SUPPORTING INFORMATION FOR

Gyroscope Like Molecules Consisting of Trigonal or Square Planar Osmium Rotators Within Three-Spoked Dibridgehead Diphosphine Stators: Syntheses, Substitution Reactions, Structures, and Dynamic Properties

Tobias Fiedler,[†‡] Nattamai Bhuvanesh,[†] Frank Hampel,[‡] Joseph H. Reibenspies,[†] and John A. Gladysz[*†]

[†]Department of Chemistry, Texas A&M University, PO Box 30012, College Station, Texas 77842-3012, USA.

[‡]Institut für Organische Chemie and Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestraße 42, 91054 Erlangen, Germany

submitted to *Dalton Transactions*

■ Experimental Section

General Data. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on standard 300-500 MHz spectrometers at ambient probe temperatures and referenced as follows (δ, ppm): ^1H, residual internal C_6D_5H (7.15) or $CHCl_3$ (7.26); ^{13}C, internal C_6D_6 (128.0) or $CDCl_3$ (77.0); ^{31}P, external H_3PO_4 (0.00). IR spectra were recorded using an ASI React-IR 1000, a Thermo Scientific Nicolet IR100 FT-IR, or a Shimadzu IRAffinity-1 spectrophotometer with a Pike MIRacle ATR system (diamond/ZnSe crystal). Mass spectra were obtained using Micromass Zabspec (FAB), Shimadzu Biotech Axima Confidence (MALDI-TOF MS), or Applied Biosystem STR Voyager (MALDI-TOF MS) instruments. Melting points were determined on an Electrothermal IA 9100 apparatus or a Stanford Research Systems (SRS) MPA100 (Opti-Melt) automated device. DSC and TGA data were recorded with a Mettler-Toledo DSC821 instrument and treated by standard methods.[s1] Microanalyses were conducted on a Carlo Erba EA1110 instrument (in house) or by Atlantic Microlab.

All reactions were conducted under dry N_2 atmospheres unless noted using standard Schlenk techniques; all chromatographies were conducted in air. Solvents were treated as follows: THF, hexanes, and CH_2Cl_2 were dried and degassed using a Glass Contour solvent purification system, or distilled from Na/benzophenone (THF/hexanes) or CaH_2 (CH_2Cl_2); MeOH was distilled from Mg; chlorobenzene was distilled by rotary evaporation, and then aspirated with N_2; 2-methoxyethanol (anhydrous, 99.8%, Aldrich), C_6D_6, and $CDCl_3$ (2 × deutero GmbH or Cambridge Isotope Laboratories) were used as received. SiO_2, neutral Al_2O_3 (2 × Macherey-Nagel or Silicycle), CO (99.97%, Linde, or 99.998%, Matheson), CF_3SO_3H (98+%, Alfa Aesar), HCl (1.0 M in Et_2O, Acros), Grubbs' catalyst $Cl_2(PCy_3)_2Ru{=}CHPh_2$ (Aldrich), PtO_2, (99%, Acros), MeLi (1.6 M in Et_2O, Acros), PhLi (2.0 M in Bu_2O, Acros), *n*-Bu_4N^+ BF_4^- (99+%, electrochemical grade, Fluka), and ferrocene (98%, Acros), used as received. $(NH_4)_2OsCl_6$,[s2a] $(NH_4)_2OsBr_6$,[s2b] the phosphines **1a-c**,[s3] C_8K,[s4] and $[H(OEt_2)_2]^+$ BAr_f^-,[s5] were synthesized by literature procedures.

***cis,cis,trans*-Os(CO)$_2$(Cl)$_2$(P((CH$_2$)$_6$CH=CH$_2$)$_3$)$_2$ (2a).** A Fischer-Porter bottle was charged with $(NH_4)_2OsCl_6$ (0.507 g, 1.16 mmol) and 2-methoxyethanol (40 mL). The red suspension was stirred at 110 °C under CO (10 bar) until it turned pale yellow (5-7 d). Then **1a** (1.55 g, 4.25 mmol) was added with stirring and the solution kept at 80 °C for 24 h. The solvent was removed by oil pump vacuum and the resulting red-brown oil chromatographed (SiO_2 column, 3.5 cm × 30 cm, 2:1 v/v hexanes/CH_2Cl_2). The solvent was removed from the product containing fractions by oil pump vacuum to give **2a** (0.883 g, 0.844 mmol, 73%) as a pale yellow oil. Anal. calcd (%) for $C_{50}H_{90}Cl_2O_2P_2Os$ (1046.33): C 57.39, H 8.67; found C 56.97, H 8.74.

NMR (C_6D_6, δ/ppm): ^{1}**H** (300 MHz)[s6] 5.77 (ddt, 6H, $^3J_{HH\mathit{trans}}$ = 16.9 Hz, $^3J_{HH\mathit{cis}}$ = 10.1 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 5.04 (br d, $^3J_{HH\mathit{trans}}$ = 17.5 Hz, 6H, =$CH_E H_Z$), 4.99 (br d, $^3J_{HH\mathit{cis}}$ = 10.8 Hz, 6H, =$CH_E H_Z$), 2.21-2.13 (br m, 12H, PCH_2), 1.98-1.92 (br m, 12H, CH_2CH=), 1.69-1.58 (br m, 12H, PCH_2CH_2), 1.35-1.21 (br m, 36H, remaining CH_2); ^{13}**C{^{1}H}** (100 MHz)[s6] 176.6 (t, $^2J_{CP}$ = 7.2 Hz, *C*O), 139.1 (s, *C*H=), 114.6 (s, =CH_2), 33.9 (s, CH_2CH=), 31.1 (virtual t,[s7] $^3J_{CP}$ = 6.4 Hz, PCH_2CH_2-CH_2), 29.0 (s, CH_2), 28.8 (s, CH_2), 23.5 (overlapping virtual t,[s7] $^1J_{CP}$ = 15.6 Hz, PCH_2),[s8] 23.3 (overlapping s, PCH_2CH_2);[s8] ^{31}**P{^{1}H}** (121 MHz) –16.3 (s).

IR (cm^{-1}, oil film): 3076 (w), 2926 (m), 2856 (w), 2019 (s, ν_{CO}), 1945 (s, ν_{CO}), 1640 (w), 1459 (w), 1440 (w), 1417 (w), 992 (w), 907 (m), 718 (w). **MS** (FAB, 3-NBA):[s9] 1011 ([**2a** – Cl]$^+$, 5%), 365 ([**1a** + 1]$^+$, 100%).

***cis,cis,trans*-$Os(CO)_2(Cl)_2(P((CH_2)_7CH{=}CH_2)_3)_2$ (2b).** $(NH_4)_2OsCl_6$ (0.500 g, 1.14 mmol), 2-methoxyethanol (40 mL), and **1b** (1.60 g, 3.95 mmol) were combined in a procedure analogous to that used for **2a**. An identical workup gave **2b** (0.854 g, 0.755 mmol, 66%) as a pale yellow oil. Anal. calcd (%) for $C_{56}H_{102}Cl_2O_2P_2Os$ (1130.49): C 59.50, H 9.09; found C 59.32, H 8.80.

NMR (C_6D_6, δ/ppm): ^{1}**H** (300 MHz)[s6] 5.78 (ddt, 6H, $^3J_{HH\mathit{trans}}$ = 16.9 Hz, $^3J_{HH\mathit{cis}}$ = 10.2 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 5.04 (br d, $^3J_{HH\mathit{trans}}$ = 17.0 Hz, 6H, =$CH_E H_Z$), 4.99 (br d, $^3J_{HH\mathit{cis}}$ = 10.1 Hz, 6H, =$CH_E H_Z$), 2.24-2.14 (br m, 12H, PCH_2), 2.01-1.94 (br m, 12H, CH_2CH=), 1.72-1.59 (br m, 12H, PCH_2CH_2), 1.36-1.18 (br m, 48H, remaining CH_2); ^{13}**C{^{1}H}** (100 MHz)[s6] 176.6 (t, $^2J_{CP}$ = 7.3 Hz, *C*O), 139.2 (s, *C*H=), 114.5 (s, =CH_2), 34.0 (s, CH_2CH=), 31.2 (virtual t,[s7] $^3J_{CP}$ = 6.4 Hz, PCH_2CH_2-CH_2), 29.24 (s, CH_2), 29.19 (s, CH_2), 29.0 (s, CH_2), 23.6 (overlapping virtual t,[s7] $^1J_{CP}$ = 15.5 Hz, PCH_2),[s8] 23.4 (overlapping s, PCH_2CH_2);[s8] ^{31}**P{^{1}H}** (121 MHz) –15.6 (s).

IR (cm^{-1}, oil film): 3076 (w), 2926 (m), 2856 (w), 2019 (s, ν_{CO}), 1945 (s, ν_{CO}), 1640 (w), 1463 (w), 1417 (w), 996 (w), 907 (m), 718 (w). **MS** (FAB, 3-NBA): 1075 ([**2b** – 2CO + 1]$^+$, 2%), 1067 ([**2b** – Cl – CO – 1]$^+$, 5%), 407 ([**1b** + 1]$^+$, 100%).

***cis,cis,trans*-Os(CO)$_2$(Cl)$_2$(P((CH$_2$)$_8$CH=CH$_2$)$_3$)$_2$ (2c).** $(NH_4)_2OsCl_6$ (0.500 g, 1.14 mmol), 2-methoxyethanol (40 mL), and **1c** (1.55 g, 3.46 mmol) were combined in a procedure analogous to that used for **2a**. An identical workup gave **2c** (0.929 g, 0.207 mmol, 67%) as a pale yellow oil. Anal. calcd (%) for $C_{62}H_{114}Br_2O_2P_2Os$ (1214.65): C 61.31, H 9.46; found C 61.05, H 9.48.

NMR (C_6D_6, δ/ppm): **^{1}H** (300 MHz)[s6] 5.79 (ddt, 6H, $^3J_{HHtrans}$ = 16.9 Hz, $^3J_{HHcis}$ = 10.2 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 5.04 (br d, $^3J_{HHtrans}$ = 18.0 Hz, 6H, =CH_EH_Z), 4.99 (br d, $^3J_{HHcis}$ = 11.1 Hz, 6H, =CH_EH_Z), 2.24-2.16 (br m, 12H, PCH_2), 2.03-1.95 (br m, 12H, CH_2CH=), 1.73-1.61 (br m, 12H, PCH$_2$CH_2), 1.37-1.18 (br m, 60H, remaining CH_2); **^{13}C{^{1}H}** (75 MHz)[s6] 176.6 (t, $^2J_{CP}$ = 7.4 Hz, *C*O), 139.2 (s, *C*H=), 114.5 (s, =*C*H$_2$), 34.2 (s, *C*H$_2$CH=CH$_2$), 31.4 (virtual t,[s7] $^3J_{CP}$ = 6.4 Hz, PCH$_2$CH$_2$-*C*H$_2$), 29.7 (s, *C*H$_2$), 29.5 (s, *C*H$_2$), 29.4 (s, *C*H$_2$), 29.3 (s, *C*H$_2$), 23.7 (overlapping virtual t,[s7] $^1J_{CP}$ = 15.5 Hz, P*C*H$_2$),[s8] 23.5 (overlapping s, PCH$_2$*C*H$_2$);[s8] **^{31}P{^{1}H}** (121 MHz) –16.3 (s).

IR (cm^{-1}, oil film): 3076 (w), 2926 (m), 2856 (w), 2019 (s, ν_{CO}), 1945 (s, ν_{CO}), 1640 (w), 1463 (w), 1417 (w), 992 (w), 907 (m), 718 (w). **MS** (FAB, 3-NBA):[s9] 1152 ([**2c** – Cl – CO + 1]$^+$, 5%), 449 ([**1c** + 1]$^+$, 100%).

***cis,cis,trans*-Os(CO)$_2$(Br)$_2$(P((CH$_2$)$_6$CH=CH$_2$)$_3$)$_2$ (3a).** A Fischer-Porter bottle was charged with $(NH_4)_2OsBr_6$ (0.500 g, 0.709 mmol) and 2-methoxyethanol (40 mL). The deep red solution was stirred at 80 °C under CO (10 bar) until it turned pale yellow (3-5 d). Then **1a** (0.950 g, 2.61 mmol) was added with stirring and the solution kept at 80 °C for 24 h. The solvent was removed by oil pump vacuum and the resulting red-brown oil chromatographed (SiO_2 column, 3.5 cm × 30 cm, 5:2 v/v hexanes/CH_2Cl_2). The solvent was removed from the product containing fractions by oil pump vacuum to give **3a** (0.441 g, 0.388 mmol, 55%) as a pale yellow oil. Anal. calcd (%) for $C_{50}H_{90}Br_2O_2P_2Os$ (1135.23): C 52.90, H 7.99; found C 53.22, H 8.26.

NMR (C_6D_6, δ/ppm): **^{1}H** (300 MHz)[s10] 5.77 (ddt, 6H, $^3J_{HHtrans}$ = 16.9 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 5.04 (br d, $^3J_{HHtrans}$ = 17.5 Hz, 6H, =CH_EH_Z), 4.99 (br d, $^3J_{HHcis}$ = 10.8 Hz, 6H, =CH_EH_Z), 2.30-2.24 (br m, 12H, PCH_2), 1.98-1.92 (br m, 12H, CH_2CH=), 1.68-1.58 (br m, 12H,

PCH_2CH_2), 1.35-1.22 (br m, 36H, remaining CH_2); **^{13}C{^{1}H}** (100 MHz)[s10] 174.0 (t, $^2J_{CP}$ = 7.5 Hz, *C*O), 139.1 (s, *C*H=), 114.4 (s, =*C*H_2), 33.6 (s, *C*H_2CH=), 30.8 (virtual t,[s7] $^3J_{CP}$ = 6.3 Hz, PCH_2CH_2-*C*H_2), 28.7 (s, *C*H_2), 28.6 (s, *C*H_2), 24.3 (virtual t,[s7] $^1J_{CP}$ = 15.9 Hz, P*C*H_2), 23.3 (s, PCH_2*C*H_2); **^{31}P{^{1}H}** (121 MHz) –25.3 (s).

IR (cm^{-1}, oil film): 3076 (w), 2926 (m), 2855 (w), 2023 (s, ν_{CO}), 1949 (s, ν_{CO}), 1640 (w), 1459 (w), 1440 (w), 1417 (w), 992 (w), 907 (m), 718 (w). **MS** (FAB, 3-NBA):[s9] 1078 ([**3a** – 2CO – 1]$^+$, 2%), 1055 ([**3a** – Br]$^+$, 5%), 365 ([**1a** + 1]$^+$, 100%).

***cis,cis,trans*-$Os(CO)_2(Br)_2(P((CH_2)_7CH=CH_2)_3)_2$ (3b).** $(NH_4)_2OsBr_6$ (0.500 g, 0.709 mmol), 2-methoxyethanol (40 mL), and **1b** (1.13 g, 2.79 mmol) were combined in a procedure analogous to that used for **3a**. An identical workup gave **3b** (0.398 g, 0.326 mmol, 46%) as a pale yellow oil. Anal. calcd (%) for $C_{56}H_{102}Br_2O_2P_2Os$ (1219.39): C 55.16, H 8.43; found C 55.06, H 8.51.

NMR (C_6D_6, δ/ppm): **^{1}H** (300 MHz)[s6] 5.79 (ddt, 6H, $^3J_{HH\mathit{trans}}$ = 16.9 Hz, $^3J_{HH\mathit{cis}}$ = 10.2 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 5.04 (br d, $^3J_{HH\mathit{trans}}$ = 17.1 Hz, 6H, =CH_EH_Z), 5.00 (br d, $^3J_{HH\mathit{cis}}$ = 10.7 Hz, 6H, =CH_EH_Z), 2.32-2.27 (br m, 12H, PCH_2), 2.01-1.94 (br m, 12H, CH_2CH=), 1.72-1.59 (br m, 12H, PCH_2CH_2), 1.34-1.21 (br m, 48H, remaining CH_2); **^{13}C{^{1}H}** (75 MHz)[s6] 175.2 (t, $^2J_{CP}$ = 7.4 Hz, *C*O), 139.1 (s, *C*H=), 114.5 (s, =*C*H_2), 34.1 (s, *C*H_2CH=), 31.3 (virtual t,[s7] $^3J_{CP}$ = 6.4 Hz, PCH_2CH_2*C*H_2), 29.4 (s, *C*H_2), 29.3 (s, *C*H_2), 29.2 (s, *C*H_2), 24.3 (virtual t,[s7] $^1J_{CP}$ = 15.9 Hz, P*C*H_2), 23.9 (s, PCH_2-*C*H_2); **^{31}P{^{1}H}** (121 MHz) –25.9 (s).

IR (cm^{-1}, oil film): 3076 (w), 2926 (m), 2856 (w), 2023 (s, ν_{CO}), 1949 (s, ν_{CO}), 1640 (w), 1463 (w), 1440 (w), 1417 (w), 996 (w), 907 (m), 718 (w). **MS** (FAB, 3-NBA):[s9] 1191 ([**3b** – CO + 1]$^+$, 0.5%), 1163 ([**3b** –2CO + 1]$^+$, 2%), 1140 ([**3b** – Br + 1]$^+$, 3%), 1110 ([**3b** – Br – CO – 1]$^+$, 5%), 407 ([**1b** + 1]$^+$, 100%).

***cis,cis,trans*-$Os(CO)_2(Br)_2(P((CH_2)_8CH=CH_2)_3)_2$ (3c).** $(NH_4)_2OsBr_6$ (0.600 g, 0.709 mmol), 2-methoxyethanol (40 mL), and **1c** (1.49 g, 3.33 mmol) were combined in a procedure analogous to that used for **6a**. An identical workup gave **3c** (0.541 g, 0.415 mmol, 49%) as a pale yellow oil. Anal. calcd (%) for $C_{62}H_{114}Br_2O_2P_2Os$ (1303.55): C 57.13, H 8.81; found C 56.80, H 8.90.

NMR (C_6D_6, δ/ppm): **^{1}H** (300 MHz)[s6] 5.79 (ddt, 6H, $^3J_{HH\mathit{trans}}$ = 16.9 Hz, $^3J_{HH\mathit{cis}}$ = 10.2 Hz,

$^3J_{HH}$ = 6.7 Hz, C*H*=), 5.04 (br d, $^3J_{HHtrans}$ = 18.1 Hz, 6H, =CH$_E$*H*$_Z$), 5.00 (br d, $^3J_{HHcis}$ = 11.2 Hz, 6H, =C*H*$_E$H$_Z$), 2.34-2.26 (br m, 12H, PC*H*$_2$), 2.03-1.96 (br m, 12H, C*H*$_2$CH=), 1.74-1.60 (br m, 12H, PCH$_2$C*H*$_2$), 1.39-1.18 (br m, 60H, remaining C*H*$_2$); **^{13}C{^{1}H}** (75 MHz)[s6] 175.2 (t, $^2J_{CP}$ = 7.3 Hz, *C*O), 139.2 (s, *C*H=), 114.5 (s, =*C*H$_2$), 34.2 (s, *C*H$_2$CH=CH$_2$), 31.3 (virtual t,[s7] $^3J_{CP}$ = 6.4 Hz, PCH$_2$CH$_2$-*C*H$_2$), 29.7 (s, *C*H$_2$), 29.5 (s, *C*H$_2$), 29.4 (s, *C*H$_2$), 29.3 (s, *C*H$_2$), 25.0 (virtual t,[s7] $^1J_{CP}$ = 15.9 Hz, P*C*H$_2$), 23.9 (s, PCH$_2$*C*H$_2$); **^{31}P{^{1}H}** (121 MHz) –25.3 (s).

IR (cm^{-1}, oil film): 3076 (w), 2926 (m), 2856 (w), 2023 (s, ν_{CO}), 1949 (s, ν_{CO}), 1640 (w), 1463 (w), 1440 (w), 1417 (w), 992 (w), 907 (m), 718 (w). **MS** (FAB, 3-NBA):[s9] 449 ([**1c** + 1]$^+$, 100%).

Alkene metathesis of 2a. A Schlenk flask was charged with **2a** (0.714 g, 0.683 mmol) and chlorobenzene (700 mL; the resulting solution was 0.0010 M). Then solid Grubbs' catalyst (0.039 g, 0.048 mmol, 7.0 mol%) was added with stirring. The solution was aspirated with N$_2$, and periodically monitored by ^{1}H NMR. After the reaction was complete (ca. 24 h), the solution was aspirated with air (30 min) to decompose the remaining catalyst. The solution was filtered through Al$_2$O$_3$ (3 cm × 5 cm), which was washed with CH$_2$Cl$_2$. The solvents were removed from the filtrate to give crude **4*a** (0.571 g, 0.594 mmol, 87%) as a light brown sticky oil.

