General. Most experimental and instrumental procedures were analogous to those in previous papers in this series.[3] Reactions of phosphorus- or metal-containing educts were conducted under dry N_2 atmospheres. Solvents were treated as follows: THF, ether, benzene, hexane, toluene, and xylene, distilled from Na/benzophenone; CH_2Cl_2 and DMF (99%, Fluka) distilled from CaH_2; $CHCl_3$ and C_6H_5Cl distilled from P_2O_5; $ClCH_2CH_2Cl$ (99%, Fluka) and ethanol, used as received. The reagents NaC≡CH (Acros, 18% in xylene/light oil, 95% purity), CH_3I (99%, Riedel-de Haën), $HPPh_2$ (Aldrich), and $KPPh_2$ (Aldrich, 0.5 M in THF) were used as received. The *n*-BuLi (Aldrich, 2.1 M in hexane) was standardized before use,[S1] and $Br(CH_2)_6Br$ (96%, EGA-Chemie) was distilled.

$Br(CH_2)_6C{\equiv}CH$ (2). A three neck flask was charged with NaC≡CH (18% in xylene/light oil, 95% purity; 9.152 g, 32.59 mmol) and DMF/xylene (100 mL, 37.5:62.5 v/v), and fitted with a dropping funnel and a condenser. The mixture was heated to 40 °C and $Br(CH_2)_6Br$ (5.010 mL, 7.946 g, 33 mmol) was added over a period of 20 min. After 12 h, the mixture was filtered. The filtrate was fractionally distilled to give **2**[12a] (bp ca. 70 °C, 1.3×10^{-3} mbar) as a colorless liquid (4.040 g, 21.4 mmol, 66%).[S2]

NMR (δ, $CDCl_3$): ^{1}H 3.41 (t, $^3J_{HH}$ = 6.6, BrCH_2), 2.22-2.17 (td, $^3J_{HH}$ = 6.9, $^4J_{HH}$ = 2.7, $CH_2C{\equiv}$), 1.95 (t, $^4J_{HH}$ = 2.7, ≡C*H*), 1.92-1.82 (m, CH_2), 1.60-1.40 (m, 3CH_2); $^{13}C\{^1H\}$ 84.6 (s, *C*≡CH), 68.5 (s, C≡*C*H), 34.0 (s, BrCH_2), 32.8 (s, BrCH_2CH_2), 28.4, 28.0, 27.5 (3s, CH_2CH_2-$CH_2CH_2C{\equiv}$), 18.5 (s, $CH_2C{\equiv}C$).

IR (cm^{-1}, CH_2Cl_2) 3306 (w, $\nu_{\equiv CH}$), 2116 (s, $\nu_{C\equiv C}$).

$Br(CH_2)_6C{\equiv}CCH_3$ (3). A Schlenk flask was charged with $Br(CH_2)_6C{\equiv}CH$ (0.943 g, 4.99 mmol) and THF (20 mL), and cooled to –45 °C (CO_2/isopropanol). Then *n*-BuLi (2.1 M in hexane; 2.5 mL, 5.3 mmol) was added with stirring. After 10 min, the –45 °C bath was replaced by a 0 °C bath. After another 10 min, CH_3I (3.0 mL, 48 mmol) was added, and the 0 °C bath was removed. After 3 h, the solution was passed through a silica gel plug (2 × 3 cm). The solvent was removed from the filtrate by oil pump vacuum. Vacuum distillation gave **3**[12b] (bp ca. 95 °C, 1.3×10^{-3} mbar) as a colorless liquid (0.721 g, 3.55 mmol, 71%).

NMR (δ, $CDCl_3$): ^{1}H 3.43 (t, $^3J_{HH}$ = 8.3, BrCH_2), 2.16-2.11 (m, $CH_2C{\equiv}C$), 1.89-1.87 (m, CH_2), 1.78 (t, $^5J_{HH}$ = 2.9, CH_3), 1.59-1.39 (m, 3CH_2); $^{13}C\{^1H\}$ 79.0 (s, $CH_2C{\equiv}C$), 75.5 (s,

C≡*C*CH$_3$), 33.8 (s, Br*C*H$_2$), 32.7 (s, BrCH$_2$*C*H$_2$), 28.8, 27.9, 27.7 (3 s, *C*H$_2$*C*H$_2$*C*H$_2$CH$_2$C≡), 18.6 (s, *C*H$_2$C≡C), 3.4 (s, C≡C*C*H$_3$).

Ph$_2$P(CH$_2$)$_6$C≡CCH$_3$ (4). A. A Schlenk flask was charged with HPPh$_2$ (2.264 g, 12.16 mmol) and THF (30 mL), and cooled to 0 °C. Then *n*-BuLi (2.1 M in hexanes; 5.8 mL, 12.2 mmol) was added dropwise with stirring. The colorless solution turned orange-red. After 10 min, a solution of **3** (2.673 g, 13.16 mmol) in THF (5 mL) was added. The mixture turned light yellow. After 10 min, the cold bath was removed. After 3 h, the solvent was removed by oil pump vacuum. Benzene (30 mL) was added, and the mixture was passed through a silica gel plug (2 × 2 cm). The solvent was removed from the filtrate by oil pump vacuum and the residue chromatographed (silica gel column, 1:1 v/v CH$_2$Cl$_2$/hexane) to give **4** as a colorless oil (3.041 g, 9.860 mmol, 81%) that was stable in air on the time scale of hours.

NMR (δ, CDCl$_3$): ^{1}H 7.47-7.32 (m, 2Ph), 2.14-2.02 (m, PC*H*$_2$ and C*H*$_2$C≡C), 1.78 (t, $^5J_{HH}$ = 3.2, C*H*$_3$), 1.52-1.36 (m, 4C*H*$_2$); ^{13}C{^{1}H} 139.2 (d, $^1J_{CP}$ = 12.6, *i*-Ph), 132.9 (d, $^2J_{CP}$ = 18.1, *o*-Ph), 128.6 (d, $^3J_{CP}$ = 9.1, *m*-Ph), 128.6 (s, *p*-Ph), 79.5 (s, *C*≡CCH$_3$), 75.6 (s, C≡*C*CH$_3$), 31.0 (d, $^3J_{CP}$ = 12.6, PCH$_2$CH$_2$*C*H$_2$),[S3] 29.1, 28.7 (2 s, *C*H$_2$*C*H$_2$CH$_2$C≡C), 28.2 (d, $^1J_{CP}$ = 11.1, P*C*H$_2$),[S3] 26.1 (d, $^2J_{CP}$ = 16.1, PCH$_2$*C*H$_2$),[S3] 18.9 (s, CH$_2$*C*H$_2$C≡C), 3.7 (s, C≡C*C*H$_3$); ^{31}P {^{1}H} −15.6 (s).

B. A Schlenk flask was charged with **3** (1.328 g, 6.54 mmol) and THF (22 mL) and cooled to 0 °C. Then KPPh$_2$ (0.5 M in THF; 13 mL, 6.5 mmol) was added dropwise with stirring over 15 min. A precipitate formed, and near the end of the addition the mixture turned red. After 30 min, the cold bath was removed. After 30 min, the solvent was removed by oil pump vacuum, giving a white solid suspended in an oil. The residue was extracted with hexanes (3 × 15 mL). The extract was filtered, and the solvent removed by rotary evaporation. The residue was vacuum distilled (150 °C, 10^{-2} mbar) to give **4** as a viscous colorless liquid (1.111 g, 3.60 mmol, 55%). Calcd for C$_{21}$H$_{25}$P: C, 81.79; H, 8.17. Found: C, 81.41; H, 8.21.

