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Facile P−C Bond Cleavage of Trimethylphosphine at a Heterodimetallic (Ni−W) Center

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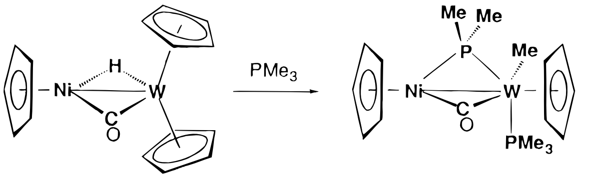
Introduction

Heterometallic complexes have attracted considerable interest as potential sites for cooperative reactions effected by two different adjacent metals.[1] In a previous report, we described the photochemical synthesis of several di- and trinuclear heterometallic complexes containing molybdenocene or tungstenocene.[2] On examining reactions of these new heterometallic compounds, we have found that a Ni−W complex shows, indeed, a synergistic activity toward trimethylphosphine, which lead to phosphorus−carbon bond cleavage under mild conditions.

Transition metal-mediated P−C bond cleavage of tertiary phosphines is relevant to homogeneous catalysis deactivation processes and has been studied extensively.[3] These examples are mainly concerned with breaking of aryl−phosphine bonds but very seldom with an alkyl−phosphine bond,[3,4] which apparently is the consequence of less favored migration of an alkyl group from phosphine to a metal center as compared to that of aryl group.[5] Extended Hückel calculations on R migration from phosphine to Pd in a model complex ($H_2(R)P-Pd(PH_3)Me_2$) have indicated barriers of 31 kcal/mol for R = Me but only 1.6 kcal/mol for R = Ph.[6] One of the rare examples is detection of ethane-d_3 and ethane-d_6 during the reductive elimination of ethane at 60 °C from *cis*-$Pd(Me)_2(PPh_2CD_3)_2$, where oxidative addition of $P-CD_3$ bound to Pd(0) was proposed.[7] In another work, butene was detected in 20% yield upon reaction of $P(n\text{-}Bu)_3$ with $Pd(OAc)_2$ at 90 °C, which has been explained as due to migration of the *n*-Bu group from P to Pd and successive β-hydride elimination.[8] In dinuclear and trinuclear complexes, it has been quite well known that μ_2-coordinating bis(diphenylphosphino)methane and derivatives are special in that they undergo P−C bond activation at the $P-CH_2$ bond rather than at the P−phenyl bond.[9−17] To the best of our knowledge, however, there has been only one example of P−C bond cleavage of trimethylphosphine in coordination complexes, which has been observed in di- and trinuclear Ru complexes.[18,19] The present work demonstrates that the coordination site provided by a suitable *hetero*dimetallic complex can activate the P−C bond of this simplest tertiary alkylphosphine under fairly mild conditions.

Results and Discussion

Treatment of $(C_5H_5)Ni(\mu\text{-}CO)(\mu\text{-}H)W(C_5H_5)_2$ (**1**) with 4 equiv of PMe_3 in THF at room temperature and successive purification by column chromatography gave a red powder formulated as $(C_5H_5)Ni(\mu\text{-}CO)(\mu\text{-}PMe_2)(C_5H_5)W(Me)(PMe_3)$ (**2**) in 58% yield. Further purification by chromatography and recrystallization gave a 36% yield of crystalline **2**. Use of a 2 equiv amount of PMe_3 resulted in a lower yield.



1 **2**

(1)

The solid-state structure of **2** has been determined by an X-ray diffraction study, as shown in Figure 1, and selected bond lengths and angles are listed in Table 1. Loss of a cyclopentadienyl and the hydride units on going from **1** to **2**, i.e., loss of six donating electrons, is compensated by addition of two lone pairs of PMe_3 and two new σ-bonds, a metal−P and W−Me, thus maintaining the 34-electron configuration of a saturated dinuclear complex. The hydride bridge in the starting complex is replaced by a phosphido bridge with two methyl substituents, while the third methyl is bound directly to W. Another trimethylphosphine ligand coordinates to the same metal.

