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Syntheses, characterization and facial–meridional isomerism of tungsten tricarbonyl diphosphine complexes

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The complexes *fac*-[W(CO)$_3$(η^2-dppf)(η^1-dppm)] **4f**, *fac*-[W(CO)$_3$(η^2-dppm)(η^1-dppf)] **5f**, *fac*-[W(CO)$_3$(η^2-dppf)-(η^1-dppe)] **6f**, *fac*-[W(CO)$_3$(η^2-dppe)(η^1-dppf)] **7f**, *fac*-[W(CO)$_3$(η^2-dppm)(η^1-dppe)] **8f** and *fac*-[W(CO)$_3$(η^2-dppe)-(η^1-dppm)] **9f** have been prepared by treating *fac*-[W(CO)$_3$(η^2-diphos)(NCMe)] **1**–**3** [diphos = 1,1′-bis(diphenylphosphino)ferrocene (dppf), dppm ($Ph_2PCH_2PPh_2$) or dppe ($Ph_2PCH_2CH_2PPh_2$)] with the corresponding diphosphines. The initially afforded facial isomers are converted into the meridional forms (**4m**–**9m**) in a subsequent, slow rearrangement process through opening of the chelated diphosphine ligand. A five-co-ordinate, square-pyramidal intermediate is presumed. In contrast, acid-assisted facial–meridional isomerization of **4f** and **6f** is likely *via* a seven-co-ordinate hydrido species. The new compounds have been characterized by elemental analyses and IR, mass and NMR spectroscopy.

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The d^6 metal tricarbonyl complexes, M(CO)$_3$L$_3$, exhibit facial (*fac*) and meridional (*mer*) isomers.[1–6] When L is a good σ donor and poor π acceptor relative to CO the *fac* isomer is expected to be more stable electronically to achieve stronger M to CO back donation. On the other hand, the *mer* isomer is less sterically encumbered and is favored when L contains bulky groups.[7] Several studies regarding their isomerization have been reported. For example, Rousche and Dobson[8] studied the thermolysis of *fac*-[Mo(CO)$_3$(η^2-dppe){P(OPr^i)$_3$}] (dppe = $Ph_2PCH_2CH_2PPh_2$) at 120 °C leading to *mer*-[Mo(CO)$_3$(η^2-dppe)-{P(OPr^i)$_3$}] *via* dissociation/association of the P(OPr^i)$_3$ ligand. Darensbourg *et al.*[9] observed that on prolonged standing a solution of *fac*-[W(CO)$_3$(^{13}CO)(η^2-dppm)] (dppm = $Ph_2PCH_2PPh_2$) at room temperature afforded a mixture of facial and meridional isomers, presumably undergoing an intramolecular CO rearrangement process. Schenk and Hilpert[10] found an interesting reaction of *fac*-[Mo(CO)$_3$(η^2-dppm)(NCMe)] and dppe giving *fac*-[Mo(CO)$_3$(η^2-dppe)(η^1-dppm)] with switch of the chelate ligand, but no subsequent isomerization of this compound was indicated. In contrast, Krishnamurthy and co-workers[11] revealed that treating *fac*-[Mo(CO)$_3$(NCMe){η^2-$Ph_2PN(Pr^i)PPh$(dmpz)}] (dmpz = 3,5-dimethylpyrazol-1-yl) with dppe produced *fac*- and *mer*-[Mo(CO)$_3${η^2-$Ph_2PN(Pr^i)PPh$(dmpz)}(η^1-dppe)], in which the four-membered diphosphazane ring was retained and the dppe was co-ordinated in an η^1 fashion. In these reactions, however, a plausible isomerization mechanism involving opening the η^2-diphosphine ring was ignored.

We recently prepared the complexes *fac*-[W(CO)$_3$(η^2-dppf)-(PMe$_3$)] and *fac*-[W(CO)$_3$(η^2-dppf)(PPh$_2$X)] [dppf = 1,1′-bis(diphenylphosphino)ferrocene, X = H or OH], which did not lead to the meridional isomers upon heating.[12] Apparently their geometries are not sterically congested enough to surpass the electronic advantages. We then investigated the analogous complexes with bulky diphosphines. This paper presents results concerning the syntheses and facial–meridional isomerism of a series of complexes of the type [W(CO)$_3$(η^2-diphos)-(η^1-diphos′)] (diphos = diphosphine). It appears that the chelated diphosphine ligand is opened up to facilitate the isomerization reaction.

Experimental

General methods

Reactions were performed on a double-manifold Schlenk line under dried nitrogen. The complexes *fac*-[W(CO)$_3$(η^2-dppf)-(NCMe)][12] **1** and *fac*-[W(CO)$_3$(η^2-dppm)(NCMe)][9] **2** were prepared by literature methods. 1,1′-Bis(diphenylphosphino)-ferrocene (dppf) was prepared from ferrocene and chlorodiphenylphosphine as described.[13] Trimethylphosphine (1.0 M in toluene), methyldiphenylphosphine, triphenylphosphine, dppm, dppe and tetrafluoroboric acid (54% in Et_2O) from Aldrich were used without further purification. Solvents were dried over appropriate agents under nitrogen and distilled before use. Thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck). Infrared spectra were recorded with a 0.1 mm path CaF_2 solution cell on a Hitachi I-2001 spectrometer, ^{1}H and ^{31}P NMR spectra on a Varian VXR-300 spectrometer at 300 and 121.4 MHz, respectively, and fast atom bombardment (FAB) mass spectra on a VG Blotch-5022 spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at the National Chung-Hsing University, Taichung, Taiwan.

Preparation of *fac*-[W(CO)$_3$(η^2-dppe)(NCMe)] 3

The complex [W(CO)$_3$(NCMe)$_3$] (500 mg, 1.28 mmol) and dppe (510 mg, 1.28 mmol) were placed in a Schlenk flask (50 cm^3) containing a magnetic stirring bar. The flask was capped with a rubber septum, evacuated and backfilled with nitrogen. After adding dichloromethane (15 cm^3), the solution was stirred at ambient temperature for 5 h, forming a yellow precipitate. The supernatant was removed *via* a cannula and the solids washed with diethyl ether (50 cm^3) and then dried under vacuum. The complex *fac*-[W(CO)$_3$(η^2-dppe)(NCMe)] **3** was afforded in 86% yield (780 mg, 1.10 mmol). Mass spectrum (FAB): *m*/*z* 707 (M^+, ^{184}W), 666 (M^+ − CH_3CN) and 666 − 28*n* (*n* = 1–3); IR (1,2-$C_2H_4Cl_2$, cm^{-1}): ν(CO) 1932vs, 1838s and 1822s. ^{31}P-{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 46.25 (s; with ^{183}W satellites, $^1J_{WP}$ = 226 Hz). ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.97 (s, 3 H, NCMe), 2.59 (m, 4 H, CH_2) and 7.30–7.80 (m, 20 H, Ph).

Reaction of complex 1 and dppm

The complex *fac*-[W(CO)$_3$(η^2-dppf)(NCMe)] **1** (50 mg, 0.058 mmol) and dppm (25 mg, 0.065 mmol) were placed in a Schlenk flask (50 cm^3) containing a magnetic stirring bar. The flask was fitted with a rubber septum, evacuated and backfilled with nitrogen. After adding dichloromethane (15 cm^3), the solution was stirred at ambient temperature for 20 h. The mixture was dried under vacuum and the residue separated by TLC, eluting

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with CH_2Cl_2–*n*-hexane (1 : 1, v/v). Three bands were obtained according to the order of appearance: yellow [W(CO)$_4$-(η^2-dppf)] (trace amount), yellow *mer*-[W(CO)$_3$(η^2-dppm)-(η^1-dppf)] **5m** (28 mg, 40%) and yellow *fac*-[W(CO)$_3$(η^2-dppf)-(η^1-dppm)] **4f** (30 mg, 43%).

