Preliminary communication

Synthesis of binuclear tungsten carbonyls bridged both by hydride and by bidentate phosphine ligands, (μ-H)(μ-Ph$_2$P(CH$_2$)$_n$PPh$_2$)W$_2$(CO)$_8^-$ (n = 1–4), (μ-*H*)(μ-(Ph$_2$PCH$_2$)$_3$CMe)W$_2$(CO)$_8^-$, and (μ-H)(μ-(η^5-C$_5$H$_4$PPh$_2$)$_2$Fe)W$_2$(CO)$_8^-$

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Abstract

Protonation of (Et$_4$N)$_2$(H$_2$W$_2$(CO)$_8$) with one equivalent of trichloroacetic acid in CH$_3$CN at $-30\,^\circ$C, followed by treatment with potentially bidentate phosphine ligands, provides 40–85% yields of yellow complexes, (Et$_4$N)((μ-H)(μ-Ph$_2$P(CH$_2$)$_n$PPh$_2$)W$_2$(CO)$_8$) (n = 1–4), (Et$_4$N)((μ-H)(μ-(Ph$_2$PCH$_2$)$_3$CMe)W$_2$(CO)$_8$), and (Et$_4$N)((μ-H)(μ-(η^5-C$_5$H$_4$PPh$_2$)$_2$Fe)W$_2$(CO)$_8$). These new complexes are characterized on the basis of elemental analyses, IR, and ^{1}H and ^{31}P NMR spectra.

Syntheses of (μ-H)(μ-Ph$_2$P(CH$_2$)$_n$PPh$_2$)Mo$_2$(CO)$_8^-$ (n = 1–4) via reaction of (μ-H)Mo$_2$(CO)$_{10}^-$ with bidentate phosphine ligands in refluxing THF was reported by Darensbourg recently [1]. In other publications, Darensbourg [2] observed that the heavier transition metal or substituent phosphine ligands in some monomeric group VI metal [3 *] hydride complexes enhanced the hydridic character of these anions toward reduction of primary alkyl halides. In a separate report, (μ-H)W$_2$(CO)$_{10}^-$ was found to be a better reducing agent than HW(CO)$_5^-$, possibly owing to the cooperation of the two tungsten centers [4].

Stimulated by Darensbourg's results, we started to examine the possibility of synthesizing tungsten analogs of (μ-H)(μ-Ph$_2$P(CH$_2$)$_n$PPh$_2$)Mo$_2$(CO)$_8^-$ (n = 1–4) in the hope of finding one with more hydridic nature toward organic substrates and with an enhanced thermal stability to fragmentation. In accord with Darensbourg's observations [5], we found that the thermal reaction of HW$_2$(CO)$_{10}^-$ with bidentate phosphine ligands was not a facile and clean process [6 *].

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* Reference number with asterisk indicates a note in the list of references.

Table 1

Elemental analyses and $\nu(CO)$ infrared data for salts of $(\mu\text{-H})(\mu\text{-L} \sim \text{L})W_2(CO)_8^-$

Compound	Analysis (%)						$\nu(CO)^a$ (cm^{-1})	Yield (%)
	C		H		N			
	Found	calcd	Found	calcd	Found	calcd		
$(Et_4N)((\mu\text{-H})(\mu\text{-Ph}_2PCH_2PPh_2)W_2(CO)_8)$ (**1**)	44.45	44.47	3.89	3.91	1.22	1.26	2011m 1987mw 1898s 1860sh 1830m	69
$(Et_4N)((\mu\text{-H})(\mu\text{-Ph}_2P(CH_2)_2PPh_2)W_2(CO)_8)$ (**2**)	45.16	44.98	4.16	4.04	1.21	1.25	2011m 1989mw 1910s 1890sh 1830m	84
$(Et_4N)((\mu\text{-H})(\mu\text{-Ph}_2P(CH_2)_3PPh_2)W_2(CO)_8)$ (**3**)	45.53	45.48	4.14	4.17	1.20	1.23	2011m 1989mw 1905s 1867sh 1824m	55
$(Et_4N)((\mu\text{-H})(\mu\text{-Ph}_2P(CH_2)_4PPh_2)W_2(CO)_8)$ (**4**)	46.06	45.97	4.34	4.30	1.26	1.22	2010m 1988mw 1902s 1887sh 1867sh 1820m	67
$(Et_4N)((\mu\text{-H})(\mu\text{-}(Ph_2PCH_2)_3CMe)W_2(CO)_8))$ (**5**)	50.39	50.80	4.51	4.49	1.02	1.04	2015m 1990mw 1924sh 1907s 1884sh 1869sh 1827m	73
$(Et_4N)((\mu\text{-H})(\mu\text{-}(\eta^5\text{-}C_5H_4PPh_2)_2Fe)W_2(CO)_8)$ (**6**)	46.91	47.01	3.83	3.87	1.23	1.10	2012m 1985mw 1906s 1862mw 1820m	41

^{a} Measured in CH$_3$CN solution

We independently synthesized $((Ph_3P)_2N)((\mu\text{-}H)(\mu\text{-}Ph_2PCH_2CH_2PPh_2)Mo_2(CO)_8)$ [7 *] in quantitative yield via protonation of $((Ph_3P)_2N)_2(H_2Mo_2(CO)_8)$ [8] followed by treatment with a phosphine ligand at $-78°C$. In this paper we report our successful extension of this method to the tungsten system. In a typical reaction, one equivalent of trichloroacetic acid dissolved in CH_3CN was added dropwise to a vigorously stirred CH_3CN solution of $(Et_4N)_2(H_2W_2(CO)_8)$ [8] prechilled to $-30°C$, and the color of the solution changed from red to yellow within 30 min. One equivalent of a bidentate phosphine ligand was then added. After another 30 min at $-30°C$, the solution was warmed slowly to room temperature (1.5 h). Subsequent work-up and recrystallization from THF/Et_2O provided yellow, analytically pure $(Et_4N)((\mu\text{-}H)(\mu\text{-}L\sim L)W_2(CO)_8)$ ($L\sim L$ is a bidentate ligand). The bidentate phosphine ligands used in this reaction include $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–4), $(Ph_2PCH_2)_3CMe$, and $(\eta^5\text{-}C_5H_4PPh_2)_2Fe$ [9].

