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Migratory insertion reaction of a phosphenium ligand into Mo– and W–alkyl bonds

Hiroshi Nakazawa [a,b,*], Mitsuru Kishishita [a,b], Shizuyo Yoshinaga [a], Yoshitaka Yamaguchi [a,b], Tsutomu Mizuta [a,b], Katsuhiko Miyoshi [a]

[a] *Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-Hiroshima 739, Japan*
[b] *Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan*

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Abstract

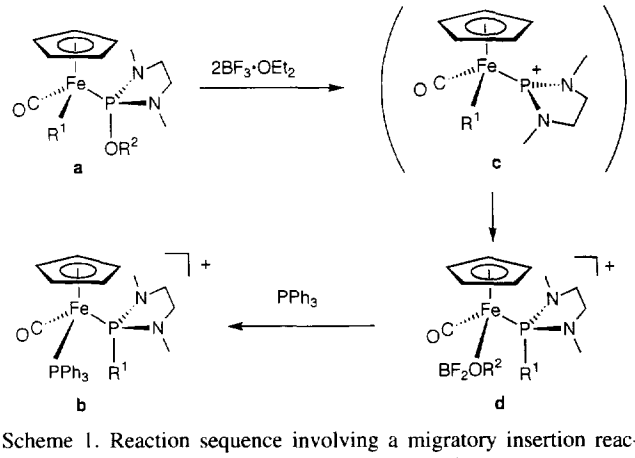
Treatment of $Cp(CO)_2MeM\{\overline{PN(Me)CH_2CH_2X(OR)}\}$ (M = Mo, W; X = NMe, O) with $BF_3 \cdot OEt_2$ and then with PPh_3 yields *trans*-$[Cp(CO)_2(PPh_3)M\{\overline{PN(Me)CH_2CH_2X(Me)}\}]BF_4$. Reaction of $Cp(CO)_2MeM\{P(OMe)_3\}$ (M = Mo, W) with $BF_3 \cdot OEt_2$ and then with PPh_3 gives a mixture of $[Cp(CO)_2(PPh_3)M\{P(OMe)_2Me\}]BF_4$ and $[Cp(CO)_2(PPh_3)M\{P(OMe)_3\}]BF_4$. These reactions reveal that migratory insertion of a phosphenium ligand into an M–alkyl bond (M = Mo, W) takes place. The structures of *trans*-$[Cp(CO)_2(PPh_3)Mo\{\overline{PN(Me)CH_2CH_2NMe(Me)}\}]OTf$ and $[Cp(CO)_2(PPh_3)W\{P(OMe)_3\}]BF_4$ were determined by single crystal X-ray diffraction studies.

Keywords: Migratory insertion reaction; Group 6 transition metal; Phosphenium ligand

1. Introduction

There is growing interest in the chemistry of transition metal complexes containing a cationic phosphenium fragment ($^+PR_2$) that can serve both as a strong π-acceptor, due to the empty p orbital on the phosphorus atom, and as a σ-donor [1,2]. Since the first report of Parry and coworkers in 1978 [3], cationic phosphenium complexes have been reported for several kinds of transition metal [4–6]. (In selected cases, neutral transition metal complexes described as $[L_nMPR_2]$ can be considered to contain formal L_nM^- and $^+PR_2$ fragments; for example, see Ref. [7]. In this paper we focus on cationic transition metal complexes described as $[L_nMPR_2]^+$.) Little has been studied, however, on the reactivity of cationic phosphenium complexes.

Recently, we found that $Cp(CO)R^1Fe\{\overline{PN(Me)CH_2CH_2X(OR^2)}\}$ (X = NMe, O) reacts with $BF_3 \cdot OEt_2$ and then PPh_3 to give $[Cp(CO)(PPh_3)Fe\{\overline{PN(Me)CH_2CH_2X(R^1)}\}]^+$ [8]. The reaction proceeds as shown in Scheme 1: **a** reacts with $BF_3 \cdot OEt_2$ to yield a cationic phosphenium complex **c** by the abstraction of the OR^2 group as an anion from the phosphorus atom, followed by migratory insertion of the phosphenium ligand into the iron–alkyl bond giving **d**, which readily reacts with PPh_3 forming the final product **b**. The migratory insertion reaction involving alkyl migration from the transition metal to the phosphenium fragment is unprecedented, though some interesting insertion reactions of phosphenium cations



Scheme 1. Reaction sequence involving a migratory insertion reaction of a phosphenium ligand into an Fe–C bond.

* Corresponding author.

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are known in organic chemistry [2] (also, for insertion reactions with a C–H bond, see for example Ref. [9]; for insertion reactions with a C–C bond, see for example Ref. [10]; for insertion reactions with a B–C bond, see for example Ref. [11]). Therefore, we have investigated the generality of this migratory insertion reaction.

Table 1
Spectroscopic data of the trans isomer of neutral molybdenum (**Mo–1a** to **Mo–4a**) and tungsten (**W–1a** to **W–4a**) complexes

Complex	IR (CH_2Cl_2) ν(CO) (cm^{-1})	^1H NMR ($CDCl_3$) δ (ppm), J_{PH} (Hz)	^{13}C NMR ($CDCl_3$) δ (ppm), J_{PC} (Hz)	^{31}P NMR (CH_2Cl_2) δ (ppm), J_{PW} (Hz)
Mo–1a	1938 1850	0.29 (d, J = 3.0, 3H, $MoCH_3$) 2.81 (d, J = 11.0, 6H, NCH_3) 3.08–3.18 (m, 2H, NCH_2) 3.38–3.45 (m, 2H, NCH_2) 3.31 (d, J = 11.8, 3H, OCH_3) 4.89 (d, J = 1.2, 5H, C_5H_5)	−19.39 (d, J = 12.2, $MoCH_3$) 33.46 (d, J = 12.3, NCH_3) 51.58 (d, J = 3.7, NCH_2) 51.98 (d, J = 11.0, OCH_3) 91.21 (s, C_5H_5) 234.87 (d, J = 31.8, CO)	178.20 (s)
W–1a	1929 1838	0.38 (d, J = 3.6, 3H, WCH_3) 2.79 (d, J = 11.2, 6H, NCH_3) 3.05–3.20 (m, 2H, NCH_2) 3.30–3.47 (m, 2H, NCH_2) 3.34 (d, J = 11.9, 3H, OCH_3) 4.94 (d, J = 1.7, 5H, C_5H_5)	−31.51 (d, J = 11.0, WCH_3) (J_{WC} = 34.2) 33.81 (d, J = 10.9, NCH_3) 51.37 (d, J = 2.4, NCH_2) 52.63 (d, J = 11.0, OCH_3) 89.74 (s, C_5H_5) 226.44 (d, J = 23.2, CO) (J_{WC} = 163.6)	141.88 (s) (J = 360.1)
Mo–2a	1935 1849	0.29 (d, J = 2.9, 3H, $MoCH_3$) 1.14 (t, J_{HH} = 6.8, 3H, CH_2CH_3) 2.81 (d, J = 13.2, 6H, NCH_3) 2.45–3.90 (m, 6H, OCH_2, NCH_2) 4.90 (d, J = 1.3, 5H, C_5H_5)	−19.36 (d, J = 11.6, $MoCH_3$) 16.27 (d, J = 4.6, OCH_2CH_3) 33.59 (d, J = 11.7, NCH_3) 51.48 (d, J = 3.5, NCH_2) 60.45 (d, J = 10.4, OCH_2) 91.29 (s, C_5H_5) 234.98 (d, J = 31.3, CO)	175.45 (s)
W–2a	1929 1838	0.37 (d, J = 3.6, 3H, WCH_3) 1.17 (t, J_{HH} = 6.9, 3H, CH_2CH_3) 2.73 (d, J = 11.2, 6H, NCH_3) 3.04–3.14 (m, 2H, NCH_2) 3.32–3.39 (m, 2H, NCH_2) 3.59–3.70 (m, 2H, OCH_2) 4.94 (d, J = 1.3, 5H, C_5H_5)	−31.48 (d, J = 12.2, WCH_3) (J_{WC} = 34.2) 16.18 (d, J = 6.1, OCH_2CH_3) 33.85 (d, J = 11.0, NCH_3) 51.23 (d, J = 2.4, NCH_2) 60.92 (d, J = 9.8, OCH_2) 89.76 (s, C_5H_5) 226.53 (d, J = 23.2, CO) (J_{WC} = 163.6)	139.62 (s) (J = 360.1)
Mo–3a	1945 1861	0.30 (d, J = 3.0, 3H, $MoCH_3$) 2.80 (d, J = 10.1, 3H, NCH_3) 3.05–3.65 (m, 2H, NCH_2) 3.49 (d, J = 11.9, 3H, OCH_3) 3.96–4.55 (m, 2H, OCH_2) 5.02 (d, J = 1.2, 5H, C_5H_5)	−21.19 (d, J = 12.2, $MoCH_3$) 31.98 (d, J = 11.0, NCH_3 50.75 (s, NCH_2) 52.26 (d, J = 8.6, OCH_3) 67.18 (d, J = 11.0, OCH_2) 91.27 (s, C_5H_5) 233.69 (d, J = 26.9, CO) 234.18 (d, J = 28.1, CO)	200.70 (s)
W–3a	1938 1850	0.34 (d, J = 3.6, 3H, WCH_3) 2.76 (d, J = 11.2, 3H, NCH_3) 3.16–3.29 (m, 1H, NCH_2) 3.33–3.41 (m, 1H, NCH_2) 3.45 (d, J = 11.9, 3H, OCH_3) 4.15–4.28 (m, 1H, OCH_2) 4.31–4.41 (m, 1H, OCH_2) 5.07 (d, J = 1.7, 5H, C_5H_5)	−33.70 (d, J = 11.0, WCH_3) (J_{WC} = 34.2) 32.25 (d, J = 8.5, NCH_3) 50.66 (s, NCH_2) 52.84 (d, J = 8.6, OCH_3) 67.09 (d, J = 11.0, OCH_2) 89.76 (s, C_5H_5) 225.11 (d, J = 23.2, CO) (J_{WC} = 162.3) 225.55 (d, J = 26.9, CO) (J_{WC} = 159.9)	164.04 (s) (J = 387.6)
Mo–4a	1949 1870	0.29 (d, J = 3.0, 3H, $MoCH_3$) 3.60 (d, J = 13.0, 9H, OCH_3) 5.03 (d, J = 1.3, 5H, C_5H_5)	−20.93 (d, J = 12.2, $MoCH_3$) 52.04 (d, J = 4.9, OCH_3) 91.23 (s, C_5H_5) 233.78 (d, J = 34.1, CO)	200.98 (s)