Complex **5m** (Found: C, 61.23; H, 4.37. $C_{62}H_{50}FeO_3P_4W$ requires C, 61.71; H, 4.18%): mass spectrum (FAB) *m*/*z* 1206 (M^+); IR (1,2-$C_2H_4Cl_2$, cm^{-1}) ν(CO) 1966w, 1864s and 1838 (sh); ^{31}P-{^{1}H} NMR (CD_2Cl_2, 20 °C) δ −25.0 (dd, J_{PP} = 31 and 24; with ^{183}W satellites, J_{WP} = 180, dppm), −16.69 (s, dppf), −11.56 (dd, J_{PP} = 31 and 67; with ^{183}W satellites, J_{WP} = 244, dppm) and 22.96 (dd, J_{PP} = 24 and 67, with ^{183}W satellites, J_{WP} = 302 Hz, dppf); ^{1}H NMR (CD_2Cl_2, 20 °C) δ 3.75 (s, 2 H), 4.00 (s, 2 H), 4.26 (s, 2 H), 4.30 (s, 2 H, C_5H_4), 5.04 (t, 2 H, J_{PH} = 9 Hz, CH_2) and 7.00–7.70 (m, 40 H, C_6H_5).

Complex **4f** (Found: C, 61.50; H, 4.19. $C_{62}H_{50}FeO_3P_4W$ requires C, 61.71; H, 4.18%): mass spectrum (FAB) *m*/*z* 1206 (M^+), 822 (M^+ − dppm) and 822 − 28*n* (*n* = 1–3); IR (1,2-$C_2H_4Cl_2$, cm^{-1}): ν(CO) 1938s, 1842s and 1826 (sh); ^{31}P-{^{1}H} NMR (CD_2Cl_2, 20 °C) δ −24.16 (d, J_{PP} = 23, dppm), 8.17 (dt, J_{PP} = 23, 26; with ^{183}W satellites, J_{WP} = 214, dppm) and 16.91 (d, J_{PP} = 26; with ^{183}W satellites, J_{WP} = 230 Hz, dppf); ^{1}H NMR (CD_2Cl_2, 20 °C) δ 3.08 (s, 2 H), 3.95 (s, 2 H), 4.27 (s, 2 H), 4.46 (s, 2 H, C_5H_4), 4.68 (s, 2 H, CH_2) and 6.90–7.50 (m, 40 H, C_6H_5).

Reaction of complex 2 and dppf

The complex *fac*-[W(CO)$_3$(η^2-dppm)(NCMe)] **2** (20 mg, 0.023 mmol) and dppf (50 mg, 0.09 mmol) and CD_2Cl_2 (2 cm^3) were placed in a dry NMR tube under nitrogen. The reaction was carried out at ambient temperature and monitored by ^{31}P NMR spectroscopy. The resonances corresponding to *fac*-[W(CO)$_3$-(η^2-dppm)(η^1-dppf)] **5f** were detected initially. However, only **5m** (17 mg, 0.014 mmol, 61%) was obtained after separation by TLC. Attempts to isolate **5f** in pure form have been unsuccessful. Complex **5f**: ^{31}P-{^{1}H} NMR (CD_2Cl_2, 20 °C) δ −22.46 (d, J_{PP} = 22, dppm), −17.03 (s, dppf) and 12.96 (t, J_{PP} = 22 Hz, dppf).

Reaction of complex 1 and dppe

The reaction of *fac*-[W(CO)$_3$(η^2-dppf)(NCMe)] **1** (50 mg, 0.058 mmol) and dppe (25 mg, 0.063 mmol) was carried out (5 h) and worked up in a fashion similar to that of **1** and dppm. Three products were obtained in order of appearance on the TLC plate: yellow [W(CO)$_4$(η^2-dppf)] (trace amount), yellow *fac*-[W(CO)$_3$(η^2-dppf)(η^1-dppe)] **6f** (38 mg, 54%) and yellow *fac*,*fac*-[{W(CO)$_3$(η^2-dppf)}$_2$(η^1 : η^1-dppe)] **6ff** (25 mg, 42%).

Complex **6f** (Found: C, 61.72; H, 4.39. $C_{63}H_{52}FeO_3P_4W$ requires C, 61.99; H, 4.29%): mass spectrum (FAB) *m*/*z* 1220 (M^+), 1220 − 28*n* (*n* = 1–3), 822 (M^+ − dppe) and 822 − 28*n* (*n* = 1–3); IR (1,2-$C_2H_4Cl_2$, cm^{-1}) ν(CO) 1938s, 1842s and 1826 (sh); ^{31}P-{^{1}H} NMR (CD_2Cl_2, 20 °C) δ −12.49 (d, J_{PP} = 31, dppe), 9.14 (dt, J_{PP} = 31, 27; with ^{183}W satellites, J_{WP} = 211, dppe) and 16.0 (d, J_{PP} = 27; with ^{183}W satellites, J_{WP} = 227 Hz, dppf); ^{1}H NMR (CD_2Cl_2, 20 °C) δ 1.82 (m, 2 H), 2.35 (m, 2 H, C_2H_4), 3.91 (s, 2 H), 4.24 (s, 2 H), 4.45 (s, 2 H), 4.67 (s, 2 H, C_5H_4) and 6.90–7.50 (m, 40 H, C_6H_5).

Complex **6ff** (Found: C, 58.92; H, 3.87. $C_{100}H_{80}Fe_2O_6P_6W_2$ requires C, 58.79; H, 3.95%): mass spectrum (FAB) *m*/*z* 1220 [M^+ − W(CO)$_3$(dppf)] and 822 [M^+ − W(CO)$_3$(dppf)(dppe)]; IR (1,2-$C_2H_4Cl_2$, cm^{-1}) ν(CO) 1938s, 1842s and 1828 (sh); ^{31}P-{^{1}H} NMR (CD_2Cl_2, 20 °C) δ 15.0 (t, J_{PP} = 27; with ^{183}W satellites, J_{WP} = 232, dppe) and 17.33 (d, J_{PP} = 27; with ^{183}W satellites, J_{WP} = 230 Hz, dppf); ^{1}H NMR (CD_2Cl_2, 20 °C) δ 2.48 (br, 4 H, C_2H_4), 3.97 (s, 4 H), 4.24 (s, 4 H), 4.49 (s, 4 H), 4.73 (s, 4 H, C_5H_4) and 6.80–7.50 (m, 60 H, C_6H_5).

Reaction of complex 3 and dppf

The complex *fac*-[W(CO)$_3$(η^2-dppe)(NCMe)] **3** (100 mg, 0.141 mmol) was treated with dppf (80 mg, 0.14 mmol) by the same method as described above (60 h). Three products were isolated: yellow [W(CO)$_4$(η^2-dppe)] (32 mg, 33%), yellow *mer*-[W(CO)$_3$(η^2-dppe)(η^1-dppf)] **7m** (45 mg, 26%) and yellow *fac*-[W(CO)$_3$(η^2-dppe)(η^1-dppf)] **7f** (50 mg, 29%).

