Organometallics **2003,** *22,* 2259−2266

Low-Valent Tungsten Aryloxide Compounds with Pyridine Ancillary Ligation: Intramolecular Reduction of Heterocyclic and Aromatic Rings Including Formation of an η^5-Cyclohexadienyl Group

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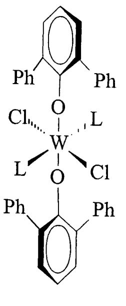
Received January 22, 2003

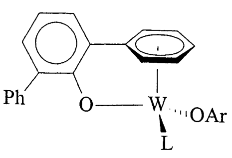
The sodium amalgam reduction (2 Na per W) of hydrocarbon solutions of [W(OC$_6$HPh$_4$-2,3,5,6)$_2$Cl$_4$] in the presence of pyridine or 4-*tert*-butylpyridine leads to the W(IV) compounds [W(OC$_6$HPh$_4$-2,3,5,6)$_2$Cl$_2$(py)$_2$] (**1**) and [W(OC$_6$HPh$_4$-2,3,5,6)$_2$Cl$_2$(4-*tert*-butylpyridine)$_2$] (**2**) in good yields. The ambient-temperature ^{1}H NMR spectra of both **1** and **2** were found to be sharp and to exhibit extensive contact shifts due to the paramagnetic tungsten center. The addition of 2,2′-bipyridine to an emerald green solution of [W(OC$_6$HPh$_3$-η^6-C$_6$H$_5$)(OC$_6$HPh$_4$-2,3,5,6)(PEt$_3$)] produced [W(OC$_6$HPh$_4$-2,3,5,6)$_2$(bipy)$_2$] (**3**), containing two bipy rings and two terminal aryloxide ligands coordinated mutually *cis*. The W−N(bipy) distances of 2.092(2), 2.093(2), 2.096(2), and 2.115(2) Å in **3** are among the shortest so far reported for bipy ligands bound to either molybdenum or tungsten. The solid state and solution data for **3** indicate that reduction of both bipy ligands has occurred, but whether this involves four-electron reduction to yield d^0-W(VI) is unclear. The addition of 4-*tert*-butylpyridine to [W(OC$_6$HPh$_3$-η^6-C$_6$H$_5$)(OC$_6$HPh$_4$-2,3,5,6)(PEt$_3$)] was found (^{1}H NMR) to lead only to partial substitution of the phosphine ligand to produce [W(OC$_6$HPh$_3$-η^6-C$_6$H$_5$)(OC$_6$HPh$_4$-2,3,5,6)(py-Bu^t-4)] (**4**). The sodium amalgam reduction (4 Na per W) of hydrocarbon solutions of [W(OC$_6$HPh$_4$-2,3,5,6)$_2$Cl$_4$] in the presence of 4-*tert*-butylpyridine produced a mixture found to contain the expected compound **4** along with a new salt compound, [W(OC$_6$HPh$_3$-η^5-C$_6$H$_6$)(OC$_6$HPh$_3$-η^1-C$_6$H$_4$)(OC$_6$HPh$_4$-2,3,5,6)][Cl] (**5**), containing a total of three aryloxide ligands. Crystals were obtained containing a 1:1 ratio of **4**/**5**. One of the aryloxides in **5** is terminally bound, the second is cyclometalated, while the third chelates to the metal center via an η^5-interaction with an ortho-cyclohexadienyl ring. The formal oxidation state of the metal center in **5** is (VI), and the unit cell contains one chloride ion to balance the positive charge on the tungsten. In compound **5** the hydride ligand formed via the cyclometalation has been transferred to the ortho-position of a phenyl ring. The structural parameters for the π-bound rings in **4** and **5** and their relevance to catalytic arene hydrogenation are discussed.

Introduction

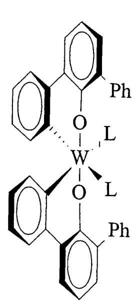
The chemistry of tungsten aryloxides continues to be an area of intense research interest.[1] Aryloxide ligands are an important component of many tungsten metathesis catalysts.[2] Also there has been an awareness that the combination of π-donating aryloxide ligands with lower valent, mononuclear tungsten metal centers can lead to interesting structures and reactivity. Previous studies by our group have shown that the sodium amalgam reduction of the tetrachloride species [W(OC$_6$H$_3$Ph$_2$-2,6)$_2$Cl$_4$], in the presence of phosphine ligands (L), typically leads (via the intermediacy of **I** and **II**) to the bis-cyclometalated compounds [W(OC$_6$H$_3$-Ph-η^1-C$_6$H$_4$)$_2$(L)$_2$] (**III**).[3] With choice of a suitable phosphine, the deep-green compound [W(OC$_6$H$_3$Ph-η^6-C$_6$H$_5$)(OC$_6$H$_3$Ph$_2$-2,6)(L)] (**II**) can be isolated and shown to thermally convert to the cyclometalated species **III** and H$_2$.[4]