Table 1 (continued)

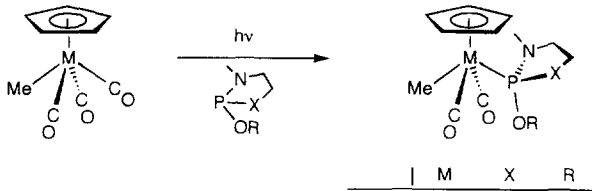
Complex	IR (CH_2Cl_2) ν(CO) (cm^{-1})	^1H NMR ($CDCl_3$) δ (ppm), J_{PH} (Hz)	^{13}C NMR ($CDCl_3$) δ (ppm), J_{PC} (Hz)	^{31}P NMR (CH_2Cl_2) δ (ppm), J_{PW} (Hz)
W–4a	1940 1853	0.39 (d, J = 4.0, 3H, WCH_3) 3.59 (d, J = 11.9, 9H, OCH_3) 5.10 (d, J = 1.6, 5H, C_5H_5)	−33.74 (d, J = 11.0, WCH_3) (J_{WC} = 33.0) 52.60 (d, J = 4.8, OCH_3) 89.70 (s, C_5H_5) 225.00 (d, J = 25.7, CO) (J_{WC} = 161.1)	165.08 (s) (J = 408.2)

In this paper, we report the comparable reaction of four-legged piano stool complexes of Mo and W containing both phosphite and alkyl ligands with $BF_3 \cdot OEt_2$ and then PPh_3.

2. Results and discussion

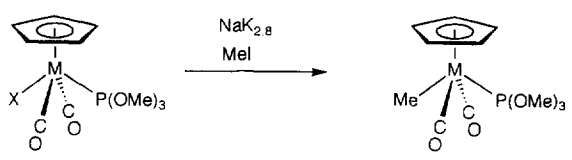
2.1. Preparation of $Cp(CO)_2MeM(phosphite)$ (M = Mo, W)

Molybdenum and tungsten complexes containing a methyl group and 'amino-substituted phosphite' were prepared from $Cp(CO)_3MeM$ (M = Mo, W) with the corresponding phosphite by the photoreaction (Eq. (1)). Trimethyl phosphite complexes of Mo (**Mo–4a**) and W (**W–4a**) were respectively prepared in the reactions of $[Cp(CO)_2Mo\{P(OMe)_3\}]_2$ and $Cp(CO)_2IW\{P(OMe)_3\}$ with $NaK_{2.8}$ and then MeI (Eq. (2)).



	M	X	R
Mo-1a	Mo	NMe	Me
W-1a	W	NMe	Me
Mo-2a	Mo	NMe	Et
W-2a	W	NMe	Et
Mo-3a	Mo	O	Me
W-3a	W	O	Me

(1)



M = Mo, X = $Cp(CO)_2Mo\{P(OMe)_3\}$ **Mo-4a**

M = W, X = I **W-4a**

(2)

The complexes thus prepared were characterized by IR, ^1H, ^{13}C and ^{31}P NMR spectra as well as elemental analyses. These spectroscopic data are shown in Table 1. It has been reported that **Mo–4a** and **W–4a** exist in solution as a mixture of the cis and trans isomers and these are in equilibrium [4]. The new methyl complexes (**Mo–1a** to **Mo–3a** and **W–1a** to **W–3a**) also exist as a cis/trans equilibrium mixture in solution, and are isolated as a cis/trans mixture. In all cases, the trans isomer is dominant; the equilibrium ratio of trans/cis is 12/1 for **Mo–1a**, 9/1 for **W–1a**, 13/1 for **Mo–2a**, 9/1 for **W–2a**, 7/1 for **Mo–3a**, 4/1 for **W–3a**, 5/1 for **Mo–4a** and 6/1 for **W–4a**. The spectroscopic data tabulated in Table 1 are for trans isomers, and the product in Eq. (1) is depicted simply as the trans isomer.

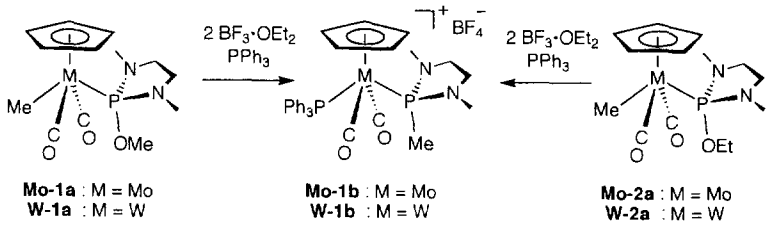
2.2. Reaction of $Cp(CO)_2MeM(phosphite)$ with $BF_3 \cdot OEt_2$ and then PPh_3

The complexes obtained in Eqs. (1) and (2) were treated first with $BF_3 \cdot OEt_2$ and then PPh_3. A CH_2Cl_2 solution containing a starting complex was cooled to −78 °C, treated with about two equivalents of $BF_3 \cdot OEt_2$, allowed to warm to room temperature, and stirred for several hours. Then, the solution was cooled to −78 °C, and an equimolar amount of PPh_3 was added. After the solution was warmed to room temperature, the resulting complex was purified by column chromatography to give a yellow powder. The spectroscopic data of the products are shown in Table 2.