Complex **7m** (Found: C, 61.82; H, 4.40. $C_{63}H_{52}FeO_3P_4W$ requires C, 61.99; H, 4.29%): mass spectrum (FAB) *m*/*z* 1221 (M^+) and 1221 − 28*n* (*n* = 1–3); IR (1,2-$C_2H_4Cl_2$, cm^{-1}) ν(CO) 1965w and 1859s; ^{31}P-{^{1}H} NMR (CD_2Cl_2, 20 °C) δ 47.10 (dd, J_{PP} = 12, 69; with ^{183}W satellites, J_{WP} = 271, dppe), 38.79 (dd, J_{PP} = 15, 12; with ^{183}W satellites, J_{WP} = 216, dppe), 18.32 (dd, J_{PP} = 15, 69; with ^{183}W satellites, J_{WP} = 295 Hz, dppf) and −17.03 (s, dppf); ^{1}H NMR (CD_2Cl_2, 20 °C) δ 2.38 (br, 4 H, C_2H_4), 3.71 (s, 2 H), 3.95 (s, 2 H), 4.17 (s, 2 H), 4.23 (s, 2 H, C_5H_4) and 6.90–7.70 (m, 40 H, C_6H_5).

Complex **7f** (Found: C, 61.85; H, 4.22. $C_{63}H_{52}FeO_3P_4W$ requires C, 61.99; H, 4.29%): mass spectrum (FAB) *m*/*z* 1221 (M^+) and 1221 − 28*n* (*n* = 1–3); IR (1,2-$C_2H_4Cl_2$, cm^{-1}) ν(CO) 1935s and 1840s; ^{31}P-{^{1}H} NMR (CD_2Cl_2, 20 °C) δ 33.68 (d, J_{PP} = 22; with ^{183}W satellites, J_{WP} = 220, dppe), 8.02 (t, J_{PP} = 22; with ^{183}W satellites, J_{WP} = 213 Hz, dppf) and −17.26 (s, dppf); ^{1}H NMR (CD_2Cl_2, 20 °C) δ 2.48 (br, 4 H, C_2H_4), 3.83 (s, 2 H), 3.97 (s, 2 H), 4.27 (s, 2 H), 4.62 (s, 2 H, C_5H_4) and 6.60–7.70 (m, 40 H, C_6H_5).

Reaction of complex 2 and dppe

Complex *fac*-[W(CO)$_3$(η^2-dppm)(NCMe)] **2** (100 mg, 0.144 mmol) was treated with dppe (60 mg, 0.15 mmol) for 50 h at 28 °C by the same method as described above. Yellow *mer*-[W(CO)$_3$(η^2-dppe)(η^1-dppm)] **9m** (70 mg, 46%) and yellow *fac*-[W(CO)$_3$(η^2-dppe)(η^1-dppm)] **9f** (58 mg, 38%) were obtained by TLC. Two intermediates corresponding to *fac*-[W(CO)$_3$(η^2-dppm)(η^1-dppe)] **8f** and *mer*-[W(CO)$_3$(η^2-dppm)(η^1-dppe)] **8m** were detected by ^{31}P NMR spectroscopy during the reaction. However, attempts to isolate them failed, leading only to **9m** and **9f**.

Complex **8f**: ^{31}P-{^{1}H} NMR (CD_2Cl_2, 20 °C) δ −21.85 (d, J_{PP} = 22, dppm), −12.53 (d, J_{PP} = 36, dppe) and 15.08 (dt, J_{PP} = 22, 36 Hz, dppe).

Complex **8m**: ^{31}P-{^{1}H} NMR (CD_2Cl_2, 20 °C) δ −24.60 (dd, J_{PP} = 23, 30, dppm), −12.35 (dd, J_{PP} = 30, 66, dppm), −12.06 (d, J_{PP} = 39, dppe) and 25.67 (ddd, J_{PP} = 23, 39, 66 Hz, dppe).

Complex **9m** (Found: C, 61.67; H, 4.46. $C_{54}H_{46}O_3P_4W$ requires C, 61.73; H, 4.41%): mass spectrum (FAB) *m*/*z* 1050 (M^+) and 1050 − 28*n* (*n* = 1–3); IR (1,2-$C_2H_4Cl_2$, cm^{-1}) ν(CO) 1966w and 1860s; ^{31}P-{^{1}H} NMR (CD_2Cl_2, 20 °C) δ 47.85 (dd, J_{PP} = 11, 69; with ^{183}W satellites, J_{WP} = 273, dppe), 40.18 (dd, J_{PP} = 15, 11; with ^{183}W satellites, J_{WP} = 220, dppe), 16.47 (ddd, J_{PP} = 15, 42, 69; with ^{183}W satellites, J_{WP} = 293, dppm) and −25.92 (d, J_{PP} = 42 Hz, dppm); ^{1}H NMR (CD_2Cl_2, 20 °C) δ 2.41 (m, 4 H, C_2H_4), 3.02 (br, 2 H, CH_2) and 6.90–7.70 (m, 40 H, C_6H_5).

Complex **9f** (Found: C, 61.65; H, 4.45. $C_{54}H_{46}O_3P_4W$ requires C, 61.73; H, 4.41%): mass spectrum (FAB) *m*/*z* 1050 (M^+) and 1050 − 28*n* (*n* = 1–3); IR (1,2-$C_2H_4Cl_2$, cm^{-1}) ν(CO) 1938s and 1844s; ^{31}P-{^{1}H} NMR (CD_2Cl_2, 20 °C) δ 36.99 (d, J_{PP} = 22; with ^{183}W satellites, J_{WP} = 225, dppe), 6.89 (dt, J_{PP} = 30, 22; with ^{183}W satellites, J_{WP} = 215, dppm) and −25.61 (d, J_{PP} = 30 Hz, dppm); ^{1}H NMR (CD_2Cl_2, 20 °C) δ 2.55 (m, 4 H, C_2H_4), 2.79 (br, 2 H, CH_2) and 6.70–7.70 (m, 40 H, C_6H_5).

Reaction of complex 1 and PPh_3

Complex *fac*-[W(CO)$_3$(η^2-dppf)(NCMe)] **1** (50 mg, 0.058 mmol) was treated with PPh_3 (16 mg, 0.06 mmol) for 20 h by the same method as described above. Three products were isolated: yellow *mer*-[W(CO)$_3$(η^2-dppf)(PPh_3)] **12f** (2 mg, 3%), yellow [W(CO)$_4$(η^2-dppf)] (14 mg, 28%) and yellow *fac*-[W(CO)$_3$-(η^2-dppf)(PPh_3)] **12m** (16 mg, 26%).

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Complex **12m** (Found: C, 60.67, H, 4.45. $C_{55}H_{43}FeO_3P_3W$ requires C, 60.91; H, 4.00%): IR (1,2-$C_2H_4Cl_2$, cm^{-1}) ν(CO) 1965w, 1856s and 1840 (sh); ^{31}P-{^1H} NMR (CD_2Cl_2, 20 °C) δ 15.16 (dd, J_{PP} = 23, 11; with ^{183}W satellites, J_{WP} = 224), 20.72 (dd, J_{PP} = 23, 66; with ^{183}W satellites, J_{WP} = 286) and 28.66 (dd, J_{PP} = 66, 11; with ^{183}W satellites, J_{WP} = 282 Hz); ^1H NMR (CD_2Cl_2, 20 °C) δ 3.98–4.40 (m, 8 H, C_5H_4) and 6.80–7.60 (m, 35 H, C_6H_5).

Complex **12f** (Found: C, 60.99; H, 3.92. $C_{55}H_{43}FeO_3P_3W$ requires C, 60.91; H, 4.00%): mass spectrum (FAB) *m*/*z* 1084 (M^+), 822 ($M^+ - PPh_3$) and 822 − 28*n* (*n* = 1–3); IR (1,2-$C_2H_4Cl_2$, cm^{-1}) ν(CO) 1940s, 1846s and 1828 (sh); ^{31}P-{^1H} NMR (CD_2Cl_2, 20 °C) δ 16.26 (d, J_{PP} = 28; with ^{183}W satellites, J_{WP} = 224) and 19.05 (t, J_{PP} = 28; with ^{183}W satellites, J_{WP} = 210 Hz); ^1H NMR (CD_2Cl_2, 20 °C) δ 3.90 (s, 2 H), 4.26 (s, 2 H), 4.53 (s, 2 H), 4.80 (s, 2 H, C_5H_4) and 6.80–7.60 (m, 35 H, C_6H_5).