The W−C(1)−O (155.9(5)°) and Ni−C(1)−O (119.6(5)°) angles indicate that the CO ligand is tilted significantly toward the Ni center. For comparison, an analog of **1**, $(C_5Me_5)Ni(\mu\text{-}H)(\mu\text{-}CO)Mo(C_5H_5)_2$ (**3**), the structure of which we reported previously has angles of 141.8(4)° (Ni−C(1)−O) and 135.4(4)° (Mo−C(1)−O).[2] Apparently, the coordination mode of the carbonyl group in **2** is semibridging. The longer W−P(1) distance as compared to the Ni−P(1) bond length may be attributed to the larger atomic radius of W, but the rather shorter W−C(co) bond than Ni−C(co) is consistent with the semibridging character of the CO ligand. This holds true also in solution: in THF, the IR carbonyl stretching absorption

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(1) Wilkinson, G.; Stone, G.; Abel, E. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, G., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 6, p 763.

(2) Nakajima, T.; Mise, T.; Shimizu, I.; Wakatsuki, Y. *Organometallics* **1995**, *14*, 5598.

(3) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171.

(4) Doel, G. R.; Feasey, N. D.; Knox, S. A. R.; Orpen, A. G.; Webster, J. *J. Chem. Soc., Chem Commun.* **1986**, *1986*, 542.

(5) Morita, D. K.; Stille, J. K.; Norton, J. R. *J. Am. Chem. Soc.* **1995**, *117*, 8576.

(6) Ortiz, J. V.; Havias, Z.; Hoffmann, R. *Helv. Chim. Acta* **1984**, *67*, 1.

(7) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933.

(8) Kikukawa, K.; Takagi, M.; Matsuda, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1493.

(9) Lugan, N.; Bonnet, J.-J.; Ibers, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4484.

(10) Doherty, N. M.; Hogarth, G.; Knox, S. A. R.; Macpherson, K. A.; Melchior, F.; Orpen, G. *J. Chem. Soc., Chem. Commun.* **1986**, *1986*, 540.

(11) Bergounhou, C.; Bonnet, J.-J.; Fompeyrine, P.; Lavigne, G.; Lugan, N.; Mansilla, F. *Organometallics* **1986**, *5*, 60.

(12) Grist, N. J.; Hogarth, G.; Knox, S. A. R.; Lloyd, B. R.; Morton, D. A. V.; Orpen, G. *J. Chem. Soc., Chem. Commun.* **1988**, *1988*, 673.

(13) Lugan, N.; Bonnet, J.-J.; Ibers, J. A. *Organometallics* **1988**, *7*, 1538.

(14) Riera, V.; Ruiz, M. A.; Villafañe, F.; Bois, C.; Jeannin, Y. *J. Organomet. Chem.* **1989**, *375*, C23.

(15) Hogarth, G.; Knox, S. A. R.; Turner, M. L. *J. Chem. Soc., Chem. Commun.* **1990**, *1990*, 145.

(16) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **1997**, *16*, 354.

(17) Shiu, K.-B.; Jean, S.-W.; Wang, H.-J.; Wang, S.-L.; Liao, F.-L.; Wang, J.-C.; Liou, L.-S. *Organometallics* **1997**, *16*, 114.

(18) Matsubara, K.; Tanaka, M.; Suzuki, H. Presented at the 68th Annual Meeting of the Japanese Chemical Society, Nagoya, October 1994.

(19) Ooki, Y.; Tanaka, M.; Suzuki, H. Presented at the 71sth Annual Meeting of the Japanese Chemical Society, Hukuoka, October 1996.

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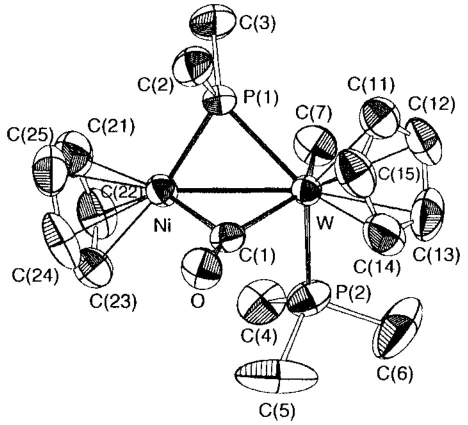
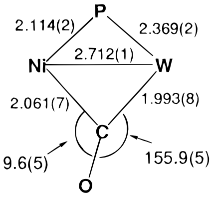


Figure 1. Molecular structure of **2**. Ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

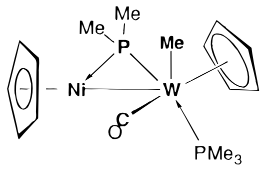
Table 1. Selected Bond Distances (Å) and Angles (deg) for **2**