In the case of the reaction of **Mo–1a**, the product is formulated as $[Cp(CO)_2(PPh_3)Mo\{\overline{PN(Me)CH_2CH_2NMe(Me)}\}]BF_4$ (**Mo–1b**) (Scheme 2) for the following reasons: (i) IR absorption bands due to ν(CO) are 30 and 40 cm^{-1} higher in frequency than those for the starting complex (**Mo–1a**) consistent with the cationic charge; (ii) the ^1H and ^{13}C NMR spectra show that the OMe group is removed from the atom (no doublet at about 3.3 ppm in ^1H NMR or at about 52 ppm in ^{13}C NMR) and replaced by a Me group (a doublet at 1.70 ppm in ^1H NMR and at 23.98 ppm in ^{13}C NMR); (iii) two resonances are observed at 55.29 and 153.26 ppm in the ^{31}P NMR spectrum as doublets with J_{PP} = 27.9 Hz, indicating that

Table 2
Spectroscopic data of cationic molybdenum (**Mo–1b, 3b, 4b**) and tungsten (**W–1b, 3b, 4c**) complexes

Complex	IR (CH_2Cl_2) ν(CO) (cm^{-1})	^1H NMR ($CDCl_3$) δ (ppm), J_{PH} (Hz)	^{13}C NMR ($CDCl_3$) δ (ppm), J_{PC} (Hz)	^{31}P NMR (CH_2Cl_2) δ (ppm), J (Hz)
Mo–1b	1968 1890	1.70 (d, J = 6.1, 3H, PCH_3) 2.83(d, J = 12.2, 6H, NCH_3) 3.25 (m, 2H, NCH_2) 3.27 (m, 2H, NCH_2) 5.18 (s, 5H, C_5H_5) 7.29–7.56 (m, 15H, C_6H_5)	23.98 (d, J = 24.4, PCH_3) 33.93 (d, J = 6.9, NCH_3) 51.76 (s, NCH_2) 95.09 (s, C_5H_5) 129.10 (d, J = 8.5, m-C_6H_5) 131.57 (s, p-C_6H_5) 132.57 (d, J = 43.9, i-C_6H_5) 132.81 (d, J = 7.3, o-C_6H_5) 233.74 (t, J = 28.4, CO)	55.29 (d, J_{PP} = 27.9) 153.26 (d, J_{PP} = 27.9)
W–1b	1959 1877	1.83 (d, J = 6.9, 3H, PCH_3) 2.79 (d, J = 11.9, 6H, NCH_3) 3.22 (d, J = 2.0, 2H, NCH_2) 3.26 (m, 2H, NCH_2) 5.29 (s, 5H, C_5H_5) 7.29–7.55 (m, 15H, C_6H_5)	23.57 (dd, J = 2.4 and 30.6, PCH_3) 33.96 (d, J = 7.3, NCH_3) 51.48 (s, NCH_2) 93.82 (s, C_5H_5) 129.38 (d, J = 9.7, m-C_6H_5) 131.85 (d, J = 52.5, i-C_6H_5) 131.95 (s, p-C_6H_5) 133.23 (d, J = 8.6, o-C_6H_5) 225.47 (t, J = 22.6, CO) (J_{WC} = 155.0)	24.98 (d, J_{PP} = 27.5) (J_{PW} = 192.3) 115.88 (d, J_{PP} = 27.5) (J_{PW} = 238.1)
Mo–3b	1979 1902	1.85 (d, J = 6.6, 3H, PCH_3) 2.81 (d, J = 11.9, 3H, NCH_3) 3.32–3.47 (m, 2H, NCH_2) 4.30–4.47 (m, 2H, OCH_2) 5.29 (s, 5H, C_5H_5) 7.28 ~ 7.53 (m, 15H, C_6H_5)	25.40 (d, J = 28.1, PCH_3) 31.81 (d, J = 7.3, NCH_3) 50.26 (s, NCH_2) 68.62 (d, J = 8.5, OCH_2) 94.84 (s, C_5H_5) 129.32 (d, J = 11.0, m-C_6H_5) 131.80 (s, p-C_6H_5) 132.29 (d, J = 48.8, i-C_6H_5) 132.88 (d, J = 9.8, o-C_6H_5) 231.94 (dd, J = 26.9 and 35.4, CO) 232.94 (dd, J = 26.9 and 33.0, CO)	53.69 (d, J_{PP} = 25.7) 201.73 (d, J_{PP} = 25.7)
W–3b	1970 1890	1.96 (d, J = 6.9, 3H, PCH_3) 2.80 (d, J = 11.9, 3H, NCH_3) 3.27–3.48 (m, 2H, NCH_2) 4.25–4.44 (m, 2H, OCH_2) 5.39 (s, 5H, C_5H_5) 7.26–7.53 (m, 15H, C_6H_5)	24.78 (dd, J = 2.5 and 34.2, PCH_3) 31.88 (d, J = 7.3, NCH_3) 50.06 (d, J = 2.4, NCH_2) 68.56 (d, J = 8.6, OCH_2) 93.48 (s, C_5H_5) 129.31 (d, J = 9.3, m-C_6H_5) 131.91 (s, p-C_6H_5) 132.00 (d, J = 51.2, i-C_6H_5) 133.03 (d, J = 9.7, o-C_6H_5) 223.50 (dd, J = 21.9 and 29.3, CO) 224.87 (dd, J = 22.0 and 24.4, CO)	23.19 (d, J_{PP} = 24.4) (J_{WP} = 204.5) 163.13 (d, J_{PP} = 24.4) (J_{WP} = 253.3)
Mo–4b	1987 1910	2.10 (d, J = 6.6, 3H, PCH_3) 3.77 (d, J = 12.2, 6H, OCH_3) 5.32 (s, 5H, C_5H_5) 7.34–7.53 (m, 15H, C_6H_5)	22.23 (d, J = 44.0, PCH_3) 54.57 (d, J = 9.8, OCH_3) 94.39 (s, C_5H_5) 129.26 (d, J = 11.0, m-C_6H_5) 131.75 (s, p-C_6H_5) 132.56 (d, J = 51.3, i-C_6H_5) 133.37 (d, J = 9.7, o-C_6H_5) 232.34 (dd, J = 28.0 and 35.4, CO)	55.70 (d, J_{PP} = 14.9) 204.90 (d, J_{PP} = 14.9)
W–4c	1978 1900	3.77 (d, J = 11.7, 9H, OCH_3) 5.45 (t, J = 1.0, 5H, C_5H_5) 7.28–7.54 (m, 15H, C_6H_5)	54.91 (d, J = 8.0, OCH_3) 92.66 (s, C_5H_5) 129.32 (s, m-C_6H_5) 131.90 (d, J = 42.8, i-C_6H_5) 131.98 (s, p-C_6H_5) 133.17 (d, J = 10.4, o-C_6H_5) 222.53 (dd, J = 22.1 and 33.6, CO) (J_{WC} = 149.3)	21.94 (d, J_{PP} = 14.7) (J_{PW} = 204.1) 133.16 (d, J_{PP} = 14.7) (J_{PW} = 354.8)



Scheme 2.

$\overline{PN(Me)CH_2CH_2NMe(Me)}$ and PPh_3 are both coordinated to the same molybdenum atom. Confirmation of the structure is proved by the X-ray diffraction analysis of $[Cp(CO)_2(PPh_3)Mo\{\overline{PN(Me)CH_2CH_2NMe(Me)}\}]$-OTf (**Mo–1b'**) (vide infra). For similar reasons, we conclude that **W–1a** is converted into **W–1b**. The cationic complexes produced (**Mo–1b** and **W–1b**) appear only in the trans configuration.

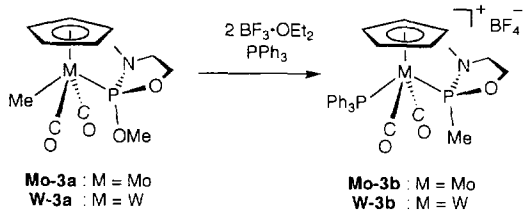
The migration of the methyl group from the Mo or W atom to the P atom is proved by the parallel reactions of **Mo–2a** and **W–2a** with $BF_3 \cdot OEt_2$ and then PPh_3 which contain an OEt group in place of an OMe group on the P atoms of **Mo–1a** and **W–1a**. The products, **Mo–1b** and **W–1b**, clearly show the OEt group on the phosphorus atom is eliminated and the Me group on the Mo or W atom migrates to the phosphorus atom.

