highly asymmetric carbonyl ligands. With use of the experimental conditions herein described, we were able to isolate 1 in nonoptimized overall yields of 16-24%. In addition to unreacted starting materials, the only other organometallic compounds that were isolated from the reaction were $Fe(CO)_5$ and the Mo-Mo single-bonded $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_6$ dimer, which is produced by the reaction of liberated CO with 2.[45]

Mixed-metal organometallic clusters such as 1 are of particular interest due to the extensive use of molybdenum-based heterogeneous catalysts. Our current research involving the synthesis and physicochemical properties of molybdenum-containing mixed-metal clusters has shown that 2 can react with $Fe_2(CO)_9$ to give such molybdenum-containing species. In subsequent articles, we will report the reaction of 2 with a assortment of carbonyl- and/or nitrosyl-containing organometallic compounds. Such reactions have resulted in the isolation of a wide variety of unusual new organometallic clusters, some of which are formed with concomitant N-O or C-O bond activation.[11-13,32]

Acknowledgment. Support for this research by the National Science Foundation is gratefully appreciated. The support of J.-S.H. as a Visiting Scholar at the UW—Madison by the People's Republic of China is also acknowledged.

Registry No. 1, 102342-15-4; 2, 12132-04-6; $Fe_2(CO)_9$, 15321-51-4; Mo, 7439-98-7; Fe, 7439-89-6.

Supplementary Material Available: Tables giving calculated positions and isotropic temperature factors for all hydrogen atoms, anisotropic thermal parameters for all non-hydrogen atoms, and a listing of observed and calculated structure factor amplitudes (44 pages). Ordering information is available on any current masthead page.

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[45] Ginley, D. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1975**, *97*, 3533-3535.

Peralkylcyclopentadienyl Tungsten Polyhydride Complexes

Jun Okuda, Robert C. Murray, John C. Dewan, and Richard R. Schrock*

Department of Chemistry, 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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$[WCp^*H_4]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) has been prepared by the reaction of $[WCp^*Cl_4]_2$ with $LiAlH_4$ followed by treatment with methanol. Analogous $\eta^5\text{-}C_5Me_4Et$, $\eta^5\text{-}C_5Me_4\text{-}n\text{-}Pr$, $\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu$, $\eta^5\text{-}C_5Et_5$, and $\eta^5\text{-}C_5Et_4\text{-}t\text{-}Bu$ complexes have been prepared similarly. Reaction of $[WCp^*H_4]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with CO under pressure gives the known dinuclear hydrido carbonyl complex $[WCp^*H(CO)_2]_2$, whereas with PMe_3 a hydrido phosphine complex $W_2Cp^*_2H_6(PMe_3)$ is formed. The dimeric unit is retained when $[WCp^*H_4]_2$ is mixed with $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_4]_2$ and during the reaction of this mixture with CO or PMe_3. A trimeric trihydride complex, $[WCp^*H_3]_3$, forms together with a small amount of $[WCp^*H_4]_2$ upon high-pressure hydrogenation of WCp^*Me_4. Reaction of $WCp^*Cl_4(PMe_3)$ with $LiAlH_4$ gives the monomeric phosphine hydride complex $WCp^*H_5(PMe_3)$. $[WCp^*H_4]_2$ can be protonated cleanly by HBF_4 to give $[W_2Cp^*_2H_9]BF_4$. With use of analogous methodology several hydride complexes containing the two-carbon-linked cyclopentadienyl ligand $\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4$ have been prepared. The octahydride complex $[WH_4]_2(\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$ crystallizes as a toluene solvate in the triclinic space group $P\bar{1}$ with $a = 14.828$ (3) Å, $b = 15.963$ (5) Å, $c = 7.854$ (3) Å, $\alpha = 93.03$ (3)°, $\beta = 98.04$ (2)°, $\gamma = 110.91$ (2)°, and $Z = 2$. Diffraction data (Mo Kα) were collected at -50 °C with a CAD4F-11 diffractometer, and the structure was refined to $R_1 = 4.3\%$ and $R_2 = 4.7\%$ for 4595 absorption corrected reflections having $3° \le 2\theta \le 50°$ and $F_o > 4\sigma(F_o)$. The complex shows a dinuclear structure with a W-W distance of 2.591 (1) Å and slightly distorted bridging ligand system. The hydride ligands could not be located, even using a data set collected at -180 °C. An interesting difference in the reactivity of $[WCp^*H_4]_2$ and $[WH_4]_2(\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$ is that the latter does not react readily with CO. ^1H NMR data for all neutral hydride complexes show intramolecular hydride exchange to be rapid on the NMR time scale under most conditions, while the exchange of terminal and bridging hydrides in $[W_2Cp^*_2H_9]^+$ is slow at -30 °C (400 MHz).

Introduction

Several years ago we discovered that a tantalum complex with the composition $[Ta(\eta^5\text{-}C_5Me_5)Cl_2H]_2$ would react readily with carbon monoxide to give a μ-hydrido μ-η^2,η^2-formyl complex, $Ta_2(\eta^5\text{-}C_5Me_5)_2Cl_4(\mu\text{-}H)(\mu\text{-}CHO)$.[1] This is a rare example of the reduction of carbon monoxide by a transition-metal hydride complex under mild conditions. Formation of a complex containing a formyl ligand is thought to be the first step in homogeneous systems in which CO is reduced.[2] Although we could show that methane could be obtained by hydrogenation in the presence of $AlCl_3$ and methanol by hydrolysis, we felt that the inherent oxophilicity of tantalum ultimately would prevent any catalytic reduction of CO to C_1 or, more desirably, C_2 products. We decided to move toward less oxophilic metals to the right of tantalum and continue to explore the possibility of bimetallic activation of carbon monoxide.

Our exploration of the reactions of alkylidyne complexes led to the discovery of $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Cl_4]_2$.[3] We found

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[1] (a) Belmonte, P. A.; Schrock, R. R.; Day, C. S. *J. Am. Chem. Soc.* **1982**, *104*, 3082. (b) Belmonte, P. A.; Cloke, F. G. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 2643.

[2] (a) Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051. (b) Wayland, B. B.; Duttaahmed, A.; Woods, B. A. *J. Chem. Soc., Chem. Comm.* **1983**, 142. (c) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302. (d) Dombek, B. D. *Adv. Catal.* **1985**, *32*, 325.

that two hydride complexes *could* be prepared by hydrogenation of W(η^5-C_5Me_4-*t*-Bu)Me_4,[4a] but we could not proceed to investigate them in any significant detail because of their tedious preparation. Fortunately, we soon discovered a simple route to $[WCp^*Cl_4]_2$ (Cp* = η^5-C_5Me_5).[4b] What we report here in part are the preparations of simple WCp^*H_x complexes and some of their reactions.

Another aspect of the problem concerning the reduction of small molecules in general is the question as to whether systems containing ligands that hold two metal centers in proximity will behave any differently from analogous systems without the connecting link. We have the opportunity to answer this question (as far as the cyclopentadienyl systems being investigated here) because we have discovered a route to $[WCl_4]_2(\eta^5,\eta^5$-$Et_4C_5CH_2CH_2C_5Et_4)$ in good yield.[5] The second goal of this report is to present some of the first comparisons between the "linked" and analogous "unlinked" (η^5-C_5Me_5) complexes.

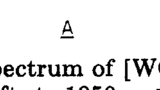
Results

Preparation of $[WCp^*H_4]_2$ (Cp* = η^5-C_5Me_5). Addition of a large excess of $LiAlH_4$ to $[WCp^*Cl_4]_2$ in ether or tetrahydrofuran at −78 °C followed by slow warming of the mixture to ~25 °C yields a nearly colorless solution. Addition of methanol at −78 °C followed by workup at 25 °C yields brown $[WCp^*H_4]_2$ in 40–50% yield (eq 1).

$$[WCp^*Cl_4]_2 \xrightarrow[\substack{\text{2. warm to 25 °C} \\ \text{3. MeOH, −78 °C}}]{\text{1. LiAlH}_4\text{, −78 °C}} [WCp^*H_4]_2 \tag{1}$$

$[WCp^*H_4]_2$ is soluble in pentane and other common organic solvents, although in chloroform or dichloromethane it decomposes immediately to an as yet uncharacterized green material.

In the ^1H NMR spectrum of $[WCp^*H_4]_2$ a single hydride resonance of area 4 (per Cp* group) is found at −0.34 ppm with ^{183}W satellite peaks characteristic of a dimeric species (Figure 1a). The first set of satellite peaks due to coupling of all eight hydrides to one ^{183}W have an area of ~25% of the total, while the two weak satellite peaks that are part of a 1:2:1 triplet resulting from coupling of the hydrides to two ^{183}W centers have an area of ~1% of the total (theory = 2% for 1:2:1 triplet). Unfortunately, the hydride resonance only broadens into the base line at 400 MHz and −120 °C. Therefore, we can only guess the structure of $[WCp^*H_4]_2$. A reasonable one is that containing a W–W bond, two bridging hydrides, and six terminal hydrides, schematically A.



A

A band in the IR spectrum of $[WCp^*H_4]_2$ is observed at 1875 cm^{-1} which shifts to 1350 cm^{-1} in $[WCp^*D_4]_2$ (see below). We assign this band to the terminal W–H stretch and can only propose that any band that would result from a mode involving the bridging hydrides is simply too weak to observe.

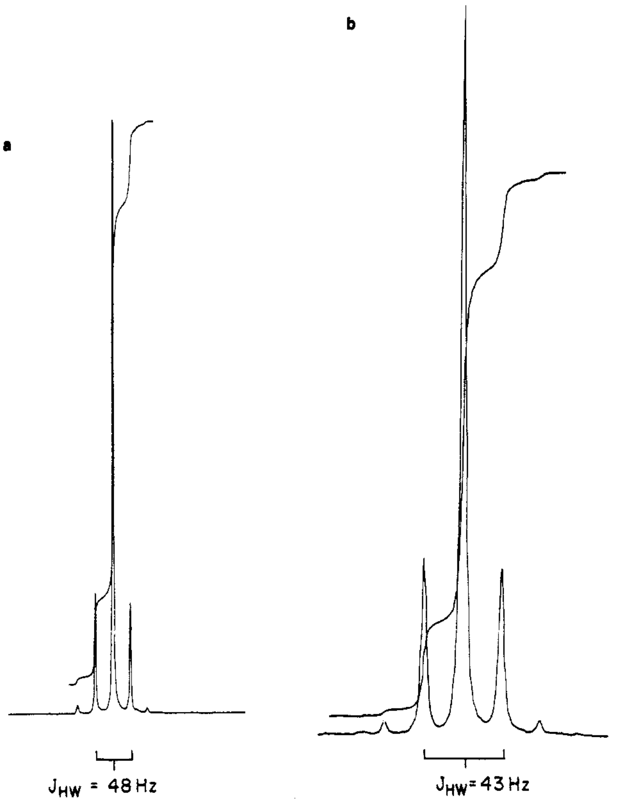


Figure 1. The hydride signal in the ^1H NMR spectrum of (a) $[WCp^*H_4]_2$ at 25 °C and (b) $[WCp^*H_3]_3$ at 60 °C.

