MS (20 V,

m/z): 676.5 $[M-2Cl]^{2+}$. HRMS ESI-TOF-MS (positive mode): $[M-Cl]^{+}$ monoisotopic peak 1387.4236, calcd 1387.4238, ε_r=0.14 ppm. Anal. Calcd. for $C_{69}H_{96}Cl_3N_6Rh_3$ (1424.60): C, 58.17; H, 6.79; N, 5.90. Found: C, 58.26; H, 7.05; N, 5.58.

1.2. Synthesis of complex 5

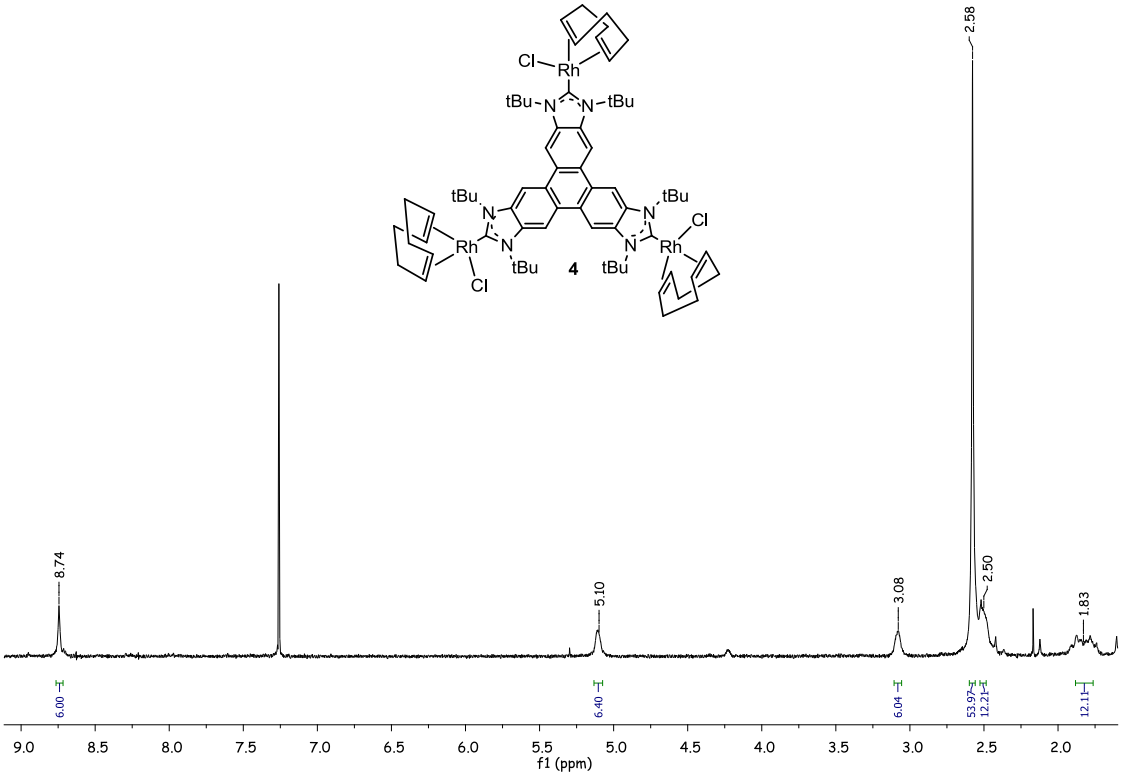
KHMDS (0.5 M in toluene, 0.54 mL, 0.27 mmol, 3.15 equiv.) was added dropwise to a suspension of **3** (81.5 mg, 0.086 mmol) in THF (10 mL) at 0ºC. After stirring at that temperature for 10 minutes, a solution of $[RhCl(CO)_2]_2$ (50 mg, 0.13 mmol) in THF (5 mL) was added *via* oven dried cannula. The resulting mixture was stirred for 10 minutes at 0ºC and for 2 hours at 50ºC. After this time, the volatile components were removed under vacuum. The crude solid was dissolved in CH_2Cl_2 and filtered through a pad of Celite. Precipitation with a mixture CH_2Cl_2/hexane afforded compound **5** as a yellow solid. Yield: 27 mg (26 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.94 (s, 6H, C*H*$_{arom}$), 2.58 (s, 54H, C(C*H*$_3$)$_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 187.5 (d, $^1J_{Rh-C}$ = 42.4 Hz, Rh-*C*$_{carbene}$), 185.8 (d, $^1J_{Rh-C}$ = 57.2 Hz, Rh-*C*O), 182.7 (d, $^1J_{Rh-C}$ = 75.7, Rh-*C*O), 135.5 (C$_{q\ arom}$), 125.0 (*C*$_{q\ arom}$), 109.4 (*C*H$_{arom}$), 61.3 (*C*(CH$_3$)$_3$), 32.9 (C(*C*H$_3$)$_3$). IR (CH_2Cl_2) = 2078 ($\nu_{C=O}$), 1999 ($\nu_{C=O}$) cm^{-1}. Electrospray MS (20 V, *m/z*): 1073.2 $[M-(Rh(CO)_2Cl)+H]^+$, 1216.1 $[M-2CO-Cl+MeCN]^+$, 1285.2 $[M-2CO-Cl+2MeCN]^+$. HRMS ESI-TOF-MS (positive mode): $[M-Cl-2CO+MeCN]^+$ monoisotopic peak 1216.1488, calcd 1216.1483, ε_r= 0.4 ppm. Slow decomposition of the compound prevented a correct elemental analysis.