I



II



III

In contrast, reduction of the compounds [W(OC$_6$HPh$_2$-2,6-R$_2$-3,5)$_2$Cl$_4$] (containing metalation-resistant aryloxides; R = Ph, Me, Bu^t) in the presence of a variety of

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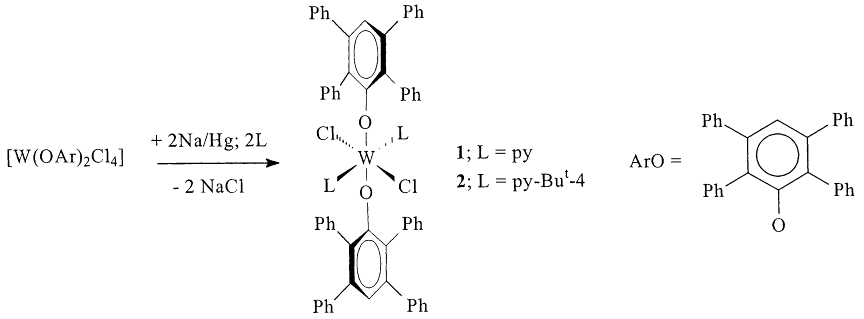
10.1021/om030054s CCC: $25.00
Publication on Web 05/01/2003

Scheme 1



phosphine ligands generates the W(II) species of type **II** [$W(OC_6HR_2Ph$-η^6-$C_6H_4)(OC_6HPh_2$-2,6-R_2-3,5)(L)] in moderate yield.[5] Solutions of these deep-green compounds in C_6D_6 are unchanged (NMR) after being heated at 100 °C for hours. These compounds prove to be valuable substrates for the four-electron reduction of a variety of small molecules.[6]

The majority of these studies have focused on the use of tertiary phosphine ligands as the ancillary Lewis base used to stabilize mononuclear, electron-deficient tungsten aryloxides. In one case it was shown that pyridine and bipyridine adducts of the bis-cyclometalated compounds **III** exhibited extremely interesting temperature-dependent NMR spectra, from which the singlet−triplet energy gap of these d^2-metal compounds were exquisitely sensitive to the π-acidity of the coordinated N-heterocycle ring.[7] Previous work has also shown that the adducts of formally titanium(II) with ligands of this type have interesting electronic and structural properties.[8] In this context we report here on an investigation of the effects of pyridine and bipyridine ligands on the reduction chemistry of the W(VI) aryloxide [$W(OC_6HPh_4$-2,3,5,6$)_2Cl_4$]. Besides generating some new adducts with interesting electronic properties, an aryloxide compound was fortuitously isolated that contains an η^5-cyclohexadienyl ring bound to tungsten. This compound is highly significant to the mechanism of arene hydrogenation, which can be catalyzed by related aryloxide compounds.[9]

Results and Discussion

Synthesis and Spectroscopic Properties of [$W(OAr)_2Cl_2(py)_2$] Compounds. The sodium amalgam reduction (2 Na per W) of hydrocarbon solutions of [$W(OC_6HPh_4$-2,3,5,6$)_2Cl_4$] in the presence of pyridine or 4-*tert*-butylpyridine leads to the W(IV) compounds **1** and **2** in good yields (Scheme 1). Both [$W(OC_6HPh_4$-2,3,5,6$)_2Cl_2(py)_2$] (**1**) and [$W(OC_6HPh_4$-2,3,5,6$)_2Cl_2$(4-*tert*-butylpyridine$)_2$] (**2**) were found to be highly insoluble in straight chain hydrocarbon solvents and somewhat soluble in aromatic hydrocarbons. Compounds **1** and **2** can be purified easily using hot toluene, yielding the pure product as small red needles. Both ^1H NMR and elemental analysis agree with the assigned formulation. The assignment of an all-trans geometry is based upon previously isolated phosphine complexes.[10] Also the direct d^1-group 5 analogues [$M(OC_6H_3Pr^i_2$-2,6$)_2Cl_2(py)_2$] (M = Nb, Ta) have been reported and fully characterized (crystallographic inversion center).[11]