W-C(1)	1.993(8)	W-Ni	2.712(1)
W-P(1)	2.369(2)	Ni-C(1)	2.061(7)
W-P(2)	2.482(2)	Ni-P(1)	2.114(2)
W-C(7)	2.290(12)		
W-Ni-P(1)	57.2(1)	W-Ni-C(1)	46.9(2)
Ni-P(1)-W	74.2(1)	Ni-C(1)-W	84.0(3)
P(1)-W-Ni	48.6(1)	C(1)-W-Ni	49.1(2)
W-C(1)-O	155.9(5)	Ni-C(1)-O	119.6(5)
P(1)-W-C(1)	78.2(2)	P(1)-W-C(7)	81.0(3)
P(2)-W-C(1)	85.0(2)	P(2)-W-C(7)	78.4(3)
Ni-P(1)-W/Ni-C(1)-W	113.8(3)		

of **2** (1907 cm^{-1}) is much higher energy than that of **3** (1741 cm^{-1}), where the CO ligand is in typical μ_2-coordination. These observations suggest some contribution of a formulation **2′**.



2



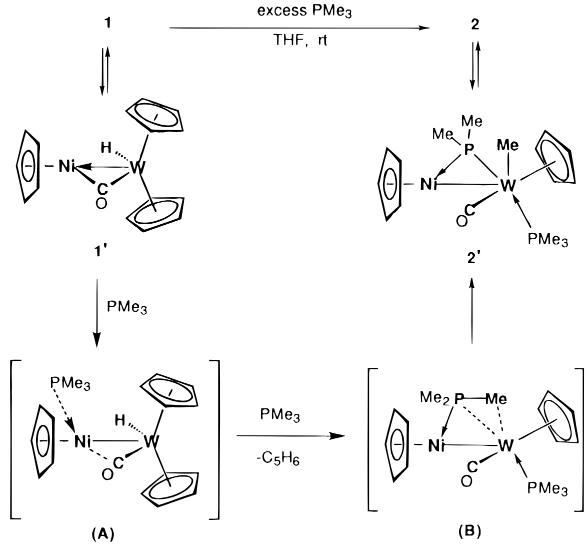
2′

In accord with the solid-state structure, the ^{1}H NMR spectra of **2** with and without ^{31}P decoupling indicated the presence of four different types of methyl groups and two cyclopentadienyl groups but the absence of a hydride signal (for the numbering of P and Me, see Figure 1): δ 0.09 (MeW, dd, $J_{H,P(1)} = 11.7$ Hz, $J_{H,P(2)} = 12.7$ Hz, and $J_{H,W} = 4.0$ Hz as satellite signals), 1.19 (Me$_3$P$_{(2)}$, d, $J_{H,P(2)} = 8.3$ Hz), 1.26 (Me$_{(2)}$P$_{(1)}$, d, $J_{H,P} = 11.5$ Hz), 1.32 (Me$_{(3)}$P$_{(1)}$, d, $J_{H,P} = 11.2$ Hz), 4.20 (C_5H_5W, dd, $J_{HP(1)} = 0.7$ Hz, $J_{HP(2)} = 1.5$ Hz), 5.31 (C_5H_5Ni, br s, $J_{H,P(1)} < 0.5$ Hz) ppm. The assignments were confirmed by the ^{1}H−^{13}C PFG-HMQC technique.[20]

In the ^{31}P{^{1}H} NMR spectrum of **2**, two phosphorus signals having satellites by the ^{183}W nucleus (14.4% natural abundance) were observed at δ −44.2 (P$_{(2)}$, d, $J_{P,P} = 38.0$ Hz and $J_{P,W} = 246.7$ Hz) and 89.1 (P$_{(1)}$, d, $J_{P,P} = 38.0$ Hz and $J_{P,W} = 227.7$ Hz) ppm, where the external standard was 85% H_3PO_4.

In contrast to the smooth reaction of **1** with PMe$_3$, no appreciable reaction was observed, even at 60 °C, when PMe$_3$ was added to a THF solution of the pentamethylcyclopentadienyl derivative, (C_5Me_5)Ni(μ-CO)(μ-H)W(C_5H_5)$_2$. Since the Ni center is sterically protected in this complex, the successful attack by PMe$_3$ in the case of **1** may well be on the Ni site. We tentatively propose that a tautomer (**1′**) is responsible for accepting this attack, giving intermediate **A** (Scheme 1). Reductive elimination of H-C_5H_5 and concomitant coordination of another PMe$_3$ molecule to W gives coordinatively unsaturated and electron-rich W center **B**. The oxidative addition of one of the Ni-coordinated P−Me bonds will then formally yield **2′**, a tautomer of the product **2**.

