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C−H versus O−H Bond Cleavage Reactions of Bis(2-hydroxyphenyl)phenylamine, $PhN(o\text{-}C_6H_4OH)_2$: Synthesis and Structural Characterization of Mononuclear and Dinuclear Tungsten Aryloxide Complexes Which Exhibit Bidentate, Tridentate, and Tetradentate Coordination Modes

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Summary: The phenylimino-bridged diphenol $PhN(o\text{-}C_6H_4OH)_2$ *reacts with* $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ *to yield a variety of mononuclear and dinuclear complexes that include* $[\kappa^2\text{-}PhN(C_6H_4OH)(C_6H_3O)]W(PMe_3)_4H_2$, $[\mu\text{-}\kappa^2,\kappa^2\text{-}PhN(C_6H_3O)_2]\{W(PMe_3)_4H_2\}_2$, $[\kappa^3\text{-}PhN(C_6H_4O)_2]W(PMe_3)_3H_2$, $[\kappa^4\text{-}N(C_6H_4)(C_6H_4O)_2]W(PMe_3)_3H$, *and* $[\kappa^2\text{-}PhN(C_6H_4O)_2]_2W(PMe_3)_2$ *via O−H and C−H bond activation reactions. Structural characterization of these compounds by X-ray diffraction demonstrates that the derived alkoxide ligand is structurally flexible and can adopt bidentate, tridentate, and tetradentate coordination modes.*

Introduction

Alkoxide (OR) and aryloxide (OAr) ligands have been employed extensively in organometallic chemistry,[1] with applications in areas as diverse as olefin and acetylene metathesis[2] and materials chemistry.[3] The widespread use of these ligands is commonly associated with their ability to stabilize a variety of coordination environments. Specifically, alkoxide and aryloxide ligands are electronically versatile due to the availability of two lone pairs on the oxygen atom that allow them to function as one-electron (X), three-electron (LX), or five-electron (L_2X) donors[4] depending upon the electronic needs of the metal center. Furthermore, the steric demands of alkoxide and aryloxide ligands may also be readily modified, as exemplified by the very bulky $OCBu^t_3$ ligand.[5] In addition to mono(aryloxide) ligands, considerable attention has been given to the application of bis- and poly(aryloxide) ligands. With respect to bis(aryloxide) ligands, the majority of studies have been devoted to biphenolate or binaphtholate derivatives in which the two aryloxide moieties are directly linked together,[6] but more recently attention has been given to derivatives in which the aryloxide groups are attached by a linker.[7−10] Since the nature of the linker modifies the chemistry of the system,[11] we are interested in developing the application of bis(aryloxide) ligands that feature a nitrogen bridge, with particular emphasis being given to the chemistry of the early transition metals. In this paper, we describe the reactivity of the phenylimino-bridged diphenol $PhN(o\text{-}C_6H_4OH)_2$[12,13] towards $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$, thereby resulting in a series of O−H and C−H bond activation reactions to give products that feature (i) bidentate $\kappa^2\text{-}O_2$ and κ^2-OC, (ii) tridentate $\kappa^3\text{-}O_2N$, and (iii) tetradentate $\kappa^4\text{-}O_2CN$ coordination modes.

Whereas the tris(phenol) $N(o\text{-}C_6H_4OH)_3$ has been used to prepare a variety of transition-metal derivatives,[14] counterparts of the structurally related diphenol $PhN(o\text{-}C_6H_4OH)_2$ have not previously been reported.[15] It is, therefore, noteworthy that an array of tungsten complexes may be obtained via treatment of

