Oxidation of phosphido-bridged complexes of molybdenum and tungsten. Isolation of [cyclic] [trans-(HPh2P)(OC)3M(.mu.-PPh2)2M(CO)3(PPh2H)][PF6]

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Oxidation of Phosphido-Bridged Complexes of Molybdenum and Tungsten. Isolation of $[(HPh_2P)(OC)_3M(\mu\text{-}PPh_2)_2M(CO)_3(PPh_2H)][PF_6]$

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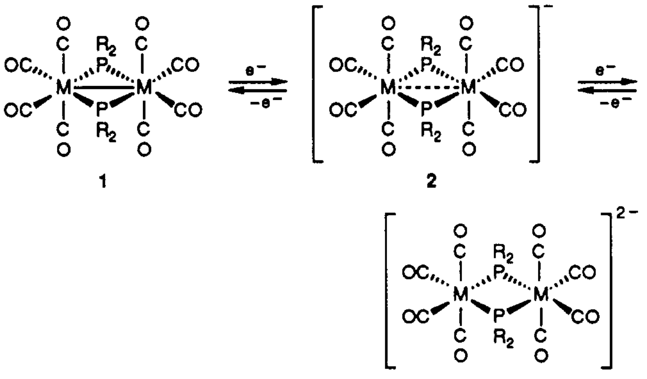
Summary: The 33-electron phosphido-bridged bimetallic cations $[(HPh_2P)(OC)_3M(\mu\text{-}PPh_2)_2M(CO)_3(PPh_2H)]^+$ (M = Mo, W) were obtained from the oxidation of $(HPh_2P)(OC)_3M(\mu\text{-}PPh_2)_2M(CO)_3(PPh_2H)$ by silver hexafluorophosphate. Analogous reactions occur with $(OC)_4M(\mu\text{-}PPh_2)_2M(CO)_4$, but the resulting cations are much more reactive and were not isolated in pure form.

Within a decade after the discovery of $(OC)_4M(\mu\text{-}PR_2)_2M(CO)_4$ (M = Cr, Mo, W) complexes,[1] it was shown that they could be reduced electrochemically or with alkali metals to stable mono- and dianions.[2] Subsequently, 3



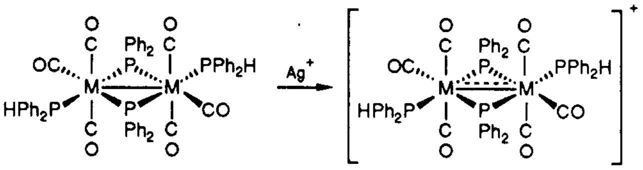
1 2 3

(Mo, W) was synthesized by the reaction of $M(CO)_5PPh_2H$ with potassium *tert*-butoxide[3] and by reduction of 1 with alumino- and borohydrides.[4] Upon exposure to O_2, 3 loses two electrons and reverts back to 1.

Structure determinations have revealed that the planar framework $M(\mu\text{-}PR_2)_2M$[5] found in 1 is maintained upon reduction to 3.[6] For the tungsten complex (R = Ph), reduction leads to a metal–metal bond lengthening of 1.07 Å.[6b] These results are consistent with W–W formal bond orders of one and zero, predicted by the 18-electron rule, for 1 (W) and 3 (W), respectively.

The absence of oxidation studies of 1 (Mo, W) in the literature and the growing importance of 17-electron complexes[7] led us to consider the possibility of obtaining stable 33-electron phosphido-bridged cations. Furthermore, it was expected that oxidation could be facilitated by replacing some carbonyl groups with phosphines, which would enhance the electron density of the complex.

We have found that $(HPh_2P)(OC)_3M(\mu\text{-}PPh_2)_2M(CO)_3(PPh_2H)$ complexes 4 (Mo, W) are readily oxidized



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by $Ag[PF_6]$ to give +1 cations, which can be isolated in pure form as hexafluorophosphate salts. Similar reactions with $(OC)_4M(\mu\text{-}PPh_2)_2M(CO)_4$ (Mo, W) led to highly reactive +1 cations that were characterized spectroscopically but were not isolated in pure form. Cationic phosphido-bridged complexes are rare, represented by the recently reported 34-electron binuclear complexes of iron and ruthenium, $[M_2(CO)_8(\mu\text{-}PPh_2)]BF_4$.[8]

Experimental Section

General Data. All reactions were carried out under an atmosphere of dry nitrogen in a Vacuum Atmospheres glovebox or on a high-vacuum line. Glassware was dried rigorously prior to use. Reagent dichloromethane was dried over P_2O_5 and distilled. Reagent toluene was predried with $CaCl_2$ and further dried with P_2O_5. The oxidant, $Ag[PF_6]$, was obtained from Strem Chemical Co. and used without further purification. The neutral phosphido-bridged complexes were synthesized by literature methods.[3a,9]

