

# Reactivity of Heterodinuclear Complexes Formed by Platinum Insertion to Phosphorus-Bridged [1]Ferrocenophane Coordinating to a Metal Fragment

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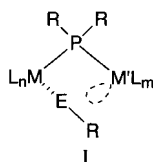
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Received September 4, 2001

A reaction of  $\text{Pt}(\text{PMe}_3)_4$  with fcpp (fcpp = 1,1'-ferrocenediylphenylphosphine) coordinating to  $\text{CpMn}(\text{CO})_2$  and  $\text{W}(\text{CO})_5$  fragments gave heterodinuclear complexes (actually they are trinuclear complexes if an iron center of a ferrocene unit is included), in which a  $\text{Pt}(\text{PMe}_3)_2$  fragment was inserted into a P–C bond of the fcpp ligand to form P–Pt and  $\eta^1\text{-C}_5\text{H}_4\text{-Pt}$  bonds with a  $\mu\text{-PPhFc}$  bridge ( $\mu\text{-PPhFc} = \mu\text{-PPh}(\text{C}_5\text{H}_4\text{FeC}_5\text{H}_4)$ ). X-ray analyses showed that the products were  $\text{Cp}(\text{CO})_2\text{Mn}(\mu\text{-PPhFc})\text{Pt}(\text{PMe}_3)_2$  and  $(\text{CO})_5\text{W}(\mu\text{-PPhFc})\text{Pt}(\text{PMe}_3)_2$ , respectively. Upon a similar reaction employing  $\text{Pt}(\text{PPh}_3)_4$  in place of  $\text{Pt}(\text{PMe}_3)_4$ ,  $\text{CpMn}(\text{CO})_2(\text{fcpp})$  gave  $\text{Cp}(\text{CO})\text{Mn}(\mu\text{-CO})(\mu\text{-PPhFc})\text{Pt}(\text{PPh}_3)$ , whereas  $\text{W}(\text{CO})_5(\text{fcpp})$  gave  $(\text{CO})_4\text{W}(\mu\text{-PPh}_2)(\mu\text{-PPh}(\text{C}_5\text{H}_4\text{FeC}_5\text{H}_4\text{Ph}))\text{Pt}(\text{PPh}_3)$ , in which cleavage of a P–Ph bond of  $\text{PPh}_3$  and migration of the Ph group to a ferrocene moiety took place. To elucidate the reaction mechanism, several reaction intermediates were isolated and characterized as  $(\text{CO})_5\text{W}(\mu\text{-PPhFc})\text{Pt}(\text{CO})(\text{PPh}_3)$ , *cis-W*- and *trans-W*-( $\text{CO})_4(\text{PPh}_3)\text{W}(\mu\text{-PPhFc})\text{Pt}(\text{CO})(\text{PPh}_3)$ , and *cis-W*-( $\text{CO})_4(\text{PPh}_3)\text{W}(\mu\text{-CO})(\mu\text{-PPhFc})\text{Pt}(\text{PPh}_3)$ .

## Introduction

Heterodinuclear complexes have attracted continuous interest, since two different metals in close proximity may provide a reaction site where both metals are engaged in multisite interactions with a substrate and/or consecutive activation and transformation of a substrate.<sup>1,2</sup> Usually such a complex contains a linker bridging two metal fragments to retain a dinuclear framework during the reaction. One such example is schematically shown in I, in which the complex has a



phosphido bridge and a vacant coordination site as well. This core structure is considered to be promising for the bimetallic activation of a substrate, because (1) the vacant coordination site on the right metal can effectively cleave an E–C bond of the substrate coordinating to the left metal, (2) the phosphido-bridged complex is readily available, and (3) the phosphido ligand can coordinate to almost any transition metal in the periodic table. Although several reports describe the

activation reaction of an E–H bond by a phosphido-bridged complex such as I,<sup>3</sup> only a limited number of reports have described the activation of the E–C bond.<sup>4</sup>

Previously, we reported that the P–C bond of phosphorus-bridged [1]ferrocenophane is cleaved through an intramolecular insertion of a  $\text{Cp}(\text{CO})\text{Fe}$  fragment (eq 1).<sup>5</sup>

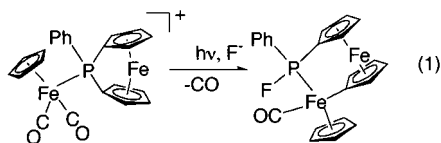
(2) See, for example: Komiya, S.; Muroi, S.; Furuya, M.; Hirano, M. *J. Am. Chem. Soc.* **2000**, *122*, 170 and references therein. (b) Torkelson, J. R.; Oke, O.; Muritu, J.; McDonald, R.; Cowie, M. *Organometallics* **2000**, *19*, 854. (c) Sterenberg, B. T.; McDonald, R.; Cowie, M. *Organometallics* **1997**, *16*, 2297. (d) Alvarez, C.; Garcia, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **1997**, *16*, 1378. (e) Nakajima, T.; Shimizu, I.; Kobayashi, K.; Koshino, H.; Wakatsuki, Y. *Inorg. Chem.* **1997**, *36*, 6440. (f) Davies, J. E.; Mays, M. J.; Raithby, P. R.; Sarveswaran, K.; Shields, G. P. *J. Organomet. Chem.* **1999**, *573*, 180. (g) King, J. D.; Mays, M. J.; Mo, C.-Y.; Raithby, P. R.; Rennie, M. A.; Solan, G. A.; Adatia, T.; Conole, G. *J. Organomet. Chem.* **2000**, *601*, 271. (h) Gade, L. H.; Schubart, M.; Findeis, B.; Fabre, S.; Bezougli, I.; Lutz, M.; Scowen, I. J.; McPartlin, M. *Inorg. Chem.* **1999**, *38*, 5282. (i) Bitterwolf, T. E.; Haener, J. L.; Shade, J. E.; Rheingold, A. L.; Yap, G. P. A. *J. Organomet. Chem.* **1997**, *547*, 23. (j) Bitterwolf, T. E.; Saygh, A. A.; Shade, J. E.; Rheingold, A. L.; Yap, G. P. A.; Lable-Sands, L. M. *Inorg. Chim. Acta* **2000**, *300–302*, 800.

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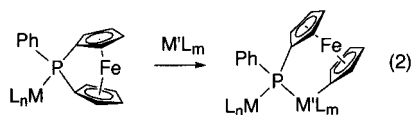
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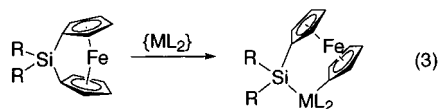


If this insertion to the [1]ferrocenophane takes place through the intermolecular attack of an external metal fragment, a phosphido-bridged dinuclear complex will be obtained (eq 2). Here, we report that such a het-

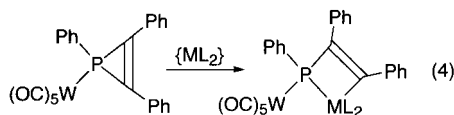


erodinuclear complex is actually obtained and it successfully cleaves a P–C bond of PPh<sub>3</sub>.

Two reactions relevant to our study have been reported. Manners et al.<sup>6</sup> and Tanaka et al.<sup>7</sup> found independently that palladium(0) and platinum(0) complexes are inserted into an Si–C bond of silicon-bridged [1]ferrocenophanes (eq 3). Furthermore, Mathey et al.



reported the insertion reaction of palladium(0) and platinum(0) complexes into the P–C bond of a phenylphosphirene tungsten complex (eq 4).<sup>8</sup> However,



they did not report the reactivities of the products in detail.

## Results and Discussion

**Insertion Reaction of a Pt(PMe<sub>3</sub>)<sub>2</sub> Fragment.** The reaction of 1,1'-ferrocenediylphenylphosphine (**1**), abbreviated as fcpp, with CpMn(CO)<sub>2</sub>(THF) or W(CO)<sub>5</sub>(THF) gave CpMn(CO)<sub>2</sub>(fcpp) (**2**) or W(CO)<sub>5</sub>(fcpp) (**3**), respectively.<sup>9</sup> **2** thus obtained was allowed to react with Pt(PMe<sub>3</sub>)<sub>4</sub> in toluene at 70 °C for 6 h. With silica gel column chromatography, the product was isolated in low yield, probably due to partial decomposition during the chromatography in the air, because the <sup>31</sup>P{<sup>1</sup>H} NMR

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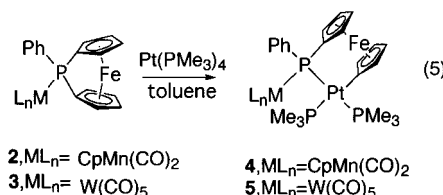
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**Table 1.** <sup>31</sup>P{<sup>1</sup>H} NMR Data for Heterodinuclear Complexes

	bridge, δ (J, Hz)	terminal, δ (J, Hz)
<b>4</b>	81.8 (d, 324, <sup>a</sup> 2074)	–27.4 (dd, 21, <sup>a</sup> 323, <sup>a</sup> 1639, <sup>c</sup> <i>trans</i> -PMe <sub>3</sub> ) –25.5 (dd, 14, <sup>a</sup> 21, <sup>a</sup> 2018, <sup>c</sup> <i>cis</i> -PMe <sub>3</sub> )
<b>5</b>	11.6 (dd, 11, <sup>a</sup> 340, <sup>a</sup> 185, <sup>b</sup> 2005 <sup>a</sup> )	–27.9 (dd, 11, <sup>a</sup> 21, <sup>a</sup> 1961, <sup>c</sup> <i>cis</i> -PMe <sub>3</sub> ) –25.9 (dd, 21, <sup>a</sup> 340, <sup>a</sup> 1820, <sup>c</sup> <i>trans</i> -PMe <sub>3</sub> )
<b>6</b>	187.2 (dd, 297, <sup>a</sup> 2126 <sup>a</sup> )	27.5 (d, 299, <sup>a</sup> 2864, <sup>c</sup> PPh <sub>3</sub> )
<b>8</b>	163.2 (dd, 51, <sup>a</sup> 219, <sup>a</sup> 145, <sup>b</sup> 2870 <sup>a</sup> ) 173.6 (dd, 44, <sup>a</sup> 221, <sup>a</sup> 157, <sup>b</sup> 2555 <sup>a</sup> )	48.9 (dd, 44, <sup>a</sup> 51, <sup>a</sup> 5186, <sup>c</sup> PPh <sub>3</sub> )
<b>9</b>	17.1 (d, 287, <sup>a</sup> 190, <sup>b</sup> 1827 <sup>a</sup> )	8.3 (d, 287, <sup>a</sup> 1625, <sup>a</sup> PPh <sub>3</sub> )
<b>10</b>	104.1 (dd, 24, <sup>a</sup> 267, <sup>a</sup> 205, <sup>b</sup> 1780 <sup>a</sup> )	16.4 (d, 24, <sup>a</sup> 75, <sup>a</sup> 256, <sup>b</sup> W–PPh <sub>3</sub> ) 28.4 (d, 266, <sup>a</sup> 2867, <sup>c</sup> Pt–PPh <sub>3</sub> )
<b>11</b>	27.7 (d, 47, <sup>a</sup> 283, <sup>a</sup> 227, <sup>b</sup> 1854 <sup>a</sup> )	8.0 (d, 283, <sup>a</sup> 1467, <sup>c</sup> Pt–PPh <sub>3</sub> ) 29.5 (d, 44, <sup>a</sup> 284, <sup>b</sup> W–PPh <sub>3</sub> )
<b>12</b>	23.1 (dd, 28, <sup>a</sup> 277, <sup>a</sup> 187, <sup>b</sup> 1842 <sup>a</sup> )	8.1 (dd, 7, <sup>a</sup> 278, <sup>a</sup> 1508, <sup>c</sup> Pt–PPh <sub>3</sub> ) 20.6 (dd, 7, <sup>a</sup> 28, <sup>a</sup> 222, <sup>b</sup> W–PPh <sub>3</sub> )