Complexes of **Mo–3a** and **W–3a** having a monoamino-substituted phosphite also react with $BF_3 \cdot OEt_2$ and then PPh_3 to give the methyl-migrated products, **Mo–3b** and **W–3b** (Scheme 3). These products display only the trans configuration.

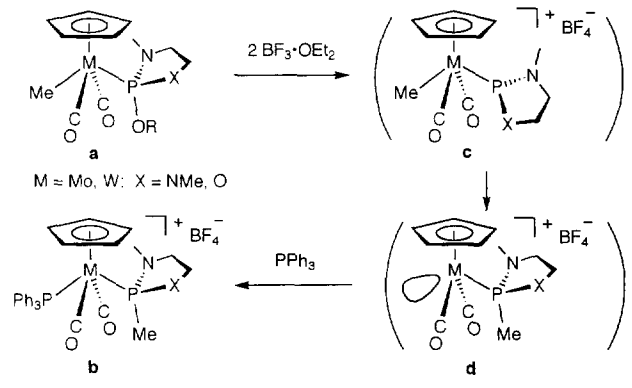
Let us consider the pathway of the reaction mentioned above (Scheme 4). In the reaction of **a** with $BF_3 \cdot OEt_2$, the OR group on the phosphorus atom is abstracted by BF_3 as an anion to give a cationic complex **c** and $[BF_3OR]^-$, the latter of which may react with BF_3 to give BF_2OR and BF_4^- serving as a counteranion of the final product **b**. After the formation of **c**, the methyl group on the central transition metal migrates to the phosphenium phosphorus atom to give **d**. Since the cationic intermediate **d** itself is a 16-electron species, it may be stabilized by weak coordination of the solvent or BF_2OR, for example. Compound **d** is readily converted into a stable and isolable complex **b** by addition of PPh_3.

In Scheme 4, **a**, **c**, and **d** are depicted in the trans isomer form. However, as mentioned above, the starting complex **a** consists of trans and cis isomers in solution. We attempted to isolate the complexes **c** or **d**, but the isolation was unsuccessful presumably due to its high reactivity. Therefore, there is no information on the geometry of **c** and **d**, though the final product, **b**, has only the trans configuration. Unfortunately, it is not clear whether the Me group can migrate to the phosphenium ligand only for the cis isomer of **c** or the migration can take place even for the trans isomer.

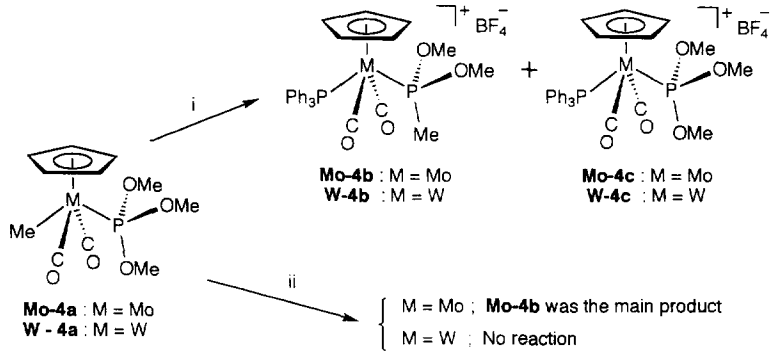
Recently, we found that combination of $Cp(CO)MeFe\{P(OMe)_3\}$ with $BF_3 \cdot OEt_2$ and then PPh_3 did not show OMe abstraction, followed by Me group migration to the phosphenium fragment. Instead, an unexpected metallacycle complex, $Cp(PPh_3)$-$\overline{FeC(Me)OBF_2OP(OMe)_2}$ formed [12]. Therefore, it was of interest to examine the reactions of **Mo–4a** and **W–4a** with $BF_3 \cdot OEt_2$ and then PPh_3. The results are summarized in Scheme 5. A CH_2Cl_2 solution containing **Mo–4a** or **W–4a** was treated with $BF_3 \cdot OEt_2$ at $-78\,^{\circ}C$, stirred for several hours at room temperature, treated with PPh_3 at $-78\,^{\circ}C$, and stirred at room temperature. The procedures are the same as employed for **Mo–1a** to **Mo–3a** and **W–1a** to **W–3a**. Two kinds of complex, **4b** and **4c**, were formed in approximately 1:1 ratio. The spectroscopic data suggest that **4b** is $[Cp(CO)_2(PPh_3)M\{PMe(OMe)_2\}]BF_4$ expected to form by OMe abstraction and then Me migration from the Mo or W atom to the P atom. Compound **4c** is $[Cp(CO)_2(PPh_3)M\{P(OMe)_3\}]BF_4$ produced by an ap-



Scheme 3.



Scheme 4. Proposed reaction pathway.



Scheme 5. (i) Add $BF_3 \cdot OEt_2$ at −78 °C, stir at room temperature, add PPh_3 at −78 °C, and stir at room temperature. (ii) Add $BF_3 \cdot OEt_2$, stir, and add PPh_3 at −78 °C, and then stir at room temperature.

parent Me/PPh_3 substitution reaction. Since **W–4c** was isolated as a single crystal, the structure was confirmed by the X-ray diffraction analysis (vide infra).

In contrast, the reaction of **Mo–4a** with $BF_3 \cdot OEt_2$ and then PPh_3 at −78 °C throughout resulted in the formation of **Mo–4b** as the main product. In the case of

Table 3
Crystal and refinement data for **Mo–1b′** and **W–4c**

	Mo–1b′	**W–4c**
Crystal data		
Formula	$C_{31}H_{33}F_3MoN_2O_5P_2S$	$C_{28}H_{29}BF_4O_5P_2W$
Formula weight	760.55	778.14
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	14.663(3)	10.457(1)
b (Å)	17.967(3)	11.133(2)
c (Å)	14.033(3)	26.122(6)
α (deg)		89.13(2)
β (deg)	116.06(2)	89.02(1)
γ (deg)		84.82(1)
V (Å^3)	3321(1)	3028.1(8)
Z	4	4
D(calc) (g cm^{-3})	1.521	1.707
Crystal dimensions (mm)	0.65 × 0.55 × 0.30	0.25 × 0.25 × 0.20
μ(Mo Kα)(cm^{-1})	6.12	39.85
Data collection and processing		
Diffractometer	Enraf–Nonius CAD4	Enraf–Nonius CAD4
X-radiation	Mo Kα (graphite monochromated)	Mo Kα (graphite monochromated)
Scan mode	ω-θ	ω-θ
ω-scan wide (deg)	1.24 + 0.35 tanθ	0.65 + 0.40 tanθ
2θ limits (deg)	50.0	49.9
No. of reflections		
total	6305	10902
unique	6059	10643
observed	3842	7626
Absorption correction (transmission factor)	DIFABS (0.7467–1.3064)	DIFABS (0.9336–1.0649)
Structure analysis and refinement		
Structure solution	direct method (SAPI91)	direct method (SAPI91)
Refinement	full-matrix least squares	full-matrix least squares
No. of parameters	407	663
Weighting scheme	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$
R	0.053	0.044
R_w	0.045	0.047

W–4a, the starting complex remained unreacted under the mild condition.

With the $P(OMe)_3$ complexes (**Mo–4a** and **W–4a**), two types of reaction proceed concurrently; one is the similar reaction observed in Schemes 2 and 3, and the other is an apparent Me/PPh_3 substitution reaction. The former reaction pathway seems to be dominant, because under a mild condition (−78 °C) **Mo–4b** was obtained as the main product in the case of the reaction of **Mo–4a**, and **Mo–4b** was not converted into **Mo–4c** by warming to room temperature. For **W–4a**, the reaction condition may be too mild to the OMe abstraction. Successively added PPh_3 deactivates BF_3 to form $BF_3 \cdot PPh_3$ adduct leading to no reaction.

