Inorg. Chem. **2005**, *44*, 9637–9639

Inorganic Chemistry
Communication

Synthesis and Structural Characterization of $M(PMe_3)_3(O_2CR)_2(OH_2)H_2$ (M = Mo, W): Aqua–Hydride Complexes of Molybdenum and Tungsten

Guang Zhu and Gerard Parkin*

Department of Chemistry, Columbia University, New York, New York 10027

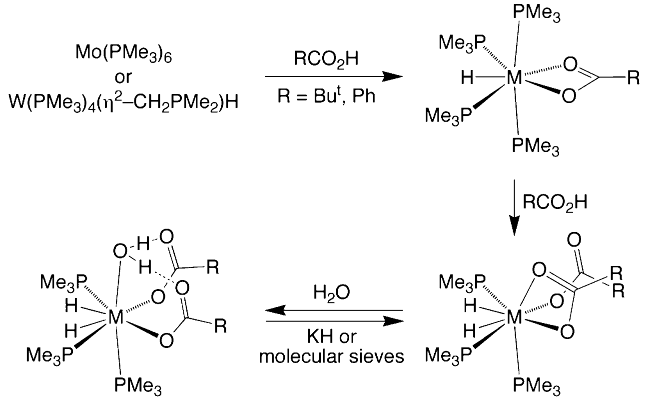
Received September 20, 2005

$Mo(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ undergo oxidative addition of the O–H bond of RCO_2H to yield sequentially $M(PMe_3)_4(\eta^2\text{-}O_2CR)H$ and $M(PMe_3)_3(\eta^2\text{-}O_2CR)(\eta^1\text{-}O_2CR)H_2$ (M = Mo and R = Ph, Bu^t; M = W and R = Bu^t). One of the oxygen donors of the bidentate carboxylate ligand may be displaced by H_2O to give rare examples of aqua–dihydride complexes, $M(PMe_3)_3(\eta^1\text{-}O_2CR)_2(OH_2)H_2$, in which the coordinated water molecule is hydrogen-bonded to both carboxylate ligands.

Aqua and hydride ligands represent unusual combinations for the early transition metals, especially in view of the fact that hydride derivatives of these metals are invariably thermodynamically unstable with respect to hydrolysis to yield either hydroxo or oxo complexes.(1) Hydride and organometallic complexes that are stable to water are, however, of considerable relevance with respect to aqueous-phase organometallic chemistry and its application to green chemistry.(2) In this paper, we report the synthesis and structural characterization of a pair of aqua−dihydride complexes, namely, $M(PMe_3)_3(\eta^1\text{-}O_2CBu^t)_2(OH_2)H_2$ (M = Mo, W).

The trimethylphosphine complexes $Mo(PMe_3)_6$(3) and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$(4) have been shown to be highly reactive towards oxidative addition of a large variety of H−X bonds. Correspondingly, $Mo(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ undergo oxidative addition of 1 equiv of RCO_2H to yield $M(PMe_3)_4(\eta^2\text{-}O_2CR)H$ (M = Mo and R = Ph, Bu^t; M = W and R = Bu^t),(5) as illustrated in Scheme 1.

Scheme 1



The molecular structure of $Mo(PMe_3)_4(\eta^2\text{-}O_2CPh)H$ has been determined by X-ray diffraction and is analogous to that of $Mo(PMe_3)_4(\eta^2\text{-}O_2CH)H$.(5a) The monocarboxylate complexes $M(PMe_3)_4(\eta^2\text{-}O_2CR)H$ (M = Mo and R = Ph, Bu^t; M = W and R = Bu^t) undergo oxidative addition of a second equivalent of RCO_2H to give $M(PMe_3)_3(\eta^2\text{-}O_2CR)(\eta^1\text{-}O_2CR)H_2$, which features both unidentate and bidentate carboxylate ligands, as demonstrated by X-ray diffraction studies on $M(PMe_3)_3(\eta^2\text{-}O_2CBu^t)(\eta^1\text{-}O_2CBu^t)H_2$ (Figure 1). The ^1H NMR spectra of $M(PMe_3)_3(\eta^2\text{-}O_2CBu^t)(\eta^1\text{-}O_2CBu^t)H_2$ at room temperature, however, exhibit a single resonance for the *tert*-butyl groups indicative of a fluxional molecule, as has been proposed for other complexes with both η^1- and η^2-carboxylate ligands.(6) It is, therefore, noteworthy that the fluxional process within $M(PMe_3)_3(\eta^2\text{-}O_2CBu^t)(\eta^1\text{-}O_2CBu^t)H_2$ may be frozen out on the NMR time scale at ca. −75 °C.

