Neighboring Metal-Induced Oxidative Addition in Conjunction with a Hydride Trap: Formation of [(η^5-MeC$_5$H$_4$)Fe(CO)(μ-η^1:η^1-PPh$_2$CH$_2$PPh$_2$)(μ-H)M(CO)$_4$] (M = W, Mo)

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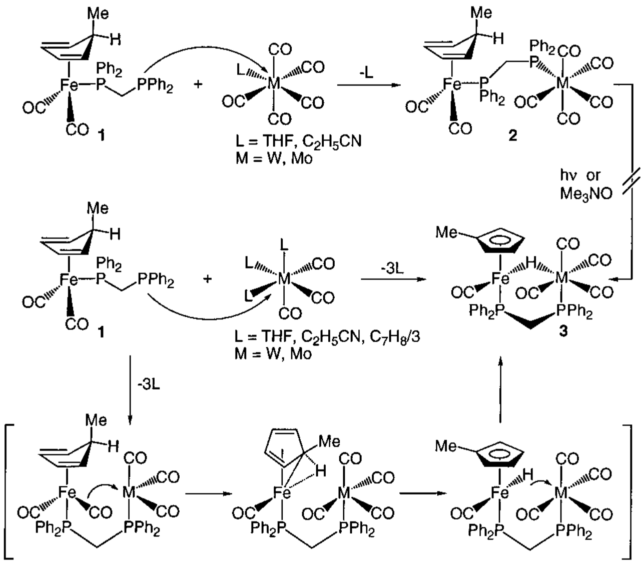
Summary: The reaction of (η^4-MeC$_5$H$_5$)Fe(CO)$_2$(η^1-dppm), **1**, *with M(CO)$_3$L$_3$ produced (η^5-MeC$_5$H$_4$)Fe(CO)(μ-η^1:η^1-dppm)(μ-H)M(CO)$_4$,* **3** *(L$_3$ = (C$_2$H$_5$CN)$_3$, (THF)$_3$, C$_7$H$_8$; M = W, Mo). The novel hydrido-bridged Fe(II)−M(0) compound was likely formed via the following steps: coordination of the monodentate dppm to M and then CO migration from Fe to M with a sequential or concerted oxidative addition of the endo-C−H bond of the η^4-MeC$_5$H$_5$ ligand to give the (η^5-MeC$_5$H$_4$)FeH complex, followed by a trapping of the Fe−H bond by M, forming a six-membered heterocyclic ring in* **3**.

Being important in catalytic or stoichiometric reactions,[1] the chemistry of organo-transition metal hydrides has been vigorously pursued for many years. The main synthetic routes to hydrides are by protonation, from hydride donors, *via* oxidative addition, or *via* β-elimination.[2] The oxidative addition of active hydrogen-containing species leads to such a formation, silanes H−SiR$_3$ resulting in silyl hydrides[3] and orthometalation of C−H giving orthometalated hydrides,[4] for example. The intramolecular oxidative addition is key to the facile loss of hydrogen in (η^4-C$_5$H$_6$)Fe(CO)$_3$ to give [(η^5-C$_5$H$_5$)Fe(CO)$_2$]$_2$, proceeding with an intermediate formation of (η^5-C$_5$H$_5$)Fe(CO)$_2$H.[5] Yet (η^5-C$_5$H$_5$)Fe(CO)$_2$H in general is synthesized independently from the acidification of (η^5-C$_5$H$_5$)Fe(CO)$_2$Na, not directly from (η^4-C$_5$H$_6$)Fe(CO)$_3$, due to competing and/or consecutive reactions.[6] In this communication, we wish to report a clean activation of *endo*-C−H bond of η^4-cyclopentadiene in the dppm derivative (η^4-MeC$_5$H$_5$)Fe(CO)$_2$(η^1-dppm), dppm = Ph$_2$PCH$_2$PPh$_2$, after its ligation to a M(CO)$_3$ unit (M = W, **a**; M = Mo, **b**). The result is a novel hydrido-bridged heterodimetallic complex, giving the first example of a metal (M) inducing an oxidative addition of C−H of η^4-cyclopentadiene on a neighboring metal (Fe) with the M intervention to finalize in “3c−2e” M−H−Fe bonding.[7]