NMR (C$_6$D$_6$, δ/ppm): **^{1}H** (300 MHz) 5.57-5.39 (br m, 5H, C*H*=), 5.27-5.20 (br m, 1H, C*H*=), 2.26-0.99 (br m, 78H, C*H*$_2$); **^{31}P{^{1}H}** (121 MHz) −10.4 (s, 53% of integral), −11.5 (s, 21%), −12.7 (s, 11%), −12.8 (s, 8%), −12.9 (s, 9%), −13.0 (s, 9%).

***cis,cis,trans*-Os(CO)$_2$(Cl)$_2$(P((CH$_2$)$_{14}$)$_3$P) (6a) and *cis,cis,trans*-Os(CO)$_2$(Cl)$_2$(P(CH$_2$)$_{13}$-CH$_2$)((CH$_2$)$_{14}$)(P(CH$_2$)$_{13}$CH$_2$) (6'a).** A Schlenk flask was charged with **4*a** (0.571 g, 0.594 mmol; the entire quantity prepared above), THF (30 mL), and PtO$_2$ (0.023 g, 0.102 mmol), connected to a gas balloon, and partially evacuated. Then H$_2$ (1 bar) was introduced, and the suspension was stirred. After 3 d, the solvent was removed by oil pump vacuum. The black residue was filtered through Al$_2$O$_3$ with CH$_2$Cl$_2$. The solvent was removed from the filtrate and the residue was chromatographed (SiO$_2$ column, 3.5 cm × 30 cm, 3:2 v/v hexanes/CH$_2$Cl$_2$). The solvents were removed from the product containing fractions by oil pump vacuum to give **6a** (0.186 g, 0.192 mmol, 28% from **2a**) as a white solid and

6'a (0.084 g, 0.087 mmol, 13% from **2a**) as a colorless sticky oil that solidified after one week.

6a: Dec. pt. (capillary) 260 °C[s11]. **DSC** ($T_i/T_e/T_p/T_c/T_f$):[s1] 32.3/39.6/41.1/42.7/56.1 °C (endotherm); 74.0/84.5/85.8/87.6/109.2 °C (endotherm); 165.6/181.5/183.1/184.8/199.0 °C (endotherm), 244.5/248.0/253.4/258.2/273.3 °C (endotherm). **TGA**: onset of mass loss, 295.0 °C. Anal. calcd (%) for $C_{44}H_{84}Cl_2O_2P_2Os$ (968.22): C 54.58, H 8.74; found C 55.01, H 8.90.

NMR (C_6D_6, δ/ppm): **^{1}H** (300 MHz)[s12] 2.09-1.97 (br m, 12H, PCH_2), 1.74-1.60 (br, 12H, P-CH_2CH_2), 1.53-1.35 (br m, 60H, remaining CH_2); **^{13}C{^{1}H}** (100 MHz)[s12] 176.6 (t, $^2J_{CP}$ = 7.5 Hz, *C*O), 30.0 (virtual t,[s7] $^3J_{CP}$ = 6.7 Hz, $PCH_2CH_2CH_2$), 28.61 (s, *C*H_2), 28.57 (s, *C*H_2), 27.8 (s, *C*H_2), 27.6 (s, *C*H_2), 24.8 (virtual t,[s7] $^1J_{CP}$ = 15.7 Hz, P*C*H_2), 22.5 (s, PCH_2CH_2); **^{31}P{^{1}H}** (121 MHz) –14.2 (s).

IR (cm^{-1}, powder film): 2922 (m), 2853 (w), 2019 (s, ν_{CO}), 1945 (s, ν_{CO}), 1459 (w), 1417 (w), 772 (w), 718 (m). **MS** (FAB, 3-NBA):[s9] 969 ([**6a** + 1]$^+$, 5%), 932 ([**6a** – CO]$^+$, 100%).

6'a: mp (capillary) 67 °C. Anal. calcd (%) for $C_{44}H_{84}Cl_2O_2P_2Os$ (968.22): C 54.58, H 8.74; found C 54.58, H 8.70.

NMR (C_6D_6, δ/ppm): **^{1}H** (300 MHz)[s13,s14] 2.40-2.26 (br m, 4H, PC'H_2), 2.15-2.00 (br m, 4H, PC'H_2), 1.99-1.88 (br m, 4H, PCH_2), 1.85-1.63 (br m, 8H, PCH_2CH_2 and $PC'H_2C'H_2$), 1.58-1.42 (br m, 20H, remaining CH_2), 1.40-1.11 (br m, 44H, $PC'H_2C'H_2$ and remaining C'H_2); **^{13}C{^{1}H}** (100 MHz)[s13,s14] 176.5 (t, $^2J_{CP}$ = 7.4 Hz, *C*O), 30.5 (virtual t,[s7] $^3J_{CP}$ = 6.8 Hz, $PCH_2CH_2CH_2$), 29.0 (virtual t,[s7] $^3J_{CP}$ = 6.0 Hz, $PC'H_2C'H_2C'H_2$), 28.5 (s, *C*H_2), 28.4 (s, *C*H_2), 28.1 (s, *C*H_2), 27.8 (s, *C*H_2), 27.1 (s, *C*'H_2), 27.0 (s, *C*'H_2), 26.8 (s, *C*'H_2), 26.1 (s, *C*'H_2), 25.5 (virtual t,[s7] $^1J_{CP}$ = 15.9 Hz, P*C*H_2), 23.4 (s, PCH_2CH_2), 22.6 (virtual t,[s7] $^1J_{CP}$ = 15.3 Hz, P*C*'H_2), 21.8 (s, $PC'H_2C'H_2$); **^{31}P{^{1}H}** (121 MHz) –14.4 (s).

IR (cm^{-1}, powder film): 2921 (m), 2851 (w), 2017 (s, ν_{CO}), 1944 (s, ν_{CO}), 1454 (w), 1411 (w), 713 (m). **MS** (MALDI+, SIN):[s9] 1008 ([**6'a** + K + 1]$^+$, 10%), 992 ([**6'a** + Na + 1]$^+$, 30%), 934 ([**6'a** – Cl + 1]$^+$, 20%), 904 ([**6'a** – Cl – CO – 1]$^+$, 40%).

Alkene metathesis of 2b. Complex **2b** (0.649 g, 0.574 mmol), chlorobenzene (600 mL; the resulting solution was 0.0010 M), and Grubbs' catalyst (0.018 g, 0.022 mmol, 7.5 mol%) were combined in a procedure analogous to that used for the metathesis of **2a**. An identical workup gave crude **4*b** (0.571 g, 0.545 mmol, 95%) as a light brown sticky oil.

NMR (C_6D_6, δ/ppm): ^{1}**H** (300 MHz) 5.66-5.58 (br m, 1H, C*H*=), 5.58-5.46 (br m, 2H, C*H*=), 5.40-5.34 (br m, 1H, C*H*=), 5.33-5.25 (br m, 2H, C*H*=), 2.54-2.34 (br m, 4H, CH_2), 2.27-1.86 (br m, 20H, CH_2), 1.85-1.64 (br m, 8H, CH_2), 1.56-1.03 (br m, 52H, CH_2); ^{31}**P{**^{1}**H}** (121 MHz) −14.0 (s, 25% of integral), −14.09 (s, 5%), −14.11 (s, 6%), −14.17 (s, 10%), −14.19 (s, 9%), −14.27 (s, 22%), −14.32 (s, 5%), −14.40 (s, 8%), −14.41 (s, 7%), −14.5 (s, 3%).

***cis,cis,trans*-Os(CO)$_2$(Cl)$_2$(P((CH$_2$)$_{16}$)$_3$P) (6b) and *cis,cis,trans*-Os(CO)$_2$(Cl)$_2$(P(CH$_2$)$_{15}$-CH$_2$)((CH$_2$)$_{16}$)(P(CH$_2$)$_{15}$CH$_2$) (6'b).** Complex **4*b** (0.571 g, 0.545 mmol; the entire quantity prepared above), PtO_2 (0.018 g, 0.080 mmol), H_2, and THF (30 mL) were combined in a procedure analogous to that used for the hydrogenation of **4*a**. A similar workup including an identical SiO_2 column gave **6b** (0.052 g, 0.049 mmol, 5% from **2b**) as a white solid and **6'b** (0.308 g, 0.293 mmol, 51% from **2b**) as a colorless sticky oil.

6b: mp (capillary) 150 °C; **DSC** ($T_i/T_e/T_p/T_c/T_f$):[s1] 56.9/67.4/77.3/87.6/89.7 °C (endotherm); 90.2/95.3/100.4/104.8/108.2 °C (endotherm, minor), 110.5/135.8/147.6/152.9/157.3 °C (endotherm). **TGA**: onset of mass loss, 268.7 °C. Anal. calcd (%) for $C_{50}H_{96}Cl_2O_2P_2Os$ (1052.38): C 57.06, H 9.19; found C 56.97, H 8.96.

NMR (C_6D_6, δ/ppm): ^{1}**H** (300 MHz)[s12] 2.12-1.99 (br m, 12H, PCH_2), 1.71-1.55 (br m, 12H, PCH$_2$CH_2), 1.51-1.31 (br m, 72H, remaining CH_2); ^{13}**C{**^{1}**H}** (100 MHz)[s12] 176.5 (t, $^{2}J_{CP}$ = 7.5 Hz, *C*O), 30.1 (virtual t,[s7] $^{3}J_{CP}$ = 6.5 Hz, PCH$_2$CH$_2$*C*H$_2$), 29.1 (s, *C*H$_2$), 28.7 (s, *C*H$_2$), 28.3 (s, *C*H$_2$), 28.1 (s, *C*H$_2$), 27.5 (s, *C*H$_2$), 23.4 (virtual t,[s7] $^{1}J_{CP}$ = 15.6 Hz, P*C*H$_2$), 22.4 (s, PCH$_2$*C*H$_2$); ^{31}**P{**^{1}**H}** (121 MHz) –13.8 (s).

IR (cm^{-1}, powder film): 2921 (m), 2850 (w), 2016 (s, ν_{CO}), 1941 (s, ν_{CO}), 1457 (w), 1417 (w), 788 (w), 715 (m). **MS** (FAB, 3-NBA):[s9] 1053 ([**6b** + 1]$^+$, 10%), 1016 ([**6b** – Cl – 1]$^+$, 100%).

6'b: Anal. calcd (%) for $C_{50}H_{96}Cl_2O_2P_2Os$ (1052.38): C 57.07, H 9.19; found C 56.92, H 8.85.

NMR (C_6D_6, δ/ppm): ^{1}**H** (300 MHz)[s13,s14] 2.45-2.30 (br m, 4H, PC'H_2), 2.20-2.03 (br m, 4H, PC'H_2), 2.01-1.89 (br m, 4H, PCH_2), 1.84-1.64 (br m, 8H, PCH$_2$CH_2 and PC'H$_2$C'H_2), 1.54-1.37 (br m, 24H, remaining CH_2), 1.36-1.06 (br m, 56H, PC'H$_2$C'H_2 and remaining C'H_2); **^{13}C{^{1}H}** (75 MHz)[s13,s14] 176.5 (t, $^2J_{CP}$ = 7.4 Hz, *C*O), 30.7 (virtual t,[s7] $^3J_{CP}$ = 6.7 Hz, PCH$_2$CH$_2$*C*H$_2$), 30.1 (virtual t, $^3J_{CP}$ = 6.0 Hz, PC'H$_2$C'H$_2$*C*'H$_2$), 28.9 (s, *C*H$_2$), 28.8 (s, *C*H$_2$), 28.5 (s, *C*H$_2$), 28.3 (s, *C*H$_2$), 28.2 (s, *C*H$_2$), 28.1 (s, *C*'H$_2$), 27.3 (s, *C*'H$_2$), 27.3 (s, *C*'H$_2$), 25.4 (virtual t,[s7] $^1J_{CP}$ = 15.7 Hz, P*C*H$_2$), 23.5 (s, PCH$_2$*C*H$_2$), 22.50 (overlapping virtual t,[s7] $^1J_{CP}$ = 15.4 Hz, P*C*'H$_2$),[s15] 22.48 (overlapping s, PC'H$_2$*C*'H$_2$).[s15] **^{31}P{^{1}H}** (121 MHz) –14.1 (s).

IR (cm^{-1}, oil film): 2922 (m), 2853 (w), 2019 (s, ν_{CO}), 1945 (s, ν_{CO}), 1459 (w), 1417 (w), 791 (w), 718 (m). **MS** (MALDI+, DHB):[s9] 1092 ([**6'b** + K + 1]$^+$, 10%), 1075 ([**6'b** + Na]$^+$, 20%), 1018 ([**6'b** – Cl + 1]$^+$, 20%), 990 ([**6'b** – Cl – CO + 1]$^+$, 30%).

Alkene metathesis of 2c. Complex **2c** (0.896 g, 0.738 mmol), chlorobenzene (750 mL; the resulting solution was 0.0010 M), and Grubbs' catalyst (0.045 g, 0.055 mmol, 7.5 mol%) were combined in a procedure analogous to that used for the metathesis of **2a**. An identical workup gave crude **4*c** (0.710 g, 0.679 mmol, 92%) as a light brown sticky oil. **NMR** (C_6D_6, δ/ppm): **^{1}H** (300 MHz) 5.56-5.45 (br m, 5H, C*H*=), 5.40-5.35 (br m, 1H, C*H*=), 2.42-1.12 (br m, 96H, CH_2); **^{31}P{^{1}H}** (121 MHz) –13.2 (s, 39% of integral), –13.48 (s, 17%), –13.52 (s, 14%), –13.66 (s, 10%), –13.69 (s, 12%), –13.8 (s, 8%).

***cis,cis,trans*-Os(CO)$_2$(Cl)$_2$(P((CH$_2$)$_{18}$)$_3$P) (6c) and *cis,cis,trans*-Os(CO)$_2$(Cl)$_2$(P(CH$_2$)$_{17}$-CH$_2$)((CH$_2$)$_{18}$)(P(CH$_2$)$_{17}$CH$_2$) (6'c).** Complex **4*c** (0.710 g, 0.679 mmol; the entire quantity prepared above), PtO$_2$ (0.025 g, 0.111 mmol), H$_2$, and THF (30 mL) were combined in a procedure analogous to that used for the hydrogenation of **4*a**. A similar workup including an identical SiO$_2$ column gave **6c** (0.192 g, 0.169 mmol, 23% from **2c**) as a white solid and **6'c** (0.100 g, 0.088 mmol, 12% from **2c**) as a colorless sticky oil.

6c: mp (capillary) 86 °C; **DSC** ($T_i/T_e/T_p/T_c/T_f$):[s1] 46.7/84.4/86.5/88.4/155.0 °C (endotherm). **TGA**: onset of mass loss, 294.6 °C. Anal. calcd (%) for $C_{56}H_{108}Cl_2O_2OsP_2$ (1136.52): C 59.18, H 9.58; found C 59.11, H 9.48.

NMR (C_6D_6, δ/ppm): **^{1}H** (300 MHz)[s12] 2.16-2.00 (br m, 12H, PCH_2), 1.73-1.54 (br m, 12H, PCH$_2$CH_2), 1.51-1.25 (br m, 84H, remaining CH_2); **^{13}C{^{1}H}** (75 MHz)[s12] 176.4 (t, $^2J_{CP}$ = 7.5 Hz,

CO), 30.5 (virtual t,[s7] $^3J_{CP}$ = 6.4 Hz, $PCH_2CH_2CH_2$), 29.2 (s, CH_2), 28.9 (s, CH_2), 28.8 (s, CH_2), 28.62 (s, CH_2), 28.59 (s, CH_2), 28.1 (s, CH_2), 23.4 (virtual t,[s7] $^1J_{CP}$ = 15.7 Hz, PCH_2), 22.8 (s, PCH_2CH_2); **^{31}P{^{1}H}** (121 MHz) –16.3 (s).

IR (cm^{-1}, powder film): 2927 (s), 2858 (s), 2016 (s, ν_{CO}), 1946 (s, ν_{CO}), 1460 (m), 1352 (w), 1305 (w), 1220 (w), 1097 (w), 1027 (w), 788 (m), 718 (m). **MS** (FAB, 3-NBA):[s9] 1101 ([**6c** – Cl]$^+$, 70%).

6'c: Anal. calcd (%) for $C_{56}H_{108}Cl_2O_2P_2Os$ (1136.52): C 59.18, H 9.58; found C 58.75, H 9.45.

NMR (C_6D_6, δ/ppm): **^{1}H** (300 MHz)[s13,s14] 2.48-2.33 (br m, 4H, $PC'H_2$), 2.21-2.04 (br m, 4H, $PC'H_2$), 2.03-1.91 (br m, 4H, PCH_2), 1.86-1.64 (br m, 8H, PCH_2CH_2 and $PC'H_2C'H_2$), 1.49-1.41 (br m, 28H, remaining CH_2), 1.40-1.15 (br m, 60H, $PC'H_2C'H_2$ and remaining $C'H_2$); **^{13}C{^{1}H}** (75 MHz)[s13,s14] 176.5 (t, $^2J_{CP}$ = 7.4 Hz, CO), 31.0 (overlapping virtual t,[s7] $^3J_{CP}$ = 6.7 Hz, PCH_2CH_2-CH_2),[s16] 30.8 (overlapping virtual t,[s7] $^3J_{CP}$ = 6.1 Hz, $PC'H_2C'H_2C'H_2$),[s16] 28.9, 28.75, 28.67, 28.64, 28.4, 28.3, 28.0, 27.4 (8 × s, CH_2 or $C'H_2$, insufficient intensity difference), 25.5 (virtual t,[s7] $^1J_{CP}$ = 15.9 Hz, PCH_2), 23.6 (s, PCH_2CH_2), 22.8 (overlapping s, $PC'H_2C'H_2$),[s8] 22.6 (overlapping virtual t,[s7] $^1J_{CP}$ = 15.6 Hz, $PC'H_2$);[s8] **^{31}P{^{1}H}** (121 MHz) –16.6 (s).

IR (cm^{-1}, oil film): 2927 (m), 2858 (w), 2024 (s, ν_{CO}), 1946 (s, ν_{CO}), 1460 (w), 1415 (w), 796 (w), 718 (m). **MS** (FAB, 3-NBA):[s9] 1137 ([**6'c**]$^+$, 5%), 1102 ([**6'c** – Cl]$^+$, 15%), 1072 ([**6'c** – Cl – CO – 1]$^+$, 5%).

Alkene metathesis of 3a. Complex **3a** (0.800 g, 0.705 mmol), chlorobenzene (700 mL; the resulting solution was 0.0010 M), and Grubbs' catalyst (0.041 g, 0.049 mmol, 7.0 mol%) were combined in a procedure analogous to that used for the metathesis of **2a**. An identical workup gave crude **5*a** (0.682 g, 0.649 mmol, 92%) as a light brown sticky oil.

NMR (C_6D_6, δ/ppm): **^{1}H** (300 MHz) 5.62-5.40 (br m, 5H, CH=), 5.27-5.20 (br m, 1H, CH=), 2.55-1.11 (br m, 72H, CH_2); **^{31}P{^{1}H}** (121 MHz) –19.1 (s, 48% of integral), –20.7 (s, 12%), –22.2 (s, 10%), –22.26 (s, 12%), –22.31 (s, 8%), –22.4 (s, 10%).

***cis,cis,trans*-Os(CO)$_2$(Br)$_2$(P((CH$_2$)$_{14}$)$_3$P) (7a) and *cis,cis,trans*-Os(CO)$_2$(Br)$_2$(P(CH$_2$)$_{13}$-**

$\overline{C}H_2)((CH_2)_{14})(P(CH_2)_{13}CH_2)$ (7'a). Complex **5*a** (0.682 g, 0.649 mmol; the entire quantity prepared above), PtO_2 (0.015 g, 0.066 mmol), H_2, and THF (30 mL) were combined in a procedure analogous to that used for the hydrogenation of **4*a**. A similar workup (SiO_2 column, 3.5 cm × 30 cm, 3:1 v/v hexanes/CH_2Cl_2) gave **7a** (0.231 g, 0.219 mmol, 31% from **3a**) as a white solid and **7'a** (0.131 g, 0.124 mmol, 18% from **3a**) as a colorless sticky oil that solidified after one week.

7a: Dec. pt. (capillary) 230 °C.[s11] **DSC** ($T_i/T_e/T_p/T_c/T_f$):[s1] 107.9/125.8/134.3/138.1/144.5 °C (endotherm); 170.8/187.6/236.9/266.7/272.7 °C (endotherm). **TGA**: onset of mass loss, 286.2 °C. Anal. calcd (%) for $C_{44}H_{84}Br_2O_2P_2Os$ (1057.12) C 49.99, H 8.01; found C 49.80, H 7.99.