The yield of $[WCp^*H_4]_2$ depends critically upon the reaction temperature, upon the mode of addition of $LiAlH_4$, and especially upon the conditions of the alcoholysis step. When $LiAlH_4$ is added to $[WCp^*Cl_4]_2$ stepwise in ether at room temperature, orange $[WCp^*Cl_4]_2$ dissolves, gas evolves (presumably hydrogen), and an intense emerald green solution results. The next discernible stage is a deep red solution. When more than 5 equiv of $LiAlH_4$ have been added, a white solid remains suspended in a nearly colorless solution. So far we have only been able to identify the green material present at the first stage. It can be prepared independently by reducing $[WCp^*Cl_4]_2$ with sodium amalgam in toluene (2Na/W) or with $LiBEt_3H$ in THF (2 equiv/W).[6] We propose that it is $[WCp^*Cl_2]_2$, probably with four bridging chloride ligands. $[WCp^*Cl_2]_2$ does react with $LiAlH_4$ to give the nearly colorless end product that yields $[WCp^*H_4]_2$ in 40–50% yield upon methanolysis at −78 °C. So far other hydride sources such as $NaBH_4$, $NaAl(OCH_2CH_2OCH_3)_2H_2$, $LiBEt_3H$, LiAl(O-*t*-Bu)$_3$H, or KH yield no significant amount of $[WCp^*H_4]_2$ in reactions similar to those employing $LiAlH_4$.

$[WCp^*D_4]_2$ can be obtained by employing $LiAlD_4$ and hydrolyzing with CH_3OD. If CH_3OH is employed in the hydrolysis step, then the product shows a hydride resonance of area ~3/Cp* group that is shifted upfield only slightly to −0.38 ppm; i.e., the average product composition is approximately $[WCp^*H_3D]_2$. An upfield shift of only ~0.04 ppm for the hydride resonance probably can be ascribed solely to a normal isotope effect, not to a preference for H to spend more time in the bridging vs. terminal positions. It is possible that the chemical shift difference between the signals for the bridging hydrides and that (or those) for the terminal hydrides in a static structure is not great enough to cause a marked shift in the average signal upon partially substituting D for H.

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[3] (a) Pederson, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808. (b) Schrock, R. R.; Pederson, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574.

[4] (a) Holmes, S. J.; Schrock, R. R. *Organometallics* **1983**, *2*, 1463. (b) Murray, R. C.; Blum, L.; Liu, A. H.; Schrock, R. R. *Organometallics* **1985**, *4*, 953.

[5] MacLaughlin, S. A.; Murray, R. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1985**, *4*, 796.

[6] Okuda, J.; Murray, R. C.; Schrock, R. R., unpublished results.

Table I. ^1H NMR Data (C_6D_6, 25 °C) for the Hydride Signal in Complexes of the Type $[W(\eta^5\text{-}C_5R_4R')H_4]_2$

C_5R_4'	δ(WH)	J_{HW}, Hz
C_5Me_5	−0.34	48.4
C_5Me_4Et	−0.41	48.4
C_5Me_4-*n*-Pr	−0.40	48.4
C_5Me_4-*t*-Bu	−0.81	48.6
C_5Et_5	−0.85	48.7
C_5Et_4-*t*-Bu	−1.28	48.7

Dimeric species analogous to $[WCp^*H_4]_2$ in which the cyclopentadienyl ring system is C_5Me_4Et, C_5Me_4-*n*-Pr, C_5Me_4-*t*-Bu, C_5Et_5, or C_5Et_4-*t*-Bu can be prepared by analogous methods from the tetrachlorides. All are obtained as brown crystalline complexes, except for $[W(\eta^5\text{-}C_5Me_4\text{-}n\text{-}Pr)H_4]_2$, which is an oil at room temperature. All can be purified by column chromatography on silica or deactivated alumina. The IR spectra all show a band at ~1890 cm^{-1} and the ^1H NMR spectra a sharp hydride signal further upfield than where it is found in $[WCp^*H_4]_2$ as shown in Table I. Structural differences could account for the different chemical shift of the average hydride resonance as the ring's substituents become bulkier, but if this is the case, we suspect that such differences are likely to be relatively subtle. As we shall see later in a related molecule, the coupling constants of terminal hydrides to ^{183}W are rather different from the coupling constants of bridging hydrides. The fact that the average coupling constants (Table I) are so similar is good evidence that the gross structures of these molecules are virtually identical.

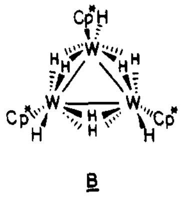
If one treats a mixture of $[WCp^*Cl_4]_2$ and $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Cl_4]_2$ with $LiAlH_4$, or a mixture of "$[WCp^*Cl_2]_2$" and "$[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Cl_2]_2$" with $LiAlH_4$, then the resulting tetrahydride complexes that are obtained are $[WCp^*H_4]_2$, $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_4]_2$, and $W_2Cp^*(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_8$, judging from the 1:1:1 pattern of hydride resonances (that for the cross-over product being at −0.62 ppm). Since we know that once a dimeric octahydride is formed, it does not readily break into monomeric fragments (see below), scrambling must occur before the octahydride is formed, possibly early in the reaction. For example, since we know that $[WCp^*Cl_4]_2$ can be cleaved readily by donor ligands such as PMe_3 or pyridine, $W_2Cp^*(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Cl_8$ may form readily when $[WCp^*Cl_4]_2$ and $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Cl_4]_2$ are mixed.

Hydrogenation of WCp^*Me_4. In pentane WCp^*Me_4 reacts with H_2 at 200–1500 psi to give a mixture of $[WCp^*H_4]_2$ and dark blue $[WCp^*H_3]_3$ (eq 2). They can

$$WCp^*Me_4 + H_2 \rightarrow [WCp^*H_4]_2 + [WCp^*H_3]_3 \quad (2)$$

be separated by column chromatography on deactivated alumina and isolated as pure crystals in ~10% yield for $[WCp^*H_4]_2$ and ~40% yield for $[WCp^*H_3]_3$. Other products have not yet been identified. Intractable mixtures result if the H_2 pressure is less than 200 psi. Increasing the pressure or varying the reaction time or temperature (0–25 °C) does not alter the 4:1 ratio of $[WCp^*H_3]_3$ to $[WCp^*H_4]_2$, or the total yield, to any significant extent. $[WCp^*H_3]_3$ is also formed in trace amounts in the reaction between $[WCp^*Cl_4]_2$ and $LiAlH_4$.

The ^1H NMR spectrum of $[WCp^*H_3]_3$ shows only one Cp* resonance at 2.33 ppm and one hydride resonance, a broadened singlet of area 9, at −1.65 ppm. At 60 °C the hydride resonance is sharp and two sets of ^{183}W satellites of intensities ~30% and ~2.5% are observed, as would be expected for a trimeric species in which all hydrides are coupled to all ^{183}W centers equally ($^{184}W_2{}^{183}W$ = 31.3% of mixture; $^{184}W^{183}W_2$ = 5.0%; Figure 1b). As the temperature is lowered to −90 °C (400 MHz), the hydride resonance broadens and at least four broad ones arise. But the Cp* resonance only splits into two in a ratio of 2:1. The static structure must be one containing only two types of Cp* ligands and at least four types of hydride ligands. A triangular framework seems plausible on the basis of the fact that several trimeric W(IV) complexes have been shown to be triangular species.[7] An attractive possibility is structure, B, in which there are six different hydrides

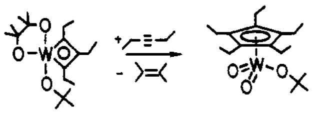


B

(1:1:1:2:2:2). It is plausible, even expected, that several hydride signals would overlap to give the observed pattern.

The IR spectrum of $[WCp^*H_3]_3$ is consistent with the presence of terminal hydrides in a more complex structure than that found for $[WCp^*H_4]_2$. Two medium strength bands are found at 1885 and 1838 cm^{-1}; the latter has a shoulder at 1850 cm^{-1}. In the spectrum of $[WCp^*D_3]_3$ only one band at 1315 cm^{-1} can be assigned unambiguously to a W–D mode.

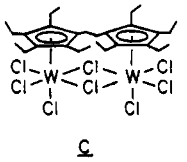
Preparation and X-ray Structure of $[WH_4]_2(\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$ ($\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4 = Cp^2$). One of the main goals of this research is to explore the differences between the systems we have just described and analogous systems containing linked cyclopentadienyl rings. The preparation of peralkylated linked cyclopentadienyl ring systems became possible as a result of the reactions shown in eq 3[3] and 4;[4b] use of 3,7-decadiyne yields



(3)

$$W(\eta^5\text{-}C_5Et_5)O_2(O\text{-}t\text{-}Bu) \xrightarrow[CH_2Cl_2]{PCl_5} [W(\eta^5\text{-}C_5Et_5)Cl_4]_2 \quad (4)$$

analogous linked complexes containing the "linked" system $\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4$ (Cp^2).[5] The exact nature of $[WCl_4]_2Cp^2$ is still unknown. It is highly insoluble but readily forms a soluble green PMe_3 adduct, $[WCl_4(PMe_3)]_2Cp^2$, a structural study of which confirmed that the configuration about each metal is pseudooctahedral and that the two metal centers are independent.[5] $[WCl_4]_2Cp^2$ itself may be either a molecule of type C or



C

a related polymeric species. In either case, there is no significant electron pairing between the W(V) centers; all tetrachloro W(V) complexes are paramagnetic.

When $[WCl_4]_2Cp^2$ is treated with a large excess of $LiAlH_4$ in ether and the reaction is worked up in a manner

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[7] (a) Cotton, F. A.; Lay, D. G.; Felthouse, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 1431. (b) Bino, A.; Cotton, F. A.; Dori, Z.; Koch, S.; Küppers, H.; Millar, M.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3245. (c) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1979**, *101*, 3842. (d) Ardon, M.; Cotton, F. A.; Dori, Z.; Fang, A.; Kapon, M.; Reisner, G. M.; Shaia, M. *J. Am. Chem. Soc.* **1982**, *104*, 5394. (e) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 3683. (f) Chisholm, M. H.; Folting, K.; Heppert, J. A.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1234.