Reaction of complex 1 and PPh_2Me

Complex **1** (50 mg, 0.058 mmol) was treated with PPh_2Me (12 mg, 0.06 mmol) for 20 h by the method described above. Three products were isolated: yellow [W(CO)$_4$(η^2-dppf)] (2 mg, 4%), yellow *mer*-[W(CO)$_3$(η^2-dppf)(PPh_2Me)] **13m** (4 mg, 7%) and yellow *fac*-[W(CO)$_3$(η^2-dppf)(PPh_2Me)] **13f** (52 mg, 88%).

Complex **13m** (Found: C, 58.50; H, 4.23. $C_{50}H_{41}FeO_3P_3W$ requires C, 58.75; H, 4.01%): mass spectrum (FAB) *m*/*z* 1022 (M^+), 994 ($M^+ - CO$), 822 ($M^+ - PPh_2Me$) and 822 − 28*n* (*n* = 1–3); IR (1,2-$C_2H_4Cl_2$, cm^{-1}) ν(CO) 1960w, 1852s and 1842 (sh); ^{31}P-{^1H} NMR (CD_2Cl_2, 20 °C) δ 1.50 (dd, J_{PP} = 13, 65; with ^{183}W satellites, J_{WP} = 272), 17.62 (dd, J_{PP} = 13, 23; with ^{183}W satellites, J_{WP} = 224) and 21.35 (dd, J_{PP} = 23, 65; with ^{183}W satellites, J_{WP} = 292 Hz); ^1H NMR (CD_2Cl_2, 20 °C) δ 1.65 (d, 3 H, J_{PH} = 7, Me), 4.16 (s, 2 H), 4.25 (br, 4 H), 4.28 (s, 2 H, C_5H_4) and 7.00–7.70 (m, 30 H, C_6H_5).

Complex **13f** (Found: C, 58.52; H, 4.13. $C_{50}H_{41}FeO_3P_3W$ requires C, 58.75; H, 4.01%): mass spectrum (FAB) *m*/*z* 1022 (M^+), 994 ($M^+ - CO$), 822 ($M^+ - PPh_2Me$) and 822 − 28*n* (*n* = 1–3); IR (1,2-$C_2H_4Cl_2$, cm^{-1}) ν(CO) 1938s, 1846s and 1830 (sh); ^{31}P-{^1H} NMR (CD_2Cl_2, 20 °C) δ −3.71 (t, J_{PP} = 27; with ^{183}W satellites, J_{WP} = 228) and 19.83 (d, J_{PP} = 27; with ^{183}W satellites, J_{WP} = 216 Hz); ^1H NMR (CD_2Cl_2, 20 °C) δ 1.90 (d, 3 H, J_{PH} = 5 Hz, Me), 3.99 (s, 2 H), 4.28 (s, 2 H), 4.50 (s, 2 H), 4.73 (s, 2 H, C_5H_4) and 7.00–7.60 (m, 30 H, C_6H_5).

Isomerizations

Complexes 4f and 7f. Typically, an NMR tube was charged with *fac*-[W(CO)$_3$(η^2-dppf)(η^1-dppm)] **4f** (15 mg) and CD_2Cl_2 (2 cm^3) under nitrogen. The isomerization was carried out at room temperature and monitored by ^{31}P NMR spectroscopy. It was complete after 72 h, showing only the resonances for **5m**. Isomerization of complex **7f** to give **7m** takes 1 week to complete at room temperature, but only 3 h are required at 80 °C.

Complexes 4m and 6m. A typical reaction: a Schlenk flask (50 cm^3) was charged with *mer*-[W(CO)$_3$(η^2-dppf)(η^1-dppm)] **4m** (40 mg) and 1,2-dichloroethane (10 cm^3). The flask was placed in an oil-bath at 80 °C and the reaction was monitored by IR spectroscopy in the CO stretching region. The spectra showed no further change after 6 h. The solvent was evaporated under vacuum and the residue separated by TLC, affording **5m** in 90% yield. Isomerization of complex **6m** was carried out at 80 °C, producing **7m** in 71% yield. No reaction was observed at ambient temperature.

Complex 4f in the presence of acid. The complex (18 mg, 0.015 mmol) and dichloromethane (10 cm^3) were placed in a Schlenk flask (50 cm^3) containing a magnetic stirring bar and a rubber septum. An ether solution of HBF_4 (20 µl, excess) was added *via* a syringe. The mixture was stirred at ambient temperature for 2 h, and evacuated under vacuum. The residue was subjected to TLC, eluting with CH_2Cl_2–*n*-hexane (1 : 1, v/v). The material from the yellow band gave *mer*-[W(CO)$_3$(η^2-dppf)(η^1-dppm)] **4m** (14 mg, 78%) (Found: C, 61.42; H, 4.22. $C_{62}H_{50}FeO_3P_4W$ requires C, 61.71; H, 4.18%): mass spectrum (FAB) *m*/*z* 1205 (M^+), 1205 − 28*n* (*n* = 1–3) and 821 (M^+ − dppm); IR (1,2-$C_2H_4Cl_2$, cm^{-1}) ν(CO) 1961w and 1853s; ^{31}P-{^1H} NMR (CD_2Cl_2, 20 °C) δ 21.66 (dd, J_{PP} = 23, 66; with ^{183}W satellites, J_{WP} = 288, dppf), 16.83 (dd, J_{PP} = 23, 33; with ^{183}W satellites, J_{WP} = 230, dppf), 14.66 (ddd, J_{PP} = 33, 38, 66; with ^{183}W satellites, J_{WP} = 275, dppm) and −25.06 (d, J_{PP} = 38 Hz, dppm); ^1H NMR (CD_2Cl_2, 20 °C) δ 3.23 (br, 2 H, CH_2), 4.12 (br, 4 H, C_5H_4), 4.21 (br, 4 H, C_5H_4) and 6.80–7.70 (m, 40 H, C_6H_5).

Complex 6f in the presence of acid. Isomerization of *fac*-[W(CO)$_3$(η^2-dppf)(η^1-dppe)] **6f** (20 mg, 0.016 mmol) in the presence of an excess amount of HBF_4 was carried out and worked up in a fashion identical to that above. Yellow *mer*-[W(CO)$_3$(η^2-dppf)(η^1-dppe)] **6m** (12 mg, 60%) was obtained as the major product. Mass spectrum (FAB): *m*/*z* 1221 (M^+), 823 (M^+ − dppe) and 823 − 28*n* (*n* = 1–3); IR (1,2-$C_2H_4Cl_2$, cm^{-1}) ν(CO) 1960w and 1854s; ^{31}P-{^1H} NMR (CD_2Cl_2, 20 °C) δ 21.53 (dd, J_{PP} = 23, 66; with ^{183}W satellites, J_{WP} = 291, dppf), 18.27 (ddd, J_{PP} = 33, 34, 66; with ^{183}W satellites, J_{WP} = 273, dppe), 16.26 (dd, J_{PP} = 23, 34; with ^{183}W satellites, J_{WP} = 225, dppf) and −13.45 (d, J_{PP} = 34 Hz, dppe); ^1H NMR (CD_2Cl_2, 20 °C) δ 1.62 (m, 2 H), 2.36 (m, 2 H, C_2H_4), 4.12 (s, 2 H), 4.18 (s, 2 H), 4.22 (s, 2 H), 4.24 (s, 2 H, C_5H_4) and 6.60–7.80 (m, 40 H, C_6H_5).