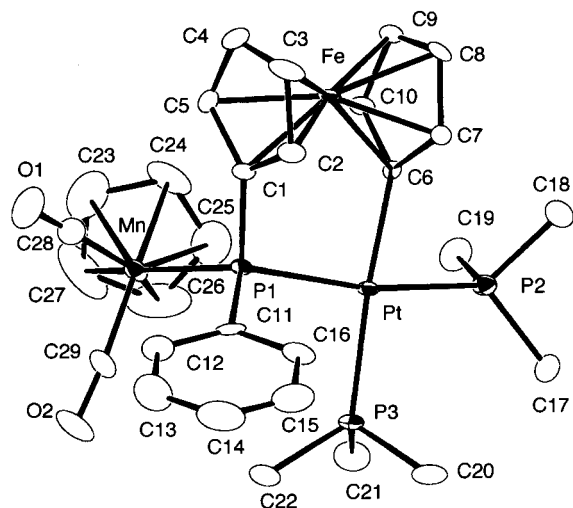
<sup>a</sup> <sup>2</sup>J<sub>PP</sub> coupling constant. <sup>b</sup> <sup>1</sup>J<sub>PW</sub> coupling constant. <sup>c</sup> <sup>1</sup>J<sub>PPT</sub> coupling constants.

spectrum of the reaction mixture showed that an isolated species was a major product. The product was characterized as **4**, shown in eq 5. The <sup>31</sup>P{<sup>1</sup>H} NMR



spectrum of the product showed three signals at –27.4, –25.5, and 81.8 ppm, which are summarized in Table 1 together with the data for the complexes reported in this work. The signal at the lowest field can be assigned to the phosphido bridge bonding to both manganese and platinum centers, judging from the following three findings: (1) the presence of satellites due to the coupling with <sup>195</sup>Pt (*J*<sub>PPT</sub> = 2074 Hz), (2) broadening of the signal due to <sup>55</sup>Mn quadrupole relaxation, which prevented an observation of the coupling with a PMe<sub>3</sub> *cis* to the platinum center, and (3) a large coupling constant (*J*<sub>PP</sub> = 324 Hz) with a *trans* PMe<sub>3</sub>. The chemical shift of this bridging phosphido group seems to be closer to that (200–100 ppm) of a phosphido-bridged dinuclear complex with a metal–metal bond than that (–50 to –150 ppm) without a metal–metal bond.<sup>10</sup> However, the X-ray crystal analysis (*vide infra*) revealed the absence of an Mn–Pt bond. Similar unusual low-field shifts of the phosphido bridge were also reported for some heterodinuclear manganese complexes without a metal–metal bond: i.e., 88.6 ppm for Cp'(CO)<sub>2</sub>Mn(*μ*-PPh<sub>2</sub>)Fe(CO)<sub>4</sub><sup>–</sup> and 60.3 ppm for Cp'(CO)<sub>2</sub>Mn(*μ*-PPh<sub>2</sub>)Cr(CO)<sub>5</sub><sup>–</sup>.<sup>11</sup> Thus, the unusual low-

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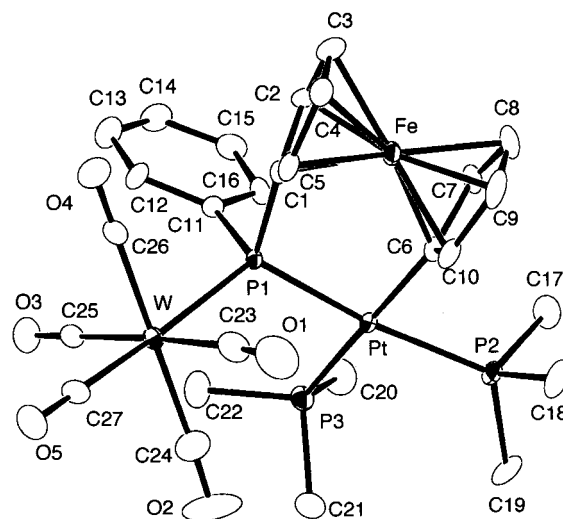


**Figure 1.** Molecular structure and numbering scheme of **4**. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pt–P1, 2.380(2); Pt–P2, 2.330(2); Pt–P3, 2.320(2); Pt–C6, 2.075(5); Mn–P1, 2.316(2); Mn–C28, 1.776(8); Mn–C29, 1.747(7); P1–C1, 1.855(6); P1–C11, 1.859(6); Pt···Mn, 3.970(1); P1–Pt–C6, 89.0(2); P1–Pt–P3, 94.77(5); P2–Pt–C6, 82.1(2); P2–Pt–P3, 94.55(5); Pt–P1–Mn, 115.44(7); Pt–P1–C1, 108.4(2); Mn–P1–C1, 109.7(2).

field shift observed for **4** is attributable to the coordination to Mn.

The other two signals at  $-27.4$  and  $-25.5$  ppm were readily assigned to the trans and cis  $\text{PMe}_3$  on the platinum center, respectively, because the former has a large coupling constant of 323 Hz with the bridging phosphido group, whereas the latter has a small one, 14 Hz. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR spectra were all consistent with the structure expected for **4** in eq 5. In addition, the structure of **4** was confirmed by X-ray analysis, as shown in Figure 1, where the  $\text{Pt}(\text{PMe}_3)_2$  fragment has been inserted into the P–C bond of the [1]ferrocenophane unit to form the phosphido-bridged Mn–Pt heterodinuclear complex. Actually, the complex should be classified as a trinuclear complex, if an iron center is included, but hereafter we adopt “dinuclear” since we focus our attention on the phosphido-bridged core structure.

When **3** was heated with  $\text{Pt}(\text{PMe}_3)_4$  in toluene, a similar platinum-insertion reaction also took place to give **5**. The characterization of the product was performed similarly on the basis of the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR and IR spectra. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, the bridging phosphido group was observed at 11.6 ppm as a doublet of doublets ( $^2J_{\text{PP}} = 11$  and 340 Hz) having satellites due to both  $^{183}\text{W}$  ( $J_{\text{PW}} = 185$  Hz) and  $^{195}\text{Pt}$  ( $J_{\text{Pt}} = 2005$  Hz). The two  $\text{PMe}_3$  ligands on the platinum center were observed at  $-27.9$  and  $-25.9$  ppm, which are assigned to the  $\text{PMe}_3$  groups cis and trans with respect to the bridging phosphido group, respectively. The structure was confirmed by X-ray analysis, as shown in Figure 2, where the  $\text{W}(\text{CO})_5$  and  $\text{Pt}(\text{PMe}_3)_2$  fragments are connected through the ferrocenylphosphido bridge in a manner similar to that found in **4**.



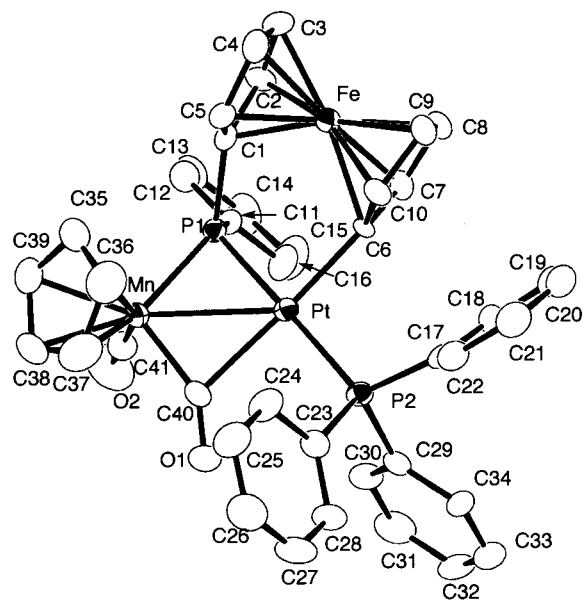
**Figure 2.** Molecular structure and numbering scheme of **5**. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pt–P1, 2.3601(8); Pt–P2, 2.3245(8); Pt–P3, 2.3329(9); Pt–C6, 2.054(3); W–P1, 2.6082(8); W–P1, 2.6082(8); W–C23, 2.040(4); W–C24, 2.048(4); W–C25, 2.061(4); W–C26, 2.043(4); W–C27, 1.988(3); P1–C1, 1.840(4); P1–C11, 1.851(3); Pt···W, 4.6255(2); P1–Pt–P3, 94.45(3); P1–Pt–C6, 88.36(9); P2–Pt–P3, 95.18(3); P2–Pt–C6, 82.11(9); Pt–P1–W, 118.22(3); Pt–P1–C1, 111.3(1); W–P1–C1, 106.2(1).

From the two reactions described above, it is found that phosphido-bridged heterodinuclear complexes can be obtained through the insertion reaction of the  $\text{Pt}(\text{PMe}_3)_2$  fragment into the P–C bond of the  $\text{fcpp}$ –metal complex (eq 5). Here, if the phosphine ligand could be removed from the position cis to the bridge, a vacant site such as that shown in structure I would be formed and is expected to serve as a reaction site. However, the isolated complexes **4** and **5** did not release the phosphine ligand and, thus, did not demonstrate the expected reactivity. We thought that the inertness of these complexes presumably arises from a strong coordination of  $\text{PMe}_3$  to the platinum center. Thus, the insertion reaction was carried out employing a  $\text{Pt}(0)$  fragment bearing a  $\text{PPh}_3$  ligand whose coordination to the platinum is not as strong as that of  $\text{PMe}_3$ .