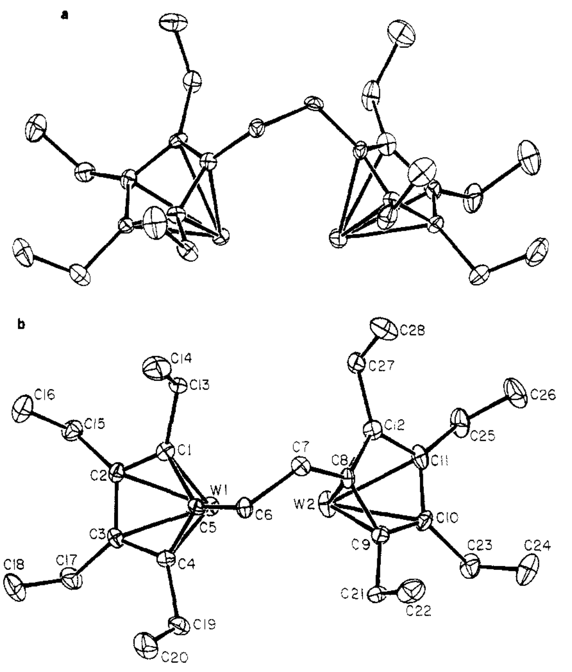

Figure 2. Ortep drawing of $[WH_4]_2(\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$ at −50 °C (30% probability ellipsoids; hydrogen atoms omitted): (a) side view; (b) top view with atom labels. The molecule possesses no crystallographically imposed symmetry. The toluene of crystallization is not shown.

analogous to that used to prepare $[WCp^*H_4]_2$, the related red-brown crystalline complex with the formula $[WH_4]_2Cp^2$ can be isolated in 10–15% yield after column chromatography on deactivated alumina. $[WH_4]_2Cp^2$ is soluble in toluene, from which it can be crystallized as a toluene solvate, and slightly soluble in pentane and ether. It decomposes in dichloromethane to give an as yet unidentified precipitate. Unfortunately, we have never been able to obtain $[WH_4]_2Cp^2$ in greater than 15% yield by varying reaction conditions, and the yield is variable, at times <5%. No other product can be isolated in significant yield, although traces of a paramagnetic purple crystalline material, as well as a diamagnetic hydride complex (δ(H) −0.77), are observed. They have not been identified. Peculiarly, hydrogenation of $[WMe_4]_2Cp^2$ (see Experimental Section) at pressures up to 1000 psi in toluene or tetrahydrofuran yielded no identifiable products, not even a trace of $[WH_4]_2Cp^2$. This result is at least consistent with the fact that $[WCp^*H_4]_2$ is only a minor product of the hydrogenation of WCp^*Me_4 (vide supra).

NMR and IR spectra of $[WH_4]_2Cp^2$ suggest that the essential features of its structure are analogous to those for $[WCp^*H_4]_2$. The hydride signal is found at 0.84 ppm with ^{183}W satellites of relative intensity ~25% of the total and J_{HW} = 44 Hz. The IR spectrum shows a medium strength band at 1855 cm^{-1}. An FD mass spectrum suggests that the molecule is not of the type $[W_2Cp^2H_8]_x$ where $x \geq 2$.

An X-ray structural study of $[WH_4]_2Cp^2$ at −50 °C showed the molecule to contain two linked tungsten centers 2.591 (1) Å apart (Figure 2; Table II). Considerable effort was expended to unambiguously locate bridging or terminal hydride ligands using a data set collected at −180 °C, but without success (see Experimental Section). The Cp^2 unit is slightly skewed, and the dihedral angle between the C_5 ring planes is 79.7°. The angles at the bridging methylene carbon atoms (119 (1)° and 120 (1)°) are significantly larger than expected, perhaps indicative of some torsional strain in the C_2H_4 bridging unit. The C–C bond length in the C_2H_4 bridge (1.53 (1) Å) is entirely normal.

Table II. Selected Bond Distances (Å) and Angles (deg) in $[WH_4]_2(\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$ at −50 °C

W(1)-W(2)	2.591 (1)	C(6)-C(7)	1.53 (1)
W(1)-C(1)	2.316 (8)	C(7)-C(8)	1.55 (1)
W(1)-C(2)	2.367 (8)	C(1)-C(13)	1.51 (1)
W(1)-C(3)	2.387 (8)	C(13)-C(14)	1.55 (1)
W(1)-C(4)	2.329 (8)	C(2)-C(15)	1.53 (1)
W(1)-C(5)	2.307 (8)	C(15)-C(16)	1.48 (1)
W(2)-C(8)	2.282 (9)	C(5)-W(1)-W(2)	97.4 (2)
W(2)-C(9)	2.323 (9)	C(8)-W(2)-W(1)	101.3 (2)
W(2)-C(10)	2.342 (9)	C(5)-C(6)-C(7)	120 (1)
W(2)-C(11)	2.361 (9)	C(6)-C(7)-C(8)	119 (1)
W(2)-C(12)	2.319 (10)	C(1)-C(13)-C(14)	113 (1)
C(5)-C(6)	1.52 (1)	C(2)-C(15)-C(16)	115 (1)

Table III. Final Positional Parameters for the Non-Hydrogen Atoms in $[WH_4]_2(\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$ at −50 °C[a]

atom	*x*	*y*	*z*
W(1)	0.56630 (3)	0.23182 (3)	0.08843 (5)
W(2)	0.38298 (3)	0.21167 (3)	0.04191 (5)
C(1)	0.6548 (6)	0.3153 (6)	−0.1062 (11)
C(2)	0.7236 (6)	0.2963 (6)	0.0122 (11)
C(3)	0.7003 (6)	0.2019 (6)	−0.0007 (11)
C(4)	0.6123 (6)	0.1600 (6)	−0.1308 (11)
C(5)	0.5840 (6)	0.2294 (6)	−0.1987 (11)
C(6)	0.5068 (6)	0.2159 (6)	−0.3578 (11)
C(7)	0.4350 (6)	0.2650 (6)	−0.3609 (11)
C(8)	0.3587 (6)	0.2411 (6)	−0.2385 (11)
C(9)	0.2854 (6)	0.1536 (6)	−0.2271 (12)
C(10)	0.2237 (6)	0.1677 (7)	−0.1138 (12)
C(11)	0.2551 (7)	0.2612 (7)	−0.0602 (12)
C(12)	0.3389 (7)	0.3079 (7)	−0.1336 (12)
C(13)	0.6611 (7)	0.4082 (6)	−0.1469 (13)
C(14)	0.6987 (9)	0.4333 (8)	−0.3185 (16)
C(15)	0.8113 (7)	0.3670 (7)	0.1302 (13)
C(16)	0.8983 (7)	0.4072 (8)	0.0479 (16)
C(17)	0.7561 (7)	0.1535 (8)	0.0979 (14)
C(18)	0.8412 (8)	0.1506 (9)	0.0146 (16)
C(19)	0.5654 (7)	0.0606 (7)	−0.1923 (13)
C(20)	0.6072 (8)	0.0347 (8)	−0.3424 (15)
C(21)	0.2669 (7)	0.0668 (7)	−0.3342 (15)
C(22)	0.2129 (9)	0.0623 (8)	−0.5172 (14)
C(23)	0.1339 (7)	0.0940 (8)	−0.0711 (14)
C(24)	0.0411 (8)	0.0759 (9)	−0.2000 (16)
C(25)	0.2067 (8)	0.3049 (9)	0.0554 (14)
C(26)	0.1300 (9)	0.3359 (9)	−0.0428 (16)
C(27)	0.3913 (7)	0.4076 (7)	−0.1198 (14)
C(28)	0.3597 (9)	0.4499 (9)	−0.2731 (18)
C(29)	0.1873 (11)	0.7504 (13)	0.4183 (19)
C(30)	0.0857 (10)	0.7207 (11)	0.4579 (15)
C(31)	0.0500 (11)	0.7844 (10)	0.5152 (19)
C(32)	−0.0427 (13)	0.7575 (13)	0.5596 (19)
C(33)	−0.0988 (12)	0.6653 (14)	0.5456 (19)
C(34)	−0.0629 (14)	0.6025 (14)	0.486 (2)
C(35)	0.0279 (12)	0.6306 (11)	0.4426 (17)

[a] Numbers in parentheses are errors in the last significant digit(s).

These values should be compared with those obtained for the only other structurally characterized bimetallic complex containing cyclopentadienyl rings linked by a two-carbon unit ($[Fe(CO)_2]_2[C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4]$[8]), 110.5 (6)°, 116.5 (6)°, and 1.54 (10) Å, respectively. *Mononuclear* titanium and zirconium dichloride complexes containing the η^5,η^5-$Me_4C_5CH_2CH_2C_5Me_4$ ligand have been reported recently.[9] The angles at the bridging carbon atoms are 111° and 113°, and the C–C bond length is 1.54 Å. The origin of the apparent strain at the bridging carbon atoms in $[WH_4]_2Cp^2$ is not obvious, as models show that the ligand can bind

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(8) Stephens, F. S. *J. Chem. Soc. A* **1970**, 1722.

(9) Wochner, F.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 69.

apparently strain-free to a single metal or to two metals up to ~5-Å apart.

Attempts to slow down the rate of hydride exchange in $[WH_4]_2Cp^2$ were unsuccessful. At 400 MHz and −90 °C the hydride signal was only slightly broadened; i.e., the rate of hydride exchange in the Cp^2 system appears to be grater than it is in $[WCp^*H_4]_2$. In spite of this fact we are not inclined to postulate any structure other than one in which there are two bridging hydride ligands and six terminal hydrides. Even in the absence of any detailed knowledge of the mechanism of hydride exchange, we can speculate that different rates of hydride exchange in $[WH_4]_2Cp^2$ and $[WCp^*H_4]_2$ could result from the fact that the Cp* ligands are more likely to be transoid in $[WCp^*H_4]_2$, while they are cisoid in $[WH_4]_2Cp^2$.

Some Reactions of Dimeric Octahydrides. A mixture of $[WCp^*H_4]_2$ and $[W(\eta^5\text{-}C_5Et_5)H_4]_2$ or $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_4]_2$ in C_6D_6 after 1 day showed only the hydride signals for starting materials. After 12 h at 80 °C signals for the crossover products $W_2Cp^*(\eta^5\text{-}C_5Et_5)H_8$ or $W_2Cp^*(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_8$ are observed, but their intensity never reaches that expected relative to the starting materials. We assume this result is due to the fact that decomposiiton is extensive at this point (~50%). If we assume that cyclopentadienyl rings do not scramble, then crossover most likely proceeds by fragmentation of the dimeric units. Decomposition of the monomeric fragments (e.g., loss of H_2) would assure that 100% dimers could not reform. (Note that no $[WCp^*H_3]_3$ is observed upon heating a solution of $[WCp^*H_4]_2$ under the same conditions, conditions where $[WCp^*H_3]_3$ is relatively stable.) On the basis of these results we can safely assume that thermally induced fragmentation of octahydride dimers is relatively slow.

A solution containing $[WCp^*D_4]_2$ and $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_4]_2$ in C_6D_6 at 25 °C shows a broad hydride signal for each of the two partially deuterated hydrides $[WCp^*H_xD_{4-x}]_2$ and $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_xD_{4-x}]_2$ but no signal for $W_2Cp^*(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_xD_{4-x}$. This H/D exchange does not proceed by loss and readdition of H_2 or D_2, as a C_6D_6 solution of $[WCp^*H_4]_2$ under D_2 (60 psi) at 25 °C shows negligible incorporation of D in 24 h. Therefore, H and D most likely scramble in an intermediate that contains H or D bridges between dimers, i.e., a tetrametallic species. We feel that an approximately linear arrangement of the four metals is more likely than a W_4 ring or tetrahedron related to the proposed $[WCp^*H_3]_3$ structure but have no evidence to back up that proposal at this time. It is interesting to note that facile H/D scrambling between complexes of the type $[TaCp^*Cl_2H]_2$ and $[TaCp'Cl_2D]_2$ (Cp′ = e.g., $\eta^5\text{-}C_5Me_4Et$) was observed, as well as halide scrambling between analogous chloride and bromide species.[1] In each case a bimolecular reaction between dimeric species to give intermediates containing new bridging hydrides, deuterides, or halides was proposed.