Scheme 1



(η^4-MeC$_5$H$_5$)Fe(CO)$_2$(η^1-dppm), **1**, could be prepared in a reaction of an equimolar amount of (η^5-C$_5$H$_5$)Fe(CO)$_2$I with MeLi in the presence of dppm at low temperature,[8] following the nucleophilic Cp-ring alkylation strategy.[9] Compound **1** could be used as a metallo ligand to construct heterodimetallic complexes in which the dppm serves as a stabilizing backbone. Examples[10] are (η^4-MeC$_5$H$_5$)Fe(CO)$_2$(μ-η^1:η^1-dppm)AuCl and (η^5-MeC$_5$H$_4$)Fe(μ-CO)$_2$(μ-η^1:η^1-dppm)RhCl$_2$.

Outlined in Scheme 1, treatment of **1** (0.17 mmol) with M(CO)$_5$(THF)[11] (0.20 mmol) in THF (20 mL) at ambient temperature for 2 h yielded (η^4-MeC$_5$H$_5$)Fe(CO)$_2$(μ-η^1:η^1-dppm)M(CO)$_5$, **2** (**2a**, 0.15 mmol, 88%

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[1] (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; John Wiley & Sons: New York, 1994. (b) Dedieu, A., Ed. *Transition Metal Hydrides*; VCH: Weinheim, Germany, 1990. (c) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.

[2] Crabtree, R. H. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; John Wiley & Sons: New York, 1994; Vol. 3, pp 1395−1396.

[3] (a) Schubert, U.; Ackermann, K.; Wörle, B. *J. Am. Chem. Soc.* **1982**, *104*, 7378. (b) Fernandez, M. J.; Bailey, P. M.; Bentz, P. O.; Ricci, J. S.; Koetzle, T. F.; Maitlis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 5458. (c) Wang, W.-D.; Eisenberg, R. *J. Am. Chem. Soc.* **1990**, *112*, 1833.

[4] (a) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73. (b) Constable, E. C. *Polyhedron* **1984**, *3*, 1037.

[5] (a) Elschenbroich, C.; Salzer, A. *Organometallics,* 2nd ed.; VCH: Weinheim, Germany, 1992; p 199. A few examples of oxidative addition of η^4-cyclopentadiene ligand to a metal: (η^5-C$_5$H$_5$)Fe(CO)$_2$H,$^{b-d}$ (η^5-C$_5$H$_5$)Ru(CO)$_2$H,^{e} (η^5-C$_5$H$_5$)Os(CO)$_2$H,^{e} (η^5-C$_5$H$_5$)Cr(CO)$_3$H,^{f} (η^5-C$_5$H$_5$)Mo(CO)$_3$H,^{f} (η^5-C$_5$H$_5$)W(CO)$_3$H,^{f} (η^5-C$_5$Me$_5$)Mo(CO)$_3$H,^{g} and (η^5-C$_5$Me$_5$)W(CO)$_3$H.^{9} (b) Davison, A.; Green, M. L. H.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3172. (c) Kochhar, R. K.; Pettit, R. *J. Organomet. Chem.* **1966**, *6*, 272. (d) Whitesides, T. H.; Shelly, J. *J. Organomet. Chem.* **1975**, *92*, 215. (e) Humphries, A. P.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1710. (f) Keppie, S. A.; Lappert, M. F. *J. Chem. Soc. A* **1971**, 3216. (g) Kubas, G. J.; Wasserman, H. J.; Ryan, R. R. *Organometallics* **1985**, *4*, 2012.

[6] Shackleton, T. A.; Mackie, S. C.; Fergusson, S. B.; Johnston, L. J.; Baird, M. C. *Organometallics* **1990**, *9*, 2248 and relevant references within.

[7] The strategy[2] used previously for the synthesis of hydrido-bridged metal clusters was either an oxidative addition to preformed cluster compounds or a metal hydride attachment to the second metal centers.