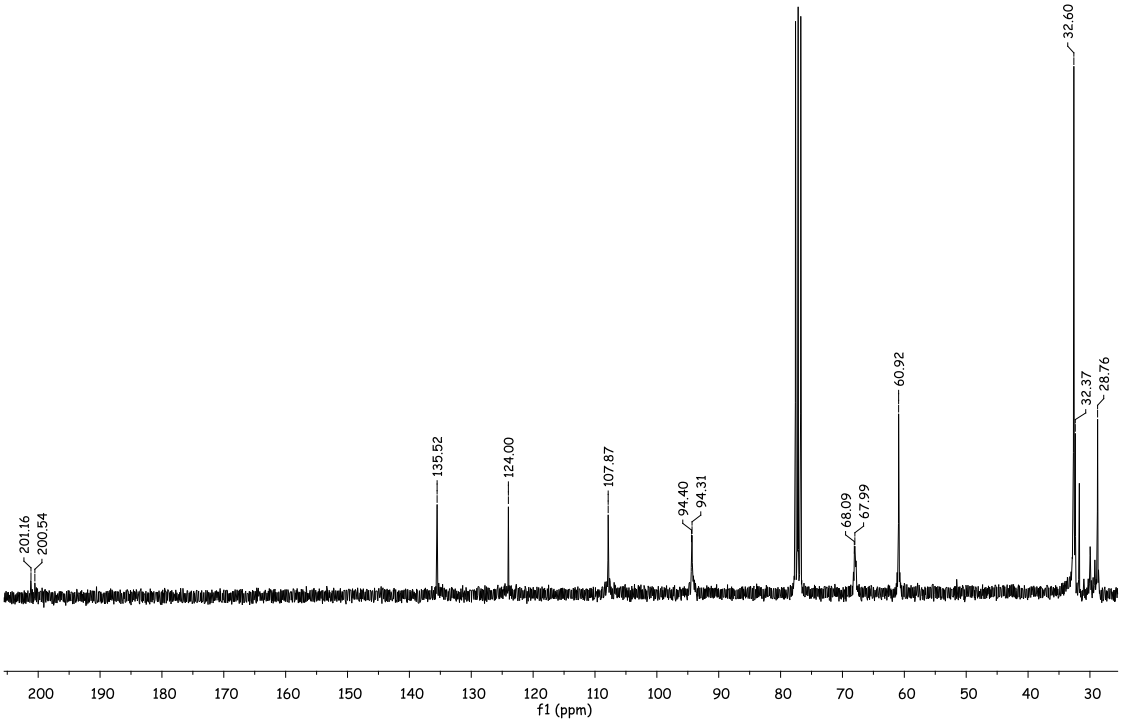
2. Electrochemical measurements

The measurements were carried out using a GPES equipped PGSTAT-30 potentiostat from Autolab at room temperature. A three-electrode configuration was used, where two Pt microelectrodes were connected to the working electrode and counter electrode and a Ag wire was used as the pseudo-reference electrode. The redox potential of ferrocene (445 mV) was used to calibrate the potential scale. Measurements performed on 10 mM analyte in CH_2Cl_2 with 0.1 mM $[NBu_4]PF_6$, at a 100 mVs^{-1} scan rate.

