Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information (ESI)

Sterically Encumbered Metalla-diphosphines: Unlocking Alkyne Rotation by Pt^{II} Coordination

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1. Crystallographic Details

1.1 Overview

Single crystals suitable for X-ray diffraction analysis were selected in Fomblin YR-1800 perfluoropolyether oil (Alfa Aesar) at ambient temperature and mounted on a glass fiber. During the measurement, the samples were cooled to 123(2) K. Diffraction data were collected on a Bruker-Nonius Apex X8 and a Bruker Kappa Apex II diffractometer using graphite monochromated Mo-K_α radiation. Structure solutions were found by direct methods (SHELXS-2013)[S1] and were refined by full-matrix least-squares procedures on F^2 (SHELXL-2013)[S2]. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included at calculated positions with fixed thermal parameters.

Table S1. Crystallographic details for **3b**, **4a** and **4b**.

	3b	**4a**	**4b**
empirical formula	$C_{33}H_{56}BIN_6OP_2W$	$C_{45}H_{48}BCl_2IN_6OP_2PtW\cdot$ $3\ CH_2Cl_2$	$C_{33}H_{56}BCl_2IN_6OP_2PtW$
M_W / g·mol^{-1}	936.33	1593.16	1202.32
colour, habit	green, block	orange, block	yellow, plate
crystal system	Triclinic	monoclinic	Monoclinic
space group	*P*-1	$P2_1/n$	$P2_1/c$
a / Å	10.7720(3)	15.4421(6)	13.0737(14)
b / Å	10.9323(3)	16.6727(6)	16.0295(14)
c / Å	18.1301(6)	21.7440(9)	20.3881(19)
α / °	100.651(1)	90	90
β / °	102.567(2)	91.937(2)	106.624(5)
γ / °	104.278(1)	90	90
V / Å^3	1954.3(1)	5595.0(4)	4094.0(7)
Z	2	4	4
$\rho_{calcd.}$ / g·cm^{-1}	1.591	1.891	1.951
μ / mm^{-1}	3.860	5.585	7.218
$\lambda_{MoK\alpha}$ / Å	0.71073	0.71073	0.71073
T / K	123(2)	123(2)	123(2)
collected refl.	64275	101541	65115
unique refl.	14059	20226	12480
refl. $I > 2\sigma(I)$	12419	14460	6555
R_{int}	0.0318	0.0677	0.1261
parameters/restraints	406/0	651/21	386/4
R_1 [$I > 2\sigma(I)$]	0.0252	0.0369	0.0585
wR_2 (all data)	0.0589	0.0641	0.0989
GooF	1.027	1.013	1.008
resid. density [eÅ^{-3}]	0.826/–0.863	1.223/–1.418	1.934/–2.296
CCDC	1541341	1541345	1541342

Table S2. Crystallographic details for **4c, 4c*** and **5**.

	4c	**4c***	**5**
empirical formula	$C_{39}H_{52}BCl_2IN_6OP_2PtW\cdot$ 2 CH_2Cl_2	$C_{39}H_{52}BCl_2IN_6OP_2PtW\cdot$ 2 CH_2Cl_2	$C_{49}H_{48}BIMoN_6O_5P_2W$
M_W / g·mol^{-1}	1435.10	1435.10	1280.37
colour, habit	yellow, block	yellow, block	orange, block
crystal system	Monoclinic	monoclinic	Monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a / Å	14.5361(6)	13.8095(4)	13.0382(4)
b / Å	25.7551(10)	19.9745(5)	22.1495(6)
c / Å	15.0081(6)	18.6144(4)	16.9858(5)
α / °	90	90	90
β / °	115.980(2)	95.971(1)	94.388(2)
γ / °	90	90	90
V / Å^3	5050.9(4)	5106.7(2)	4890.9(2)
Z	4	4	4
$\rho_{\text{calcd.}}$ / g·cm^{-1}	1.910	1.873	1.739
μ / mm^{-1}	6.074	6.006	3.356
$\lambda_{\text{MoK}\alpha}$ / Å	0.71073	0.71073	0.71073
T / K	123(2)	123(2)	173(2)
collected refl.	90447	97722	85417
unique refl.	18268	18470	17626
refl. $I > 2\sigma(I)$	15563	15752	14427
R_{int}	0.0567	0.0352	0.0468
parameters/restraints	583/16	597/32	595/0
R_1 [$I > 2\sigma(\text{I})$]	0.0260	0.0233	0.0302
wR_2 (all data)	0.0608	0.0527	0.0673
GooF	1.029	1.053	1.035
resid. density [eÅ^{-3}]	1.121/–1.428	0.968/–0.940	0.913/–0.981
CCDC	1541343	1541346	1541344

1.2 Molecular Structures of 3b, 4a-c, 4c* and 5

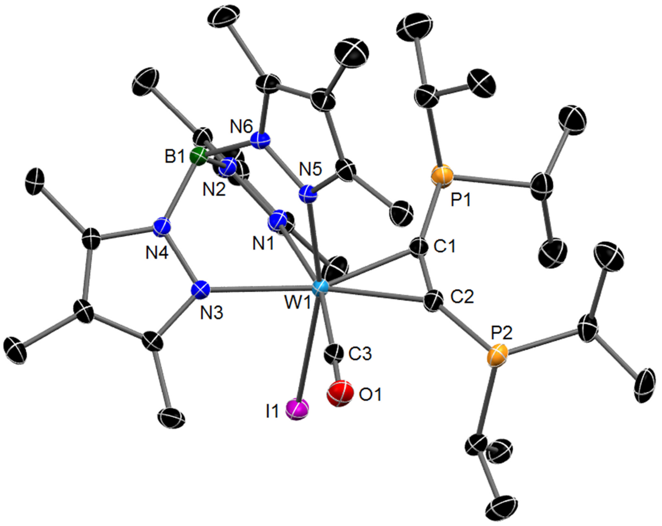


Figure S1. Molecular structure of **3b**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: W1–I1 2.7940(2), W1–C1 2.060(2), W1–C2 2.106(2), W1–C3 1.951(2), W1–N1 2.269(2), W1–N3 2.266(2), W1–N5 2.165(2), C1–C2 1.318(3), C1–P1 1.821(2), C2–P2 1.806(2), C1–C2–P2 150.9(2), C2–C1–P1 154.3(2).

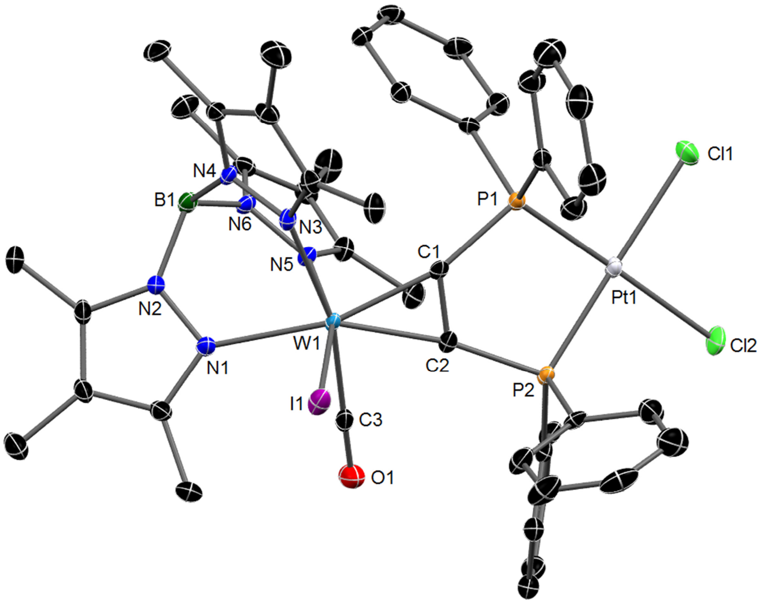


Figure S2. Molecular structure of **4a** in the crystal. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and three molecules of co-crystallized CH_2Cl_2 were omitted for clarity. Selected bond lengths [Å] and angles [°]: W1–I1 2.7710(3), W1–N1 2.228(3), W1–N3 2.238(3), W1–N5 2.175(3), W1–C1 2.034(3), W1–C2 2.035(3), W1–C3 1.982(4), C1–C2 1.326(5), C1–P1 1.808(3), C2–P2 1.824(3), P1–Pt1 2.233(1), P2–Pt1 2.221(1), Pt1–Cl1 2.349(1), Pt1–Cl2 2.345(1), C1–C2–P2 118.9(3), C2–C1–P1 117.9(2), P1–Pt1–P2 88.27(3), Cl1–Pt1–Cl2 90.51(3).

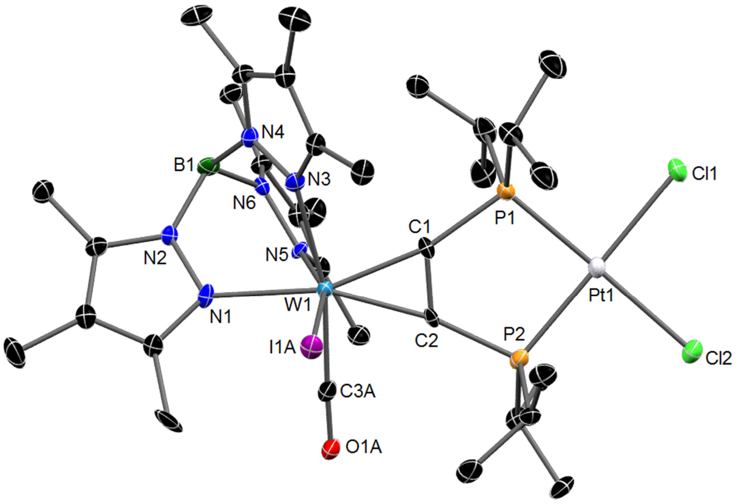


Figure S3. Molecular structure of **4b** in the crystal. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms were omitted for clarity. Only one of two disordered Iodide/Carbonyl position groups is displayed. Selected bond lengths [Å] and angles [°]: W1–I1A 2.7801(7), W1–N1 2.223(6), W1–N3 2.261(7), W1–N5 2.160(6), W1–C1 2.043(7), W1–C2 2.076(8), W1–C3A 1.964(9), C1–C2 1.335(10), C1–P1 1.819(8), C2–P2 1.811(8), P1–Pt1 2.227(2), P2–Pt1 2.233(2), Pt1–Cl1 2.363(2), Pt1–Cl2 2.376(2), C1–C2–P2 119.6(6), C2–C1–P1 119.2(6), P1–Pt1–P2 89.44(8), Cl1–Pt1–Cl2 91.13(7).

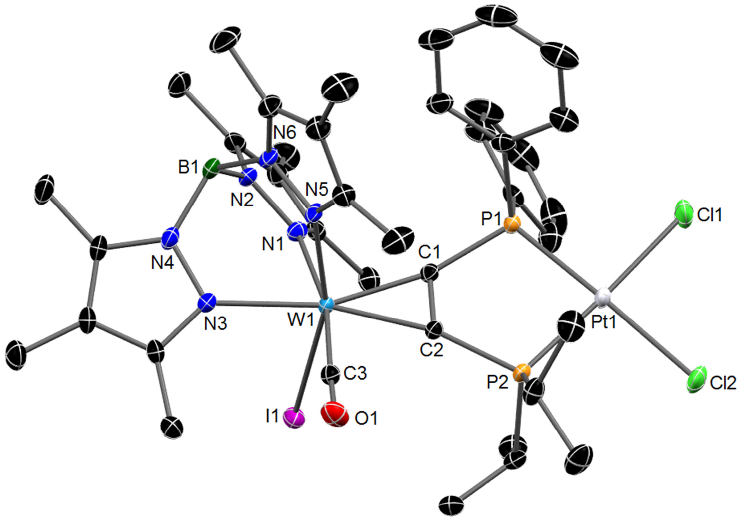


Figure S4. Molecular structure of **4c** in the crystal. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and two molecules of co-crystallized CH$_2$Cl$_2$ were omitted for clarity. Selected bond lengths [Å] and angles [°]: W1–I1 2.7810(2), W1–C1 2.041(2), W1–N1 2.229(2), W1–N3 2.235(2), W1–N5 2.144(2), W1–C2 2.075(2), W1–C3 1.986(2), C1–C2 1.329(3), C1–P1 1.803(3), C2–P2 1.826(3), P1–Pt1 2.214(1), P2–Pt1 2.235(1), Pt1–Cl1 2.360(1), Pt1–Cl2 2.361(1), C1–C2–P2 120.0(2), C2–C1–P1 117.6(2), P1–Pt1–P2 88.97(2), Cl1–Pt1–Cl2 91.99(2).