NMR (C_6D_6, δ/ppm): **^{1}H** (300 MHz)[s10] 2.16-2.05 (br m, 12H, PCH_2), 1.72-1.58 (br m, 12H, PCH_2CH_2), 1.55-1.35 (br m, 60H, remaining CH_2); **^{13}C{^{1}H}** (100 MHz)[s10] 175.2 (t, $^2J_{CP}$ = 7.2 Hz, *C*O), 29.8 (virtual t,[s7] $^3J_{CP}$ = 6.6 Hz, $PCH_2CH_2CH_2$), 28.7 (s, CH_2), 28.6 (s, CH_2), 27.8 (s, CH_2), 27.6 (s, CH_2), 26.3 (virtual t,[s7] $^1J_{CP}$ = 16.0 Hz, PCH_2), 22.8 (s, PCH_2CH_2); **^{31}P{^{1}H}** (121 MHz) –23.2 (s).

IR (cm^{-1}, powder film): 2922 (m), 2853 (w), 2019 (s, ν_{CO}), 1949 (s, ν_{CO}), 1459 (w), 1413 (w), 768 (w), 718 (m). **MS** (FAB, 3-NBA):[s9] 1056 ([**7a**]$^+$, 10%), 1028 ([**7a** – CO]$^+$, 10%), 977 ([**7a** – Br]$^+$, 100%), 949 ([**7a** – Br – CO]$^+$, 30%).

7'a: mp (capillary) 74 °C. **DSC** ($T_i/T_e/T_p/T_c/T_f$):[s1] 39.5/52.5/56.5/59.0/71.8 °C (endotherm). **TGA**: onset of mass loss, 255.0 °C. Anal. calcd (%) for $C_{44}H_{84}Br_2O_2P_2Os$ (1057.12): C 49.99, H 8.01; found C 50.10, H 7.99.

NMR (C_6D_6, δ/ppm): **^{1}H** (300 MHz)[s13,s14] 2.50-2.36 (br m, 4H, $PC'H_2$), 2.23-2.08 (br m, 4H, $PC'H_2$), 2.06-1.95 (br m, 4H, PCH_2), 1.83-1.61 (br m, 8H, PCH_2CH_2 and $PC'H_2C'H_2$), 1.56-1.40 (br m, 20H, remaining CH_2), 1.39-1.12 (br m, 44H, $PC'H_2C'H_2$ and remaining $C'H_2$); **^{13}C{^{1}H}** (126 MHz)[s13,s14] 175.1 (t, $^2J_{CP}$ = 7.3 Hz, *C*O), 30.4 (virtual t,[s7] $^3J_{CP}$ = 6.8 Hz, $PCH_2CH_2CH_2$), 28.9 (virtual t,[s7] $^3J_{CP}$ = 6.0 Hz, $PC'H_2C'H_2C'H_2$), 28.52 (s, CH_2), 28.48 (s, CH_2), 28.3 (s, CH_2), 27.9 (s, CH_2), 27.1 (s, $C'H_2$), 26.9 (s, $C'H_2$), 26.8 (overlapping s, $C'H_2$),[s8] 26.6 (overlapping virtual t,[s7] $^1J_{CP}$ = 16.3 Hz, PCH_2),[s8] 26.1 (s, $C'H_2$), 24.0 (virtual t,[s7] $^1J_{CP}$ = 15.7 Hz, $PC'H_2$), 23.6 (s, PCH_2CH_2), 22.1 (s, $PC'H_2C'H_2$); **^{31}P{^{1}H}** (121 MHz) –24.0 (s).

IR (cm^{-1}, powder film): 2920 (m), 2851 (w), 2019 (s, ν_{CO}), 1946 (s, ν_{CO}), 1455 (w), 1411 (w), 766 (w), 719 (m). **MS** (MALDI+, THAP):s9 1097 ([**7'a** + K]$^+$, 25%), 1039 ([**7'a** – 2CO + K]$^+$, 50%), 951s17 ([**7'a** – Br – CO + 2]$^+$, 100%).

Alkene metathesis of 3b. Complex **3b** (0.565 g, 0.463 mmol), chlorobenzene (470 mL; the resulting solution was 0.0010 M), and Grubbs' catalyst (0.035 g, 0.042 mmol, 7.5 mol%) were combined in a procedure analogous to that used for the metathesis of **2a**. An identical workup gave crude **5*b** (0.473 g, 0.417 mmol, 90%) as a light brown sticky oil.

NMR (C_6D_6, δ/ppm): **^{1}H** (300 MHz) 5.68-5.57 (br m, 1H, C*H*=), 5.57-5.46 (br m, 2H, C*H*=), 5.41-5.34 (br m, 1H, C*H*=), 5.33-5.25 (br m, 2H, C*H*=), 2.65-2.45 (br m, 4H, CH_2), 2.34-1.91 (br m, 20H, CH_2), 1.89-1.64 (br m, 8H, CH_2), 1.59-1.01 (br m, 52H, CH_2); **^{31}P{^{1}H}** (121 MHz) –23.5 (s, 28% of integral), –23.70 (s, 9%), –23.73 (s, 11%), –23.75 (s, 16%), –23.87 (s, 5%), –23.90 (s, 11%), –23.94 (s, 13%), –23.98 (s, 7%).

***cis,cis,trans*-Os(CO)$_2$(Br)$_2$(P((CH$_2$)$_{16}$)$_3$P) (7b) and *cis,cis,trans*-Os(CO)$_2$(Br)$_2$(P(CH$_2$)$_{15}$-CH$_2$)((CH$_2$)$_{16}$)(P(CH$_2$)$_{15}$CH$_2$) (7'b).** Complex **5*b** (0.473 g, 0.417 mmol; the entire quantity prepared above), PtO_2 (0.016 g, 0.070 mmol), H_2, and THF (30 mL) were combined in a procedure analogous to that used for the hydrogenation of **4*a**. A similar workup (SiO_2 column, 3.5 cm × 30 cm, 3:1 v/v hexanes/CH_2Cl_2) gave **7b** (0.025 g, 0.022 mmol, 5% from **3b**) as a white solid and **7'b** (0.213 g, 0.187 mmol, 40% from **3b**) as a colorless sticky oil that solidified after one week.

7b: mp (capillary) 199 °C; **DSC** ($T_i/T_e/T_p/T_c/T_f$):s1 86.9/89.9/100.8/107.0/111.2 °C (endotherm, minor); 158.9/199.1/204.7/206.9/240.1 °C (endotherm). **TGA**: onset of mass loss, 307.9 °C. Anal. calcd (%) for $C_{50}H_{96}Br_2O_2P_2Os$ (1141.28): C 52.62, H 8.48; found C 52.19, H 8.48.

NMR (C_6D_6, δ/ppm): **^{1}H** (300 MHz)s12 2.22-2.12 (br m, 12H, PCH_2), 1.69-1.56 (br m, 12H, PCH$_2$CH_2), 1.49-1.36 (br m, 72H, remaining CH_2); **^{13}C{^{1}H}** (100 MHz)s12 175.1 (t, $^2J_{CP}$ = 7.4 Hz, *C*O), 30.1 (virtual t,s7 $^3J_{CP}$ = 6.3 Hz, PCH$_2$CH$_2$*C*H$_2$), 29.4 (s, *C*H$_2$), 28.8 (s, *C*H$_2$), 28.5 (s, *C*H$_2$), 28.2 (s, *C*H$_2$), 27.6 (s, *C*H$_2$), 24.9 (virtual t,s7 $^1J_{CP}$ = 15.9 Hz, P*C*H$_2$), 22.9 (s, PCH$_2$*C*H$_2$); **^{31}P{^{1}H}** (121 MHz) –24.9 (s).

IR (cm^{-1}, powder film): 2920 (m), 2851 (w), 2019 (s, ν_{CO}), 1947 (s, ν_{CO}), 1455 (w), 1415 (w), 785 (w), 718 (m). **MS** (MALDI+, THAP):s9 1179 ([**7b** + K]$^+$, 5%), 1164 ([**7b** + Na + 1]$^+$, 8%), 1062

([**7b** – Br]$^+$, 8%), 1034 ([**7b** – Br – CO]$^+$, 8%), 790 ([(OP((CH$_2$)$_{16}$)$_3$PO) + Na]$^+$, 100%), 768[s17] ([(OP((CH$_2$)$_{16}$)$_3$PO) + 2]$^+$, 75%).

7'b: mp (capillary) 54 °C. **TGA**:[s1] onset of mass loss, 293.1 °C. Anal. calcd (%) for $C_{50}H_{96}$-$Br_2O_2P_2Os$ (1141.28): C 52.62, H 8.48; found C 52.66, H 8.20.

NMR (C_6D_6, δ/ppm): **^{1}H** (300 MHz)[s10,s14] 2.58-2.42 (br m, 4H, PC'H_2), 2.31-2.15 (br m, 4H, PC'H_2), 2.09-1.97 (br m, 4H, PCH_2), 1.86-1.64 (br m, 8H, PCH$_2$CH_2 and PC'H$_2$C'H_2), 1.53-1.41 (br m, 24H, remaining CH_2), 1.36-1.16 (br m, 56H, PC'H$_2$C'H_2 and remaining C'H_2); **^{13}C{^{1}H}** (126 MHz)[s10,s14] 175.1 (t, $^2J_{CP}$ = 7.5 Hz, *C*O), 30.6 (virtual t,[s7] $^3J_{CP}$ = 6.5 Hz, PCH$_2$CH$_2$*C*H$_2$), 30.1 (virtual t,[s7] $^3J_{CP}$ = 6.0 Hz, PC'H$_2$C'H$_2$*C*'H$_2$), 28.9 (s, *C*H$_2$), 28.8 (s, *C*H$_2$), 28.5 (s, *C*H$_2$), 28.33 (s, *C*H$_2$), 28.31 (s, *C*H$_2$), 28.2 (s, *C*'H$_2$), 27.83 (s, *C*'H$_2$), 26.80 (s, *C*'H$_2$), 27.3 (s, *C*'H$_2$), 26.4 (virtual t,[s7] $^1J_{CP}$ = 16.2 Hz, P*C*H$_2$), 24.1 (virtual t,[s7] $^1J_{CP}$ = 15.8 Hz, P*C*'H$_2$), 23.8 (s, PCH$_2$*C*H$_2$), 23.0 (s, PC'H$_2$*C*'H$_2$); **^{31}P{^{1}H}** (121 MHz) –25.4 (s).

IR (cm^{-1}, powder film): 2921 (m), 2851 (w), 2018 (s, ν_{CO}), 1946 (s, ν_{CO}), 1454 (w), 1411 (w), 802 (w), 713 (m). **MS** (MALDI+, THAP):[s9] 1032 ([**7'b** – Br – CO – 1]$^+$, 50%), 790 ([(OP(CH$_2$)$_{15}$-CH$_2$)((CH$_2$)$_{16}$)(OP(CH$_2$)$_{15}$CH$_2$) + Na]$^+$, 80%), 768[s17] ([(OP(CH$_2$)$_{15}$CH$_2$)((CH$_2$)$_{16}$)(OP(CH$_2$)$_{15}$CH$_2$) + 2]$^+$, 100%).

Alkene metathesis of 3c. Complex **3c** (0.692 g, 0.531 mmol), chlorobenzene (550 mL; the resulting solution was 0.0010 M), and Grubbs' catalyst (0.033 g, 0.040 mmol, 7.5 mol%) were combined in a procedure analogous to that used for the alkene metathesis of **2a**. An identical workup gave crude **5*c** (0.565 g, 0.462 mmol, 87%) as a light brown sticky oil.

NMR (C_6D_6, δ/ppm): **^{1}H** (300 MHz) 5.58-5.45 (br m, 5H, C*H*=), 5.41-5.35 (br m, 1H, C*H*=), 2.59-2.37 (br m, 4H, CH_2), 2.33-1.92 (br m, 20H, CH_2), 1.87-1.14 (br m, 72H, CH_2); **^{31}P{^{1}H}** (121 MHz) –22.6 (s, 50% of integral), –23.0 (s, 11%), –23.2 (s, 12%), –22.28 (s, 9%), –22.20 (s, 9%), –22.4 (s, 9%).

***cis,cis,trans*-Os(CO)$_2$(Br)$_2$(P((CH$_2$)$_{18}$)$_3$P) (7) and *cis,cis,trans*-Os(CO)$_2$(Br)$_2$(P(CH$_2$)$_{17}$-CH$_2$)((CH$_2$)$_{18}$)(P(CH$_2$)$_{17}$CH$_2$) (7'c)** Complex **5*c** (0.565 g, 0.462 mmol; the entire quantity prepared above), PtO$_2$ (0.018 g, 0.080 mmol), H$_2$, and THF (30 mL) were combined in a procedure analogous to that used for the hydrogenation of **4*a**. A similar workup (SiO_2 column, 3.5 cm × 30 cm, 3:1 v/v hexanes/CH_2Cl_2) gave **7c** (0.237 g, 0.193 mmol, 27% from **3c**) as a white solid and **7'c** (0.210 g, 0.171 mmol, 24% from **3c**) as a colorless sticky oil.

7c: mp (capillary) 92 °C; **DSC** ($T_i/T_e/T_p/T_c/T_f$):[s1] 61.2/91.5/93.6/96.0/162.9 °C (endotherm). **TGA**: onset of mass loss, 259.3 °C. Anal. calcd (%) for $C_{56}H_{108}Br_2O_2OsP_2$ (1225.44): C 54.89, H 8.88; found C 54.66, H 8.92.

NMR (C_6D_6, δ/ppm): ^{1}**H** (300 MHz)[s12] 2.24-2.13 (br m, 12H, PCH_2), 1.69-1.55 (br m, 12H, PCH_2CH_2), 1.48-1.32 (br m, 84H, remaining CH_2); ^{13}**C{^{1}H}** (75 MHz)[s12] 175.1 (t, $^2J_{CP}$ = 7.6 Hz, *C*O), 30.4 (virtual t,[s7] $^3J_{CP}$ = 6.4 Hz, $PCH_2CH_2CH_2$), 29.2 (s, CH_2), 28.9 (s, CH_2), 28.8 (s, CH_2), 28.6 (s, CH_2), 28.5 (s, CH_2), 28.1 (s, CH_2), 24.6 (virtual t,[s7] $^1J_{CP}$ = 16.0 Hz, PCH_2), 23.1 (s, PCH_2CH_2); ^{31}**P{^{1}H}** (121 MHz) –25.8 (s).

IR (cm^{-1}, powder film): 2920 (m), 2850 (w), 2020 (s, ν_{CO}), 1946 (s, ν_{CO}), 1456 (w), 1415 (w), 785 (w), 715 (m). **MS** (FAB, 3-NBA):[s9] 1224 ([**7c**]$^+$, 3%), 1146 ([**7c** – Br + 1]$^+$, 10%), 1116 ([**7c** – Br – CO – 1]$^+$, 5%).

7'c: Anal. calcd for (%) for $C_{56}H_{108}Br_2O_2P_2Os$ (1225.44): C 54.89, H 8.88; found C 54.40, H 8.59.

NMR (C_6D_6, δ/ppm): ^{1}**H** (300 MHz)[s13,s14] 2.56-2.41 (br m, 4H, PC'H_2), 2.28-2.13 (br m, 4H, PC'H_2), 2.11-2.00 (br m, 4H, PCH_2), 1.83-1.64 (br m, 8H, PCH_2CH_2 and PC'H_2C'H_2), 1.48-1.39 (br m, 28H, remaining CH_2), 1.38-1.20 (br m, 60H, PC'H_2C'H_2 and remaining C'H_2); ^{13}**C{^{1}H}** (100 MHz)[s13,s14] 175.2 (t, $^2J_{CP}$ = 7.3 Hz, *C*O), 30.7 (overlapping virtual t,[s7] $^3J_{CP}$ = 6.7 Hz, $PCH_2CH_2CH_2$),[s18] 30.6 (overlapping virtual t,[s7] $^3J_{CP}$ = 6.1 Hz, PC'H_2C'H_2C'H_2),[s18] 28.83 (s, CH_2), 28.78 (s, CH_2), 28.7 (s, CH_2), 28.62 (s, CH_2 or C'H_2), 28.60 (s, CH_2 or C'H_2), 28.59 (s, CH_2 or C'H_2), 28.5 (s, CH_2 or C'H_2), 28.23 (s, C'H_2), 28.13 (s, C'H_2), 27.8 (s, C'H_2), 27.3 (s, C'H_2), 26.3 (virtual t,[s7] $^1J_{CP}$ = 16.1 Hz, PCH_2), 24.0 (virtual t,[s7] $^1J_{CP}$ = 15.9 Hz, PC'H_2), 23.7 (s, PCH_2CH_2), 23.1 (s, PC'H_2C'H_2); ^{31}**P{^{1}H}** (121 MHz) –26.1 (s).

IR (cm^{-1}, oil film): 2920 (m), 2850 (w), 2018 (s, ν_{CO}), 1947 (s, ν_{CO}), 1456 (w), 1415 (w), 791 (w), 714 (m). **MS** (MALDI+, SIN):[s9] 1197 ([**7'c** – CO + 1]$^+$, 3%), 1146 ([**7'c** – Br + 1]$^+$, 4%).

***cis,cis,trans*-Os(CO)$_2$(Br)$_2$(P(*n*-C$_8$H$_{17}$)$_3$)$_2$ (8a).** A Schlenk flask was charged with **3a** (0.500 g, 0.440 mmol), PtO_2 (0.015 g, 0.066 mmol), and THF (20 mL), connected to a gas balloon, and partially evacuated. Then H_2 (1 bar) was introduced, and the suspension stirred. After 24 h, the solvent was removed by oil pump vacuum. The residue was filtered through Al_2O_3 using CH_2Cl_2. The solvent was removed from the filtrate by oil pump vacuum to give **8a** (0.427 g, 0.372 mmol, 85%) as a colorless oil. Anal. calcd (%) for $C_{50}H_{102}Br_2O_2P_2Os$ (1147.33): C 52.34, H 8.96; found C 52.50, H 8.75.

NMR (C_6D_6, δ/ppm): **^{1}H** (500 MHz)[s6] 2.22-2.15 (br m, 12H, PCH_2), 1.58-1.49 (br m, 12H, PCH$_2$CH_2), 1.44-1.36 (br m, 12H, PCH$_2$CH$_2$CH_2), 1.36-1.22 (br m, 48H, remaining CH_2), 0.88 (t, $^3J_{HH}$ = 7.0 Hz, 18H, CH_3); **^{13}C{^{1}H}** (126 MHz)[s6] 173.9 (t, $^2J_{CP}$ = 7.5 Hz, *C*O), 31.8 (s, *C*H$_2$), 31.0 (virtual t,[s7] $^3J_{CP}$ = 6.4 Hz, PCH$_2$CH$_2$*C*H$_2$), 29.2 (s, *C*H$_2$), 29.1 (s, *C*H$_2$), 24.3 (virtual t,[s7] $^1J_{CP}$ = 16.0 Hz, P*C*H$_2$), 23.4 (s, PCH$_2$*C*H$_2$), 22.6 (s, *C*H$_2$), 14.1 (s, *C*H$_3$); **^{31}P{^{1}H}** (202 MHz) –24.8 (s).

IR (cm^{-1}, oil film): 2953 (w), 2922 (s), 2853 (m), 2019 (s, ν_{CO}), 1950 (s, ν_{CO}), 1456 (w), 1441 (m), 1377 (w), 1015 (w), 791 (m), 718 (m). **MS** (MALDI+, THAP):[s9] 1170 ([**8a** + Na + 1]$^+$, 40%), 1068 ([**8a** – Br + 1]$^+$, 60%), 1041[s17] ([**8a** – Br – CO + 2]$^+$, 100%).

***trans*-$\overline{\text{Os}}$(CO)$_3$(P((CH$_2$)$_{14}$)$_3\overline{\text{P}}$) (9a).** A Schlenk flask was charged with **6a** (0.100 g, 0.107 mmol) or **7a** (0.100 g, 0.098 mmol) and THF (10 mL). The solution was aspirated with CO (15 min). Then a suspension of C_8K (0.331 g, 2.45 mmol or 0.361 g, 2.68 mmol) in THF (10 mL) was slowly added. The reaction was monitored by ^{31}P NMR. After the educt has been consumed, graphite powder and unreacted C_8K were removed by cannula filtration. The filtrate was concentrated to 5 mL by oil pump vacuum, and MeOH (20 mL) was added. The colorless precipitate was isolated by filtration and washed with MeOH. The filter was rinsed with CH_2Cl_2 to dissolve the product and remove insoluble solids. The solvent was removed from the filtrate and the residue dried by oil pump vacuum to give **9a** (0.086 g, 0.093 mmol, 87%, or 0.074 g, 0.080 mmol, 82%) as a white solid, mp 248 °C, dec (gradual darkening, >180 °C; capillary). **DSC** ($T_i/T_e/T_p/T_c/T_f$):[s1] 94.7/95.3/118.1/127.8/127.8 °C (endotherm, minor); 127.9/144.9/148.3/150.5/155.8 °C (endotherm). **TGA**: onset of mass loss, 230.6 °C. Anal. calcd (%) for $C_{45}H_{84}O_3P_2Os$ (925.32): C 58.41, H 9.15; found C 58.38, H 8.80.