**Reaction of 2 with  $\text{Pt}(\text{PPh}_3)_4$ .** The reaction of **2** with  $\text{Pt}(\text{PPh}_3)_4$  was carried out in a manner similar to that described above to give the product **6**, whose  $^{31}\text{P}\{^1\text{H}\}$  NMR signals are listed in Table 1. In the region of the terminal  $\text{PPh}_3$ , only one resonance was observed at 27.5 ppm ( $J_{\text{PP}} = 299$  Hz,  $J_{\text{Pt}} = 2864$  Hz), indicating that only one  $\text{PPh}_3$  coordinates to the platinum center, as we expected. Since this terminal  $\text{PPh}_3$  has a large coupling constant with the bridging phosphido ligand, it is considered to occupy the position trans to the bridging phosphido group. The signal assigned to the phosphido bridge was observed at 187.2 ppm, which is at considerably lower field than 81.8 ppm for the corresponding phosphido bridge of **4**, indicating the presence of a metal–metal bond bridged by the phosphido ligand.<sup>10</sup>

The molecular structure of the product was confirmed by X-ray analysis. The structure **6** is shown in Figure 3, where only one  $\text{PPh}_3$  is bound to the platinum center at the position trans to the bridging phosphido group.

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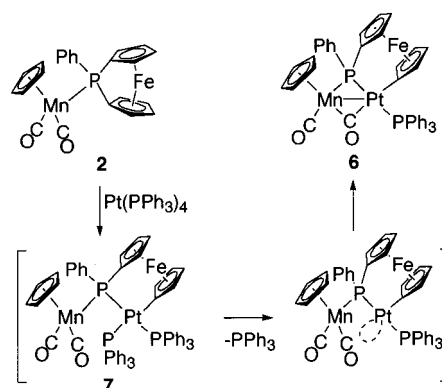


**Figure 3.** Molecular structure and numbering scheme of **6**. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pt–Mn, 2.7411(8); Pt–P1, 2.251(1); Pt–P2, 2.331(1); Pt–C6, 2.059(5); Pt–C40, 2.230(5); Mn–P1, 2.221(2); Mn–C40, 1.853(6); Mn–C41, 1.766(7); P1–C1, 1.808(6); P1–C11, 1.807(5); Mn–Pt–P1, 51.71(4); Mn–Pt–C40, 42.2(2); P1–Pt–C6, 88.5(1); Pt–Mn–P1, 52.68(4); Pt–Mn–C40, 54.0(2); Pt–Mn–C41, 106.5(2); Pt–P1–Mn, 75.61(5); Pt–P1–C1, 112.6(2); Mn–P1–C1, 128.1(2); Pt–C40–O1, 127.0(4); Mn–C40–O1, 149.2(5).

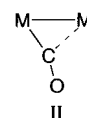
Several points are notable in this structure. The Mn–Pt separation is 2.7411(8) Å, which is much smaller than 3.970(1) Å for **4** in Figure 1 and is close to 2.864(1) Å of the Mn–Pt distance reported for  $(OC)_4Mn(\mu\text{-PPh}_2)(\mu\text{-H})Pt(Ph)(PPh_3)$ ,<sup>11</sup> indicating the presence of the Mn–Pt bond in **6**. In addition to the phosphido bridge, one of the two carbonyl ligands on the manganese center also bridges the manganese and platinum centers. The presence of the bridging CO is evident also from the IR spectrum in solution.  $\nu_{CO}$  absorptions of **6** were observed at 1917 and 1778  $\text{cm}^{-1}$ . The considerably low wavenumber of the latter is characteristic of the bridging CO,<sup>12</sup> whereas 1906 and 1836  $\text{cm}^{-1}$  for **4** are usual for two terminal CO ligands.<sup>13</sup>

A plausible mechanism for the formation of **6** is shown in Scheme 1. Assuming a reaction analogous to eq 5, the first step of the reaction is the insertion of the  $Pt(PPh_3)_2$  fragment into the P–C bond to give **7**. However, **7** could not be observed, even in the spectroscopic measurements of the reaction mixture. Because of great steric repulsion between one  $PPh_3$  cis to the phosphido

Scheme 1



ligand and both the manganese fragment and the other  $PPh_3$ , the cis  $PPh_3$  may readily dissociate from the platinum center to relax the repulsion. The vacant site thus formed is occupied by forming the CO bridge and the Mn–Pt bond to give **6**. In this case, the formation of a pair of diastereomeric isomers is expected in principle, depending on which CO ligand bridges the manganese and platinum centers, but in practice only one isomer, shown in Figure 3, was observed. Since the bridging carbonyl readily dissociates from the platinum center (vide infra), the other diastereomer, if formed, would be converted to the diastereomer **6** through an exchange between the bridging and terminal carbonyls. With regard to the CO bridge in Figure 3, it is noteworthy that a bond angle of the manganese side, Mn–C40–O1 = 149.2(5)°, is significantly wider than that of the platinum side, Pt–C40–O1 = 127.0(4)°. In addition, a Pt–C40 length of 2.230(5) Å is greater by 0.377 Å than an Mn–C40 length of 1.853(6) Å, while with regard to the phosphido bridge on the opposite side of the Mn–Pt bond, a Pt–P1 length of 2.251(1) Å is almost comparable to an Mn–P1 length of 2.221(1) Å. These asymmetric bond lengths and angles around the bridging carbonyl indicate that the bridging carbonyl bears to some extent a semibridging coordination mode (structure II).<sup>14</sup> A contribution of such a semibridge mode



probably makes the carbonyl–platinum bond in **6** weaker than that of a usual bridging carbonyl.

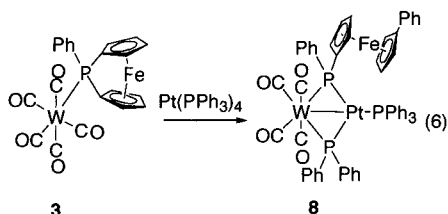
**Reaction of 3 with  $Pt(PPh_3)_2$  Fragment.** Although the reactions with the  $Pt(PMe_3)_2$  fragment proceeded analogously for both the manganese and tungsten complexes **2** and **3**, the reaction of **3** with the  $Pt(PPh_3)_2$  fragment was far more complicated, compared with the manganese case described in the previous section.

When **3** was heated with  $Pt(PPh_3)_4$  at 90 °C in toluene for 15 h, the product isolated was characterized as **8**, shown in eq 6. The molecular structure of this product

(12) (a) Leonhard, K.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 649. (b) Fong, R.; Hersh, W. H. *Organometallics* **1985**, *4*, 1468. (c) King, R. B.; Fu, W.-K.; Holt, E. M. *Inorg. Chem.* **1985**, *24*, 3094. (d) King, R. B.; Fu, W.-K.; Holt, E. M. *Inorg. Chem.* **1965**, *25*, 2394. (e) Bars, O.; Braunstein, P.; Geoffroy, G. L.; Metz, B. *Organometallics* **1986**, *5*, 2021. (f) Arif, A. M.; Chandler, D. J.; Jones, R. A. *Inorg. Chem.* **1987**, *26*, 1780. (g) Zhuang, J.-M.; Batchelor, R. J.; Einstein, F. W. B.; Jones, R. H.; Hader, R.; Sutton, D. *Organometallics* **1990**, *9*, 2723. (h) Fong, R. H.; Lin, C.-H.; Idmoumaz, H.; Hersh, W. H. *Organometallics* **1993**, *12*, 503.

(13) (a) Alcock, H. R.; Lavin, K. D.; Tollefson, N. M.; Evans, T. L. *Organometallics* **1983**, *2*, 267. (b) Barre, C.; Kubicki, M. M.; Leblanc, J.-C.; Moïse, C. *Inorg. Chem.* **1990**, *29*, 5244. (c) Lin, J.-T.; Yeh, A.-C.; Chou, Y.-C.; Tsai, T. Y.-R.; Wen, Y.-S. *J. Organomet. Chem.* **1995**, *486*, 147.

(14) (a) Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1. (b) Colton, R.; McCormick, M. J. *Coord. Chem. Rev.* **1980**, *31*, 1. (c) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Coord. Chem. Rev.* **1985**, *65*, 219. (d) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219. (e) Howard, J. A. K.; Jeffery, J. C.; Laguna, M.; Navarro, R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1981**, 751. (f) Crabtree, R. H.; Lavin, M. *Inorg. Chem.* **1986**, *25*, 805.

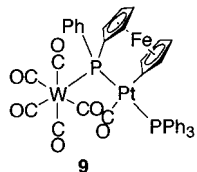


was determined by X-ray analysis. The structure is depicted in Figure 4, where  $W(CO)_4$  and  $Pt(PPh_3)$  fragments are connected by a  $W-Pt$  bond and two different bridging phosphido groups. This structure was also consistent with the  $^1H$ ,  $^{13}C$ , and  $^{31}P$  NMR and IR spectral data as well as elemental analysis. The yield was 56%. In the  $^{31}P\{^1H\}$  NMR, two sets of double doublets were observed at 173.6 and 163.2 ppm, both of which have  $^{183}W$  and  $^{195}Pt$  satellites. These chemical shifts are close to 173.8 ppm for  $(OC)_4W(\mu-PPh_2)_2Pt(PPh_3)$ , which has a  $W-Pt$  bond.<sup>15</sup> The signal of the terminal  $PPh_3$  of **8** was observed as a double doublet with  $^{195}Pt$  satellites at 48.9 ppm, which is also close to 47.9 ppm for the corresponding  $PPh_3$  in  $(OC)_4W(\mu-PPh_2)_2Pt(PPh_3)$ .

The most notable point concerning the molecular structure of **8** is that the phenyl group is attached to the ferrocene moiety. This phenyl group is considered to have come from  $PPh_3$ , because the remaining  $PPh_2$  exists as the bridging group, which connects the  $W$  and  $Pt$  fragments. To elucidate why such a product was obtained from the reaction of **3** with  $Pt(PPh_3)_4$ , the same reaction was carried out under milder conditions.