Reactions of complex 4f

With dppe. The complex (23 mg, 0.019 mmol) and dppe (75 mg, 0.19 mmol) were placed in a Schlenk flask (50 cm^3) containing a magnetic stirring bar. The flask was fitted with a rubber septum, evacuated, and backfilled with nitrogen. After introducing dichloromethane (15 cm^3), the solution was stirred at ambient temperature for 48 h. The mixture was then dried under vacuum and the residue separated by TLC, eluting with CH_2Cl_2–*n*-hexane (1 : 1, v/v). Three products were isolated in order of appearance on the TLC plate: yellow *mer*-[W(CO)$_3$(η^2-dppm)(η^1-dppf)] **5m** (11 mg, 48%), yellow *fac*-[W(CO)$_3$(η^2-dppf)(η^1-dppe)] **6f** (60 mg, 25%) and yellow *fac*-[W(CO)$_3$(η^2-dppf)(η^1-dppm)] **4f** (50 mg, 21%).

With PMe_3. A Schlenk flask (50 cm^3) was charged with *fac*-[W(CO)$_3$(η^2-dppf)(η^1-dppm)] **4f** (10 mg, 0.008 mmol) and 1,2-dichloroethane (10 cm^3) under nitrogen. A toluene solution of PMe_3 (12 µl, 0.012 mmol) was introduced by a microsyringe. The mixture was stirred at ambient temperature for 30 h. The solvents were removed under vacuum and the residue separated by TLC, eluting with *n*-hexane–dichloromethane (1 : 1, v/v). The known complex *fac*-[W(CO)$_3$(η^2-dppf)(PMe_3)] [12] **10f** (6 mg, 83%) and **5m** (1 mg, 10%) were obtained.

With CO. A two-necked flask (100 cm^3) was equipped with a magnetic stir bar. One neck was connected to an oil bubbler and the other had an inlet tube for introduction of carbon monoxide gas into the solution. A solution of *fac*-[W(CO)$_3$(η^2-dppf)(η^1-dppm)] **4f** (20 mg, 0.017 mmol) in 1,2-dichloroethane (10 cm^3) was transferred to the flask and saturated with CO gas. The mixture was stirred at ambient temperature for 48 h with slow bubbling of CO through the solution. The mixture was dried under vacuum and the residue separated by TLC. The known complex [W(CO)$_4$(η^2-dppf)] [14] **11** (10 mg, 70%) and **5** (3 mg, 15%) were obtained.

Results and Discussion

Preparation of compound 3

The syntheses of *fac*-[W(CO)$_3$(η^2-dppf)(NCMe)] [12] **1** and *fac*-

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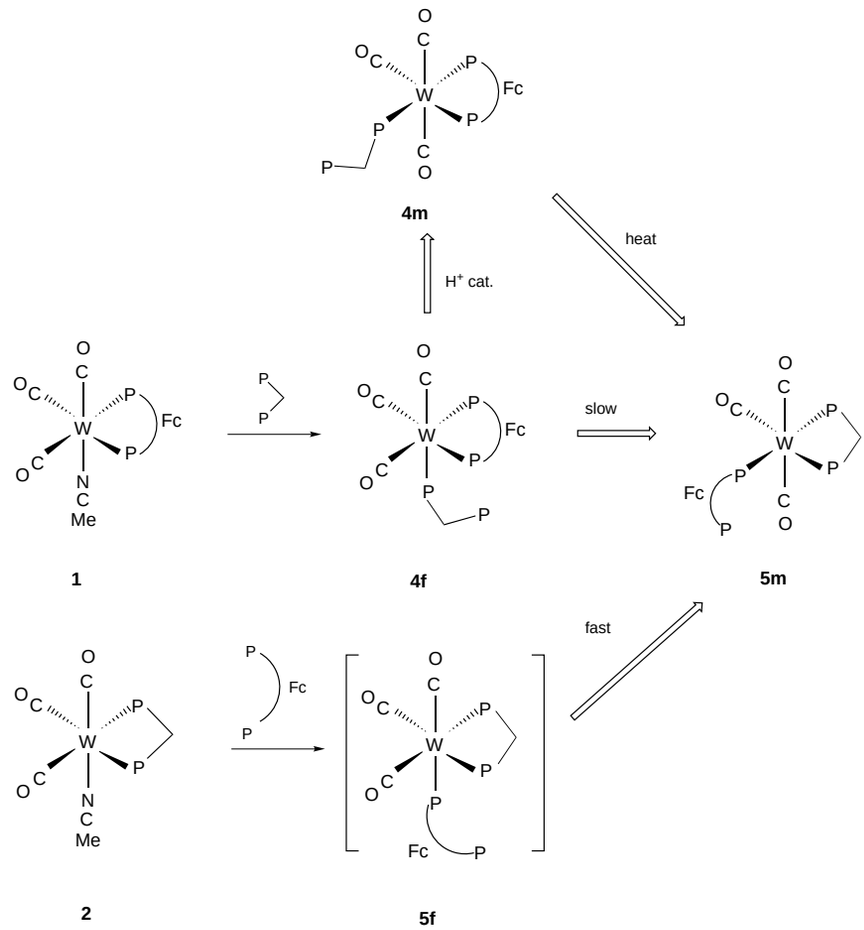
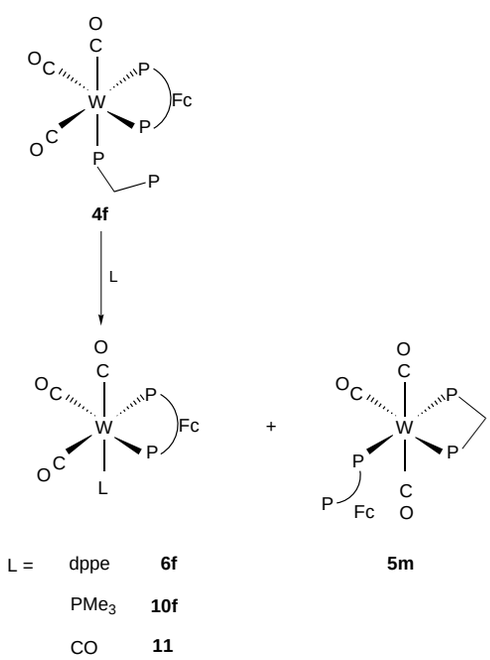


Scheme 1



Scheme 2

$[W(CO)_3(\eta^2\text{-dppm})(NCMe)]$[9] **2** have been previously described. The analogous complex *fac*-$[W(CO)_3(\eta^2\text{-dppe})(NCMe)]$ **3** is prepared in a similar fashion by treating $[W(CO)_3(NCMe)_3]$ with equimolar dppe at room temperature. The IR spectrum of **3** in the carbonyl region resembles those recorded for **1** and **2**, indicating similar structures. The ^{31}P NMR spectrum of **3** displays one resonance at δ 46.25, which is significantly downfield from those recorded for **1** (δ 22.4) and **2** (δ −11.06).

Preparation and isomerization of complexes 4f and 5f

The complex *fac*-$[W(CO)_3(\eta^2\text{-dppf})(\eta^1\text{-dppm})]$ **4f** is initially afforded from the reaction of *fac*-$[W(CO)_3(\eta^2\text{-dppf})(NCMe)]$ **1** and dppm at ambient temperature. Isomerization of **4f** readily takes place at 25 °C to give *mer*-$[W(CO)_3(\eta^2\text{-dppm})(\eta^1\text{-dppf})]$ **5m** together with a switch of the chelate ligand from dppf to dppm. Complete transformation from **4f** to **5m** takes 72 h at 25 °C, but only 4 h are required at 50 °C. In the presence of acid, however, *mer*-$[W(CO)_3(\eta^2\text{-dppf})(\eta^1\text{-dppm})]$ **4m** is obtained as the sole product. Compound **4m** is indefinitely stable at room temperature, but it slowly converts into **5m** in hot 1,2-dichloroethane solution (80 °C). The other isomer *fac*-$[W(CO)_3(\eta^2\text{-dppm})(\eta^1\text{-dppf})]$ **5f** is not isolable but only detected by ^{31}P NMR spectroscopy as an intermediate during the reaction of *fac*-$[W(CO)_3(\eta^2\text{-dppm})(NCMe)]$ **2** and dppf, leading to **5m**. The results are summarized in Scheme 1.