NMR (C_6D_6, δ/ppm): **^{1}H** (300 MHz)[s10] 1.53-1.35 (br m, 24H, PCH_2 and PCH$_2$CH_2), 1.52-

1.35 (br m, 60H, remaining CH_2); ^{13}**C{**^{1}**H}** (100 MHz)[s10] 197.5 (t, $^{2}J_{CP}$ = 12.2 Hz, *C*O), 31.2 (virtual t,[s7] $^{1}J_{CP}$ = 17.1 Hz, PCH_2), 30.4 (virtual t,[s7] $^{3}J_{CP}$ = 7.0 Hz, $PCH_2CH_2CH_2$), 28.1 (s, CH_2), 27.1 (s, CH_2), 26.8 (s, CH_2), 24.4 (s, PCH_2CH_2); ^{31}**P{**^{1}**H}** (121 MHz) –2.6 (s).

IR (cm^{-1}, powder film): 2926 (m), 2853 (m), 1864 (s, ν_{CO}), 1459 (w), 1409 (w), 826 (w), 787 (w), 760 (w), 737 (m), 718 (m). **MS** (FAB, 3-NBA):[s9] 925 ([**9a** – 1]$^+$, 40%), 897 ([**9a** – CO – 1]$^+$, 45%).

***trans*-Os(CO)$_3$(P(CH$_2$)$_{15}$CH$_2$)((CH$_2$)$_{16}$)(P(CH$_2$)$_{15}$CH$_2$) (9'b).** Complex **6'b** (0.103 g, 0.098 mmol) or **7'b** (0.110 g, 0.096 mmol), C_8K (0.391 g, 2.89 mmol or 0.377 g, 2.79 mmol), and THF (20 ml or 20 mL) were combined in a procedure analogous to that used for **9a**. Identical workups gave **9'b** (0.052 g, 0.052 mmol, 53%, or 0.082 g, 0.081 mmol, 84%) as a colorless waxy solid, mp 104 °C (capillary). **DSC** ($T_i/T_e/T_p/T_c/T_f$):[s1] 70.2/94.7/99.9/103.5/122.0 °C (endotherm). **TGA**: onset of mass loss, 262.4 °C. Anal. calcd (%) for $C_{51}H_{96}O_3P_2Os$ (1009.48): C 60.68, H 9.59; found C 60.61, H 9.66.

NMR (C_6D_6, δ/ppm): ^{1}**H** (500 MHz)[s10,s14] 1.97-1.84 (br m, 8H, PC'H_2), 1.83-1.72 (br m, 4H, PCH_2 and PCH_2CH_2), 1.68-1.58 (br m, 4H, PC'H$_2$C'H_2), 1.56-1.40 (br m, 28H, PC'H$_2$C'H_2 and remaining CH_2), 1.36-1.20 (br m, 48H, remaining C'H_2); ^{13}**C{**^{1}**H}** (126 MHz)[s10,s14] 198.8 (t, $^{2}J_{CP}$ = 11.9 Hz, *C*O), 31.0 (virtual t,[s7] $^{3}J_{CP}$ = 6.0 Hz, $PCH_2CH_2CH_2$), 30.55 (overlapping virtual t,[s7] $^{1}J_{CP}$ = 16.6 Hz, PCH_2),[s18] 30.53 (overlapping virtual t,[s7] $^{1}J_{CP}$ = 17.4 Hz, P*C*'H$_2$),[s18] 29.8 (virtual t,[s7] $^{3}J_{CP}$ = 6.2 Hz, PC'H$_2$C'H$_2$*C*'H$_2$), 28.9 (s, CH_2), 28.6 (s, CH_2), 28.5 (s, CH_2), 28.05 (s, CH_2), 27.97 (s, *C*'H$_2$), 27.91 (s, *C*'H$_2$), 27.89 (s, *C*'H$_2$), 27.87 (s, *C*'H$_2$), 27.7 (s, *C*'H$_2$), 27.5 (s, CH_2), 24.9 (s, PCH_2CH_2), 23.8 (s, PC'H$_2$*C*'H$_2$); ^{31}**P{**^{1}**H}** (202 MHz) –8.9 (s).

IR (cm^{-1}, oil film): 2922 (m), 2853 (w), 1856 (s, ν_{CO}), 1458 (w), 1408 (w), 797 (w), 750 (m), 718 (m). **MS** (MALDI+, THAP):[s9] 1011 ([**9'b** + 1]$^+$, 100%), 983 ([**9'b** – CO + 1]$^+$, 10%).

***trans*-Os(CO)$_3$(P((CH$_2$)$_{18}$)$_3$P) (9c).** Complex **7c** (0.100 g, 0.082 mmol), C_8K (0.327 g, 2.42 mmol), and THF (20 mL) were combined in a procedure analogous to that used for **9a**. An identical workup gave **9c** (0.071 g, 0.065 mmol, 79%) as a white solid, mp 61 °C (capillary). **DSC** ($T_i/T_e/T_p/T_c/T_f$):[s1] 46.6/60.0/62.8/65.3/73.5 °C (endotherm). **TGA**: onset of mass loss, 145.7 °C. Anal. calcd (%) for $C_{57}H_{108}O_3P_2Os$ (1093.64): C 62.60, H 9.95; found C 63.00, H 9.94.

NMR (C_6D_6, δ/ppm): **^{1}H** (500 MHz)[s19] 1.83-1.77 (br m, 12H, PCH_2), 1.72-1.62 (br m, 12H, PCH_2CH_2), 1.46-1.36 (br m, 84H, remaining CH_2); **^{13}C{^{1}H}** (126 MHz)[s19] 198.0 (t, $^2J_{CP}$ = 11.8 Hz, *C*O), 30.8 (overlapping virtual t,[s7] $^3J_{CP}$ = 7.0 Hz, $PCH_2CH_2CH_2$),[s16] 30.7 (overlapping virtual t,[s7] $^1J_{CP}$ = 16.8 Hz, PCH_2),[s16] 29.0 (s, CH_2), 28.90 (s, CH_2), 28.86 (s, CH_2), 28.6 (s, CH_2), 28.3 (s, CH_2), 27.9 (s, CH_2), 24.5 (s, PCH_2CH_2); **^{31}P{^{1}H}** (202 MHz) –6.8 (s).

IR (cm^{-1}, powder film): 2922 (m), 2851 (w), 1863 (s, ν_{CO}), 1458 (w), 1410 (w), 742 (m), 719 (m). **MS** (MALDI+, THAP):[s9] 1096[s17] ([**9c** + 2]$^+$, 100%), 1067 ([**9c** – CO + 1]$^+$, 30%).

***mer,trans*-[$\overline{\text{Os}(H)(CO)_3(P((CH_2)_{14})_3\text{P}}$)]$^+$ $CF_3SO_3^-$ (9a-H$^+$ $CF_3SO_3^-$).** A 5 mm NMR tube was charged with **9a** (0.010 g, 0.011 mmol), $CDCl_3$ (0.5 mL), and CF_3SO_3H (0.002 mL, 0.02 mmol). NMR spectra showed the quantitative generation of **9a**-H$^+$ $CF_3SO_3^-$.

NMR ($CDCl_3$, δ/ppm): **^{1}H** (400 MHz)[s19] 2.06-1.97 (br m, 12H, PCH_2), 1.58-1.45 (br m, 24 H, PCH_2CH_2 and $PCH_2CH_2CH_2$), 1.44-1.24 (br m, 48H, remaining CH_2), –8.50 (t, $^2J_{PH}$ = 15.3 Hz, 1H, Os*H*); **^{13}C{^{1}H}** (100 MHz)[s19] 176.8 (t, $^2J_{CP}$ = 9.5 Hz, *C*O *cis* to H), 174.9 (t, $^2J_{CP}$ = 5.9 Hz, *C*O *trans* to H), 118.3 (q, $^1J_{CF}$ = 317.7 Hz, $CF_3SO_3^-$), 30.0 (virtual t,[s7] $^1J_{CP}$ = 17.3 Hz, PCH_2), 29.3 (virtual t,[s7] $^3J_{CP}$ = 7.3 Hz, $PCH_2CH_2CH_2$), 27.6 (s, CH_2), 27.3 (s, CH_2), 27.2 (s, CH_2), 27.0 (s, CH_2), 23.8 (s, PCH_2CH_2); **^{31}P{^{1}H}** (161 MHz) –10.2 (s).

***mer,trans*-[$\overline{\text{Os}(H)(CO)_3(P((CH_2)_{14})_3\text{P}}$)]$^+$ BAr_f^- (9a-H$^+$ BAr_f^-).** A Schlenk flask was charged with **9a** (0.047 g, 0.051 mmol), CH_2Cl_2 (10 mL), and $[H(OEt_2)_2]^+$ BAr_f^- (0.052 g, 0.051 mmol) with stirring. After 24 h, the solvent was removed by oil pump vacuum. The residue was washed with hexanes and dried by oil pump vacuum to give **9a**-H$^+$ BAr_f^- (0.073 g, 0.041 mmol, 80%) as a colorless powder, mp 181 °C (capillary). **TGA**:[s1] onset of mass loss, 190.9 °C. Anal. calcd (%) for $C_{77}H_{97}BF_{24}O_3P_2Os$ (1789.54): C 51.68, H 5.46; found C 51.96, H 5.63.

NMR ($CDCl_3$, δ/ppm): **^{1}H** (500 MHz)[s20] 7.73-7.69 (m, 8H, C_6H_3 *o* to B), 7.54-7.52 (m, 4H, C_6H_3 *p* to B), 2.01-1.94 (br m, 12H, PCH_2), 1.53-1.44 (br m, 24H, PCH_2CH_2 and $PCH_2CH_2CH_2$), 1.39-1.23 (br m, 48H, remaining CH_2), –8.53 (t, $^2J_{PH}$ = 15.3 Hz, 1H, Os*H*); **^{13}C{^{1}H}** (126 MHz)[s20] 176.5 (t, $^2J_{CP}$ = 9.5 Hz, *C*O *cis* to H), 174.7 (t, $^2J_{CP}$ = 5.4 Hz, *C*O *trans* to H), 161.7 (q, $^1J_{BC}$ = 49.9 Hz, C_6H_3 *i* to B), 134.8 (s, C_6H_3 *o* to B), 128.8 (q, $^2J_{CF}$ = 30.5 Hz, C_6H_3 *m* to B), 124.6 (q, $^1J_{CF}$ =

272.5 Hz, CF_3), 117.4 (s, C_6H_3 *p* to B), 30.0 (virtual t,[s7] $^1J_{CP}$ = 16.9 Hz, PCH_2), 29.3 (virtual t,[s7] $^3J_{CP}$ = 6.5 Hz, $PCH_2CH_2CH_2$), 27.6 (s, CH_2), 27.3 (s, CH_2), 27.2 (s, CH_2), 27.0 (s, CH_2), 23.8 (s, PCH_2CH_2); **^{31}P{^{1}H}** (202 MHz) –10.8 (s).

IR (cm^{-1}, powder film): 2932 (m), 2860 (m), 2114 (w, ν_{CO}), 2054 (m, ν_{CO}), 2031 (s, ν_{CO}), 1964 (br w), 1462 (w), 1416 (w), 1352 (s), 1277 (s), 1163 (s), 1121 (vs), 887 (m), 839 (m), 762 (w), 745 (w), 716 (s), 685 (s), 669 (s). **MS** (MALDI+, THAP):[s9] 927 ([**9a**-H]$^+$, 100%); (MALDI–, THAP):[s9] 863 (BAr_f^-, 100%).

***mer,trans*-[Os(H)(CO)$_3$(P(CH$_2$)$_{15}$CH$_2$)((CH$_2$)$_{16}$)(P(CH$_2$)$_{15}$CH$_2$)]$^+$ BAr$_f^-$ (9'b-H$^+$ BAr$_f^-$).** Complex **9'b** (0.052 g, 0.052 mmol), CH_2Cl_2 (10 mL), and $[H(OEt_2)_2]^+$ BAr_f^- (0.052 g, 0.052 mmol) were combined in a procedure analogous to that used for **9a**-H$^+$ BAr_f^-. An identical workup gave **9'b**-H$^+$ BAr_f^- (0.066 g, 0.035 mmol, 68%) as a yellow gum. Anal. calcd (%) for $C_{83}H_{109}BF_{24}O_3P_2Os$ (1873.70): C 53.20, H 5.86; found C 53.38, H 5.94.

NMR ($CDCl_3$, δ/ppm): **^{1}H** (500 MHz)[s14,s21] 7.72-7.69 (m, 8H, C_6H_3 *o* to B), 7.54-7.52 (m, 4H, C_6H_3 *p* to B), 2.14-2.05 (br m, 4H, PC'H_2), 2.04-1.97 (br m, 4H, PCH_2), 1.95-1.86 (br m, 4H, PC'H_2), 1.51-1.41 (br m, 24H, PCH_2CH_2, PC'H$_2$C'H_2, $PCH_2CH_2CH_2$, PC'H$_2$C'H$_2$C'H_2), 1.39-1.24 (br m, 60H, remaining CH_2 and remaining C'H_2), –8.48 (t, $^2J_{PH}$ = 16.3 Hz, 1H, OsH); **^{13}C{^{1}H}** (126 MHz)[s14,s21] 176.2 (t, $^2J_{CP}$ = 9.4 Hz, *C*O *cis* to H), 174.5 (t, $^2J_{CP}$ = 5.4 Hz, *C*O *trans* to H), 161.7 (q, $^1J_{BC}$ = 49.9 Hz, C_6H_3 *i* to B), 134.8 (s, C_6H_3 *o* to B), 128.8 (q, $^2J_{CF}$ = 31.5 Hz, C_6H_3 *m* to B), 124.6 (q, $^1J_{CF}$ = 272.5 Hz, CF_3), 117.5 (s, C_6H_3 *p* to B), 29.9 (virtual t,[s7] $^3J_{CP}$ = 7.1 Hz, $PCH_2CH_2CH_2$), 29.3 (virtual t,[s7] $^3J_{CP}$ = 5.9 Hz, PC'H$_2$C'H$_2$*C*'H$_2$), 29.0 (virtual t,[s7] $^1J_{CP}$ = 17.8 Hz, PCH_2), 28.5 (virtual t,[s7] $^1J_{CP}$ = 17.3 Hz, P*C*'H$_2$), 28.1 (s, CH_2), 27.88 (s, CH_2), 28.85 (s, CH_2), 27.6 (s, CH_2 or *C*'H$_2$), 27.4 (s, CH_2 or *C*'H$_2$), 27.33 (s, CH_2 or *C*'H$_2$), 27.27 (s, CH_2 or *C*'H$_2$), 27.2 (s, CH_2 or *C*'H$_2$), 27.0 (s, CH_2 or *C*'H$_2$), 24.0 (s, PCH_2CH_2), 23.0 (s, PC'H$_2$*C*'H$_2$); **^{31}P{^{1}H}** (202 MHz) –16.5 (s).

IR (cm^{-1}, solid film): 2928 (m), 2859 (m), 2114 (w, ν_{CO}), 2052 (m, ν_{CO}), 2027 (s, ν_{CO}), 1967 (br w), 1462 (w), 1418 (w), 1352 (s), 1273 (s), 1161 (s), 1119 (vs), 887 (m), 839 (m), 745 (w), 712 (s), 681 (s), 669 (s). **MS** (MALDI+, THAP):[s9] 1012 ([**9'b**-H + 1]$^+$, 100%), 983 ([**9'b**-H – CO]$^+$, 20%); (MALDI–, THAP):[s9] 863 (BAr_f^-, 100%).

***mer,trans*-[$\overline{\mathbf{Os(H)(CO)_3(P((CH_2)_{18})_3P}}$)]$^+$ BAr$_f^-$ (9c-H$^+$ BAr$_f^-$).** Complex **9c** (0.051 g, 0.047 mmol), CH_2Cl_2 (10 mL), and $[H(OEt_2)_2]^+$ BAr$_f^-$ (0.047 g, 0.047 mmol) were combined in a procedure analogous to that used for **8a**-H$^+$ BAr$_f^-$. An identical workup gave **9c**-H$^+$ BAr$_f^-$ (0.073 g, 0.041 mmol, 80%) as a yellow gum. Anal. calcd (%) for $C_{89}H_{121}BF_{24}O_3P_2Os$ (1957.86): C 54.60, H 6.23; found C 54.74, H 6.05.

NMR ($CDCl_3$, δ/ppm): **^{1}H** (500 MHz)[s20] 7.74-7.68 (m, 8H, C_6H_3 *o* to B), 7.55-7.52 (m, 4H, C_6H_3 *p* to B), 2.04-1.96 (br m, 12H, PCH_2), 1.53-1.41 (br m, 24H, PCH$_2$CH_2 and PCH$_2$CH$_2$CH_2), 1.38-1.21 (br m, 72H, remaining CH_2), –8.45 (t, $^2J_{PH}$ = 16.3 Hz, 1H, Os*H*); **^{13}C{^{1}H}** (126 MHz)[s20] 176.5 (t, $^2J_{CP}$ = 9.4 Hz, *C*O *cis* to H), 174.6 (t, $^2J_{CP}$ = 5.5 Hz, *C*O *trans* to H), 161.7 (q, $^1J_{BC}$ = 49.8 Hz, C_6H_3 *i* to B), 134.8 (s, C_6H_3 *o* to B), 128.8 (q, $^2J_{CF}$ = 30.9 Hz, C_6H_3 *m* to B), 124.6 (q, $^1J_{CF}$ = 272.5 Hz, *C*F$_3$), 117.4 (s, C_6H_3 *p* to B), 29.8 (virtual t,[s7] $^3J_{CP}$ = 6.4 Hz, PCH$_2$CH$_2$*C*H$_2$), 28.9 (virtual t,[s7] $^1J_{CP}$ = 17.3 Hz, P*C*H$_2$), 28.3 (s, *C*H$_2$), 28.22 (s, *C*H$_2$), 28.18 (s, *C*H$_2$), 27.9 (s, *C*H$_2$), 23.7 (s, PCH$_2$*C*H$_2$); **^{31}P{^{1}H}** (202 MHz) –15.0 (s).

IR (cm^{-1}, solid film): 2928 (m), 2857 (m), 2112 (w, ν_{CO}), 2050 (m, ν_{CO}), 2025 (s, ν_{CO}), 1965 (br w), 1462 (w), 1418 (w), 1352 (s), 1273 (s), 1161 (s), 1119 (vs), 887 (m), 839 (m), 745 (w), 712 (s), 681 (s), 669 (s). **MS** (MALDI+, THAP):[s9] 1096 ([**9c**-H + 1]$^+$, 100%), 1068 ([**9c**-H$^+$ – CO + 1]$^+$, 10%); (MALDI–, THAP):[s9] 863 (BAr$_f^-$, 100%).

***cis,cis,trans*-Os(CO)$_3$(P(*n*-C$_8$H$_{17}$)$_3$)$_2$ (10a).** A Schlenk flask was charged with **8a** (0.299 g, 0.261 mmol) and THF (10 mL). The solution was aspirated with CO (15 min). Then a suspension of C_8K (0.993 g, 7.35 mmol) in THF (10 mL) was slowly added. The reaction was monitored by ^{31}P NMR. After the educt had been consumed, graphite powder and unreacted C_8K were removed by cannula filtration. The solvent was removed from the filtrate by oil pump vacuum and the residue filtered through celite using CH_2Cl_2. The solvent was removed from the filtrate by oil pump vacuum to give **13a** (0.225 g, 0.222 mmol, 85%) as a colorless oil. Anal. calcd (%) for $C_{51}H_{102}O_3OsP_2$ (1015.53): C 60.32, H 10.12; found C 60.98, H 10.13.

NMR (C_6D_6, δ/ppm): **^{1}H** (500 MHz)[s12] 1.92-1.86 (br m, 12H, PCH_2), 1.70-1.61 (br m, 12H, PCH$_2$CH_2), 1.38-1.18 (br m, 60H, remaining CH_2), 0.9 (t, $^3J_{HH}$= 7.0 Hz, 18H, CH_3); **^{13}C{^{1}H}** (126

MHz)[s12] 198.7 (t, $^2J_{CP}$ = 11.8 Hz, *C*O), 32.2 (s, CH_2), 31.3 (virtual t,[s7] $^3J_{CP}$ = 6.7 Hz, $PCH_2CH_2CH_2$), 30.9 (virtual t,[s7] $^1J_{CP}$ = 17.0 Hz, PCH_2), 29.6 (s, CH_2), 24.7 (s, PCH_2CH_2), 23.1 (s, CH_2), 14.4 (s, CH_3); ^{31}**P{^{1}H}** (121 MHz) –9.1 (s).