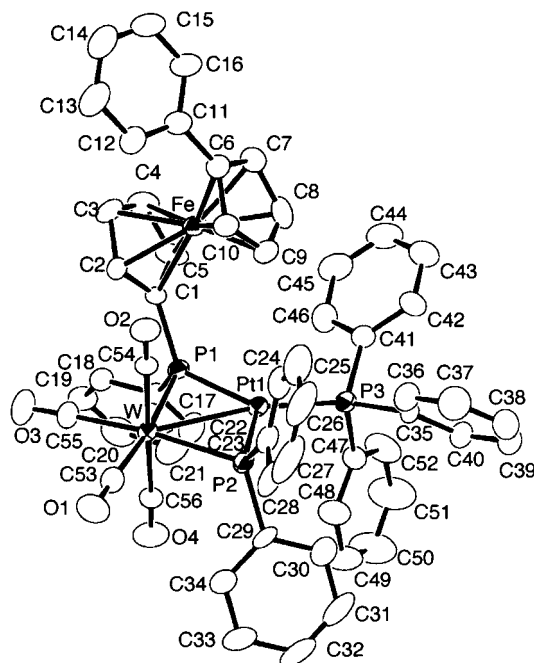
**Characterization of Intermediates.** When the reaction was carried out at 40 °C, the amount of the starting complex **3** gradually decreased. After 12 h, the  $^{31}P\{^1H\}$  NMR spectrum of the reaction mixture showed that the signal due to **3** disappeared completely and that a number of new signals (over 50) appeared. Detailed analyses of their chemical shifts and coupling constants, however, revealed that almost all signals were assignable to complexes **9–12** in Table 1.

With silica gel chromatography, the mixture of the four species was separated into two fractions. The  $^{31}P\{^1H\}$  NMR spectrum of the first fraction showed that it consists of one complex, whereas that of the second fraction showed that it is the mixture of three complexes. The product in the first fraction was isolated and characterized as **9** by X-ray analysis (Figure 5) as well

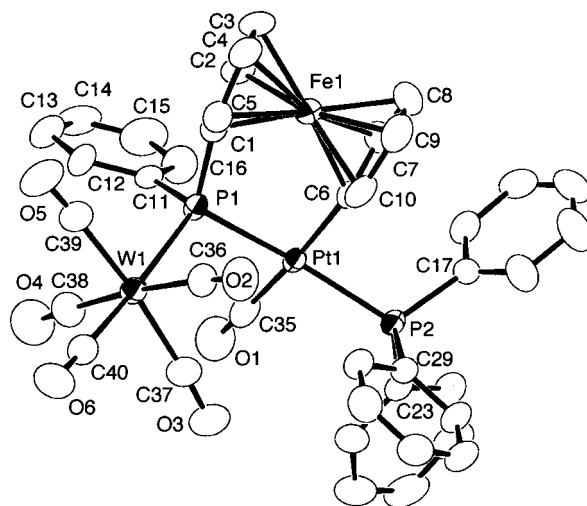


as the spectroscopic data. As shown in Figure 5, five CO ligands and the phosphido ligand coordinate to the tungsten center, and the platinum center has the phosphido bridge, the ferrocene moiety, a  $PPh_3$ , and a terminal CO. In the  $^{31}P\{^1H\}$  NMR spectrum, two resonances were observed at 17.1 and 8.3 ppm with a

(15) (a) Morrison, E. D.; Harley, A. D.; Maecelli, M. A.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* **1984**, *3*, 1407. (b) Powell, J.; Couture, C.; Gregg, M. R.; Sawyer, J. F. *Inorg. Chem.* **1989**, *28*, 3437.

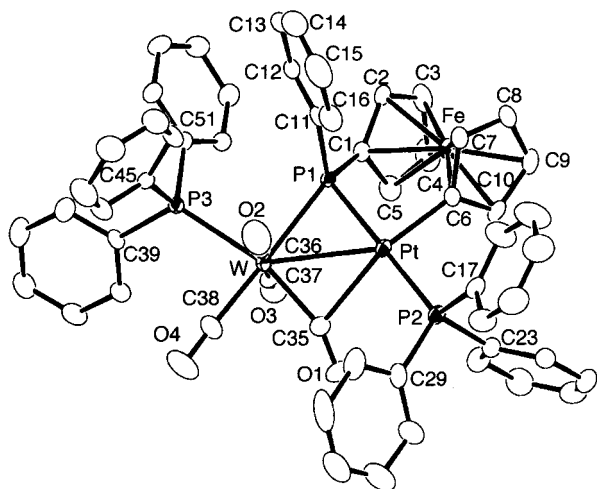


**Figure 4.** Molecular structure and numbering scheme of **8**. Only one of the two independent molecules in a unit cell is depicted. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg):  $Pt1-W1$ , 2.7656(3);  $Pt1-P1$ , 2.264(2);  $Pt1-P2$ , 2.267(2);  $Pt1-P3$ , 2.237(2);  $W1-P1$ , 2.512(2);  $W1-P2$ , 2.493(2);  $P1-C1$ , 1.817(6);  $P1-C17$ , 1.818(7);  $C6-C11$ , 1.472(10);  $W1-Pt1-P1$ , 58.92(4);  $W1-Pt1-P2$ , 58.38(4);  $P1-Pt1-P2$ , 117.23(6);  $P1-Pt1-P3$ , 121.96(6);  $P2-Pt1-P3$ , 120.12(6);  $Pt1-W1-P1$ , 50.52(4);  $Pt1-W1-P2$ , 50.75(4);  $P1-W1-P2$ , 101.23(5);  $Pt1-P1-W1$ , 70.55(4);  $Pt1-P2-W1$ , 70.87(5).



**Figure 5.** Molecular structure and numbering scheme of **9**. Only one of the two independent molecules in a unit cell is depicted. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg):  $Pt1-P1$ , 2.354(1);  $Pt1-P2$ , 2.352(1);  $Pt1-C6$ , 2.067(4);  $Pt1-C35$ , 1.910(5);  $W1-P1$ , 2.575(1);  $W1-C36$ , 2.033(5);  $W1-C37$ , 2.041(6);  $W1-C38$ , 2.043(6);  $W1-C39$ , 2.043(5);  $W1-C40$ , 1.990(5);  $Pt1\cdots W1$ , 3.8972(2);  $P1-Pt1-C6$ , 89.2(1);  $P1-Pt1-C35$ , 89.5(1);  $P2-Pt1-C6$ , 86.4(1);  $P2-Pt1-C35$ , 96.7(1);  $Pt1-P1-W1$ , 104.43(4);  $Pt1-P1-C1$ , 111.2(1).

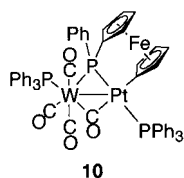
large  $J_{PP}$  coupling constant of 287 Hz. The former resonance was assigned to the bridging phosphido



**Figure 6.** Molecular structure and numbering scheme of **10**. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pt–W, 2.9156(1); Pt–P1, 2.2712(7); Pt–P2, 2.3193(8); Pt–C6, 2.057(3); Pt–C35, 2.431(3); W–P1, 2.4836(8); W–P3, 2.5155(8); W–C35, 2.020(3); W–C36, 2.048(3); W–C37, 2.019(3); W–C38, 2.007(4); P1–C1, 1.817(3); P1–C11, 1.826(3); W–Pt–P1, 55.55(2); W–Pt–C35, 43.23(8); P1–Pt–C6, 87.91(9); P2–Pt–C6, 93.65(9); P2–Pt–C35, 85.86(8); Pt–W–P1, 48.95(2); Pt–W–C35, 55.51(9); Pt–P1–W, 75.50(2); Pt–P1–C1, 108.8(1); Pt–C35–W, 81.3(1); Pt–C35–O1, 120.4(3); W–C35–O1, 156.8(3).

ligand, since it had both  $^{183}\text{W}$  ( $J_{\text{PW}} = 190$  Hz) and  $^{195}\text{Pt}$  ( $J_{\text{PPT}} = 1827$  Hz) satellites, and therefore the latter was assigned to the terminal  $\text{PPh}_3$  on the platinum center. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum at a CO region showed three resonances at 201.6 (doublet), 199.3 (doublet), and 179.3 (triplet) with relative intensities of 1:4:1. Since the signal at the highest field was coupled with two phosphorus atoms, it was assigned to the CO ligand coordinating to the platinum center. Two signals at 201.6 ppm ( $J_{\text{CP}} = 16$  Hz) and 199.3 ppm ( $J_{\text{CP}} = 6$  Hz) were assigned to the five CO ligands bonding to the tungsten center at the trans and cis positions, respectively, with respect to the bridging phosphido group.

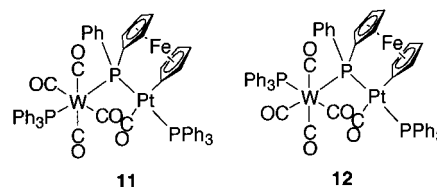
After the solvents of the other fraction containing the three species were removed under reduced pressure, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the residue in  $\text{CH}_2\text{Cl}_2$  showed that the amount of one species increased and those of the other two decreased. To isolate the increased species, the residue was dissolved again in toluene, and the solvent was removed in vacuo. After this procedure was repeated several times, one of the three species became a major component, and then it was isolated by recrystallization from  $\text{CH}_2\text{Cl}_2$ –hexane. The molecular structure of this product was determined as **10** by X-ray



analysis (Figure 6) as well as by the spectroscopic data. Figure 6 shows that **10** has the bridging phosphido group, a metal–metal bond, a bridging carbonyl group, a ferrocene moiety, and only one terminal  $\text{PPh}_3$  on the

platinum. All these structural dispositions are the same as those of the previously described manganese complex **6** shown in Figure 3. One unexpected structural difference is the presence of  $\text{PPh}_3$  on the tungsten center. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, this  $\text{PPh}_3$  was observed at 16.4 ppm, having a coupling ( $J_{\text{PP}} = 24$  Hz) with the bridging phosphido ligand at the cis position. Another  $\text{PPh}_3$  on the platinum center was observed at 28.4 ppm having a large coupling ( $J_{\text{PP}} = 266$  Hz) with the phosphido group. The bridging phosphido ligand was observed as a double doublet at significantly low field ( $\delta$  104.1 ppm), consistent with the presence of the W–Pt bond.<sup>10</sup>

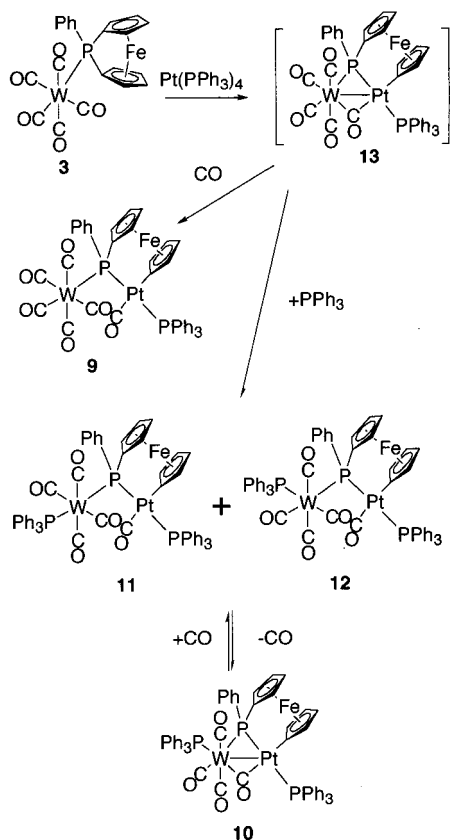
Judging from the fact that the remaining two species (**11** and **12**) could be converted to **10** just by removing the solvent under reduced pressure, a plausible reaction leading to **10** under such conditions is decarbonylation.