The migratory insertion reaction of a phosphenium ligand into a transition-metal–alkyl bond was demonstrated first for iron complexes in 1995 [8]. The results obtained in this paper show that this migratory insertion reaction applies also to Group 6 transition metals such as Mo and W.

Table 4
Final fractional coordinates and thermal parameters for the non-hydrogen atoms of **Mo–1b′**

Atom	x	y	z	B_{eq} (Å^2)
Mo	0.87441(4)	0.17731(3)	0.57775(5)	3.76(1)
S	0.2000(3)	0.0360(2)	0.9471(3)	10.1(1)
P(1)	0.9915(1)	0.20250(9)	0.4981(2)	4.51(4)
P(2)	0.7179(1)	0.10028(9)	0.5351(1)	3.64(4)
F(1)	0.2339(9)	−0.0588(6)	1.0795(7)	20.9(4)
F(2)	0.0778(7)	−0.0439(5)	0.983(1)	23.5(5)
F(3)	0.1573(6)	−0.1025(4)	0.9185(7)	16.0(3)
O(1)	0.9437(4)	0.0166(3)	0.5596(4)	6.2(1)
O(2)	0.7300(3)	0.2346(3)	0.3521(4)	7.2(2)
O(3)	0.1884(8)	0.0891(5)	1.0105(8)	17.4(4)
O(4)	0.2976(6)	0.0156(6)	0.9614(8)	17.0(4)
O(5)	0.1204(10)	0.0324(7)	0.8342(7)	25.8(5)
N(1)	1.1152(4)	0.1878(4)	0.5719(5)	6.0(2)
N(2)	1.0094(4)	0.2920(3)	0.4783(5)	6.6(2)
C(1)	0.9571(10)	0.1850(7)	0.7641(7)	10.6(4)
C(2)	0.9995(9)	0.236(1)	0.719(1)	15.6(8)
C(3)	0.933(1)	0.2845(8)	0.665(1)	14.2(7)
C(4)	0.8430(8)	0.2710(5)	0.6714(7)	8.4(3)
C(5)	0.8582(6)	0.2084(5)	0.7302(6)	5.8(2)
C(6)	0.9177(4)	0.0761(4)	0.5626(5)	3.8(2)
C(7)	0.7830(5)	0.2118(4)	0.4327(6)	4.9(2)
C(8)	0.9581(5)	0.1559(4)	0.3736(5)	5.8(2)
C(9)	1.1602(5)	0.1221(5)	0.6302(7)	7.8(2)
C(10)	1.1763(6)	0.2498(5)	0.5667(8)	8.6(3)
C(11)	1.1113(7)	0.3100(6)	0.5031(8)	9.9(3)
C(12)	0.9314(6)	0.3430(4)	0.4156(8)	9.7(3)
C(13)	0.6293(4)	0.1479(4)	0.5726(5)	3.9(2)
C(14)	0.5909(5)	0.2170(4)	0.5262(5)	4.8(2)
C(15)	0.5251(5)	0.2564(4)	0.5549(6)	6.2(2)
C(16)	0.4983(6)	0.2295(5)	0.6299(7)	6.3(2)
C(17)	0.5340(6)	0.1615(5)	0.6745(7)	7.1(3)
C(18)	0.6005(5)	0.1205(4)	0.6465(6)	5.6(2)
C(19)	0.6409(5)	0.0746(3)	0.3970(5)	3.9(2)
C(20)	0.5363(5)	0.0695(3)	0.3573(5)	4.5(2)
C(21)	0.4783(5)	0.0450(4)	0.2536(6)	5.4(2)
C(22)	0.5255(7)	0.0262(4)	0.1912(6)	5.9(2)
C(23)	0.6297(6)	0.0312(4)	0.2305(6)	6.0(2)
C(24)	0.6866(5)	0.0557(4)	0.3329(5)	4.8(2)
C(25)	0.7407(4)	0.0098(3)	0.6009(5)	3.9(2)
C(26)	0.6865(5)	−0.0521(4)	0.5513(6)	5.7(2)
C(27)	0.7070(6)	−0.1212(4)	0.6001(7)	6.7(2)
C(28)	0.7828(6)	−0.1277(4)	0.7008(7)	6.3(2)
C(29)	0.8349(7)	−0.0677(5)	0.7506(6)	8.6(3)
C(30)	0.8154(7)	0.0010(4)	0.7010(6)	7.9(2)
C(31)	0.1642(9)	−0.0516(7)	0.983(1)	11.6(4)

Table 5
Selected bond lengths (Å) and angles (deg) for **Mo–1b′** with estimated standard deviations in parentheses

Lengths			
Mo–P(1)	2.467(2)	Mo–P(2)	2.516(2)
Mo–C(6)	1.968(6)	Mo–C(7)	1.982(8)
P(1)–N(1)	1.668(5)	P(1)–N(2)	1.673(6)
P(1)–C(8)	1.800(7)	P(2)–C(13)	1.817(6)
P(2)–C(19)	1.822(6)	P(2)–C(25)	1.827(6)
N(1)–C(9)	1.424(9)	N(1)–C(10)	1.451(9)
N(2)–C(11)	1.414(9)	N(2)–C(12)	1.427(9)
C(10)–C(11)	1.46(1)		
Angles			
P(1)–Mo–P(2)	137.42(6)	P(1)–Mo–C(6)	78.4(2)
P(1)–Mo–C(7)	76.6(2)	P(2)–Mo–C(6)	76.7(2)
P(2)–Mo–C(7)	78.0(2)	C(6)–Mo–C(7)	106.5(3)
Mo–P(1)–N(1)	118.3(2)	Mo–P(1)–N(2)	116.3(2)
Mo–P(1)–C(8)	114.0(2)	N(1)–P(1)–N(2)	92.7(3)
N(1)–P(1)–C(8)	106.7(3)	N(2)–P(1)–C(8)	106.4(3)
Mo–P(2)–C(13)	111.4(2)	Mo–P(2)–C(19)	117.9(2)
Mo–P(2)–C(25)	115.1(2)	C(13)–P(2)–C(19)	103.8(3)
C(13)–P(2)–C(25)	105.5(3)	C(19)–P(2)–C(25)	101.7(3)

2.3. X-ray structures of *Mo–1b′* and *W–4c*

Single crystals of **Mo–1b′** and **W–4c** were obtained from CH_2Cl_2 and CH_2Cl_2–pentane respectively. The cell constants and the data collection parameters are summarized in Table 3. The fractional coordinates and important bond lengths and angles are listed in Tables 4–7. The ORTEP drawings of **Mo–1b′** and **W–4c** are shown in Figs. 1 and 2 respectively. For **W–4c**, there are two crystallographically independent molecules in the unit cell. The structures of the two molecules are basically identical. The only difference is the orientation of the OMe groups. Therefore, only one crystal structure out of two crystallographically independent molecules is shown in Fig. 2.