Infrared spectra of dichloromethane solutions were measured with a Nicolet 20 DXB spectrometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN. Magnetic susceptibility measurements were made with a Cahn RTL (Faraday) electrobalance. The susceptibility standard was $Hg[Co(SCN)_4]$. Electrochemical experiments were carried out with a PAR Model 173 potentiostat/galvanostat that was controlled by a PAR 175 universal programmer. A standard three-electrode system was used. The working electrode was a platinum disk (0.203 cm^2 in area), and a coiled platinum wire was used as the auxiliary electrode. The reference electrode, $Ag/AgNO_3$ (0.10 M), was separated from the solvent system employed (0.10 M tetrabutylammonium perchlorate, TBAP, in CH_3CN) by a salt bridge containing 0.10 M TBAP in CH_3CN. All potentials are quoted vs $Ag/AgNO_3$ and are uncompensated for solution resistance and the effects of liquid-junction potentials. With the use of this reference the $E_{1/2}$ value for ferrocenium/ferrocene was 0.15 V in CH_2Cl_2. Scan rates were varied between 1.0 and 50 V/min with 2.0 V/min as the standard scan rate.

Preparation of $[(HPh_2P)(OC)_3W(\mu\text{-}PPH_2)_2W(CO)_3(PPh_2H)][PF_6]$ (5) (M = W). To 1.45 g (1.13 mmol) of *trans*-$(HPh_2P)(OC)_3W(\mu\text{-}PPh_2)_2W(CO)_3(PPh_2H)$ dissolved in 50

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† Deceased May 17, 1986.

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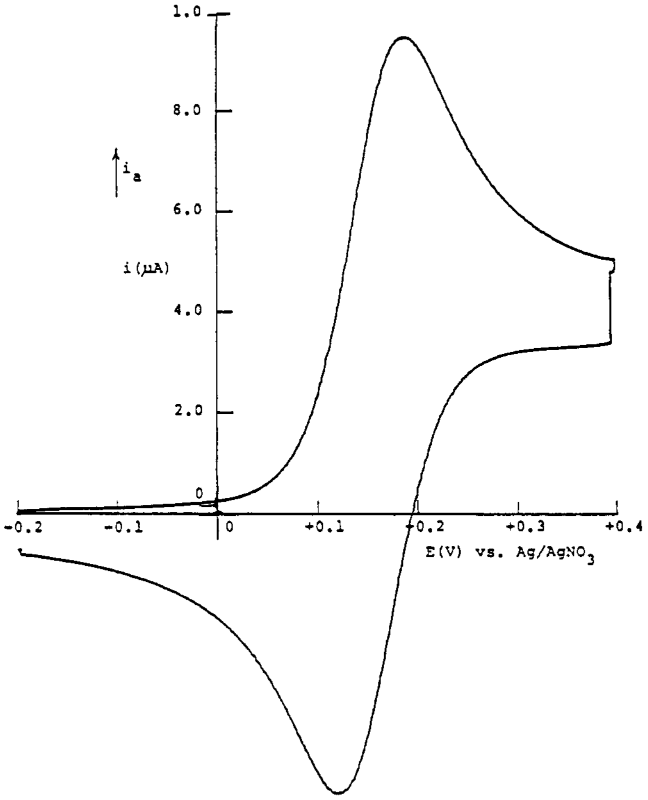

Figure 1. Cyclic voltammogram of 4 (W) in CH_2Cl_2 (0.1 M TBAP as the electrolyte; scan rate 2.0 V/min).

mL of dry dichloromethane was added 0.286 g (1.13 mmol) of Ag[PF_6]. Immediately, the original bright red color of the solution changed to dark green. The colloidal solution was filtered through a medium frit to remove metallic silver. Solvent from the filtrate was rapidly removed under vacuum, and the residue was washed with three successive portions (50 mL) of toluene to remove unreacted starting materials. The dried green product (1.29 g, 80%) was stable in the solid state but slowly decomposed in solution to regenerate starting material. The magnetic moment of the sample was determined to be 1.7 μ_B at 298 K.

Anal. Calcd for $C_{54}H_{42}F_6O_6P_5W_2$: C, 45.56; H, 2.97; P, 10.87. Found: C, 45.18; H, 3.21; P, 11.05.

A similar procedure was followed for the preparation of $[(HPh_2P)(OC)_3\overline{Mo(\mu\text{-}PPh_2)_2M}(CO)_3(PPh_2H)][PF_6]$ (5) (M = Mo).