Scheme 1



Experimental Section

Most manipulations were performed in a dry, oxygen-free argon atmosphere. THF was purified by standard methods and freshly distilled from sodium benzophenone under argon before use. The starting complex (C_5H_5)Ni(μ-CO)(μ-H)W(C_5H_5)$_2$ (**1**) was obtained as published before.[2] All other reagents were commercially obtained. ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were measured on a JEOL JNM-A400 spectrometer, and IR spectra were recorded on a Perkin Elmer FT-1650 spectrometer using CaF$_2$ liquid cell. Elemental analyses were performed by the Chemical Analysis Laboratory of RIKEN institute.

Reaction of 1 with PMe$_3$. To a solution of **1** (50.0 mg, 0.11 mmol) in THF (10 mL) was added PMe$_3$ (45.5 μL, 0.44 mmol) at room temperature until most of **1** was consumed (ca. 48 h) as monitored by IR spectra. The initially red solution became dark red. The solvent was evaporated under reduced pressure. The residual dark red oil was extracted with hexane and then filtered through a Celite column. The filtrate was dried under vacuum. The dark red solid was chromatographed on alumina (deactivated with 10 wt % H_2O, 18 × 2 cm). Elution with hexane gave a red band. The red eluted was collected and evaporated to dryness to yield dark red crystalline solid (23.1 mg, 0.04 mmol, 36%). ^{13}C NMR (C_6D_6): δ −19.1 (MeW, t, $J_{C,P(1)} = 12.8$ Hz, $J_{C,P(2)} = 12.8$ Hz), 11.4 (Me$_{(3)}$P$_{(1)}$, d, $J_{C,P} = 14.7$ Hz), 19.5 (MeP$_{(2)}$, d, $J_{C,P} = 26.9$ Hz), 22.0 (Me$_{(2)}$P$_{(1)}$, d, $J_{C,P} = 26.9$ Hz), 85.9 (C_5H_5W, s), 91.6 (C_5H_5Ni, s), 260.0 (CO, s). The analytically pure sample, also suitable for X-ray analysis, was obtained by recrystallization from hexane as red plates (mp 142−144 °C). Anal. Calcd for $C_{17}H_{28}NiOP_2W$: C, 36.93; H, 5.13. Found: C, 37.33; H, 5.23.

X-ray Crystallographic Analysis of 2. Reflection data were collected at room temperature on a CAD-4 diffractometer using graphite-monochromated Mo Kα radiation and the $\omega-2\theta$ scan technique. The intensity data were corrected for absorption anisotropy effects. The structure was solved from direct and Fourier methods and refined by full-matrix least squares with anisotropic thermal parameters in the last cycles for all non-hydrogen atoms. Hydrogen atoms for the cyclopentadienyl rings and the W-CH$_3$ group were located from a difference Fourier map, while other methyl hydrogens were placed in calculated positions. These hydrogen atoms were included in subse-

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(20) Hurd, R. E.; John, B. K. *J. Magn. Reson.* **1991**, *91*, 648.

quent refinements with isotropic thermal parameters. The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$. The computational program package used in the analysis was the UNICS-III program system.[21] Neutral atomic scattering factors were taken from *International Tables for X-ray Crystallography*.[22] Crystal and refinement data: crystal size, 0.50 × 0.36 × 0.14 mm, monoclinic $P21/C$, $a = 14.627(2)$ Å, $b = 9.424(1)$ Å, $c = 15.245(2)$ Å, $\beta = 109.17(1)°$, $Z = 4$, $d_{calc} = 1.855$ g·cm^{-3}, $F(000) = 1048$, $\mu = 70.3$ cm^{-1}, 2θ range 4.0−55.0°, no. of unique reflections 3713 ($F_o \geq 3\sigma(F_o)$), $R = 0.037$, $R_w = 0.040$.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for **2** is available on the Internet only. Access information is given on any current masthead page.

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(21) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyuusho Hokoku* **1979**, *55*, 69.

(22) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.