In addition to their spectroscopic properties, there are several other features of $M(PMe_3)_3(\eta^2\text{-}O_2CR)(\eta^1\text{-}O_2CR)H_2$ (R = Ph, Bu^t) that are noteworthy. For example, the bis(carboxylates) $M(PMe_3)_3(\eta^2\text{-}O_2CR)(\eta^1\text{-}O_2CR)H_2$ (R = Ph, Bu^t) are of a completely different nature than the cationic complex $[W(PMe_3)_4(\eta^2\text{-}O_2CCF_3)H_2][CF_3CO_2]$ that is obtained from the corresponding reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with 2 equiv of CF_3CO_2H.(7) Another interesting

---

* To whom correspondence should be addressed. E-mail: parkin@columbia.edu.

(1) For example, see: Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472−5478.

(2) (a) Horváth, I. T.; Joó, F. *Aqueous Organometallic Chemisty and Catalysis*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995. (b) Joó, F. *Aqueous Organometallic Catalysis*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001.

(3) Murphy, V. J.; Parkin, G. *J. Am. Chem. Soc.* **1995**, *117*, 3522−3528.

(4) Gibson, V. C.; Graimann, C. E.; Hare, P. M.; Green, M. L. H.; Bandy, J. A.; Grebenik, P. D.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1985**, 2025−2035.

(5) For $Mo(PMe_3)_4(\eta^2\text{-}O_2CR)H$ (R = H, Me, Et, CF_3), see: (a) Lyons, D.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 695−700. (b) Alvarez, R.; Carmona, E.; Galindo, A.; Gutiérrez, E.; Marín, J. M.; Monge, A.; Poveda, M. L.; Ruiz, C.; Savariault, J. M. *Organometallics* **1989**, *8*, 2430−2439.

(6) For example, see: Boyer, P. M.; Roy, C. P.; Bielski, J. M.; Merola, J. S. *Inorg. Chim. Acta* **1996**, *245*, 7−15.

10.1021/ic051617q CCC: $30.25

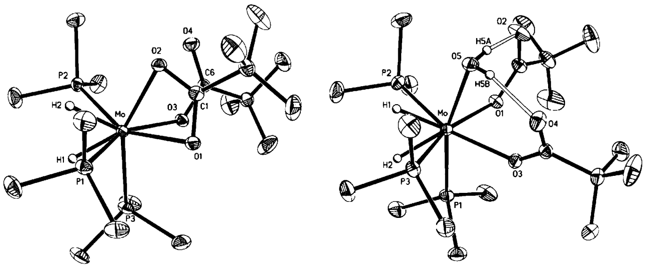


Figure 1. Molecular structures of Mo(PMe$_3$)$_3$(η^2-O$_2$CBu^t)(η^1-O$_2$CBu^t)H$_2$ and Mo(PMe$_3$)$_3$(η^1-O$_2$CBu^t)$_2$(OH$_2$)H$_2$.