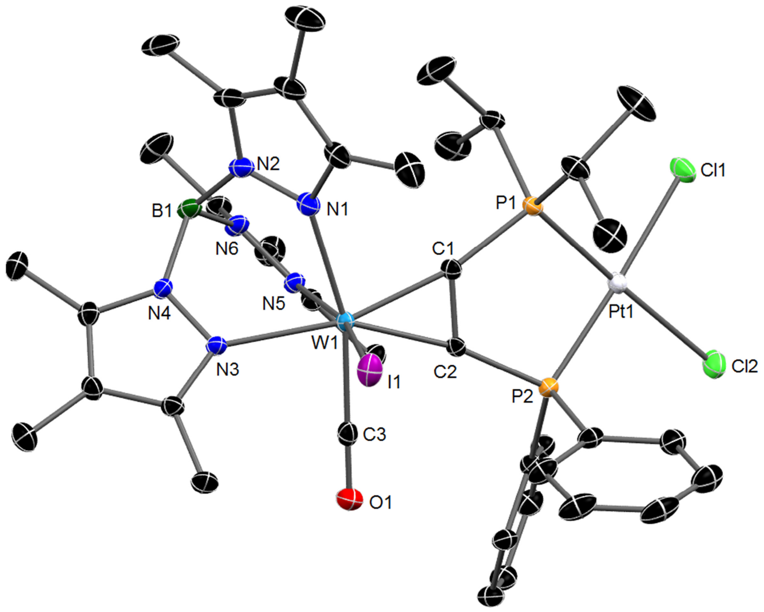


Figure S5. Molecular structure of **4c*** in the crystal. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and two molecules of co-crystallized CH_2Cl_2 were omitted for clarity. Selected bond lengths [Å] and angles [°]: W1–I1 2.7786(2), W1–C1 2.045(2), W1–C2 2.052(2), W1–C3 1.976(2), W1–N1 2.245(2), W1–N3 2.235(2), W1–N5 2.179 (2), C1–C2 1.333(3), C1–P1 1.810(2), C2–P2 1.826(2), P1–Pt1 2.239(1), P2–Pt1 2.229(1), Pt1–Cl1 2.352(1), Pt1–Cl2 2.384(1), C1–C2–P2 119.6(2), C2–C1–P1 118.5(2), P1–Pt1–P2 88.08(2), Cl1–Pt1–Cl2 89.33(2).

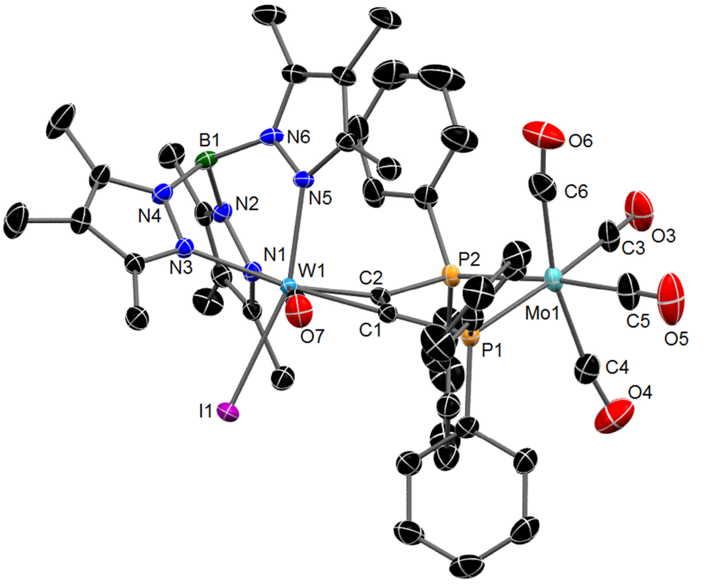


Figure S6. Molecular structure of **5** in the crystal. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: W1–I1 2.7802(2), W1–N1 2.241(2), W1–N3 2.260(2), W1–N5 2.153(2), W1–C1 2.079(2), W1–C2 2.032(2), W1–C7 1.978(3), C1–C2 1.325(3), C1–P1 1.833(2), C2–P2 1.829(2), Mo1–P1 2.5234(7), Mo1–P2 2.5379(7), Mo1–C3 1.996(3), Mo1–C4 2.042(3), Mo1–C5 1.995(3), Mo1–C6 2.025(3), P1–C1–C2 121.3(2), C1–C2–P2 122.5(2), P1–Mo1–P2 80.81(2), C3–Mo1–C5 96.05(12), C4–Mo1–C6 167.11(13).

2. Experimental Section

2.1. General Information

All operations were carried out in an atmosphere of dry argon using Schlenk and glove box techniques. Solvents were dried and saturated with argon by standard methods and freshly distilled prior to use. One- and two-dimensional NMR spectra were recorded at 300 K using Bruker Avance 250, 300 or 500 MHz spectrometer, respectively. In ^{1}H and ^{13}C NMR, the chemical shifts were internally referenced to the solvent residual peak. IR spectroscopy was conducted on a Nicolet 380 FT-IR with a Smart Orbit ATR module. Elemental analyses were performed with a Thermo Finnigan Flash EA 1112 Series. The starting materials Tp*W(CO)(I)(HC_2H)[S3] **1**, Tp*W(CO)(I)(Ph_2PC_2H)[S3] **2a**, Tp*W(CO)(I)($Ph_2PC_2PPh_2$)[S3] **3a**, (1,5-cyclooctadiene)$PtCl_2$[S4] and $Mo(CO)_4$(piperidine)$_2$[S5] were synthesized according to literature procedures. All other reagents were used as purchased from commercial sources.

2.2. Synthetic Procedures

i. Tp*W(CO)(I)($^{i}Pr_2PC_2H$) 2b

A blue green solution of Tp*W(CO)(I)(C_2H_2) (1.06 g, 1.51 mmol) in 190 ml THF was cooled to -78 °C for 30 min, before *n*-butyllithium (2.5 M solution in *n*-hexane, 0.72 ml) was added dropwise. The resulting black solution was stirred for 30 min at -78 °C to complete the reaction. After the addition of $ClP^{i}Pr_2$ (0.33 ml, 2.07 mmol) the solution turned green and was allowed to warm up. At room temperature, the volatiles were removed *in vacuo* leaving a green residue, which was subjected to rapid chromatographic purification on silica. Using a 1:1 mixture of petroleum ether and CH_2Cl_2 a green band was eluted. The solvents were removed yielding a green powder. NMR data indicates the formation of two isomers (**2b´**: H_{syn}, 33 %; **2b´´**: H_{anti}, 67 %). Yield: 995 mg (1.21 mmol, 81 %).

Elemental analysis $C_{27}H_{43}BIN_6OPW$ (820.20 g mol^{-1}): C 39.54 (calcd. 39.54), H 5.18 (5.28), N 10.22 (10.25) %. **^{1}H NMR** ($CDCl_3$, 300 MHz, 300 K): **2b´**: δ = 13.48 (s, 1 H, CCH_{syn}), 2.74 (s, 3 H, CCH_3), 2.55 (d, J_{HP} = 2.5 Hz, 3 H, CCH_3), 2.50 (s, 3 H, CCH_3), 2.36 (s, 3 H, CCH_3), 2.24 (s, 3 H, CCH_3), 2.03 (sep, $^{3}J_{HH}$ = 7.0 Hz, partially superimposed, 1 H, $CH(CH_3)_2$), 2.01 (s, 3 H, CCH_3), 1.81 (s, 3 H, CCH_3), 1.76 (s, 3 H, CCH_3), 1.74 (s, 3 H, CCH_3), 1.41 (dd, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{PH}$ = 14.9 Hz, partially superimposed, 3 H, $CH(CH_3)_2$), 1.10 (dd, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{PH}$ = 15.5 Hz, partially superimposed, 3 H, $CH(CH_3)_2$), 0.95 (sep, $^{3}J_{HH}$ = 7.6 Hz, superimposed, 1 H, $CH(CH_3)_2$), 0.74 (dd, $^{3}J_{HH}$ = 7.6 Hz, $^{3}J_{PH}$ = 18.5 Hz, 3 H, $CH(CH_3)_2$), 0.07 (dd, $^{3}J_{HH}$ = 7.6 Hz, $^{3}J_{PH}$ = 7.9 Hz, 3 H, $CH(CH_3)_2$); **2b´´**: δ = 12.54 (s, 1 H, CCH_{anti}), 2.97 (sep, $^{3}J_{HH}$ = 7.6 Hz, 1 H, $CH(CH_3)_2$), 2.78 (s, 3 H, CCH_3), 2.60 (sep, $^{3}J_{HH}$ = 7.0 Hz, 1 H, $CH(CH_3)_2$), 2.52 (s, 3 H, CCH_3), 2.51 (s, 3 H, CCH_3), 2.37 (s, 3 H, CCH_3), 2.28 (s, 3 H, CCH_3), 2.01 (s, 3 H, CCH_3), 1.83 (s, 3 H, CCH_3), 1.72 (s, 3 H, CCH_3), 1.68 (s, 3 H, CCH_3), 1.48 (dd, $^{3}J_{HH}$ = 7.6 Hz, $^{3}J_{PH}$ = 18.3 Hz, 3 H, $CH(CH_3)_2$), 1.35 (dd, $^{3}J_{HH}$ = 7.0 Hz,

$^3J_{\mathrm{PH}}$ = 15.1 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.24 (dd, $^3J_{\mathrm{HH}}$ = 7.0 Hz, $^3J_{\mathrm{PH}}$ = 15.1 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.35 (dd, $^3J_{\mathrm{HH}}$ = 7.6 Hz, $^3J_{\mathrm{PH}}$ = 7.6 Hz, 3 H, CH(C*H*$_3$)$_2$) ppm. **^{13}C NMR** (CDCl$_3$, 75 MHz, 300 K): *δ* = **2b´**: 232.7 (d, superimposed, $^3J_{\mathrm{CP}}$ = not resolved, W*C*O), 214.2 (d, $^1J_{\mathrm{CP}}$ = 76.3 Hz, W*C*$_{\mathrm{anti}}$), 200.8 (d, $^2J_{\mathrm{CP}}$ = 13.6 Hz, W*C*$_{\mathrm{syn}}$), 154.1, 152.4, 147.5, 143.0, 141.5, 140.8, 114.0, 112.9, 112.8 (*C*CH$_3$), 25.7 (d, $^1J_{\mathrm{CP}}$ = 15.4 Hz, *C*H(CH$_3$)$_2$), 25.1 (d, $^1J_{\mathrm{CP}}$ = 10.8 Hz, *C*H(CH$_3$)$_2$), 22.5–19.6 (br, 4 signals, superimposed, CH(*C*H$_3$)$_2$), 18.0 (d, J_{CP} = 1.5 Hz, C*C*H$_3$), 16.7, 14.7, 11.1, 10.7, 10.6, 8.4, 8.3 (C*C*H$_3$), 8.2 (superimposed, C*C*H$_3$); **2b´´**: 232.7 (d, partially superimposed, $^3J_{\mathrm{CP}}$ = 5.4 Hz, W*C*O), 213.3 (d, $^2J_{\mathrm{CP}}$ = 17.7 Hz, W*C*$_{\mathrm{anti}}$), 206.4 (d, $^1J_{\mathrm{CP}}$ = 61.7 Hz, W*C*$_{\mathrm{syn}}$), 152.9, 152.6 (*C*CH$_3$), 149.8 (d, J_{CP} = 1.5 Hz (*C*CH$_3$), 143.1, 141.7, 140.5, 113.8, 113.2, 112.7 (*C*CH$_3$), 25.4 (d, $^1J_{\mathrm{CP}}$ = 13.9 Hz, *C*H(CH$_3$)$_2$), 25.2 (d, $^1J_{\mathrm{CP}}$ = 10.8 Hz, *C*H(CH$_3$)$_2$), 22.5–18.6 (br, 4 signals, superimposed, CH(*C*H$_3$)$_2$), 17.1, 17.1 (C*C*H$_3$), 15.2 (d, J_{CP} = 9.3 Hz, C*C*H$_3$), 11.1, 10.9, 10.8, 8.4, 8.2, 8.2 (C*C*H$_3$) ppm. **^{31}P{H} NMR** (CDCl$_3$, 121 MHz, 300 K): *δ* = **2b´**: 40.0; **2b´´**: 24.7 ppm. All assignments were confirmed by ^{13}C DEPT and multinuclear 2D NMR experiments. **IR** (THF, cm^{-1}): *isomeric mixture* $\tilde{\nu}$ = 2551 (w, BH), 1908 (vs, CO); (ATR, cm^{-1}): $\tilde{\nu}$ = 2547 (w, BH), 1899 (vs, CO).

ii. Tp*W(CO)(I)(^{i}Pr$_2$PC$_2$P^{i}Pr$_2$) 3b

A green-blue solution of **2b** (487 mg, 0.59 mmol) in 120 ml THF was cooled to -78 °C for 15 min, before *n*-butyllithium (2.5 M solution in *n*-hexane, 0.33 ml) was added dropwise. The resulting intense blue solution was stirred for 30 min at -78 °C to complete the reaction. Addition of ClP^{i}Pr$_2$ (0.14 ml, 0.88 mmol) resulted a dark green solution, which was allowed to warm up. At room temperature, the volatiles were removed *in vacuo* leaving a dark green residue, which was subjected to a rapid chromatographic purification on silica. A bright green band was eluted with toluene. The solvent was removed yielding a green powder. Single crystals suitable for XRD analysis could be obtained by layering a concentrated solution of **3b** in CH$_2$Cl$_2$ with *n*-pentane. Yield: 323 mg (0.34 mmol, 58 %).