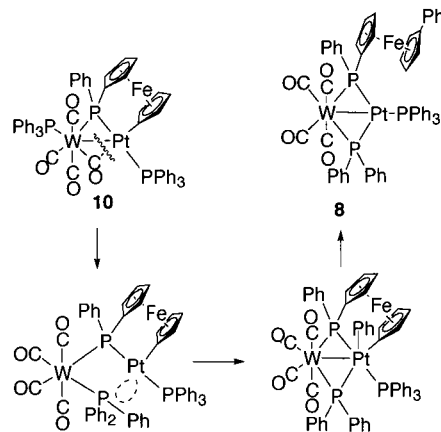
Therefore, two species were assumed to be **11** and **12**, each of which has an additional CO ligand on the platinum center but does not have the semibridging carbonyl. Furthermore, one of them (**11**) has  $\text{PPh}_3$  trans to and the other (**12**) has  $\text{PPh}_3$  cis to the bridging phosphido ligand around the tungsten. To confirm this assumption, the isolated **10** was dissolved in  $\text{CH}_2\text{Cl}_2$  and was treated with CO. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the products indicated the formation of the expected two species in about a 2:1 ratio. On the basis of thorough analyses of the  $^{13}\text{C}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectra, the major and minor products were confirmed to be **11** and **12**, respectively. In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **11**, a triplet at 180.1 ppm was assigned to the CO ligand coordinating to the platinum center. Four equivalent CO ligands on the tungsten center were observed as a triplet at 206.6 ppm ( $J_{\text{CP}} = 5$  Hz) due to the coupling with both the bridging phosphido ligand and the terminal  $\text{PPh}_3$  on the tungsten center. On the other hand, the four CO ligands on the tungsten center in **12** are all magnetically inequivalent. Two of the four CO ligands were observed at 208.1 ( $J_{\text{CP}} = 6$  and 21 Hz) and 209.0 ppm ( $J_{\text{CP}} = 26$  Hz). Their relatively large C–P coupling constants indicate that these two CO ligands are at the positions trans to the phosphorus ligands. The signals of the two remaining CO ligands were observed at 206.3 ppm as an overlapped multiplet. For the CO ligand on the platinum center in **12**, a triplet was observed at 180.2 ppm, which is almost identical with 180.1 ppm for **11** as well as 179.3 ppm for **9**. In the  $^{31}\text{P}$  NMR spectrum of **11**, the bridging phosphido ligand was observed at 27.7 ppm, indicating the absence of a W–Pt bond. Signals assigned to the two terminal  $\text{PPh}_3$  ligands on the tungsten and platinum centers were at 29.5 and 8.0 ppm, respectively. **12** also had three signals at 23.1 (phosphido), 20.6 ( $\text{PPh}_3$  on W), and 8.1 ( $\text{PPh}_3$  on Pt) ppm, which are similar to those of **11**.

In this way, all of the four species were characterized as **9**–**12**. Scheme 2 shows plausible reaction sequences. The first step is considered to be platinum insertion into

Scheme 2



Scheme 3



of the reaction mixture showed that the final product **8** was formed, indicating that **10** is an intermediate of the reaction shown in eq 6. A similar thermal reaction of **9** in the presence of  $\text{PPh}_3$  was also followed by  $^{31}\text{P}$  NMR. In this case, the formation of **10** as well as the final product **8** was observed, indicating that, at  $90^\circ\text{C}$ , decarbonylation of **9** probably takes place to regenerate **13**, which is converted to **10** according to the mechanism in Scheme 2, and **10** is eventually converted to **8**. A plausible reaction mechanism for the formation of **8** from **10** is shown in Scheme 3. The first step is a dissociation of the bridging carbonyl group from the Pt center together with the W–Pt bond cleavage. The facile dissociation of the bridging carbonyl is understandable from the molecular structure of **10**, which is indicative of some contribution of the asymmetric semibridging mode of the CO bridge: the W–C35–O1 angle of  $156.8(3)^\circ$  vs the Pt–C35–O1 angle of  $120.4(3)^\circ$  and the W–C35 length of  $2.020(3)\text{ \AA}$  vs the Pt–C35 length of  $2.431(3)\text{ \AA}$ . Through the rotation along the W–P(bridge) bond, the  $\text{PPh}_3$  on the W center approaches the vacant coordination site. Then, the P–Ph bond of  $\text{PPh}_3$  is cleaved by the platinum center. Bitterwolf et al. reported a similar P–C bond activation of  $\text{PPh}_3$  by a Mo–Ru heterodinuclear complex, in which a coordinatively unsaturated ruthenium center was generated by photolytic decarbonylation and it cleaved the P–Ph bond of the  $\text{PPh}_3$  on an adjacent molybdenum center to form a Ru–Ph bond and a  $\mu\text{-PPh}_2$  bridge.<sup>21,j</sup> In Scheme 3, the Ph group of  $\text{PPh}_3$  is similarly transferred to the platinum center, and the Ph group and the ferrocenyl group are coupled by a reductive elimination to give the final product **8**.

## Conclusion

Low-valent platinum complexes having two phosphine ligands cleave the P–C bond of the fcpp ligand coordinating to the manganese or tungsten complex to give ferrocenyl phosphido bridged heterodinuclear complexes. When the two phosphine ligands on the platinum center are bulky like  $\text{PPh}_3$ , one of the two phosphine ligands is released from the platinum center to form a coordinatively unsaturated species. In the tungsten case, released  $\text{PPh}_3$  is trapped by the tungsten center and then the P–Ph bond of the  $\text{PPh}_3$  is cleaved by the platinum center upon heating. In other words, the tungsten and platinum centers in this heterodi-

the P–C bond of the fcpp ligand coordinating to the tungsten. In the reaction of the manganese complex **2** with the platinum(0) fragment having bulky  $\text{PPh}_3$ , the product had only one  $\text{PPh}_3$  on the platinum center (Scheme 1). Therefore, the product of the first step in Scheme 2 is considered to be **13**. However, in this case, the reaction does not terminate at this stage, but **13** is readily attacked by  $\text{PPh}_3$  present in solution to give both **11** and **12**. The attack is considered relatively fast compared with the formation of **13**, since the presence of **13** could not be detected even spectroscopically. Such smooth addition of a phosphine ligand has been reported by Shyu et al.<sup>16</sup> and other groups<sup>17</sup> for  $\mu\text{-PPh}_2$ -bridged tungsten dinuclear complexes having the CO bridge. In complexes **11** and **12**, the platinum center readily releases the CO ligand to give **10**. **13** is also attacked by the free CO ligand thus formed to give **9**. Consequently, the four dinuclear complexes **9–12** are formed through the reaction of the starting **3** with the  $\text{Pt}(\text{PPh}_3)$  fragment.

**Thermolysis of 9 and 10 To Give 8.** When the isolated **10** was heated to  $90^\circ\text{C}$  in toluene, the  $^{31}\text{P}$  NMR

(16) (a) Shyu, S.-G.; Lin, P.-J.; Lin, K.-J.; Chang, M.-C.; Wen, M.-C. *Organometallics* **1995**, *14*, 2253. (b) Shyu, S.-G.; Hsiao, S.-M.; Lin, S.-M.; Gau, H.-M. *Organometallics* **1995**, *14*, 4300. (c) Shyu, S.-G.; Wu, W.-J.; Wen, Y.-S.; Peng, S.-M.; Lee, G.-H. *J. Organomet. Chem.* **1995**, *489*, 113. (d) Hsiao, S.-M.; Shyu, S.-G. *Organometallics* **1998**, *17*, 1151.

(17) (a) Mercer, W. C.; Whittle, R. R.; Burkhardt, E. W.; Geoffroy, G. L. *Organometallics* **1985**, *4*, 68. (b) Mercer, W. C.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1985**, *4*, 1418. (c) Powell, J.; Gregg, M. R.; Sawyer, J. F. *Inorg. Chem.* **1989**, *28*, 4451. (d) Powell, J.; Sawyer, J. F.; Stainer, M. V. R. *Inorg. Chem.* **1989**, *28*, 4461. (e) Powell, J.; Fuchs, E.; Gregg, M. R.; Phillips, J.; Stainer, M. V. R. *Organometallics* **1990**, *9*, 387. (f) Powell, J.; Fuchs, E.; Sawyer, J. F. *Organometallics* **1990**, *9*, 1722. (g) Mays, M. J.; Owen, S. M.; Raithby, P. R.; Reinisch, P. F.; Shields, G. P.; Solan, G. A. *J. Organomet. Chem.* **1997**, *528*, 123.

nuclear complex play clearly different roles in the activation of the  $\text{PPh}_3$ ; that is, the tungsten center traps the substrate, whereas the coordinatively unsaturated platinum center cleaves the P–C bond.

### Experimental Section

**General Remarks.** All reactions were carried out under an atmosphere of dry nitrogen using Schlenk tube techniques. All solvents were dried and purified by distillation:  $\text{CH}_2\text{Cl}_2$  was distilled from  $\text{P}_2\text{O}_5$ , toluene and THF were distilled from sodium/benzophenone, and hexane was distilled from sodium metal. These purified solvents were stored under an  $\text{N}_2$  atmosphere. Other reagents were used as received. **1–3**<sup>9</sup> and the platinum complexes  $\text{Pt}(\text{PMe}_3)_4$ <sup>18</sup> and  $\text{Pt}(\text{PPh}_3)_4$ <sup>19</sup> were prepared according to the previously described methods.

