Synthesis and Characterization of Novel Phosphido-Bridged Bimetallic Complexes of Molybdenum and Tungsten

Makoto Minato, Takashi Nakamura, Takashi Ito,* Takeaki Koizumi,† and Kohtaro Osakada†
Department of Materials Chemistry, Faculty of Engineering, Yokohama National University, 156 Tokiwadai, Hodogaya-ku, Yokohama 240
†*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226*

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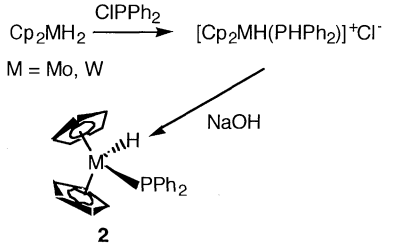
The phosphido-bridged molybdenum and tungsten complexes $[Cp_2M(H)(\mu\text{-}PPh_2)M'(H)Cp_2]^+(OTs)^-$ (M, M' = Mo, W) were prepared and characterized. The X-ray crystallography for the complex (M = M' = Mo) indicated that it has a novel symmetrical structure with regard to two metal centers.

The bis(η^5-cyclopentadienyl)molybdenum and tungsten dihydrides Cp_2MH_2 (M = Mo or W), which were first synthesized by Green and co-workers,[1] have proved to be useful starting materials for the syntheses of a number of molybdenocene and tungstenocene complexes.[2] Recently, we have shown that the trihydrido compounds $[Cp_2MH_3]^+(OTs)^-$ (OTs = p-$CH_3C_6H_4SO_3$) are formed by reaction of the dihydrides with p-toluenesulfonic acid and these compounds are readily converted to monohydrido tosylato complexes $Cp_2MH(OTs)$ (M = Mo (**1a**) and W (**1b**)) with accompanying evolution of 1 mol of H_2.[3] Subsequently, we have been studying these complexes and have found them to undergo a number of interesting reactions.[4] For example, they were found to react with tertiary phosphines, such as PPh_3, PEt_3, PBu^n_3, and $P(OEt)_3$, to give the cationic monohydrido complexes $[Cp_2MH(PR_3)]^+(OTs)^-$ (eq (1)).

$$Cp_2MH(OTs) + PR_3 \rightarrow [Cp_2MH(PR_3)]^+(OTs)^- \quad (1)$$

M = Mo (**1a**), W (**1b**) R = Ph, Et, ^{n}Bu, OEt

Of particular interest to us are bimetallic compounds,[5] and we have been trying to extend the reaction (1) to prepare bimetallic compounds which are held together through bridging phosphide ligand. In 1990, Kubicki and co-workers reported the synthesis of novel phosphide complexes $Cp_2MH(PPh_2)$ (M = Mo (**2a**) and W (**2b**)), which were prepared by treatment of $[Cp_2MH(PPh_2H)]^+Cl^-$ with aqueous NaOH (Scheme 1).[6]



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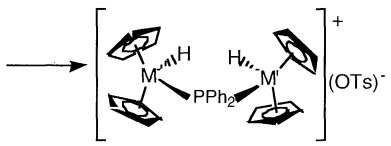
Scheme 1.

The observation that these phosphide complexes exhibit a chemical behavior similar to that of the tertiary phosphines prompted us to investigate reactions between **1** and **2**. It was to be anticipated that the reactions could give symmetric bimetallic hydrido complexes. Recently phosphido-bridged complexes have gained much attention, especially with respect to synthesis, structure, and bonding.[7] In these complexes, central atoms are usually surrounded by different supporting ligands and the enviroments of metal atoms much differ from one another. In view of its relevance to a simple model for heterogeneous catalysts, studying a bimetallic complex which has symmetric structure is important.

In analogy to the procedure for the synthesis of $[Cp_2MH(PR_3)]^+(OTs)^-$, the reaction of **1** with **2** in ethanol at ambient temperature straightforwardly gave the new complexes in satisfactory yields.

$$Cp_2MH(OTs) + Cp_2MH(PPh_2) \rightarrow \quad (2)$$

M, M' = Mo, W



3 : M = M' = Mo 67%
4 : M = Mo, M' = W 75%
5 : M = M' = W 75%

The ^{1}H NMR spectrum of molybdenum complex **3** in CD_3OD displays a doublet resonance at δ -9.10 ($^2J_{HP}$ = 26.6 Hz) assignable to the hydride ligands and one singlet resonance at δ 4.74 due to the Cp ligands. These results indicate that the complex has a symmetrical structure and two molybdenum atoms are equivalent. Therefore the positive charge can be regarded as being spread over two metal centers as well as a bridging phosphorus atom. Both the resonances of hydride and Cp ligands are at higher field than those of the related complex $[Cp_2MoH(PPh_3)]^+$ by ca. 1 and 0.2 ppm respectively.[4] This highfield shift presumably reflects a considerable degree of a drift of electron density from phosphide ligand to the cationic molybdenum metal center. The hydridic W—*H* protons of tungsten complex **5** appeared as doublet at δ -11.77 ($^2J_{HP}$ = 26.8 Hz) with ^{183}W satellites ($^1J_{WP}$ = 67.5 Hz). The doublet at δ 5.10 which corresponded to the Cp ligands of **5** shows coupling to the phosphine atom ($^3J_{HP}$ = 2.4 Hz). In the ^{1}H NMR spectrum of hetero-bimetallic complex **4**, the Mo—*H* resonance appeared as doublet at δ -9.17 ($^2J_{HP}$ = 26.6 Hz) and the W—*H* resonance appeared also as doublet at -12.32 ($^2J_{HP}$ = 22.9 Hz) with ^{183}W satellites ($^1J_{WP}$ = 71.9 Hz). These resonances were obviously distinguishable and the interchange of the hydride ligands did not take place at room temperature. The spectrum of **4** shows peaks at δ 4.74 for Mo—*Cp* and at δ 4.86 for W—*Cp* groups. By IR spectroscopy, the M—H stretching vibrations are observed at 1856 cm^{-1} for **3** and 1916 cm^{-1} for **5**.