It is obvious that complexes **4f** and **5f** are the kinetic products of the reactions, while **5m** is most stable thermodynamically. However, when dppe, PMe_3 or CO is present, **5m** is obtained together with *fac*-$[W(CO)_3(\eta^2\text{-dppf})(\eta^1\text{-dppe})]$ **6f**, *fac*-$[W(CO)_3(\eta^2\text{-dppf})(PMe_3)]$ **10f** and $[W(CO)_4(\eta^2\text{-dppf})]$ **11**, respectively (Scheme 2). This indicates that substitution of the η^1-diphosphine ligand is a competitive reaction. Nevertheless, once the meridional isomer is formed, it is quite resistant to ligand dissociation, such that **5m** does not react with PMe_3 at 50 °C.

The different reactivity between complexes **4f** and **5f** can be rationalized in terms of the structures of parent compounds **1** and **2**. Since the dppf ligand of **1** can modify its steric bite by twisting the cyclopentadienyl rings, the phenyl groups and the NCMe ligand are staggered.[12] However, the four-membered dppm ring of **2** constrains the phenyl groups to being eclipsed to the axial NCMe and CO ligands.[9] So compound **5f** would

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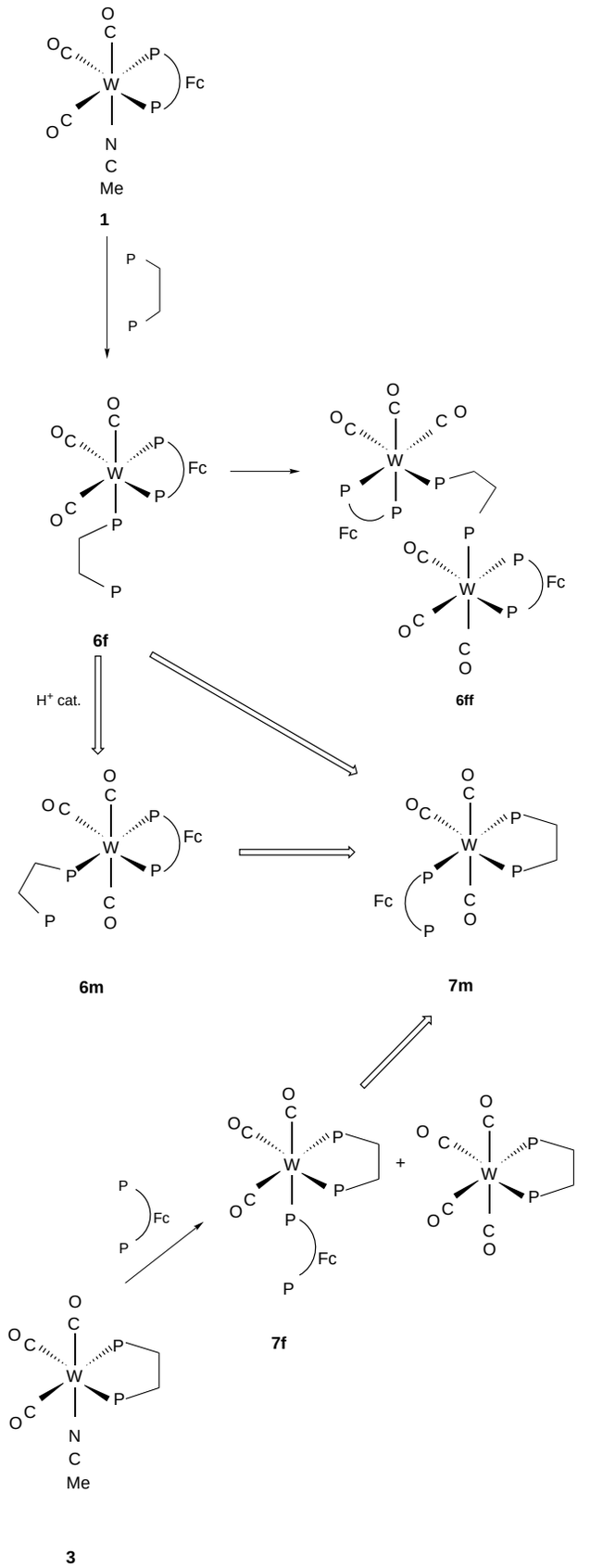

Scheme 3

sustain stronger steric repulsions between phosphine ligands than **4f** and is more susceptible to isomerization.

Preparation and isomerization of complexes 6f and 7f

Reactions of *fac*-[W(CO)$_3$(η^2-dppf)(NCMe)] **1** with dppe and its subsequent isomerization processes are summarized in Scheme 3. The results closely resemble the reactions with dppm shown above, except that a dimetallic complex *fac*,*fac*-[{W(CO)$_3$(η^2-dppf)}$_2$(η^1 : η^1-dppe)] **6ff** is produced and both **6f** and **7f** are isolable. Standing a solution of pure **6f** at 25 °C yields **7m** and **6ff**, but under acidic conditions **6m** is obtained solely without forming the dimetallic species. It is apparent that eliminating a dppe ligand from **6f** is essential to give **6ff**, while **6m** is resistant to ligand dissociation. Furthermore, no isomerization of **6ff** is evidenced. This is contrary to the reaction of *fac*-[Mo(CO)$_3$(NCMe){η^2-Ph$_2$PN(Pr^i)PPh(dmpz)}] and dppe to produce *mer*,*mer*-[{Mo(CO)$_3$[η^2-Ph$_2$PN(Pr^i)PPh(dmpz)]}$_2$-(η^1 : η^1-dppe)].[11]

On the other hand, treating *fac*-[W(CO)$_3$(η^2-dppe)(NCMe)] **3** with dppf at room temperature produces [W(CO)$_4$(η^2-dppe)] (33%), *fac*-[W(CO)$_3$(η^2-dppe)(η^1-dppf)] **7f** (29%) and *mer*-[W(CO)$_3$(η^2-dppe)(η^1-dppf)] **7m** (26%). It is likely compound **7f** is afforded initially, following by isomerization to give **7m** as well as disproportionation to yield the W(CO)$_4$ complex.

Preparation and isomerization of complex 8f

The acetonitrile ligand of *fac*-[W(CO)$_3$(η^2-dppm)(NCMe)] **2** is readily replaced by dppe, but leading to *fac*-[W(CO)$_3$(η^2-dppe)(η^1-dppm)] **9f** and *mer*-[W(CO)$_3$(η^2-dppe)(η^1-dppm)] **9m** (Scheme 4). Phosphorus-31 NMR spectroscopy has been applied to assess the progress of reaction. The spectrum of reaction mixture after 2 h shows the presence of *fac*-[W(CO)$_3$(η^2-dppm)(η^1-dppe)] **8f** along with small quantities of *mer*-[W(CO)$_3$(η^2-dppm)(η^1-dppe)] **8m** and **9f**. The quantities of **8f**, **8m** and **9f** are about equal in 24 h. After 3 d, **9f** and **8m** are present as the major products together with a minor amount of **8f** and **9m**. Although this transformation is slow, attempts to isolate all the components by TLC only afford **9f** and **9m**. It is probable that the conversion of **8** into **9** is accelerated by acid contaminant on the silica gel. Schenk and Hilpert[10] previously reported an analogous reaction of *fac*-[Mo(CO)$_3$(η^2-dppm)-(NCMe)] and dppe to yield *fac*-[Mo(CO)$_3$(η^2-dppe)(η^1-dppm)], where the four-membered chelate ring of dppm is opened up to leave an η^1-co-ordinated dppm while a more stable five-membered chelate ring is formed by dppe. The ultimate formation of **9m** indicates the operation of ring strains in determining the products.