Elemental analysis C$_{33}$H$_{56}$BIN$_6$OP$_2$W (936.34 g mol^{-1}): C 42.10 (calcd. 42.33), H 5.86 (6.03), N 8.98 (9.02) %. **^{1}H NMR** (CDCl$_3$, 300 MHz, 300 K): *δ* = 3.47 (dsep, $^3J_{\mathrm{HH}}$ = 7.6 Hz, J_{PH} = 2.8 Hz, 1 H, C*H*(CH$_3$)$_2$), 2.86 (m, $^3J_{\mathrm{HH}}$ = 6.8 Hz, J_{PH} = not resolved, 1 H, C*H*(CH$_3$)$_2$), 2.76 (s, 3 H, CC*H*$_3$), 2.50 (s, 3 H, CC*H*$_3$), 2.39 (s, 3 H, CC*H*$_3$), 2.35 (d, J_{HP} = 3.4 Hz, 3 H, CC*H*$_3$), 2.22 (s, 3 H, CC*H*$_3$), 1.96 (s, 3 H, CC*H*$_3$), 1.79 (s, partially superimposed, 3 H, CC*H*$_3$), 1.78 (s, partially superimposed, 3 H, CC*H*$_3$), 1.75 (m, superimposed, 1 H, C*H*(CH$_3$)$_2$), 1.74 (s, 3 H, CC*H*$_3$), 1.57 (dd, $^3J_{\mathrm{HH}}$ = 7.6 Hz, $^3J_{\mathrm{PH}}$ = 19.6 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.42 (dd, $^3J_{\mathrm{HH}}$ = 6.8 Hz, $^3J_{\mathrm{PH}}$ = 17.6 Hz, partially superimposed, 3 H, CH(C*H*$_3$)$_2$), 1.34 (dd, $^3J_{\mathrm{HH}}$ = 7.0 Hz, $^3J_{\mathrm{PH}}$ = 13.6 Hz, partially superimposed, 3 H, CH(C*H*$_3$)$_2$), 1.08 (dd, $^3J_{\mathrm{HH}}$ = 6.8 Hz, $^3J_{\mathrm{PH}}$ = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.03–0.71 (br, superimposed, *J* not resolved, 10 H, 1x C*H*(CH$_3$)$_2$, 9x CH(C*H*$_3$)$_2$), 0.51 (br, *J* not resolved, 3 H, CH(C*H*$_3$)$_2$) ppm. **^{13}C NMR** (CDCl$_3$, 63 MHz, 300 K): *δ* = 236.6 (dd, $^3J_{\mathrm{CP}}$ = 2.3 Hz, $^3J_{\mathrm{CP}}$ = 10.8 Hz, W*C*O), 214.8 (dd, $^1J_{\mathrm{CP}}$ = 77.1 Hz, $^2J_{\mathrm{CP}}$ = 22.3 Hz, W*C*$_{\mathrm{anti}}$), 204.0 (dd, $^1J_{\mathrm{CP}}$ = 80.9 Hz, $^2J_{\mathrm{CP}}$ = 22.4 Hz, W*C*$_{\mathrm{syn}}$), 154.4, 152.6, 150.6, 143.2, 141.3, 140.8, 113.9, 113.0, 113.0 (*C*CH_3), 25.4 (d, $^1J_{\mathrm{CP}}$ = 12.3 Hz, *C*H$(CH_3)_2$), 24.6 (br, 2 signals, $^1J_{\mathrm{CP}}$ = not resolved, *C*H$(CH_3)_2$), 24.2 (d, $^1J_{\mathrm{CP}}$ = 16.2 Hz, *C*H$(CH_3)_2$), 23.4–19.9 (br, 8 signals, superimposed, CH(*C*H_3)$_2$), 20.7 (d, J_{CP} = 18.5 Hz, partially superimposed, C*C*H_3), 17.3 (C*C*H_3), 15.5 (d, J_{CP} = 9.3 Hz, C*C*H_3), 11.2, 10.8, 10.6, 8.7, 8.3, 8.2 (C*C*H_3) ppm. **^{31}P{H} NMR** ($CDCl_3$, 121 MHz, 300 K): *δ* = 40.9 (br), 38.0 (s) ppm. All assignments were confirmed by ^{13}C DEPT and multinuclear 2D NMR experiments. **IR** (THF, cm^{-1}): $\tilde{\nu}$ = 2553 (w, BH), 1907 (vs, CO); (CH_2Cl_2 cm^{-1}): $\tilde{\nu}$ = 2557 (w, BH), 1902 (vs, CO); (ATR, cm^{-1}): $\tilde{\nu}$ = 2549 (w, BH), 1891 (vs, CO).

iii. Tp*W(CO)(I)($Ph_2PC_2P^iPr_2$) 3c

Complex **3c** was obtained following the procedure for **3b** using [Tp*W(CO)(I)(Ph_2PC_2H)] (250 mg, 0.281 mmol) instead of **2b** and a 1:1 mixture of CH_2Cl_2 and petroleum ether as eluent in the chromatography step. The solvent of the collected green band was removed yielding a green powder. Yield: 189 mg (0.188 mmol, 70 %).

Elemental analysis $C_{39}H_{52}BIN_6OP_2W$ (1004.73 g mol^{-1}): C 46.25 (calcd. 46.64), H 5.00 (5.22), N 8.70 (8.37) %. **^{1}H NMR** ($CDCl_3$, 250 MHz, 300 K): *δ* = 7.34 (m, 1 H, Ph-*H$_p$*), 7.31–7.24 (m, 4 H, Ph-*H$_{o,m}$*), 7.03 (m, 1 H, Ph-*H$_p$*), 6.92 (m, 2 H, Ph-*H$_{o,m}$*), 6.33 (m, 2 H, Ph-*H$_{o,m}$*), 3.56 (dsep, $^3J_{\mathrm{HH}}$ = 7.4 Hz, J_{PH} = 3.1 Hz, 1 H, C*H*$(CH_3)_2$), 2.83 (s, 3 H, CC*H$_3$*), 2.59 (s, 3 H, CC*H$_3$*), 2.22 (s, 3 H, CC*H$_3$*), 2.21 (s, 3 H, CC*H$_3$*), 2.10 (s, 3 H, CC*H$_3$*), 1.95 (sep, $^3J_{\mathrm{HH}}$ = 6.9 Hz, J_{PH} = not resolved, partially superimposed, 1 H, C*H*$(CH_3)_2$), 1.89 (s, 3 H, CC*H$_3$*), 1.77 (s, 3 H, CC*H$_3$*), 1.73 (s, 3 H, CC*H$_3$*), 1.52 (dd, $^3J_{\mathrm{HH}}$ = 7.4 Hz, $^3J_{\mathrm{PH}}$ = 19.6 Hz, 3 H, CH(C*H$_3$*)$_2$), 1.35 (s, 3 H, CC*H$_3$*), 1.20 (dd, $^3J_{\mathrm{HH}}$ = 6.9 Hz, $^3J_{\mathrm{PH}}$ = 6.9 Hz, 3 H, CH(C*H$_3$*)$_2$), 1.10 (dd, $^3J_{\mathrm{HH}}$ = 7.4 Hz, $^3J_{\mathrm{PH}}$ = 19.1 Hz, partially superimposed, 3 H, CH(C*H$_3$*)$_2$), 1.01 (dd, $^3J_{\mathrm{HH}}$ = 6.9 Hz, $^3J_{\mathrm{PH}}$ = 13.2 Hz, partially superimposed, 3 H, CH(C*H$_3$*)$_2$) ppm. **^{13}C NMR** ($CDCl_3$, 63 MHz, 300 K): δ = 238.5 (dd, $^3J_{\mathrm{CP}}$ = 2.3 Hz, $^3J_{\mathrm{CP}}$ = 10.0 Hz, W*C*O), 214.0 (d, $^1J_{\mathrm{CP}}$ = 65.5 Hz, $^2J_{\mathrm{CP}}$ = not resolved, W*C*$_{\mathrm{anti}}$), 213.2 (dd, $^1J_{\mathrm{CP}}$ = 53.2 Hz, $^2J_{\mathrm{CP}}$ = 18.5 Hz, W*C*$_{\mathrm{syn}}$), 152.9, 152.5 (*C*CH_3), 149.3 (d, J_{CP} = 1.5 Hz, *C*CH_3), 143.0, 141.4, 140.1 (*C*CH_3), 136.0, 135.8 (*C*$_{\mathrm{ipso}}$), 134.8, 134.4, 132.4, 132.0 (Ph-*C*$_{\mathrm{o,m}}$), 129.2 (Ph-*C*$_{\mathrm{p}}$), 128.4, 128.1 (Ph-*C*$_{\mathrm{o,m}}$), 127.4 (Ph-*C*$_{\mathrm{p}}$), 127.1, 127.0 (Ph-*C*$_{\mathrm{o,m}}$), 113.3, 113.0, 112.8 (*C*CH_3), 26.3 (d, J_{CP} = 11.6 Hz, *C*H$(CH_3)_2$), 23.6 (d, J_{CP} = 14.6 Hz, *C*H$(CH_3)_2$), 23.2 (d, J_{CP} = 27.0 Hz, CH(*C*H_3)$_2$), 23.0 (d, J_{CP} = 23.9 Hz, CH(*C*H_3)$_2$), 21.6 (d, J_{CP} = 4.6 Hz, CH(*C*H_3)$_2$), 20.7 (d, J_{CP} = 13.1 Hz, CH(*C*H_3)$_2$), 19.5 (d, J_{CP} = 3.9 Hz, C*C*H_3), 17.7 (C*C*H_3), 14.9 (dd, J_{CP} = 8.5 Hz, J_{CP} = 3.1 Hz, C*C*H_3), 11.1, 11.0, 10.7, 8.5 (C*C*H_3), 8.3 (superimposed, 2 signals, C*C*H_3) ppm. **^{31}P{H} NMR** ($CDCl_3$, 121 MHz, 300 K): *δ* = 45.0 (s, *P*^{i}Pr$_2$), 18.2 (s, *P*Ph$_2$) ppm. All assignments were confirmed by ^{13}C DEPT and multinuclear 2D NMR experiments. **IR** (THF, cm^{-1}): $\tilde{\nu}$ = 2554 (b, BH), 1908 (s, CO); (CH_2Cl_2 cm^{-1}): $\tilde{\nu}$ = 2558 (w, BH), 1905 (vs, CO); (ATR, cm^{-1}): $\tilde{\nu}$ = 2549 (w, BH), 1895 (vs, CO).

iv. General Procedure for the Synthesis of $\{Tp^*W(CO)(I)(R_2PC_2PR_2)\}PtCl_2$ 4a-c

To a CH_2Cl_2 solution (10 ml) of complex ligand **3a-c** (100 mg) was added a CH_2Cl_2 (5 ml) solution of (1,5-cyclooctadiene)$PtCl_2$ (1 equivalent). After stirring until *in situ* IR spectroscopy indicates full conversion (1 h for **4a**, 5 h for **4b**, 20 h for **4c**), volatiles were removed *in vacuo*. The crude product was washed two times with 5 ml Et_2O, before it was recrystallized from CH_2Cl_2 / Et_2O. Single crystals suitable for XRD analysis could be obtained by layering a concentrated solution of the product in CH_2Cl_2 with excess Et_2O. Yield: 74 % for **4a**, 64 % for **4b**, 83 % for **4c**.

4a: **Elemental analysis** $C_{45}H_{48}BCl_2IN_6OP_2PtW$ (1338.39 g mol^{-1}): C 40.40 (calcd. 40.38), H 3.51 (3.61), N 6.26 (6.28) %. **^{1}H NMR** (CD_2Cl_2, 300 MHz, 300 K): δ = 8.20 (m, 4 H, Ph-*H*), 7.70–7.44 (m, 7 H, Ph-*H*), 7.38–7.21 (m, 7 H, Ph-*H*), 7.02 (m, 2 H, Ph-*H*), 2.62 (s, 3 H, $C\mathit{H_3}$), 2.58 (s, 3 H, $C\mathit{H_3}$), 2.36 (s, 3 H, $C\mathit{H_3}$), 2.17 (s, 3 H, $C\mathit{H_3}$), 1.82 (s, 3 H, $C\mathit{H_3}$), 1.72 (s, 3 H, $C\mathit{H_3}$), 1.46 (s, 3 H, $C\mathit{H_3}$), 1.32 (s, 3 H, $C\mathit{H_3}$), 1.02 (s, 3 H, $C\mathit{H_3}$) ppm. **^{31}P{H} NMR** (CD_2Cl_2, 121 MHz, 300 K): δ = 34.3 (s, $J_{\mathrm{P}^{195}\mathrm{Pt}}$ = 4026 Hz), 22.1 (s, $J_{\mathrm{P}^{195}\mathrm{Pt}}$ = 3901 Hz) ppm. **IR** (CH_2Cl_2, cm^{-1}): $\tilde{\nu}$ = 2563 (w, BH), 1958 (s, CO); (ATR, cm^{-1}): $\tilde{\nu}$ = 2563 (w, BH), 1948 (s, CO).

