

Reactive Hydroxo and Hydroxycarbyne Cyclopentadienyl Complexes. Proton Transfer and Oxidative Addition of O–H Bonds at Unsaturated Ditungsten Centers

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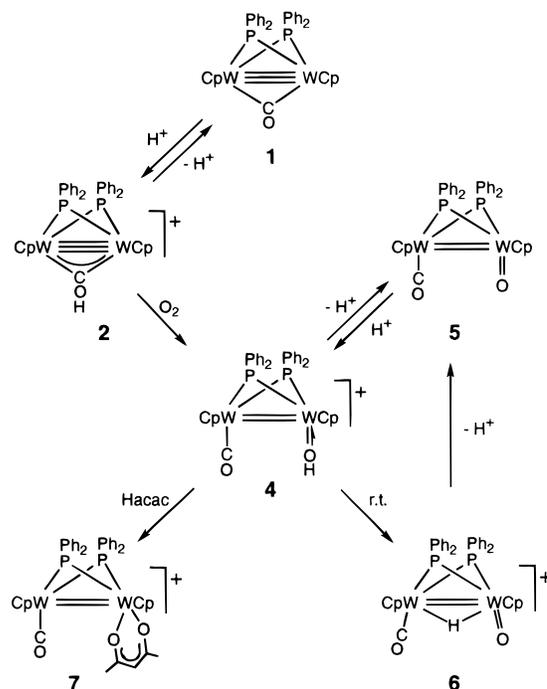
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Recently we reported the preparation and some reactions of the binuclear hydroxycarbyne complex $[W_2(\mu-CO)Cp_2(CO)_2(\mu-Ph_2PCH_2PPh_2)]BF_4$ ($Cp = \eta^5-C_5H_5$).¹ Interest in hydroxycarbyne complexes arises from two main considerations. In the first place, their chemistry is virtually unexplored due to the lack of available compounds with enough thermal stability. Second, their transformations can be of relevance in the context of some important reactions as, for example, carbon monoxide reduction.^{1,2} Thus, we sought to prepare new thermally stable binuclear hydroxycarbyne complexes to better study their chemical behavior. In this paper we report the preparation of the new compound $[W_2(\mu-CO)Cp_2(\mu-PPh_2)]BF_4$ (**2**), and some unusual transformations derived thereof (Scheme 1). This hydroxycarbyne complex readily reacts with oxygen to afford, after proton transfer, the hydroxo carbonyl derivative $[W_2Cp_2(OH)(\mu-PPh_2)(CO)]BF_4$ (**4**), which in turn experiences an intramolecular oxidative addition of the O–H bond at rt to give the oxohydroido complex $[W_2Cp_2(\mu-H)(O)(\mu-PPh_2)(CO)]BF_4$ (**6**). The latter represents a rare example of oxidative O–H bond addition occurring at a dimetal center. In fact, we are aware of just one previous complex experiencing this rearrangement in a detectable way.³ More importantly, the unsaturated nature of **4** makes the terminal hydroxo ligand quite reactive toward organic substrates having acidic protons, a property held by different late metal hydroxo complexes,⁴ and this gives a considerable synthetic potential to this compound. We note here that the chemistry of hydroxo complexes is of relevance in the context of different metal-catalyzed reactions of organic substrates such as oxidation or hydrolysis, the latter including a large number of biological transformations such as those induced by zinc enzymes.^{4d,5}

The triply bonded dimer $[W_2(\mu-CO)Cp_2(\mu-PPh_2)]$ (**1**) can be obtained in high yield through the photochemical reaction of the hydride $[W_2Cp_2(\mu-H)(\mu-PPh_2)(CO)_4]$ and $HPPPh_2$.^{6,7} This synthetic

Scheme 1



method can be equally used with other primary or secondary phosphines $HPRR'$, whereby a wide range of mixed phosphido complexes with tunable steric and electronic characteristics can be prepared. We recall here that the dimolybdenum analogue of **1** has been previously prepared in a two-step reaction starting from $[Mo_2Cp_2(CO)_6]$ and P_2Ph_4 .⁸