Table 1. Temperature Dependence of the ^1H NMR Chemical Shifts of the 4-*tert*-Butylpyridine Signals in [$W(OC_6HPh_4$-2,3,5,6$)_2Cl_2(py$-Bu^t-4$)_2$]

temp (°C)	δ ortho-H (ppm)	δ meta-H (ppm)	δ Bu^t (ppm)
95	−30.99	14.85	0.58
85	−31.52	14.75	0.52
75	−32.04	14.64	0.45
65	−32.62	14.51	0.38
55	−33.18	14.39	0.31
45	−33.75	14.26	0.24
35	−34.32	14.11	0.16
25	−34.92	13.96	0.09
15	−35.50	13.80	0.01
5	−36.06	13.63	−0.08
−5	−36.63	13.45	−0.16
−15	−37.21	13.27	−0.25

The ambient-temperature ^1H NMR spectra of both **1** and **2** were found to be sharp and to exhibit extensive contact shifts due to the paramagnetic tungsten center. At 25 °C the aryloxide protons are unusually spread apart but still remain close to the aromatic region, with the exception of the singlet from the phenoxy proton, which is located at δ 5.00 and 4.93 ppm for **1** and **2**, respectively. The protons that exhibited the most contact shift were those of the pyridine rings. In both compounds the ortho-protons were found to resonate at very high field, δ −26.14 and −34.92 ppm for **1** and **2**, respectively. The para-protons of the pyridine ring in **1** are also upfield shifted to δ −23.71. In contrast the meta-protons appear downfield at δ 12.15 and 13.96 ppm for **1** and **2**, respectively. The CMe_3 protons in **2**

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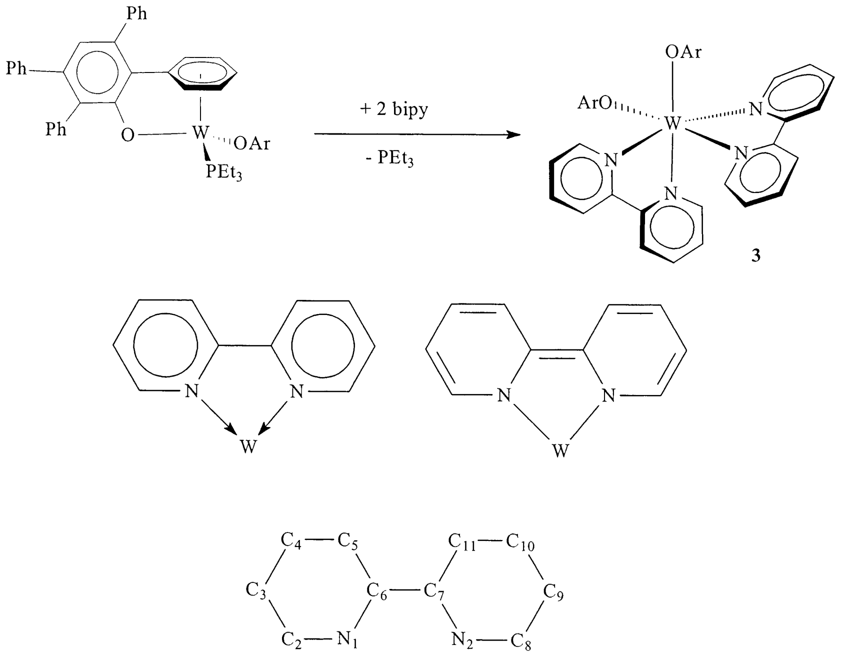
Scheme 2



Atoms	W-bipy 1/Å	W-bipy 2/Å	bipy/Å
N(1)-C(2)	1.366(6)	1.374(3)	1.341(2)
C(2)-C(3)	1.365(5)	1.360(3)	1.384(2)
C(3)-C(4)	1.411(5)	1.409(4)	1.383(3)
C(4)-C(5)	1.358(5)	1.357(4)	1.385(2)
C(5)-C(6)	1.414(4)	1.403(4)	1.394(2)
C(6)-N(1)	1.383(3)	1.380(3)	1.346(2)
C(6)-C(7)	1.412(4)	1.409(4)	1.490(3)
C(7)-N(2)	1.383(3)	1.380(3)	1.346(2)
N(2)-C(8)	1.381(4)	1.374(3)	1.341(2)
C(8)-C(9)	1.356(4)	1.370(4)	1.384(2)
C(9)-C(10)	1.415(4)	1.399(5)	1.383(3)
C(10)-C(11)	1.357(5)	1.362(5)	1.385(2)
C(11)-C(7)	1.414(4)	1.410(4)	1.394(2)

appear as a sharp singlet at δ 0.09 ppm, upfield of the normal diamagnetic position for these protons.