4b: **Elemental analysis** $C_{33}H_{56}BCl_2IN_6OP_2PtW\cdot 0.5\ CH_2Cl_2$ (1244.80 g mol^{-1}): C 32.42 (calcd. 32.32), H 4.55 (4.62), N 6.69 (6.75) %. **^{1}H NMR** (CD_2Cl_2, 300 MHz, 300 K): δ = 3.52 (m, $^3J_{HH}$ = 7.2 Hz, J_{PH} = not resolved, 1 H, $C\mathit{H}(CH_3)_2$), 2.97 (sep, $^3J_{HH}$ = 7.2 Hz, J_{PH} = not resolved, 1 H, $C\mathit{H}(CH_3)_2$), 2.71 (sep, $^3J_{HH}$ = 7.0 Hz, J_{PH} = not resolved, 1 H, $C\mathit{H}(CH_3)_2$), 2.56 (s, 3 H, $C\mathit{H_3}$), 2.55 (s, 3 H, $C\mathit{H_3}$), 2.51 (s, 3 H, $C\mathit{H_3}$), 2.40 (s, 3 H, $C\mathit{H_3}$), 2.26 (dsep, $^3J_{HH}$ = 7.0 Hz, J_{PH} = 1.3 Hz, 1 H, $C\mathit{H}(CH_3)_2$), 2.15 (s, 3 H, $C\mathit{H_3}$), 2.13 (s, 3 H, $C\mathit{H_3}$), 2.02 (s, 3 H, $C\mathit{H_3}$), 1.81 (s, 3 H, $C\mathit{H_3}$), 1.81 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 16.1 Hz, partially superimposed, 3 H, $CH(C\mathit{H_3})_2$), 1.75 (s, 3 H, $C\mathit{H_3}$), 1.74 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 16.1 Hz, partially superimposed, 3 H, $CH(C\mathit{H_3})_2$), 1.62 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 20.0 Hz, 3 H, $CH(C\mathit{H_3})_2$), 1.43 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 8.9 Hz, partially superimposed, 3 H, $CH(C\mathit{H_3})_2$), 1.37 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 13.4 Hz, partially superimposed, 3 H, $CH(C\mathit{H_3})_2$), 1.34 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 19.6 Hz, partially superimposed, 3 H, $CH(C\mathit{H_3})_2$), 0.42 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 19.6 Hz, 3 H, $CH(C\mathit{H_3})_2$), 0.31 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 15.3 Hz, 3 H, $CH(C\mathit{H_3})_2$) ppm. **^{31}P{H} NMR** (CD_2Cl_2, 121 MHz, 300 K): δ = 64.8 (s, $J_{\mathrm{P}^{195}\mathrm{Pt}}$ = 3985 Hz), 54.1 (s, $J_{\mathrm{P}^{195}\mathrm{Pt}}$ = 3875 Hz) ppm. **IR** (CH_2Cl_2, cm^{-1}): $\tilde{\nu}$ = 2563 (w, BH), 1949 (s, CO); (ATR, cm^{-1}): $\tilde{\nu}$ = 2551 (w, BH), 1940 (s, CO).

4c: **Elemental analysis** $C_{39}H_{52}BCl_2IN_6OP_2PtW\cdot 0.5\ CH_2Cl_2$ (1312.83 g mol^{-1}): C 36.19 (calcd. 36.14), H 4.05 (4.07), N 6.33 (6.40) %. **^{1}H NMR** ($CDCl_3$, 300 MHz, 300 K): δ = 7.71 (m, 2 H, Ph-*H*), 7.50–7.33 (m, 5 H, Ph-*H*), 7.20 (m, 1 H, Ph-*H*), 6.88 (m, 2 H, Ph-*H*), 3.52 (sep, $^3J_{HH}$ = 7.1 Hz, J_{PH} = not resolved, 1 H, $C\mathit{H}(CH_3)_2$), 3.30 (sep, $^3J_{HH}$ = 6.9 Hz, J_{PH} = not resolved, 1 H, $C\mathit{H}(CH_3)_2$), 2.63 (s, 3 H, $C\mathit{H_3}$), 2.59 (s, 3 H, $C\mathit{H_3}$), 2.57 (s, 3 H, $C\mathit{H_3}$), 2.21 (s, 3 H, $C\mathit{H_3}$), 1.92 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{PH}$ = 16.4 Hz, 3 H, $CH(C\mathit{H_3})_2$), 1.79 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{PH}$ = 16.4 Hz, partially superimposed, 3 H, $CH(C\mathit{H_3})_2$), 1.75 (s, 3 H, $C\mathit{H_3}$), 1.74

(s, 3 H, CCH_3), 1.58 (dd, $^3J_{\text{HH}}$ = 6.9 Hz, $^3J_{\text{PH}}$ = 20.0 Hz, partially superimposed, 6 H, CH(CH_3)$_2$), 1.52 (s, 3 H, CCH_3), 1.35 (s, 3 H, CCH_3), 1.24 (s, 3 H, CCH_3) ppm. **^{31}P{H} NMR** (CDCl$_3$, 101 MHz, 300 K): δ = 69.2 (s, $J_{\text{P}^{195}\text{Pt}}$ = 3825 Hz, P^{i}Pr$_2$), 23.0 (s, $J_{\text{P}^{195}\text{Pt}}$ = 4133 Hz, *P*Ph$_2$) ppm. **IR** (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2564 (w, BH), 1943 (s, CO); (ATR, cm^{-1}): $\tilde{\nu}$ = 2559 (w, BH), 1938 (s, CO).

v. {Tp*W(CO)(I)($^{\text{i}}$Pr$_2$PC$_2$PPh$_2$)}PtCl$_2$ 4c*

Complex **4c** isomerizes within days in solution giving a 1 : 1.86 mixture of **4c** and **4c*** according to ^{1}H NMR spectroscopy. To isolate pure **4c***, freshly prepared **4c** (made from 0.997 mmol **3c** (100 mg)) is stirred for additional 7 days in CH$_2$Cl$_2$ (10 ml) before being concentrated to half the volume and layered with Et$_2$O (40 ml). The first crop of crystals, which were also suitable for XRD analysis, were collected the next day and dried *in vacuo*. Because the supernatant is now **4c** enriched, an immediate recrystallization would lead to crystals of **4c** or of a mixture of both isomers. In solution, **4c*** interconverts back to **4c** until the equilibrium is reached. Yield: 31 mg (0.024 mmol, 25 %).

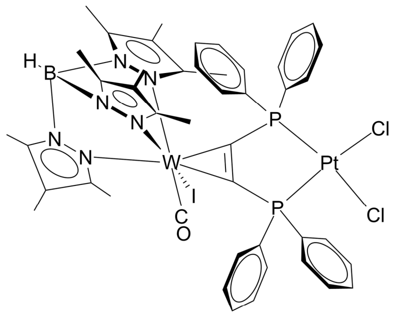
^{1}H NMR (CDCl$_3$, 300 MHz, 300 K): δ = 8.46 (m, 2 H, Ph-*H*), 8.17 (m, 2 H, Ph-*H*), 7.57–7.39 (m, 6 H, Ph-*H*), 2.89 ($^3J_{\text{HH}}$ = 7.2 Hz, $^2J_{\text{PH}}$ = 2.3 Hz, 1 H, C*H*(CH$_3$)$_2$), 2.63 (s, 3 H, CCH_3), 2.59 (m, $^3J_{\text{HH}}$ and J_{PH} not resolved, superimposed, 1 H, C*H*(CH$_3$)$_2$), 2.56 (s, 3 H, CCH_3), 2.48 (s, 3 H, CCH_3), 2.42 (s, 3 H, CCH_3), 2.16 (s, 3 H, CCH_3), 1.97 (s, 3 H, CCH_3), 1.73 (s, 3 H, CCH_3), 1.73 (s, superimposed, 3 H, CCH_3), 1.48 (s, 3 H, CCH_3), 1.37 (dd, $^3J_{\text{HH}}$ = 7.0 Hz, $^3J_{\text{PH}}$ = 17.4 Hz, 3 H, CH(CH_3)$_2$), 0.53 (dd, $^3J_{\text{HH}}$ = 6.8 Hz, $^3J_{\text{PH}}$ = 19.3 Hz, partially superimposed, 3 H, CH(CH_3)$_2$), 0.45 (dd, $^3J_{\text{HH}}$ = 7.0 Hz, $^3J_{\text{PH}}$ = 15.7 Hz, partially superimposed, 3 H, CH(CH_3)$_2$), 0.34 (dd, $^3J_{\text{HH}}$ = 7.2 Hz, $^3J_{\text{PH}}$ = 20.0 Hz, 3 H, CH(CH_3)$_2$) ppm. **^{31}P{H} NMR** (CD$_2$Cl$_2$, 101 MHz, 300 K): δ = 60.5 (s, $J_{\text{P}^{195}\text{Pt}}$ = 3631 Hz, P^{i}Pr$_2$), 32.3 (s, $J_{\text{P}^{195}\text{Pt}}$ = 4129 Hz, *P*Ph$_2$) ppm. **IR** (CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$ = 2564 (w, BH), 1953 (s, CO); (ATR, cm^{-1}): $\tilde{\nu}$ = 2559 (w, BH), 1951 (s, CO).

vi. {Tp*W(CO)(I)(Ph$_2$PC$_2$PPh$_2$)}Mo(CO)$_4$ 5

A green solution of **3a** (300 mg, 0.280 mmol) in CH$_2$Cl$_2$ (10 ml) was added to a yellow solution of Mo(CO)$_4$(piperidine)$_2$ (106 mg, 0.280 mmol) in CH$_2$Cl$_2$ (10 ml). The resulting brown mixture was stirred for 12 h, before all volatiles were removed *in vacuo*. The residue was washed with toluene (2x 10 ml) and Et$_2$O (10 ml) and subsequently dried *in vacuo*. Single-crystals of **5** could be obtained by slow diffusion of *n*-pentane into a concentrated CH$_2$Cl$_2$ solution (50 mg in 12 ml). Yield: 254 mg (71 %).

Elemental analysis $C_{49}H_{48}BIMoN_6O_5P_2W$ (1280.41 g mol^{-1}): C 45.72 (calcd. 45.96), H 3.67 (3.78), N 6.42 (6.56) %. **^{1}H NMR** (CD$_2$Cl$_2$, 300 MHz, 298 K): δ = 7.98 (m, 2 H, Ph-*H*), 7.67 (m, 2 H, Ph-*H*), 7.53-7.43 (m, 6 H, Ph-*H*), 7.26 (m, 2 H, Ph-*H*), 7.13 (m, 2 H, Ph-*H*), 7.02-6.98 (m, 4 H, Ph-*H*), 6.82 (m, 2 H, Ph-*H*), 2.55 (s, 3 H, CH_3), 2.55 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 2.13 (s, 3 H, CH_3), 1.76 (s, 3 H, CH_3), 1.70 (s, 3 H, CH_3), 1.58 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 1.46 (s, superimposed, 3 H, CH_3) ppm. **^{31}P{H} NMR** ($CDCl_3$, 122 MHz, 298 K): δ = 62.2 (d, $^2J_{PP}$ = 15.61 Hz, *P*Ph_2), 48.5 (d, $^2J_{PP}$ = 15.61 Hz, *P*Ph_2). **IR** (CH_2Cl_2, cm^{-1}): ν = 2560 (w, BH), 2021 (s, CO), 1947 (s, CO), 1927 (s, CO), 1904 (vs, CO), 1889 (sh, CO); (ATR, cm^{-1}): ν = 2552 (w, BH), 2021 (s, CO), 1948 (s, CO), 1918 (s, CO), 1889 (s, CO), 1874 (vs, CO).