[8] Liu, L.-K.; Luh, L.-S.; Eke, U. B. *Organometallics* **1995**, *14*, 440.

[9] (a) Liu, L.-K.; Luh, L.-S. *Organometallics* **1994**, *13*, 2816. (b) Luh, L.-S.; Liu, L.-K. *Bull. Inst. Chem., Acad. Sin.* **1994**, *41*, 39.

[10] Liu, L.-K.; Luh, L.-S.; Wen, Y.-S.; Eke, U. B.; Mesubi, M. A. *Organometallics* **1995**, *14*, 4474.

[11] (a) Kolodziej, R. M.; Lee, A. J. *Organometallics* **1986**, *5*, 450. (b) Arndt, L. W.; Darensbourg, M. Y.; Delord, T.; Bancroft, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 2617.

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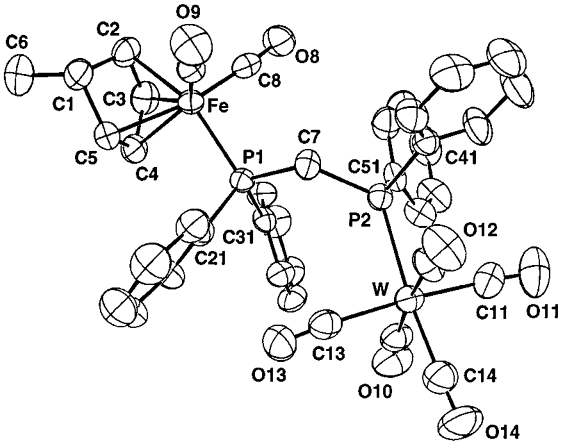

Figure 1. Thermal ellipsoid drawing (50%) of complex **2a**. The H atoms are omitted for clarity. Selected bond lengths (Å): Fe−P1 2.206(1), Fe−C2 2.086(5), Fe−C3 2.037(6), Fe−C4 2.045(5), Fe−C5 2.117(5), Fe−C8 1.763(7), Fe−C9 1.776(6), W−P2 2.551(2), W−C10 2.030(6), W−C11 2.015(8), W−C12 2.045(6), W−C13 2.043(7), W−C14 1.989(7). Selected bond angles (deg): P1−Fe−C8 94.5(2), P1−Fe−C9 97.6(2), Fe−P1−C7 111.6(2), W−P2−C7 122.6(2), P1−C7−P2 127.7(3).

yield; **2b**, 0.13 mmol, 76% yield), after chromatographic workup on a silica column using 1:8 ethylacetate/*n*-hexane as an eluent.[12] Complex **2a** revealed in its ^{1}H NMR spectra the characteristic peaks at δ 4.80 (2H), 2.58 (1H), and 2.07 (2H), consistent with a η^4-MeC$_5$H$_5$ bonding mode. In the ^{31}P NMR spectra, a simple AB pattern was observed with one of them having the tungsten satellite. Spectroscopically complex **2b** behaved in a similar way, except for the difference between W and Mo. Stable in the solid state at ambient temperature, complex **2** gradually decomposed in chlorinated solvents. The structure of **2a** was confirmed by X-ray crystallography.[13] An ORTEP drawing is shown in Figure 1. The two metal centers are seen linked by one dppm bridge [Fe⋯W = 7.035(1) Å]. The torsion angle of Fe−P⋯P−W is 162.0(1)°. The ring Me group is *exo* on the cyclopentadiene from Fe. The coordination geometry around Fe(0) is a distorted square pyramid with one of the CO ligands at the apical position. The second CO ligand is in the basal plane *trans* to one of the double bonds of the cyclopentadiene, and the PPh$_2$-CH$_2$− ligand is *trans* to the second double bond. An octahedral geometry around W(0) is revealed. Despite that the dppm ligand has been broadly used as a stabilizing backbone to construct heterodimetallic complexes,[14] complex **2a** is interestingly the first structurally characterized FeW unit linked by dppm. One close example is {FeW(μ-CC$_6$H$_4$Me-4)(μ-CO)(μ-dmpm)(CO)$_2$-[HB(pz)$_3$]}[15] (dmpm = Me$_2$PCH$_2$PMe$_2$, pz = pyrazolyl) which has, however, a Fe−W multiple bond [Fe−W = 2.650(1) Å].