aspect of M(PMe$_3$)$_3$(η^2-O$_2$CR)(η^1-O$_2$CR)H$_2$ is that one of the oxygen donors of the bidentate carboxylate ligand may be displaced by H$_2$O to give the corresponding aqua−dihydride complex, M(PMe$_3$)$_3$(η^1-O$_2$CR)$_2$(OH$_2$)H$_2$.[8] Mo(PMe$_3$)$_3$(η^1-O$_2$CBu^t)$_2$(OH$_2$)H$_2$ and W(PMe$_3$)$_3$(η^1-O$_2$CBu^t)$_2$(OH$_2$)H$_2$ have been structurally characterized by X-ray diffraction, as illustrated in Figure 1 for the molybdenum derivative; the Mo−OH$_2$ [2.242(1) Å] and W−OH$_2$ [2.224(2) Å] bond lengths in the two aqua complexes are comparable.[9]

The structures of M(PMe$_3$)$_3$(η^1-O$_2$CBu^t)$_2$(OH$_2$)H$_2$ are noteworthy because there are no structurally characterized neutral metal aqua−dihydrides listed in the Cambridge Structural Database;[10−13] several cationic derivatives are, however, known.[14,15]

The formation of the aqua adducts is reversible, and treatment of a solution of M(PMe$_3$)$_3$(η^1-O$_2$CBu^t)$_2$(OH$_2$)H$_2$ with either molecular sieves or KH to remove water regenerates M(PMe$_3$)$_3$(η^2-O$_2$CBu^t)(η^1-O$_2$CBu^t)H$_2$; the coordinated water may also be removed by exposing a sample of M(PMe$_3$)$_3$(η^1-O$_2$CBu^t)$_2$(OH$_2$)H$_2$ to vacuum for a period of 3 days. Furthermore, ^{1}H NMR spectroscopic studies indicate that dissociation is facile on the NMR time scale. For example, while a solution composed of a mixture of Mo(PMe$_3$)$_3$(η^2-O$_2$CBu^t)(η^1-O$_2$CBu^t)H$_2$ and Mo(PMe$_3$)$_3$(η^1-O$_2$CBu^t)$_2$(OH$_2$)H$_2$ exhibits distinct signals for the hydride ligands of each complex at −30 °C, the signals coalesce at ca. 35 °C. Assuming that the mechanism for exchange proceeds via rate-determining dissociation of water from Mo(PMe$_3$)$_3$(η^1-O$_2$CBu^t)$_2$(OH$_2$)H$_2$, the activation parameters for this process are $\Delta H^\ddagger = 18.0(6)$ kcal mol^{-1} and $\Delta S^\ddagger = 11(2)$ eu; the corresponding activation parameters for the tungsten complex W(PMe$_3$)$_3$(η^1-O$_2$CBu^t)$_2$(OH$_2$)H$_2$ are $\Delta H^\ddagger = 18.6(3)$ kcal mol^{-1} and $\Delta S^\ddagger = 10(1)$ eu.[16]

The coordination mode of water to a metal center has been extensively investigated, both in classical coordination compounds[17] and in organometallic and hydride derivatives.[6,14] These studies indicate that a common feature of coordinated water is that both hydrogen atoms participate in hydrogen-bonding interaction. In accord with this observation, the coordinated water molecule within M(PMe$_3$)$_3$(η^1-O$_2$CBu^t)$_2$(OH$_2$)H$_2$ (M = Mo, W) is hydrogen-bonded to both carboxylate ligands with O···O distances of 2.559(2) and 2.655(2) Å (M = Mo) and 2.537(3) and 2.631(3) Å (M = W). This hydrogen-bonding motif is similar to that in Cp*Rh(η^1-O$_2$CR)$_2$(OH$_2$) (R = Ph,[18] Me[6]) and a variety of other derivatives[19] for which the water and carboxylate ligands adopt a *fac* disposition.[20,21]

While the presence of two hydrogen bonds is common to the majority of metal−aqua compounds, there exist a variety of coordination geometries for the water ligand. For compounds in which the water is attached to a single metal center,

---

(7) Green, M. L. H.; Parkin, G.; Chen, M.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1986**, 2227−2236.