2.3 NMR Spectra of Dinuclear Complexes 4a-c, 4c*



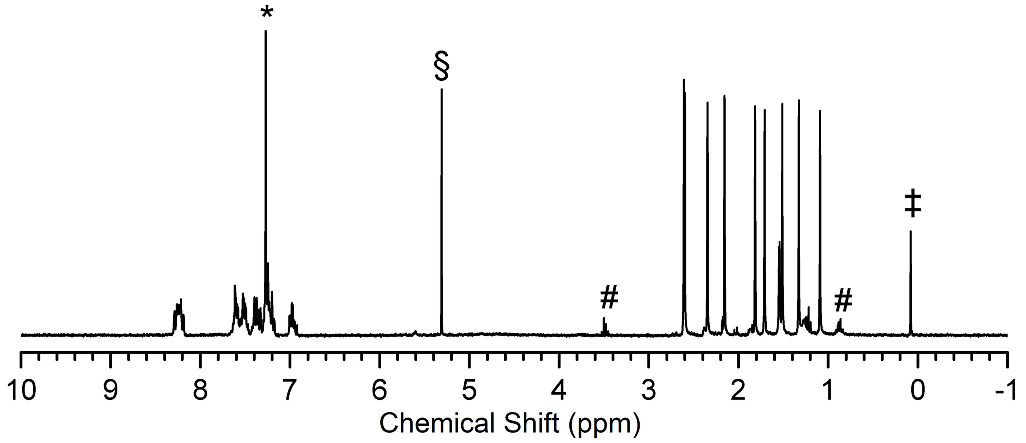


Figure S7. ^{1}H NMR spectra of crystalline **4a** in $CDCl_3$ showing residual $CHCl_3$ (*) and TMS (‡) as well as traces of recrystallization solvents CH_2Cl_2 (§) and Et_2O (#).

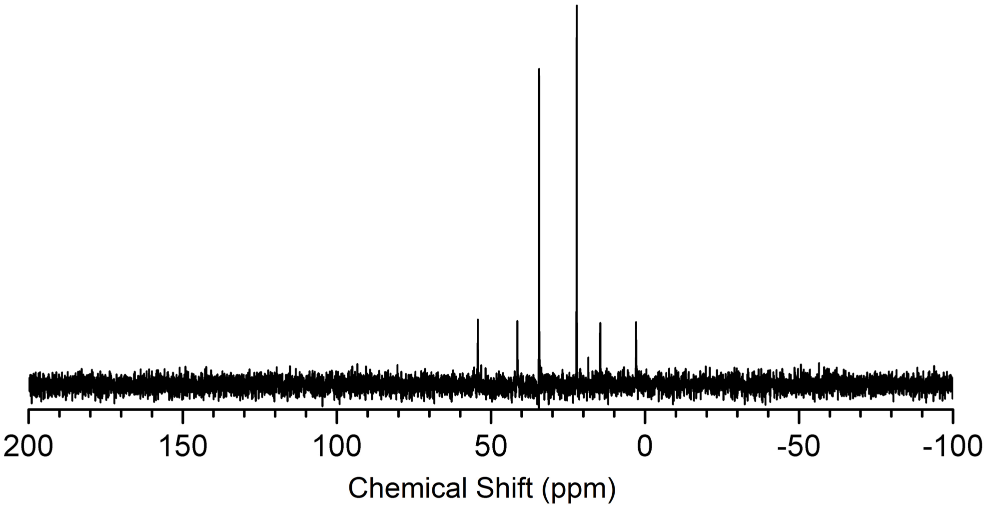
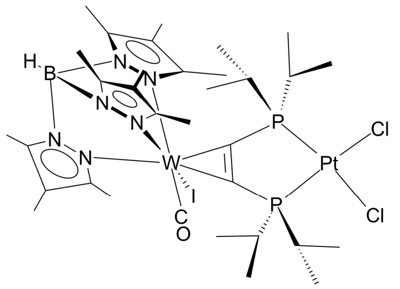


Figure S8. ^{31}P NMR spectra of crystalline **4a** in $CDCl_3$.



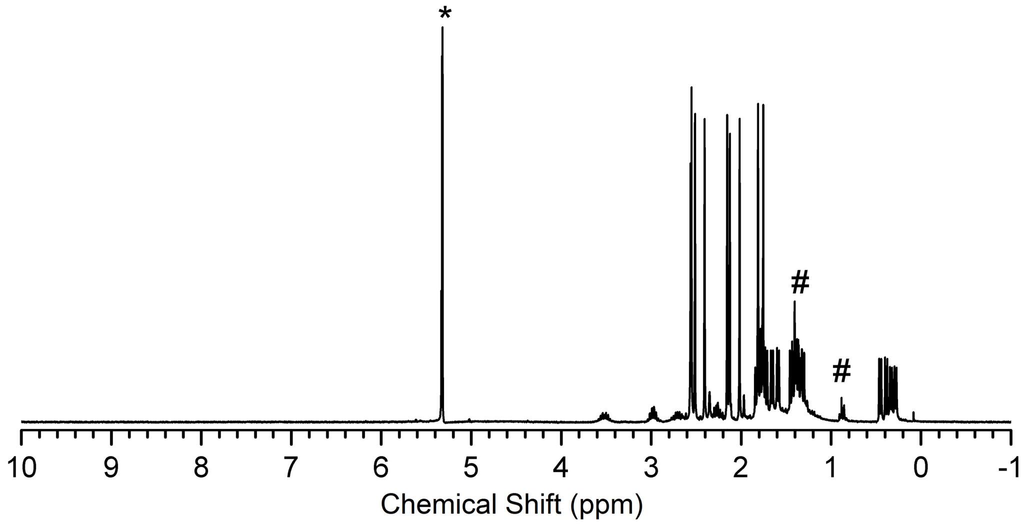


Figure S9. ^{1}H NMR spectra of crystalline **4b** in CD_2Cl_2 showing residual $CHDCl_2$ (*) and traces of recrystallization solvents CH_2Cl_2 (*) and C_5H_{12} (#).

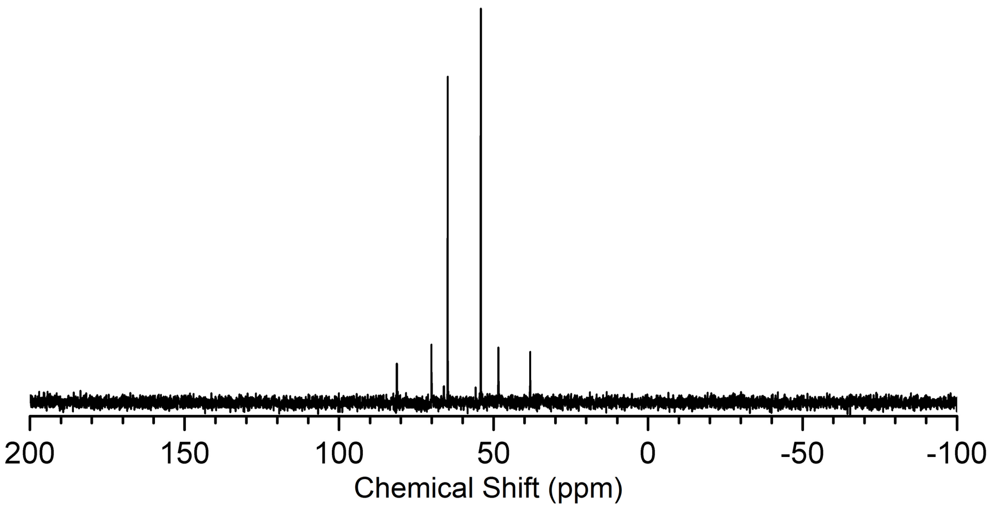


Figure S10. ^{31}P NMR spectra of crystalline **4b** in $CDCl_3$.

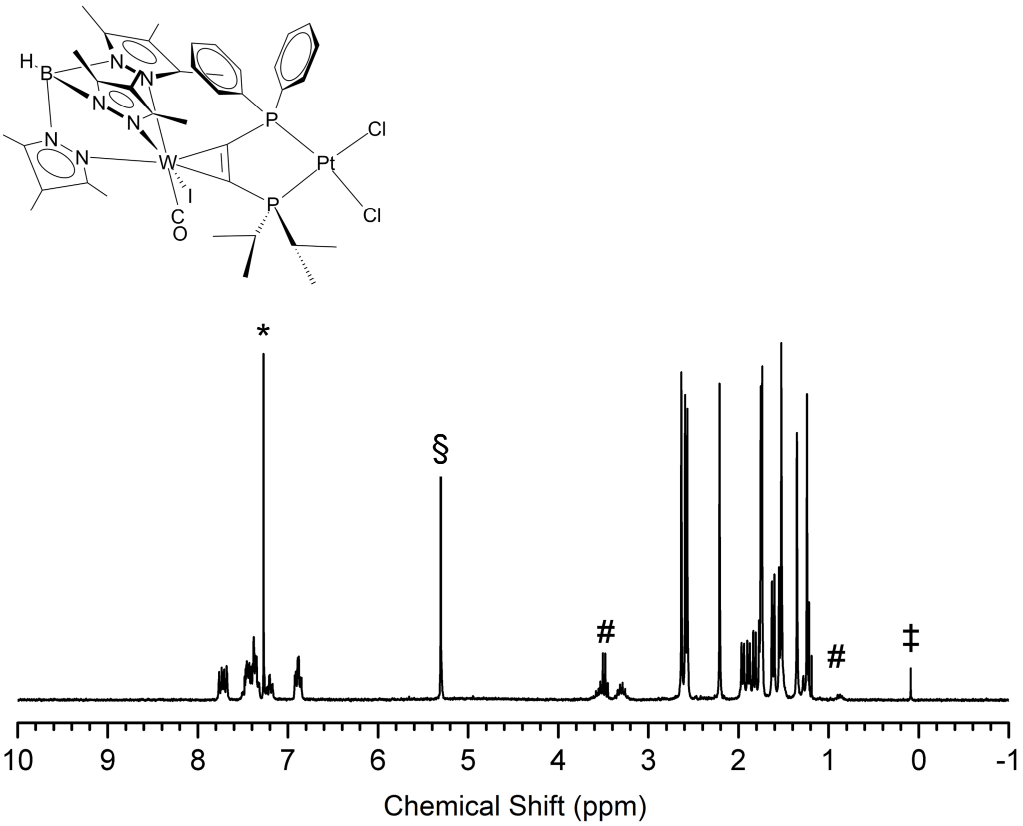


Figure S11. ^{1}H NMR spectra of crystalline **4c** in $CDCl_3$ showing residual $CHCl_3$ (*) and TMS (‡) as well as traces of recrystallization solvents CH_2Cl_2 (§) and Et_2O (#).

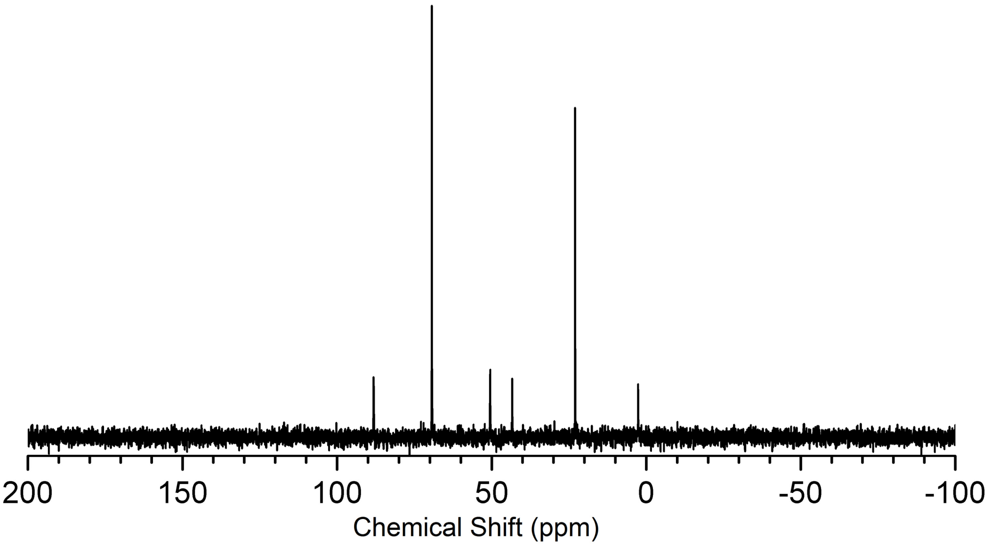


Figure S12. ^{31}P NMR spectra of crystalline **4c** in $CDCl_3$.