NMR (δ, CDCl$_3$), ^{1}H 7.52-7.27 (m, 2Ph), 2.11-2.03 (m, PC*H*$_2$ and C*H*$_2$C≡C), 1.78 (s, C*H*$_3$), 1.45-1.27 (m, 4C*H*$_2$); ^{31}P{^{1}H} −15.4 (s).

IR (cm^{-1}, liquid film) 3073 (w), 3053 (w), 2930 (m), 2856 (m), 1482 (s), 1432 (s), 1096 (m), 1027 (m), 737 (s), 695 (s).

***fac*-(CO)$_3$Re(Br)(Ph$_2$P(CH$_2$)$_6$C≡CCH$_3$)$_2$ (5)**. A Schlenk flask was charged with

$(CO)_5Re(Br)$ (0.289 g, 0.713 mmol),[S4] **4** (0.440 g, 1.427 mmol), and $CHCl_3$ (12 mL), and fitted with a condenser with a nitrogen inlet/bubbler on top. The mixture was refluxed (46 h) under a continuous nitrogen flow.[S5] The solvent was removed by oil pump vacuum. The residue was chromatographed (12 × 2.5 cm column; neutral Al_2O_3, 1:1 v/v CH_2Cl_2/hexanes). The solvent was removed from the product fraction by oil pump vacuum to give **5** as a colorless oil (0.344 g, 0.356 mmol, 50%), which solidified after several days. Calcd for $C_{45}H_{50}BrO_3P_2Re$: C, 55.90; H, 5.21. Found: C, 55.20; H, 5.18.

NMR (δ, $CDCl_3$): ^{1}H 7.43-7.28 (m, 4Ph), 2.63-2.58 (m, 2PC*H*H'), 2.08-2.04 (m, 2CH_2C≡), 1.92 (m, 2PCH*H'*), 1.78-1.77 (t, $^5J_{HH}$ = 5.0, 2CH_3), 1.36-1.30 (m, 2CH_2), 1.20 (m, 4CH_2), 1.00-0.99 (m, 2CH_2); $^{13}C\{^1H\}$ 189.8 (br s, *C*O), 189.2 (br s, 2*C*O), 133.5-131.8 (complex, *i*-Ph), 133.1 (virtual t,[S6] J_{CP} = 4.5, o-Ph), 132.8 (virtual t, J_{CP} = 4.7, *o*-Ph'), 130.0 (s, *p*-Ph), 128.2 (m, *m*-Ph), 79.1 (s, *C*≡CCH$_3$), 75.4 (s, C≡*C*CH$_3$), 30.4 (virtual t, J_{CP} = 5.9, *C*H$_2$), 28.8 (s, *C*H$_2$), 28.2 (s, *C*H$_2$), 26.3 (virtual t, J_{CP} = 13.4, *C*H$_2$), 23.8 (br s, *C*H$_2$), 18.6 (s, ≡C*C*H$_2$), 3.5 (s, *C*H$_3$); $^{31}P\{^1H\}$ –8.5 (s).

IR (cm^{-1}, powder film) 3057 (w), 2934 (m), 2856 (m), 2104 (m), 2026 (s, ν_{CO}), 1999 (sh), 1938 (s, ν_{CO}), 1895 (s, ν_{CO}), 1482 (m), 1436 (m), 1096 (m), 741 (s), 695 (s); (cm^{-1}, $CHCl_3$, partial) 2033 (s, ν_{CO}), 1952 (s, ν_{CO}), 1906 (s, ν_{CO}). MS (FAB, 3-NBA, *m/z*) 966 (**5**$^+$, <5%), 910 ([**5**-2CO]$^+$, 20%), 987 ([**5**-Br]$^+$, 30%), 600 ([**5**-Ph_2PR-2CO]$^+$, 20%), 574 ([**5**-Ph_2PR-3CO]$^+$, 40%), 549 ([**5**-Ph_2PR-Br-CO]$^+$, 35%), 309 (Ph_2PR^+, 100%).

(η^5-C_5H_5)Ru(Cl)($Ph_2P(CH_2)_6C{\equiv}CCH_3)_2$ (6). A Schlenk flask was charged with (η^5-C_5H_5)Ru(Cl)(PPh_3)$_2$ (0.235 g, 0.324 mmol),[S7] **4** (0.250 g, 0.811 mmol) and toluene (2.5 mL), and fitted with a condenser with a nitrogen inlet/bubbler on top. The orange suspension was refluxed (18 h) under a continuous nitrogen flow. The solvent was removed by oil pump vacuum. The residue was chromatographed using a Chromatotron® (2 cm silica gel plate, 1:1 v/v Et_2O/hexanes). The solvent was removed from the product fraction by oil pump vacuum to yield **6** as an orange oil (0.080 g, 0.098 mmol, 30%). Calcd for $C_{47}H_{55}ClP_2Ru$: C, 68.98; H, 6.77. Found: C, 69.07; H, 6.85.

NMR (δ, $CDCl_3$): ^{1}H 7.40-7.18 (m, 4Ph), 4.19 (s, C_5H_5), 2.54-2.48 (m, 2PC*H*H'), 2.07-2.03 (m, 2CH_2C≡), 1.77 (t, $^5J_{HH}$ = 5.0, 2CH_3), 1.49-1.47 (m, 2PCH*H'*), 1.36-1.30 (m, 2CH_2); 1.18-1.05 (m, 6CH_2); $^{13}C\{^1H\}$ 138.8-138.4 (complex, *i*-Ph), 132.8 (virtual t,[S6] J_{CP} = 4.8, *o*-Ph), 132.1

(virtual t, J_{CP} = 4.2, *o*-Ph'), 128.8 (s, *p*-Ph), 128.6 (s, *p*-Ph'), 127.9 (virtual t, J_{CP} = 4.0, *m*-Ph), 127.5 (virtual t, J_{CP} = 4.4, *m*-Ph'), 79.9 (s, C_5H_5), 79.3 (s, $C{\equiv}CCH_3$), 75.3 (s, $C{\equiv}CCH_3$), 30.7 (virtual t, J_{CP} = 5.7, CH_2), 28.9 (s, CH_2), 28.4 (s, CH_2), 26.5 (m, CH_2), 24.5 (br s, CH_2), 18.6 (s, ${\equiv}CCH_2$), 3.5 (s, CH_3); $^{31}P\{^1H\}$ 37.5 (s).

IR (cm^{-1}, powder film) 3049 (w), 2922 (m), 2856 (m), 1432 (m), 1092 (m). MS (FAB, 3-NBA, *m/z*) 818 (**6**$^+$, 100%), 783 ([**6**-Cl]$^+$, 45%), 510 ([**6**-Ph_2PR]$^+$, 75%), 473 ([**6**-Ph_2PR-Cl]$^+$, 85%), 309 (Ph_2PR^+, 95%).