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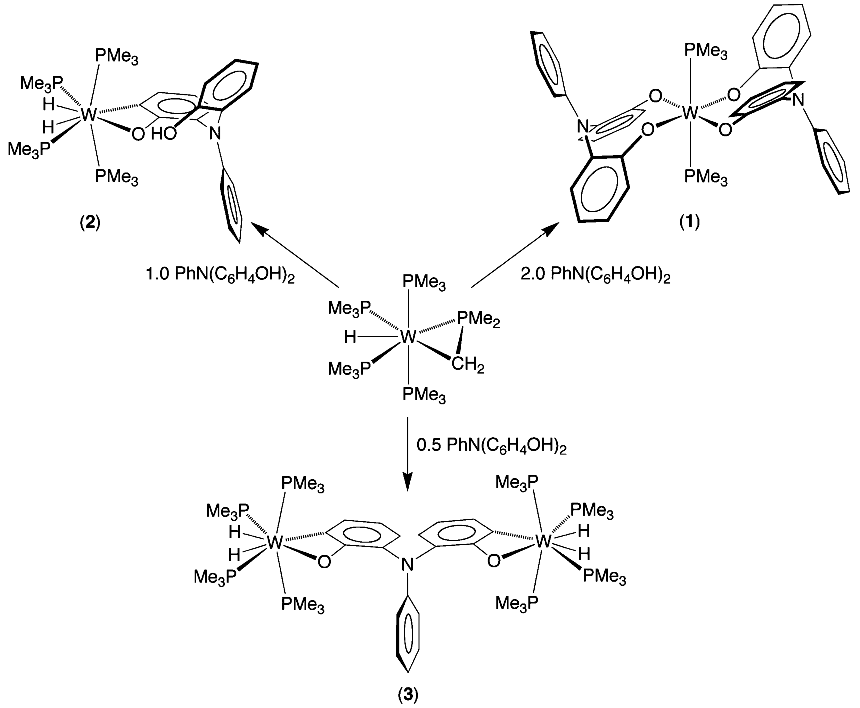
Scheme 1



$W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with $PhN(o\text{-}C_6H_4OH)_2$, with the nature of the product being critically dependent on stoichiometry (Scheme 1). For example, $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ reacts with $PhN(o\text{-}C_6H_4OH)_2$ in a 1:2 molar ratio to yield the octahedral bis(diphenolate) complex $[\kappa^2\text{-}PhN(C_6H_4O)_2]_2W(PMe_3)_2$ (**1**) via reaction with the O−H bonds of two $PhN(o\text{-}C_6H_4OH)_2$ molecules.[16] In contrast, the corresponding reaction with a 1:1 molar ratio results in both O−H and C−H bond activation, yielding $[\kappa^2\text{-}PhN(C_6H_4OH)(C_6H_3O)]W(PMe_3)_4H_2$ (**2**) (Scheme 1), in which one of the O−H bonds remains intact and participates in a O−H···O hydrogen-bonding interaction with the oxygen atom of the aryloxide moiety (Figure 1). Despite the hydrogen-bonding interaction, the O−H bond in $[\kappa^2\text{-}PhN(C_6H_4OH)(C_6H_3O)]W(PMe_3)_4H_2$ (**2**) is reactive and treatment with $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ results in the formation of the dinuclear complex $[\mu\text{-}\kappa^2,\kappa^2\text{-}PhN(C_6H_3O)_2]\{W(PMe_3)_4H_2\}_2$ (**3**), which corresponds to an overall 2:1 stoichiometry.

The formation of $[\kappa^2\text{-}PhN(C_6H_4OH)(C_6H_3O)]W(PMe_3)_4H_2$ (**2**) in the 1:1 reaction is of particular note, because the bidentate κ^2-O,C coordination mode demonstrates that oxidative addition of the C−H bond of the aryloxy ligand is favored over oxidative addition of the second O−H bond. In this regard, we have previously demonstrated that ortho C−H bond activation to give four-membered oxametallacycles is a common feature of the reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with phenols and have established that this preference is kinetic in origin.[17,18] Supporting this notion, the C−H bond cleavage reaction is reversible and $[\kappa^2\text{-}PhN(C_6H_4OH)(C_6H_3O)]W(PMe_3)_4H_2$ (**2**) converts to $[\kappa^3\text{-}PhN(C_6H_4O)_2]W(PMe_3)_3H_2$ (**4**) upon heating at ca. 60 °C (Scheme 2).[19] The molecular structure of $[\kappa^3\text{-}PhN(C_6H_4O)_2]W(PMe_3)_3H_2$ (**4**) has been determined by X-ray diffraction (Figure 2), thereby demonstrating that, in contrast to $[\kappa^2\text{-}PhN(C_6H_4O)_2]_2W(PMe_3)_2$ (**2**), the nitrogen atom also coordinates to the metal center;[20] as such, the ligand adopts a tridentate $\kappa^3\text{-}O_2N$ mode.