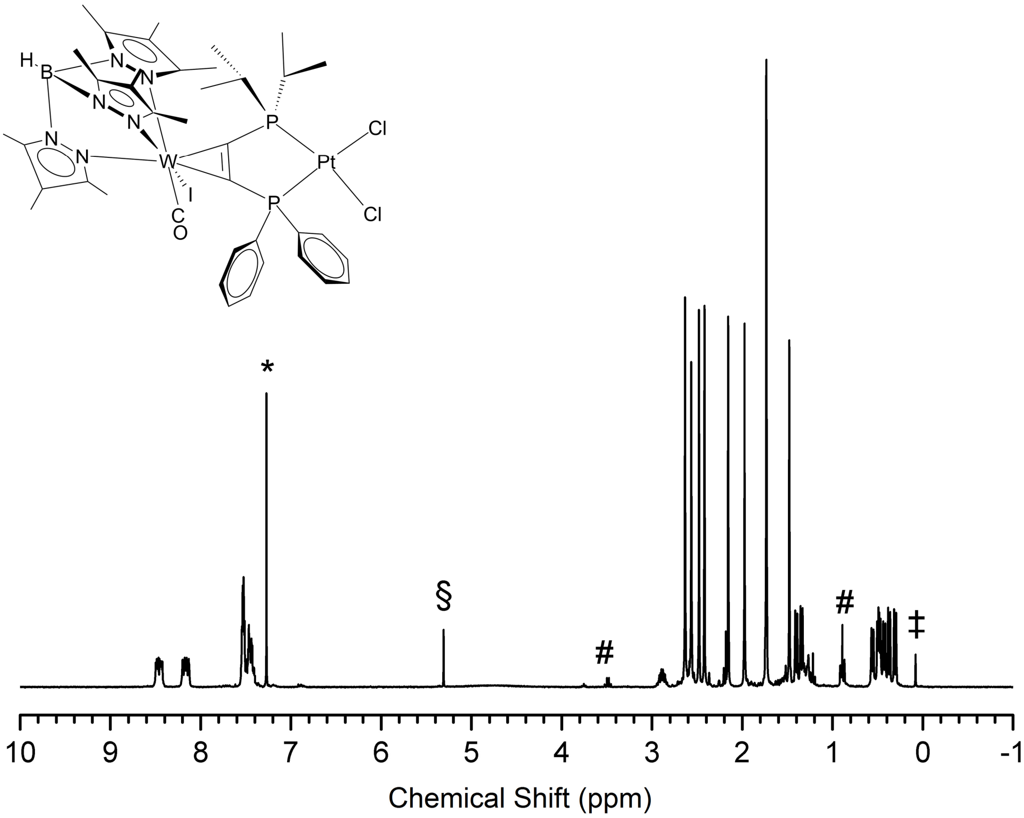


Figure S13. ^{1}H NMR spectra of crystalline **4c*** in $CDCl_3$ showing residual $CHCl_3$ (*) and TMS (‡) as well as traces of recrystallization solvents CH_2Cl_2 (§) and Et_2O (#).

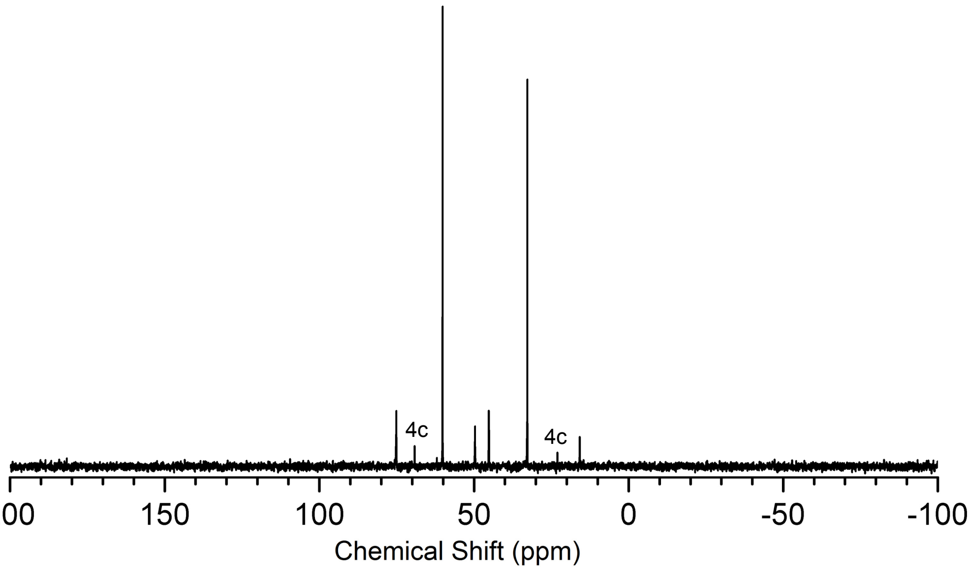


Figure S14. ^{31}P NMR spectra of crystalline **4c*** in $CDCl_3$ showing traces of **4c**.

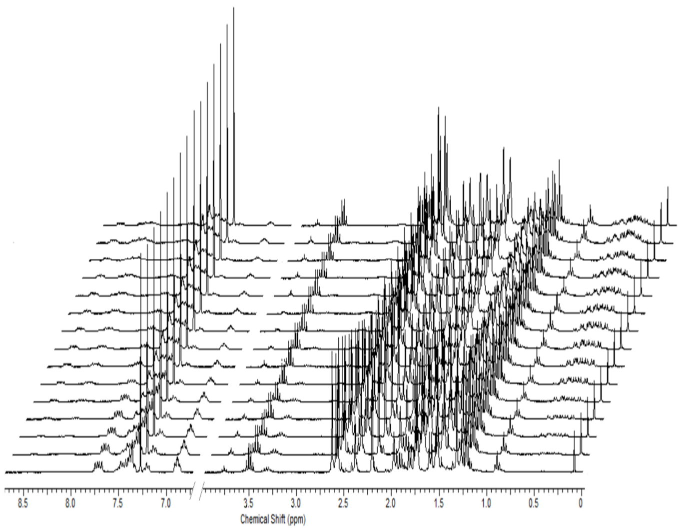


Figure S15. ^{1}H NMR spectra of **4c** in $CDCl_3$ ($c = 0.0118$ mol l^{-1}) over the course of 14 d measured at 298 K.

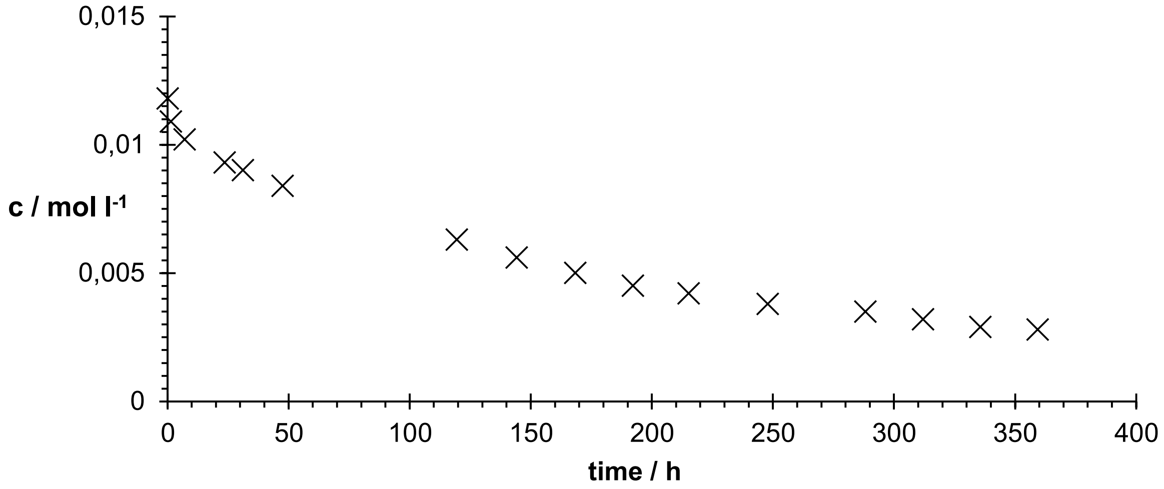


Figure S16. Plot of concentration c(**4c**) versus time.

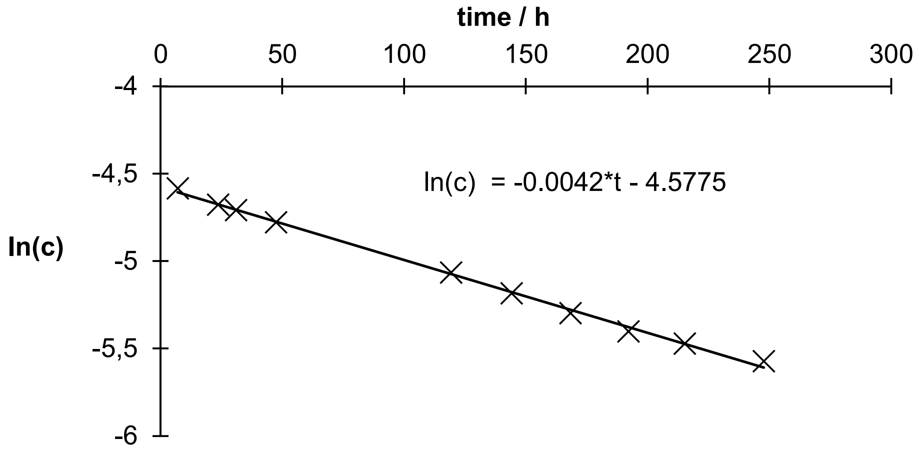


Figure S17. Plot of ln(c) versus time resulting $k = 0.0042$ h^{-1} and $t_{0.5} = 6.88$ d.

2.4 Cyclic Voltammetry

Cyclic voltammetry was performed using a Princeton Applied Research VersaSTAT 3. A three-electrode arrangement with a glassy carbon working electrode, a platinum wire counter electrode and a Ag/AgBF$_4$ in CH$_3$CN reference electrode and 0.15 M *n*-Bu$_4$NPF$_6$ as supporting electrolyte was employed. The ferrocene/ferrocenium (Fc/Fc$^+$) redox couple was used as internal standard. Comments on reversibility are based on additional experiments varying scan rates.

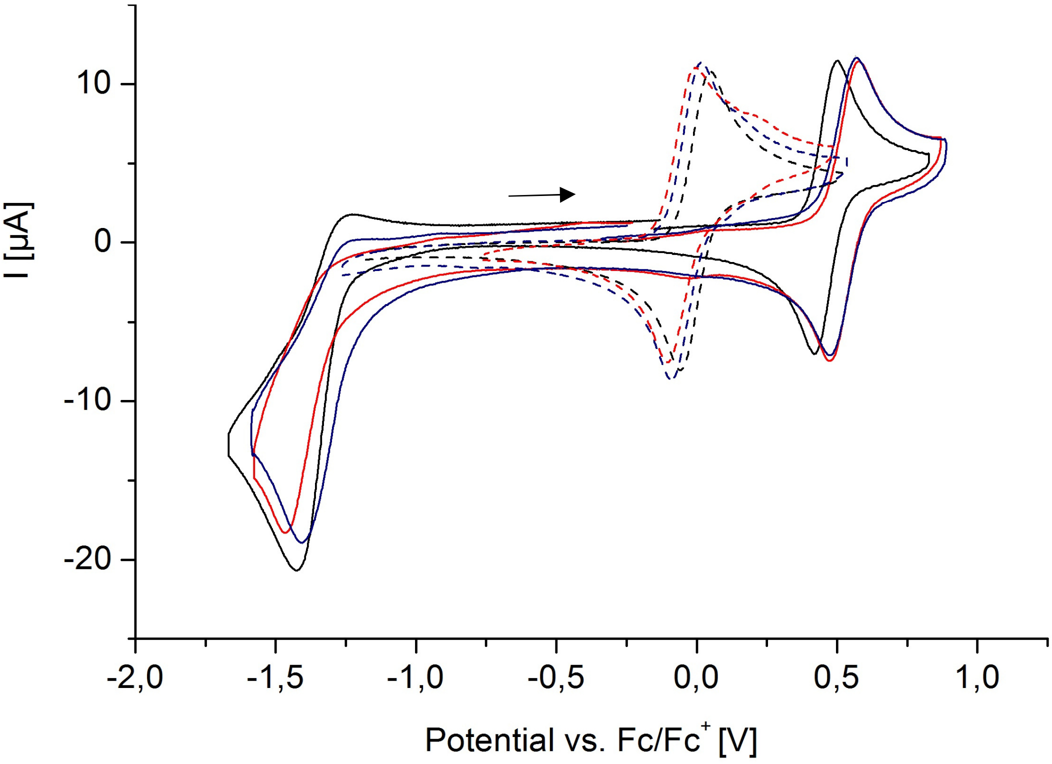


Figure S18. Selected cyclic voltammetry of bisphosalkyne complexes (dashed lines) **3a** (black), **3b** (red), **3c** (blue) and their respective Pt coordination compounds (solid lines) **4a** (black), **4b** (red) and **4c**[1] (blue) measured in CH$_2$Cl$_2$ comparing the reversible oxidation waves for the putative W$^{II/III}$ redox process and irreversible reduction of Pt^{II}.

Table S3. CV details for **3a-c**, **4a-c** and **5**.

	irreversible reduction E(Peak) [V]	reversible oxidation E$_{1/2}$ = [V]
3a	n/a	–0.05
3b	n/a	–0.54
3c	n/a	–0.37
4a	–1.425	+0.46
4b	–1.467	+0.53
4c	–1.405	+0.52
5	n/a	+0.29

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[1] Complex **4c*** was not measured, because of its faster isomerization to **4c** in solution.