$[WCp^*H_4]_2$ reacts with CO at 60–1000 psi in pentane at 25 °C to give $[WCp^*(CO)_2H]_2$ quantitatively. NMR and IR data are in full agreement with those reported by Alt, who first prepared $[WCp^*(CO)_2H]_2$ by hydrogenating $WCp^*(CO)_3H$ under photochemical conditions.[10] Since we could not detect any organic product(s) by ^1H NMR, we assume that hydrogen is lost in the process (eq 5).

$$[WCp^*H_4]_2 + 4CO \rightarrow [WCp^*(CO)_2H]_2 + 3H_2 \quad (5)$$

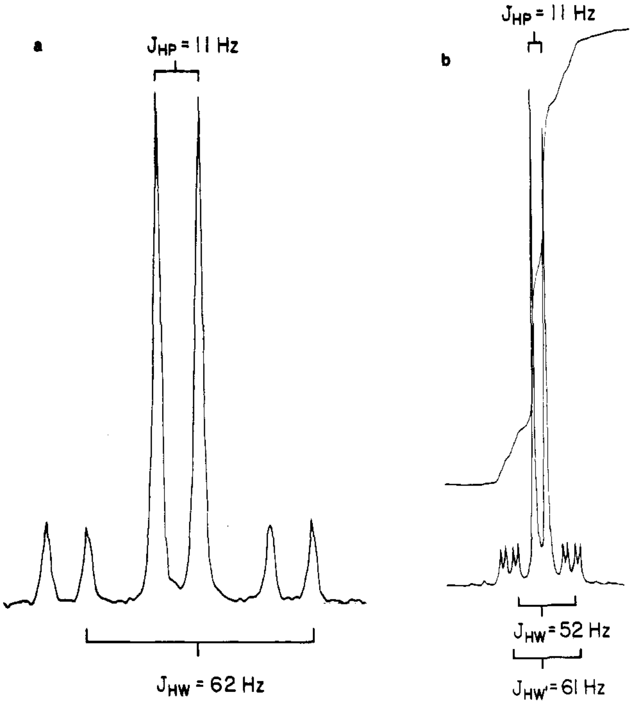

Figure 3. The hydride signal in the ^1H NMR spectrum of (a) $W_2Cp^*_2H_6(PMe_3)$ at 100 °C and (b) $W_2Cp^2H_6(PMe_3)$ at 25 °C.

Substitution of H_2 by CO is common in polyhydride complexes,[11] and the reaction that is to be expected. The carbonylation takes place without fragmenting the dimer, since a mixture of $[WCp^*H_4]_2$ and $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_4]_2$ is carbonylated to give a mixture of $[WCp^*(CO)_2H]_2$ and $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)(CO)_2H]_2$; no $W_2Cp^*(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)(CO)_4H_2$ could be detected by ^1H NMR (~5% detectable). The control experiment showed that a mixture of $[WCp^*H_4]_2$, $W_2Cp^*(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_8$, and $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_4]_2$ was carbonylated to the expected mixture of products.

One of the most interesting results, the first of what may be some important differences between the reactions of $[WCp^*H_4]_2$ and those of $[WH_4]_2Cp^2$ is the fact that $[WH_4]_2Cp^2$ does *not* react with CO at 25 °C up to a pressure of 750 psi. Since $[WCp^*H_4]_2$ does not fragment when it reacts with CO, the lack of reaction between $[WH_4]_2Cp^2$ and CO cannot be ascribed solely to the fact that the hydride-bridged structure in $[WH_4]_2Cp^2$ is less likely to be broken up to give isolated tungsten centers than that in $[WCp^*H_4]_2$.

$[WCp^*H_4]_2$ reacts with excess PMe_3 in ether/pentane at 25 °C to give brown $W_2Cp^*_2H_6(PMe_3)$ which can be isolated from pentane in >80% yield (eq 6). The ^1H NMR

$$[WCp^*H_4]_2 \xrightarrow{\text{excess } PMe_3} W_2Cp^*_2H_6(PMe_3) \quad (6)$$

spectrum of $W_2Cp^*_2H_6(PMe_3)$ shows two signals for the Cp* groups and a single broad doublet hydride resonance at −0.91 ppm. At 100 °C two Cp* signals are still observed (implying that PMe_3 exchange between W and W′ is slow), and the hydride signal is now a sharp doublet (J_{HP} = 11.5 Hz) with one set of ^{183}W satellite peaks (Figure 3a). Although the tungsten centers are different and all hy-

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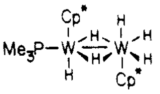
[10] Alt, H. G.; Mahmoud, K. A.; Rest, A. J. *Angew. Chem.* **1983**, *95*, 569; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 544; *Angew. Chem. Suppl.* **1983**, 803.

[11] Examples for group 5 metals: (a) Schrock, R. R. *J. Organomet. Chem.* **1976**, *121*, 373. (b) Mayer, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 2157. Examples for group 6 metals: (c) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1981**, 1204. Examples for group 7 metals: (d) Girolami, G. S.; Howard, C. G.; Wilkinson, G.; Dawes, H. M.; Thornton-Pett, M.; Montevalli, M.; Hursthouse, M. B. *Ibid.* **1985**, 921.

drides see each tungsten center, J_{HW} must be essentially the same as $J_{HW'}$. When the sample is cooled to -90 °C, the hydride signal collapses to yield three resonances at 0.86, -2.02, and -5.52 ppm in a ratio of ~3:2:1. That at -2.02 ppm (area 2) is a doublet with $J_{HP} \approx 50$ Hz. If two bridging hydrides are still present, then the signal at -2.02 ppm can be ascribed to them. The PMe_3 ligand on the tungsten center that has only one hydride attached to it must be roughly *trans* to the bridging hydrides in order to account for the relatively large J_{HP} of 50 Hz. We have placed the single hydride trans to the Cp* ligand in order that J_{HP} be small and that the bridging hydrides be equivalent. The result is shown schematically as D. The only significant problem with this postulated structure is that the three terminal hydrides on the right-hand W cannot occupy equivalent positions. Either they are still exchanging rapidly at -90 °C or their chemical shifts are too similar.



D

$[WH_4]_2Cp^2$ also reacts with PMe_3 to give a brown crystalline monophosphine adduct, $W_2Cp^2H_6(PMe_3)$, practically quantitatively. In the 25 °C ^1H NMR spectrum of $W_2Cp^2H_6(PMe_3)$ a sharp doublet hydride resonance is observed at -2.49 ppm flanked by *two* sets of ^{183}W satellite peaks since J_{HW} (60.7 Hz) and $J_{HW'}$ (52.1 Hz) are no longer identical (Figure 3b). Apparently the hydrides again are more mobile in the Cp^2 system, and now perhaps because the C_5 rings are cisoid instead of transoid, the coupling of the hydrides to one tungsten is significantly different from the coupling to the other tungsten. The Cp^2 ligand gives rise to a relatively complex set of signals, but one consistent with the inequivalence of the two ends of the molecule.

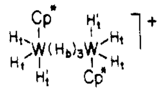
During the preparation of $W_2Cp*_2H_6(PMe_3)$ using a large excess of PMe_3 traces of $WCp*H_5(PMe_3)$ are observed. Under H_2 pressure (60 psi) at 60 °C in toluene it is possible to convert $W_2Cp*_2H_6(PMe_3)$ in the presence of PMe_3 slowly to $WCp*H_5(PMe_3)$. Colorless $WCp*H_5(PMe_3)$ can be obtained straightforwardly in 40% yield by reacting monomeric $WCp*Cl_4(PMe_3)$ with excess $LiAlH_4$ in ether in a manner analogous to that used to prepare $[WCp*H_4]_2$. It can be purified by column chromatography on silica gel. Its NMR and IR spectra (δ(H) -2.56 (J_{HP} = 41.5 Hz, J_{HW} = 42.3 Hz); ν_{WH} = 1838 cm^{-1}) are similar to those of the η^5-C_5H_5 analogue reported by Green.[12] A monomeric structure is suggested by the FD mass spectrum which shows an ion that can be assigned as $M^+ - 2H$.

$[WH_5(PMe_3)]_2Cp^2$ can also be prepared in modest yield by treating $[WCl_4(PMe_3)]_2Cp^2$ with $LiAlH_4$. However, it cannot be prepared by treating $W_2Cp_2H_6(PMe_3)$ with H_2 in the presence of excess PMe_3 in toluene (80 °C, 60 psi).

Protonation of $[WCp*H_4]_2$. When 1 equiv of HBF_4·ether is added to $[WCp*H_4]_2$ at -80 °C, a white precipitate forms rapidly and quantitatively. The product $[W_2Cp*_2H_9]BF_4$ is soluble in acetone, acetonitrile, dichloromethane, or methanol, but such solutions quickly turn brown at 25 °C (no product can be identified), a process that is not significantly slower under 1 atm of molecular hydrogen. Addition of NEt_3 to $[W_2Cp*_2H_9]^+$ yields $[WCp*H_4]_2$ quantitatively. Attempts to prepare a cationic species by adding HCl to $[WCp*H_4]_2$ yielded only insoluble, unidentifiable green precipiates.

The ^1H NMR spectrum of $[W_2Cp*_2H_9]BF_4$ at 25 °C in acetone shows broad hydride resonances at ~2.8 ppm (area 2) and ~-2.2 ppm (area 3). At -30 °C in CD_2Cl_2, however, a well-resolved spectrum showing three hydride resonances is obtained (Figure 4). The intense satellites of the quintet resonance at -2.30 ppm (area 3) are consistent only with this signal being associated with bridging hydrides that are coupled to four other hydrides. Note the large value for J_{HW} (72 Hz), nearly twice that for the terminal hydride ligands in this molecule and in related species such as $WCp*H_5(PMe_3)$ (J_{HW} = 42 Hz). The quartet signal for the four terminal hydrides to which the three bridging hydrides are coupled is found at 2.24 ppm. Unfortunately, only the upfield ^{183}W satellite can be observed, but its intensity, along with the more normal value for J_{HW}, leave little doubt that the 2.24 ppm signal can be ascribed to terminal hydrides. Finally, a singlet ascribable to two terminal hydrides is found at 2.65 ppm with J_{HW} = 44 Hz. We must propose that the three bridging hydrides, which cannot be equivalent formally in any structure, are still exchanging rapidly with each other at this temperature (-30 °C) where bridge/terminal exchange is relatively slow on the NMR time scale.

An attractive proposed structure for $[W_2Cp*_2H_9]^+$ is E, obtained by adding a proton to the W-W bond in A. It seems plausible that H_t can be coupled to H_b, while H_t' is not coupled to any significant extent to either. It is interesting to compare this structure with D where two bridging hydrides are strongly coupled to phosphorus ($J_{HP} \approx 50$ Hz) while the unique hydride cis to the phosphine ligand (trans to Cp*) is not coupled strongly to phosphorus. It is also interesting to note that if one uses the values found for J_{H_tW}, $J_{H_t'}$, and J_{H_bW} in $[W_2Cp*_2H_9]^+$ to calculate an average J_{HW} for the *parent* $[WCp*H_4]_2$ (assuming structure A), then the answer is 48 Hz, essentially that which is found (Table I).