(8) Ammonia also reacts with M(PMe$_3$)$_3$(η^2-O$_2$CBu^t)(η^1-O$_2$CBu^t)H$_2$. By analogy to the aqua complexes, we postulate that the products are M(PMe$_3$)$_3$(η^1-O$_2$CBu^t)$_2$(NH$_3$)H$_2$, in which the ammonia is involved in a hydrogen-bonding interaction with the carboxylate ligands. However, the ammonia is not coordinated strongly and readily regenerates M(PMe$_3$)$_3$(η^2-O$_2$CBu^t)(η^1-O$_2$CBu^t)H$_2$ upon removal of the ammonia atmosphere.

(9) The average Mo−OH$_2$ and W−OH$_2$ bond lengths for complexes listed in the Cambridge Structural Database are 2.18 and 2.14 Å, respectively.

(10) Cambridge Structural Database (Version 5.26). *3D Search and Research Using the Cambridge Structural Database*. Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8* (1), 1 and 31−37.

(11) The molecular structure of the octahedral aqua−dihydride Ru(Imes)$_2$(CO)(OH$_2$)H$_2$ has been recently reported (see ref 11a), but it is now recognized that the structure actually corresponds to a disordered square-pyramidal hydroxy−hydride complex, Ru(Imes)$_2$(CO)(OH)H (see ref 11b). (a) Jazzar, R. F. R.; Bhatia, P. H.; Mahon, M. F.; Whittlesey, M. K. *Organometallics* **2003**, *22*, 670−683. (b) Chatwin, S. L.; Davidson, M. G.; Doherty, C.; Donald, S. M.; Jazzar, R. F. R.; Macgregor, S. A.; McIntyre, G.; Mahon, M. F.; Whittlesey, M. K., to be submitted for publication.

(12) The complex [W(PMe$_3$)$_4$H$_2$(OH$_2$)F][F] has been reported, but the complex is now recognized to be [W(PMe$_3$)$_4$H$_2$F(FHF)]. See: Murphy, V. J.; Rabinovich, D.; Hascall, T.; Klooster, W. T.; Koetzle, T. F.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 4372−4387.

(13) The complex [Os(PPr$^i_3$)$_2$(OTf)$_2$(H$_2$O)H$_2$] has been reported, but the X-ray data were not of sufficient quality to determine either the presence or number of hydrides or to verify the identity of the coordinated water on two of the four crystallographically independent molecules. See: Kuhlman, R.; Streib, W. E.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1996**, *118*, 6934−6945.

(14) Luo, X.-L.; Schulte, G. K.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 682−686.

(15) Eremenko, I. L.; Rosenberger, S.; Nefedov, S. E.; Berke, H. *Inorg. Chem.* **1995**, *34*, 830−840.

(16) The calculated energies for dissociation of water from M(PMe$_3$)$_3$(η^1-O$_2$CBu^t)$_2$(OH$_2$)H$_2$ to give M(PMe$_3$)$_3$(η^2-O$_2$CBu^t)(η^1-O$_2$CBu^t)H$_2$ ($\Delta H^{SCF} = 17.7$ kcal mol^{-1}, Mo; $\Delta H^{SCF} = 16.7$ kcal mol^{-1}, W) are comparable to the barrier for dissociation of water as determined by dynamic ^{1}H NMR spectroscopy.

(17) (a) Ferraris, G.; Franchini-Angela, M. *Acta Crystallogr.* **1972**, *B28*, 3572−3583. (b) Chiari, G.; Ferraris, G. *Acta Crystallogr.* **1986**, *B38*, 2331−2341. (c) Lutz, H. D. *Struct. Bond.* **1988**, *69*, 97−125.

(18) Kisenyi, J. M.; Sunley, G. J.; Cabeza, J. A.; Smith, A. J.; Adams, H.; Salt, N. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1987**, 2459−2466.