When **1** (0.13 mmol) was reacted with M(CO)$_3$(C$_2$H$_5$-CN)$_3$[16] (0.20 mmol) in THF (20 mL) for 6 h at ambient temperature, the reaction mixture changed color from yellow to maroon, the new ν_{CO} bands in the IR spectra being at lower wavenumbers than those of **1** and **2**. After chromatographic workup (silica, 1:4 ethylacetate/*n*-hexane), red powders of **3**, (η^5-MeC$_5$H$_4$)Fe(CO)(μ-η^1:η^1-dppm)(μ-H)M(CO)$_4$, were collected (**3a**, 0.11 mmol, 85% yield; **3b**, 0.11 mmol, 85% yield).[17] Compound **3** could also be obtained in comparable yields from the reaction of **1** with either M(CO)$_3$(THF)$_3$[18] or M(CO)$_3$(η^6-C$_7$H$_8$)[19] (see Scheme 1). The ^{1}H NMR data for **3a** indicated that the 2:1:2 integration ratios for the η^4-MeC$_5$H$_5$ fragment of **1** disappeared whereas a 4-peak, equal intensity pattern characteristic of an η^5-MeC$_5$H$_4$ connected to a chiral metal center appeared. Also observed in the ^{1}H NMR is a doublet of doublets with a tungsten satellite (J_{HW} = 37 Hz) centered at δ −16.92, suggesting the existence of a bridging hydride in **3a**.[20] The doublet without tungsten satellite in the ^{31}P NMR spectrum shifted downfield to δ 83.40. In addition, the J_{PP} coupling constant of 60 Hz was considerably larger than that of **2** [24 Hz (**2a**), 19 Hz (**2b**)], suggesting more than one through-bond connectivity in **3a**. Compound **3b** was very similar in spectroscopic data, taking into consideration the difference of W and Mo. Finally the structure of novel hydrido-bridged complex **3a** was confirmed by a single-crystal X-ray diffraction study.[21]

The molecular structure of **3a** is shown in Figure 2, revealing both a hydride bridge and a dppm bridge between two metal centers. The Fe−H−W vector is bent at 128.6°, with W−H and Fe−H distances of 1.812

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(12) Spectroscopic and analytical data for **2a**: IR (*n*-hexane) ν_{CO} 2069 (m), 1968 (s), 1941 (b, vs), 1916 (sh) cm^{-1}; ^{31}P NMR (CDCl$_3$) δ 68.45 (d, $^2J_{PP}$ = 24 Hz), 10.78 (d, $^2J_{PP}$ = 24 Hz, $^1J_{PW}$ = 245 Hz); ^{1}H NMR (CDCl$_3$) δ 7.34−7.17 (m, 20H, Ph), 4.80 (m, 2H, −C*H*=CHCHMe−), 3.70 (m, 2H, PC*H*$_2$P), 2.58 (m, 1H, −CH=CHC*H*Me−), 2.07 (m, 2H, −CH=C*H*CHMe−), 0.24 (d, 3H, $^3J_{HH}$ = 5 Hz, Me); MS (FAB) *m/z* 901 (M$^+$). Anal. Calcd for C$_{38}$H$_{30}$FeO$_7$P$_2$W: C, 50.70; H, 3.33. Found: C, 50.88; H, 3.33. **2b**: IR (*n*-hexane) ν_{CO} 2070 (m), 1968 (s), 1942 (b, vs), 1915 (sh) cm^{-1}; ^{31}P NMR (CDCl$_3$) δ 69.97 (d, $^2J_{PP}$ = 19 Hz), 30.35 (d, $^2J_{PP}$ = 19 Hz); ^{1}H NMR (CDCl$_3$) δ 7.35−7.14 (m, 20H, Ph), 4.79 (m, 2H, −C*H*=CHCHMe−), 3.70 (m, 2H, PC*H*$_2$P), 2.58 (m, 1H, −CH=CHC*H*Me−), 2.06 (m, 2H, −CH=C*H*CHMe−), 0.23 (d, 3H, $^3J_{HH}$ = 5 Hz, Me); MS (FAB) *m/z* 814 (M$^+$). Anal. Calcd for C$_{38}$H$_{30}$-FeMoO$_7$P$_2$: C, 56.13; H, 3.69. Found: C, 56.20; H, 3.62.