Anal. Calcd for $C_{54}H_{42}F_6O_6P_5Mo_2$: C, 51.98; H, 3.39; P, 12.41. Found: C, 51.55; H, 3.31; P, 12.06.

Attempted Preparation of $[(OC)_4\overline{M(\mu\text{-}PPh_2)_2M}(CO)_4][PF_6]$ (6) (M = W, Mo). To a slurry of $(OC)_4\overline{W(\mu\text{-}PPh_2)_2W}(CO)_4$ (0.255 g, 0.267 mmol) in 55 mL of CH_2Cl_2 was added Ag[PF_6] (0.075 g, 0.29 mmol). The color of the mixture instantly changed from bright red to medium green. The solution was filtered immediately through a medium frit, and the solvent was vacuum-evaporated from the filtrate as quickly as possible. During the evaporation process, a red solid collected on the sides of the flask. An infrared spectrum of the residue identified it as a mixture of starting material and product. Within 2 h all traces of the green color, characteristic of the product, had disappeared. The product was not obtained in pure form. Similar results were obtained for the analogous molybdenum reaction.

Results and Discussion

Early electrochemical work by Dessy[10] on phosphido-bridged bimetallic species revealed quite clearly that success in bringing about radical-anion, radical-cation, dianion, or dication formation depends strongly on the nature of the bridging group, the metal, and ancillary ligands. For example, $(OC)_4\overline{W(\mu\text{-}PMe_2)_2W}(CO)_4$ shows one polarographic wave corresponding to a two-electron reduction of its dianion, while $[(\eta^5\text{-}C_5H_5)Fe(CO)(\mu\text{-}PPh_2)]_2$ can be oxidized to its radical cation and even further to its dication.

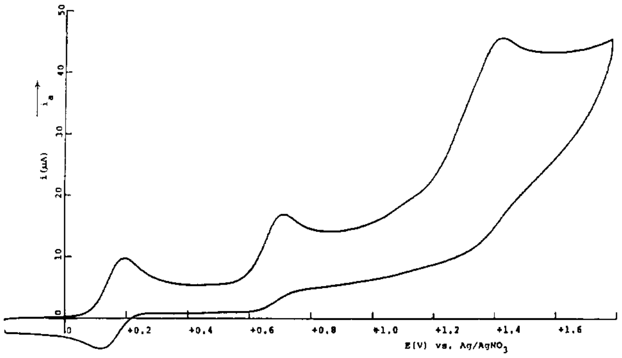

Figure 2. Cyclic voltammogram of 4 (W) in CH_2Cl_2 (0.1 M TBAP as the electrolyte; scan rate 2.0 V/min).

Preliminary electrochemical measurements were carried out in order to assess the feasibility of obtaining stable oxidation products from 4 (Mo, W) and 1 (Mo, W). The cyclic voltammogram of 4 (W) (Figure 1) shows facile reversible loss of one electron at a potential (0.19 V) which is only 0.04 V more positive than that observed for ferrocene. A CV peak separation of 62 mV was measured when the scan rate was 1.0 V min^{-1}. In accordance with a diffusion-controlled process, the current function was constant over the scan range examined. A second electron (Figure 2) is lost irreversibly at 0.72 V, characteristic of a one-electron transfer followed by a fast chemical reaction. A third poorly defined anodic wave was observed at 1.4 V.

The ease of removing one electron from 4 (W) and the apparent stability of the radical cation suggested that its isolation would be possible. Such indeed was the case as addition of stoichiometric amounts of Ag[PF_6] to 4 (W) led to quantitative formation of 5 (W). The molybdenum salt 5 (Mo) was obtained similarly. These cations react with dichloromethane (or perhaps with traces of impurities in dichloromethane) or disproportionate to regenerate their neutral precursors. These reactions can be observed visually because the neutral compounds are red and their +1 salts are green.

Attempts to convert 1 (W, Mo) to pure cationic complexes were not successful. Addition of stoichiometric quantities of the oxidant gave radical cations 6 (W, Mo), as noted by color change (red to green) and by infrared spectroscopy, but isolation efforts were accompanied by reversion of the product to starting material. The cyclic voltammogram of 1 (W) showed a well-defined current maximum at 0.75 V that was consistent with quasi-reversible one-electron oxidation of each metal center when compared to ferrocene. The magnitude of the cathodic peak current was also consistent with two one-electron transfers. A second anodic wave was observed at 1.02 V and was characteristic of irreversible electron transfer.

Complex 4 differs from 1 in having two secondary phosphines in place of two carbonyl groups. This has the effect of increasing the electron density of 4 relative to 1, and as a result, oxidation of 4 is more favorable than oxidation of 1, all of which is consistent with the greater stability of 5 relative to 6. Of course 5 is sterically more encumbered than 6 and its energy of activation for accepting an electron may be higher as a result. Thus, we may be able to isolate 5 in pure form but not 6, because of both thermodynamic and kinetic reasons.