Both complexes have typical four-legged piano-stool structures, and two phosphorus ligands are coordinated to the central metal in mutually trans position. The Mo–P bond lengths (Mo–P1 = 2.467 Å and Mo–P2 = 2.516 Å) in **Mo–1b′** fall in the range of normal Mo–P dative bond distances (2.40–2.57 Å) [1]. The corresponding bond lengths and bond angles are quite similar between **Mo–1b′** and **W–4c**. The reason presumably

Table 6
Final fractional coordinates and thermal parameters for the non-hydrogen atoms of **W–4c**

Atom	x	y	z	B_{eq} (Å^2)
W(1)	0.01438(4)	−0.49439(3)	−0.66905(2)	2.701(9)
W(2)	0.17206(4)	0.18334(4)	0.11264(2)	2.977(10)
P(1)	−0.1513(3)	−0.6303(3)	−0.6548(1)	3.89(7)
P(2)	0.2275(2)	−0.4727(2)	−0.62958(10)	3.18(6)
P(3)	0.2436(3)	0.2423(3)	0.0281(1)	4.84(8)
P(4)	0.1194(2)	−0.0082(2)	0.1567(1)	3.10(6)
F(1) [a]	0.334(1)	0.0291(9)	0.5776(3)	16.4
F(2) [a]	0.1565(7)	0.0663(10)	0.6248(4)	16.4
F(3) [a]	0.3474(10)	0.0558(10)	0.6614(3)	16.4
F(4) [a]	0.286(1)	0.2109(6)	0.6103(4)	16.4
F(5) [a]	0.7398(9)	0.4271(9)	0.1697(3)	15.4
F(6) [a]	0.7411(9)	0.3467(9)	0.0924(3)	15.4
F(7) [a]	0.5882(9)	0.3100(8)	0.1490(4)	15.4
F(8) [a]	0.5912(9)	0.4923(7)	0.1136(4)	15.4
O(1)	0.1588(7)	−0.7446(6)	−0.6912(3)	4.5(2)
O(2)	−0.0553(7)	−0.4601(8)	−0.5535(3)	5.5(2)
O(3)	−0.1667(8)	−0.7083(7)	−0.7032(3)	5.8(2)
O(4)	−0.2948(7)	−0.5705(8)	−0.6482(3)	5.7(2)
O(5)	−0.1485(8)	−0.7134(8)	−0.6054(3)	6.5(3)
O(6)	0.4294(7)	0.0220(7)	0.0990(3)	6.0(2)
O(7)	−0.0428(7)	0.1072(7)	0.0418(3)	5.2(2)
O(8)	0.307(1)	0.1505(10)	−0.0093(4)	11.0(4)
O(9)	0.1327(9)	0.3191(9)	−0.0015(3)	7.9(3)
O(10)	0.3499(9)	0.3322(10)	0.0274(4)	8.7(3)
C(1)	0.052(1)	−0.4263(9)	−0.7520(4)	3.9(3)
C(2)	−0.074(1)	−0.4551(10)	−0.7478(4)	4.7(3)
C(3)	−0.1408(10)	−0.376(1)	−0.7129(5)	4.7(3)
C(4)	−0.054(1)	−0.2972(9)	−0.6961(4)	4.3(3)
C(5)	0.064(1)	−0.3300(9)	−0.7201(4)	4.0(3)
C(6)	0.1056(9)	−0.6544(9)	−0.6802(4)	3.1(2)
C(7)	−0.0259(9)	−0.4773(9)	−0.5958(4)	3.5(2)
C(8)	−0.269(1)	−0.788(1)	−0.7086(6)	8.6(5)
C(9)	−0.337(1)	−0.499(1)	−0.6061(5)	6.3(4)
C(10)	−0.043(1)	−0.796(1)	−0.5911(6)	8.5(5)
C(11)	0.3480(8)	−0.4388(9)	−0.6783(4)	3.2(2)
C(12)	0.3716(9)	−0.5158(10)	−0.7189(4)	4.0(3)
C(13)	0.4622(10)	−0.492(1)	−0.7570(4)	4.5(3)
C(14)	0.5253(9)	−0.389(1)	−0.7544(4)	4.7(3)
C(15)	0.503(1)	−0.313(1)	−0.7138(5)	4.9(3)
C(16)	0.4139(9)	−0.3369(9)	−0.6764(4)	4.2(3)
C(17)	0.2957(9)	−0.6074(10)	−0.5957(4)	3.9(3)
C(18)	0.388(1)	−0.689(1)	−0.6141(4)	4.2(3)
C(19)	0.426(1)	−0.795(1)	−0.5894(6)	6.3(4)
C(20)	0.368(1)	−0.819(1)	−0.5440(6)	7.0(4)
C(21)	0.278(1)	−0.742(1)	−0.5229(5)	7.2(4)
C(22)	0.238(1)	−0.636(1)	−0.5493(5)	5.9(3)
C(23)	0.235(1)	−0.355(1)	−0.5831(4)	4.2(3)
C(24)	0.335(1)	−0.357(1)	−0.5494(5)	7.4(4)
C(25)	0.346(2)	−0.264(2)	−0.5168(6)	10.3(6)
C(26)	0.258(2)	−0.166(2)	−0.5163(6)	9.3(5)
C(27)	0.156(2)	−0.160(1)	−0.5495(6)	8.4(5)
C(28)	0.144(1)	−0.256(1)	−0.5821(4)	5.5(3)
C(29)	0.257(1)	0.3481(10)	0.1455(4)	4.3(3)
C(30)	0.142(1)	0.3901(9)	0.1207(4)	4.5(3)
C(31)	0.039(1)	0.3445(10)	0.1474(5)	4.6(3)
C(32)	0.089(1)	0.2733(10)	0.1874(4)	4.5(3)
C(33)	0.223(1)	0.2760(10)	0.1873(4)	4.5(3)
C(34)	0.3311(10)	0.0782(9)	0.1033(4)	3.9(3)
C(35)	0.0380(10)	0.1310(9)	0.0683(4)	3.7(3)
C(36)	0.275(2)	0.048(2)	−0.0258(7)	11.3(6)
C(37)	0.147(2)	0.374(2)	−0.0505(6)	11.7(7)
C(38)	0.474(2)	0.314(2)	0.018(1)	17.8(9)
C(39)	0.176(1)	−0.0157(8)	0.2227(4)	3.7(2)
C(40)	0.092(1)	−0.0252(9)	0.2633(4)	4.1(3)
C(41)	0.141(1)	−0.0297(10)	0.3139(4)	5.1(3)
C(42)	0.267(2)	−0.022(1)	0.3216(5)	6.2(4)
C(43)	0.351(1)	−0.010(1)	0.2808(5)	6.0(4)
C(44)	0.305(1)	−0.0082(10)	0.2326(4)	4.7(3)
C(45)	0.1901(9)	−0.1458(9)	0.1264(4)	3.5(2)
C(46)	0.278(1)	−0.2270(9)	0.1513(4)	4.2(3)
C(47)	0.329(1)	−0.327(1)	0.1243(5)	5.5(3)
C(48)	0.293(1)	−0.350(1)	0.0757(5)	5.2(3)
C(49)	0.205(1)	−0.271(1)	0.0521(4)	5.0(3)
C(50)	0.155(1)	−0.1713(9)	0.0775(4)	4.4(3)
C(51)	−0.0495(9)	−0.0375(8)	0.1631(3)	3.0(2)
C(52)	−0.1471(10)	0.0539(9)	0.1608(4)	4.1(3)
C(53)	−0.273(1)	0.030(1)	0.1672(5)	5.3(3)
C(54)	−0.304(1)	−0.088(1)	0.1745(5)	6.2(4)
C(55)	−0.208(1)	−0.179(1)	0.1768(5)	5.4(3)
C(56)	−0.084(1)	−0.1545(10)	0.1708(4)	4.4(3)
B(1) [a]	0.2810(7)	0.0905(6)	0.6185(3)	16.4
B(2) [a]	0.6651(6)	0.3940(6)	0.1312(2)	15.4

[a] Treated as a rigid molecule.

comes from the similar radii of Mo (1.36 Å) and W (1.37 Å).