E

Since triethylamine deprotonates $[W_2Cp*_2H_9]^+$ so easily, we suspect that $[W_2Cp*_2H_9]^+$ might lose a proton in a polar solvent to give highly fluxional $[WCp*H_4]_2$. Intramolecular bridge/terminal hydride exchange in $[W_2Cp*_2H_9]^+$, if it could be observed, therefore might be quite slow relative to what it is in $[WCp*H_4]_2$. We might then propose that it *is* slow in $[W_2Cp*_2H_9]^+$ because three bridging hydrides are present or, alternatively, that it is fast in $[WCp*H_4]_2$ because a terminal hydride (most likely the equivalent of H_t' in the parent molecule A) can move easily into a bridging position to give an unsymmetrical intermediate containing three bridging hydrides and a total of five terminal hydrides.

Discussion

The reaction of early transition-metal halides with $LiAlH_4$ or other main-group hydride reagents is one of the most common methods for the preparation of polyhydride complexes.[13] However, the mechanistic details of this transformation remain unclear, and only recently[14] has it

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[12] Green, M. L. H.; Parkin, G. *J. Chem. Soc., Chem. Comm.* **1984**, 1467.

[13] (a) Muetterties, E. L., Ed. *Transition Metal Hydrides*; Marcel Dekker: New York, 1971. (b) Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415.

[14] (a) Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3508. (b) Davies, S. G.; Moon, S. D.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1278.

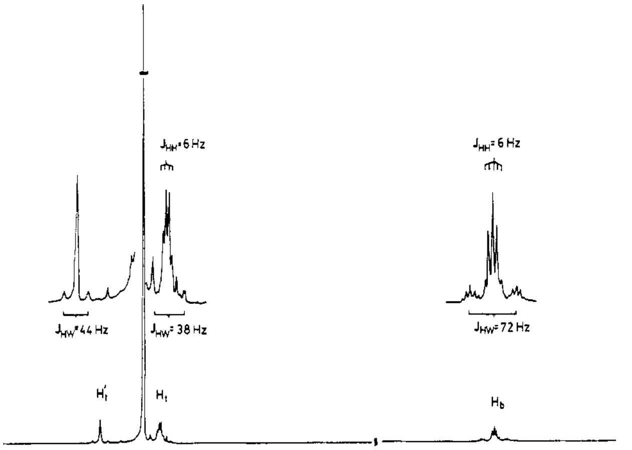

Figure 4. The 400-MHz ^1H NMR spectrum of $[W_2(\eta^5\text{-}C_5Me_5)_2H_9]BF_4$ in CD_2Cl_2 at −30 °C.

been recognized that the metal complex is oxidized by hydrogen generated during the hydrolysis step. Thus it seems that a crucial reaction is the formation and hydrolysis of an intermediate aluminohydride[15] or borohydride[14] complex. In this respect it makes sense that $[WCp^*Cl_4]_2$ is first reduced to a tungsten(III) aluminohydride complex that is then hydrolyzed to yield a tungsten(V) hydride product. We have few good ideas as to why this reaction sequence (apparently) cannot proceed in an analogous fashion in the system containing the Cp^2 system. One possibility is that the aluminohydride ligand system forms on metal centers that are turned away from one another and that upon hydrolysis an oligomeric system forms that contains hydrides bridging between tungsten centers that are not linked also through the Cp^2 ligand system.

To our knowledge $[WCp^*H_4]_2$ is the only example of a W(V) dimer containing one or more hydride ligands (we assume two) in the bridging positions. On the basis of the compound's diamagnetism and relatively short W–W bond (in $[WH_4]_2Cp^2$) compared to other W(V) dimers[16] the best description is that a single W–W bond is present. $[WCp^*H_4]_2$ could be viewed as being derived from $[Cp^*H_3W{\equiv}WCp^*H_3]^{2-}$, with an 18e count around each metal center, by addition of two protons to the W≡W bond.[17] Therefore, unlike $[TaCp^*Cl_2H]_2$, $[WCp^*H_4]_2$ is electronically saturated, at least as long as the two hydrides remain in bridging positions. Like $[TaCp^*Cl_2H]_2$, however, cleavage of the M–M bond in $[WCp^*H_4]_2$ to give odd-electron monomeric fragments is not facile. This behavior contrasts with that of $Rh_2Cp^*{}_2Cl_3H$ and $Ir_2Cp^*{}_2Cl_3H$ which rapidly form the mixed dimer $RhIrCp^*{}_2Cl_3H$ at ambient temperatures.[18] It is also known that $[IrCp^*H_2]_2$ is cleaved by PMe_3 to give $IrCp^*H_2(PMe_3)$.[19] In both the Rh and Ir systems, however, even-electron, M(III) fragments result when the dimer is cleaved.

To us, one of the more interesting findings of this study is that some features of the chemistry of $[WH_4]_2Cp^2$ are different from those of $[WCp^*H_4]_2$. Most dramatic is the fact that $[WH_4]_2Cp^2$ does not react readily with CO to yield a molecule analogous to $[WCp^*(CO)_2H]_2$. Since we do not yet know the gross structure of $[WCp^*H_4]_2$ (we assume the Cp* ligands are transoid), we cannot begin to formulate a reason for the differing reactivity. We believe that there are other examples of differing reactivity of the "linked" system in the offing and therefore will continue to explore the "linked" and "unlinked" systems side by side, if a suitable preparation of $[WH_4]_2Cp^2$ can be found.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres HE43-2 drybox or by using standard Schlenk techniques. Reagent grade ether, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl under nitrogen. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Methanol was distilled from magnesium methoxide under nitrogen. All deuterated NMR solvents were passed through a column of activated alumina. Chromatography adsorbants (Davidson-brand silica gel and Camag-brand alumina) were dried at 150 °C and kept under vacuum overnight. Alumina was deactivated by adding 7% water.

PMe_3 was prepared by the method of Wolfsberger and Schmidbaur[20a] in dibutyl ether.[20b] $[W(\eta^5\text{-}C_5R_4R')Cl_4]_2$ compounds were prepared by treating $W(\eta^5\text{-}C_5R_4R')(CO)_3Me$ with PCl_5 ($\eta^5\text{-}C_5Me_5$; $\eta^5\text{-}C_5Me_4Et$; $\eta^5\text{-}C_5Me_4\text{-}n\text{-}Pr$),[4b] by treating $W(C\text{-}t\text{-}Bu)(dme)Cl_3$ with $RC{\equiv}CR$ ($\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu$; $\eta^5\text{-}C_5Et_4\text{-}t\text{-}Bu$),[3] or by treating $W(\eta^5\text{-}C_5Et_5)(O\text{-}t\text{-}Bu)O_2$ in dichloromethane with 3 equiv of PCl_5. $W(\eta^5\text{-}C_5Me_5)Cl_4(PMe_3)$ and $W(\eta^5\text{-}C_5Me_5)Me_4$ were prepared as described before.[4b]

NMR data are listed in parts per million (positive downfield) relative to Me_4Si for ^1H and ^{13}C and relative to 85% H_3PO_4 for ^{31}P. Coupling constants are quoted in hertz. Obvious multiplicities and aliphatic coupling constants in the range 125–130 Hz are not noted specifically. Spectra were obtained in C_6D_6 at 25 °C unless otherwise noted.

Preparation of Compounds. $[W(\eta^5\text{-}C_5Me_5)H_4]_2$. Solid $LiAlH_4$ (865 mg, 22.8 mmol) was slowly added to a suspension of $[WCp^*Cl_4]_2$ (1.5 g, 3.3 mmol) in ether (50 mL) at −78 °C. Gas evolved and a dark brown suspension formed. Upon removal of the cooling bath, the mixture turned grass green within 1 h and almost colorless overnight. Methanol (3.0 g, 94 mmol) in 10 mL of ether was added dropwise to this mixture at −78 °C with vigorous stirring. After the viscous mixture was stirred at −78 °C for 1 h, it was warmed to room temperature and stirred for 1 h, during which time the color of the mixture became dark brown. The mixture was filtered through Celite, and the solvent was removed from the filtrate leaving a brown residue. The residue was dissolved in ether, and the solution was passed through a short column of alumina. The column was eluted with pentane/ether (1:1) and the eluate concentrated in vacuo and cooled to −20 °C to give brown platelets (450 mg, 42%): ^1H NMR δ 2.19 (s, 15, C_5Me_5), −0.34 (s, 4, J_{HW} = 48.4, W–H); $^{13}C\{^1H\}$ NMR δ 99.2 (C_5Me_5), 13.2 ($C_5\mathit{Me}_5$); IR (KBr, cm^{-1}) 1900 (sh), 1875 (ms, br, W–H); FD/MS, m/e 646 (^{184}W; expected isotope pattern). Anal. Calcd for $WC_{10}H_{19}$: C, 37.17; H, 5.93. Found: C, 37.22; H, 5.93.

$[W(\eta^5\text{-}C_5Me_5)D_4]_2$. $[WCp^*D_4]_2$ was prepared by reacting $[WCp^*Cl_4]_2$ with a large excess of $LiAlD_4$ and working up with methanol-d_1, as described above for $[WCp^*H_4]_2$.

Other $[WCp'H_4]_2$ Species ($Cp' = C_5Me_4Et$, $C_5Me_4\text{-}n\text{-}Pr$, $C_5Me_4\text{-}t\text{-}Bu$, C_5Et_5, $C_5Et_4\text{-}t\text{-}Bu$). These compounds were pre-

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pared in a manner analogous to that used to prepared [W(η^5-C$_5$Me$_5$)H$_4$]$_2$ and were isolated by column chromatography. The crude material was dissolved in a minimum amount of toluene and placed on an alumina column (1.5 × 15 cm) made up in pentane. Elution with pentane/toluene (1:1) removed a small band of blue green [WCp′H$_3$]$_3$. With use of pentane/ether (1:1) as eluent, a broad brown band was separated and collected. The solvent was evaporated and the residue recrystallized.

[W(η^5-C$_5$Me$_4$Et)H$_4$]$_2$: brown needles from pentane; yield 24%; ^{1}H NMR δ 2.66 (q, 2, *J* = 7.6, C*H*$_2$CH$_3$), 2.24 (s, 6, ring–CH$_3$), 2.19 (s, 6, ring–CH$_3$), 0.82 (t, 3, *J* = 7.6, CH$_2$C*H*$_3$), −0.41 (s, 4, J_{HW} = 48.4, W–H); ^{13}C{^{1}H} NMR δ 104.8 (*C*CH$_2$CH$_3$), 99.7 and 98.7 (*C*CH$_3$), 22.0 (*C*H$_2$CH$_3$), 17.2 (CH$_2$*C*H$_3$), 13.1 and 13.2 (ring–CH$_3$); IR (Nujol, cm^{-1}) 1890 (ms, br, W–H). Anal. Calcd for WC$_{11}$H$_{21}$: C, 39.19; H, 6.28. Found: C, 39.26; H, 6.14.