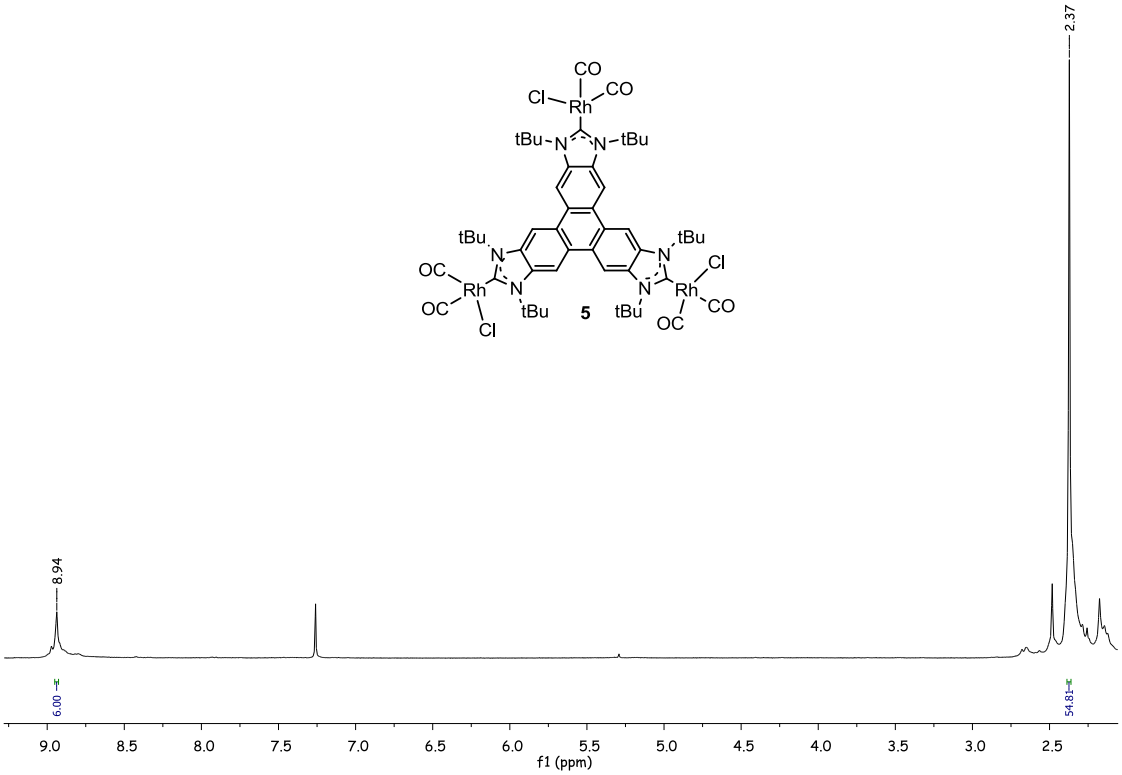
3. Spectra

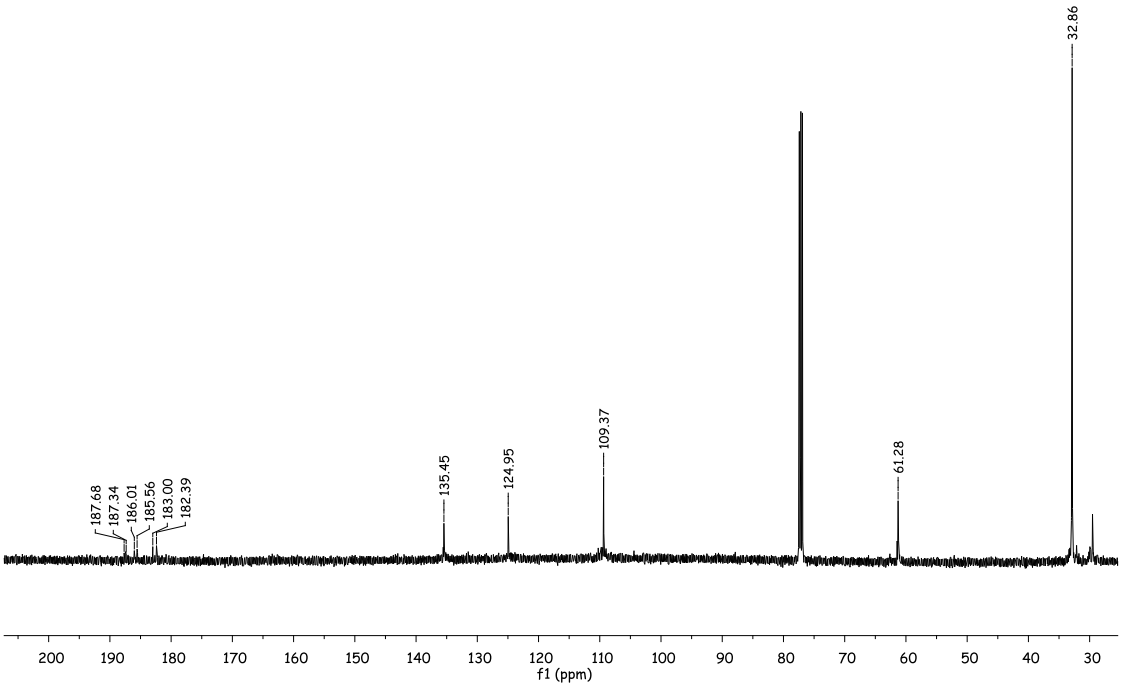
3.1. ^{1}H and ^{13}C NMR spectra of 4





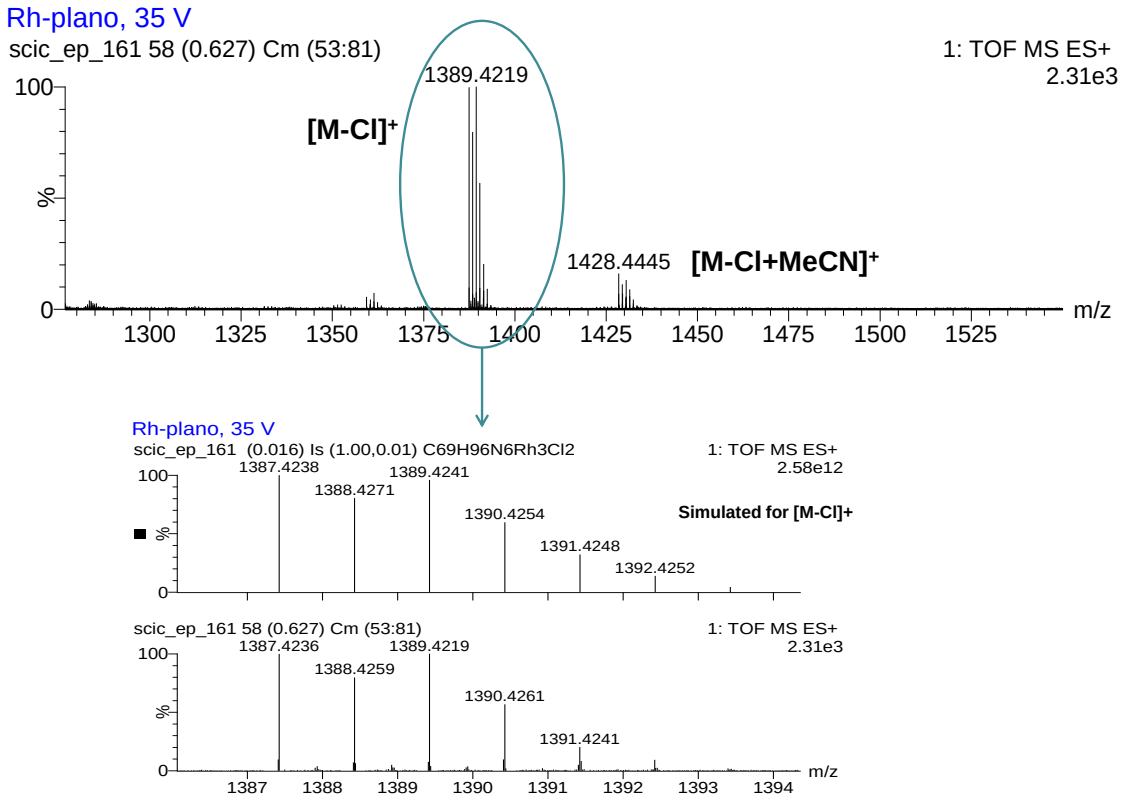
3.2. ^{1}H and ^{13}C NMR spectra of 5



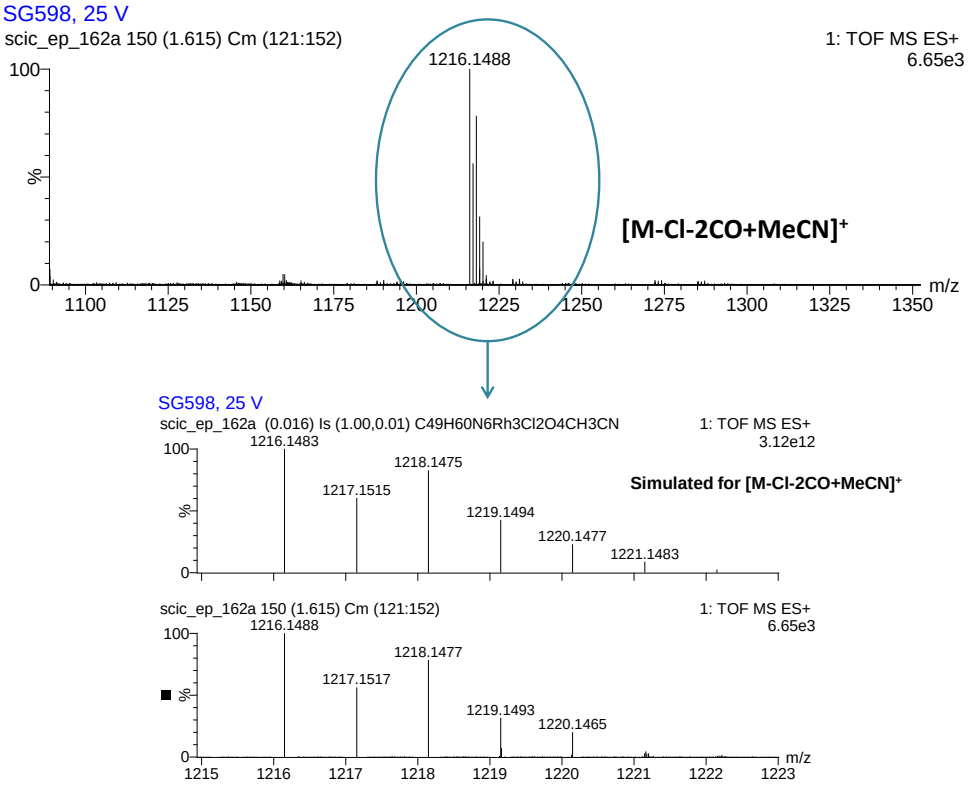


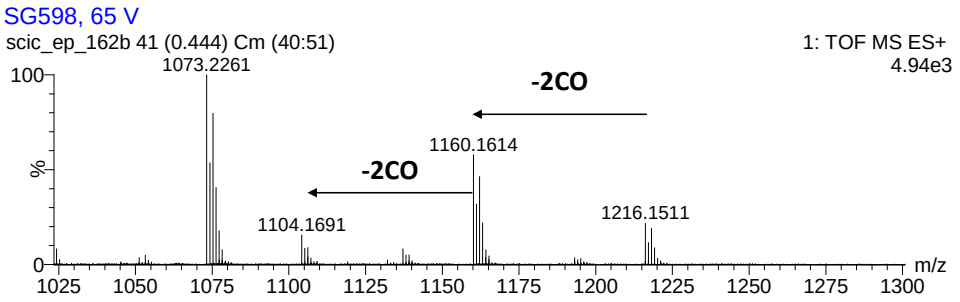
3.3. High Resolution Mass Spectra of 4 and 5

HR MS of 4



HR MS of 5


SG598, 25 V
scic_ep_162a 150 (1.615) Cm (121:152)
1: TOF MS ES+
6.65e3
1216.1488
[M-Cl-2CO+MeCN]+
m/z
SG598, 25 V
scic_ep_162a (0.016) Is (1.00,0.01) C49H60N6Rh3Cl2O4CH3CN
1: TOF MS ES+
3.12e12
1216.1483
1218.1475
1217.1515
1219.1494
1220.1477
1221.1483