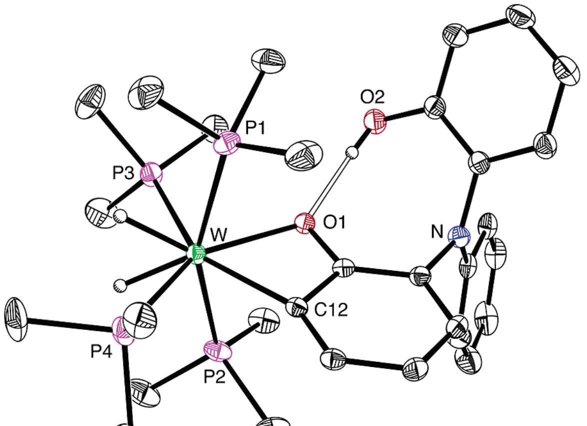


Figure 1. Molecular structure of $[\kappa^2\text{-}PhN(C_6H_4OH)(C_6H_3O)]W(PMe_3)_4H_2$ (**2**).

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[10] Other linkers include Te,[10a] S(O),[10b] S_2,[10c] SCH_2CH_2S,[10d] CH_2CH_2,[10e] and N(H)C(O)C(O)NH:[10f] (a) Nakayama, T.; Watanabe, K.; Ueyama, N.; Nakamura, A.; Harada, A.; Okuda, J. *Organometallics* **2000**, *19*, 2498−2503. (b) Okuda, J.; Fokken, S.; Kang, H.-C.; Massa, W. *Polyhedron* **1998**, *17*, 943−946. (c) Okuda, J.; Fokken, S.; Kleinhenn, T.; Spaniol, T. P. *Eur. J. Inorg. Chem.* **2000**, 1321−1326. (d) Capacchione, C.; Proto, A.; Ebeling, H.; Mülhaupt, R.; Möller, K.; Manivannan, R.; Spaniol, T. P.; Okuda, J. *J. Mol. Catal. A: Chem.* **2004**, *213*, 137−140. (e) Fokken, S.; Spaniol, T. P.; Okuda, J.; Sernetz, F. G.; Mülhaupt, R. *Organometallics* **1997**, *16*, 4240−4242. (f) Jimenez-Pérez, V. M.; Camacho-Camacho, C.; Güizado-Rodríguez, M.; Nöth, H.; Contreras, R. *J. Organomet. Chem.* **2000**, *614−615*, 283−293.

[11] For example, sulfur−bridged bis(aryloxide) ligands create more active titanium olefin polymerization catalysts than the corresponding methylene-bridged derivatives. See: Miyatake, T.; Mizunuma, K.; Kakugo, M. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 203−214.

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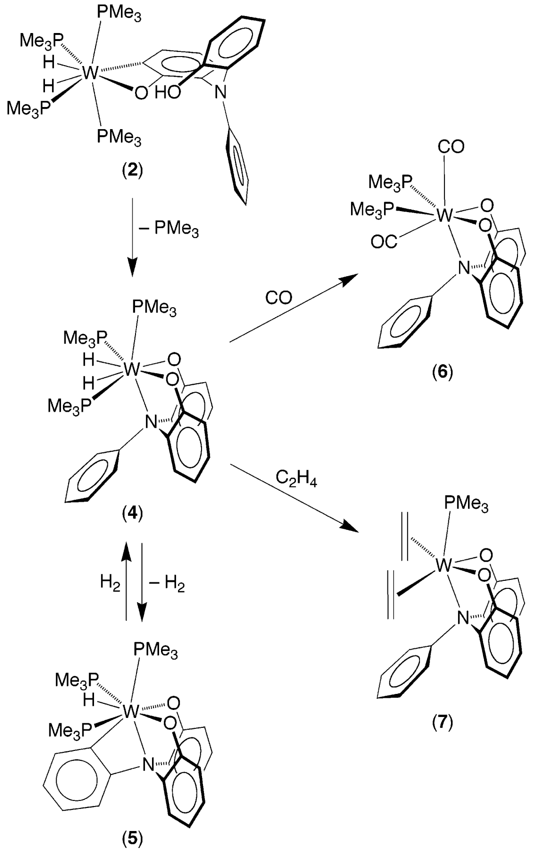
[15] For antimony complexes of this ligand, see: Tanski, J. M.; Kelly, B. V.; Parkin, G. *Dalton Trans.* **2005**, 2442−2447.