***trans*-(Cl)(C_6F_5)Pt($Ph_2P(CH_2)_6C{\equiv}CCH_3$)$_2$ (7).** A Schlenk flask was charged with [Pt(μ-Cl)(C_6F_5)(SR_2)]$_2$ (0.394 g, 0.405 mmol; SR_2 = tetrahydrothiophene),[S8] **4** (0.500 g, 1.621 mmol) and CH_2Cl_2 (23 mL). The mixture was stirred (16 h) and the solvent was removed by oil pump vacuum. The residue was chromatographed (10 × 2.5 cm column; neutral Al_2O_3, 1:1 v/v CH_2Cl_2/hexanes). The solvent was removed from the product fraction by oil pump vacuum to give **7** as a colorless oil (0.444 g, 0.438 mmol, 54%), which solidified after several days. Calcd for $C_{48}H_{50}ClF_5PPt$: C, 56.84; H, 4.97. Found: C, 56.96; H, 5.10.

NMR (δ, $CDCl_3$): ^1H 7.45-7.41 (m, 8 H of 4Ph), 7.28-7.18 (m, 12 H of 4Ph), 2.53-2.52 (m, $2PCH_2$), 2.06-2.05 (m, $2CH_2C{\equiv}$), 1.85 (m, $2PCH_2CH_2$), 1.72 (t, $^5J_{HH}$ = 5.0, $2CH_3$), 1.44-1.30 (m, $6CH_2$); $^{13}C\{^1H\}$[S9] 133.0 (virtual t,[S6] J_{CP} = 6, *o*-Ph), 130.8 (virtual t, J_{CP} = 26, *i*-Ph), 130.2 (s, *p*-Ph), 128.0 (virtual t, J_{CP} = 6, *m*-Ph), 79.2 (s, $C{\equiv}CCH_3$), 75.5 (s, $C{\equiv}CCH_3$), 30.9 (virtual t, J_{CP} = 7, CH_2), 28.8 (s, CH_2), 28.5 (s, CH_2), 25.9 (virtual t, J_{CP} = 17, CH_2), 25.5 (s, CH_2), 18.7 (s, CH_2) 3.5 (s, CH_3); $^{31}P\{^1H\}$ 16.3 (s, $^1J_{PPt}$ = 2655).[S10]

IR (cm^{-1}, powder film) 3057 (w), 2934 (m), 2856 (m), 1502 (s), 1459 (s), 1436 (s), 1100 (m), 1058 (s), 953 (s), 807 (m), 737 (s), 691 (s). MS (FAB, 3-NBA, *m/z*) 1013 (**7**$^+$, 15%), 978 ([7-Cl]$^+$, 80%), 810 ([**7**-Cl-C_6F_5]$^+$, 20%), 501 ([**7**-Cl-C_6F_5-Ph_2PR]$^+$, 100%).

***fac*-$(CO)_3$Re(Br)($Ph_2P(CH_2)_6C{\equiv}C(CH_2)_6PPh_2$) (8).** A Schlenk flask was charged with **5** (0.052 g, 0.054 mmol), chlorobenzene (5.9 mL; the resulting solution is 0.022 M in **5**) and ca. half of the catalyst (*t*-BuO)$_3$W≡(C-*t*-Bu) (**1**; 0.004 g, 0.008 mmol, 15 mol%).[10] A nitrogen stream was bubbled through the solution, which was stirred at 80 °C. After 1 h, the remaining catalyst was added. After 1 h, the solvent was removed by oil pump vacuum. A ^{31}P NMR spectrum showed ca. 75% conversion. The residue was extracted with CH_2Cl_2/hexanes (1:1 v/v). The extract was filtered

through neutral Al_2O_3 (2.5 × 4 cm pad, 1:1 v/v CH_2Cl_2/hexanes). The solvent was removed by rotary evaporation and oil pump vacuum. The residue was dissolved in a minimum of CH_2Cl_2, layered with ethanol, and stored at –18°C. After 4 days, the white crystals were collected by filtration and dried by oil pump vacuum (losing crystallinity) to give **8** as a white powder (0.023 g, 0.025 mmol, 47%). Calcd for $C_{41}H_{44}BrO_3P_2Re$: C, 53.95; H, 4.86. Found: C, 54.14; H, 5.06.

NMR (δ, $CDCl_3$): ^{1}H 7.80-7.70 (m, 4 H of 4Ph), 7.37-7.28 (m, 16 H of 4Ph), 2.86-2.82 (m, 2PC*H*H'), 2.25-2.17 (m, 2PCH*H'* and 2CH_2CH≡), 1.56-1.25 (m, 8CH_2); ^{13}C{^{1}H} 189.7 (br s, *C*O), 189.4 (br s, 2*C*O), 134-132.5 (complex, *i*-Ph), 133.0 (virtual t,[S6] J_{CP} = 4.5, *o*-Ph), 132.6 (virtual t, J_{CP} = 4.6, *o*-Ph'), 129.91 (s, *p*-Ph), 129.86 (s, *p*-Ph'), 128.5 (virtual t, J_{CP} = 4.5 *m*-Ph), 128.1 (virtual t, J_{CP} = 4.7 *m*-Ph'), 80.5 (s, *C*≡), 30.2 (virtual t, J_{CP} = 6.0, *C*H_2), 28.7 (s, *C*H_2), 27.7 (s, *C*H_2), 25.6 (virtual t, J_{CP} = 12.1, *C*H_2), 24.2 (br s, *C*H_2), 18.6 (s, ≡*C*CH_2); ^{31}P{^{1}H} –8.3 (s).

IR (cm^{-1}, powder film) 3053 (w), 2926 (m), 2856 (m), 2023 (s, ν_{CO}), 1949 (sh), 1926 (s, ν_{CO}), 1876 (s, ν_{CO}), 1482 (m), 1436 (m), 1096 (m), 741(s), 695 (s). MS (FAB, 3-NBA, *m/z*) 912 (**8**$^+$, 40%), 856 ([**8**-2CO]$^+$, 65%), 833 ([**8**-Br]$^+$, 100%).

(η^5-C_5H_5)Ru(Cl)($Ph_2P(CH_2)_6C{\equiv}C(CH_2)_6PPh_2$) (9). A Schlenk flask was charged with **6** (0.227 g, 0.277 mmol), chlorobenzene (12.5 mL; the resulting solution is 0.022 M in **6**), and ca. half of the catalyst **1** (0.013 g, 0.028 mmol, 10 mol%).[10] The solution was stirred at 80 °C.[S11] After 1 h, the remaining catalyst was added. After 1 h, the solvent was removed by oil pump vacuum. A ^{31}P NMR spectrum showed ca. 70% conversion. The residue was extracted with Et_2O/hexanes (1:1 v/v). The extract was chromatographed (10 × 2.5 cm column; neutral Al_2O_3, 1:1 v/v hexanes/Et_2O). The product fractions were concentrated to ca. 10 mL and stored at –18 °C (16 h). The precipitate was collected by filtration and dried by oil pump vacuum to give **9** as an orange powder (0.111 g, 0.145 mmol, 52%). Calcd for $C_{43}H_{49}ClP_2Ru$: C, 67.57; H, 6.46. Found: C, 66.74; H, 6.62.[S12]