Reaction of complex 1 and bulky monophosphine

Treatment of *fac*-[W(CO)$_3$(η^2-dppf)(NCMe)] **1** with PPh$_3$ and PPh$_2$Me affords *fac*-[W(CO)$_3$(η^2-dppf)(PPh$_3$)] **12f** and *fac*-[W(CO)$_3$(η^2-dppf)(PPh$_2$Me)] **13f**, respectively, which then rearrange to give *mer*-[W(CO)$_3$(η^2-dppf)(PPh$_3$)] **12m** and *mer*-[W(CO)$_3$(η^2-dppf)(PPh$_2$Me)] **13m**. The analogous complexes *fac*-[W(CO)$_3$(η^2-dppf)(L)] (L = PMe$_3$, PPh$_2$H, or PPh$_2$OH) are stable under similar conditions.[12] Obviously, the energy barrier for *fac* ⟶ *mer* transformation is reduced as the steric bulk of the ligands increases.

Characterization of new compounds

Compounds **5f**, **8m** and **8f** cannot be isolated in a pure form and were characterized only by ^{31}P NMR spectroscopy. The remaining complexes form crystalline solids and give satisfactory analyses (C, H). Their FAB mass spectra display the molecular ion and ions corresponding to successive loss of three carbonyls. The IR spectra in the carbonyl region for the facial isomers show three strong bands, presumably due to a disrupted C_3 symmetry for the W(CO)$_3$ group, while the meridional geometry is indicated by one weak and two medium to strong absorption bands.[2–6,9,15]

Identification of these new complexes is unambiguously substantiated by ^{31}P NMR spectroscopy. Their spectra are assigned on the basis of chemical shifts and coupling patterns.[2–4,10,16] In general, the facial isomers have a plane of symmetry and would

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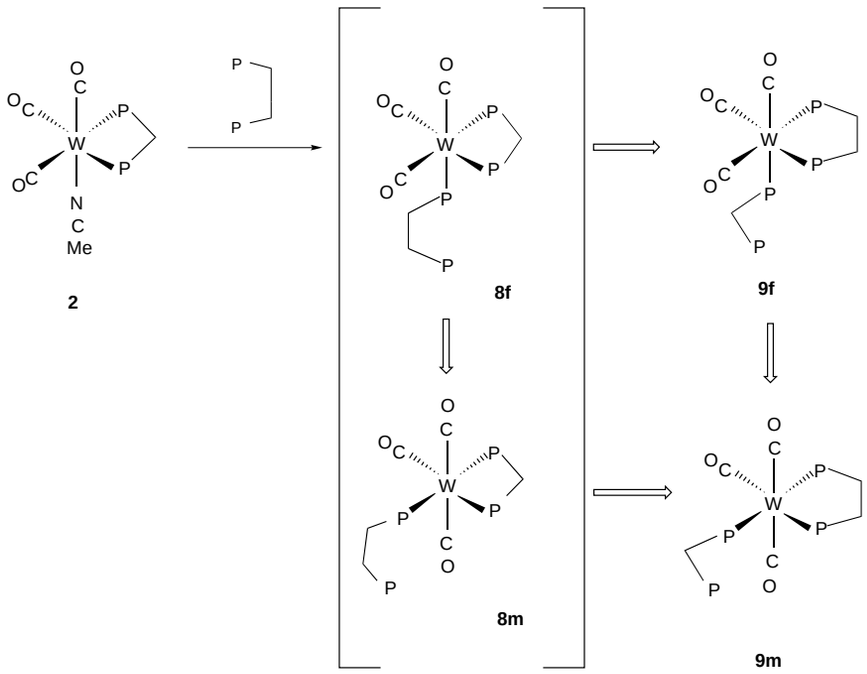

Scheme 4

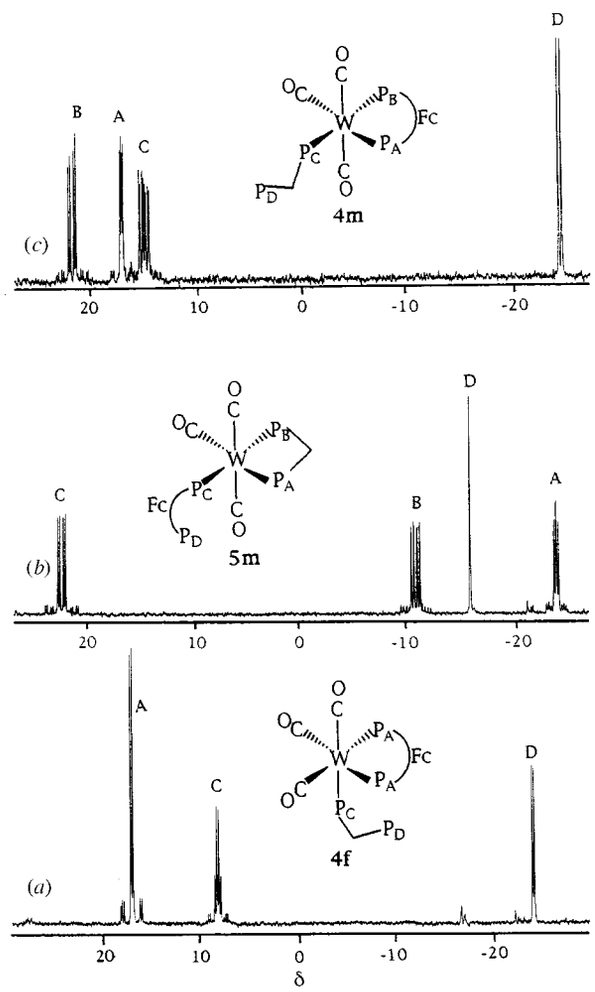

Fig. 1 The ^{31}P-{^{1}H} NMR spectra of (*a*) *fac*-[W(CO)$_3$(η^2-dppf)(η^1-dppm)] **4f**, (*b*) *mer*-[W(CO)$_3$(η^2-dppm)(η^1-dppf)] **5m** and (*c*) *mer*-[W(CO)$_3$(η^2-dppf)(η^1-dppm)] **4m** in CD_2Cl_2 solution

display two ^{31}P resonances for the co-ordinated phosphines and one resonance for the pendant phosphine group, while the meridional isomers present four resonance signals. Typical spectra of **4f**, **4m** and **5m** are illustrated in Fig. 1 for comparison. For **4f** a doublet signal at δ 16.91 and a doublet of doublets at δ 8.17 accompanied by ^{183}W satellites are assigned to the co-ordinated dppf and dppm moieties, respectively, and an upfield doublet resonance at δ −24.16 without ^{183}W satellites is assigned to the pendant dppm group. On the other hand, **4m** and **5m** display three complex resonances for the co-ordinated phosphines due to coupling between the inequivalent phosphorus atoms and to the ^{183}W atom.