IR spectra were recorded on a Shimadzu FTIR-8100A spectrometer. NMR spectra were recorded on JEOL LA-300 and LA-500 spectrometers.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts were reported relative to  $\text{Me}_4\text{Si}$  and were determined by reference to the residual solvent peaks.  $^{31}\text{P}$  NMR chemical shifts were reported relative to  $\text{H}_3\text{PO}_4$  (85%) used as an external reference. Elemental analyses were performed on a Perkin-Elmer 2400CHN elemental analyzer.

**Preparation of 4.**  $\text{CpMn}(\text{CO})_2(\text{fcpp})$  (**2**; 100 mg, 0.214 mmol),  $\text{Pt}(\text{PMe}_3)_4$  (100 mg, 0.200 mmol), and toluene (3 mL) were placed in a Pyrex Schlenk tube, and the solution was heated at 70 °C for 6 h. After the solvent was removed in vacuo, the residue was loaded on a silica gel column and eluted with  $\text{CH}_2\text{Cl}_2$ . A yellow band was collected and dried. To purify the product further, the residue was loaded again on the silica gel column and eluted with a mixture of hexane and  $\text{CH}_2\text{Cl}_2$  (1:1). After workup, **4** was obtained as a yellow powder (48 mg, 0.053 mmol, 29%).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.20–1.65 (m, 18H,  $\text{PMe}_3$ ), 3.74 (br, 2H, Fc), 4.06–4.23 (5H, Fc), 4.92 (br, 5H, Cp–Mn), 4.99 (br, 1H, Fc), 7.34–7.67 (5H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  15.7 (d,  $J_{\text{CP}} = 30.2$  Hz,  $J_{\text{CpT}} = 28.7$  Hz,  $\text{Me}_3\text{P}$ ), 17.5 (d,  $J_{\text{CP}} = 30.2$  Hz,  $J_{\text{CpT}} = 24.9$  Hz,  $\text{Me}_3\text{P}$ ), 66.8 (d,  $J_{\text{CP}} = 6.0$  Hz, Fc), 68.0 (br, Fc), 70.5 (d,  $J_{\text{CP}} = 4.5$  Hz,  $J_{\text{CpT}} = 51.3$  Hz, Fc), 71.9 (d,  $J_{\text{CP}} = 6.0$  Hz,  $J_{\text{CpT}} = 48.2$  Hz, Fc), 73.9 (br,  $J_{\text{CpT}} = 51.3$  Hz, Fc), 74.2 (br, Fc), 74.7 (d,  $J_{\text{CP}} = 6.0$  Hz,  $J_{\text{CpT}} = 49.0$  Hz, Fc), 77.2 (d,  $J_{\text{CP}} = 16.6$  Hz, Fc), 83.1 (s, Cp–Mn), 128.5 (br, Ph), 135.4 (br, Ph), 147.4 (br, Ph), 234.6 (br, CO), 235.9 (br, CO). IR ( $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$ ): 1906, 1836. Anal. Calcd for  $\text{C}_{29}\text{H}_{36}\text{FeMnO}_2\text{P}_3\text{Pt}\cdot\text{CH}_2\text{Cl}_2$ : C, 40.02; H, 4.25. Found: C, 40.29; H, 4.35.

**Preparation of 5.**  $\text{W}(\text{CO})_5(\text{fcpp})$  (**3**; 202 mg, 0.328 mmol),  $\text{Pt}(\text{PMe}_3)_4$  (115 mg, 0.230 mmol), and toluene (5 mL) were placed in a Pyrex Schlenk tube, and the solution was heated at 45 °C for 5 h. After the solvent was removed in vacuo, the residue was loaded on a silica gel column and eluted with  $\text{CH}_2\text{Cl}_2$ . An orange band was collected and dried. For a further purification, the residue was loaded again on the silica gel column and eluted with a mixture of hexane and  $\text{CH}_2\text{Cl}_2$  (2:1). After workup, **5** was obtained as an orange powder (67 mg, 0.062 mmol, 30%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.26 (dd,  $J_{\text{HP}} = 1.8$  Hz,  $J_{\text{HPt}} = 8.8$  Hz,  $J_{\text{HPt}} = 25.2$  Hz, 9H,  $\text{PMe}_3$ ), 1.31 (d,  $J_{\text{HP}} = 8.8$  Hz,  $J_{\text{HPt}} = 17.7$  Hz, 9H,  $\text{PMe}_3$ ), 3.81 (br, 1H, Fc), 3.95 (br, 1H, Fc), 4.08 (br, 1H, Fc), 4.13 (br,  $J_{\text{HPt}} = 22.3$  Hz, 1H, Fc), 4.32 (br, 1H, Fc), 4.38 (br, 1H, Fc), 4.41 (br,  $J_{\text{HPt}} = 18.0$  Hz, 1H, Fc), 5.11 (br, 1H, Fc), 7.25–7.40 (m, 3H, Ph), 8.10 (t,  $J_{\text{HH}} = 16.3$  Hz, 2H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  16.0 (d,  $J_{\text{CP}} = 29.7$  Hz,  $J_{\text{CpT}} = 28.9$  Hz,  $\text{Me}_3\text{P}$ ), 17.1 (d,  $J_{\text{CP}} = 31.6$  Hz,  $J_{\text{CpT}} = 21.1$  Hz,  $\text{Me}_3\text{P}$ ), 60.6 (dd,  $J_{\text{CP}} = 17.3$  Hz,  $J_{\text{CP}} = 106.7$  Hz, Fc), 66.8 (d,  $J_{\text{CP}} = 7.4$  Hz, Fc), 69.6 (m, Fc), 70.2 (m,  $J_{\text{CpT}} = 50.8$  Hz, Fc), 72.2 (m,  $J_{\text{CpT}} = 49.0$  Hz, Fc), 73.6 (m,  $J_{\text{CpT}} = 51.5$  Hz, Fc), 74.7 (br, Fc), 75.0 (br,  $J_{\text{CpT}} = 48.4$  Hz, Fc), 78.6 (d,  $J_{\text{CP}} = 18.6$  Hz, Fc), 96.2 (dd,  $J_{\text{CP}} = 5.5$  Hz,  $J_{\text{CP}} = 29.8$  Hz,

Fc), 128.0 (d,  $J_{\text{CP}} = 7.4$  Hz, Ph), 128.4 (s, Ph), 136.1 (m, Ph), 145.4 (m, Ph), 200.3 (d,  $J_{\text{CP}} = 5.0$ ,  $J_{\text{CpT}} = 13.5$  Hz,  $J_{\text{CW}} = 125.3$  Hz, 4OC–W), 201.5 (d,  $J_{\text{CP}} = 14.7$  Hz, OC–W). IR ( $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$ ): 2057, 1966, 1918. Anal. Calcd for  $\text{C}_{27}\text{H}_{31}\text{FeO}_5\text{P}_3\text{PtW}\cdot\text{CDCl}_3$ : C, 31.04; H, 3.07. Found: C, 31.04; H, 2.95.

**Preparation of 6.**  $\text{CpMn}(\text{CO})_2(\text{fcpp})$  (**2**; 127 mg, 0.271 mmol),  $\text{Pt}(\text{PPh}_3)_4$  (374 mg, 0.301 mmol), and toluene (5 mL) were placed in a Pyrex Schlenk tube, and the suspension was heated at 90 °C for 6 h. After the solvent was removed in vacuo, the residue was loaded on a silica gel column and eluted with  $\text{CH}_2\text{Cl}_2$ . A reddish orange band was collected and dried. The residue was repeatedly washed with pentane to remove free  $\text{PPh}_3$ . After workup, **6** was obtained as a reddish orange powder (134 mg, 0.133 mmol, 53%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.04 (br,  $J_{\text{HPt}} = 24.8$  Hz, 1H, Fc), 3.61 (br, 1H, Fc), 3.80 (br, 1H, Fc), 4.30 (br, 2H, Fc), 4.37 (br, 5H, Cp), 4.62 (br,  $J_{\text{HPt}} = 23.9$  Hz, 1H, Fc), 4.79 (br, 1H, Fc), 4.83 (br, 1H, Fc), 7.30–7.57 (18H, Ph), 7.98 (m, 2H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  38.8 (d,  $J_{\text{CP}} = 10.2$  Hz, Fc), 68.6 (br, Fc), 70.5 (br,  $J_{\text{CpT}} = 72.6$  Hz, Fc), 71.5 (d,  $J_{\text{CP}} = 10.2$  Hz, Fc), 72.2 (d,  $J_{\text{CP}} = 20.4$  Hz, Fc), 74.7 (br,  $J_{\text{CpT}} = 50.9$  Hz, Fc), 76.8 (br,  $J_{\text{CpT}} = 72.9$  Hz, Fc), 78.4 (br, Fc), 78.8 (d,  $J_{\text{CP}} = 36.5$  Hz, Fc), 83.6 (br,  $J_{\text{CpT}} = 96.7$  Hz, Fc), 84.0 (s, Cp–Mn), 127.9 (d,  $J_{\text{CP}} = 10.1$  Hz,  $\text{Ph}_3\text{P}$ ), 128.1 (d,  $J_{\text{CP}} = 14.0$  Hz, Ph), 128.9 (d,  $J_{\text{CP}} = 2.6$  Hz, Ph), 129.8 (d,  $J_{\text{CP}} = 47.8$  Hz,  $\text{Ph}_3\text{P}$ ), 132.3 (dd,  $J_{\text{CP}} = 3.8$  Hz,  $J_{\text{CP}} = 10.2$  Hz, Ph), 132.4 (dd,  $J_{\text{CP}} = 1.7$  Hz,  $J_{\text{CP}} = 45.9$  Hz,  $\text{Ph}_3\text{P}$ ), 134.6 (d,  $J_{\text{CP}} = 11.2$  Hz,  $\text{Ph}_3\text{P}$ ), 140.5 (d,  $J_{\text{CP}} = 43.3$  Hz, Ph), 235.9 (d,  $J_{\text{CP}} = 15.7$  Hz, CO), 237.7 (br, CO). IR ( $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$ ): 1917, 1778. Anal. Calcd for  $\text{C}_{41}\text{H}_{33}\text{FeMnO}_2\text{P}_2\text{Pt}$ : C, 53.21; H, 3.59. Found: C, 53.57; H, 3.45.