NMR (δ, $CDCl_3$): ^{1}H 7.76-7.74 (m, 4 H of 4Ph), 7.34-7.32 (m, 6 H of 4Ph), 7.31-7.28 (m, 2H of 4Ph), 7.13-7.10 (m, 4H of 4Ph), 6.92 (m, 4H of 4Ph), 4.07 (s, C_5H_5), 2.95-2.88 (m, 2PC*H*H'), 2.20 (m, 2CH_2C≡), 1.97 (m, 2PCH*H'*), 1.64-1.18 (m, 8CH_2); ^{13}C{^{1}H} 139.8-139.4 (complex, *i*-Ph), 137.1-136.7 (complex, *i*-Ph'), 133.0 (virtual t, J_{CP} = 5.0, *o*-Ph), 131.3 (virtual t,[S6] J_{CP} = 4.6, *o*-Ph'), 128.7 (s, *p*-Ph), 128.2 (s, *p*-Ph'), 128.0 (virtual t, J_{CP} = 4.2, *m*-Ph), 127.4 (virtual t, J_{CP} = 4.7, *m*-Ph'), 81.0 (s, C_5H_5), 80.3 (s, *C*≡), 30.5 (virtual t, J_{CP} = 5.2, *C*H_2), 29.1 (s, *C*H_2), 27.5 (s, *C*H_2), 25.4

(m, CH_2), 25.0 (virtual t, J_{CP} = 9.9, CH_2), 18.3 (s, $\equiv CCH_2$); $^{31}P\{^1H\}$ 40.4 (s).

IR (cm^{-1}, powder film) 3053 (w), 2930 (m), 2856 (m), 1482 (m), 1432 (m), 1092 (m). MS (FAB, 3-NBA, *m/z*) 764 (**9**$^+$, 100%), 729 ([**9**-Cl]$^+$, 60%).

***trans*-(Cl)(C_6F_5)Pt($PPh_2(CH_2)_6C\equiv C(CH_2)_6PPh_2$) (10)**. A Schlenk flask was charged with **7** (0.210 g, 0.207 mmol), chlorobenzene (10.0 mL; the resulting solution is 0.021 M in **7**), and ca. half of the catalyst **1** (0.016 g, 0.031 mmol, 15 mol%).[10] A nitrogen stream was bubbled through the solution, which was stirred at 80 °C. After 1 h, the remaining catalyst was added. After 1 h, the solvent was removed by oil pump vacuum. A ^{31}P NMR spectrum showed ca. 90% conversion. The tan powder was extracted with CH_2Cl_2. The extract was chromatographed (12 × 2.5 cm column; neutral Al_2O_3; 1:1 v/v CH_2Cl_2/hexanes). The solvent was removed by rotary evaporation and oil pump vacuum to give **10** as a white powder (0.117 g, 0.122 mmol, 59%). Calcd for $C_{44}H_{44}ClF_5P_2Pt$: C 55.03, H 4.62; found: C 54.76, H 4.82.

NMR (δ, $CDCl_3$): ^1H 7.49-7.44 (m, 8 H of 4Ph), 7.32-7.21 (m, 12 H of 4Ph), 2.70-2.66 (m, $2PCH_2$), 2.34-2.33 (t, $^3J_{HH}$ = 11, $2CH_2C\equiv$), 2.23 (m, $2PCH_2CH_2$), 1.77-1.70 (m, $2PCH_2CH_2CH_2$), 1.68-1.25 (m, $4CH_2$); $^{13}C\{^1H\}$ 145.0 (dm, $^1J_{CF}$ = 210 Hz, *o*-C_6F_5), 136.0 (dm, $^1J_{CF}$ = 237 Hz, *m/p*-C_6F_5), 132.7 (virtual t,[S6] J_{CP} = 5.8, *o*-Ph), 131.8 (virtual t, J_{CP} = 27.5, *i*-Ph), 130.1 (s, *p*-Ph), 128.0 (virtual t, J_{CP} = 5.5, *m*-Ph), 80.7 (s, $C\equiv$), 31.7 (virtual t, J_{CP} = 8.5, CH_2), 28.9 (s, CH_2), 28.6 (s, CH_2), 27.4 (s, CH_2), 26.9 (virtual t, J_{CP} = 17.4, CH_2), 18.7 (s, CH_2); $^{31}P\{^1H\}$ 18.1 (s, $^1J_{PPt}$ = 2683).[S10]

IR (cm^{-1}, powder film) 3057 (w), 2934 (m), 2856 (m), 1502 (s), 1459 (s), 1436 (s), 1100 (m), 1058 (s), 1023 (m), 953 (s), 803 (m), 737 (s), 691 (s). MS (FAB, 3-NBA, *m/z*) 960 (**10**$^+$, <1%), 924 ([**10**-Cl]$^+$, 100%), 755 ([**10**-Cl-C_6F_5]$^+$, 95%).

***trans*-(Cl)(C_6F_5)Pt($PPh_2(CH_2)_{14}PPh_2$) (11)**.[1] A Schlenk flask was charged with **10** (0.045 g, 0.0562 mmol), 10% Pd/C (0.006 g, 0.0056 mmol Pd), $ClCH_2CH_2Cl$ (3 mL), and ethanol (3 mL), flushed with H_2, and fitted with a balloon of H_2. The mixture was stirred for 45 h. The solvent was removed by rotary evaporation, and the residue chromatographed (6 × 2.5 cm column; silica gel, 1:2 v/v CH_2Cl_2/hexanes). The solvent was removed from the product fraction by oil pump vacuum to give the known compound **11**[1] as a white powder (0.047 g, 0.049 mmol, 87%).

NMR (δ, $CDCl_3$): ^1H 7.52-7.47 (m, 8 H of 4Ph), 7.33-7.25 (m, 12 H of 4Ph), 2.71-2.66 (m,

$2PCH_2$), 2.18-2.15 (m, $2PCH_2CH_2$), 1.56-1.30 (m, $10CH_2$); $^{13}C\{^1H\}$[S9] 132.8 (virtual t,[S6] J_{CP} = 6, *o*-Ph), 131.4 (virtual t, J_{CP} = 27, *i*-Ph), 130.1 (s, *p*-Ph), 127.9 (virtual t, J_{CP} = 5, *m*-Ph), 31.0 (virtual t, J_{CP} = 7, CH_2), 27.7 (s, CH_2), 27.6 (s, CH_2), 27.2 (s, CH_2), 26.5 (s, CH_2), 26.2 (virtual t, J_{CP} = 17, CH_2), 25.7 (s, CH_2); $^{31}P\{^1H\}$ 16.9 (s, $^1J_{PPt}$ = 2673).[S10]

IR (cm^{-1}, powder film) 3049 (w), 2930 (m), 2860 (m), 1502 (s), 1463 (s), 1436 (s), 1104 (m), 1058 (s), 1023 (m), 957 (s), 807 (m), 737 (s), 691 (s). MS (FAB, 3-NBA, *m/z*) 964 (**11**$^+$, 20%), 928 ([**11**-Cl]$^+$, 100%), 760 ([**11**-Cl-C_6F_5]$^+$, 60%)]$^+$, 565 ([$Ph_2P(CH_2)_{14}PPh_2$]$^+$, 20%).