3. DFT computational results

The calculations were carried out as closed shell calculations applying the DFT method and either the G09w[S6] or the ORCA[S7] program package. Molecular geometries of **4c**, **4c***, as well as the metallo-ligands **3c** and its isomer **3c*** (which was not isolated) were optimized without truncation and symmetry constraints in the gas phase using the BP86 functional.[S8] Quasi-relativistic effective core potentials of the Stuttgart/Cologne group were used for W, Pt (ECP60) and I (ECP46) in combination with (8s7p6d2f1g)/[6s5p3d2f1g] basis set for W as well as Pt and a (4s5p)/[2s3p] basis set for I.[S9] Split valence triple ζ-basis sets (def2-TZVP) of the Ahlrich group were used for the other elements.[S10] In doing so a reasonable match between the calculated and the experimentally determined structures was achieved. A comparison of calculated and experimentally determined metric parameters for the pair **4c**/**4c*** are given in Table S4. The strongest deviations (2.8 %) arise for the W–N bonds of the Tp* ligand, while all trends are well reflected showing mostly deviations below 2 %. Frequency calculations were performed to identify all stationary points as minima. The final energies were computed at higher level using the hybrid functional PBE0[S11] in combination with the scalar-relativistic ZORA method[S12] and the D3BJ dispersion correction of Grimme.[S13] The frontier Kohn-Sham orbitals of **3c** (isosurface value 0.05) are based on the high level calculation (Fig. S19). The Gibbs free energies (Δ*G*) were calculated using the total electronic energy from the higher level calculation and the thermal correction to Gibbs free energy from the frequency calculation.

Table S4. Comparison of essential bond lengths [Å] obtained by X-ray structure analysis and single molecule geometry optimization in the gas phase, the calculated bond lengths were rounded for clarity.

	4c (calc.)	**4c** (exp.)	**4c*** (calc.)	**4c*** (exp.)
W1–C1	2.076	2.041(2)	2.067	2.045(2)
W1–C2	2.077	2.075(2)	2.077	2.052(2)
W1–I1	2.829	2.7810(2)	2.834	2.7786(2)
W1–N1	2.276	2.229(2)	2.292	2.245(2)
W1–N3	2.295	2.235(2)	2.303	2.235(2)
W1–N5	2.205	2.144(2)	1.195	2.179 (2)
W1–C3	1.975	1.986(2)	1.977	1.976(2)
C1–C2	1.346	1.329(3)	1.348	1.333(3)
C1–P1	1.839	1.803(3)	1.836	1.810(2)
C2–P2	1.851	1.826(3)	1.852	1.826(2)
P1–Pt1	2.242	2.214(1)	2.256	2.239(1)
P2–Pt1	2.251	2.235(1)	2.248	2.229(1)
Pt1–Cl1	2.373	2.360(1)	2.369	2.352(1)
Pt1–Cl2	2.374	2.361(1)	2.376	2.384(1)

HOMO–1 (–5.72, –5.78 eV) LUMO (–1.91, –1.79 eV)

HOMO–4 (–6.28, –6.30 eV) HOMO (–4.92, –5.00 eV)

Figure S19. Selected frontier orbitals of **3c**, orbital energies in brackets: first value **3c**, second value **3c*** (orbitals exhibit a very similar composition, HOMO–2 and HOMO–3 are essentially lone pairs at iodide, the admixture of H–4 into H–3 and H–2 and *vice versa* is more pronounced in **3c***)

For the truncated model systems (Figure S20) PH_2 substituents were used in place of the PR_2 group and hydrido-tris(pyrazolyl)borate was applied as spectator ligand. The C_{sp}–C_{sp}–W–C_{CO} torsion angle was systematically changed and frozen at certain values. Subsequently the geometry was optimized as described above (BP86, ECP60 (W) and ECP46 (I) in combination with (8s7p6d2f1g)/[6s5p3d2f1g] basis set for W, a (4s5p)/[2s3p] basis set for I and def2-SVP for the other elements. The calculated total electronic energies without any correction were employed as criteria, because thermodynamic influences are considered as negligible due to the high structural similarity of the isomers compared.

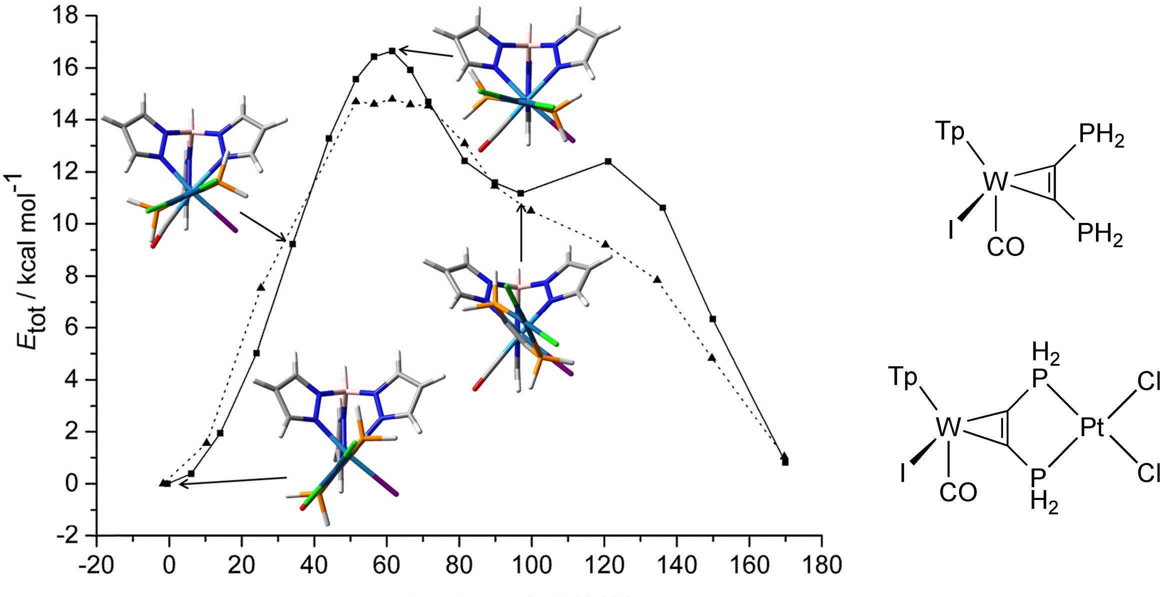

Figure S20. Calculated energy profile (E_{tot}) of alkyne rotation for the truncated model systems depicted; mononuclear W complex (dotted), dinuclear W/Pt complex (line, selected geometry optimized structures).

Table S5. Cartesian coordinates of the geometry optimized structures of **3c** (left) and **3c*** (right) in the gas phase; PB86/def2-TZVP/ECP(W, I).

W	-0.436908	-0.721680	0.068854	P	1.671448	-2.855845	0.246926
I	-0.470598	-2.008123	-2.482760	P	3.084062	0.556905	1.354334
N	-1.085201	1.096712	-1.128224	C	4.796141	-1.654020	1.458917
N	-2.652312	-1.227700	0.074666	C	4.182620	3.071763	1.655001
N	-1.183158	0.432941	1.805060	C	1.014795	-1.146266	0.085556
C	1.404590	0.232694	0.348553	C	2.286597	-3.285550	-1.490709
C	1.627341	-1.093268	0.354086	C	0.287111	-4.121187	0.466901
C	-0.318596	-2.372749	1.127258	C	1.621931	-0.001818	0.469305
N	-2.273061	1.715533	-0.834289	C	4.536236	-0.441617	0.793867
C	-0.590384	1.709826	-2.229393	C	3.511755	2.234625	0.745059
N	-3.572367	-0.210832	0.165878	C	5.934541	-2.404204	1.152611
C	-3.358277	-2.389345	0.002589	C	4.595642	4.350346	1.273243
N	-2.248323	1.288912	1.657288	W	-0.396390	0.383488	0.048272
C	-0.764556	0.543720	3.091179	I	0.029918	1.739582	-2.432378
P	2.323338	1.665235	0.864859	N	-1.748981	-0.970144	-1.219010
P	3.168938	-2.078113	0.410995	N	-2.337763	1.650375	0.125915
O	-0.272741	-3.299085	1.851370	N	-1.431871	-0.440670	1.803653
C	0.708618	1.376040	-2.881119	C	0.274159	1.902994	1.099235
B	-3.107120	1.250143	0.368246	N	-3.040449	-1.197268	-0.806064
C	-2.532097	2.697845	-1.741982	C	-1.628082	-1.557503	-2.434890
C	-1.473599	2.727277	-2.650152	N	-3.539361	1.007491	0.297606
C	-4.833283	-0.716115	0.142138	C	-2.610147	2.982029	0.091166
C	-2.761577	-3.752125	-0.104917	N	-2.726408	-0.894030	1.701756
C	-4.738109	-2.107135	0.037362	C	-1.038141	-0.649559	3.086868
C	-2.499074	1.928837	2.833214	O	0.614107	2.794366	1.779419
C	0.370424	-0.226903	3.671220	C	-0.377646	-1.615961	-3.243667
C	-1.560232	1.491246	3.770771	C	-1.602735	4.072149	-0.060241
C	3.974094	1.613319	0.057282	B	-3.584850	-0.527684	0.466082
C	1.556368	3.201637	0.204049	C	-3.725288	-1.900828	-1.750999
C	2.973533	-3.731855	-0.464315	C	-2.852031	-2.152955	-2.808739
C	3.277545	-2.499997	2.259441	C	-4.553438	1.911273	0.360376
C	-3.766533	3.539854	-1.701700	C	-3.999232	3.186379	0.229197
C	-1.275954	3.631182	-3.827178	C	-3.144856	-1.373143	2.906451
C	-3.621635	2.901831	3.001700	C	0.323526	-0.336887	3.602021
C	-1.414710	1.908699	5.202859	C	-2.088937	-1.248353	3.812779
C	5.032628	2.224072	0.753531	C	-5.160425	-2.291179	-1.599090
C	4.235506	1.017935	-1.187747	C	-3.117045	-2.898961	-4.079853
C	0.374476	3.661329	0.813787	C	-5.984835	1.516990	0.536134
C	2.182390	4.015654	-0.755181	C	-4.700613	4.510104	0.229685
C	3.206151	-3.519891	-1.972085	C	-4.519794	-1.916116	3.129140
C	1.765086	-4.632030	-0.196033	C	-2.053589	-1.659482	5.253844
C	3.858494	-1.283147	2.996380	C	5.457834	0.014385	-0.163691
C	4.161747	-3.731275	2.500293	C	6.600890	-0.732769	-0.462505
C	6.319509	2.256368	0.209887	C	6.841214	-1.945153	0.191603

C	5.524343	1.044032	-1.727059	C	4.326864	4.815345	-0.018104
C	-0.181851	4.887985	0.448553	C	3.648075	3.994990	-0.924098
C	1.631107	5.252251	-1.106370	C	3.249318	2.708122	-0.550201
C	6.567304	1.664919	-1.032613	C	2.938544	-4.677625	-1.461446
C	0.446520	5.691212	-0.509596	C	3.266600	-2.244030	-2.039442
C	-5.849360	-3.109811	-0.031111	C	-0.338224	-3.983532	1.861745
C	-6.054642	0.143159	0.213401	C	-0.783483	-4.305379	-0.609176
H	0.550634	1.080456	-3.929662	H	4.099381	-2.013089	2.217795
H	1.372249	2.255840	-2.876627	H	4.374811	2.718931	2.671379
H	1.213782	0.545974	-2.377922	H	1.405607	-3.320218	-2.148981
H	-4.064305	1.963714	0.500972	H	0.912284	-5.035302	0.488405
H	-3.468726	-4.423080	-0.613060	H	6.119113	-3.344654	1.676330
H	-1.826053	-3.740171	-0.677760	H	5.116193	4.988951	1.990072
H	-2.549286	-4.179824	0.887444	H	-0.449236	-0.965158	-4.127826
H	0.238270	-0.326954	4.757868	H	-0.698915	3.732219	-0.576727
H	0.440135	-1.229153	3.233929	H	-0.214911	-2.645818	-3.602570
H	1.329059	0.286618	3.498524	H	0.495608	-1.292997	-2.669787
H	3.877692	-4.236854	-0.072872	H	-2.039519	4.897519	-0.641680
H	2.265091	-2.713984	2.633589	H	-1.306248	4.477919	0.920191
H	-3.723325	4.299381	-2.493145	H	-4.717956	-0.880053	0.654421
H	-4.677168	2.942179	-1.861589	H	0.334164	-0.418358	4.697152
H	-3.881250	4.060497	-0.739420	H	1.077208	-1.035508	3.206067
H	-0.367771	4.245959	-3.717194	H	0.651068	0.673884	3.327104
H	-1.169592	3.060916	-4.764188	H	-5.445569	-2.979895	-2.405259
H	-2.123783	4.318400	-3.956627	H	-5.350120	-2.793384	-0.639769
H	-3.560469	3.373458	3.991055	H	-5.832391	-1.420458	-1.653431
H	-3.591397	3.697938	2.243891	H	-2.383884	-3.706659	-4.237856
H	-4.604993	2.413267	2.922417	H	-4.115170	-3.358692	-4.078518
H	-1.492074	1.048810	5.887621	H	-3.060994	-2.238619	-4.960577
H	-0.441914	2.389009	5.394547	H	-6.624429	2.407927	0.490774
H	-2.196164	2.624588	5.493016	H	-6.318237	0.821709	-0.248114
H	4.844059	2.675092	1.731186	H	-6.161717	1.026694	1.505477
H	3.431177	0.526141	-1.735284	H	-4.505661	5.073964	-0.696945
H	-0.105161	3.058789	1.588408	H	-5.789454	4.389259	0.314928
H	3.112398	3.688839	-1.223256	H	-4.374648	5.146451	1.068130
H	4.126199	-2.946833	-2.161507	H	-4.580315	-2.380529	4.121968
H	3.299265	-4.495644	-2.476249	H	-5.287520	-1.128559	3.080510
H	2.362543	-2.987006	-2.434169	H	-4.783613	-2.678311	2.382180
H	1.605256	-4.818764	0.874126	H	-1.823046	-0.808987	5.914867
H	0.847516	-4.188706	-0.606359	H	-3.021388	-2.066890	5.577151
H	1.913694	-5.605649	-0.693483	H	-1.292924	-2.433904	5.441875
H	3.300296	-0.358260	2.791944	H	5.283970	0.961567	-0.676059
H	3.843999	-1.453447	4.085616	H	7.305582	-0.364496	-1.211316
H	4.902372	-1.110920	2.692030	H	7.736660	-2.525861	-0.039821
H	3.709371	-4.657149	2.120769	H	4.638735	5.819123	-0.314632
H	5.153916	-3.613625	2.034421	H	3.422864	4.354184	-1.930442