3. Experimental section

3.1. General remarks

All reactions were carried out under an atmosphere of dry nitrogen by using standard Schlenk tube techniques. Column chromatography was done quickly in

Table 7
Selected bond lengths (Å) and angles (deg) for **W–4c** with estimated standard deviations in parentheses

Lengths			
W(1)–P(1)	2.421(3)	W(1)–P(2)	2.504(3)
W(1)–C(6)	1.965(10)	W(1)–C(7)	1.96(1)
P(1)–O(3)	1.564(9)	P(1)–O(4)	1.594(8)
P(1)–O(5)	1.575(10)	P(2)–C(11)	1.83(1)
P(2)–C(17)	1.83(1)	P(2)–C(23)	1.81(1)
O(1)–C(6)	1.14(1)	O(2)–C(7)	1.16(1)
O(3)–C(8)	1.46(2)	O(4)–C(9)	1.41(2)
O(5)–C(10)	1.42(2)		
Angles			
P(1)–W(1)–P(2)	134.16(10)	P(1)–W(1)–C(6)	76.7(3)
P(1)–W(1)–C(7)	76.9(3)	P(2)–W(1)–C(6)	77.9(3)
P(2)–W(1)–C(7)	76.0(3)	C(6)–W(1)–C(7)	108.7(4)
W(1)–P(1)–O(3)	110.7(4)	W(1)–P(1)–O(4)	116.8(4)
W(1)–P(1)–O(5)	119.8(4)	O(3)–P(1)–O(4)	100.0(5)
O(3)–P(1)–O(5)	109.6(5)	O(4)–P(1)–O(5)	97.6(5)
W(1)–P(2)–C(11)	111.2(3)	W(1)–P(2)–C(17)	114.3(4)
W(1)–P(2)–C(23)	117.3(4)	C(11)–P(2)–C(17)	105.7(5)
C(11)–P(2)–C(23)	103.8(5)	C(17)–P(2)–C(23)	103.3(5)

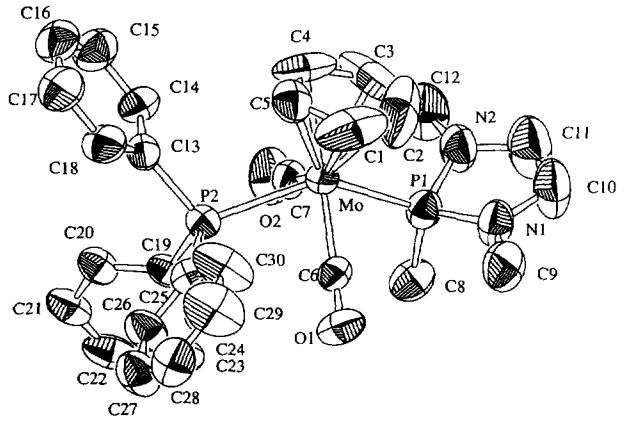


Fig. 1. Crystal structure of $[Co(CO)_2(PPh_3)Mo\{PN(Me)CH_2CH_2NMe(Me)\}]^+$ in **Mo–1b′** with the numbering scheme. Thermal ellipsoids are drawn at 50% probability. OTf^- was eliminated for clarity.

the air (aluminum oxide, 200–300 mesh purchased from Katayama, and silica gel 60, 230–400 mesh purchased from Merck). All solvents were purified by distillation: CH_2Cl_2 was distilled from P_2O_5, and ether, THF, benzene, and hexane were distilled from sodium metal. These were stored under an N_2 atmosphere. Acetone as an eluent was obtained from a common commercial source and was used without further purification. $BF_3 \cdot OEt_2$ was distilled prior to use. All other reagents were used without further purification.

IR spectra were recorded on a Shimadzu FTIR-8100A spectrometer. ^1H, ^{13}C and ^{31}P NMR spectra were measured on Jeol EX-270 and EX-400 spectrometers. ^1H and ^{13}C NMR data were referred to $Si(CH_3)_4$ as an internal standard. ^{31}P NMR data were referred to 85% H_3PO_4 as an external standard.

Phosphorus(III) compounds, PN(Me)CH_2CH_2NMe(OMe) [13], PN(Me)CH_2CH_2NMe(OEt) [13] and PN(Me)CH_2CH_2O(OMe) [14] were prepared according to the literature method. $Cp(CO)_3MeM$ (M = Mo and W) was prepared by the reported method [15].

3.2. Typical preparation of $[Cp(CO)_2MeM\{PN(Me)CH_2CH_2X(OMe)\}]$ (M = Mo, W; X = NMe, O)

In a typical procedure, $Cp(CO)_3MeMo$ (2000 mg, 7.7 mmol), PN(Me)CH_2CH_2NMe(OMe) (1.4 ml, 9.3 mmol) and benzene (120 ml) were put in a Pyrex Schlenk tube, and the solution was irradiated with a 400 W medium-pressure mercury arc lamp at 0 °C for 6 h. After the solvent had been removed, the residue was loaded on an alumina column and eluted with hexane and then hexane–CH_2Cl_2 (1/1). The band eluted with hexane–CH_2Cl_2 (1/1) was collected, and the solvents were removed in vacuo to give a yellow powder of **Mo–1a** (1960 mg, 5.2 mmol, 67%). Anal. Found: C, 41.12; H, 5.50; N, 7.23. $C_{13}H_{21}MoN_2O_3P$. Calc.: C, 41.06; H, 5.57; N, 7.37%.

For **W–1a**, yield: 62%. Anal. Found: C, 33.28; H, 4.36; N, 5.93. $C_{13}H_{21}N_2O_3PW$. Calc.: C, 33.35; H, 4.52; N, 5.98%. For **Mo–2a**, yield 56%. Anal. Found: C, 42.93; H, 5.86; N, 7.00. $C_{14}H_{23}MoN_2O_3P$. Calc.: C, 42.65; H, 5.88; N, 7.11%. For **W–2a**, yield 61%. Anal. Found: C, 34.91; H, 4.65; N, 5.82. $C_{14}H_{23}N_2O_3PW$. Calc.: C, 34.87; H, 4.81; N, 5.81%. For **Mo–3a**, yield 48%. Anal. Found: C, 39.49; H, 4.95; N, 3.81. $C_{12}H_{18}MoNO_4P$. Calc.: C, 39.25; H, 4.94; N, 3.82%. For **W–3a**, yield 49%. Anal. Found: C, 31.50; H, 3.77; N, 3.10. $C_{12}H_{18}NO_4PW$. Calc.: C, 31.67; H, 3.99; N, 3.08%.

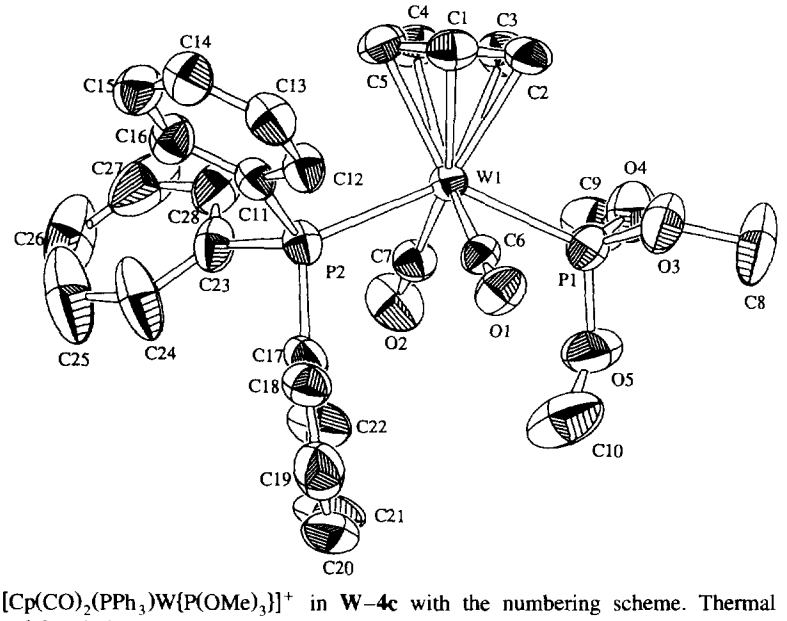


Fig. 2. Crystal structure of $[Cp(CO)_2(PPh_3)W\{P(OMe)_3\}]^+$ in **W–4c** with the numbering scheme. Thermal ellipsoids are drawn at 50% probability. BF_4^- was eliminated for clarity.

3.3. Preparation of $[Cp(CO)_2MeMo\{P(OMe)_3\}]$ (Mo–4a)

The preparative method of **Mo–4a** has been reported in the literature [16], but it involves a mercury complex. Therefore, we found a new preparative route. $[Cp(CO)_2Mo\{P(OMe)_3\}]_2$ (500 mg, 0.72 mmol) was treated with $NaK_{2.8}$ (1 ml, 6.5 mmol) in THF (40 ml) at room temperature for 1.5 h. After filtration, the filtrate was added to a THF solution (10 ml) containing MeI (0.5 ml, 8 mmol), and the solution was stirred at room temperature for 3 h. After some insoluble materials were removed by filtration, the filtrate was dried in vacuo to give a yellow powder of **Mo–4a** (400 mg, 1.1 mmol, 78%).