(19) (a) Albers, M. O.; Liles, D. C.; Singleton, E. *Acta Crystallogr.* **1987**, *C43*, 860−863. (b) Chaudhuri, P.; Stockheim, C.; Wieghardt, K.; Deck, W.; Gregorzik, R.; Vahrenkamp, H.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1992**, *31*, 1451−1457. (c) Mieczynska, E.; Trzeciak, A. M.; Ziólkowski, J. J.; Lis, T. *J. Chem. Soc., Dalton Trans.* **1995**, 105−109. (d) Chuan H.; Lippard, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 105−113. (e) Ye, B. H.; Chen, X.-M.; Xue, F.; Ji, L. N.; Mak, T. C. W. *Inorg. Chim. Acta* **2000**, *299*, 1−8. (f) Malik, K. Z.; Robinson, S. D.; Steed, J. W. *Polyhedron* **2000**, *19*, 1589−1592. (g) Speier, G.; Tyeklár, Z.; Tóth, P.; Speier, E.; Tisza, S.; Rockenbauer, A.; Whalen, A. M.; Alkire, N.; Pierpont, C. G. *Inorg. Chem.* **2001**, *40*, 5653−5659. (h) Warzeska, S. T.; Miccichè, F.; Mimmi, M. C.; Bouwman, E.; Kooijman, H.; Spek, A. L.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **2001**, 3507−3512. (i) Liu, G.-F.; Ye, B.-H.; Ling, G.-H.; Chen, X.-M. *Chem. Commun.* **2002**, 1442−1443.

(20) Complexes that exhibit a similar motif but with a trans arrangement of carboxylate ligands and a *mer* arrangement with the aqua ligand are also known. See: (a) Wu, X.-L.; Tong, Y.-X.; Chen, X.-M.; Mak, T. C. W. *Acta Crystallogr.* **1998**, *C54*, 606−608. (b) Kuznetsov, V. P.; Yap, G. P. A.; Alper, H. *Organometallics* **2001**, *20*, 1300−1309. (c) Jensen, D. R.; Schultz, M. J.; Mueller, J. A.; Sigman, M. S. *Angew. Chem., Int. Ed.* **2003**, *42*, 3810−3813.

(21) For an example in which the aqua ligand also bridges two metals, see: Coucouvanis, D.; Reynolds, R. A., III; Dunham, W. R. *J. Am. Chem. Soc.* **1995**, *117*, 7570−7571.

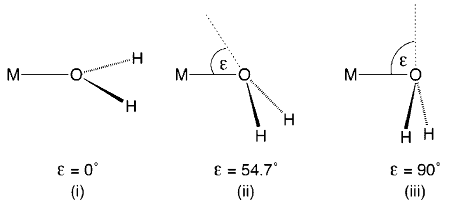


Figure 2. Metal−aqua coordination modes.

the M−OH_2 coordination modes may be differentiated by the magnitude of the displacement of the metal from the plane defined by the three atoms of the water moiety,[17] as illustrated in Figure 2. Several idealized geometries may be considered and classified according to the magnitude of the displacement, viz., (i) $\epsilon = 0°$, for which the oxygen is trigonal planar and the bonding may formally be considered to involve lone-pair donation from an sp^2 hybrid on oxygen, (ii) $\epsilon = 54.7°$, for which the oxygen is pyramidal and the bonding involves lone-pair donation from an sp^3 hybrid on oxygen, and (iii) $\epsilon = 90°$, for which the oxygen is highly angular and the bonding involves lone-pair donation from a p orbital of an sp^2-hybridized oxygen atom. Not surprisingly, many compounds that contain a water molecule bonded to a single metal atom adopt a geometry that most closely corresponds to class ii, with the interaction involving lone-pair donation from an sp^3 hybrid. While the bonding in the extreme class i[14] and iii[22] geometries may be formally discussed in terms of sp^2-hybridized oxygen coordinating through either an sp^2 hybrid orbital or a p orbital, respectively, it has also been suggested that the bonding between the metal and oxygen may be ionic in nature and thus relatively nondirectional, such that the geometry is determined by the positions of the hydrogen-bond acceptors.[6,14]