(13) Crystallographic data for **2a**: C$_{38}$H$_{30}$FeO$_7$P$_2$W, fw 900.30, monoclinic, *C*2/*c*, a = 28.394(4) Å, b = 13.550(1) Å, c = 19.447(2) Å, β = 102.99(1)°, V = 7290(1) Å^3, Z = 8, $F(000)$ = 3551, D_{calcd} = 1.641 g·cm^{-3}; Nonius CAD-4 data, Mo Kα radiation, λ = 0.710 7 Å, μ = 37.51 cm^{-1}. R = 0.024, R_w = 0.026, and GOF = 1.19 with 79 atoms and 442 parameters for 3578 out of 4756 measured reflections.

(14) (a) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99. (b) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191. (c) Braunstein, P.; de Meric de Bellefon, C.; Oswald, B. *Inorg. Chem.* **1993**, *32*, 1638. (d) Braunstein, P.; Knorr, M.; Strampfer, M.; Dusausoy, Y.; Bayeul, D.; DeCian, A.; Fischer, J.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1994**, 1533.

(15) Green, M.; Howard, J. A. K.; James, A. P.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1986**, 1697.

(16) *Inorg. Synth.* **1990**, *28*, 29−33.

(17) Spectroscopic and analytical data for **3a**: IR (THF) ν_{CO} 2010 (s), 1927 (vs), 1890 (sh), 1886 (s), 1855 (s) cm^{-1}; ^{31}P NMR (CDCl$_3$) δ 83.49 (d, $^{2+4}J_{PP}$ = 60 Hz), 13.20 (d, $^{2+4}J_{PP}$ = 60 Hz, $^1J_{PW}$ = 243 Hz); ^{1}H NMR (CDCl$_3$) δ 7.62−7.00 (m, 20H, Ph), 4.59 (m, 1H), 4.46 (m, 1H), 4.41 (m, 1H), 4.00 (m, 1H) for MeC$_5$*H*$_4$, 3.65 (m, 1H), 2.78 (m, 1H) for PC*H*$_2$P, 1.82 (s, 3H, Me), −16.92 (dd, 1H, μ-H, $^2J_{HP}$ = 53 Hz, 8 Hz, $^1J_{HW}$ = 37 Hz); MS (FAB) *m/z* 846 (M$^+$ + 1). Anal. Calcd for C$_{36}$H$_{30}$FeO$_5$P$_2$W·$^1/_2$Et$_2$O: C, 51.80; H, 3.97. Found: C, 52.13; H, 4.67. **3b**: IR (THF) ν_{CO} 2015 (s), 1927 (vs), 1900 (sh), 1894 (s), 1859 (s) cm^{-1}; ^{31}P NMR (CDCl$_3$) δ 81.62 (d, $^{2+4}J_{PP}$ = 61 Hz), 32.25 (d, $^{2+4}J_{PP}$ = 61 Hz); ^{1}H NMR (CDCl$_3$) δ 7.58−7.02 (m, 20H, Ph), 4.54 (m, 1H), 4.40 (m, 1H), 4.11 (m, 1H), 4.00 (m, 1H) for MeC$_5$*H*$_4$, 3.38 (m, 1H), 2.78 (m, 1H) for PC*H*$_2$P, 1.81 (s, 3H, Me), −18.12 (dd, 1H, μ-H, $^2J_{HP}$ = 53 Hz, 8 Hz); MS (FAB) *m/z* 758 (M$^+$). Anal. Calcd for C$_{36}$H$_{30}$FeMoO$_5$P$_2$·$^1/_2$-Et$_2$O: C, 57.87; H, 4.82. Found: C, 57.54; H, 4.41.