[W(η^5-C$_5$Me$_4$-*n*-Pr)H$_4$]$_2$: red-brown oil; yield 35%; ^{1}H NMR δ 2.68 (t, 2, *J* = 7.8, C*H*$_2$CH$_2$CH$_3$), 2.26 (s, 6, ring–CH$_3$), 2.20 (s, 5, ring–CH$_3$), 1.22 (sextet, 2, *J* = 7.8, CH$_2$C*H*$_2$CH$_3$), 0.76 (t, 3, *J* = 7.3, CH$_2$CH$_2$C*H*$_3$), −0.40 (s, 4, J_{HW} = 48.4, W–H); ^{13}C{^{1}H} NMR δ 103.6 (*C*CH$_2$CH$_2$CH$_3$), 99.7 and 99.0 (*C*CH$_3$), 30.8 (*C*H$_2$CH$_2$CH$_3$), 26.0 (CH$_2$*C*H$_2$CH$_3$), 14.1 (CH$_2$CH$_2$*C*H$_3$), 13.3 and 13.2 (ring–CH$_3$); IR (Nujol, cm^{-1}) 1890 (ms, br, W–H).

[W(η^5-C$_5$Me$_4$-*t*-Bu)H$_4$]$_2$: brown crystals from pentane; yield 40%; ^{1}H NMR δ 2.33 (s, 6, ring–CH$_3$), 2.22 (s, 6, ring–CH$_3$), 1.47 (s, 9, *t*-Bu), −0.81 (s, 4, J_{HW} = 48.6, W–H); ^{13}C NMR δ 113.1 (*C*-*t*-Bu), 100.4 and 97.7 (*C*CH$_3$), 33.7 (*C*Me$_3$), 33.7 (C*Me*$_3$), 13.9 (ring–CH$_3$); IR (Nujol, cm^{-1}) 1915 and 1890 (ms, br, WH); FD/MS, *m/e* 730. Anal. Calcd for WC$_{13}$H$_{25}$: C, 42.76; H, 6.90. Found: C, 42.74; H, 6.73.

[W(η^5-C$_5$Et$_5$)H$_4$]$_2$: brown flakes from pentane/ether; yield 35%; ^{1}H NMR δ 2.69 (q, 10, *J* = 7.6, C*H*$_2$CH$_3$), 1.04 (t, 15, *J* = 7.6, CH$_2$C*H*$_3$), −0.85 (s, 4, J_{HW} = 48.7, W–H); ^{13}C{^{1}H} NMR δ 105.5 (*C*$_5$Et$_5$), 21.8 (*C*H$_2$CH$_3$), 18.6 (CH$_2$*C*H$_3$); IR (Nujol, cm^{-1}) 1895 (ms, br, W–H). Anal. Calcd for WC$_{15}$H$_{29}$: C, 45.81; H, 7.43. Found: C, 45.88; H, 7.31.

[W(η^5-C$_5$Et$_4$-*t*-Bu)H$_4$]$_2$: brown needles from pentane/ether; yield 38%; ^{1}H NMR δ 2.88 (m, 2, C*H*$_2$CH$_3$), 2.69 (m, 2, C*H*$_2$CH$_3$), 2.73 (q, 4, C*H*$_2$CH$_3$), 1.53 (s, 9, C-*t*-Bu), 1.10 (t, 6, *J* = 7.4, CH$_2$C*H*$_3$), 1.04 (t, 6, *J* = 7.6, CH$_2$C*H*$_3$), −1.28 (s, 4, J_{HW} = 48.7, W–H); ^{13}C{^{1}H} NMR δ 113.2 (*C*-*t*-Bu), 106.1 and 104.9 (*C*CH$_2$CH$_3$), 34.0 (*C*Me$_3$), 33.7 (C*Me*$_3$), 22.5 and 21.9 (*C*H$_2$CH$_3$), 18.6 and 19.9 (CH$_2$*C*H$_3$); IR (Nujol, cm^{-1}) 1885 (ms, br, W–H). Anal. Calcd for WC$_{17}$H$_{33}$: C, 48.47; H, 7.90. Found: C, 48.48; H, 8.01.

W(η^5-C$_5$Me$_5$)H$_5$(PMe$_3$). WCp*Cl$_4$(PMe$_3$) (835 mg, 1.56 mmol) was added in small portions to a suspension of LiAlH$_4$ (550 mg, 14.5 mmol) in ether at room temperature. The mixture was stirred at room temperature overnight and cooled to −30 °C. Methanol (1.85 g, 58 mmol) in ether (5 mL) was added dropwise. When the mixture started to darken, the solvent was removed in vacuo and the residue was extracted with toluene (50 mL). The extract was filtered through Celite, concentrated to a few milliliters, placed on a silica column (2 × 10 cm) made up in pentane, and eluted with toluene (50 mL). Then pentane/ether was used as eluent to separate a red band which was shown by ^{1}H NMR to contain traces of a mixture of [WCp*H$_4$]$_2$ and WCp*H$_5$(PMe$_3$). The pale orange brown band was collected, and the solvent was removed in vacuo. The off-white residue was recrystallized twice from pentane to give the pure product as colorless plates (250 mg, 40%): ^{1}H NMR δ 2.30 (s, 15, C$_5$Me$_5$), 1.35 (d, 9, J_{HP} = 9.6, PMe$_3$), −2.56 (d, 5, J_{HP} = 41.5, J_{HW} = 42.3, W–H); ^{13}C NMR δ 98.8 (*C*$_5$Me$_5$), 29.0 (dq, J_{CH} = 132, J_{CP} = 34, PMe$_3$), 13.2 (C$_5$*Me*$_5$); ^{31}P{^{1}H} NMR δ −19.9 (J_{PW} = 49.7); selective decoupling of the PMe$_3$ methyl group protons revealed the signal to be a sextet with J_{HP} = 42 Hz; IR (KBr, cm^{-1}) 1875 (sh), 1838 (ms, br, W–H); FD/MS, *m/e* 398 (M$^+$ − 2H). Anal. Calcd for WC$_{13}$H$_{29}$P: C, 39.02; H, 7.30. Found: C, 38.91; H, 7.14.

[W(η^5-C$_5$Me$_5$)H$_3$]$_3$. A solution of WCp*Me$_4$ (570 mg, 1.5 mmol) in pentane (20 mL) was placed in a Parr pressure bomb. The bomb was flushed and pressurized with hydrogen (500 psi) at room temperature. After 2 h the solvent was removed in vacuo from the resulting green-black reaction mixture. The residue was dissolved in a few milliliters of toluene and placed on an alumina column (1.5 × 25 cm) made up in pentane. A broad blue band was eluted with toluene. The toluene was removed in vacuo, and the residue was recrystallized from pentane/THF at −20 °C to give blue microcrystals (200 mg, 41%): ^{1}H NMR δ 2.33 (s, 15, C$_5$Me$_5$), −1.65 (s, 3, W–H); ^{1}H NMR (toluene-*d*$_8$, 60 °C) δ 2.29 (s, 15, C$_5$Me$_5$), −1.76 (s, 3, J_{HW} = 43, W–H); ^{1}H NMR (toluene-*d*$_8$, −90 °C, 400 MHz) 2.30 (s, 30, C$_5$Me$_5$), 2.19 (s, 15, C$_5$Me$_5$), 0.17 (s, br, ~5, WH), −0.45 (s br, ~1, WH), −3.10 (s br, ~2, WH), −5.28 (s br, ~1, WH); ^{13}C{^{1}H} NMR δ 97.7 (*C*$_5$Me$_5$), 14.1 (C$_5$*Me*$_5$); IR (KBr, cm^{-1}) 1885, 1838 (ms, br, W–H). Anal. Calcd for WC$_{10}$H$_{18}$: C, 37.29; H, 5.63. Found: C, 37.14; H, 5.74.

A brown band that was eluted with a mixture of pentane and ether (1:1) afforded [WCp*H$_4$]$_2$ in 10% yield.

[WCp*D$_3$]$_3$. [WCp*D$_3$]$_3$ was prepared by reacting WCp*Me$_4$ in pentane with deuterium under 200 psi pressure at room temperature. Separation from [WCp*D$_4$]$_2$ was accomplished by column chromatography on alumina deactivated with 7% D$_2$O.

W$_2$(η^5-C$_5$Me$_5$)$_2$H$_6$(PMe$_3$). PMe$_3$ (115 mg, 1.51 mmol) was added to a solution of [WCp*H$_4$]$_2$ (160 mg, 0.5 mmol) in 15 mL of a 1:1 mixture of pentane and ether. After 6 h the solvent was evaporated and the semisolid, brown residue was crystallized from a minimum amount of pentane at −20 °C to give brown crystals: yield ca. 150 mg (83%); ^{1}H NMR δ 2.31 (s, 15, C$_5$Me$_5$), 2.27 (s, 15, C$_5$Me$_5$), 1.79 (d, 9, J_{HP} = 8.5, PMe$_3$), −0.91 (br d, 6, J_{HP} = 10.5, J_{HW} not resolved, W–H); ^{1}H NMR (toluene-*d*$_8$, 100 °C) δ 2.28 (s, 15, C$_5$Me$_5$), 2.26 (s, 15, C$_5$Me$_5$), 1.79 (d, 9, J_{HP} = 8.6, PMe$_3$), −1.06 (d, 6, J_{HP} = 11.5, J_{HW} = 61.9); ^{1}H NMR (toluene-*d*$_8$, −90 °C, 400 MHz) δ 2.40 (s, 15, C$_5$Me$_5$), 2.27 (s, 15, C$_5$Me$_5$), 1.80 (br, 9, PMe$_3$), 0.86 (s, 3, WH), −2.02 (d, 2, J_{HP} ≈ 50, WH), −5.52 (br, 1, WH); ^{13}C{^{1}H} NMR δ 99.2 (*C*$_5$Me$_5$), 98.2 (*C*$_5$Me$_5$), 30.8 (d, J_{CP} = 31.1, PMe$_3$), 15.2 (C$_5$*Me*$_5$), 13.3 (C$_5$*Me*$_5$); ^{31}P{^{1}H} NMR δ −28.4 (J_{PW} = 244, $J_{PW'}$ < 35); IR (KBr, cm^{-1}), 1885, 1780 (br, W–H). Anal. Calcd for W$_2$C$_{23}$H$_{45}$P: C, 38.35; H, 6.30. Found: C, 38.50; H, 6.42.

Reaction of [W(η^5-C$_5$Me$_5$)H$_4$]$_2$ with CO. A solution of [WCp*H$_4$]$_2$ (150 mg, 0.46 mmol) in 20 mL of pentane was placed in a Parr pressure bomb. The bomb was cooled to −78 °C and then flushed and pressurized with carbon monoxide to 1000 psi. The bomb was allowed to warm to room temperature and the pressure released after 1 h. The yellow-brown supernatant was decanted from dark brown crystals which were recrystallized from pentane/toluene at −20 °C to give 120 mg (69%) of black crystalline product: ^{1}H NMR δ 1.87 (C$_5$Me$_5$), −9.23 (J_{HW} = 82.8, W–H); ^{13}C NMR δ 258.4 (CO), 108.8 (*C*$_5$Me$_5$), 12.0 (C$_5$*Me*$_5$); IR (Nujol, cm^{-1}) 1900, 1830 (s, CO). The carbonylation can also be performed at 60 psi, in which case the reaction time is 12 h.