Simulated for [M-Cl-2CO+MeCN]+
scic_ep_162a 150 (1.615) Cm (121:152)
1: TOF MS ES+
6.65e3
1216.1488
1218.1477
1217.1517
1219.1493
1220.1465
m/z


SG598, 65 V
scic_ep_162b 41 (0.444) Cm (40:51)
1: TOF MS ES+
4.94e3
1073.2261
-2CO
1160.1614
-2CO
1104.1691
1216.1511
m/z

4. X-Ray Crystallography

X-Ray Diffraction studies for complex 4. Crystals suitable for X-ray study of **4** were obtained by slow diffusion of diethyl ether into a concentrated solution of the complex in acetonitrile. Diffraction data was collected on a Agilent SuperNova diffractometer equipped with an Atlas CCD detector using Mo-Kα radiation (λ = 0.71073 Å). Single crystals were mounted on a MicroMount® polymer tip (MiteGen) in a random orientation. Absorption corrections based on the multiscan method were applied.[5] The structures were solved by direct methods in SHELXS-97 and refined by the full-matrix method based on F^2 with the program SHELXL-97 using the OLEX software package.[6, 7]

Key details of the crystal and structure refinement data are summarized in Supplementary Table S1. Further crystallographic details may be found in the respective CIF which was deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The reference number for **4** was assigned as 936175.