(18) (a) Muetterties, E. L.; Bleeke, J. R.; Sievert, A. C. *J. Organomet. Chem.* **1979**, *178*, 197. (b) Hoff, C. D. *J. Organomet. Chem.* **1985**, *282*, 201. (c) Nolan, S. P.; de la Vega, R. L.; Hoff, C. D. *Organometallics* **1986**, *5*, 2529.

(19) (a) Abel, E. W.; Bennett, M. A.; Wilkinson, G. *Proc. Chem. Soc.* **1958**, 152. (b) Abel, E. W.; Bennett, M. A.; Burton, R.; Wilkinson, G. *J. Chem. Soc.* **1958**, 4559. (c) King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837. (d) Kubas, G. J. *Inorg. Chem.* **1983**, *22*, 692. (e) *Inorg. Synth.* **1990**, *27*, 4−6.

(20) (a) The observed J_{HW} is in the range of (μ-H)W$_2$(CO)$_{10}^-$ (42 Hz)[b] and (μ-H)$_2$W$_2$(CO)$_8^{2-}$ (30 Hz).[c] (b) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176. (c) Lin, J. T.; Hagen, G. P.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2296.

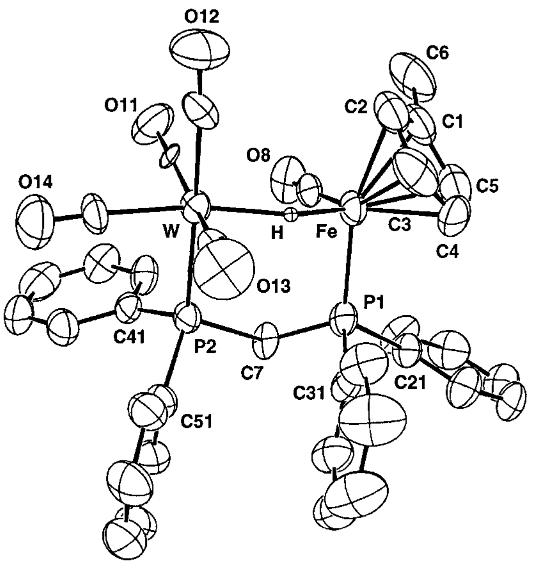

Figure 2. Thermal ellipsoid drawing (50%) of complex **3a**. The H atoms except for the bridging hydride are omitted for clarity. Selected bond lengths (Å): Fe–P1 2.174(4), Fe–C1 2.107(1), Fe–C2 2.090(1), Fe–C3 2.087(1), Fe–C4 2.074(1), Fe–C5 2.069(1), Fe–C8 1.738(1), Fe–H 1.722, W–P2 2.504(3), W–C11 1.917(2), W–C12 1.925(1), W–C13 1.985(2), W–C14 1.934(1), W–H 1.812. Selected bond angles (deg): P1–Fe–C8 92.0(4), Fe–P1–C7 112.9(4), W–P2–C7 115.3(3), P1–C7–P2 111.9(5), Fe–H–W 128.6.

and 1.722 Å, respectively. To our knowledge, this is the first structurally characterized, six-membered heterodimetallic species bridged by just one hydride and one dppm. Most of analogous[22] heterodimetallic structures known are bridged by one hydride and two dppm in an "A-frame" skeleton. In **3a**, the Fe(II) center is in a slightly distorted octahedral bonding environment and so is the W(0) center. Especially noted are the five CO ligands (originally two with Fe, three with W) now redistributed to one with Fe and four with W, the total remaining unchanged. The Fe–W distance, 3.185(2) Å, is about 0.2 Å longer than 2.989(2) Å found in $[Ph_2PNPPh_2]^+[Fe(CO)_4(\mu\text{-}H)W(CO)_5]^-$,[11b,23] which has a formal Fe–W single bond. The torsion angle of Fe–P1···P2–W, 22.4(1)°, indicates that in **3a** the metal centers are likely attractive whereas in **2a** the metal centers are likely repulsive. If the Fe–H moiety is considered as a two electron donor to the W(0) center, an EAN rule fits well on both metal centers in **3a**.