IR (cm^{-1}, oil film): 2955 (w), 2922 (s), 2853 (m), 1863 (s, ν_{CO}), 1456 (w), 1412 (w), 1377 (w), 1030 (w), 797 (w), 758 (w), 721 (m). **MS** (MALDI+, THAP):[s9] 1018[s17] ([**10a** + 2]$^+$, 100%), 989 ([**10a** – CO + 1]$^+$, 20%).

***cis,cis,trans*-$Os(CO)_2(Me)_2(P((CH_2)_{14})_3P)$ (11a).** A Schlenk flask was charged with **6a** (0.100 g, 0.104 mmol) and THF (10 mL) and cooled to 0 °C. Then MeLi (1.6 M in Et_2O, 1.35 mL, 2.16 mmol) was added with stirring. After 24 h, a few drops of water were added. The solvent was removed by oil pump vacuum and the residue filtered through Al_2O_3 using CH_2Cl_2. The solvent was removed from the filtrate by oil pump vacuum to give **11a** (0.095 g, 0.102 mmol, 98%) as a colorless powder, mp 247 °C (capillary). **DSC** ($T_i/T_e/T_p/T_c/T_f$):[s1] 36.6/39.0/47.0/49.8/53.5 °C (endotherm); 53.5/54.3/ 56.6/58.8/60.7 °C (endotherm, minor); 61.0/61.8/68.5/74.7/77.3 °C (endotherm, minor); 79.8/85.0/91.1 /95.7/97.5 °C (endotherm, minor); 201.9/210.5/213.8/215.6/220.9 °C (endotherm, minor). **TGA**: onset of mass loss, 230.3 °C. Anal. calcd (%) for $C_{46}H_{90}O_2P_2Os$ (927.38): C 59.58, H 9.78; found C 59.87, H 9.52.

NMR (C_6D_6, δ/ppm): ^{1}**H** (500 MHz)[s12] 1.80-1.74 (br m, 12H, PCH_2), 1.61-1.53 (br m, 12H, PCH_2CH_2), 1.51-1.39 (br m, 60H, remaining CH_2), 0.05 (t, 6H, $^3J_{HP}$ = 7.5 Hz, $OsCH_3$); ^{13}**C{^{1}H}** (126 MHz)[s12] 184.5 (t, $^2J_{CP}$ = 7.9 Hz, *C*O), 30.1 (virtual t,[s7] $^3J_{CP}$ = 6.3 Hz, $PCH_2CH_2CH_2$), 28.73 (s, CH_2), 28.70 (s, CH_2), 27.90 (s, CH_2), 27.88 (s, CH_2), 26.5 (virtual t,[s7] $^1J_{CP}$ = 14.9 Hz, PCH_2), 23.1 (s, PCH_2CH_2), –22.2 (t, $^2J_{CP}$ = 9.1 Hz, $OsCH_3$); ^{31}**P{^{1}H}** (202 MHz) –21.0 (s).

IR (cm^{-1}, powder film): 2922 (m), 2853 (w), 1967 (s, ν_{CO}), 1886 (s, ν_{CO}), 1458 (w), 1414 (w), 1384 (w), 1086 (w), 1007 (w), 781 (w), 764 (w), 714 (m). **MS** (MALDI+, THAP):[s9] 929 ([**11a** + 1]$^+$, 10%), 914 ([**11a** – Me + 1]$^+$, 20%), 899 ([**11a** – 2Me + 1]$^+$, 100%).

***cis,cis,trans*-$Os(CO)_2(Me)_2(P(CH_2)_{15}CH_2)((CH_2)_{16})(P(CH_2)_{15}CH_2)$ (11'a).** Complex **6'b** (0.63 g, 0.060 mmol), THF (10 mL), and MeLi (1.6 M in Et_2O, 0.75 mL, 1.2 mmol) were combined in a procedure analogous to that used for **11a**. An identical workup gave **11'b** (0.056 g, 0.055 mmol, 98%)

as a colorless gum. Anal. calcd (%) for $C_{52}H_{102}O_2P_2Os$ (1011.54): C 61.74, H 10.16; found C 61.95, H 10.21.

NMR (C_6D_6, δ/ppm): **^{1}H** (500 MHz)[s13,s14] 2.05-1.96 (br m, 4H, PC'H_2), 1.95-1.87 (br m, 4H, PC'H_2), 1.86-1.80 (br m, 4H, PCH_2), 1.75-1.66 (br m, 4H, PCH$_2$CH_2), 1.65-1.55 (br m, 4H, PC'H$_2$-C'H_2), 1.52-1.42 (br m, 24H, remaining CH_2), 1.41-1.19 (br m, 56H, PC'H$_2$C'H_2 and remaining C'H_2), 0.20 (t, 6H, $^3J_{HP}$ = 7.7 Hz, OsCH_3); **^{13}C{^{1}H}** (126 MHz)[s13,s14] 184.1 (t, $^2J_{CP}$ = 7.6 Hz, *C*O), 30.9 (virtual t,[s7] $^3J_{CP}$ = 6.4 Hz, PCH$_2$CH$_2$*C*H$_2$), 30.3 (virtual t,[s7] $^3J_{CP}$ = 5.6 Hz, PC'H$_2$C'H$_2$*C*'H$_2$), 28.83 (s, *C*H$_2$), 28.80 (s, *C*H$_2$), 28.51 (s, *C*H$_2$), 28.47 (s, *C*H$_2$), 28.27 (s, *C*H$_2$), 28.26 (s, *C*'H$_2$), 27.88 (s, *C*'H$_2$), 27.86 (s, *C*'H$_2$), 27.4 (s, *C*'H$_2$), 26.5 (virtual t,[s7] $^1J_{CP}$ = 15.2 Hz, P*C*H$_2$), 24.0 (virtual t,[s7] $^1J_{CP}$ = 14.5 Hz, P*C*'H$_2$), 23.6 (s, PCH$_2$*C*H$_2$), 22.8 (s, PC'H$_2$*C*'H$_2$), –22.5 (t, $^2J_{CP}$ = 9.4 Hz, OsCH_3); **^{31}P{^{1}H}** (202 MHz) –25.3 (s).

IR (cm^{-1}, solid film): 2922 (m), 2853 (w), 1971 (s, ν_{CO}), 1896 (s, ν_{CO}), 1458 (w), 1418 (w), 781 (w), 718 (m). **MS** (MALDI+, THAP):[s9] 999[s17] ([**11'b** – Me + 2]$^+$, 40%), 983 ([**11'b** – 2Me + 1]$^+$, 100%).

***cis,cis,trans*-$\overline{\text{Os}(\text{CO})_2(\text{Ph})_2(\text{P}((\text{CH}_2)_{14})_3\text{P}}$) (12a).** A Schlenk flask was charged with **7a** (0.205 g, 0.194 mmol) and THF (20 mL) and cooled to 0 °C. Then PhLi (2.0 M in Bu_2O, 1.00 mL, 2.16 mmol) was added with stirring. The cold bath was removed. After 2 h, the solution was refluxed. After 1 h, a few drops of water were added. The solvents were removed by oil pump vacuum and the residue chromatographed (SiO_2 column, 2.5 cm × 30 cm, 3:1 v/v hexanes/CH_2Cl_2). The solvents were removed from the product-containing fractions by oil pump vacuum to give **12a** (0.118 g, 0.112 mmol, 58%) as a colorless oil that solidified after one week, mp 162-164°C (capillary). Anal. calcd (%) for $C_{56}H_{94}$-O_2P_2Os (1051.52): C 63.96, H 9.01; found C 63.70, H 8.96.

NMR ($CDCl_3$, δ/ppm): **^{1}H** (500 MHz)[s22] 7.99 (d, $^3J_{HH}$ = 7.2 Hz, 4H, *o*-Ph), 7.02 (apparent t, $^3J_{HH}$ = 7.2 Hz, 4H, *m*-Ph), 6.96 (apparent t, $^3J_{HH}$ = 7.1 Hz, 2H, *p*-Ph), 1.92-1.82 (m, 4H, PCH_2), 1.79-1.69 (m, 4H, PCH_2), 1.53-1.15 (br m, 68H, CH_2), 1.12-0.98 (br m, 8H, CH_2); **^{13}C{^{1}H}** (126 MHz)[s22,s23] 184.0 (t, $^2J_{CP}$ = 7.0 Hz, *C*O), 145.7 (t, $^2J_{CP}$ = 12.5 Hz, *i*-Ph), 145.2 (s, *o*-Ph), 126.9 (s, *m*-Ph), 121.9 (s, *p*-Ph), 29.8-29.4 (three overlapping virtual t,[s7] P*C*'H$_2$, PC'H$_2$C'H$_2$*C*'H$_2$, PCH$_2$CH$_2$*C*H$_2$), 29.4 (s, CH_2), 29.2 (s, CH_2), 28.8 (s, $C'H_2$), 28.5 (s, $C'H_2$), 28.1 (s, CH_2), 27.8 (s, $C'H_2$), 27.7 (s, $C'H_2$), 27.5 (s, CH_2), 25.3 (virtual t,[s7] $^1J_{CP}$ = 16.0 Hz, PCH_2), 21.8 (s, $PC'H_2C'H_2$), 21.3 (s, PCH_2CH_2); **^{31}P{^{1}H}** (202 MHz) –27.8 (s).

IR (cm^{-1}, powder film): 3042 (w), 2922 (m), 2851 (m), 1983 (s, ν_{CO}), 1911 (s, ν_{CO}), 1572 (w), 1460 (w), 1418 (w), 1069 (w), 1015 (w), 735 (s), 708 (m). **MS** (MALDI+, THAP):[s9] 1053 ([**12a**]$^+$, 2%), 976 ([**12a** – Ph]$^+$, 15%).

Cyclic Voltammetry. A BAS*i* Epsilon Electrochemical Workstation (Cell Stand C3) with the program Epsilon EC (version 2.13.77) was employed. Cells were fitted with Pt working and counter electrodes, and a silver wire pseudoreference electrode. Per a previous study,[s24] CH_2Cl_2 solutions that were 0.0010 M in substrate, 0.20 M in *n*-Bu_4N^+ PF_6^-, and prepared under N_2 were employed; scan rates were 200 mV/sec. Ferrocene (0.46 V) was added after each measurement and calibration voltammograms were recorded. The ambient laboratory temperature was 22 ± 1 °C.

Crystallography. Refer to Table s2 for selected aspects of data collection.[25]

A. A CH_2Cl_2 solution of **6a** was layered with MeOH. After 7 d, data were collected on the resulting colorless prisms. Cell parameters were obtained from 10 frames using a 10° scan and refined with 9288 reflections. Lorentz, polarization, and absorption corrections[s26] were applied. The space group was determined from systematic absences and subsequent least squares refinement. The structure was solved by direct methods. The parameters were refined with all data by full matrix least squares on F^2 using SHELXL-97.[s27] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in idealized positions using a riding model. One chloride and one CO ligand showed disorder over two positions and were refined to a 51:49 occupancy ratio. Scattering factors were taken from literature.[s28]

B. A C_6D_6 solution of **6b** was layered with MeOH. After 7 d, data were collected on the resulting colorless thin plates. Cell parameters were obtained from 180 data frames using a 0.5° scan and refined with 83787 reflections using the program Cell Now.[s29] Integrated intensity information for each reflection was obtained by reduction of the data frames with SAINTplus.[s30] Data were scaled, and absorption corrections were applied using the program SADABS[s31]. The structure was solved by direct methods using SHELXTL (SHELXS)[s27] and refined (weighted least squares refinement on F^2) using SHELXTL (X-Seed).[s27,s32] Two independent molecules were found in the asymmetric unit. The first molecule (Os1_Mol) could be easily located. While the heavier atoms of the second (Os2_Mol) could be located, strong Q peaks around Os2 suggested possible whole molecule disorder. Also, the thermal ellipsoids of Os2, P51, and P52 were elongated. Four partially occupied chlorine atoms (Cl51, Cl52, Cl53, Cl54) were located. While some of the carbon atoms bonded close to P51 could be established, the remaining carbon atoms linking P51 to P52 could not be accurately determined.

The whole molecule disorder of Os2_Mol was modeled with strong restraints, making it similar to Os1_Mol. This decreased reliability factors significantly, and the disorder refined to a 53:47 occupancy ratio. Finally, the thermal ellipsoids of the carbon atoms in the methylene chains were also strongly restrained to avoid rendering them non-positive definite. At the end of the refinement, many of the carbon atoms were large, indicating only partial modeling of the disorder. Non-hydrogen atoms were refined with anisotropic thermal parameters.

C. A C_6D_6 solution of **6c** was layered with MeOH. After 7 d, data were collected on the resulting colorless multi-faceted crystals. Cell parameters were obtained from 60 data frames using a 0.5° scan and refined with 67059 reflections. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX 2.[s33] Lorentz and polarization reduction and corrections were applied. Data were scaled, and absorption corrections were applied using the program SADABS.[s31] The structure was solved by direct methods using SHELXTL (SHELXS)[s27] and refined (weighted least squares refinement on F^2) using SHELXTL (X-Seed).[s27,s32] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in idealized positions, and refined using a riding model. Upon refinement, the Os1-C2 distance was too long, and the C2-O2 distance too short ($R1$ and $wR2$ were 0.0314 and 0.0711 respectively). Also, the principal mean square atomic displacements for Cl1 were large relative to the corresponding values for Cl2, suggesting a possible lower occupancy for Cl1. This raised the possibility of a rotational disorder (2-fold along Cl2-Os1-(C1-O1) axis) between Cl1 and C2-O2. Upon modeling this disorder, the reliability factors decreased ($R1$ = 0.0288; $wR2$ = 0.0637) and the thermal parameters and bond lengths of Os1-C2 and C2-O2 were well behaved. A twofold rotation along the Cl2-Os1-(C1-O1) axis should also lead to disorder in the methylene chains. No effort was made to model this, considering the large increase in the number of refinement parameters, and given the low degree of disorder.

D. A THF solution of **7'a** was layered with MeOH. After several weeks, data were collected on the resulting colorless multi-faceted crystals. The structure was solved and refined in a manner identical to that of **6c** (cell parameters from 60 frames using a 0.5° scan and refined with 31737 reflections). There were two independent molecules in the asymmetric unit. Most of the atoms were symmetrically related, pointing to *C*2/*c* as a possible space group (additional symmetry was sought with the program PLATON).[s34] However, in monoclinic *C*2/*c* some of the disorder of the methylene chains was difficult to model and gave non-positive definite thermal parameters for some of the carbon atoms (even when strong restraints were set). The structure was ultimately refined in the triclinic *P*-1.

No observable reflections were seen above a 2Θ value of 45°. Several Q peaks were found in the Fourier difference map along the methylene chains. Efforts to model this disorder resulted in a large increase in the number of parameters as well as the number of restraints with no significant improvement in the reliability factors. Restraints were used to keep the bond lengths and the thermal ellipsoids meaningful. Thus, some of the C-C-C angles in the methylene chains deviated from idealized values, resulting in short H-H and meaningless C-H contacts.

Several rationales, e.g., twinning, insufficient modeling, presence of undetected disordered solvents, incorrect space group, etc., were evaluated. All the possible triclinic and monoclinic space groups were also evaluated. The best results were obtained for *P*-1, followed by *C*2/*c*. Alternative methods for absorption corrections including face indexing did not improve the results. Relatively high reliability factors again indicated insufficient agreement between the model and the data. A second data set was collected with a Cu-source as opposed to a Mo-source; the results were comparable.

E. A C_6D_6 solution of **7b** was layered with MeOH. After 7 d, data were collected on the resulting colorless multi-faceted crystals. The structure was solved and refined in a manner identical to that of **6c** (cell parameters from 60 frames using a 0.3° scan and refined with 103619 reflections). After refinement, residual electron densities (Q peaks, 1.0-1.6 eÅ^{-3}) were found around 0.70-0.85 Å from the osmium and bromine atoms. The distances between these Q peaks agreed well with the osmium-bromine distance (2.58 Å), suggesting a small degree of whole molecule disorder. No attempts were made to model this disorder. Also, the carbon atoms C37 to C47 showed larger thermal ellipsoids, indicating disorder of this methylene chain. The thermal parameters were restrained for these carbon atoms.

F. A C_6D_6 solution of **7c** was layered with MeOH. After 7 d, data were collected on the resulting colorless multi-faceted crystals. The structure was solved and refined in a manner identical to that of **6c** (cell parameters from 60 frames using a 0.3° scan and refined with 31866 reflections).

G. A CH_2Cl_2 solution of **9a** was layered with MeOH. After several weeks, data were collected on the resulting colorless prisms. The structure was solved and refined in a manner identical to that of **6a** (cell parameter from 10 frames using a 10° scan and refined with 5313 reflections).

H. A $CHCl_3$ solution of **9a**-H^+ BAr_f^- was layered with MeOH. After 7 d, data were collected on the resulting colorless thin plates. Cell parameters were obtained from 180 data frames using a 0.5° scan and refined with 63051 reflections using the program Cell Now.[s29] Integrated intensity information for each reflection was obtained by reduction of the data frames with APEX 2.[s33] Data were scaled, and absorption corrections were applied using the program SADABS.[s31] The structure was solved by direct methods using SHELXTL (SHELXS)[s27] and refined (weighted least squares refinement on F^2) using SHELXTL (X-Seed).[s27,s32] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in idealized positions, and refined using a riding model. Some fluorine atoms of the BAr_f^- anion and some carbon atoms of the methylene chains showed elongation, suggesting disorder. Efforts to model the disorder increased the number of parameters as well as the number of very strong restraints, and yielded much increased reliability factors. Relaxing the restraints resulted in divergence of the refinement. SIMU and DELU commands were used to slightly reduce the elongation.

A small electron density peak was located near the osmium atom that geometrically fit the anticipated hydride ligand. This was designated H1OS. However, the exact location of the hydrogen atom could not be determined, and was only modeled to account for the formulation supported by the NMR data. The bond distance reported in the CIF file (1.3800 Å) has no physical meaning, as the hydrogen atom position could not be refined.

I. A C_6D_6 solution of **11a** was layered with MeOH. After 7 d, data were collected on the resulting colorless multi-faceted crystals. Cell parameters were obtained from 60 data frames using a 0.3° scan and refined with 44786 reflections. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX 2.[s33] Lorentz and polarization reduction and corrections were applied. Data were scaled and absorption corrections were applied using the program SADABS.[s31] The structure was solved by direct methods using SHELXTL (SHELXS)[s27] and refined (weighted least squares refinement on F^2) using SHELXTL (X-Seed).[s27,s32] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in idealized positions, and refined using a riding model. Two *cis* positions exhibited disorder, with each refining to a 50:50 CO/methyl occupancy.

J. A CH_2Cl_2 solution of **12a** was layered with MeOH. After 7 d, data were collected on the resulting colorless multi-faceted crystals. The structure was solved and refined in a manner identical to that of **6c** (cell parameters from 60 frames using a 0.5° scan and refined with 33979 reflections). No observable reflections were seen above a 2Θ value of 42°. Even longer collection times per frame (exposure time 40 s instead of 20 s) did not increase the intensity at higher angles. Significant disorder of the methylene chains, the carbon atoms of which were seen as elongated thermal ellipsoids, could account for the absence of higher angle reflections. Trials to model this disorder, while increasing the number of restraints, did not improve the refinement results. Hence, SIMU and DELU commands were used to make the thermal ellipsoids reasonable.