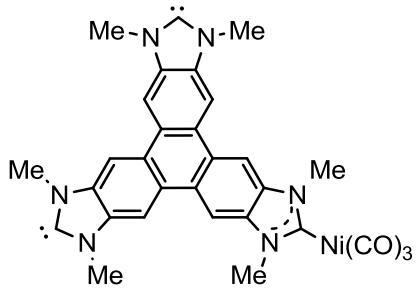
Supplementary Table S1. Summary of crystal data, data collection, and structure refinement details.

	4
Empirical formula	$C_{69}H_{96}Cl_3N_6Rh_3$, ($C_4H_6N_2$)
Sum formula	$C_{73}H_{102}Cl_3N_8Rh_3$
Formula weight	1506.71
Temperature	199.95(10)
Crystal System	monoclinic
Space group	C2/m
Unit cell dimensions	a = 16.9664(10) Å α = 90° b = 20.9747(7) Å β = 107.965(6) c = 21.9872(9) Å γ = 90
Volume	7443.0(6)
Z	2
Density (calculated)	1.345 mg/mm^3
Absorption coefficient	6.644 m/mm^{-1}
F(000)	3128.0
Crystal size	0.13 × 0.11 × 0.09 mm^3
Theta range for data collection	6.92 to 146.44°
Index ranges	$-20 \le h \le 20$, $-25 \le k \le 21$, $-27 \le l \le 26$
Reflections collected	34869
Independent reflections	7563[R(int) = 0.0517]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7563/20/416
Goodness-of-fit on F^2	1.079
Final R indices [I>2sigma(I)]	R_1 = 0.0711, wR_2 = 0.2116
R indices (all data)	R_1 = 0.0948, wR_2 = 0.2281
Largest diff. peak and hole	1.89 and -0.60 e.Å^{-3}

5. Computational details

The DFT calculations presented in this work were carried out as reported in the literature for ditopic NHC complexes.[8] The calculated atomic coordinates are collected in Supplementary Tables S2, S3 and S4.

Supplementary Table S2

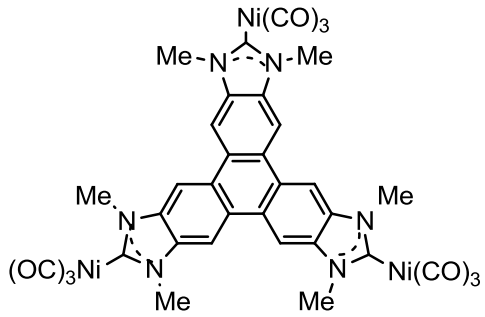


mono-Ni(CO)$_3$ complex, E = -3220.254582

Ni	-6.82814200	-3.77135000	-0.04423800
C	-5.11770400	-2.78136300	0.05112800
C	-6.65582300	-5.08902300	-1.25936200
C	-8.20929400	-2.76742600	-0.61687800
C	-7.17315300	-4.40768500	1.60295900
N	-4.90581300	-1.43439400	0.06390400
N	-3.86995200	-3.33220600	0.07518800
O	-6.58397500	-5.91181300	-2.04764600
O	-9.12704400	-2.20610400	-1.00107600
O	-7.39423100	-4.80339300	2.65035300
C	-3.55297300	-1.13390500	0.06781900
C	-5.93637400	-0.42261200	0.08193900
C	-2.88502200	-2.35842700	0.07662000
C	-3.58062100	-4.74708800	0.11291200
C	-2.85820800	0.05220600	0.06752400
H	-5.67974500	0.34518300	0.81391500
H	-6.05098300	0.03902100	-0.90155800
H	-6.87242700	-0.88846100	0.37314200
C	-1.51181200	-2.41786300	0.08680600
H	-2.87101800	-4.95644800	0.91585900
H	-3.16084100	-5.08427300	-0.83776400
H	-4.50626200	-5.28107400	0.30762100
C	-1.45169900	0.02660900	0.07854600
H	-3.40042900	0.98553400	0.05395700
C	-0.77099900	-1.22200900	0.08793400
H	-1.02222800	-3.37999300	0.08955200