[WO$_2$(O-*t*-Bu)]$_2$(η^5,η^5-Et$_4$C$_5$CH$_2$CH$_2$C$_5$Et$_4$). 3,7-Decadiyne (280 mg, 2.1 mmol) was added to a solution of W(C$_3$Et$_3$)(OCMe$_2$CMe$_2$O)(O-*t*-Bu) (2.30 g, 4.6 mmol) in 10 mL of pentane at room temperature. (The reaction is uncontrollably exothermic under more concentrated conditions.) The mixture warmed up slightly and was then heated to reflux overnight. Off-white crystals were filtered off, washed with pentane, and dried: yield ca. 1.23 g (61%); ^{1}H NMR δ 2.94 (CH$_2$CH$_2$), 2.57, 2.47 (C*H*$_2$CH$_3$), 1.27 (O-*t*-Bu), 1.09, 1.05 (CH$_2$C*H*$_3$); ^{13}C NMR δ 124.3, 124.0 (*C*CH$_2$CH$_3$), 120.8 (*C*CH$_2$CH$_2$C), 80.1 (O*C*Me$_3$), 30.2 (OC*Me*$_3$), 27.8 (*C*H$_2$*C*H$_2$), 19.6, 19.3 (*C*H$_2$CH$_3$), 15.9, 15.5 (CH$_2$*C*H$_3$); IR (Nujol, cm^{-1}) 948, 913, 903, 892 (ν_{WO}). Anal. Calcd for WC$_{18}$H$_{31}$O$_3$: C, 45.11; H, 6.52. Found: C, 44.90; H, 6.41.

[WCl$_4$]$_2$(η^5,η^5-Et$_4$C$_5$CH$_2$CH$_2$C$_5$Et$_4$). PCl$_5$ (2.11 g, 10.14 mmol) was added slowly as a solid to a vigorously stirred solution of [WO$_2$(O-*t*-Bu)]$_2$(η^5,η^5-Et$_4$C$_5$CH$_2$CH$_2$C$_5$Et$_4$) (1.50 g, 1.56 mmol) in 75 mL of dichloromethane at 25 °C. A copper-colored precipitate formed rapidly. The reaction mixture was heated to reflux for 6 h, and the orange-red microcrystals were filtered off, washed with dichloromethane and ether, and dried to give 1.30–1.37 g of crude product (80–85%). This compound can be crystallized and thereby purified by the following unusual procedure. A sample was suspended in dichloromethane that contained ~1 equiv of PPh$_3$. The mixture was heated to reflux temperature overnight to yield small well-formed orange crystals in high yield. We propose that a slightly soluble, weak PPh$_3$ adduct of W$_2$Cp^{2}Cl$_8$ is formed during this procedure. Anal. Calcd for WC$_{14}$H$_{12}$Cl$_4$: C, 32.59; H, 4.30; Cl, 27.48. Found: C, 32.40; H, 4.44; Cl, 27.31.

[WMe$_4$]$_2$(η^5,η^5-Et$_4$C$_5$CH$_2$CH$_2$C$_5$Et$_4$). ZnMe$_2$ (900 mg, 9.43 mmol) was added to a suspension of [WCl$_4$(PMe$_3$)]$_2$(η^5,η^5-Et$_4$C$_5$CH$_2$CH$_2$C$_5$Et$_4$) (500 mg, 0.48 mmol) in 30 mL of toluene. Within 10 min all starting material had dissolved and an orange precipitate had formed. The mixture was stirred overnight and filtered through a pad of silica. The solvent was removed in vacuo leaving a brown-yellow solid. Repeated recrystallization from THF at −20 °C afforded orange-yellow crystals (180 mg, 43%): EPR (CH_2Cl_2, 25 °C) $g = 2.008$; FD/MS, *m/e* 868 (M^+), 853 ($M^+ - CH_3$). Anal. Calcd for $WC_{18}H_{34}$: C, 49.78; H, 7.97. Found: C, 49.91; H, 7.61.

Hydrogenation of $[WMe_4](\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$ under conditions analogous to those used to prepare $[WCp^*H_3]_3$ (vide supra) yielded no recognizable hydride product.

$[WH_4]_2(\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$. A suspension of $[WCl_4]_2(\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$ (515 mg, 0.5 mmol) in 15 mL of ether was slowly treated with solid $LiAlH_4$ (266 mg, 7 mmol) at −20 °C. First a green color developed and the starting material rapidly went into solution to give a dark brown mixture which changed color to a green-gray after 1 h. The reaction mixtue was stirred for 12 h, cooled to −78 °C, and treated with a mixture of methanol and ether (1:1, 4 mL). The resulting brown suspension was stirred for 1 h and filtered through Celite. The filtrate was taken to dryness in vacuo. The residue was dissolved in toluene (1 mL) and the solution placed on an alumina column (1 × 10 cm) made up in pentane. Elution with pentane/toluene (1:1) gave a pale violet band which contained traces of an unidentified, paramagnetic compound. A brown band was eluted with pentane/ether (1:1). The solvent was removed in vacuo, and the residue was crystallized from toluene at −20 °C to give well-fomed red-brown cubes. Toluene of crystallization could be removed by pumping on samples in vacuo for 24 h. The yield was typically 40 mg (11%): ^1H NMR δ 3.28 (s, 2, CH_2CH_2), 3.08 (m, 1, $J = 15.3$, 7.6, $CH_AH_BCH_3$), 2.82 (m, 1, $J = 15.3$, 7.6, $CH_AH_BCH_3$), 2.31 (m, 1, $J = 15.3$, 7.6, $CH_AH_BCH_3$), 2.05 (m, 1, $J = 15.3$, 7.6, $CH_AH_BCH_3$), 1.07 (t, 3, $J = 7.6$, CH_2CH_3), 0.84 (s, 2, $J_{HW} = 43.7$, W–H), 0.82 (t, 3, $J = 7.6$, CH_2CH_3); ^{13}C NMR δ 108.2 and 108.0 (CCH_2CH_3), 100.3 (CCH_2CH_2C), 30.3 (CH_2CH_2), 22.1 (CH_2CH_3), 20.0 (CH_2CH_3), 18.2 (CH_2CH_3), 17.1 (CH_2CH_3); IR (KBr, cm^{-1}) 1895 (sh), 1855 (ms, br, W–H); FD/MS, *m/e* 756. The sample for analysis was freed to toluene in vacuo and recrystallized from ether. Anal. Calcd for $WC_{14}H_{26}$: C, 44.46; H, 6.93. Found: C, 44.25; H, 6.84.

$[WH_5(PMe_3)]_2(\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$. Solid $LiAlH_4$ (380 mg, 10 mmol) was added slowly to a stirred solution of $[WCl_4(PMe_3)]_2(\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$ (516 mg, 0.5 mmol) in 30 mL of ether at 0 °C. The starting material slowly dissolved to give a grass green mixture which became gray after being stirred at room temperature overnight. The mixtue was cooled to −20 °C, and methanol (1.28 g, 40 mmol) in 2 mL of ether was added carefully. After the mixture was warmed to 25 °C and stirred for 15 min, all volatile components were removed in vacuo, and the residue was extracted three times with 10 mL of toluene. The pale brown extracts were filtered through a pad of silica, and the filtrate was concentrated to 2 mL. Pentane (5 mL) was added, and the solution was cooled to −20 °C to afford fine colorless crystals that contained toluene of crystallization (135 mg in two crops, 30%): ^1H NMR δ 3.25 (s, CH_2CH_2), 2.99 and 2.87 (q, CH_2CH_3), 1.34 (d, 9, $J_{HP} = 9.7$, PMe_3), 1.24 and 1.17 (t, CH_2CH_3), −2.81 (d, $J_{HP} = 41.9$, $J_{HW} = 43.0$, W–H); ^{13}C NMR δ 106.1 (CCH_2CH_3), 103.9 (CCH_2CH_2C), 33.6 (CH_2CH_2), 29.2 (dq, $J_{CP} = 34$, PMe_3), 22.1 and 21.8 (CH_2CH_3), 19.0 and 18.6 (CH_2CH_3); $^{31}P\{^1H\}$ NMR δ −20.3 ($J_{PW} = 50$); IR (KBr, cm^{-1}) 1875 (sh), 1835 (m, br, W–H); FD/MS, *m/e* 906 ($M^+ - 4H$). Anal. Calcd for $WC_{19}H_{38.4}P(0.3C_7H_8)$: C, 47.50; H, 8.01. Found: C, 47.66; H, 7.39. The toluene of crystallization could be observed and quantitated by ^1H NMR. It could not be removed completely at high vacuum and 25 °C in 24 h (analysis sample).

$[W_2H_6(PMe_3)](\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$. PMe_3 (50 mg, 0.66 mmol) was added to a solution of $[WH_4]_2(\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$ (50 mg, 0.066 mmol) in 5 mL of a 1:1 mixture of ether and pentane. After 6 h at room temperature all solvents and excess PMe_3 were removed in vacuo. The residue was crystallized from a minimum amount of pentane to give red-brown platelets (50 mg, 91%): ^1H NMR δ 3.2 (m, 2, CH_2CH_2), 2.9–3.1 (overlapping m, 8, CH_2CH_2 and three CH_2CH_3 protons), 2.72 (m, 2, CH_2CH_3), 2.47 (m, 2, CH_2CH_3), 2.10 (m, 2, CH_2CH_3), 1.73 (m, 2, CH_2CH_3), 1.38 (d, 9, $J_{HP} = 8.6$, PMe_3), 1.26 (CH_2CH_3), 1.16 (CH_2CH_3), 1.04 (CH_2CH_3) 0.99 (CH_2CH_3), −2.49 (d, 6, $J_{HP} = 11.3$, $J_{HW} = 60.7$, $J_{HW'} = 52.1$, W–H); $^{13}C\{^1H\}$ NMR δ 106.6, 106.3, 99.7, 97.3, 93.7, 87.4 (ring carbons), 33.5, 28.2 (CH_2CH_2), 28.0 (d, $J_{CP} = 29.3$, PMe_3), 24.2, 23.3, 21.1, 19.7 (CH_2CH_3), 19.0, 18.7, 18.0, 17.7 (CH_2CH_3); $^{31}P\{^1H\}$ NMR δ −23.8 ($J_{PW} = 202$, $J_{PW'} = 31.7$); IR (KBr, cm^{-1}) 1855 (m, br, W–H), 1835 (sh).

$[W_2(\eta^5\text{-}C_5Me_5)_2H_9]BF_4$. A solution of HBF_4·ether (192 mg, 0.6 mmol, 50% in ether) in 10 mL of ether was slowly added to a solution of $[WCp^*H_4]_2$ (320 mg, 0.5 mmol) in ether (20 mL) at −80 °C. A white flocculent precipitate formed quickly which was filtered off from the almost colorless mother liquor and washed liberally with ether. The gray, powdery product was recrystallized twice from methanol/ether at −20 °C to give colorless crystals (350 mg, 95%): ^1H NMR (acetone-d_6, 25 °C) δ 2.82 (s br, 2, W–H), 2.47 (s, 30, C_5Me_5), −2.18 (s br, ~3, W–H); ^1H NMR (CD_2Cl_2, −30 °C, 400 MHz) δ 2.65 (s, 2, $J_{HW} = 43.8$, W–H), 2.37 (s, 30, C_5Me_5), 2.24 (q, 4, $J_{HH} = 6.0$, $J_{HW} = 37.5$), −2.30 (quin, 3, $J_{HH} = 6.0$, $J_{HW} = 71.6$); $^{13}C\{^1H\}$ NMR (acetone-d_6, 25 °C) δ 106.1 (C_5Me_5), 12.5 (C_5Me_5); IR (KBr, cm^{-1}) 1965 (w), 1940 (m, W–H). Anal. Calcd for $W_2C_{20}H_{39}BF_4$: C, 32.73; H, 5.36. Found: C, 32.81; H, 5.31.