The variation of these shifts around the pyridine ring is indicative of considerable spin density from the metal being transferred through the aromatic ring of the pyridine by a hyperconjugative mechanism.[12] The temperature dependence of the ^{1}H NMR spectrum of **2** in d_8-toluene was measured. In Table 1 are collected the variation of the chemical shifts of the *tert*-butylpyridine ligand as a function of temperature. This behavior is dramatically different from that observed for the biscyclometalated compounds of type **III** [W(OC$_6$H$_3$Ph-η^1-C$_6$H$_4$)$_2$(L)$_2$] (L = pyridines or bipyridines), where chemical shifts approached their diamagnetic positions as the temperature was lowered.[7] This was interpreted in terms of a ground state diamagnetic singlet state for the d^2-tungsten metal center with a thermally populated triplet state. The ground state electronic structure has also been shown to be very sensitive to the nature of the aryloxide in [W(OAr)$_2$Cl$_2$(PR$_3$)$_2$] species.[10] It appears that compounds **1** and **2** contain triplet ground states, which generate the hyperfine shifts and Curie temperature dependence. Other d^2 octahedral systems that exhibit this type of behavior, such as [WCl$_4$(PR$_3$)$_2$], can be found in the literature.[13]

Synthesis, Structure, and Spectroscopic Properties of [W(OAr)$_2$(bipy)$_2$]. The compounds [W(OC$_6$HPh$_3$-η^6-C$_6$H$_5$)(OC$_6$HPh$_4$-2,3,5,6)(L)] (L = tertiary phosphines) have been shown to react with aromatic diazines to cleave the N=N bond and yield novel seven-membered diaza-metallacycles.[6e] The addition of 2,2′-bipyridine to an emerald green solution of the PEt$_3$ adduct was found to produce a deep-purple solution after a few minutes. The solution was layered with pentanes to induce crystal formation of the product **3** (Scheme 2). Compound **3** was found to be diamagnetic and soluble in both straight chain and aromatic hydrocarbon solutions. The material was analyzed by 1-D and 2-D NMR techniques, elemental analysis, and X-ray diffraction, and all results corresponded to the structure of [W(OC$_6$HPh$_4$-2,3,5,6)$_2$(bipy)$_2$] containing two bipy rings and two terminal aryloxide ligands coordinated mutually cis.

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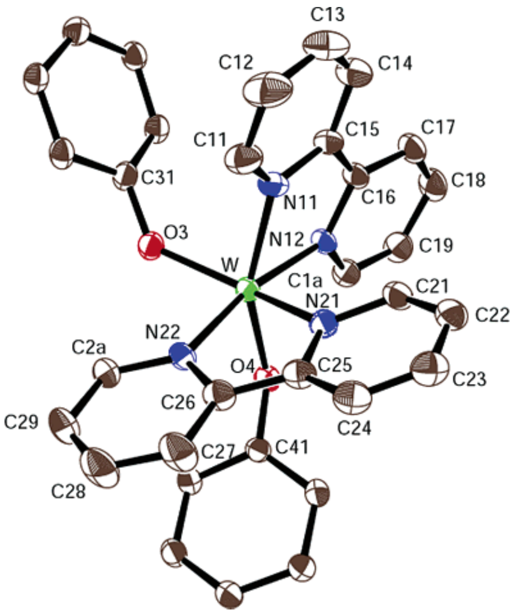

Figure 1. Molecular structure of [W(OC$_6$HPh$_4$-2,3,5,6)$_2$-(bipy)$_2$], **3**. The phenyl rings attached to the aryloxide nucleus have been removed for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [W(OC$_6$HPh$_4$-2,3,5,6)$_2$(bipy)$_2$] 3

W−O(3)	1.999(2)	W−O(4)	2.005(2)
W−N(11)	2.092(2)	W−N(12)	2.093(2)
W−N(21)	2.096(2)	W−N(22)	2.115(2)
N(11)−C(11)	1.366(4)	N(11)−C(15)	1.383(3)
N(12)−C(1A)	1.381(4)	N(12)−C(16)	1.383(3)
N(21)−C(21)	1.374(3)	N(21)−C(25)	1.380(3)
N(22)−C(2A)	1.374(3)	N(22)−C(26)	1.380(3)
C(15)−C(16)	1.412(4)	C(25)−C(26)	1.409(4)
O(3)−W−O(4)	110.24(7)	N(11)−W−N(12)	74.00(9)
N(21)−W−N(22)	73.45(8)	N(11)−W−N(21)	79.57(8)
N(12)−W−N(22)	169.30(8)	W−O(3)−C(31)	134.2(2)
W−O(4)−C(41)	127.7(2)	W−N(11)−C(15)	119.2(2)
W−N(12)−C(16)	119.2(2)	W−N(21)−C(25)	120.1(2)
W−N(22)−C(26)	118.7(2)		