Compound **1** has a bridging CO ligand, and it is therefore expected to experience electrophilic attack at the oxygen atom of this ligand. Indeed, **1** is easily protonated with $HBF_4 \cdot OEt_2$ or methylated with $MeSO_3CF_3$ to give with good yields the corresponding hydroxycarbyne **2** or methoxycarbyne analogue $[W_2(\mu-COMe)Cp_2(\mu-PPh_2)]SO_3CF_3$ (**3**). Although quite reactive in general, both compounds are stable at room temperature. Moreover, spectroscopic data for these species indicate that they have the same structure,^{9,10} confirmed through an X-ray study carried out on the latter (Figure 1).¹¹ This 30-electron complex formally retains a triple W–W bond, which is consistent with the intermetallic distance of 2.5324(8) Å (for comparison, M–M distances are 2.5144(5) Å for $[W_2Cp_2(\mu-Ph_2PCH_2PPh_2)(CO)_2]$ ¹² or 2.515(2) Å for $[Mo_2(\mu-CO)Cp_2(\mu-PPh_2)]$).⁸ As for the carbyne ligand, its C-donor atom is placed on a C_2 axis of the crystal, and therefore, the methoxy group is disordered in two positions (only one of them is shown in Figure 1). Interatomic distances

(1) Alvarez, M. A.; Bois, C.; García, M. E.; Riera, V.; Ruiz, M. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 102–104.

(2) (a) Miller, R. L.; Toreki, R.; LaPointe, R. E.; Wolczanski, P. T.; Van Duyne, G. D.; Roe, D. C. *J. Am. Chem. Soc.* **1993**, *115*, 5570–5588. (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117–130.

(3) Tahmassebi, S. K.; McNeil, W. S.; Mayer, J. M. *Organometallics* **1997**, *16*, 5342–5353.

(4) (a) Ritter, J. C. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 2580–2581. (b) Kaplan, A. W.; Bergman, R. G. *Organometallics* **1997**, *16*, 1106–1108. (c) Gilje, J. W.; Roesky, H. W. *Chem. Rev.* **1994**, *94*, 895–910. (d) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163–1188.

(5) (a) Mayer, J. M. *Polyhedron* **1995**, *22*, 3273–3292. (b) Bergman, R. G. *Polyhedron* 3227–3237. (c) Bertini, I.; Luchinat, C. In *Bioinorganic Chemistry*; Bertini, I., Gray, H. B., Lippard, S. J., Valentine, J. S., Eds.; University Science Books: Mill Valley, CA, 1994; pp 37–106.

(6) Selected spectroscopic data for **1**: $\nu(CO)$ (CH_2Cl_2) 1635 cm^{-1} . $^{31}P\{^1H\}$ NMR (81.03 MHz, CD_2Cl_2) δ 144.7 [s, $J(PW)$ 389]. $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2) δ 303.9 (s, $\mu-CO$).

(7) $[W_2Cp_2(\mu-H)(\mu-PPh_2)(CO)_4]$ is synthesized from PPh_2H and $[W_2Cp_2(CO)_4]$ (prepared in situ from $[W_2Cp_2(CO)_6]$ as described in ref 20) at 333 K. Selected spectroscopic data: $\nu(CO)$ (CH_2Cl_2) 1947 (vw, sh), 1926 (vs), 1853 (s) cm^{-1} . $^{31}P\{^1H\}$ NMR (121.50 MHz, CD_2Cl_2) δ 109.2 [s, $J(PW)$ 209]. 1H NMR (300.13 MHz, CD_2Cl_2) δ -14.83 [d, $J(HP)$ 27, $J(HW)$ 39].

(8) Adatia, T.; McPartlin, M.; Mays, M. J.; Morris, M. J.; Raitby, P. R. *J. Chem. Soc., Dalton Trans.* **1989**, 1555–1564.

(9) Selected spectroscopic data for **2**: $^{31}P\{^1H\}$ NMR (81.01 MHz, CD_2Cl_2) δ 186.8 [s, $J(PW)$ 364]. 1H NMR (400.13 MHz, CD_2Cl_2 , 233 K) δ 13.71 (br, 1H, $\mu-COH$), 6.25 (s, 10H, Cp). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2) δ 367.9 [t, $J(CP)$ 6, $\mu-COH$].

(10) Selected spectroscopic data for **3**: $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2) δ 191.5 [s, $J(PW)$ 364]. $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2) δ 366.9 (s, $\mu-COMe$).