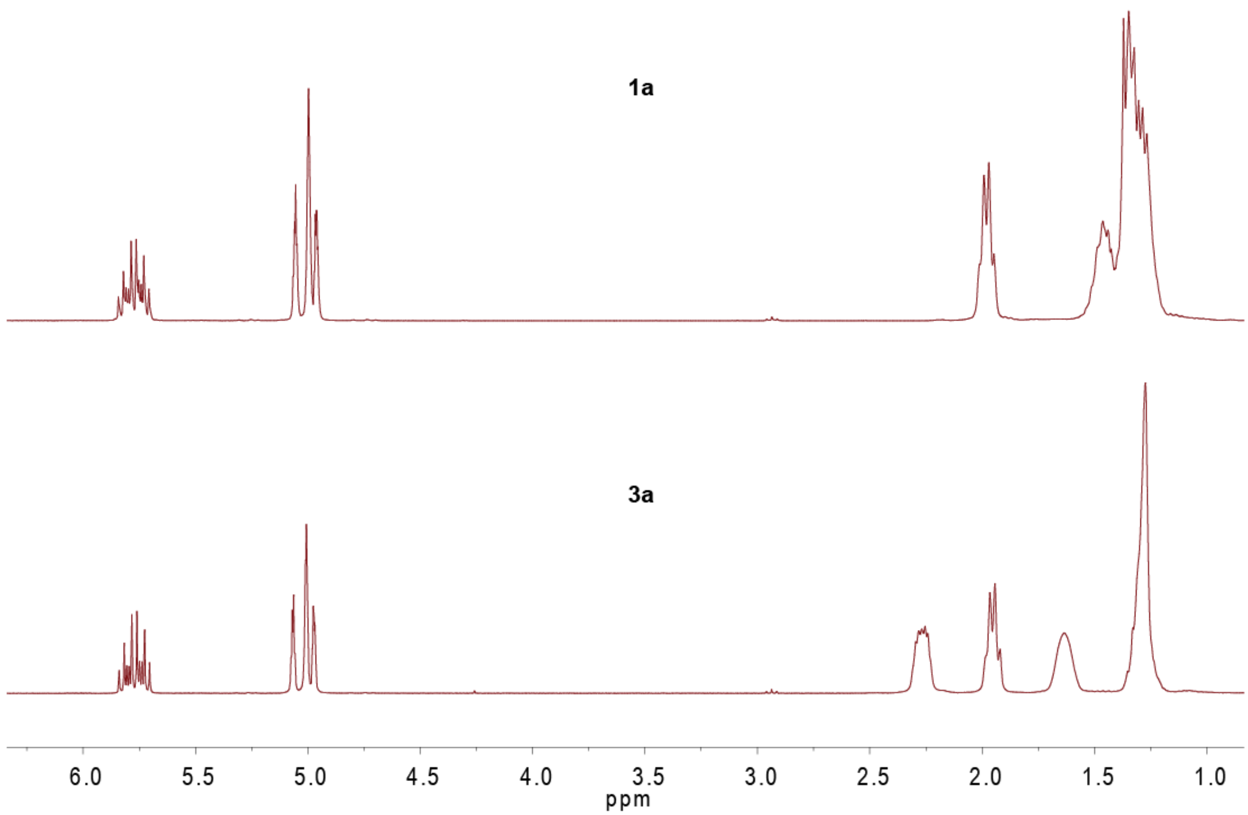

Figure s1. ^{1}H NMR spectra (300 MHz) of **1a** (top) and **3a** (bottom).

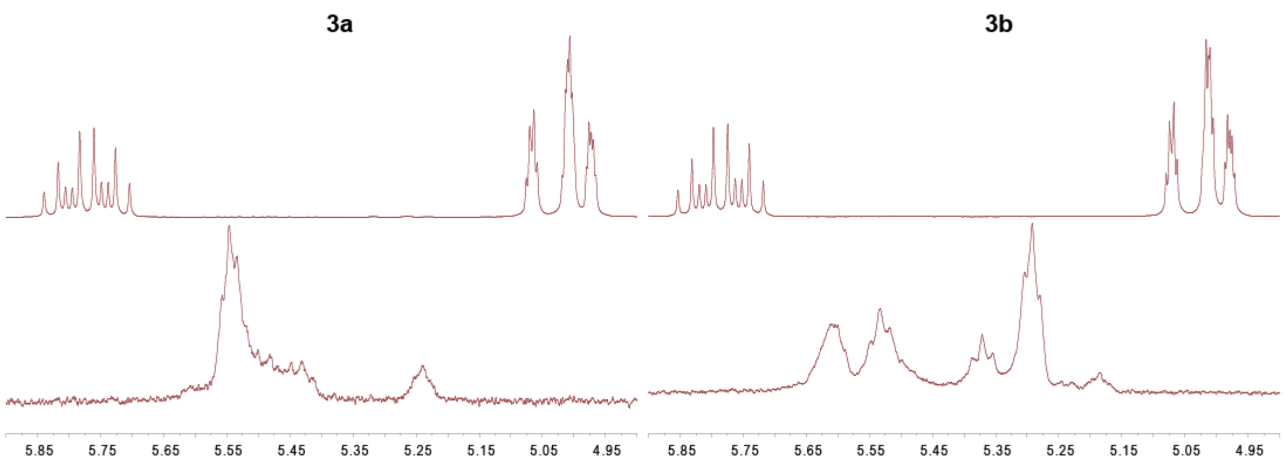

Figure s2. Representative partial ^{1}H NMR spectra (300 MHz) showing the alkene region before (top) and after (bottom) metathesis reactions of **3a** (left) and **3b** (right).

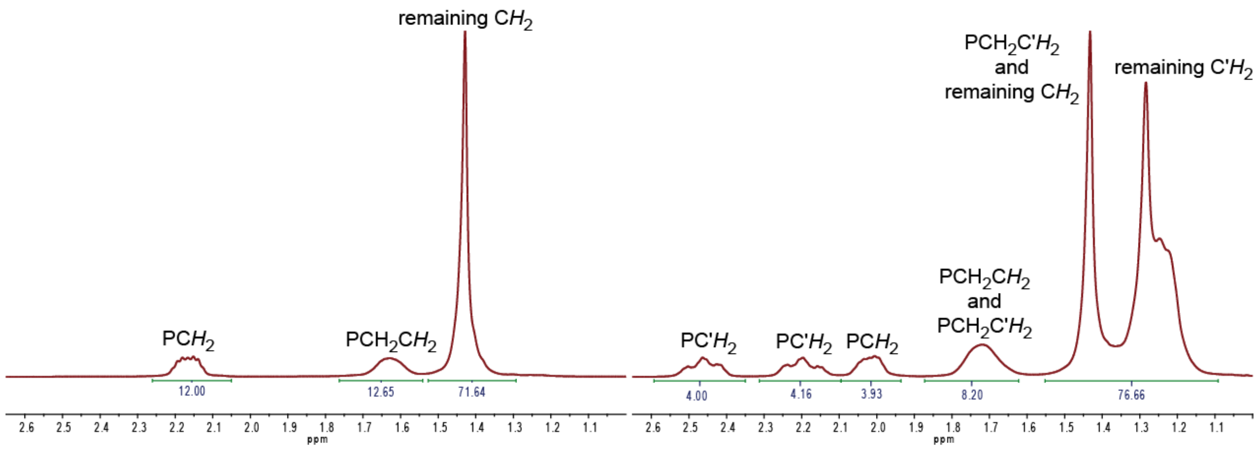

Figure s3. Representative partial [1]H NMR spectra (300 MHz) of **7b** (left) and **7'b** (right).

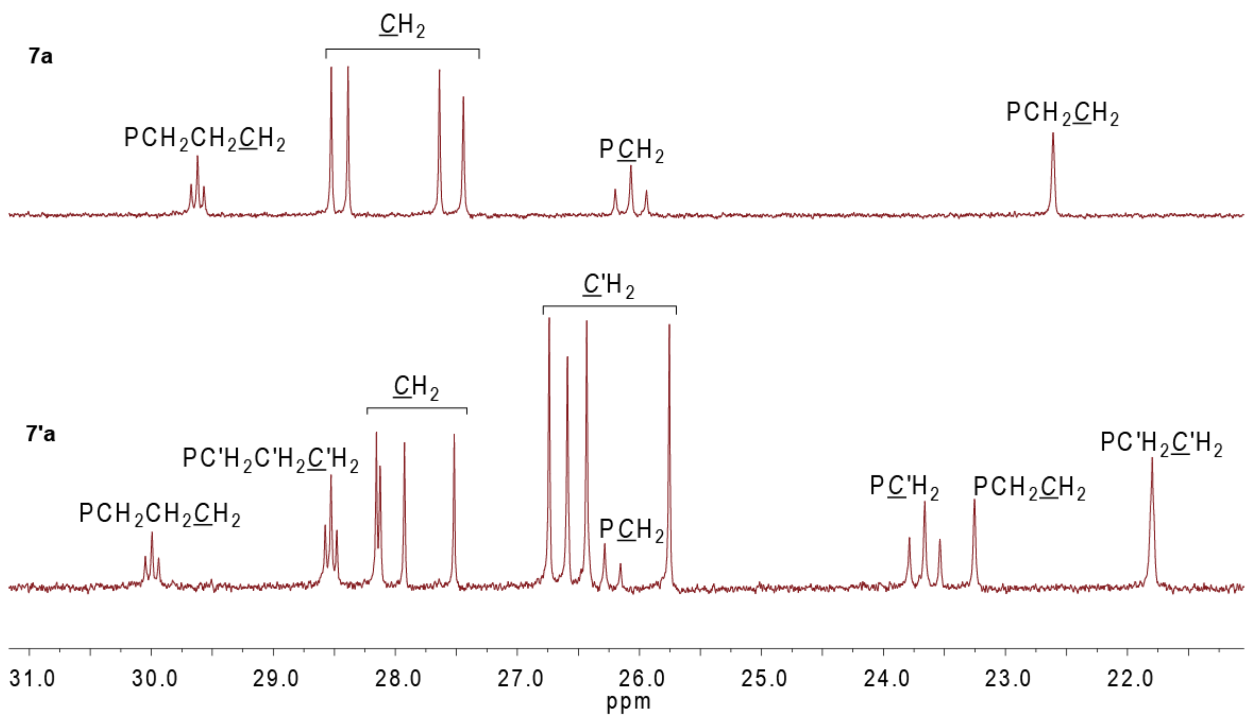

Figure s4. Representative partial $^{13}C\{^1H\}$ NMR spectra of **7a** (top, 100 MHz) and **7'a** (bottom, 126 MHz). Methylene carbon signals that are doubled in intensity are assigned to the two phosphacycles $\overline{P(CH_2)_{n-1}CH_2}$ and denoted by primes.

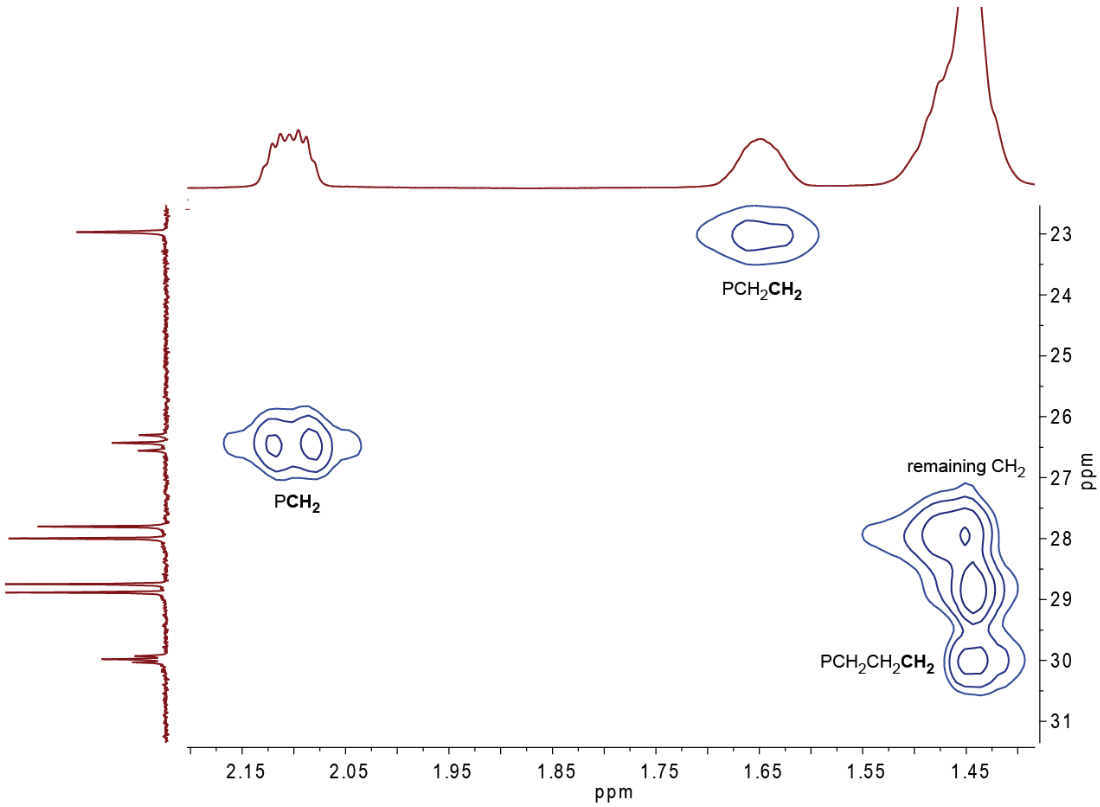

Figure s5. Partial ^{1}H, ^{13}C{^{1}H} gHMQC NMR spectrum (500 MHz) of **7a**.

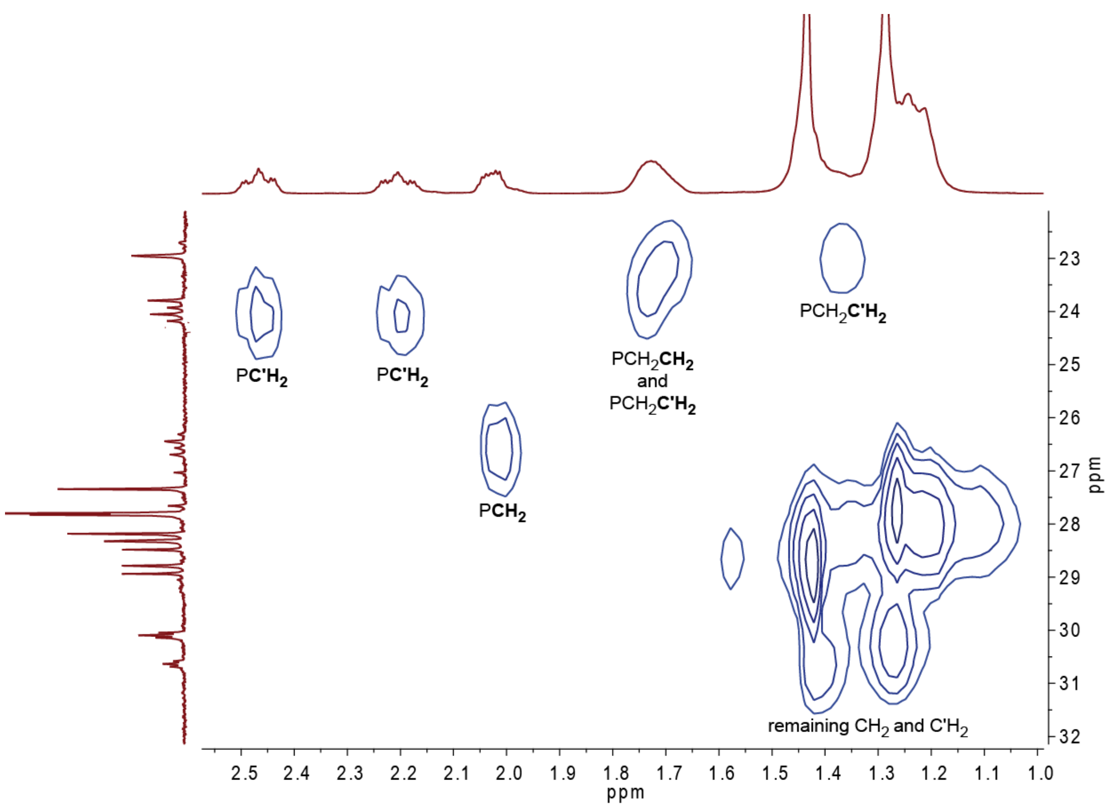

Figure s6. Partial ^{1}H, ^{13}C{^{1}H} gHSQC NMR spectrum (500 MHz) of **7'b**.

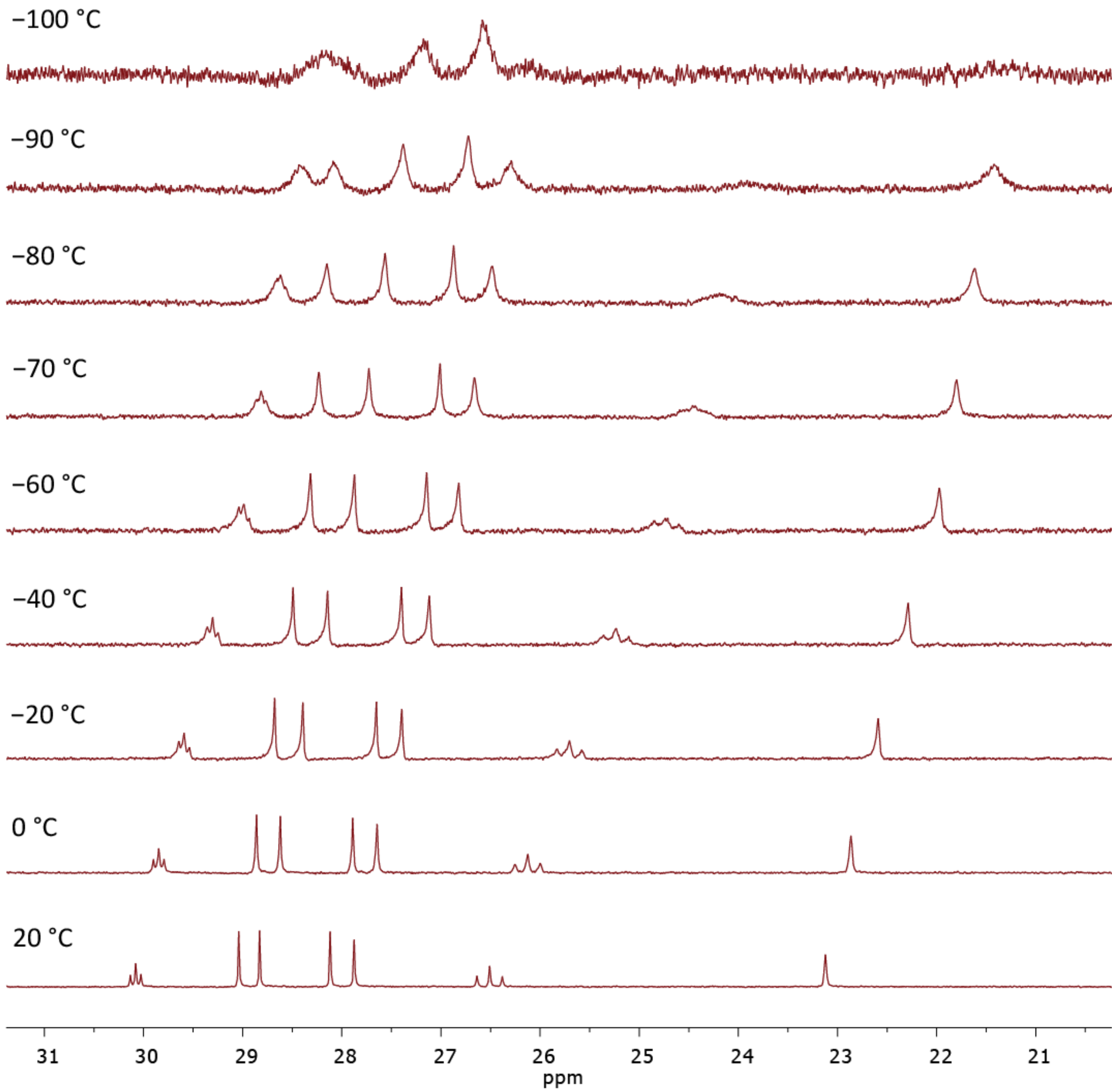

Figure s7. Variable temperature $^{13}C\{^{1}H\}$ NMR spectra (126 MHz) of **7a** in CD_2Cl_2.

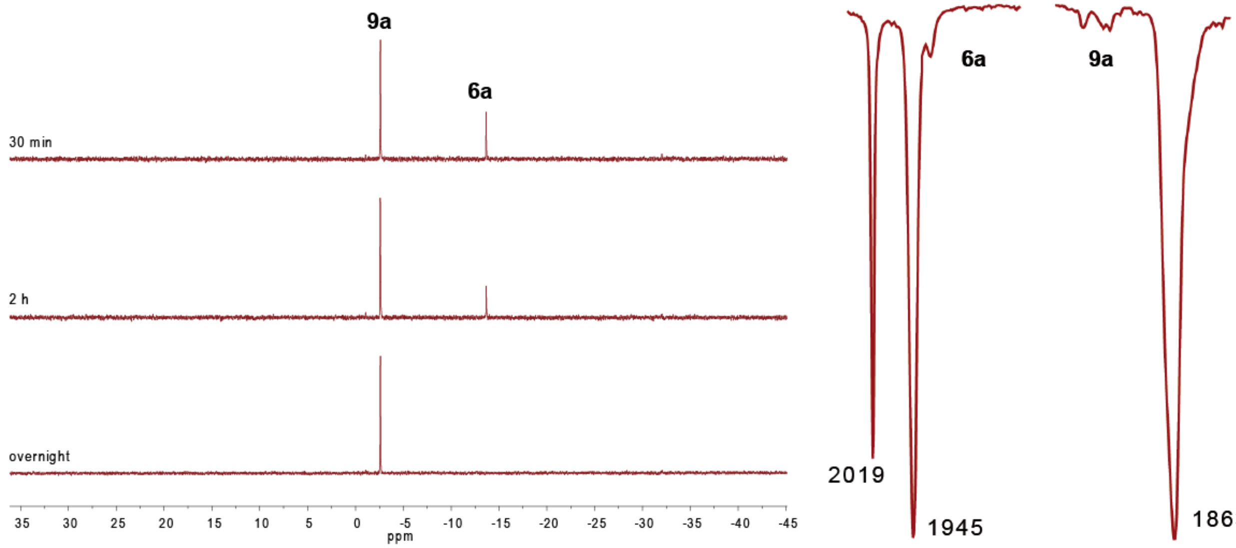

Figure s8. Monitoring the reduction of **6a** to **9a** with C_8K by $^{31}P\{^1H\}$ NMR (left, 121 MHz) and IR spectroscopy (right).