Crystal Structure of $[WH_4]_2(\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$. Data were collected at −50 °C on an Enraf-Nonius CAD4F-11 diffractometer using Mo Kα radiation. Data collection, reduction, and refinement have been explained in detail elsewhere.[21] A total of 5995 reflections ($\pm h,\pm k,+l$) were collected in the range $3° \le 2\theta \le 50°$ with the 4595 having $F_o > 4\sigma(F_o)$ being used in the structure refinement by full-matrix least-squares techniques (337 variables) using SHELX-76 to final values of $R_1 = 0.043$ and $R_2 = 0.047$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the $(\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$ ligand were placed in calculated positions (C–H = 0.95 Å) and were constrained to ride on their respective carbon atoms. The crystal contained one molecule of toluene per asymmetric unit. Methyl group hydrogen atoms on the toluene were ignored during refinement while the remainder were treated as for the Cp^2 ligand. An empirical absorption correction was applied. Crystal data at −50 °C are $a = 14.828$ (3) Å, $b = 15.963$ (5) Å, $c = 7.854$ (3) Å, $\alpha = 93.03$ (3)°, $\beta = 98.04$ (2)°, $\gamma = 110.91$ (2)°, $V = 1708.9$ Å^3, space group $P\bar{1}$, $Z = 2$, M_r 756.4 (without toluene), ρ(calcd) = 1.470 g cm^{-3}, and $\mu = 64.2$ cm^{-1}.

A second data set was collected at −180 °C. A total of 5891 reflections ($\pm h,\pm k,+l$) were collected in the range $3° \le 2\theta \le 50°$ with the 4968 having $F_o > 4\sigma(F_o)$ being used in the structure refinement by full-matrix least-squares techniques (337 variables) using SHELX-76 to final values of $R_1 = 0.029$ and $R_2 = 0.035$. Unit-cell dimensions at −180 °C are $a = 14.707$ (4) Å, $b = 15.854$ (9) Å, $c = 7.777$ (4) Å, $\alpha = 93.20$ (5)°, $\beta = 98.15$ (4)°, $\gamma = 110.57$ (4)°, and $V = 1669.6$ Å^3.

The crystal used for data collection at −180 °C was bounded by the faces (100) and ($\bar{1}00$), 0.075-mm apart, (010) and ($0\bar{1}0$), 0.075-mm apart, and (001) and ($00\bar{1}$), 0.2-mm apart. The long dimension of the crystal was approximately parallel to the glass fiber on which it was mounted. An absorption correction was applied, using the program ORABS; the maximum and minimum transmission factors were 0.493 and 0.346, respectively. All hydrogen atoms (except those of the toluene methyl group) were placed in calculated positions (C–H = 0.95 Å). The hydrogen atoms of the toluene methyl group C(29) were located easily in a difference-Fourier map and were included in the refinement as invariants. All non-hydrogen atoms were refined anisotropically.

Attempts to locate hydride atoms in a final difference-Fourier map were unsuccessful. Using only low-angle data to calculate the map, as outlined in the SHELX-76 manual, also proved fruitless.

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Registry No. $[WCp^*H_4]_2$, 102615-24-7; $[W(C_5Me_4Et)H_4]_2$, 102615-25-8; $[W(C_5Me_4\text{-}n\text{-}Pr)H_4]_2$, 102615-26-9; $[W(C_5Me_4\text{-}t\text{-}Bu)H_4]_2$, 102615-27-0; $[W(C_5Et_5)H_4]_2$, 102615-28-1; $[W(C_5Et_4\text{-}t\text{-}Bu)H_4]_2$, 102630-11-5; $WCp^*H_5(PMe_3)$, 102615-29-2; $[WCp^*H_3]_3$,

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96055-91-3; $W_2Cp^*{}_2H_6(PMe_3)$, 102630-12-6; $[WCp^*(CO)_2H]_2$, 86307-89-3; $[WO_2(O\text{-}t\text{-}Bu)]_2Cp^2$, 95045-00-4; $[WCl_4]_2Cp^2$, 102615-30-5; $[WMe_4]_2Cp^2$, 102615-31-6; $[WH_4]_2Cp^2$, 102630-13-7; $[WH_5(PMe_3)]_2Cp^2$, 102630-14-8; $[W_2H_6(Pme_3)]Cp^2$, 102615-32-7; $[W_2Cp^*{}_2H_9]BF_4$, 102615-34-9; $[WCp^*Cl_4]_2$, 102615-35-0; $WCp^*Cl_4PMe_3$, 96055-86-6; WCp^*Me_4, 96055-89-9; $W(C_3Et_3)(OCMe_2CMe_2O)(O\text{-}t\text{-}Bu)$, 102615-36-1; $ZnMe_2$, 544-97-8; $[WCl_4(PMe_3)]_2Cp^2$, 95045-02-6; 3,7-decadiyne, 33840-20-9.

Supplementary Material Available: Tables of final atomic coordinates, thermal parameters, and structure factor tables for the structures determined at −50 and −180 °C and selected bond distances and angles in the −180 °C structure (46 pages). Ordering information is given on any current masthead page.

A Heteronuclear μ-Alkyne Complex, $[\mu\text{-}(CF_3)_2C_2]CoMo(CO)_5(\eta\text{-}C_5H_5)$

Simon D. Jensen, Brian H. Robinson,* and Jim Simpson*

Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand

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Exchange of a $Co(CO)_3$ unit in $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_6$ (**1**) by the isoelectronic fragment $Mo(CO)_2Cp$ is effected by the addition of an electron to **1** in the presence of $[Mo(CO)_3Cp]_2$ or by the thermal reaction between **1** and $Mo(CO)_3Cp^-$. $(CO)_3Co[\mu\text{-}(CF_3)_2C_2]Mo(CO)_2Cp$ (**2**) crystallized in space group $P2_1/c$ ($Z = 8$, $a = 16.903$ (3) Å, $b = 12.110$ (2) Å, $c = 18.149$ (3) Å, $\beta = 111.32$ (1)°), and its X-ray crystal structure was refined to $R = 0.0348$ and $R_w = 0.0387$ for 3510 reflections ($I > 3\sigma(I)$). Insertion of a $Mo(CO)_2Cp$ group does not significantly distort the μ-alkyne–M_2 geometry of **1**; Co–Mo = 2.692 Å. A PPh_3 derivative was also characterized. **2** undergoes chemically reversible one-electron reductions at two separate redox centers. The thermal or photochemical reaction between **1** and $[Mo(CO)_3Cp]_2$ does not give **2**, and, while an electron assists the synthesis, it is not a catalyzed reaction. A novel reaction of **1** with the radical initiator AIBN gives $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_5[NC(CH_3)_2CN_2C(CH_3)_2CN]$.

Metal carbonyl anions can function as nucleophiles in electron transfer chain (ETC) catalyzed reactions with metal carbonyl clusters.[1] One potential advantage of these reactions is that heteronuclear metal clusters can be synthesized under relatively mild conditions, obviating the problems of thermal instability encountered in thermal metal exchange reactions. It was of interest to establish whether metal fragment exchange would occur where the metal–metal backbone is clamped by an electronically demanding organic group; in this instance, a μ-alkyne group. The complex $[\mu\text{-}(CF_3)_2C_2]Co_2(CO)_6$ (**1**) is a good ETC substrate,[2] with a relatively stable radical anion, and a reaction with a metal nucleophile would give a rare example[3] of a heterodinuclear monoalkyne complex; an example is $(CO)_3Co[\mu\text{-}R_2C_2]NiCp$.[4] In this paper we describe the synthesis, structure, and reactivity of $(CO)_3Co[\mu\text{-}(CF_3)_2C_2]Mo(CO)_2Cp$ (**2**).

Experimental Section

All reactions were carried out in argon-degassed solvents, dried, and purified as outlined before[2] and under an Ar atmosphere. $[Mo(CO)_3Cp]_2$,[6] $K[Mo(CO)_3Cp]$,[7] $Na[Mo(CO)_3Cp]$,[8] **1**,[9] and PPN^+Cl^-[10] were prepared by literature procedures. Benzophenone ketyl (BPK) was prepared as a THF solution as described elsewhere.[11] 2,2′-Azobis(2-methylpropionitrile) (AIBN) was used as received (Aldrich).

Conventional current–voltage curves were recorded on a PAR 174 Analyzer equipped with a PAR 175 Universal Programmer and a Bryans X-Y recorder (scan rates < 1 V s^{-1}) or Tectronix Storage oscilloscope or on an interfaced Apple //e microcomputer. Standard cells were used for the transient and bulk electrochemistry, and all measurements and electrode reactions were carried out under Ar with TBAP (CH_2Cl_2, THF) or TEAP (acetone) as supporting electrolytes. Electrodes were rigorously cleaned, and all potentials are with respect to Ag/AgCl referenced against ferrocene.[11] The cyclic voltammograms were simulated at 200 mV s^{-1} by using programs based on Feldberg's statements.[12] Reductions (electrochemically or alkali metal) for ESR measurements were carried out by the methods described elsewhere.[13] Infrared spectra were recorded on Nicolet FT or Perkin-Elmer 225 spectrometers and NMR on 60-MHz JEOL or 90-MHz Perkin-Elmer spectrometers with internal Me_4Si standard.

Preparation of 2. (i) Reaction with $[Mo(CO)_3Cp]_2$ in THF. A 98.2-mg (0.200-mmol) sample of $[Mo(CO)_3Cp]_2$ was added to a solution of 89.2 mg (0.199 mmol) of **1** in 20 cm^3 of THF. A purple solution of BPK was added, via an air-tight syringe, in 0.1-cm^3 portions until all of **1** was consumed (monitored by IR); during this time the solution changed from red to yellow-green. At this stage an IR spectrum showed ν(CO) bands at 2069, 2024, 2010, and 2006 cm^{-1} as well as bands due to $Mo(CO)_3Cp^-$ and $[Mo(CO)_3Cp]_2$. The THF solution was reduced to dryness in vacuo to give a green solid. Extraction of this solid with hexane gave an orange-red solution plus a residue, and chromatographic separation of the solution on silica gel plates (hexane/ether/CH_2Cl_2, 10:1:1) gave three bands; orange (**1**), pink ($[Mo(CO)_3Cp]_2$), and orange-red. The last band was removed and eluted with CH_2Cl_2, and the residue after removal of the CH_2Cl_2 was crystallized from hexane/CH_2Cl_2 to yield orange-red crystals of **2** (17%). Anal. Calcd for $C_{14}H_5CoF_6MoO_5$: C, 32.21; H, 0.97. Found: C, 32.53; H, 0.97. Mass spectrum (70 eV): *m/e* (relative

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