The infrared spectral pattern of these new complexes in CO stretching region is very similar to that of molybdenum analogues [1], suggesting that they might have very similar structure; i.e., binuclear metal carbonyls bridged both by a hydride and a bidentate phosphine ligand. Four prominent $\nu(CO)$ absorptions are observed: two medium-to-weak narrow bands around 2000 cm^{-1}, a strong band around 1910 cm^{-1}, and a medium band at ca. 1825 cm^{-1} (Table 1). The region between the lower two bands shows increasing complexity as n i.e. chain length increases. The ^{1}H and ^{31}P NMR spectra (Table 2) also support our proposed structure. The proton chemical shifts of the hydrides are triplets with $J(P\text{-}H)$ 15–20 Hz, which are centered between 10 to 11 ppm upfield from Me_4Si. These chemical shifts [10] and P–H coupling constants [1,11] of the hydrides are consistent with the existence of a bridged W–H–W linkage and that the hydride is cis to two ligated phosphorus atoms of the bridged phosphine ligand. It is also clear that the two tungsten atoms are magnetically equivalent toward the bridged hydride since each peak from the triplet is flanked by only one set of tungsten satellites. The ^{183}W–H coupling constant for the bridged hydrides are comparable with those reported in literature [8,10,12,13]. It is important to note that complex, $(\mu\text{-}H)(\mu\text{-}(Ph_2PCH_2)_3CMe)\text{-}W_2(CO)_8^-$, contains two ligated and one unligated PPh_2 as shown by ^{31}P NMR.

Infrared monitoring showed that the formation of these complexes proceeded quantitatively, the moderate yields reported (Table 2) are due to handling losses during the small scale preparations. In the case of the complex, $(Et_4N)((\mu\text{-}H)(\mu\text{-}(\eta^5\text{-}C_5H_4PPh_2)_2Fe)W_2(CO)_8)$, a second product which was insoluble in THF was isolated at slightly lower yield. The two products have essentially superimposable CO stretching frequencies. Whether the second product is an oligomer of the first product is presently not known. The mechanism responsible for the formation of the aforementioned complexes, $(Et_4N)((\mu\text{-}H)(\mu\text{-}L\sim L)W_2(CO)_8)$, is not certain. Similar to the protonation of $H_2Os_3(CO)_{10}$ [14], an electron deficient intermediate formulated as $H_3W_2(CO)_8^-$ might form upon protonation of $H_2W_2(CO)_8^{2-}$. Extrusion of H_2 could accompany the addition of phosphine donors, similar to ligand promoted elimination of H_2 reported by Puddephatt [15] and Ellis [8]. Alternatively, extrusion of H_2 could occur prior to ligand coordination.

Our preliminary results indicated that the aforementioned complexes could also be obtained in slightly lower yields if $(C_6H_5)_3C^+BF_4^-$, a potent hydride abstracting reagent, was used instead of trichloroacetic acid. Intermediates formed from these reactions seem to be stable at low temperature, although they are reactive toward

Table 2

^{1}H and ^{31}P NMR data for salts of $(\mu\text{-H})(\mu\text{-L} \sim \text{L})W_2(CO)_8^-$ in CD_3CN

Com-pound	^{1}H NMR [a,b,c]				^{31}P NMR [d]	
	W–H–W(J(P–H); J(^{183}W–H) [e] (H2)	$(CH_2)_n$	CH_3	C_5H_4	W–P(^2J (^{183}W–P)(H$_2$)	unligated P
1	−10.7(15.5; 43.2)	3.72(t)			14.5(173)	
2	−12.1(19.6; 41.5)	2.70(m)			37.7(202)	
3	−10.9(20.2; 42.5)	2.82(m, 4 H); 1.60(m, 2 H)			41.4(231)	
4	−10.4(16.3; 46.1)	2.76(m, 4 H); 1.41(m, 4 H)				
5	−10.6(19.0; 39.8)	2.80(m, 2 H), 2.45(m, 2 H), 1.00(m, 2 H)	0.80(s)		−5.46(204)	−26.1
6	−9.35(17.5; 47.3)			4.36(m, 4 H) 4.23(m, 4 H)	10.1(219)	

[a] Reported in ppm relative to $\delta(Me_4Si)$ 0 ppm. Abbreviations: s = singlet, t = triplet, m = multiplet. [b] Counterion, Et$_4$N$^+$, appears at 3.14(q, CH$_2$), 1.19(tt, CH$_3$). [c] Phenyl protons show multiplet from 7.8–7.0. [d] Reported in ppm relative to δ(aqueous 85% H$_3$PO$_4$) 0 ppm. [e] All hydrides appear as triplet flanked by tungsten satellites.

phosphine ligands. Extension of these strategies to the preparation of complexes with ligands other than phosphines and hetero-nuclear metal clusters are in progress.

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3 The periodic group notation is in accord with recent decisions taken by IUPAC and ACS nomenclature committees.

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