H	4.320998	-3.859692	3.583587	H	2.707596	2.085200	-1.263373
H	7.130478	2.735779	0.762130	H	2.232138	-5.473183	-1.183851
H	5.714465	0.572471	-2.693421	H	3.334462	-4.923142	-2.460497
H	-1.100599	5.228884	0.930390	H	3.779819	-4.705375	-0.751568
H	2.134746	5.875197	-1.849043	H	2.830656	-1.235584	-2.072491
H	7.573466	1.681689	-1.456567	H	4.182613	-2.196722	-1.433293
H	0.019900	6.659024	-0.780917	H	3.559122	-2.517334	-3.066513
H	-6.833128	-2.620847	-0.015797	H	0.430957	-3.891222	2.643407
H	-5.798080	-3.711841	-0.952575	H	-0.991907	-3.102763	1.921120
H	-5.819521	-3.812816	0.816538	H	-0.952523	-4.869221	2.092893
H	-6.953807	-0.476743	0.103092	H	-0.353909	-4.446821	-1.611390
H	-6.129156	0.674297	1.174466	H	-1.390849	-5.198837	-0.384999
H	-6.067907	0.902066	-0.582327	H	-1.458930	-3.442083	-0.646829

Table S6. Cartesian coordinates of the geometry optimized structures of **4c** (left) and **4c*** (right) in the gas phase; PB86/def2-TZVP/ECP(W, Pt, I).

W	-1.369238	-0.660964	-0.025957	Pt	3.494688	-1.060670	0.271153
I	-1.679531	-1.996502	-2.500823	P	1.603311	-1.961614	-0.566926
N	-2.161650	1.143246	-1.165579	P	2.511896	0.959962	0.189665
N	-3.603029	-1.128010	0.215545	C	4.325330	2.045133	-1.603595
N	-1.915878	0.456820	1.794483	C	3.251555	1.604875	2.817825
C	0.525903	0.180241	-0.133338	C	0.326810	-0.646939	-0.449998
C	0.636790	-1.087900	0.303949	C	1.694212	-2.417767	-2.376185
C	-1.164999	-2.368841	0.945477	C	0.990417	-3.488203	0.302686
N	-3.252209	1.827709	-0.686166	C	0.714212	0.574093	-0.031553
C	-1.824600	1.729157	-2.342671	C	2.958439	1.964886	-1.277968
N	-4.478758	-0.086473	0.410044	C	2.780665	2.109274	1.594601
C	-4.346657	-2.268118	0.207109	C	4.733117	2.823338	-2.688180
N	-2.963389	1.348237	1.777605	C	3.491769	2.470723	3.886723
C	-1.400475	0.481035	3.051619	W	-1.359084	0.505746	-0.132938
P	2.061495	1.192308	-0.141499	I	-1.794442	1.848971	-2.590205
P	2.282838	-1.915860	0.476024	N	-2.574823	-1.185743	-1.088194
O	-1.043464	-3.358125	1.560874	N	-3.469424	1.260891	0.397752
C	-0.706808	1.306668	-3.231984	N	-1.762616	-0.422225	1.815053
B	-3.956427	1.358060	0.591167	C	-0.780716	2.228496	0.644773
C	-3.600021	2.826148	-1.543289	N	-3.611781	-1.744354	-0.381519
C	-2.705188	2.798605	-2.613535	C	-2.544833	-1.821892	-2.287259
C	-5.750288	-0.555792	0.510743	N	-4.407892	0.336156	0.794219
C	-3.812167	-3.650430	0.037796	C	-4.075612	2.478401	0.450745
C	-5.707378	-1.946922	0.383573	N	-2.866318	-1.225214	1.987006
C	-3.107022	1.918567	3.005114	C	-1.088526	-0.420534	2.996313
C	-0.217408	-0.307806	3.481690	O	-0.451774	3.259030	1.083725
C	-2.116068	1.400711	3.843074	C	-1.591647	-1.544681	-3.399527
Pt	3.756684	-0.243199	0.162864	C	-3.431089	3.785549	0.130764

C	2.182983	2.194856	-1.673748	B	-4.031155	-1.154542	0.970333
C	1.747650	2.413556	1.191928	C	-4.226911	-2.710011	-1.117070
C	2.349235	-3.227953	-0.851253	C	-3.567173	-2.793299	-2.343449
C	2.366607	-2.805509	2.132567	C	-5.585144	0.954660	1.077337
C	-4.757751	3.740806	-1.300456	C	-5.413501	2.325132	0.866963
C	-2.665503	3.686726	-3.818857	C	-2.883411	-1.725427	3.252276
C	-4.182569	2.908986	3.317090	C	0.181508	0.314144	3.235145
C	-1.843081	1.739250	5.277175	C	-1.754035	-1.247900	3.923193
C	1.710054	3.512960	-1.762010	C	-5.401969	-3.489988	-0.620429
C	2.833421	1.620028	-2.778181	C	-3.863764	-3.698121	-3.499617
C	2.821688	2.822815	2.000717	C	-6.806241	0.216313	1.523175
C	0.473796	2.976035	1.385539	C	-6.418065	3.423500	1.038717
C	2.475629	-2.595886	-2.244303	C	-3.971060	-2.620236	3.752235
C	1.231070	-4.278156	-0.802116	C	-1.319790	-1.535665	5.328459
C	2.960072	-1.870091	3.199739	C	2.013174	2.656273	-2.050328
C	3.183680	-4.108947	2.087703	C	2.432770	3.425632	-3.140897
C	1.874279	4.238787	-2.945430	C	3.790167	3.513831	-3.458694
C	2.985936	2.344115	-3.961040	C	3.274702	3.844154	3.740898
C	2.619241	3.792073	2.986720	C	2.823121	4.353056	2.519543
C	0.282340	3.947152	2.372696	C	2.582111	3.491909	1.447128
C	2.507416	3.655563	-4.047186	C	2.570351	-3.656064	-2.618376
C	1.353383	4.356491	3.173339	C	2.181095	-1.222156	-3.206161
C	-6.847436	-2.918252	0.420866	C	0.915199	-3.271789	1.818769
C	-6.932440	0.335624	0.716444	C	-0.311819	-4.063100	-0.265769
Cl	5.332804	1.503465	-0.149489	Cl	4.476812	-3.214268	0.356708
Cl	5.502994	-1.831317	0.418559	Cl	5.539243	-0.122368	1.035366
H	-1.098489	0.791128	-4.122428	H	5.058432	1.496632	-1.004970
H	-0.142567	2.187354	-3.573204	H	3.466758	0.540268	2.914826
H	-0.016455	0.622488	-2.732174	H	0.655002	-2.650301	-2.654806
H	-4.874094	2.089897	0.843142	H	1.828003	-4.181528	0.109667
H	-4.573694	-4.280202	-0.443772	H	5.794899	2.883643	-2.935465
H	-2.911257	-3.671378	-0.585936	H	3.871468	2.070950	4.828959
H	-3.569778	-4.109549	1.009168	H	-2.092148	-0.988307	-4.207004
H	-0.152659	-0.320871	4.577511	H	-2.670790	3.694305	-0.653378
H	-0.259408	-1.343094	3.122537	H	-1.231428	-2.492560	-3.830617
H	0.710509	0.146170	3.101839	H	-0.735937	-0.945346	-3.077921
H	3.318701	-3.696807	-0.603419	H	-4.196073	4.493996	-0.217289
H	1.319885	-3.045238	2.380327	H	-2.954129	4.225785	1.020461
H	-4.790935	4.513169	-2.079711	H	-4.973627	-1.760527	1.400145
H	-5.718485	3.203937	-1.322654	H	0.389513	0.361778	4.312141
H	-4.687328	4.246310	-0.326179	H	1.035831	-0.192564	2.759745
H	-1.672573	4.145201	-3.950684	H	0.148708	1.338922	2.847259
H	-2.886401	3.129174	-4.743469	H	-5.668736	-4.265030	-1.350440
H	-3.398658	4.501659	-3.744094	H	-5.192337	-3.986905	0.337921
H	-4.015315	3.340236	4.312459	H	-6.286586	-2.851964	-0.472747
H	-4.205394	3.733377	2.590153	H	-2.981578	-4.289764	-3.792918

H	-5.180842	2.445236	3.317039	H	-4.667210	-4.407754	-3.259125
H	-1.844230	0.840646	5.913964	H	-4.181558	-3.132180	-4.390195
H	-0.863577	2.227381	5.402968	H	-7.641093	0.918071	1.645522
H	-2.604527	2.421000	5.679670	H	-7.112840	-0.547429	0.793493
H	1.230246	3.984904	-0.903717	H	-6.651844	-0.292822	2.486215
H	3.245977	0.612953	-2.694073	H	-6.548650	4.002922	0.110889
H	3.813021	2.394385	1.834553	H	-7.404021	3.026392	1.316054
H	-0.366161	2.651574	0.768772	H	-6.117914	4.134433	1.824897
H	3.337244	-1.916012	-2.293074	H	-3.700442	-3.022342	4.736846
H	2.622438	-3.392983	-2.990138	H	-4.927104	-2.085463	3.859336
H	1.563094	-2.047448	-2.523211	H	-4.142775	-3.468627	3.074700
H	1.069805	-4.701191	0.197755	H	-1.283175	-0.619629	5.939308
H	0.278430	-3.859314	-1.154328	H	-2.010883	-2.229542	5.825936
H	1.494330	-5.108424	-1.477073	H	-0.317337	-1.989870	5.361566
H	2.485598	-0.881167	3.218392	H	0.947219	2.588676	-1.825963
H	2.841075	-2.327957	4.194649	H	1.688149	3.952061	-3.741205
H	4.031636	-1.716553	3.009610	H	4.114602	4.115356	-4.310512
H	2.757218	-4.866558	1.418500	H	3.472366	4.520926	4.574908
H	4.219756	-3.905974	1.782547	H	2.664052	5.425919	2.395508
H	3.204777	-4.538293	3.102055	H	2.246277	3.900366	0.493410
H	1.516625	5.269104	-3.000258	H	2.172455	-4.557759	-2.132062
H	3.499073	1.889317	-4.810296	H	2.612854	-3.851833	-3.701863
H	3.459354	4.109341	3.607669	H	3.593780	-3.502590	-2.249373
H	-0.708758	4.381695	2.516147	H	1.545131	-0.332385	-3.088478
H	2.641672	4.227961	-4.967351	H	3.206308	-0.943925	-2.921469
H	1.200934	5.116029	3.943250	H	2.183937	-1.493077	-4.273634
H	-7.814235	-2.401004	0.487933	H	1.862817	-2.875019	2.209052
H	-6.874728	-3.545965	-0.484003	H	0.099450	-2.584560	2.086778
H	-6.778750	-3.599043	1.284410	H	0.718282	-4.234719	2.315812
H	-7.853650	-0.260950	0.709820	H	-0.238628	-4.303745	-1.335694
H	-6.884009	0.867790	1.678339	H	-0.556220	-4.997535	0.264489
H	-7.016262	1.094692	-0.074966	H	-1.152810	-3.368383	-0.127686

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