**Preparation of 8.**  $\text{W}(\text{CO})_5(\text{fcpp})$  (**3**; 86 mg, 0.140 mmol),  $\text{Pt}(\text{PPh}_3)_4$  (200 mg, 0.161 mmol), and toluene (10 mL) were placed in a Pyrex Schlenk tube, and the suspension was heated at 90 °C for 15 h. After the solvent was removed in vacuo, the residue was loaded on a silica gel column and eluted with a mixture of hexane and  $\text{CH}_2\text{Cl}_2$  (2:1). A red fraction was collected, and the solvents were removed in vacuo. The residue was washed three times with pentane (2 mL) and dried to give **7** as a red powder (103 mg, 0.074 mmol, 56%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.05 (br, 3H, Fc), 4.24 (br, 3H, Fc), 4.39 (br, 1H, Fc), 4.53 (br, 1H, Fc), 7.05–7.55 (m, 35H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  67.2 (s, 2Fc), 71.8 (s, Fc), 72.5 (d,  $J_{\text{CP}} = 7.5$  Hz, Fc), 74.8 (d,  $J_{\text{CP}} = 6.9$  Hz, Fc), 76.2 (d,  $J_{\text{CP}} = 11.2$  Hz, Fc), 84.5 (dd,  $J_{\text{CP}} = 5.6$  Hz,  $J_{\text{CP}} = 27.3$  Hz, Fc), 85.8 (s, Fc), 126.0 (s, Ph), 126.1 (s, Ph), 127.4 (d,  $J_{\text{CP}} = 10.6$  Hz, Ph), 127.7 (d,  $J_{\text{CP}} = 9.9$  Hz, Ph), 127.8 (d,  $J_{\text{CP}} = 10.0$  Hz, Ph), 128.2 (s, Ph), 128.3 (d,  $J_{\text{CP}} = 9.9$  Hz,  $\text{Ph}_3\text{P}$ ), 128.5 (br, Ph), 130.1 (br, Ph), 132.3 (d,  $J_{\text{CP}} = 12.4$  Hz, Ph), 133.0 (d,  $J_{\text{CP}} = 10.5$  Hz, Ph), 133.5 (d,  $J_{\text{CP}} = 11.2$  Hz, Ph), 134.0 (d,  $J_{\text{CP}} = 13.0$  Hz,  $\text{Ph}_3\text{P}$ ), 135.8 (dt,  $J_{\text{CP}} = 50.9$  Hz,  $J_{\text{CP}} = 3.7$  Hz, Ph), 138.5 (s, Ph), 139.9 (dd,  $J_{\text{CP}} = 4.4$  Hz,  $J_{\text{CP}} = 28.5$  Hz, Ph), 141.5 (dd,  $J_{\text{CP}} = 3.7$  Hz,  $J_{\text{CP}} = 27.9$  Hz, Ph), 143.1 (dd,  $J_{\text{CP}} = 3.7$  Hz,  $J_{\text{CP}} = 29.7$  Hz, Ph), 194.0 (br, CO), 196.0 (br, CO), 208.4 (dd,  $J_{\text{CP}} = 12.7$  Hz,  $J_{\text{CP}} = 18.3$  Hz, CO), 209.1 (dd,  $J_{\text{CP}} = 12.4$  Hz,  $J_{\text{CP}} = 19.8$  Hz, CO). IR ( $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$ ): 2029, 1939, 1921. Anal. Calcd for  $\text{C}_{56}\text{H}_{43}\text{FeO}_4\text{P}_3\text{PtW}$ : C, 51.44; H, 3.31. Found: C, 51.46; H, 3.29.

**Reaction of 3 with  $\text{Pt}(\text{PPh}_3)_4$  under Mild Conditions.**  $\text{W}(\text{CO})_5(\text{fcpp})$  (**3**; 255 mg, 0.414 mmol),  $\text{Pt}(\text{PPh}_3)_4$  (515 mg, 0.414 mmol), and toluene (25 mL) were placed in a Pyrex Schlenk tube, and the suspension was heated at 40 °C for 12 h. After the solvent was removed in vacuo, the residue was loaded on a silica gel column and eluted with a mixture of hexane and  $\text{CH}_2\text{Cl}_2$  (2:1). The faster orange band and a deep red band were collected separately. After the solvent of the former band was removed, the residue was washed with pentane (2 mL  $\times$  3) and dried in vacuo to give **9** as an orange powder (120 mg, 0.109 mmol, 26%). The solvent of the other band was removed, and the residue was used for the isolation of **10**.

(18) Schunn, R. A. *Inorg. Chem.* **1976**, *15*, 208.

(19) Ugo, R.; Cariati, F.; Monica, G. L. *Inorg. Synth.* **1968**, *11*, 105.



Table 2. Crystal and Structure Refinement Data for Compounds 4–6 and 8–10

	4	5	6	8	9	10
chem formula	C <sub>30</sub> H <sub>38</sub> Cl <sub>2</sub> Fe-MnO <sub>2</sub> P <sub>3</sub> Pt	C <sub>28</sub> H <sub>32</sub> Cl <sub>3</sub> Fe-O <sub>5</sub> P <sub>3</sub> PtW	C <sub>42</sub> H <sub>35</sub> Cl <sub>2</sub> Fe-MnO <sub>2</sub> P <sub>2</sub> Pt	C <sub>57</sub> H <sub>45</sub> Cl <sub>2</sub> Fe-O <sub>4</sub> P <sub>3</sub> PtW	C <sub>40</sub> H <sub>28</sub> Fe-O <sub>6</sub> P <sub>2</sub> PtW	C <sub>57</sub> H <sub>45</sub> Cl <sub>2</sub> Fe-O <sub>4</sub> P <sub>3</sub> PtW
fw	900.33	1082.63	1010.47	1392.59	1101.39	1392.59
color, habit	yellow, stick	orange, stick	black, stick	orange, stick	orange, stick	orange, stick
cryst dimens (mm)	0.60 × 0.05 × 0.03	0.30 × 0.25 × 0.25	0.35 × 0.08 × 0.04	0.30 × 0.30 × 0.20	0.30 × 0.20 × 0.20	0.35 × 0.20 × 0.15
cryst syst	monoclinic	triclinic	monoclinic	triclinic	triclinic	triclinic
unit cell dimens						
<i>a</i> (Å)	15.9600(4)	10.8950(2)	11.1890(2)	10.8560(2)	12.0900(2)	10.5230(2)
<i>b</i> (Å)	10.4450(2)	11.5390(2)	28.1330(7)	21.1610(5)	15.5870(2)	13.1970(2)
<i>c</i> (Å)	20.7660(5)	15.2300(3)	12.8430(3)	24.4190(5)	20.5300(3)	20.3970(2)
$\alpha$ (deg)		83.743(1)		74.161(1)	74.204(1)	93.510(1)
$\beta$ (deg)	104.682(1)	69.254(1)	109.269(2)	77.528(1)	82.494(1)	102.285(1)
$\gamma$ (deg)		73.010(1)		86.148(1)	85.736(1)	109.530(1)
<i>V</i> (Å <sup>3</sup> )	3348.7(1)	1712.35(6)	3816.2(1)	5269.1(2)	3687.76(10)	2581.39(8)
space group (No.)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (14)	<i>P</i> 1 (2)	<i>P</i> 2 <sub>1</sub> / <i>a</i> (14)	<i>P</i> 1 (2)	<i>P</i> 1 (2)	<i>P</i> 1 (2)
<i>Z</i>	4	2	4	4	4	2
$\mu$ (cm <sup>-1</sup> )	52.78	82.40	46.02	53.27	74.05	54.37
no. of rflns						
measd	7436	7405	8532	22 472	16 123	11 136
obsd ( <i>I</i> > 3.00 $\sigma$ ( <i>I</i> ))	5000	7183	7345	19 343	14 435	10 740
struct soln	direct	Patterson	direct	Patterson	direct	Patterson
methods (SIR92)	methods (SIR92)	methods (DIRDIF92 PATTY)	methods (SIR92)	methods (DIRDIF92 PATTY)	methods (SIR92)	methods (DIRDIF92 PATTY)
no. of params	382	298	611	1244	920	620
<i>R</i> (%)	4.1	2.6	4.6	4.9	2.8	2.8
<i>R</i> <sub>w</sub> (%)	6.4	4.6	7.2	7.6	4.5	5.2

Data for **9** are as follows. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  3.62 (br, 1H, Fc), 3.78 (br, 1H, Fc), 3.84 (br, 1H, Fc), 3.97 (br, 1H, Fc), 4.09 (br, 1H, Fc), 4.21 (br, 1H, Fc), 4.53 (br, 1H, Fc), 5.30 (br, 1H, Fc), 7.29–7.48 (m, 18H, Ph), 8.01 (m, 2H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  53.4 (d, *J*<sub>CP</sub> = 16.7 Hz, Fc), 67.4 (d, *J*<sub>CP</sub> = 8.7 Hz, Fc), 70.2 (d, *J*<sub>CP</sub> = 4.3 Hz, Fc), 71.2 (s, *J*<sub>CPt</sub> = 57.0 Hz, Fc), 72.7 (s, *J*<sub>CPt</sub> = 53.3 Hz, Fc), 73.9 (s, *J*<sub>CPt</sub> = 54.2 Hz, Fc), 75.1 (br, *J*<sub>CPt</sub> = 50.8 Hz, Fc), 75.1 (s, Fc), 78.2 (d, *J*<sub>CP</sub> = 20.5 Hz, Fc), 92.6 (d, *J*<sub>CP</sub> = 31.0 Hz, Fc), 128.1 (d, *J*<sub>CP</sub> = 8.8 Hz, Ph), 128.7 (s, Ph), 128.7 (d, *J*<sub>CP</sub> = 10.5 Hz, Ph<sub>3</sub>P), 129.1 (dd, *J*<sub>CP</sub> = 3.1 Hz, *J*<sub>CP</sub> = 46.5 Hz, Ph<sub>3</sub>P), 131.3 (s, Ph<sub>3</sub>P), 134.0 (d, *J*<sub>CP</sub> = 11.2 Hz, Ph<sub>3</sub>P), 134.7 (dd, *J*<sub>CP</sub> = 3.7 Hz, *J*<sub>CP</sub> = 10.0 Hz, Ph), 144.9 (dd, *J*<sub>CP</sub> = 4.1 Hz, *J*<sub>CP</sub> = 24.5 Hz, Ph), 179.3 (t, *J*<sub>CP</sub> = 7.5 Hz, OC–Pt), 199.3 (d, *J*<sub>CP</sub> = 5.6 Hz, *J*<sub>CW</sub> = 125.3 Hz, 4OC–W), 201.6 (d, *J*<sub>CP</sub> = 16.1 Hz, *J*<sub>CW</sub> = 146.4 Hz, OC–W). IR ( $\nu_{CO}$ , cm<sup>-1</sup>): 2081, 2059, 1971, 1922. Anal. Calcd for C<sub>40</sub>H<sub>28</sub>FeO<sub>6</sub>P<sub>2</sub>Pt·CH<sub>2</sub>Cl<sub>2</sub>: C, 43.62; H, 2.56. Found: C, 43.80; H, 2.45.