(11) X-ray data: black crystals of **3**, monoclinic ($C2/c$), $a = 15.458(2)$ Å, $b = 13.507(2)$ Å, $c = 19.326(3)$ Å, $\beta = 113.90(1)^\circ$, $V = 3689(1)$ Å³, $Z = 4$, $R = 0.044$, $GOF = 0.8$.

(12) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Falvello, L. R.; Bois, C. *Organometallics* **1997**, *16*, 354–364.

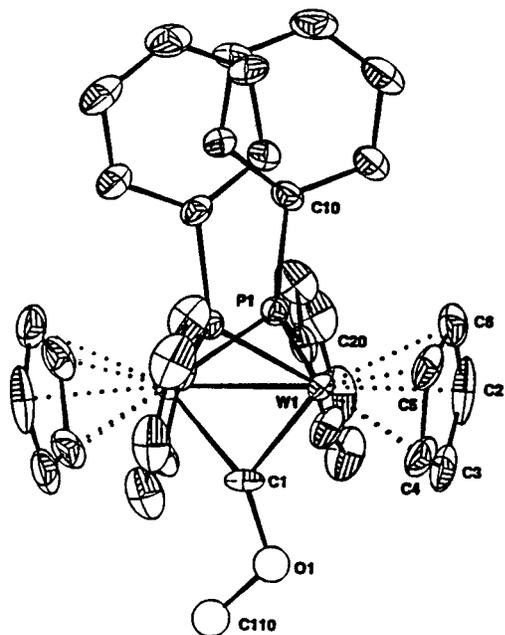


Figure 1. View of the molecular structure of the cation in complex **3** (ellipsoids at 20% probability and H atoms omitted; only symmetry-independent atoms labeled). Selected bond distances (Å) and angles (deg): W(1)–P(1) = 2.372(3), W(1)–C(1) = 1.97(1), C(1)–O(1) = 1.390(9), O(1)–C(110) = 1.40(1); W(1)–P(1)–W(1') = 64.44(7), W(1)–C(1)–W(1') = 80.2(5), C(1)–O(1)–C(110) = 113.8(14).

involving this group are otherwise similar to those measured at the 32-electron species $[\text{W}_2(\mu\text{-COMe})\text{Cp}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\text{CO})_2]\text{-BF}_4$.¹ To our knowledge, compound **3** is the first complex having an alkoxycarbonyl ligand bridging a triple metal–metal bond to be structurally characterized.

In the presence of small amounts of oxygen, the hydroxycarbonyl **2** readily transforms into the hydroxo derivative **4**.¹³ In this way, compound **4** can be isolated from the solution, provided the reaction is carried out below 253 K, otherwise further transformation occurs rapidly (see below). The unusual formation of this hydroxo complex possibly involves electrophilic attack of oxygen on the carbonyl (a similar reaction has been previously observed between sulfur and arylcarbonyl-bridged complexes),¹⁴ followed by H transfer between oxygen atoms, an hypothesis which is under current study. It is clear, in any case, that the hydroxycarbonyl ligand can act as an H reservoir for molecules approaching the unsaturated dimetal center.

As expected, the hydroxo complex **4** can be deprotonated with base to afford quantitatively the corresponding oxo complex $[\text{W}_2\text{-Cp}_2(\text{O})(\mu\text{-PPh}_2)_2(\text{CO})]$ (**5**), which is selectively formed as the cis isomer.^{15,16} This reaction can be reversed by just adding $\text{HBF}_4 \cdot \text{OEt}_2$ at 253 K to the latter. However, compound **4** isomerizes

(13) Selected spectroscopic data for **4**: IR (Nujol mull) 3500 [$\nu(\text{OH})$], 1893 [$\nu(\text{CO})$] cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR (161.99 MHz, CD_2Cl_2 , 263 K) δ 109.9 [s, $J(\text{PW})$ 372, 281]. ^1H NMR (400.13 MHz, CD_2Cl_2 , 263 K) δ 5.92, 5.51 (2 \times s, 2 \times 5H, Cp); the resonance of the O–H proton could not be identified.