The co-ordination shifts, $\Delta = \delta_{monodentate} - \delta_{free\ ligand}$, and chelation shifts, $\Delta_R = \delta_{chelate} - \delta_{monodentate}$, of the diphosphine ligands are of interest in these complexes. The co-ordination shifts for dppm, dppe and dppf are comparable, averaging +32, +24 and +28 ppm, respectively. In contrast, the chelation shifts are more diverse, where the four-membered dppm rings are shielded (−30 ppm), the five-membered dppe rings are deshielded (+25 ppm) and the dppf rings are only slightly affected (+5 ppm). Although the theoretical aspects of the ring contribution remain elusive, Garrou[17] has proposed the general utility of Δ and Δ_R for structural assignments of transition-metal phosphine complexes.

Possible isomerization mechanism

The facial–meridional isomerism may be reasonably accounted for by the reaction sequence shown in Scheme 5. Apparently, three bulky phosphines in a facial arrangement cause considerable steric repulsions, leading to ready dissociation of the η^1-disphosphine ligand to give **I**, or opening up the η^2-disphosphine ring to give **II**. The resulting square-pyramidal intermediates could then undergo site exchange, presumably through a trigonal-bipyramidal transient with one of the diphosphine ligands at the axial position and ring closing to yield the final products.[18,19] Alternatively, an associative mechanism to generate a seven-co-ordinate, 20-electron intermediate [W(CO)$_3$(η^2-diphos)(η^2-diphos′)] seems improbable based on the steric considerations.

Since isomerization of complex **4f** produces **5m** solely without forming **4m**, the site-exchange rate for **II** should be much faster than that for **I**. One possible explanation is the ring constraints of **I** increasing the energy separation between the more stable square-pyramidal and less stable trigonal-bipyramidal structures. Furthermore, adding PMe_3 to a solution of **4f** does not give [W(CO)$_3$(η^1-dppm)(η^1-dppf)(PMe$_3$)] or [W(CO)$_3$(η^2-dppm)(PMe$_3$)]. This means that, once the intermediate **II** is

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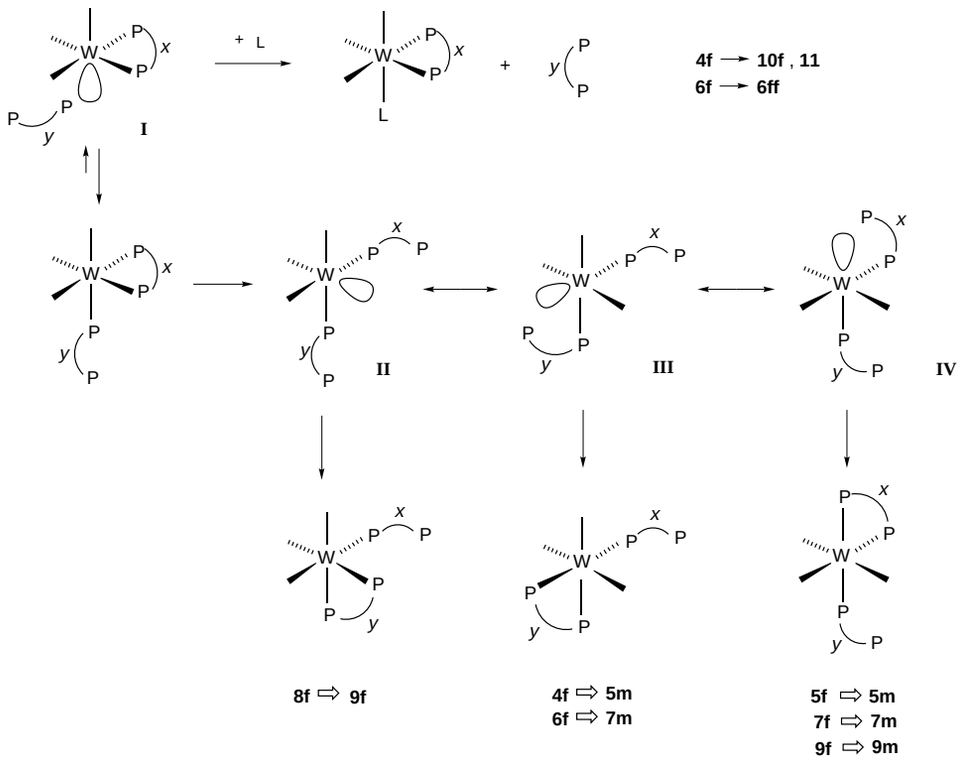
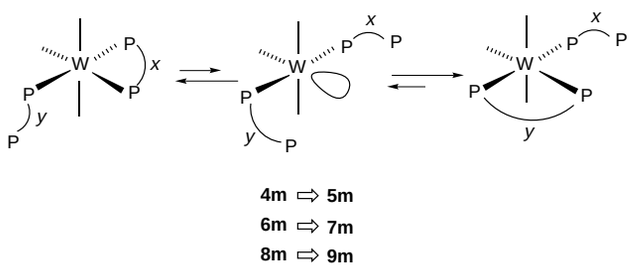
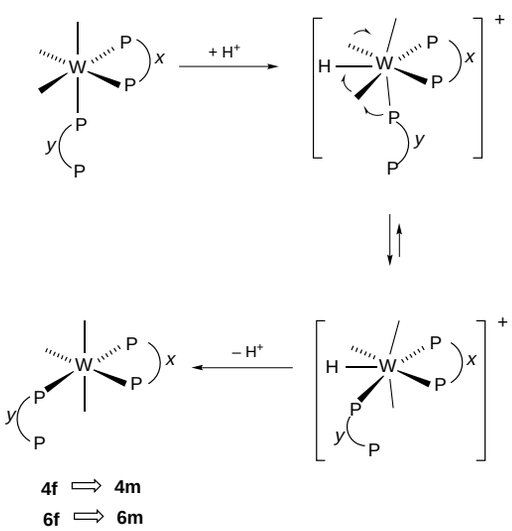


Scheme 5



Scheme 6



Scheme 7

formed, the subsequent site exchange and ring-closing processes must be very rapid.

This mechanism is further supported by a kinetic study. The rate constants measured for the reaction of complex **4f** with CO and PMe_3 at 25 °C are comparable, being 2.17×10^{-5} and 2.13×10^{-5} s^{-1}, respectively. Furthermore, both reactions are observed to be first order in metal substrate and zero order in PMe_3 or CO concentration at a pressure close to 1 atm (*ca.* 101 325 Pa). This clearly indicates that the rate-determining step is fission of the W–dppm bond.

Rearrangement of complex **4m** to **5m**, **6m** to **7m** and **8m** to **9m** probably occurs *via* the pathway shown in Scheme 6. It is apparent the ability of diphosphine ligands to form a chelate ring is dppe > dppm > dppf. The five-membered dppe ring is obviously preferable to the strained, four-membered dppm ring. On the other hand, though the chelated dppf ligand presents little ring strain, its large bite angle (*ca.* 98°)[12] combined with the steric bulk of the phenyl groups could impose strong steric interactions with the adjacent ligands. This makes dppf less favorable as a chelate ligand than dppm.

Vila and Shaw[20] previously reported a trace of acid-induced rapid interconversion between the facial and meridional isomers of $[W(CO)_3(\eta^2\text{-dppm})(PEt_3)]$ and a hydrido intermediate, $[WH(CO)_3(\eta^2\text{-dppm})(PEt_3)]^+$, was evidenced.[20] It is likely that protonation of complex **4f** or **6f** generates a fluxional seven-co-ordinate species, which then undergoes fast intramolecular rearrangement by placing the η^1-diphosphine ligand *trans* to the η^2-disphosphine group to reduce steric crowding. Subsequent deprotonation of this species could afford the meridional isomer (Scheme 7). A pseudo-three-fold rotation is likely involved to account for this facile rearrangement. It has been shown that the energy barrier for a ligand three-fold rotation decreases dramatically as the co-ordination number of the metal changes from six to seven.[21]

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