Identification of the coordination geometry requires knowledge of the positions of the hydrogen atoms, but in view of the difficulty associated with locating hydrogen atom positions by X-ray diffraction, the positions of the hydrogen-bond receptors have instead frequently been used to define the O−H bond vector on the basis that hydrogen bonds involving water are typically linear.[6,14,17a,23] However, the hydrogen atoms of the water ligands of $M(PMe_3)_3(\eta^1\text{-}O_2CBu^t)_2(OH_2)H_2$ (M = Mo, W) were located and refined to chemically reasonable positions, thereby indicating that the hydrogen atoms are displaced from the [O···O···O] plane. As a result, the values of ϵ calculated on the basis of the hydrogen atom positions differ considerably from the values obtained by assuming that the O−H···O bonds are linear, as summarized in Table 1. In view of this discrepancy and the fact that it is imprudent to rely on the location of the hydrogen atoms as determined by X-ray diffraction, we have performed density functional theory calculations to establish more details pertaining to the coordination mode of the water molecule in $M(PMe_3)_3(\eta^1\text{-}O_2CBu^t)_2(OH_2)H_2$.

Table 1. Displacement of the Metal Atom from the Aqua Plane (ϵ) As Evaluated by M−[OH_2(plane)] and M−[O···O_2(plane)] Angles[a]

	M−[OH_2(plane)]	M−[O···O_2(plane)]
Mo	71.3 (70.7)	85.4 (85.7)
W	70.0 (66.8)	83.8 (83.4)

[a] Values in parentheses are for the geometry-optimized structures.

The geometry-optimized structures of $M(PMe_3)_3(\eta^1\text{-}O_2CBu^t)_2(OH_2)H_2$ compare favorably with the experimental structures. In particular, the values of ϵ calculated on the basis of the hydrogen atom positions are comparable to the experimental structures, as are the values of ϵ based on the O···O···O plane (Table 1). Thus, while the values of ϵ based on the position of the hydrogen-bond acceptors imply that the metal is almost orthogonal to the aqua plane (geometry iii of Figure 2) and is hence coordinated via a single p orbital, consideration of the hydrogen atom positions indicates that the metal−aqua geometry more closely resembles that of structure ii, in which the oxygen coordinates via an orbital with $\approx sp^3$ character. It is, therefore, evident that the assumption that O−H···O bonds are linear in metal−aqua compounds can result in a misleading description of the bonding in metal−aqua complexes.[24]

In conclusion, $Mo(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ undergo oxidative addition of the O−H bond of RCO_2H to yield sequentially $M(PMe_3)_4(\eta^2\text{-}O_2CR)H$ and $M(PMe_3)_3(\eta^2\text{-}O_2CR)(\eta^1\text{-}O_2CR)H_2$ (M = Mo and R = Ph, Bu^t; M = W and R = Bu^t), the latter of which features both unidentate and bidentate carboxylate ligands. One of the oxygen donors of the bidentate carboxylate ligand may be displaced by H_2O to give examples of rare aqua−dihydride complexes, $M(PMe_3)_3(\eta^1\text{-}O_2CR)_2(OH_2)H_2$, in which the water molecule is hydrogen-bonded to both carboxylate ligands. Despite this hydrogen-bonding interaction, however, the water may be readily removed by treatment with either molecular sieves or KH.

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences (Grant DE-FG02-93ER14339), for support of this research.

Supporting Information Available: Experimental data, computational data for geometry-optimized structures, and crystallographic data (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

IC051617Q

---

(22) For example, see ref 6.

(23) Pedersen, B. *Acta Crystallogr.* **1974**, *B30*, 289−291.

(24) In this regard, it should be noted that while strong hydrogen bonds are typically close to linear, the angle for weaker hydrogen bonds is reduced to 160 ± 20°. See: Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: New York, 1991.