A single-crystal X-ray analysis of **3** was undertaken to establish the molecular structure, and this is shown in Figure 1 along with some pertinent structural parameters.[8] A red crystal

suitable for X-ray analysis was obtained by recrystallization from ethanol-diethyl ether. The crystals belong to the monoclinic system. Fairly weak reflection intensities prevent us from defining the hydride ligands of the complex, but their location was postulated at the site *cis* to the phosphine atom on the basis of the orbital configuration of molybdenum atom[9] and it seems reasonable to assume that the coordination geometry around molybdenum is essentially distorted tetrahedral.

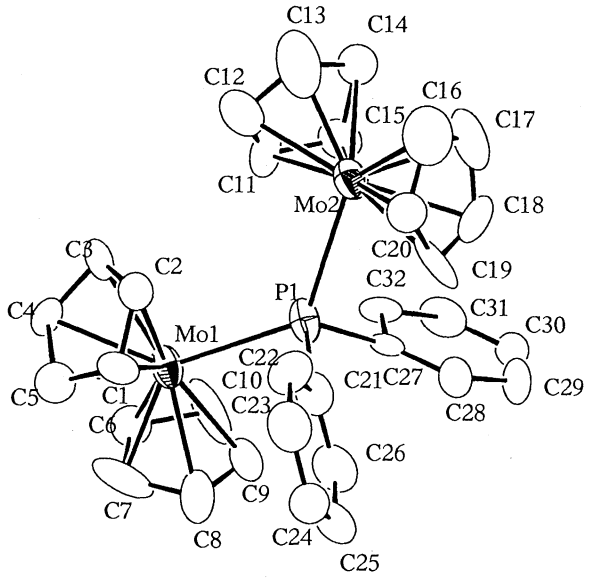


Figure 1. ORTEP drawing of **3**. Selected bond lengths (Å): Mo1—P1 = 2.654(5), Mo2—P1 = 2.657(6), Mo1—C1 = 2.28(2), Mo1—C2 = 2.33(2), Mo1—C3 = 2.30(2), Mo1—C4 = 2.24(2), Mo1—C5 = 2.28(2), Mo1—C6 = 2.26(2), Mo1—C7 = 2.20(2), Mo1—C8 = 2.29(3), Mo1—C9 = 2.33(2), Mo1—C10 = 2.27(2). Selected bond angles (°): Mo1—P1—Mo2 = 128.8(2), Mo1—P1—C21 = 97.9(6), Mo2—P1—C21 = 112.6(7), Mo1—P1—C27 = 144.0(6), Mo2—P1—C27 = 97.6(6).

The structure can be compared and contrasted with that of the known complex $Cp_2Mo(H)(\mu\text{-}PPh_2)Mn(CO)_2Cp$ (**6**).[6] The Mo1—P1 bond distance of 2.654(5) Å is very close to that of Mo2—P1 (2.657(6) Å). These results are in good agreement with the ^1H NMR spectrum of **3**. Namely, Mo1 and Mo2 are substantially equivalent and these two atoms are of the same charge. The Mo—P bond lengths are slightly longer than that in **6** (2.602(2) Å) and these values are unusual, since the Mo—P bond lengths in some related cyclopentadienyl complexes of molybdenum fall in the range 2.329—2.487 Å.[6] The Mo1—P1—Mo2 angle is 128.8(2)° and is significantly larger than that found in **6** (124.47(7)°). This large angle may result from the electrostatic repulsion of the positive Cp_2MoH fragments, and suggests that the Mo···Mo separation (4.79 Å) is nonbonding. The C—P—C (C is the ipso carbon atom of the phenyl ring) angle is 104.2° and is larger than that found in **6** by 2°. Taking into account the large Mo—P—Mo angle in **3**, this observation is intriguing.

The cyclopentadienyl rings are bound to molybdenum in an η^5 fashion, and each of the ring carbon atoms are coplanar. The mean Mo—CP (CP is the centroid of the cyclopentadienyl ligand) bond distance is 1.941 Å, and it closely resembles that found in the neutral phosphine complex $Cp_2Mo(PBu^n_3)$ (1.95 Å) **7**, which was previously synthesized by our group.[10] The internal ligand C—C—C bond angles average 107.4°, which is approximately equal to that of complex **7** (107.9°) and is compared favorably with the expected internal angle, 108°, for a planar pentagon.

We have successfully extended the reaction (1) to the synthesis of the symmetric phosphido-bridged molybdenum and tungsten complexes $[Cp_2M(H)(\mu\text{-}PPh_2)M(H)Cp_2]^+(OTs)^-$ where two metal centers are found to be electronically and structurally identical. The new type of these bimetallic dihydrido complexes thus prepared are expected to undergo interesting reactions similar to those of the related phosphido-bridged complexes.[7]

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8 Crystal data for **3** at 276 K with MoKα (l = 0.1069 Å) radiation: empirical formula = $C_{39}H_{39}O_3PSMo_2$, FW = 810.65, monoclinic, space group $P2_1/n$(# = 14), a = 9.495(4) Å, b = 13.004(6) Å, c = 26.35(1) Å, β = 93.66(4)°, V = 3246(2) Å^3, Z = 4, Dc = 1.658 g/cm^3, R = 0.093, Rw = 0.077 for 2550 observed reflections.
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