Crystallography. A CH_2Cl_2 solution of **8** was layered with ethanol and stored at –20 °C. After one month, a colorless prism was taken directly to a Nonius KappaCCD area detector for data collection as outlined in Table 1. Cell parameters were obtained from 10 frames using a 10° scan and refined with 8156 reflections. Lorentz, polarization, and absorption corrections[S13] 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.[S14] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in idealized positions using a riding model. Scattering factors were taken from literature.[S15]

Additional References

(S1) Burchat, A. F.; Chong, M. J.; Nielsen, N. *J. Organomet. Chem.* **1997**, *542*, 281.

(S2) As usually isolated, **2** contains small amounts of $Br(CH_2)_6Br$ and $HC{\equiv}C(CH_2)_6C{\equiv}CH$ (up to 10% total). These materials can be carried on in the synthesis of **3** and **4**. They are removed when the much heavier **4** is chromatographed or distilled.

(S3) These ^{13}C NMR assignments were made by analogy to those established (by COSY and INADEQUATE pulse sequences) for other compounds with $Ar_2P(CH_2)_6X$ linkages: (a) Stahl, J.; Bohling, J. C.; Bauer, E. B.; Peters, T. B.; Mohr, W.; Martín-Alvarez, J. M.; Hampel, F.; Gladysz, J. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1871; *Angew. Chem.* **2002**, *114*, 1951. (b) Mohr, W.; Horn, C. R.; Stahl, J.; Gladysz, J. A. submitted to *Synthesis*.

(S4) Schmidt, S. P.; Trogler, W. C.; Basolo, F. *Inorg. Synth.* **1989**, *23*, 41.

(S5) The reaction can be monitored by IR. Data for $Re(Br)(CO)_5$ (cm^{-1}, $CHCl_3$): 2150 (s,

ν_{CO}), 2045 (s, ν_{CO}), 2016 (s, ν_{CO}), 1984 (m, ν_{CO}).

(S6) Pregosin, P. S.; Venanzi, L. M. *Chem. Brit.* **1978**, 276.

(S7) Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorg. Synth.* **1982**, *21*, 78.

(S8) Usón, R.; Forniés, J.; Espinet, P.; Alfranca, G. *Synth. React. Inorg. Met.-Org. Chem.* **1980**, *10*, 579.

(S9) The C_6F_5 carbon resonances were not observed. These require larger numbers of transients due to the fluorine and platinum couplings.

(S10) This coupling represents a satellite (d; ^{195}Pt = 33.8%), and is not reflected in the peak multiplicity given.

(S11) When nitrogen was bubbled through this reaction mixture, better results were not obtained.

(S12) The NMR spectra of **9** show baseline purity, but it is the most labile in this study and a correct microanalysis could not be obtained.

(S13) (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.

(S14) Sheldrick, G. M.; SHELX-97, Program for refinement of crystal structures, University of Göttingen, 1997.

(S15) Cromer, D. T.; Waber, J. T. In International Tables for X-ray Crystallography; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974.

Table S1. Crystal data and structure refinement for **8**

Empirical formula	$C_{41}H_{44}BrO_3P_2Re$	
Formula weight	912.81	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 17.9002(2) Å	α= 90°
	b = 10.54090(10) Å	β= 111.074(6)°
	c = 22.1519(4) Å	γ = 90°
Volume	3900.16(9) Å^3	
Z	4	
Density (calculated)	1.555 Mg/m^3	
Absorption coefficient	4.258 mm^{-1}	
F(000)	1816	
Crystal size	0.30 × 0.30 × 0.20 mm^3	
Θ range for data collection	1.91 to 27.47°	
Index ranges (*h*, *k*, *l*)	–22 to 22, –13 to 11, –28 to 28	
Reflections collected	15263	
Independent reflections	8887 [R(int) = 0.0247]	
Reflections [I>2σ(I)]	7175	
Completeness to Θ = 27.47°	99.5%	
Absorption correction	empirical (Scalepack)	
Max. and min. transmission	0.4830 and 0.3615	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8887 / 0 / 433	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2σ(I)]	R1 = 0.0358, wR2 = 0.0898	
R indices (all data)	R1 = 0.0499, wR2 = 0.0963	
Largest diff. peak and hole	1.277 and –1.919 eÅ^{-3}	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **8**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Re(1)	1553(1)	4031(1)	857(1)	29(1)
Br(1)	2786(1)	5483(1)	1495(1)	56(1)
P(1)	2450(1)	2525(1)	549(1)	29(1)
P(2)	1627(1)	2934(1)	1877(1)	29(1)
C(1)	3246(3)	1639(4)	1170(2)	36(1)
C(2)	3834(3)	2516(5)	1682(2)	48(1)
C(3)	4429(3)	1816(6)	2231(3)	64(2)
C(4)	4944(4)	2784(6)	2777(3)	77(2)
C(5)	5318(4)	2197(6)	3399(3)	73(2)
C(6)	5851(4)	3144(7)	3906(3)	76(2)
C(7)	5421(4)	4222(7)	4031(3)	63(2)
C(8)	5097(4)	5116(7)	4134(3)	67(2)
C(9)	4696(5)	6297(9)	4250(4)	105(3)
C(10)	3857(5)	6207(8)	4139(4)	90(2)
C(11)	3342(4)	5785(6)	3461(3)	74(2)
C(12)	2504(3)	5531(5)	3401(2)	53(1)
C(13)	1984(3)	4970(4)	2760(2)	37(1)
C(14)	2275(3)	3661(4)	2637(2)	36(1)
O(20)	1339(2)	5413(4)	–414(2)	63(1)
C(20)	1433(3)	4907(4)	47(3)	42(1)
O(30)	94(2)	2523(4)	194(2)	44(1)
C(30)	554(4)	2996(5)	390(3)	45(1)
O(40)	584(2)	6248(3)	1119(2)	52(1)
C(40)	932(3)	5387(4)	1033(2)	40(1)
C(51)	3019(2)	3214(4)	81(2)	33(1)
C(52)	3269(3)	4478(5)	150(3)	51(1)
C(53)	3733(4)	4932(5)	–183(3)	66(2)
C(54)	3962(3)	4157(5)	–585(3)	54(1)
C(55)	3719(3)	2913(5)	–658(2)	47(1)
C(56)	3256(3)	2444(4)	–324(2)	42(1)
C(61)	1879(3)	1288(4)	–3(2)	34(1)
C(62)	2012(3)	–2(4)	124(2)	45(1)
C(63)	1534(4)	–886(5)	–316(3)	61(2)
C(64)	941(4)	–492(6)	–877(3)	66(2)
C(65)	811(3)	760(6)	–1017(3)	60(2)
C(66)	1276(3)	1661(5)	–579(2)	47(1)
C(71)	1939(3)	1265(4)	1960(2)	35(1)
C(72)	1483(3)	429(4)	1475(2)	41(1)
C(73)	1688(4)	–855(4)	1516(3)	58(2)
C(74)	2330(4)	–1301(5)	2025(3)	63(2)
C(75)	2778(4)	–489(5)	2504(3)	60(2)

C(76)	2577(3)	796(4)	2474(3)	49(1)
C(81)	682(3)	2780(4)	2030(2)	33(1)
C(82)	661(4)	1947(5)	2515(3)	58(2)
C(83)	–6(4)	1891(6)	2676(3)	71(2)
C(84)	–656(3)	2636(4)	2384(2)	45(1)
C(85)	–658(3)	3429(4)	1899(2)	42(1)
C(86)	17(3)	3496(4)	1717(2)	40(1)

Table S3. Bond lengths [Å] and angles [°] for **8**.