The monomeric complex crystallized with a molecule of benzene per unit cell (Figure 1, Table 2). The structural parameters are worthy of some discussion. There have been a number of alkoxides and aryloxides of general formula [M(OAr)$_2$(bipy)$_2$] that have been structurally characterized. All of the compounds contain a cis-arrangement of aryloxide or alkoxide ligands. In compound **3** the O−W−O angle is 110°, whereas this parameter is smaller at 105° in [Mo(OPr^i)$_2$(bipy)$_2$],[14] 94° in [Ti(OC$_6$H$_3$Pr^i$_2$-2,6)$_2$(bipy)$_2$],[8] and 101° and 102° in the d^{10}-[M(OC$_6$H$_4$Cl-2-NO$_2$-4)$_2$(bipy)$_2$] (M = Zn, Cd).[15] Of particular interest are the coordination parameters for the bipy ligands in **3**. It is well known that bipyridine ligands can undergo reduction when coordinated to electron-rich, reducing metal centers. The electron density located on the bipy rings typically leads to a shortening of the M−N bond length below values typical for dative interactions. In the case of **3** the W−N bond lengths are all very short. Their values of 2.092(2), 2.093(2), 2.096(2), and 2.115(2) Å are among the shortest so far reported for bipy ligands bound to either molybdenum or tungsten. In [Mo(OPr^i)$_2$(bipy)$_2$] the Mo−N distances are 2.108(2), 2.123(2), 2.115(2), and 2.126(2) Å, while those for the titanium compound are in the 2.1−2.2 Å range. The only comparable W−N(bipy) distances are found in [WCl$_2$(PMe$_3$)$_2$(bipy)], 2.085(6) and 2.071(7) Å,[16] and [WBr$_2$(py-Me-4)$_2$(bipy)], 2.081(6) and 2.079(6) Å.[17]

These short W−N distances raise the question as to the formal oxidation state of tungsten in **3**. Reduction of each bipy ring by two electrons would lead to a W(VI) metal center bound to two diamido ligands (Scheme 2). A comparison of the interatomic distances within the bipryridine ligands of **3** is inconclusive (Scheme 2). However, possible support for this resonance picture comes from the ^{1}H NMR spectrum of diamagnetic **3**. The aromatic signals for the tetraphenylphenoxide ligands appear in the "normal" aromatic region. There are eight distinct proton resonances for the bipy ligands in **3**, which can be assigned using a ^{1}H COSY spectrum. Five of these bipy ligand signals are shifted upfield, appearing at δ 4.65−5.07 ppm (4 triplets and 1 doublet). This is the region normally occupied by olefinic protons. A caveat to the argument of olefinic protons, however, is the fact that 2,3,5,6-tetraphenylphenoxide ligands are well known to cause upfield shifting of adjacent ligand protons due to the diamagnetic shielding caused by the ortho-phenyl rings. Hence the data for **3** indicate that reduction of bipy ligands has occurred, but whether this involves four-electron reduction to yield d^0-W(VI) is unclear.

Isolation and Structural Characterization of [W(OC$_6$HPh$_3$-η^6-C$_6$H$_5$)(OC$_6$HPh$_4$-2,3,5,6)(py-Bu^t-4)] (4) and [W(OC$_6$HPh$_3$-η^5-C$_6$H$_6$)(OC$_6$HPh$_3$-η^1-C$_6$H$_4$)-(OC$_6$HPh$_4$-2,3,5,6)][Cl] (5). Although bipy was found to react with [W(OC$_6$HPh$_3$-η^6-C$_6$H$_5$)(OC$_6$HPh$_4$-2,3,5,6)-(PEt$_3$)], leading to displacement of the π-arene, addition of 4-*tert*-butylpyridine was found (^{1}H NMR) to lead only to partial substitution of the phosphine ligand. Hence [W(OC$_6$HPh$_3$-η^6-C$_6$H$_5$)(OC$_6$HPh$_4$-2,3,5,6)(py-Bu^t-4)] (**4**) was observed in solution only as a component of an equilibrium mixture. In an attempt to generate this compound directly, the sodium amalgam reduction (4 Na per W) of hydrocarbon solutions of [W(OC$_6$HPh$_4$-2,3,5,6)$_2$Cl$_4$] in the presence of 4-*tert*-butylpyridine was attempted. This reaction led to a very dark reaction mixture from which red crystals of **2** could be isolated from toluene/pentane mixtures. In one experiment further treatment of the supernatant led to the isolation of a few deep-green crystals, one of which was subjected to X-ray diffraction analysis (Figures 2 and 3, Tables 3 and 4). These crystals were found to contain the expected compound **4** along with a new salt compound **5** (Scheme 3).