C	-0.68964000	1.27612600	0.07905200
C	0.69203000	-1.25854700	0.09601100
C	-1.35544900	2.51618300	0.07180100
C	0.73104400	1.24020100	0.08802300
C	1.43163900	-0.04502500	0.09572500
C	1.37334500	-2.49013800	0.10367500
C	-0.61987600	3.67726000	0.07320400
H	-2.43381400	2.57437800	0.06522800
C	1.45656800	2.44618600	0.08964900
C	2.83833500	-0.08875700	0.10286300
C	2.74774500	-2.50110100	0.11068200
H	0.83772000	-3.42789100	0.10375400
N	-0.95984200	5.02105700	0.06762900
C	0.77901900	3.64218500	0.08213100
H	2.53637900	2.45004800	0.09689200
C	3.47630800	-1.30633500	0.11023500
H	3.42677600	0.81666800	0.10233700
N	3.69288300	-3.51501600	0.11862200
C	0.13389700	5.83413300	0.07245500
C	-2.31425600	5.51976800	0.05762300
N	1.18565500	4.96712500	0.08136900
N	4.81016600	-1.68255700	0.11794100
C	4.96890200	-3.03635400	0.12320000
C	3.37805600	-4.92362600	0.12148300
H	-2.85729200	5.18667500	0.94579900
H	-2.84622300	5.18092500	-0.83504700
H	-2.26326500	6.60572000	0.05446900
C	2.56343000	5.39733700	0.08892800
C	5.91840600	-0.75777700	0.12004400
H	2.80032800	-5.19062100	1.01009100
H	2.80851400	-5.19605200	-0.77074100
H	4.31836200	-5.46923500	0.12748400
H	3.07774500	5.03696900	0.98348500
H	3.08894900	5.03234300	-0.79720100
H	2.56692800	6.48448200	0.08612400
H	5.89117300	-0.12119400	1.00809700
H	5.89966000	-0.12733800	-0.77259900
H	6.83393700	-1.34401200	0.12642200

Supplementary Table S3



tris-Ni(CO)$_3$ complex, E = -6917.184023

Ni	-6.80784000	-3.76247800	0.01584300
C	-5.09847100	-2.77593500	0.09511600
C	-6.64471200	-5.10605000	-1.17339300
C	-8.18260700	-2.76151500	-0.58068200
C	-7.16290400	-4.36991500	1.67244500
N	-4.88706200	-1.42797500	0.10299700
N	-3.84917900	-3.32564700	0.11004900
O	-6.58078900	-5.94503600	-1.94458600
O	-9.09397000	-2.20084500	-0.97943500
O	-7.38996300	-4.74792100	2.72468300
C	-3.53574700	-1.12695900	0.09352700
C	-5.92002100	-0.41801500	0.12897800
C	-2.86629700	-2.35169600	0.09954600
C	-3.55959800	-4.74093100	0.15002000
C	-2.84188100	0.05951100	0.08280500
H	-5.65417500	0.35575000	0.85119400
H	-6.05166800	0.03491200	-0.85630100
H	-6.84991100	-0.88427700	0.43884800
C	-1.49309700	-2.40978200	0.09664400
H	-2.83523400	-4.94593200	0.94069100
H	-3.15932900	-5.08412100	-0.80678300
H	-4.48174600	-5.27263800	0.36619000
C	-1.43538700	0.03437100	0.08015200
H	-3.38602700	0.99168400	0.07087700
C	-0.75394600	-1.21301100	0.08707200
H	-1.00381200	-3.37201300	0.09673200
C	-0.67380500	1.28407800	0.06805400
C	0.70910500	-1.24763700	0.08134400
C	-1.34064400	2.52261200	0.06199600
C	0.74722300	1.25049100	0.06027700

C	1.44883500	-0.03393500	0.06710000
C	1.39072700	-2.47809300	0.08736300
C	-0.60389600	3.68281500	0.04792200
H	-2.41860300	2.57991000	0.06365500
C	1.47207300	2.45600600	0.04543100
C	2.85493100	-0.07562500	0.05910200
C	2.76509300	-2.48521600	0.07914700
H	0.85630900	-3.41597500	0.09391500
N	-0.95602000	5.02103500	0.04132100
C	0.79147100	3.65017300	0.04021400
H	2.55142800	2.46118800	0.03289500
C	3.49180700	-1.29366500	0.06612100
H	3.44271500	0.82959000	0.04242600
N	3.70066800	-3.50470200	0.08349000
C	0.14458200	5.82780000	0.01333700
C	-2.32631000	5.47857800	0.07820600
N	1.20633700	4.97099400	0.03127500
N	4.82738700	-1.65845900	0.06588800
C	4.97451900	-3.01495700	0.05851900
C	3.34429800	-4.90455200	0.12695700
Ni	0.14894500	7.80007800	-0.09329400
H	-2.86643800	4.95729100	0.87087800
H	-2.82331000	5.29965100	-0.87805300
H	-2.32557700	6.54388800	0.29007800
C	2.59734400	5.36150300	0.05125000
C	5.90700700	-0.69839200	0.08194300
Ni	6.63312100	-4.08410000	-0.03227600
H	2.62350300	-5.07625900	0.92878500
H	2.91302300	-5.22633900	-0.82379200
H	4.24335100	-5.48006500	0.32769700
C	-1.11837600	8.32456000	-1.26164200
C	1.69389900	8.46957900	-0.73567100
C	-0.16079300	8.43547700	1.56183500
H	3.13551500	4.75302800	0.78002500
H	3.05456200	5.23789100	-0.93309000
H	2.65826600	6.40353700	0.34907800
H	5.68525500	0.08652600	0.80702900
H	6.04998200	-0.25141500	-0.90447500
H	6.81686300	-1.20826200	0.38228400
C	8.05893200	-3.15017500	-0.61750600