Re(1)-C(40)	1.936(5)
Re(1)-C(20)	1.961(5)
Re(1)-C(30)	2.032(7)
Re(1)-P(2)	2.4987(10)
Re(1)-P(1)	2.5203(10)
Re(1)-Br(1)	2.6387(5)
P(1)-C(61)	1.827(4)
P(1)-C(51)	1.843(4)
P(1)-C(1)	1.840(4)
P(2)-C(14)	1.833(4)
P(2)-C(71)	1.835(4)
P(2)-C(81)	1.847(4)
C(1)-C(2)	1.546(6)
C(2)-C(3)	1.492(7)
C(3)-C(4)	1.596(8)
C(4)-C(5)	1.439(8)
C(5)-C(6)	1.547(9)
C(6)-C(7)	1.454(10)
C(7)-C(8)	1.171(9)
C(8)-C(9)	1.505(11)
C(9)-C(10)	1.434(11)
C(10)-C(11)	1.521(8)
C(11)-C(12)	1.482(9)
C(12)-C(13)	1.511(6)
C(13)-C(14)	1.533(6)
O(20)-C(20)	1.109(6)
O(30)-C(30)	0.926(6)
O(40)-C(40)	1.154(5)
C(51)-C(56)	1.386(6)
C(51)-C(52)	1.396(6)
C(52)-C(53)	1.380(7)
C(53)-C(54)	1.374(8)
C(54)-C(55)	1.372(7)
C(55)-C(56)	1.386(6)
C(61)-C(62)	1.391(6)
C(61)-C(66)	1.399(7)
C(62)-C(63)	1.397(7)
C(63)-C(64)	1.376(9)
C(64)-C(65)	1.356(9)
C(65)-C(66)	1.399(7)
C(71)-C(76)	1.382(7)
C(71)-C(72)	1.402(6)
C(72)-C(73)	1.397(6)
C(73)-C(74)	1.372(9)

C(74)-C(75)	1.375(9)
C(75)-C(76)	1.397(7)
C(81)-C(86)	1.368(6)
C(81)-C(82)	1.399(6)
C(82)-C(83)	1.365(7)
C(83)-C(84)	1.360(8)
C(84)-C(85)	1.360(7)
C(85)-C(86)	1.407(6)

C(40)-Re(1)-C(20)	87.41(18)
C(40)-Re(1)-C(30)	91.97(19)
C(20)-Re(1)-C(30)	90.00(19)
C(40)-Re(1)-P(2)	90.36(13)
C(20)-Re(1)-P(2)	176.85(13)
C(30)-Re(1)-P(2)	87.85(13)
C(40)-Re(1)-P(1)	171.21(12)
C(20)-Re(1)-P(1)	85.41(13)
C(30)-Re(1)-P(1)	93.09(12)
P(2)-Re(1)-P(1)	97.00(3)
C(40)-Re(1)-Br(1)	83.93(14)
C(20)-Re(1)-Br(1)	90.69(14)
C(30)-Re(1)-Br(1)	175.80(12)
P(2)-Re(1)-Br(1)	91.29(3)
P(1)-Re(1)-Br(1)	91.09(3)
C(61)-P(1)-C(51)	101.19(19)
C(61)-P(1)-C(1)	103.6(2)
C(51)-P(1)-C(1)	100.7(2)
C(61)-P(1)-Re(1)	111.92(14)
C(51)-P(1)-Re(1)	115.98(14)
C(1)-P(1)-Re(1)	120.95(14)
C(14)-P(2)-C(71)	103.8(2)
C(14)-P(2)-C(81)	100.8(2)
C(71)-P(2)-C(81)	99.40(19)
C(14)-P(2)-Re(1)	116.54(15)
C(71)-P(2)-Re(1)	116.70(14)
C(81)-P(2)-Re(1)	116.88(14)
C(2)-C(1)-P(1)	112.7(3)
C(3)-C(2)-C(1)	113.6(4)
C(2)-C(3)-C(4)	110.4(5)
C(5)-C(4)-C(3)	113.2(5)
C(4)-C(5)-C(6)	111.8(6)
C(7)-C(6)-C(5)	114.4(5)
C(8)-C(7)-C(6)	177.7(7)
C(7)-C(8)-C(9)	177.7(8)
C(10)-C(9)-C(8)	116.8(7)
C(9)-C(10)-C(11)	114.4(7)

C(12)-C(11)-C(10)	112.1(6)
C(11)-C(12)-C(13)	114.6(5)
C(12)-C(13)-C(14)	112.7(4)
C(13)-C(14)-P(2)	113.3(3)
O(20)-C(20)-Re(1)	177.6(4)
O(30)-C(30)-Re(1)	177.5(5)
O(40)-C(40)-Re(1)	175.6(4)
C(56)-C(51)-C(52)	118.0(4)
C(56)-C(51)-P(1)	119.5(3)
C(52)-C(51)-P(1)	122.4(3)
C(53)-C(52)-C(51)	120.3(5)
C(54)-C(53)-C(52)	121.1(5)
C(55)-C(54)-C(53)	119.3(5)
C(54)-C(55)-C(56)	120.2(4)
C(51)-C(56)-C(55)	121.2(4)
C(62)-C(61)-C(66)	118.6(4)
C(62)-C(61)-P(1)	123.2(4)
C(66)-C(61)-P(1)	118.2(3)
C(61)-C(62)-C(63)	119.6(5)
C(64)-C(63)-C(62)	120.6(5)
C(65)-C(64)-C(63)	120.9(5)
C(64)-C(65)-C(66)	119.5(6)
C(61)-C(66)-C(65)	120.9(5)
C(76)-C(71)-C(72)	119.2(4)
C(76)-C(71)-P(2)	123.8(4)
C(72)-C(71)-P(2)	117.0(4)
C(73)-C(72)-C(71)	119.5(5)
C(74)-C(73)-C(72)	120.6(5)
C(73)-C(74)-C(75)	120.3(5)
C(74)-C(75)-C(76)	119.9(6)
C(71)-C(76)-C(75)	120.5(5)
C(86)-C(81)-C(82)	118.4(4)
C(86)-C(81)-P(2)	123.1(3)
C(82)-C(81)-P(2)	118.4(4)
C(83)-C(82)-C(81)	119.7(5)
C(84)-C(83)-C(82)	122.0(5)
C(83)-C(84)-C(85)	119.3(5)
C(84)-C(85)-C(86)	120.0(5)
C(81)-C(86)-C(85)	120.5(4)