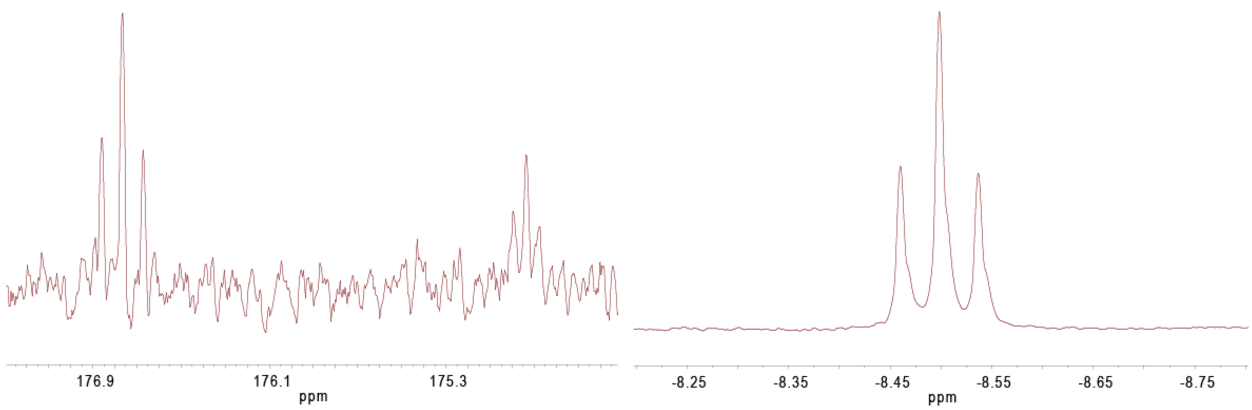

Figure s9. Partial $^{13}C\{^1H\}$ NMR spectrum (left, 100 MHz) of **9a**-H+ $CF_3SO_3^-$ showing the carbonyl region and partial ^1H NMR spectrum (right, 400 MHz) showing the hydride region.

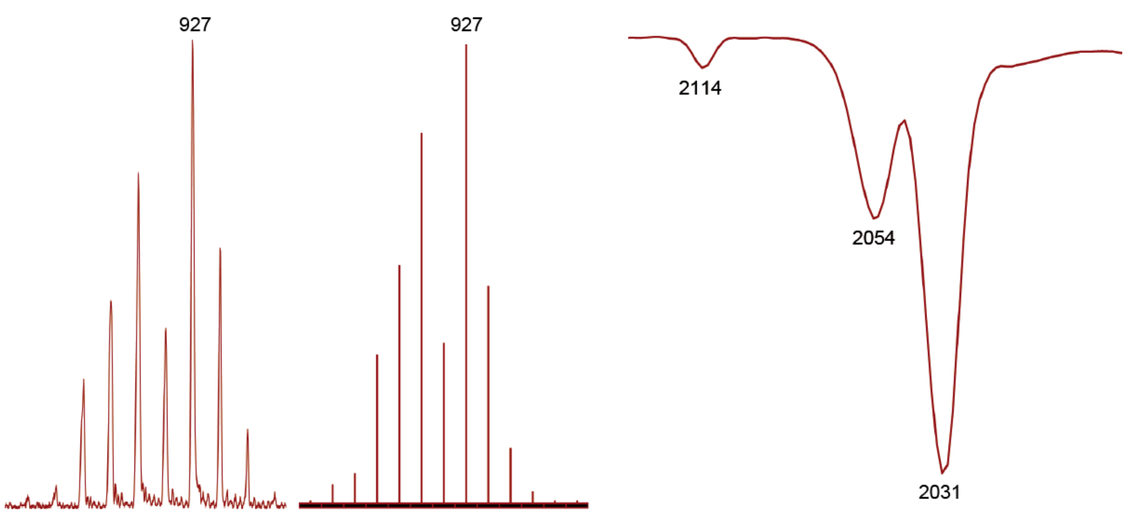

Figure s10. Observed (left) and calculated isotope patterns for the ion **9a**-H+, and a partial IR spectrum of **9a**-H+ BAr_f^-.

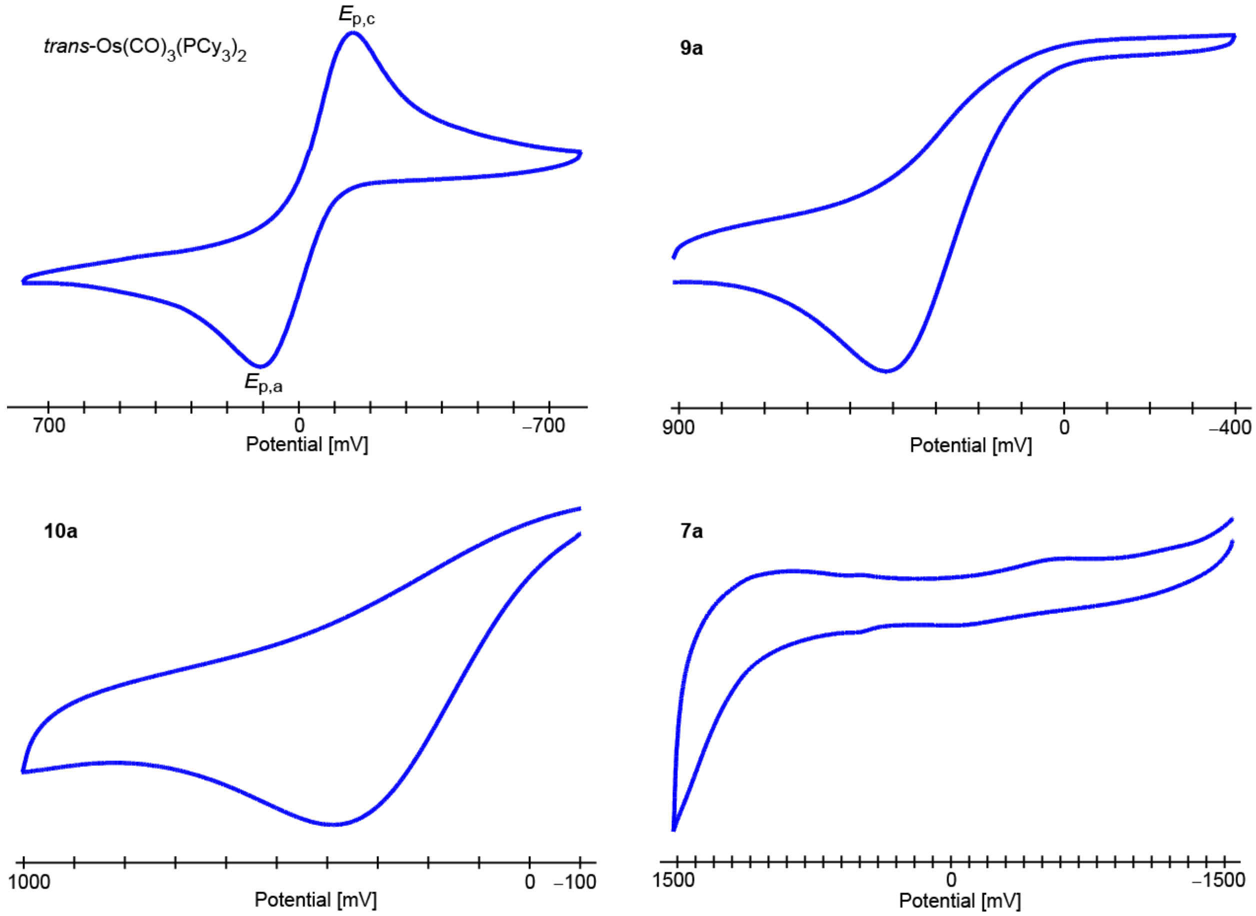

Figure s11. Representative cyclic voltammograms of *trans*-$Os(CO)_3(PCy)_3$, **9a**, **7a**, and **10a** (0.001 M, 0.2 M *n*-Bu_4N^+ PF_6^-, CH_2Cl_2; 22 ± 1 °C; Pt working and counter electrodes, potential vs. Ag wire pseudoreference; scan rate 200 mVs^{-1}; ferrocene = 0.46 V).

Table s1. Thermal stability data (°C) for selected complexes.

Complex	TGA mass loss (onset)	DSC (T_i/T_e/T_p/T_c/T_f)[a]	mp[b] capillary
6a	295	32.3/39.6/41.1/42.7/56.1[c] 74.0/84.5/85.8/87.6/109.2[c] 165.6/181.5/183.1/184.8/199.0[c] 244.5/248.0/253.4/258.2/273.3[c]	260[d]
6b	269	56.9/67.4/77.3/87.6/89.7[c] 90.2/95.3/100.4/104.8/108.2 (minor)[c] 110.5/135.8/147.6/152.9/157.3[c]	150
6c	295	46.7/84.4/86.5/88.4/155.0[c]	86
7a	286	107.9/125.8/134.3/138.1/144.5[c] 170.8/187.6/236.9/266.7/272.7[c]	230[d]
7b	308	86.9/89.9/100.8/107.0/111.2(minor)[c] 158.9/199.1/204.7/206.9/240.1[c]	199
7c	259	61.2/91.5/93.6/96.0/162.9[c]	92
6'a	-	-	67
6'b	-	-	-(oil)
6'c	-	-	- (oil)
7'a	255	39.5/52.5/56.5/59.0/71.8[c]	74
7'b	293	-	54
7'c	-	-	- (oil)
9a	231	94.7/95.3/118.1/127.8/127.8 (minor)[c] 127.9/144.9/148.3/150.5/155.8[c]	248 (>180)[d]
9'b	262	70.2/94.7/99.9/103.5/122.0[c]	104
9c	146	46.6/60.0/62.8/65.3/73.5[c]	61
9a-H^+ BAr_f^-	191	-	181

[a]See reference s1. The T_e values best represent the temperature of the phase transition or exotherm. [b]Conventional melting point apparatus. [c]Endotherm. [d]Gradual darkening without melting above this temperature.

Table s2. Summary of crystallographic data.

	6a	**6b**	**6c**
empirical formula	$C_{44}H_{84}Cl_2O_2OsP_2$	$C_{50}H_{96}Cl_2O_2OsP_2$	$C_{56}H_{108}Cl_2O_2OsP_2$
formula weight	968.15	1052.31	1136.46
Diffractometer	Nonius Kappa CCD	Bruker GADDS	Bruker APEX 2
Temperature [K]	173(2)	110(2)	110(2)
Wavelength [Å]	0.71073	1.54178	0.71073
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1$/n	$P2_1$/c	$P2_1$/c
unit cell dimensions:			
a [Å]	13.5196(2)	17.4907(12)	14.6538(15)
b [Å]	17.5887(4)	16.8895(10)	15.7020(16)
c [Å]	19.9465(4)	36.622(2)	26.920(3)
α [°]	90	90	90
β [°]	96.774(1)	91.261(3)	105.2720(10)
γ [°]	90	90	90
V [Å^3]	4710.01(16)	10815.9(12)	5975.4(11)
Z	4	8	4
ρ_{calc} [Mg/m^{-3}]	1.365	1.292	1.263
μ [mm^{-1}]	2.921	6.169	2.313
F(000)	2016	4416	2400
crystal size [mm^3]	0.25 × 0.20 × 0.20	0.25 × 0.16 × 0.02	0.40 × 0.09 × 0.05
Θ limit [°]	1.73 to 27.51	2.41 to 60.00	2.39 to 27.50
index range (h, k, l)	−17,17; −20, 22; −25, 25	−19, 19; −18, 18; −40, 36	−19, 18; −20, 20; −34, 34
reflections collected	17404	83787	67050
independent reflections	10779	15622	13559
R(int)	0.0167	0.0838	0.0459
completeness to Θ	99.6 (27.51)	97.4 (60.00)	98.8 (27.50)
max. and min. transmission	0.5927 and 0.5287	0.8866 and 0.3077	0.8931 and 0.4581
data/restraints/parameters	10779/6/488	15622/1904/1373	13559/5/578
goodness-of-fit on F^2	1.013	1.024	1.029
R indices (final) [$I > 2\sigma(I)$]			
R_1	0.0248	0.0624	0.0288
wR_2	0.0613	0.1488	0.0854
R indices (all data)			
R_1	0.0391	0.0893	0.0423
wR_2	0.0680	0.1642	0.0680
Largest diff. peak and hole [eÅ^{-3}]	0.544 and −1.125	2.007 and −1.736	1.090 and –0.399

Table s2 continued.

	7'a	**7b**	**7c**
empirical formula	$C_{44}H_{84}Br_2O_2OsP_2$	$C_{50}H_{96}Br_2O_2OsP_2$	$C_{56}H_{108}Br_2O_2OsP_2$
formula weight	1057.07	1141.23	1225.38
Diffractometer	Bruker APEX 2	Bruker APEX 2	Bruker APEX 2
Temperature [K]	110(2)	110(2)	150(2)
Wavelength [Å]	0.71073	0.71073	0.71073
crystal system	triclinic	tetragonal	triclinic
space group	*P–1*	$P4_1$	*P–1*
unit cell dimensions:			
a [Å]	12.1297(14)	16.9141(7)	14.087(5)
b [Å]	20.476(2)	16.9141(7)	14.893(6)
c [Å]	20.998(2)	19.2307(11)	16.063(6)
α [°]	90	90	87.847(7)
β [°]	97.266(1)	90	68.832(6)
γ [°]	90	90	73.272(6)
V [$Å^3$]	4751.8(10)	5501.6(5)	3001.1(19)
Z	4	4	2
ρ_{calc} [Mg/m^{-3}]	1.478	1.378	1.356
μ [mm^{-1}]	4.465	3.862	3.545
F(000)	2160	2352	1272
crystal size [mm^3]	0.43 × 0.04 × 0.03	0.24 × 0.20 × 0.17	0.60 × 0.12 × 0.02
Θ limit [°]	1.39 to 22.40	1.70 to 27.50	2.45 to 27.51
index range (h, k, l)	−12, 12; −21, 21; −22, 22	−21, 21; −21, 21; −24, 24	−18, 18; −19, 19; −20, 20
reflections collected	31737	103619	31866
independent reflections	12121	12592	13513
R(int)	0.0341	0.0925	0.0539
completeness to Θ	99.0 (22.40)	99.8 (27.50)	98.0 (27.50)
max. and min. transmission	0.8777 and 0.2498	0.5597 and 0.4575	0.9325 and 0.2249
data/restraints/parameters	12121/696/913	12592/49/514	13513/0/568
goodness-of-fit on F^2	1.034	1.036	1.094
R ind. (final) [$I > 2\sigma(I)$]			
R_1	0.0845	0.0407	0.0374
wR_1	0.2209	0.0989	0.0854
R indices (all data)			
R_2	0.0985	0.0529	0.0543
wR_2	0.2291	0.1076	0.0923
Largest diff. peak and hole [$eÅ^{-3}$]	2.337 and –4.271	3.745 and −1.489	1.546 and –1.896

Table s2 continued.

	9a	**9a**-H^+ BAr_f^-	**11a**	**12a**
empirical formula	$C_{45}H_{84}O_3OsP_2$	$C_{77}H_{97}BF_{24}O_3OsP_2$	$C_{46}H_{90}O_2OsP_2$	$C_{56}H_{94}O_2OsP_2$
formula weight	925.26	1789.49	927.32	1051.52
diffractometer	Nonius Kappa CCD	Bruker GADDS	Bruker SMART 1000	Bruker APEX 2
Temperature [K]	173(2)	110.0	110(2)	110(2)
Wavelength [Å]	0.71073	1.54178	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	*C*2/c	$P2_1$/n	$P2_1$/n	$P2_1$/n
unit cell dimensions:				
a [Å]	21.6848(5)	15.1764(10)	13.496(8)	15.622(3)
b [Å]	14.0336(2)	23.3573(14)	17.609(10)	18.229(3)
c [Å]	18.2091(4)	22.9450(13)	19.880(11)	18.907(3)
α [°]	90	90	90	90
β [°]	122.109(1)	95.723(3)	96.549(7)	97.607(2)
γ [°]	90	90	90	90
V [$Å^3$]	4693.71(16)	8093.0(9)	4694(5)	5336.7(15)
Z	4	4	4	4
ρ_{calc} [Mg/m^{-3}]	1.309	1.469	1.312	1.309
μ [mm^{-1}]	2.820	4.233	2.818	2.488
F(000)	1936	3640	1952	2208
crystal size [mm^3]	0.25 × 0.20 × 0.20	0.25 × 0.15 × 0.15	0.30 × 0.30 × 0.10	0.40 × 0.20 × 0.12
Θ limit [°]	2.22 to 27.47	2.71 to 60.00	1.55 to 25.00	1.56 to 21.00
index range (*h*, *k*, *l*)	−27, 28; −16, 18; −23, 23	−17,17; −26, 26; −25, 25	−16, 16; −20, 20; −23, 23	−15, 15; −18, 18; −19, 19
reflections collected	10253	63051	44786	33979
independent reflections	5368	12017	8233	5728
R(int)	0.0150	0.0792	0.0340	0.0411
completeness to Θ	99.9 (27.47)	99.9 (60.00)	99.7 (25.00)	100.0 (21.00)
max. and min. transmission	0.6024 and 0.5391	0.7522 and 0.5923	0.7658 and 0.4852	0.7545 and 0.4361
data/restraints/parameters	5368/0/232	12017/175/973	8233/28/489	5728/397/550
goodness-of-fit on F^2	1.104	1.088	1.014	1.147
R indices (final) [$I > 2\sigma(I)$]				
R_1	0.0197	0.0628	0.0177	0.0700
wR_1	0.0474	0.1705	0.0468	0.1778
R indices (all data)				
R_2	0.0213	0.0839	0.0267	0.0959
wR_2	0.0481	0.1812	0.0591	0.2262
Largest diff. peak and hole [$eÅ^{-3}$]	0.585 and −1.221	1.615 and −2.163	0.424 and −0.597	1.493 and −1.138

Table s3. Key crystallographic angles (°).