[16] The structurally related molybdenum complex $Mo(PMe_3)_2(OPh)_4$ has been reported. See: (a) Hascall, T.; Murphy, V. J.; Parkin, G. *Organometallics* **1996**, *15*, 3910−3912. (b) Hascall, T.; Murphy, V. J.; Janak, K. E.; Parkin, G. *J. Organomet. Chem.* **2002**, *652*, 37−49.

Scheme 2



A further example of the structural versatility of this system is provided by the observation that $[\kappa^3\text{-PhN}(C_6H_4O)_2]W(PMe_3)_3H_2$ (**4**) reductively eliminates H_2 at ca. 80 °C to give $[\kappa^4\text{-N}(C_6H_4)(C_6H_4O)_2]W(PMe_3)_3H$ (**5**) via oxidative addition of the ortho C−H bond of the phenyl substituent, thereby generating a *tetradentate* tripodal ligand. $[\kappa^4\text{-N}(C_6H_4)(C_6H_4O)_2]W(PMe_3)_3H$ (**5**) has been structurally characterized by X-ray diffraction (Figure 3), and the W−N bond length (2.271(8) Å) is substantially shorter than that in the κ^3 precursor, $[\kappa^3\text{-PhN}(C_6H_4O)_2]W(PMe_3)_3H_2$ (**4**) (2.451(4) Å), an observation that may be associated with the geometrical constraint imposed by formation of the W−C bond. The formation of $[\kappa^4\text{-N}(C_6H_4)(C_6H_4O)_2]W(PMe_3)_3H$ (**5**) is reversible, and treatment with H_2 (1 atm) regenerates $[\kappa^3\text{-PhN}(C_6H_4O)_2]W(PMe_3)_3H_2$ (**4**) ($K \approx 10^3$ M^{-1} at 80 °C).

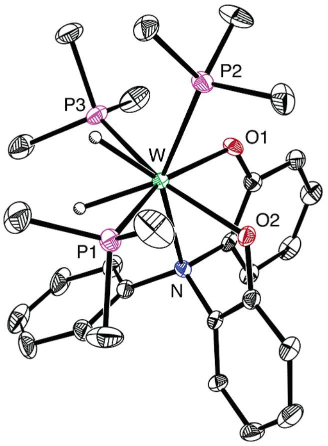


Figure 2. Molecular structure of $[\kappa^3\text{-PhN}(C_6H_4O)_2]W(PMe_3)_3H_2$ (**4**).

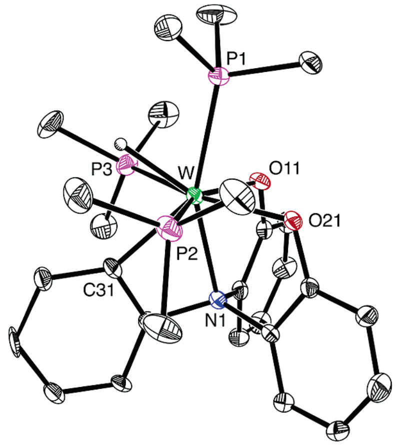


Figure 3. Molecular structure of $[\kappa^4\text{-N}(C_6H_4)(C_6H_4O)_2]W(PMe_3)_3H$ (**5**).