Compound **5** can be seen to contain a total of three aryloxide ligands. One of them is terminally bound, the second is cyclometalated, while the third chelates to the metal center via an η^5-interaction with an ortho-cyclohexadienyl ring. The formal oxidation state of the metal center in **5** is (VI), and the unit cell contains one chloride ion to balance the positive charge on the tungsten. The origin of **5** is uncertain. However, one

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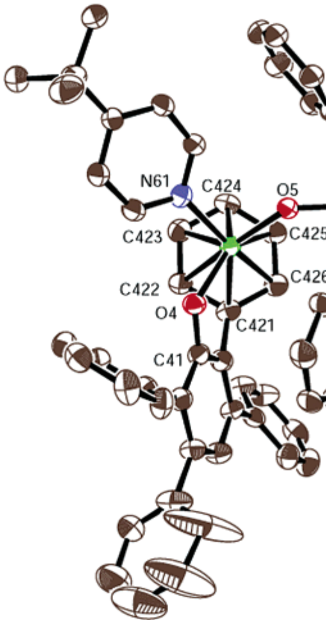

Figure 2. Molecular structure of [W(OC$_6$HPh$_3$-η^6-C$_6$H$_5$)(OC$_6$HPh$_4$-2,3,5,6)(py-Bu^t-4)], **4**, in crystals of **4**/**5**.

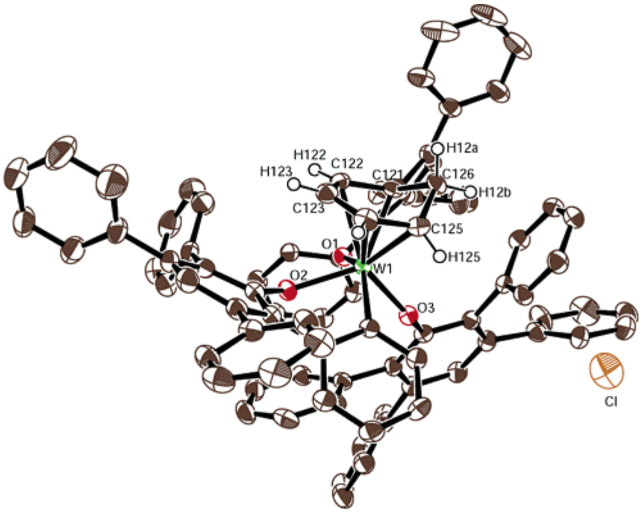

Figure 3. Molecular structure of [W(OC$_6$HPh$_3$-η^5-C$_6$H$_6$)(OC$_6$HPh$_3$-η^1-C$_6$H$_4$)(OC$_6$HPh$_4$-2,3,5,6)][Cl], **5**, in crystals of **4**/**5**.

Table 3. Selected Bond Distances (Å) and Angles (deg) for [W(OC$_6$HPh$_3$-η^6-C$_6$H$_5$)(OC$_6$HPh$_4$-2,3,5,6)(py-Bu^t-4)], 4

W(2)−O(4)	2.010(4)	W(2)−O(5)	1.987(4)
W(2)−N(61)	2.199(5)	W(2)−C(421)	2.161(6)
W(2)−C(422)	2.320(6)	W(2)−C(423)	2.252(6)
W(2)−C(424)	2.202(6)	W(2)−C(425)	2.248(6)
W(2)−C(426)	2.239(6)		
O(4)−W(2)−O(5)	114.5(2)	O(4)−W(2)−N(61)	81.3(2)
O(5)−W(2)−N(61)	80.3(2)	W(2)−O(4)−C(41)	119.3(3)
W(2)−O(5)−C(51)	135.6(3)	C(421)−C(422)−C(423)	120.5(6)
C(422)−C(423)−C(424)	118.6(6)	C(423)−C(424)−C(425)	119.1(6)
C(424)−C(425)−C(426)	123.1(6)	C(425)−C(426)−C(421)	117.0(6)
C(426)−C(421)−C(422)	119.1(5)		