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **8**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Re(1)	36(1)	23(1)	35(1)	–2(1)	21(1)	–2(1)
Br(1)	66(1)	44(1)	72(1)	–24(1)	43(1)	–23(1)
P(1)	31(1)	27(1)	33(1)	–7(1)	16(1)	–4(1)
P(2)	37(1)	22(1)	33(1)	–3(1)	18(1)	–1(1)
C(1)	35(2)	40(2)	36(2)	–4(2)	16(2)	2(2)
C(2)	44(3)	53(3)	43(3)	–14(2)	11(2)	–4(2)
C(3)	49(3)	88(4)	48(3)	5(3)	7(3)	–7(3)
C(4)	69(4)	75(4)	65(4)	12(3)	–3(3)	–18(3)
C(5)	65(4)	75(4)	77(4)	8(3)	24(3)	11(3)
C(6)	60(4)	84(5)	75(4)	–15(4)	15(3)	–9(3)
C(7)	43(3)	86(4)	54(3)	–3(3)	11(3)	–12(3)
C(8)	44(3)	90(5)	52(3)	–6(3)	–1(3)	–6(3)
C(9)	72(5)	136(7)	86(6)	–47(5)	3(4)	–10(5)
C(10)	74(5)	95(5)	76(5)	–36(4)	–5(4)	–2(4)
C(11)	58(4)	69(4)	74(4)	–34(3)	–2(3)	10(3)
C(12)	70(4)	39(2)	40(3)	–9(2)	7(3)	7(2)
C(13)	42(2)	35(2)	34(2)	–5(2)	16(2)	1(2)
C(14)	43(2)	28(2)	34(2)	–4(2)	12(2)	2(2)
O(20)	76(3)	66(2)	64(3)	28(2)	45(2)	21(2)
C(20)	42(3)	38(2)	56(3)	–4(2)	29(2)	4(2)
O(30)	42(2)	57(2)	40(2)	7(2)	23(2)	8(2)
C(30)	72(4)	38(3)	47(3)	17(2)	49(3)	25(3)
O(40)	69(2)	40(2)	64(2)	8(2)	43(2)	16(2)
C(40)	57(3)	32(2)	41(2)	6(2)	31(2)	0(2)
C(51)	30(2)	38(2)	36(2)	–5(2)	16(2)	–4(2)
C(52)	62(3)	38(2)	73(4)	–13(2)	47(3)	–12(2)
C(53)	85(4)	42(3)	99(5)	–5(3)	67(4)	–16(3)
C(54)	55(3)	58(3)	63(3)	2(2)	38(3)	–7(2)
C(55)	53(3)	57(3)	42(3)	–10(2)	29(2)	1(2)
C(56)	46(3)	42(2)	43(3)	–6(2)	24(2)	–3(2)
C(61)	36(2)	35(2)	37(2)	–11(2)	19(2)	–7(2)
C(62)	66(3)	35(2)	48(3)	–11(2)	36(2)	–6(2)
C(63)	92(5)	36(3)	71(4)	–22(2)	49(4)	–29(3)
C(64)	76(4)	68(4)	69(4)	–42(3)	46(4)	–41(3)
C(65)	49(3)	81(4)	50(3)	–27(3)	17(3)	–23(3)
C(66)	47(3)	51(3)	42(3)	–15(2)	15(2)	–6(2)
C(71)	49(3)	23(2)	46(3)	–1(2)	32(2)	–2(2)
C(72)	55(3)	32(2)	46(3)	–6(2)	31(2)	–7(2)
C(73)	97(5)	26(2)	76(4)	–13(2)	64(4)	–14(2)
C(74)	100(5)	26(2)	87(4)	8(3)	63(4)	8(3)
C(75)	75(4)	41(3)	74(4)	18(3)	41(3)	22(3)

C(76)	64(3)	34(2)	57(3)	3(2)	32(3)	9(2)
C(81)	41(2)	28(2)	38(2)	–3(2)	23(2)	–6(2)
C(82)	68(4)	61(3)	62(3)	26(3)	43(3)	19(3)
C(83)	92(5)	70(4)	78(4)	25(3)	65(4)	11(3)
C(84)	55(3)	41(2)	55(3)	–11(2)	39(3)	–10(2)
C(85)	44(3)	39(2)	52(3)	–3(2)	28(2)	–3(2)
C(86)	45(3)	32(2)	51(3)	2(2)	28(2)	–6(2)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **8**.

	x	y	z	U(eq)
H(1A)	2999	1042	1389	43
H(1B)	3548	1133	958	43
H(2A)	4124	3045	1470	57
H(2B)	3523	3092	1856	57
H(3A)	4790	1321	2071	77
H(3B)	4146	1214	2418	77
H(4A)	5363	3167	2640	93
H(4B)	4590	3475	2816	93
H(5A)	5650	1475	3358	87
H(5B)	4900	1860	3550	87
H(6A)	6118	2684	4317	91
H(6B)	6273	3463	3755	91
H(9A)	4977	6566	4704	126
H(9B)	4770	6977	3968	126
H(10A)	3666	7047	4224	109
H(10B)	3783	5600	4454	109
H(11A)	3346	6453	3148	89
H(11B)	3573	5006	3350	89
H(12A)	2259	6336	3467	63
H(12B)	2509	4942	3751	63
H(13A)	1977	5553	2408	44
H(13B)	1428	4894	2751	44
H(14A)	2305	3091	3000	43
H(14B)	2822	3745	2628	43
H(52A)	3118	5028	426	62
H(53A)	3898	5795	–133	79
H(54A)	4284	4479	–809	64
H(55A)	3869	2373	–938	57
H(56A)	3098	1578	–374	50
H(62A)	2426	–279	508	54
H(63A)	1619	–1767	–227	73
H(64A)	618	–1105	–1169	79
H(65A)	407	1022	–1409	72
H(66A)	1181	2539	–673	57
H(72A)	1039	734	1121	49
H(73A)	1379	–1424	1189	69
H(74A)	2467	–2176	2046	75
H(75A)	3223	–801	2855	72
H(76A)	2881	1353	2810	58
H(82A)	1109	1422	2731	70
H(83A)	–16	1314	3003	85

H(84A)	−1105	2603	2517	54
H(85A)	−1115	3937	1684	51
H(86A)	11	4042	1374	47

Table S6. Torsion angles [°] for **8**.