(14) Byrne, P. G.; García, M. E.; Jeffery, J. C.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 1215–1219.

irreversibly above ca. 273 K to yield quantitatively the oxohydroxo complex **6**,¹⁷ which can be also deprotonated with base to give selectively **5** (cis isomer). Thus, both **4** and **6** are thought to display a cis disposition of their CO and oxygen-donor ligands. The isomerization **4/6** equally occurs in the solid state at room temperature. On that basis, we trust that a genuinely intramolecular α -migration of the hydroxylic H atom (from oxygen to tungsten) takes place in this substrate. In CH_2Cl_2 solution, isomerization is complete in ca. 15 min at 291 K, a rate far higher than that measured for the α -migration in $[\text{Re}(\text{OH})(\text{C}_2\text{Et}_2)_3]$.³ This difference can be possibly ascribed to the electronic and (specially) coordinative unsaturation of **4**.

Although thermally quite unstable, complex **4** can be safely handled by working below 253 K, so that its chemistry can be explored in detail. Preliminary studies indicate that it readily reacts with a variety of molecules having acidic hydrogens such as thiols, carboxylic acids, or ketones such as acetone or acetylacetone. The reaction seems to proceed analogously in all cases, and it is exemplified for the latter reagent: the hydroxo ligand deprotonates the incoming molecule and the corresponding 3-e donor anion (acac) occupies the vacant position after water elimination. The resulting complex, i.e., $[\text{W}_2\text{Cp}_2(\text{O}, \text{O}'\text{-acac})(\mu\text{-PPh}_2)_2(\text{CO})]\text{BF}_4$ (**7**),^{18,19} is presumably isoelectronic with the starting material and also retains a cis disposition of the new ligand relative to the carbonyl group.

In summary, we have described efficient synthetic methods for new binuclear hydroxycarbonyl and hydroxo complexes which experience unusual H rearrangements. Moreover, these complexes are highly unsaturated molecules and therefore quite reactive under mild conditions, with the hydroxo derivative displaying a useful nucleophilic behavior. All of these properties allow us to anticipate a wide chemistry to be developed around these species, and further studies in this direction are now in progress.

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Supporting Information Available: Experimental procedures for the preparation of new complexes and microanalytical data. Data collection, refinement details and listings of atomic coordinates, thermal parameters, bond lengths and bond angles for the X-ray study on complex **3** (PDF).

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(15) Selected spectroscopic data for **5**: $\nu(\text{CO})$ (CH_2Cl_2) 1851 cm^{-1} . $\nu(\text{W}-\text{O})$ (Nujol mull) 888 cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR (81.01 MHz, CD_2Cl_2) δ 102.2 [s, $J(\text{PW})$ 381, 322]. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, CD_2Cl_2) δ 224.0 (s, CO), 100.4, 83.7 (2 \times s, Cp).

(16) A mixture of cis and trans isomers of the dimolybdenum analogue of **5** has been reported from the reaction of $[\text{Mo}_2\text{Cp}_2(\mu\text{-PPh}_2)_2(\mu\text{-CO})]$ with oxygen.⁸

(17) Selected spectroscopic data for **6**: $\nu(\text{CO})$ (CH_2Cl_2) 1977 cm^{-1} . $\nu(\text{W}-\text{O})$ (Nujol mull) 964 cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR (81.01 MHz, CD_2Cl_2) δ 31.3 [s, $J(\text{PW})$ 280, 246]. ^1H NMR (400.13 MHz, CD_2Cl_2) δ -9.83 [t, $J(\text{HP})$ 52, $J(\text{HW})$ 38, 6, $\mu\text{-H}$].

(18) Selected spectroscopic data for **7**: $\nu(\text{CO})$ (CH_2Cl_2) 1882 cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, CD_2Cl_2) δ 123.7 [s, $J(\text{PW})$ 346, 199]. ^1H NMR (300.13 MHz, CD_2Cl_2) δ 5.80, 5.30 (2 \times s, 2 \times 5H, Cp), 5.47 (s, 1H, CH), 1.09 (s, 6H, CH_3).

(19) The analogous dimolybdenum complex has been characterized through an X-ray study (results to be published).

(20) Curtis, M. D.; Fotinos, N. A.; Messerle, L.; Sattelberger, A. P. *Inorg. Chem.* **1983**, 22, 1559–1561.