Table 4. Selected Bond Distances (Å) and Angles (deg) for [W(OC$_6$HPh$_3$-η^5-C$_6$H$_6$)(OC$_6$HPh$_3$-η^1-C$_6$H$_4$)(OC$_6$HPh$_4$-2,3,5,6)][Cl], 5

W(1)−O(1)	2.144(3)	W(1)−O(2)	2.029(3)
W(1)−O(3)	1.951(4)	W(1)−C(121)	2.202(5)
W(1)−C(122)	2.253(5)	W(1)−C(123)	2.407(6)
W(1)−C(124)	2.331(5)	W(1)−C(125)	2.231(6)
W(1)−C(222)	2.221(5)		
O(1)−W(1)−O(2)	79.4(1)	O(2)−W(1)−O(3)	112.9(2)
O(1)−W(1)−O(3)	78.6(1)	W(1)−O(1)−C(11)	115.6(3)
W(1)−O(2)−C(21)	124.3(3)	W(1)−O(3)−C(31)	145.8(3)
O(2)−W(1)−C(222)	81.7(2)	C(121)−C(122)−C(123)	118.9(5)
C(122)−C(123)−C(124)	117.9(5)	C(123)−C(124)−C(125)	118.1(5)
C(124)−C(125)−C(126)	117.3(5)	C(125)−C(126)−C(121)	97.7(4)
C(126)−C(121)−C(122)	115.9(5)		

scenario involves the presence of the tris(aryloxide) [W(OAr)$_3$Cl$_3$] in the initial starting material. Reduction to the W(IV) intermediate is followed by cyclometalation of one of the aryloxide ligands and then transfer of the generated hydride ligand to one of the ortho-phenyl rings (Scheme 3). The cyclometalation of 2,6-diphenylphenoxide by Mo(IV) has precedence in previous work.[18,19] Although metalation-resistant due to the buttressing effect of the meta-phenyl rings, the tetraphenylphenoxide ligand is not immune to this type of reaction.[20] The intramolecular hydrogenation of ortho-phenyl rings also has precedence (see final discussion section).

The structural parameters for the π-bound rings in **4** and **5** are of interest. The η^6-interaction in the pyridine adduct **4** is very similar to that observed in related phosphine adducts. There is a shortening of the W−C(ipso) and W−C(para) distances, with an elongation of the W−C(ortho) trans to the terminal aryloxide in the three-legged piano stool geometry. This has been ascribed to a tungsta-norbornadiene resonance contribution. A comparison of the W−C distances for **4** and the PMe$_3$ analogue is shown in Figure 4. There is a slight shortening of the W-arene distances overall on replacing the phosphine by pyridine. Also shown in Figure 4 are the W−C distances to the η^5-cyclohexadienyl ring in **5**. The W−CH$_2$ distance is 2.861 Å. Three of the remaining W−C distances are close to those found in **4**, while two of them are slightly longer. The overall geometry for **5** is best described as a four-legged piano stool with the W−C σ-bond trans to the oxygen of the aryloxide containing the η^5-cyclohexadienyl ring. The W−C(phenyl) bond distance of 2.202(5) Å demonstrates how short the W−C π-interactions are in both **4** and **5**.

The demonstrated ability of early transition metal hydrido aryloxides to carry out the catalytic hydrogenation of arene rings has raised many mechanistic questions. We have focused particular attention on the identification and study of potential intermediates within the catalytic cycle. Especially important are the structures and reactivity of compounds containing partially hydrogenated arene rings. The literature contains examples for all η^n-fragments, $n = 5$,[21,22] 4,[23] 3,[24] 2,[25] 1,[26] bound to group 4−6 metals. Previous work by our group has allowed the isolation of η^4-cyclohexa-

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[18] Kerschner, J. L.; Yu, J.; Fanwick. P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1989**, *8*, 1414.

[19] The cyclometalation of a variety of aryloxide ligands by low-valent Mo,W systems has been demonstrated, see: (a) Hascall, T.; Murphy, V. J.; Janak, K. E.; Parkin, G, *J. Organomet. Chem.* **2002**, *652*, 37. (b) Hascall, T.; Baik, M. H.; Bridgewater, B. A.; Shin, J. H.; Churchill, D. G.; Friesner, R. A.; Parkin, G. *J. Chem Soc., Chem. Commun.* **2002**, 2644. (c) Rabinovich, D.; Zelman, R.; Parkin, G. *J. Am. Chem. Soc.* **1990**, *112*, 9632. (d) Rabinovich, D.; Zelman, R.; Parkin, G. *J. Am. Chem. Soc.* **1992**, *114*, 4611.