**Isolation of 10.** A part of the mixture obtained above (178 mg) was dissolved in toluene (5 mL). To the solution was added PPh<sub>3</sub> (100 mg), in order to prevent the dissociation of PPh<sub>3</sub> during the treatment. The solvent was removed slowly at 60 °C under reduced pressure for 2 h. Then toluene (5 mL) was added and removed again similarly. This treatment was repeated twice. At this stage, the amount of **10** increased up to about 90%. The crude product was dissolved in toluene (4 mL), and then hexane (10 mL) was added. The solution was stored at –30 °C overnight to give **10** as a precipitate, which was collected, washed with hexane (10 mL × 2), and dried (89 mg, 0.064 mmol).

Data for **10** are as follows. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  3.30 (br, 1H, Fc), 3.53 (br, 1H, Fc), 3.72 (br, 1H, Fc), 4.16 (br, 1H, Fc), 4.30 (br, 2H, Fc), 4.49 (br, 1H, Fc), 4.94 (br, 1H, Fc), 7.22–7.43 (m, 29H, Ph), 7.59 (m, 6H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  34.6 (ddd, *J*<sub>CP</sub> = 2.4 Hz, *J*<sub>CP</sub> = 3.7 Hz, *J*<sub>CP</sub> = 13.0 Hz, Fc), 68.4 (br, Fc), 70.7 (br, *J*<sub>CPt</sub> = 73.3 Hz, Fc), 71.5 (br, Fc), 71.7 (br, Fc), 74.4 (br, *J*<sub>CPt</sub> = 50.9 Hz, Fc), 76.4 (br, *J*<sub>CPt</sub> = 76.4 Hz, Fc), 78.3 (br, Fc), 79.0 (d, *J*<sub>CP</sub> = 37.9 Hz, Fc), 82.7 (d, *J*<sub>CPt</sub> = 92.5 Hz, Fc), 127.8 (d, *J*<sub>CP</sub> = 10.0 Hz, Ph), 128.3 (d, *J*<sub>CP</sub> = 9.9 Hz, Ph<sub>3</sub>P), 128.6 (d, *J*<sub>CP</sub> = 9.9 Hz, Ph<sub>3</sub>P), 128.7 (br, Ph), 130.2 (d, *J*<sub>CP</sub> = 1.8 Hz, Ph<sub>3</sub>P), 130.4 (d, *J*<sub>CP</sub> = 1.8 Hz,

Ph<sub>3</sub>P), 132.7 (dd, *J*<sub>CP</sub> = 1.8 Hz, 45.9 Hz, Ph<sub>3</sub>P), 133.1 (dd, *J*<sub>CP</sub> = 4.3 Hz, *J*<sub>CP</sub> = 10.6 Hz, Ph), 133.8 (d, *J*<sub>CP</sub> = 11.8 Hz, Ph<sub>3</sub>P), 135.2 (d, *J*<sub>CP</sub> = 11.8 Hz, Ph<sub>3</sub>P), 136.4 (dd, *J*<sub>CP</sub> = 1.8 Hz, *J*<sub>CP</sub> = 42.8 Hz, Ph<sub>3</sub>P), 139.0 (dd, *J*<sub>CP</sub> = 1.2 Hz, *J*<sub>CP</sub> = 44.7 Hz, Ph), 199.9 (t, *J*<sub>CP</sub> = 6.5 Hz, CO), 201.3 (dd, *J*<sub>CP</sub> = 6.2 Hz, *J*<sub>CP</sub> = 7.5 Hz, CO), 207.8 (dd, *J*<sub>CP</sub> = 9.3 Hz, *J*<sub>CP</sub> = 21.1 Hz, CO), 229.2 (m,  $\mu$ -CO). IR ( $\nu_{CO}$ , cm<sup>-1</sup>): 2015, 1911, 1772. Anal. Calcd for C<sub>56</sub>H<sub>43</sub>FeO<sub>4</sub>P<sub>3</sub>PtW·CH<sub>2</sub>Cl<sub>2</sub>: C, 49.16; H, 3.26. Found: C, 49.32; H, 3.09.

**Reaction of 10 with CO.** An appropriate amount of **10** was dissolved in a small amount of CH<sub>2</sub>Cl<sub>2</sub>. Into this solution, CO gas was bubbled for 15 min, and then the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum was recorded immediately, showing that the solution contained both **11** and **12**. After that, the solvent was removed in vacuo, and the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR of the CD<sub>2</sub>Cl<sub>2</sub> solution were recorded.

Data for **11** are as follows. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  3.56 (br, 1H, Fc), 3.64 (br, 1H, Fc), 3.68 (br, 1H, Fc), 3.81 (br, 1H, Fc), 3.95 (br, 1H, Fc), 4.21 (br, 1H, Fc), 4.35 (br, 1H, Fc), 5.29 (br, 1H, Fc), 7.00–8.10 (m, 35H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (125.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  67.3 (d, *J*<sub>CP</sub> = 8.2 Hz, Fc), 70.0 (d, *J*<sub>CP</sub> = 5.1 Hz, Fc), 71.2 (br, Fc), 72.7 (br, Fc), 74.7 (br, Fc), 75.2 (br, Fc), 75.9 (br, Fc), 78.8 (d, *J*<sub>CP</sub> = 20.7 Hz, Fc), 96.1 (d, *J*<sub>CP</sub> = 30.0 Hz, Fc), 128.2 (d, *J*<sub>CP</sub> = 8.3 Hz, Ph), 128.4 (d, *J*<sub>CP</sub> = 9.3 Hz, Ph<sub>3</sub>P), 129.0 (d, *J*<sub>CP</sub> = 10.3 Hz, Ph<sub>3</sub>P), 129.6 (br, Ph<sub>3</sub>P), 131.5 (d, *J*<sub>CP</sub> = 2.1 Hz, Ph<sub>3</sub>P), 133.6 (d, *J*<sub>CP</sub> = 11.4 Hz, Ph<sub>3</sub>P), 134.5 (d, *J*<sub>CP</sub> = 10.4 Hz, Ph<sub>3</sub>P), 135.5 (dd, *J*<sub>CP</sub> = 2.2 Hz, *J*<sub>CP</sub> = 10.2 Hz, Ph), 139.3 (d, *J*<sub>CP</sub> = 40.3 Hz, Ph<sub>3</sub>P), 147.7 (dd, *J*<sub>CP</sub> = 4.1 Hz, *J*<sub>CP</sub> = 23.8 Hz, Ph), 180.1 (t, *J*<sub>CP</sub> = 7.3 Hz, OC–Pt), 206.6 (t, *J*<sub>CP</sub> = 5.1 Hz, 4OC–W).

Data for **12** are as follows. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  3.56 (br, 1H, Fc), 3.60 (br, 1H, Fc), 3.64 (br, 1H, Fc), 3.77 (br, 1H, Fc), 3.90 (br, 1H, Fc), 4.16 (br, 1H, Fc), 4.40 (br, 1H, Fc), 5.08 (br, 1H, Fc), 7.00–8.10 (m, 35H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (125.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  67.6 (d, *J*<sub>CP</sub> = 8.3 Hz, Fc), 69.7 (d, *J*<sub>CP</sub> = 4.1 Hz, Fc), 71.6 (br, Fc), 72.8 (br, Fc), 74.3 (br, Fc), 75.6 (br, Fc), 75.9 (br, Fc), 78.1 (d, *J*<sub>CP</sub> = 21.7 Hz, Fc), 94.7 (d, *J*<sub>CP</sub> = 22.7 Hz, Fc), 127.8 (d, *J*<sub>CP</sub> = 8.3 Hz, Ph), 128.3 (d, *J*<sub>CP</sub> = 9.3 Hz, Ph<sub>3</sub>P), 129.0 (d, *J*<sub>CP</sub> = 10.4 Hz, Ph<sub>3</sub>P), 129.8 (br, Ph<sub>3</sub>P), 130.1 (d, *J*<sub>CP</sub> = 47.5 Hz, Ph<sub>3</sub>P), 131.5 (d, *J*<sub>CP</sub> = 2.0 Hz, Ph<sub>3</sub>P), 134.0 (d, *J*<sub>CP</sub> = 11.4 Hz, Ph<sub>3</sub>P), 134.6 (d, *J*<sub>CP</sub> = 10.3 Hz, Ph<sub>3</sub>P), 136.2

(dd,  $J_{CP} = 3.1$  Hz,  $J_{CP} = 10.4$  Hz, Ph), 136.9 (d,  $J_{CP} = 36.2$  Hz,  $\text{Ph}_3\text{P}$ ), 143.9 (d,  $J_{CP} = 17.6$  Hz, Ph), 180.2 (t,  $J_{CP} = 8.3$  Hz, OC–Pt), 206.1 (m, 2OC–W), 208.1 (dd,  $J_{CP} = 6.1$  Hz,  $J_{CP} = 20.7$  Hz, OC–W), 209.0 (d,  $J_{CP} = 25.8$  Hz, OC–W).

**X-ray Crystallography.** Suitable crystals of **4–6** and **8–10** were mounted on glass fibers and cooled to 200 K with a cold nitrogen gas flow. All measurements were made on a Mac Science DIP2030 imaging plate area detector. The data were collected up to a maximum  $2\theta$  value of  $55^\circ$ . Cell parameters and intensities for the reflection were estimated using the program packages of MacDENZO.<sup>20</sup> The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using a teXsan crystallographic software package

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(20) MacDENZO: Gewirth, D. (with the cooperation of the program authors Z. Otwinowski and W. Minor) In *The MacDenzo Manual—A Description of the Programs DENZO, XDISPLAYF, and SCALEPACK*; Yale University: New Haven, CT, 1995.

from the Molecular Structure Corp.<sup>21</sup> Crystallographic data are collected in Table 2.

**Acknowledgment.** This work was supported by Grants-in-Aid for Science Research (Nos. 12640540 and 13640560) from the Ministry of Education, Science, Sports and Culture of Japan. Some of the measurements of NMR spectra was made with the JEOL LA-500 instrument at the Instrument Center for Chemical Analysis, Hiroshima University.

**Supporting Information Available:** Tables giving positional and thermal parameters, crystallographic data, and bond lengths and angles for **4–6** and **8–10**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(21) teXsan: Single-Crystal Structure Analysis Software, Version 1.6; Molecular Structure Corp., The Woodlands, TX, 1993.