The formation of **2** from **1** is not unusual. However, the formation of **3** from **1** is unexpected. A proposed reaction pathway is included in Scheme 1, consisting of coordination of the monodentate dppm to M, the second metal center, and then CO migration from Fe to M with a sequential or concerted oxidative addition of the *endo*-C–H bond of the η^4-MeC_5H_5 ligand to give the (η^5-MeC_5H_4)FeH complex that is followed by a trapping of the Fe–H bond by M, forming a six-membered ring. The CO migration from one metal center to another is facile,[1a] yet it is crucial here to have the Fe center vacate one site immediately before the oxidative addition. The attempt to convert **2** to **3** failed with either oxidative decarbonylation by Me_3NO or photolysis for a long time, only resulting in decomposition. The reaction of **1** with $Mo(CO)_4$(norbornadiene)[24] gave a low yield of **2b** (<20%) without giving **3b** at all.[25] Thus, it seems reasonable to propose that three weakly-coordinated ligands on the second metal center are required in order to produce **3** from **1**, the first weakly-coordinated ligand being replaced during the initial phosphine coordination, the second formally during the CO relocation from Fe to M, and the third formally during the formation of "3c–2e" M–H–Fe bond. The Fe–H moiety is stabilized as a consequence. The hydride in the 3c–2e bond is derived from cyclopentadiene because given various $M(CO)_3$ precursors reacting with **1**, all yield the same product **3**. THF as a possible hydride source has been ruled out because when the reaction was performed in THF-d_8, the hydride resonance could still be recorded in the ^1H NMR spectrum with no change in intensity; i.e., complex **3** did not exchange its hydride for the active hydrogen of THF in the experiment. Works on the above hypothesis and the reactivity of **3** are currently being undertaken.

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Supporting Information Available: For the structures of (η^4-MeC_5H_5)$Fe(CO)_2$(μ-η^1:η^1-dppm)$W(CO)_5$, **2a**, and (η^5-MeC_5H_4)Fe(CO)(μ-η^1:η^1-dppm)(μ-H)$W(CO)_4$, **3a**, listings of crystallographic data, positional and isotropic and anisotropic thermal parameters, and bond distances and angles (13 pages). Ordering information is given on any current masthead page.

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(21) Crystallographic data for **3a**: $C_{36}H_{30}FeO_5P_2W\cdot{}^1/_2Et_2O$, fw 881.34, triclinic, $P\bar{1}$, $a = 10.920(6)$ Å, $b = 11.571(2)$ Å, $c = 16.516(3)$ Å, $\alpha = 89.68(2)°$, $\beta = 75.54(3)°$, $\gamma = 65.24(3)°$, $V = 1823(1)$ Å^3, $Z = 2$, $F(000) = 874$, $D_{calcd} = 1.605$ g·cm^{-3}; Nonius CAD-4 data, Mo Kα radiation, $\lambda = 0.710\,7$ Å, $\mu = 37.45$ cm^{-1}. $R = 0.048$, $R_w = 0.056$, and GOF = 2.52 with 81 atoms and 427 parameters for 3913 out of 4763 measured reflections. The hydride position was found from the final difference Fourier map. The oxygen atom of the diethyl ether solvate was located on the crystallographic inversion center, the diethyl ether being disordered. Currently a neutron diffraction study is being in progress in order to locate the exact position of hydride.

(22) (a) Delavaux, B.; Chaudret, B.; Dahan, F.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* **1985**, 805. (b) Markhm, D. P.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1987**, 1005. (c) Antonelli, D. M.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 4039.

(23) Arndt, L. W.; Delord, T.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1984**, *106*, 456.

(24) Bennett, M. A.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1971**, 2037.

(25) Only **2b** and a trace of $Mo(CO)_4$(dppm) were isolated with a sizable amount of **1** recovered.