C(40)-Re(1)-P(1)-C(61)	–119.2(10)
C(20)-Re(1)-P(1)-C(61)	–83.9(2)
C(30)-Re(1)-P(1)-C(61)	5.8(2)
P(2)-Re(1)-P(1)-C(61)	94.02(16)
Br(1)-Re(1)-P(1)-C(61)	–174.55(16)
C(40)-Re(1)-P(1)-C(51)	–3.8(10)
C(20)-Re(1)-P(1)-C(51)	31.4(2)
C(30)-Re(1)-P(1)-C(51)	121.2(2)
P(2)-Re(1)-P(1)-C(51)	–150.59(15)
Br(1)-Re(1)-P(1)-C(51)	–59.16(15)
C(40)-Re(1)-P(1)-C(1)	118.3(10)
C(20)-Re(1)-P(1)-C(1)	153.6(2)
C(30)-Re(1)-P(1)-C(1)	–116.6(2)
P(2)-Re(1)-P(1)-C(1)	–28.43(17)
Br(1)-Re(1)-P(1)-C(1)	63.00(17)
C(40)-Re(1)-P(2)-C(14)	–72.0(2)
C(20)-Re(1)-P(2)-C(14)	–117(2)
C(30)-Re(1)-P(2)-C(14)	–163.9(2)
P(1)-Re(1)-P(2)-C(14)	103.21(16)
Br(1)-Re(1)-P(2)-C(14)	11.95(16)
C(40)-Re(1)-P(2)-C(71)	164.6(2)
C(20)-Re(1)-P(2)-C(71)	120(2)
C(30)-Re(1)-P(2)-C(71)	72.7(2)
P(1)-Re(1)-P(2)-C(71)	–20.20(17)
Br(1)-Re(1)-P(2)-C(71)	–111.46(17)
C(40)-Re(1)-P(2)-C(81)	47.2(2)
C(20)-Re(1)-P(2)-C(81)	2(2)
C(30)-Re(1)-P(2)-C(81)	–44.73(19)
P(1)-Re(1)-P(2)-C(81)	–137.58(14)
Br(1)-Re(1)-P(2)-C(81)	131.16(14)
C(61)-P(1)-C(1)-C(2)	177.6(3)
C(51)-P(1)-C(1)-C(2)	73.2(4)
Re(1)-P(1)-C(1)-C(2)	–56.1(4)
P(1)-C(1)-C(2)-C(3)	173.5(4)
C(1)-C(2)-C(3)-C(4)	–173.3(5)
C(2)-C(3)-C(4)-C(5)	159.4(6)
C(3)-C(4)-C(5)-C(6)	176.7(6)
C(4)-C(5)-C(6)-C(7)	61.6(9)
C(5)-C(6)-C(7)-C(8)	–143(18)
C(6)-C(7)-C(8)-C(9)	38(30)
C(7)-C(8)-C(9)-C(10)	132(17)
C(8)-C(9)-C(10)-C(11)	–57.2(11)
C(9)-C(10)-C(11)-C(12)	171.8(7)
C(10)-C(11)-C(12)-C(13)	–173.6(5)

C(11)-C(12)-C(13)-C(14)	63.1(6)
C(12)-C(13)-C(14)-P(2)	177.5(4)
C(71)-P(2)-C(14)-C(13)	–164.9(3)
C(81)-P(2)-C(14)-C(13)	–62.2(4)
Re(1)-P(2)-C(14)-C(13)	65.3(4)
C(40)-Re(1)-C(20)-O(20)	–39(11)
C(30)-Re(1)-C(20)-O(20)	53(11)
P(2)-Re(1)-C(20)-O(20)	6(13)
P(1)-Re(1)-C(20)-O(20)	146(11)
Br(1)-Re(1)-C(20)-O(20)	–123(11)
C(40)-Re(1)-C(30)-O(30)	–62(12)
C(20)-Re(1)-C(30)-O(30)	–149(12)
P(2)-Re(1)-C(30)-O(30)	29(12)
P(1)-Re(1)-C(30)-O(30)	125(12)
Br(1)-Re(1)-C(30)-O(30)	–50(13)
C(20)-Re(1)-C(40)-O(40)	–34(6)
C(30)-Re(1)-C(40)-O(40)	–124(6)
P(2)-Re(1)-C(40)-O(40)	148(6)
P(1)-Re(1)-C(40)-O(40)	1(7)
Br(1)-Re(1)-C(40)-O(40)	57(6)
C(61)-P(1)-C(51)-C(56)	–32.6(4)
C(1)-P(1)-C(51)-C(56)	73.8(4)
Re(1)-P(1)-C(51)-C(56)	–153.9(3)
C(61)-P(1)-C(51)-C(52)	151.7(4)
C(1)-P(1)-C(51)-C(52)	–102.0(4)
Re(1)-P(1)-C(51)-C(52)	30.4(5)
C(56)-C(51)-C(52)-C(53)	0.4(8)
P(1)-C(51)-C(52)-C(53)	176.2(5)
C(51)-C(52)-C(53)-C(54)	–0.2(10)
C(52)-C(53)-C(54)-C(55)	0.4(10)
C(53)-C(54)-C(55)-C(56)	–0.7(9)
C(52)-C(51)-C(56)-C(55)	–0.7(7)
P(1)-C(51)-C(56)-C(55)	–176.7(4)
C(54)-C(55)-C(56)-C(51)	0.9(8)
C(51)-P(1)-C(61)-C(62)	111.7(4)
C(1)-P(1)-C(61)-C(62)	7.7(4)
Re(1)-P(1)-C(61)-C(62)	–124.1(4)
C(51)-P(1)-C(61)-C(66)	–68.8(4)
C(1)-P(1)-C(61)-C(66)	–172.8(4)
Re(1)-P(1)-C(61)-C(66)	55.4(4)
C(66)-C(61)-C(62)-C(63)	–1.2(7)
P(1)-C(61)-C(62)-C(63)	178.3(4)
C(61)-C(62)-C(63)-C(64)	0.8(8)
C(62)-C(63)-C(64)-C(65)	0.5(9)
C(63)-C(64)-C(65)-C(66)	–1.3(9)
C(62)-C(61)-C(66)-C(65)	0.4(7)

P(1)-C(61)-C(66)-C(65)	–179.1(4)
C(64)-C(65)-C(66)-C(61)	0.9(8)
C(14)-P(2)-C(71)-C(76)	–5.3(5)
C(81)-P(2)-C(71)-C(76)	–109.0(4)
Re(1)-P(2)-C(71)-C(76)	124.4(4)
C(14)-P(2)-C(71)-C(72)	173.2(3)
C(81)-P(2)-C(71)-C(72)	69.5(4)
Re(1)-P(2)-C(71)-C(72)	–57.1(4)
C(76)-C(71)-C(72)-C(73)	–0.8(7)
P(2)-C(71)-C(72)-C(73)	–179.3(4)
C(71)-C(72)-C(73)-C(74)	–0.2(7)
C(72)-C(73)-C(74)-C(75)	0.5(8)
C(73)-C(74)-C(75)-C(76)	0.2(9)
C(72)-C(71)-C(76)-C(75)	1.5(7)
P(2)-C(71)-C(76)-C(75)	179.9(4)
C(74)-C(75)-C(76)-C(71)	–1.2(8)
C(14)-P(2)-C(81)-C(86)	109.9(4)
C(71)-P(2)-C(81)-C(86)	–143.9(4)
Re(1)-P(2)-C(81)-C(86)	–17.4(4)
C(14)-P(2)-C(81)-C(82)	–66.2(4)
C(71)-P(2)-C(81)-C(82)	40.0(4)
Re(1)-P(2)-C(81)-C(82)	166.4(4)
C(86)-C(81)-C(82)-C(83)	–1.8(8)
P(2)-C(81)-C(82)-C(83)	174.5(5)
C(81)-C(82)-C(83)-C(84)	–0.8(10)
C(82)-C(83)-C(84)-C(85)	2.5(10)
C(83)-C(84)-C(85)-C(86)	–1.7(8)
C(82)-C(81)-C(86)-C(85)	2.6(7)
P(2)-C(81)-C(86)-C(85)	–173.6(3)
C(84)-C(85)-C(86)-C(81)	–0.9(7)