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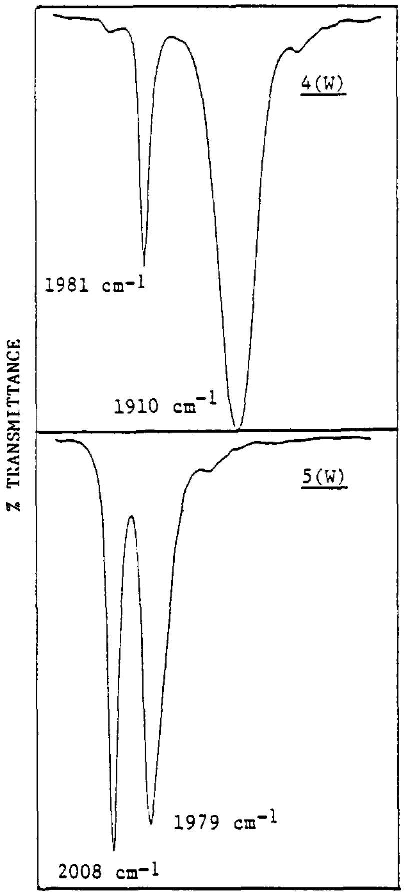

Figure 3. Infrared spectra in the carbonyl region for 4 (W) and 5 (W).

Table I. Infrared Data for Phosphido-Bridged Group 6 Carbonyl Complexes (CH_2Cl_2)

complex	C–O str freq, cm^{-1}		complex	C–O str freq, cm^{-1}	
1 (Mo)[a]	1967 (s)	2034 (s)	4 (Mo)[b]	1919 (s)	1987 (s)
6 (Mo)	2031 (s)	2057 (s)	5 (Mo)	1993 (s)	2013 (s)
1 (W)[a]	1958 (s)	2032 (s)	4 (W)[b]	1910 (s)	1981 (s)
6 (W)	2017 (s)	2055 (s)	5 (W)	1979 (s)	2008 (s)

[a] For literature values, see refs 1a, 1d, 3a, 6b, and 9. [b] For literature values see ref 9.

The infrared spectra of 4 (W) and 5 are shown in Figure 3, and infrared data are presented in Table I. The carbonyl stretching frequencies of the radical cations lie at higher values than those of their neutral precursors in accordance with the expectation that the C–O bond strength will increase as electron density on the complex decreases (i.e. reduced M–C π-bonding). A second important feature is that the number and appearance of the carbonyl absorptions are little changed upon oxidation. This suggests that the symmetries of the oxidized and reduced forms are the same. Thus, the planar framework, M(–PPh$_2$)$_2$M, appears to remain intact during oxidation. One of the infrared bands, however, shifts much more than the other upon oxidation, and this observation may be connected to some kind of structural change. We have not been able to assess this possibility with a crystal structure of 5 (Mo, W), however, because decomposition of the complex in solution competes well with crystal growth.

Electrons added to 1 or 4 in the reduction process go to an antibonding orbital, and as a result, the bond order is reduced. Various molecular orbital calculations support the view that formal metal–metal bond orders of 1, 0.5, and 0.0 are present in complexes like 1, 2, and 3, respectively.[11] Oxidation of the neutral complexes 1 and 4 to give the cations 5 and 6 would be expected to result in the loss of an electron from an antibonding molecular orbital, and therefore, a formal metal–metal bond order of 1.5 would be predicted. Thus, oxidation should lead to a shortening of the metal–metal bond. It remains to be seen whether this prediction is borne out experimentally.

It may be possible to isolate dications if the terminal secondary phosphines of 4 are replaced with better electron-donating terminal (e.g. trimethylphosphine) or bridging ligands (e.g. dimethylphosphido). It becomes apparent that bimetallic phosphido-bridged complexes may be regulated to function as "electron banks" into which electrons may be deposited or withdrawn.

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Registry No. 4 (W), 120638-06-4; 4 (Mo), 120638-07-5; 5 (W), 137465-48-6; 5 (Mo), 137465-50-0; 6 (W), 137465-52-2; 6 (Mo), 137465-54-4; Ag[PF$_6$], 26042-63-7; (OC)$_4\overline{\text{W}(\mu\text{-PPh}_2)_2\text{W}}(CO)_4$, 80049-82-7; (OC)$_4\overline{\text{Mo}(\mu\text{-PPh}_2)_2\text{Mo}}(CO)_4$, 20909-82-4.

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