3.4. Preparation of $[Cp(CO)_2MeW\{P(OMe)_3\}]$ (W–4a)

Complex **W–4a** was prepared from $Cp(CO)_2IW\{P(OMe)_3\}$, $NaK_{2.8}$, and MeI in a similar manner to **Mo–4a**. The product was purified by an alumina column (eluent: hexane–CH_2Cl_2 (1/1)) to give a yellow powder (68%).

3.5. Preparation of $[Cp(CO)_2(PPh_3)Mo\{\overline{PN(Me)CH_2CH_2NMe(Me)}\}]BF_4$ (Mo–1b)

A solution of **Mo–1a** (380 mg, 1.0 mmol) of CH_2Cl_2 (5 ml) was cooled to −78 °C and then $BF_3 \cdot OEt_2$ (0.25 ml, 2.0 mmol) was added. The solution was allowed to warm to room temperature and stirred for 1 h. Then, the solution was cooled again to −78 °C, and PPh_3 (320 mg, 1.2 mmol) was added. The cooling bath was removed, and the solution was stirred for 12 h. The resulting dark brown solution was concentrated to 1 ml under reduced pressure, and the solution was loaded on an alumina column. The reddish orange band eluted with only CH_2Cl_2 was discarded, and the yellow band eluted with CH_2Cl_2–acetone (10/1) was collected. The solvents were removed under reduced pressure to give a yellow powder of **Mo–1b** (450 mg, 0.65 mmol, 65%). Anal. Found: C, 51.71; H, 4.72; N, 4.02. $C_{30}H_{33}BF_4MoN_2O_2P_2$. Calc.: C, 51.60; H, 4.76; N, 4.01%. **Mo–1b** was prepared also from **Mo–2a** in the same manner as mentioned above. $[Cp(CO)_2(PPh_3)Mo\{\overline{PN(Me)CH_2CH_2NMe(Me)}\}]OTf$ (**Mo–1b′**) was obtained from **Mo–1a**, TMS · OTf and PPh_3, and a single crystal of this salt was subjected to X-ray analysis.

3.6. Preparation of $[Cp(CO)_2(PPh_3)W\{\overline{PN(Me)CH_2CH_2NMe(Me)}\}]BF_4$ (W–1b)

A solution of **W–1a** (350 mg, 0.75 mmol) of CH_2Cl_2 (17 ml) was cooled to −78 °C and then $BF_3 \cdot OEt_2$ (0.20 ml, 1.6 mmol) was added. The solution was allowed to warm to room temperature and stirred for 4.5 h. Then, the solution was cooled again to −78 °C, and PPh_3 (240 mg, 0.92 mmol) was added. The cooling bath was removed, and the solution was stirred for 19 h. The resulting dark brown solution was concentrated to 1 ml under reduced pressure, and the solution was loaded on a silica gel column. The reddish orange band eluted with only CH_2Cl_2 was discarded, and the yellow band eluted with CH_2Cl_2–acetone (10/1) was collected. The solvents were removed under reduced pressure to give a yellow powder of **W–1b** (250 mg, 0.32 mmol, 43%). Anal. Found: C, 45.53; H, 4.07; N, 3.54. $C_{30}H_{33}BF_4N_2O_2P_2W$. Calc.: C, 45.83; H, 4.23; N, 3.56%. **W–1b** was prepared also from **W–2a** in the same manner as mentioned above.

3.7. Preparation of $[Cp(CO)_2(PPh_3)Mo\{\overline{PN(Me)CH_2CH_2O(Me)}\}]BF_4$ (Mo–3b)

Mo–3b was prepared as a yellow powder from **Mo–3a** in a similar manner to **Mo–1b**. Yield 48%. Anal. Found: C, 50.54; H, 4.30; N, 2.03. $C_{29}H_{30}BF_4MoNO_3P_2$. Calc.: C, 50.83; H, 4.41; N, 2.04%.

3.8. Preparation of $[Cp(CO)_2(PPh_3)W\{\overline{PN(Me)CH_2CH_2O(Me)}\}]BF_4$ (W–3b)

W–3b was prepared as a yellow powder from **W–3a** in a similar manner to **W–1b**. Yield 45%. Anal. Found: C, 45.23; H, 3.89; N, 1.78. $C_{29}H_{30}BF_4NO_3P_2W$. Calc.: C, 45.05; H, 3.91; N, 1.81%.

3.9. Preparation of $[Cp(CO)_2(PPh_3)Mo\{P(Me)(OMe)_2\}]BF_4$ (Mo–4b)

A solution of **Mo–4a** (376 mg, 1.06 mmol) of CH_2Cl_2 (3 ml) was cooled to −78 °C, and then $BF_3 \cdot OEt_2$ (0.27 ml, 2.15 mmol) was added. After the solution had been stirred for 1.5 h at −78 °C, PPh_3 (280 mg, 1.07 mmol) was added, and then the solution was allowed to warm to room temperature and stirred for 22 h. After the solvent had been removed under reduced pressure, the residue was loaded on an alumina column. After elution with CH_2Cl_2, a yellow complex eluted with CH_2Cl_2–acetone (1/1) was collected and dried in vacuo to give a yellow powder which was recrystallized from CH_2Cl_2–ether to give a pure complex of **Mo–4b** (307 mg, 0.46 mmol, 43%). Anal. Found: C, 49.86; H, 4.31. $C_{28}H_{29}BF_4MoO_4P_2$. Calc.: C, 49.88; H, 4.34%.

3.10. Preparation of $[Cp(CO)_2(PPh_3)W\{P(OMe)_3\}]BF_4$ (W–4c)

A solution of **W–4a** (197 mg, 0.44 mmol) of CH_2Cl_2 (10 ml) was cooled to −78 °C, and then $BF_3 \cdot OEt_2$ (0.10 ml, 0.80 mmol) was added. The solution was allowed to warm to room temperature, stirred for 7 h, and

then cooled again to −78 °C. After the addition of PPh_3 (190 mg, 0.72 mmol), the solution was allowed to warm to room temperature and stirred for 10 h. The solvent was removed under reduced pressure, and the residue was dissolved in a small amount of CH_2Cl_2. Dropwise addition of ether to the solution caused a yellow powder to form which was collected by filtration and then loaded on a silica gel column. The yellow complex eluted with CH_2Cl_2–acetone (9/1) was collected and dried in vacuo to give a pure **W–4c** (70 mg, 0.09 mmol, 20%). Anal. Found: C, 43.24; H, 3.74. $C_{28}H_{29}BF_4O_5P_2W$. Calc.: C, 43.22; H, 3.76%.

3.11. Crystal structure determination

Crystallographic and experimental details of X-ray crystal structure analyses are given in Table 3. Suitable crystals of **Mo–1b′** and **W–4c** were mounted independently on an Enraf–Nonius CAD-4 automatic diffractometer. Data were collected at room temperature. Intensities were collected for Lorentz and polarization effects in the usual manner. The structures were solved by a combination of direct methods [17] and Fourier synthesis [18] and refined by full matrix least squares calculations. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated isotropically. Final values of $R = 0.053$ and $Rw = 0.045$ for compound **Mo–1b′** and $R = 0.044$ and $Rw = 0.047$ for compound **W–4c**, were obtained ($Rw = [\sum w||F_o| - |F_c||^2/\sum w|F|^2]^{1/2}$ and $w = 4F_o^2/\sigma^2(F_o)$). All calculations were performed using teXsan [19] with neutral atom scattering factors from Cromer and Waber [20], Δf and $\Delta f'$ values [21], and mass attenuation coefficients [22]. Anomalous dispersion coefficients were included in F_{calc}.

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