C	6.39926400	-5.40384700	-1.23619600
C	6.95719200	-4.72600700	1.61774200
O	-1.89023800	8.68663700	-2.02053200
O	2.63000200	8.96299100	-1.16477400
O	-0.35092700	8.83613500	2.61300600
O	8.99985100	-2.63512500	-1.00915100
O	6.28958300	-6.22925000	-2.01681500
O	7.16533800	-5.12552600	2.66593800

Supplementary Table S4

[Ni(CO)$_3$(BimN*t*Bu$_2$)]

C1	2.7770	4.9276	9.9669
N2	1.8436	5.0739	8.9741
N3	3.2790	6.1837	10.1879
Ni4	3.9174	3.2013	10.1962
C5	0.7365	4.1185	8.6464
C6	1.9041	6.3575	8.4350
C7	4.0078	6.6474	11.4125
C8	2.8233	7.0681	9.2123
C9	3.4287	2.2465	11.6456
C10	3.8657	2.2013	8.6979
C11	5.6748	3.5989	10.2293
C12	0.5953	4.8759	8.7739
C13	0.6632	2.9752	9.6536
C14	0.9215	3.5583	7.2354
C15	1.3094	6.9468	7.3195
C16	4.0263	5.5744	12.4965
C17	5.4390	7.0510	11.0549
C18	3.2281	7.8313	12.0073
C19	3.1646	8.3810	8.8884
O20	3.1333	1.6289	12.5588
O21	4.0013	1.4982	7.8067
O22	6.8150	3.6717	10.1887
H23	-1.4137	4.1751	8.5998
H24	-0.7048	5.2794	9.7828

H25	-0.7071	5.6961	8.0691
H26	-0.2296	2.3888	9.4256
H27	1.5261	2.3185	9.6101
H28	0.5761	3.3524	10.6736
H29	0.9454	4.3408	6.4769
H30	1.8482	2.9911	7.1606
H31	0.0931	2.8872	6.9979
H32	0.6241	6.4073	6.6837
C33	1.6471	8.2536	7.0078
H34	4.4643	6.0168	13.3939
H35	3.0166	5.2377	12.7364
H36	4.6141	4.7051	12.2198
H37	5.9969	6.2006	10.6656
H38	5.4733	7.8444	10.3082
H39	5.9508	7.4116	11.9499
H40	2.2062	7.5285	12.2455
H41	3.7141	8.1388	12.9349
H42	3.1787	8.7006	11.3561
H43	3.8976	8.9381	9.4518
C44	2.5646	8.9629	7.7836
H45	1.2047	8.7212	6.1367
H46	2.8291	9.9770	7.5103

References

1. S. Gonell, M. Poyatos and E. Peris, *Angew. Chem. Int. Edit. Engl.*, 2013, **52**, DOI: 10.1002/anie.201302686.
2. G. Giordano and R. H. Crabtree, *Inorg. Synth.*, 1990, **28**, 88.
3. F. Malbosc, V. Chauby, C. Serra-Le Berre, M. Etienne, J. C. Daran and P. Kalck, *Eur. J. Inorg. Chem.*, 2001, 2689.
4. J. A. V. Er, A. G. Tennyson, J. W. Kamplain, V. M. Lynch and C. W. Bielawski, *Eur. J. Inorg. Chem.*, 2009, 1729.
5. R. C. Clark and J. S. Reid, *Acta Crystallogr. Sect. A*, 1995, **51**, 887.
6. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.
7. G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112.
8. D. G. Gusev and E. Peris, *Dalton Trans.*, 2013, **42**, 7359.