	6a[a]	**6b**(1)[b]	**6b**(2)[b]	**6c**[a]
P-Os-P	172.325(19)	176.96(8)	174.05(16)	174.66(2)
OC-Os-CO	90.8(8)	92.131(18)	91.8(4)	92.03(15)
X-Os-X[c]	92.4(13)	90.22(8)	89.86(14)	90.65(3)
Os-C-O	176(2)/179.6(2)	176.721(11)/178.047(11)	170.9(11)/174.6(11)	177.2(3)/178.9(2)
OC-Os-X_{trans}[c]	177.6(8)/179.63(8)	177.29(6)/177.83(5)	177.1(3)/179.5(3)	177.69(13)/178.04(8)
OC-Os-X_{cis}[c]	88.15(15)/89.0(8)	87.99(5)/89.74(6)	87.7(3)/90.6(3)	87.65(13)/89.73(8)
P-Os-CO	92.6(8)/94.13(7)	89.45(6)/92.41(5)	90.1(3)/93.8(3)	92.10(8)/93.63(12)
	87.9(8)/93.51(7)	89.06(6)/93.16(6)	91.7(3)/91.9(3)	87.85(12)/92.98(8)
P-Os-X[c]	86.186(19)/89.55(13)	88.38(7)/89.57(8)	87.69(15)/90.01(16)	86.00(2)/87.81(3)
	86.170(19)/90.03(13)	88.87(8)/89.01(7)	86.66(14)/88.08(15)	88.94(2)/90.56(3)
	7'a(1)[b]	**7'a**(2)[b]	**7b**	**7c**
P-Os-P	175.62(17)	175.52(17)	178.83(6)	175.07(3)
OC-Os-CO	91.9(10)	92.3(9)	94.0(3)	92.97(16)
X-Os-X[c]	91.83(7)	91.89(7)	88.88(2)	91.09(2)
Os-C-O	175(2)/176(2)	175(19)/175.2(2)	177.3(7)/177.3(6)	178.2(4)/178.6(4)
OC-Os-X_{trans}[c]	176.1(7)/177.4(7)	175.8(6)/177.0(6)	177.0(2)/177.6(2)	177.58(11)/178.05(11)
OC-Os-X_{cis}[c]	85.7(7)/90.6(7)	85.4(6)/90.4(7)	88.3(2)/88.7(2)	86.84(11)/89.14(12)
P-Os-CO	91.0(6)/91.5(6)	89.8(6)/93.1(6)	88.3(2)/90.2(2)	91.15(12)/93.73(11)
	90.3(6)/92.6(6)	91.1(6)/91.6(6)	91.0(2)/91.3(2)/	88.55(11)/93.10(12)
P-Os-X[c]	87.62(12)/92.11(12)	86.83(13)/88.10(13)	88.91(4)/91.34(4)	86.93(4)/87.41(3)
	86.75(13)/88.19(13)	87.62(12)/92.02(12)	89.01(4)/89.98(4)	88.84(4)/90.15(3)
	9a	**9a**-H^+ BAr_f^-	**11a**[d]	**12a**
P-Os-P	178.75(2)	168.76(7)	172.50(2)	175.05(17)
OC-Os-CO	118.44(6)/118.44(6)/123.11(12)	94.6(3)/96.8(3)/168.5(3)	93.2(3)/93.3(3)/173.5(4)	88.3(7)
X-Os-X[c]	-	-	91.9(3)/92.0(3)/176.2(4)	96.3(6)
Os-C-O	178.92/178.92/180.000(1)	175.4(7)/178.5(8)/179.7(8)	177.0(8)/179.2(8)/179.6(2)	173.2(15)/176.3(16)
OC-Os-X_{trans}[c]	-	173.6	178.6(4)/178.6(4)/179.57(9)	174.5(6)/176.6(7)
OC-Os-X_{cis}[c]	-	78.0/90.5	86.7(3)/86.8(3)/88.0(3)/88.2(3)	87.0(7)/88.4(6)
P-Os-CO	89.00(6)/90.40(6)/90.627(10)	89.3(2)/90.4(2)/95.5(2)	89.0(3)/90.8(3)/93.56(9)	88.4(5)/94.1(5)
	89.00(6)/90.40(6)/90.627(10)	87.8(3)/90.2(2)/95.5(2)	88.1(3)/91.2(3)/93.91(9)	90.6(5)/93.4(5)
P-Os-X[c]	-	88.4	86.03(8)/89.5(3)/90.6(2)	86.0(4)/89.2(4)
	-	80.8	86.50(8)/89.0(2)/91.3(3)	89.4(4)/89.4(4)

Table s3 continued.

	6a[a]	**6b**(1)[b]	**6b**(2)[b]	**6c**[a]
C^{e}-P-P-C^{e}	–25.25	50.23	–26.32	–28.97
C^{f}-P-P-C^{f}	–22.67	46.77	–20.16	–31.00
C^{g}-P-P-C^{g}	–23.09	48.04	–8.26	–26.88
C^{h}-P-Os-$\underline{C}$O(1)	–13.18/–11.26	10.45/37.30	12.92/–33.60	–12.92/–13.35
C^{h}-P-Os-$\underline{C}$O(2)	14.71/38.89	37.59/9.20	–16.27/8.23	12.69/–40.47
C^{h}-P-Os-X(1)[c]	–43.35/19.86	–19.08/69.90	39.90/–66.97	–46.31/16.66
C^{h}-P-Os-X(2)[c]	48.73/–72.19	71.76/–20.33	–52.13/43.89	44.49/–73.97
P1-C1-C2-C3[i]	–159.31/174.45/–154.95	–172.70/169.86/173.97	–169.17/–78.25/–168.34	164.71/171.72/171.52
C1-C2-C3-C4[i]	–71.29/174.87/173.66	176.97/–177.16/57.77	56.01/175.81/166.95	–173.92/174.35/61.00
C2-C3-C4-C5[i]	174.62/–69.59/–173.04	–174.34/63.20/61.14	169.89/–165.35/–177.73	70.33/–63.38/176.78
C3-C4-C5-C6[i]	–64.11/179.56/63.99	–179.67/61.26/–176.84	–157.57/176.71/71.20	73.69/–54.90/62.05
C4-C5-C6-C7[i]	–58.90/170.87/64.94	–52.07/–176.73/126.71	–37.92/–57.17/69.04	–175.89/–58.65/64.85
C5-C6-C7-C8[i]	–171.62/65.59/–167.53	–62.67/173.03/–143.91	–58.57/–72.99/–166.89	–173.44/–177.77/173.49
C6-C7-C8-C9[i]	179.40/–179.67/–175.02	173.27/–171.27/133.37	174.83/–175.54/87.98	–171.97/–60.05/69.49
C7-C8-C9-C10[i]	66.16/–172.76/–168.87	–179.30/179.64/–127.31	–175.95/174.66/–154.34	–172.73/–57.63/66.82
C8-C9-C10-C11[i]	172.60/–58.26/66.62	177.10/–69.00/–156.46	174.78/176.96/–127.14	–56.21/–176.15/–179.63
C9-C10-C11-C12[i]	–178.43/–66.56/63.70	–58.01/–69.21/–57.49	–161.05/–51.51/–73.55	–54.48/–173.27/–178.99
C10-C11-C12-C13[i]	–68.58/177.40/–169.45	–55.65/178.28/–151.86	45.88/–60.13/120.16	–64.22/179.41/–165.93
C11-C12-C13-C14[i]	173.89/–72.82/173.83	178.39/179.15/84.60	116.51/177.35/167.15	175.37/–179.19/–176.87
C12-C13-C14-P2[i]	–163.58/170.90/–154.67	-	-	-
C12-C13-C14-C15[i]	-	–176.83/57.14/69.22	–81.03/–175.87/78.95	–68.18/179.43/–173.22
C13-C14-C15-C16[i]	-	179.80/51.51/–163.39	–162.01/70.92/83.47	–176.63/–59.46/66.71
C14-C15-C16-P2[i]	-	–168.08/174.70/172.88	174.15/–159.86/172.63	-
C14-C15-C16-C17[i]	-	-	-	170.15/–58.99/63.86
C15-C16-C17-C18[i]	-	-	-	60.07/–179.57/–177.32
C16-C17-C18-P2[i]	-	-	-	–173.94/–176.59/169.50
anti segments	8/8/9	11/9/6	9/9/7	10/10/10
gauche segments	5/5/4	4/6/5	5/6/6	7/7/7

Table s3 continued.

	7'a(1)	**7'a**(2)	**7b**	**7c**
C^e-P-P-C^e	–19.77	–19.84	28.64	–29.86
C^f-P-P-C^f	–17.75^j	–17.42^j	26.98	–27.34
C^g-P-P-C^g	–24.35^j	–24.73^j	22.60	–26.83
C^h-P-Os-$\underline{C}$O(1)	89.51/–109.27	88.98/–108.81	37.54/–10.43	–15.58/–11.21
C^h-P-Os-$\underline{C}$O(2)	–178.52/158.78	–178.67/159.88	13.86/8.66	–40.43/13.42
C^h-P-Os-X(1)^c	3.37/–23.70	3.52/–23.70	73.29/–44.57	15.34/–45.91
C^h-P-Os-X(2)^c	–88.01/68.23	–88.28/68.42	–15.57/44.31	46.44/–73.21
P1-C1-C2-C3^i	169.59/–158.38/165.05^k	–171.95/–172.87/–155.16^k	–178.42/170.22/–177.74	169.99/169.97/175.50
C1-C2-C3-C4^i	163.84/174.50/171.92	–62.56/–65.49/–174.98	176.64/–72.19/72.21	171.52/–176.36/64.11
C2-C3-C4-C5^i	59.39/–156.45/60.25	–59.28/–63.10/–59.98	60.68/173.36/–168.79	–64.12/66.16/–175.74
C3-C4-C5-C6^i	71.63/30.96/53.54	–161.37/–162.30/–58.11	58.07/–70.37/–171.38	–49.79/69.63/62.86
C4-C5-C6-C7^i	176.17/118.04/–179.32	178.01/–176.46/–171.46	175.91/–70.02/–75.81	–57.54/–176.12/61.04
C5-C6-C7-C8^i	58.49/–153.93/162.08	74.51/78.72/–172.04	68.27/176.52/–179.57	–176.01/175.87/173.05
C6-C7-C8-C9^i	54.73/163.41/–49.07	–94.98/–172.17/59.06	174.95/–62.91/–81.88	–60.78/–172.64/67.08
C7-C8-C9-C10^i	–172.38/–70.51/–57.05	161.54/80.66/56.02	173.82/–170.16/–74.74	–60.56/–167.81/67.34
C8-C9-C10-C11^i	–169.65/–146.81/–157.63	–179.56/149.28/176.38	162.03/60.33/170.63	–177.24/–50.50/–177.43
C9-C10-C11-C12^i	–57.77/–174.74/–52.88	54.54/–91.37/73.73	173.62/51.42/170.42	–177.89/–57.20/–177.49
C10-C11-C12-C13^i	–58.90/–61.02/–53.97	61.56/–98.21/56.14	50.61/168.54/–175.09	–177.14/–64.13/–169.43
C11-C12-C13-C14^i	–173.16/–70.02/–56.34	171.47/177.50/166.31	60.08/163.50/–59.65	–176.27/–179.42/–172.88
C12-C13-C14-P2^i	155.55^l/–172.88/–170.69	165.75^l/–158.43/169.87	-	-
C12-C13-C14-C15^i	-	-	–167.63/59.43/–66.04	178.42/–67.53/–165.88
C13-C14-C15-C16^i	-	-	74.19/–178.84/174.91	–58.06/–177.95/69.18
C14-C15-C16-P2^i	-	-	178.38/167.05/178.11	-
C14-C15-C16-C17^i				–57.56/164.40/65.38
C15-C16-C17-C18^i				178.34/62.98/–178.17
C16-C17-C18-P2^i				–175.58/–174.04/165.67
anti segments	8/8/6	7/6/7	9/8/9	10/10/10
gauche segments	5/4/7	5/4/6	6/7/6	7/7/7

Table s3 continued.

	9a	**9a**-H$^+$ BAr$_f^-$	**11a**[d]	**12a**
C^e-P-P-C^e	–38.42	–0.11	–25.44	36.80
C^f-P-P-C^f	–37.98	–2.87	–21.55	37.54
C^g-P-P-C^g	–37.98	–3.71	–21.50	38.52
C^h-P-Os-C̲O(1)	–77.51/39.62	35.43/–39.06	–34.79/12.28//15.38/37.90	63.31/–25.18
C^h-P-Os-C̲O(2)	–78.82/40.94	14.78/–14.94	–11.03/–13.59	32.33/5.52
C^h-P-Os-C̲O(3)	–77.51/39.62	–10.39/7.44	-	-
C^h-P-Os-X(1)^c	-	–54.89/50.94	20.57/–43.01//–39.94/17.46	–25.19/63.17
C^h-P-Os-X(2)^c	-	-	–71.29/48.94	–1.76/18.32
P1-C1-C2-C3^i	175.14/–172.73/–163.26	178.09/–175.83/–175.43	–163.78/–153.51/169.64	–178.94/177.25/167.53
C1-C2-C3-C4^i	168.27/58.21/174.02	168.27/–97.51/176.63	175.03/173.97/–73.30	–159.19/–150.17/160.86
C2-C3-C4-C5^i	62.01/158.90/–178.86	57.90/–51.53/44.72	–67.23/–169.36/177.19	–52.05/–50.65/48.60
C3-C4-C5-C6^i	173.03/–72.72/–177.71	59.02/151.04/176.63	–179.24/64.00/–67.29	63.82/–179.46/74.25
C4-C5-C6-C7^i	58.27/–62.81/–58.77	171.56/169.06/177.69	173.83/66.47/–58.45	–76.47/–64.83/163.37
C5-C6-C7-C8^i	62.18/–174.03/–61.71	–177.60/64.96/88.22	65.68/–169.16/–171.12	–60.82/–56.52/90.59
C6-C7-C8-C9^i	178.18/178.18/–174.98	–69.36/76.61/–166.75	179.51/–175.34/–179.54	175.08/160.69/87.60
C7-C8-C9-C10^i	–174.03/62.18/–61.71	–61.69/–177.14/72.38	–170.45/–167.11/64.76	–174.45/173.82/–168.15
C8-C9-C10-C11^i	–62.81/58.27/–58.77	–166.70/–170.42/62.77	–58.89/64.45/171.93	168.06/130.16/167.61
C9-C10-C11-C12^i	–72.72/173.03/–177.71	–176.95/–64.53/173.65	–64.25/63.66/178.84	–73.73/–167.14/–171.99
C10-C11-C12-C13^i	158.90/62.01/–178.86	74.35/–69.81/69.59	174.51/–172.76/–68.10	–71.63/110.34/74.40
C11-C12-C13-C14^i	58.21/168.27/174.02	89.02/177.60/154.93	–71.07/174.32/175.27	168.43/55.92/77.62
C12-C13-C14-P2^i	–172.73/175.14/163.26	–171.15/–170.34/175.38	174.57/–154.24/–159.71	–165.73/–175.04/178.71
anti segments	7/7/8	7/7/8	8/9/8	7/7/7
gauche segments	6/5/5	6/5/5	5/4/5	6/4/5

[a]Values for the dominant $Os(CO)_2(Cl)_2$ rotamer (**6a**,**c**). [b]Values for the two independent molecules of **6b** and **7'a** in the unit cell. [c]X = Cl, Br, H, CH_3, or C_{ipso}/C_{para}/H_{para}. [d]One CO and one methyl ligand are disordered (50:50 occupancy ratio). Hence, values are given for each conformation.[e]First macrocyclic methylene chain that is located between two X ligands (for **6a-c**, **7b**,**c**, **7'a**, and **12a**), or along the C_2 axis (**9a**), or opposite to the hydride ligand (**9a**-H$^+$ BAr$_f^-$), or opposite to the non-disordered methyl ligand (C4, **11a**). See also Figure 13. [f]Second macrocyclic methylene chain. [g]Third macrocyclic methylene chain. [h]Torsion angles between the ligand and the nearest macrocyclic chain (first carbon atom of macrocycle). See also Figure 13. [i]The numbering of the carbon atoms does not represent the numbering in the CIF file. For ease of comparison, the carbon atoms of each chain are numbered from C1 to C14 or C16 or C18. See also Figure 13. [j]These values represent the smallest torsion angles between the two *trans* disposed phosphacycles. [k]This value represents the torsion angle P2-C1-C2-C3 rather than P1-C1-C2-C3 (the angles in this column are within one phosphacycle). [l]This value represents the torsion angle C11-C12-C13-P1 rather than C11-C12-C13-P2 (the angles in this column are within one phosphacycle).

■ REFERENCES

(s1) DSC and TGA data were treated as recommended by Cammenga, H. K.; Epple, M. *Angew. Chem., Int. Ed.* **1995**, *34*, 1171-1187; *Angew. Chem.* **1995**, *107*, 1284-1301. The T_e values best represent the temperature of the phase transition or exotherm.

(s2) (a) Dwyer, F. P.; Hogarth, J. W. *Inorg Synth.* **1957**, *5*, 204-206. (b) Dwyer, F. P.; Hogarth, J. W. *Inorg Synth.* **1957**, *5*, 206-207.

(s3) Nawara-Hultzsch, A. J.; Skopek, K.; Shima, T.; Barbasiewicz, M.; Hess, G. D.; Skaper, D.; Gladysz, J. A. *Z. Naturforsch.* **2010**, *65b*, 414-424.

(s4) Bergbreiter, D. E.; Killough, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 2126-2134.

(s5) (a) Taube, R.; Wache, S. *J. Organomet. Chem.* **1992**, *428*, 431-442. (b) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920-3922.

(s6) The ^{1}H and $^{13}C\{^{1}H\}$ NMR assignments were made by analogy to those of **3a**.

(s7) The *J* values given for the virtual triplets represent the *apparent* couplings between adjacent peaks, and not the mathematically rigorous coupling constants. The indices ^{n}J represent the number of bonds between the atom of interest and the *nearest* phosphorus atom. Hersh, W. H. *J. Chem. Educ.* **1997**, *74*, 1485-1488.

(s8) These two signals overlap, such that one of the outer peaks of the virtual triplet is obscured. The coupling constant is derived from the two peaks of the virtual triplet that are visible.

(s9) The most intense peak of the isotope envelope is given; *m*/*z* (relative intensity, %). Matrices used: DHB (2,5-dihydroxybenzoic acid), 3-NBA (3-nitrobenzyl alcohol), SIN (sinapinic acid), THAP (2,4,6-trihydroxyacetophenone).

(s10) The ^{1}H and $^{13}C\{^{1}H\}$ NMR assignments were made by $^{1}H,^{1}H$ COSY and ^{1}H, $^{13}C\{^{1}H\}$ COSY (gHMQC) experiments.

(s11) The sample gradually darkened without melting above this temperature

(s12) The ^{1}H and $^{13}C\{^{1}H\}$ NMR assignments were made by analogy to those of **7a**.

(s13) The ^{1}H and $^{13}C\{^{1}H\}$ NMR assignments were made by analogy to those of **7'b**.

(s14) Methylene carbon signals that are doubled in intensity are assigned to the phosphacycles $P(CH_2)_{n-1}CH_2$ and denoted by primes.

(s15) These two signals overlap, such that the outer peaks of the virtual triplet are visible on each side of a broadened central peak.

(s16) These two virtual triplets overlap, but at least two peaks of each are distinguishable, allowing the coupling constants to be derived.

(s17) This signal deviates by +2 mass units from that expected for the given ion. However, the isotope envelope is otherwise in good agreement with that calculated.

(s18) These two virtual triplets overlap, but all six peaks are distinguishable, allowing the coupling constants to be derived.

(s19) The ^{1}H and ^{13}C{^{1}H} NMR assignments were made by analogy to **9a**.

(s20) The ^{1}H and ^{13}C{^{1}H} NMR assignments were made by analogy to those of **9a** and $[H(OEt_2)_2]^+$ BAr_f^-.

(s21) The ^{1}H and ^{13}C{^{1}H} NMR assignments were made by ^{1}H,^{1}H COSY and ^{1}H, ^{13}C{^{1}H} COSY (gHMQC) experiments and by analogy to those of $[H(OEt_2)_2]^+$ BAr_f^-.

(s22) The ^{1}H and ^{13}C{^{1}H} NMR assignments were made by analogy to those of *mer,trans*-Re-$(CO)_3(Ph)(P((CH_2)_{14})_3P)$ as described in Heß, G. D. Doctoral Dissertation, Universität Erlangen-Nürnberg, 2010.

(s23) Unprimed carbon atoms are assigned to the unique methylene chain (located between the two phenyl ligands in the solid state; see Figure 12), and primed carbon atoms (doubled in intensity) to the other two symmetry equivalent chains.

(s24) Song, L.; Trogler, W. C. *J. Am. Chem. Soc.* **1992**, *114*, 3355-3361.

(s25) CCDC 1446694 (**6a**), 1446695 (**6b**), 1446696 (**6c**), 1446697 (**7'a**), 1446698 (**7b**), 1446699 (**7c**), 1446700 (**9a**), 1446701 (**9a**-H^+ BAr_f^-), 1446702 (**11a**), and 1446703 (**12a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(s26) (a) Collect. Data collection software, Nonius B.V., 1998. (b) Scalepack. Data processing software: Otwinowski, Z.; Minor, W. in *Methods in Enzymology* **1997**, *276* (Macromolecular Crystallography, Part A), 307-326.

(s27) SHELXTL, Sheldrick, G.M. *Acta Cryst.* **2008**, *A64*, 112-122.

(s28) Cromer, D. T.; Waber, J. T. in *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974.

(s29) Sheldrick, G. M.; Cell Now, version 2008/1. Program for Obtaining Unit Cell Constants from Single Crystal Data, University of Göttingen, Germany, 2008.

(s30) Bruker SAINT, version 7, 2007. Program for Data Integration from Area Detector Frames, Bruker-Nonius Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373, USA.

(s31) Sheldrick, G. M.; SADABS, version 2008/1. Program for Absorption Correction for Data from Area Detector Frames, University of Göttingen, Germany, 2008.

(s32) Barbour, L. J. *J. Supramol. Chem.* **2001**, *1*, 189-191.

(s33) APEX 2, Program for Data Collection on Area Detectors, BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373, USA.

(s34) Spek, A. L.; Platon. A Multipurpose Crystallographic Tool, *J. Appl. Cryst.* **2003**, 36, 7-13.