The interconversion of $[\kappa^3\text{-PhN}(C_6H_4O)_2]W(PMe_3)_3H_2$ (**4**) and $[\kappa^4\text{-N}(C_6H_4)(C_6H_4O)_2]W(PMe_3)_3H$ (**5**) presumably proceeds via the 16-electron intermediate $\{[\kappa^3\text{-PhN}(C_6H_4O)_2]W(PMe_3)_3\}$. Evidence in support of this statement is provided by the observation that $[\kappa^3\text{-PhN}(C_6H_4O)_2]W(PMe_3)_3H_2$ (**4**) reacts with CO and C_2H_4 to give the bis(carbonyl) and bis(ethylene) complexes $[\kappa^3\text{-PhN}(C_6H_4O)_2]W(PMe_3)_2(CO)_2$ (**6**) and $[\kappa^3\text{-PhN}(C_6H_4O)_2]W(PMe_3)(C_2H_4)_2$ (**7**), which may be viewed as derivatives of $\{[\kappa^3\text{-PhN}(C_6H_4O)_2]W(PMe_3)_3\}$. While the carbonyl complex is an 18-electron derivative, the ethylene complex is formally a 16-electron compound; closely related precedents are, nevertheless, provided by $W(PMe_3)_2(C_2H_4)_2Cl_2$ and $W(PMe_3)_2(C_2H_4)_2(Me)(ClAlMe_2Cl)$.[21]

In summary, the diphenol PhN(*o*-$C_6H_4OH)_2$ has proven to be a useful reagent for preparing a variety of tungsten aryloxide compounds. Structural characterization of these compounds by X-ray diffraction demonstrates that the derived alkoxide ligand is structurally flexible and can adopt bidentate, tridentate, and tetradentate coordination modes and can also link two metal centers together. The ability to synthesize the dinuclear complex $[\mu\text{-}\kappa^2\kappa^2\text{-PhN}(C_6H_3O)_2]\{W(PMe_3)_4H_2\}_2$ (**3**) suggests that the reactivity of the O−H bond in $[\kappa^2\text{-PhN}(C_6H_4OH)(C_6H_3O)]W$-

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(17) For example, of the monosubstituted phenols 2-RC_6H_4OH (R = Me, Et, Pr^i, Bu^t) for which a variety of potential C−H bond activation reactions are possible, leading to the formation of four-, five- or six-membered oxametallacycles, only 2-methylphenol gives the five-membered oxametallacycle $W(PMe_3)_4[\kappa^2\text{-OC}_6H_3(CH_2)]H_2$, with all other derivatives giving the four-membered ortho-metalated alternative $W(PMe_3)_4[\kappa^2\text{-OC}_6H_3R]H_2$. See: (a) Rabinovich, D.; Zelman, R.; Parkin, G. *J. Am. Chem. Soc.* **1990**, *112*, 9632−9633. (b) Rabinovich, D.; Zelman, R.; Parkin, G. *J. Am. Chem. Soc.* **1992**, *114*, 4611−4621.

(18) For other examples of structurally characterized compounds with four-membered ortho-metalated aryloxide ligands, see: (a) Bag, N.; Choudhury, S. B.; Lahiri, G. K.; Chakravorty, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1626−1627. (b) Bag, N.; Choudhury, S. B.; Lahiri, G. K.; Chakravorty, A. *Inorg. Chem.* **1990**, *29*, 5013−5014. (c) Aneetha, H.; Rao, C. R. K.; Rao, K. M.; Zacharias, P. S.; Feng, X.; Mak, T. C. W.; Srinivas, B.; Chiang, M. Y. *Dalton Trans.* **1997**, 1697−1703.

(19) An interesting aspect of the conversion of $[\kappa^2\text{-PhN}(C_6H_4OH)(C_6H_3O)]W(PMe_3)_4H_2$ to $[\kappa^3\text{-PhN}(C_6H_4O)_2]W(PMe_3)_3H_2$ is that the overall oxidative addition of the second O−H bond is inhibited by PMe_3 and catalyzed by H_2.

(20) The W−N bond length in $W(PMe_3)_3[\kappa^3\text{-N}(C_6H_4O)_2(Ph)]H_2$ is 2.451(4) Å. For comparison, the average $W{-}NR_3$ bond length for compounds listed in the Cambridge Structural Database is 2.31 Å (Cambridge Structural Database, Version 5.27). Allen, F. H.; Kennard, O. 3D Search and Research Using the Cambridge Structural Database. *Chemical Design Automation News* **1993**, *8*(1), 1, 31−37.

(21) Sharp, P. R. *Organometallics* **1984**, *3*, 1217−1223.

$(PMe_3)_4H_2$ (**2**) may enable the synthesis of heterobimetallic complexes, an area that is currently being investigated.

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Supporting Information Available: Text, figures, and tables giving experimental details and CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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