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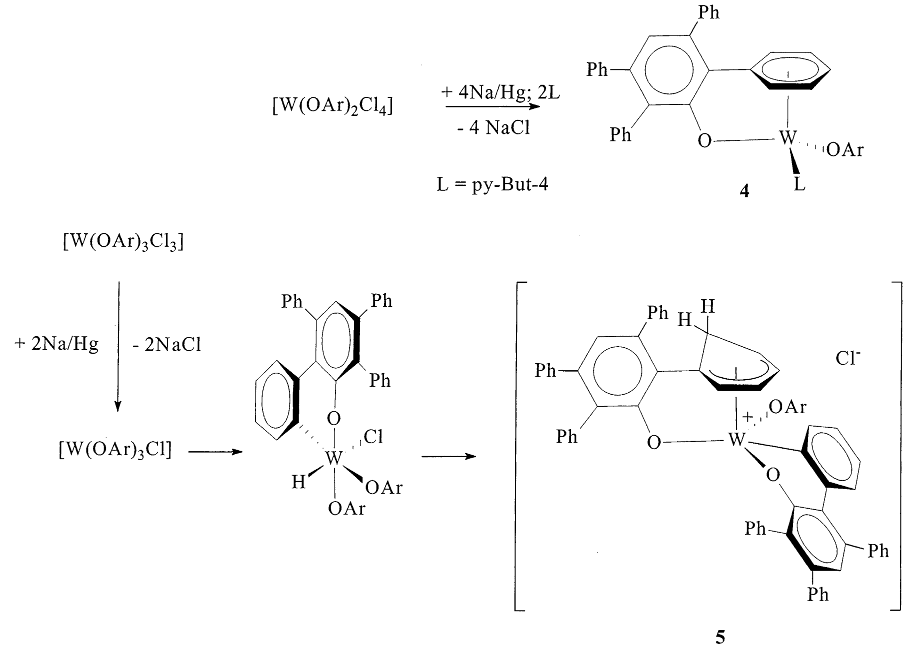
[21] Fryzuk, M. D.; Kozak, C. M.; Bowridge, M. R.; Patrick, B. O. *Organometallics* **2002**, *21*, 5047.

Scheme 3



diene,[27] η^2-cyclohexene,[28] and η^1-cyclohexyl,[29] examples supported by aryloxide ligation, formed either via intramolecular hydrogenation of phenyl rings or by other routes. The first key intermediate proposed in the mechanistic pathway (Scheme 4) is an η^5-cyclohexadienyl formed by initial attack of a metal-hydride on an arene ring.[21] This has previously been missing in aryloxide chemistry. Recently Fryzuk et al. have reported cyclohexadienyl complexes of niobium amidophosphine ligands.[21] Tilley and Gavenonis have also demonstrated the formation of an η^5-cyclohexadienyl ring by hydride transfer from tantalum to an ortho-aryl ring in an amido ligand. In this case reversible transfer to the meta-position of a [Ta-NHAr*] ring (Ar* = 2,6-dimesitylphenyl) takes place.[30] In compound **5** the hydride ligand formed via the cyclometalation has been transferred to the ortho-position of a phenyl ring. The intramolecular hydrogenation of ortho-phenylphenoxide rings to chelated cyclohexadiene, cyclohexene, and nonbound cyclohexyl groups has been observed. The site of

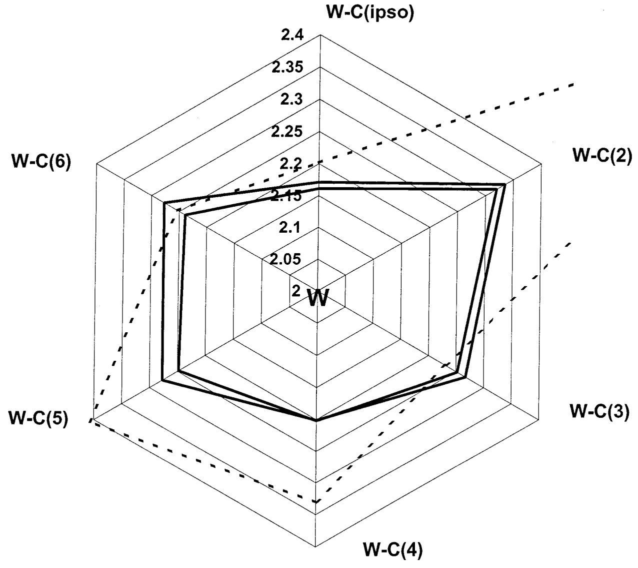


Figure 4. "Radar" plot of the W–C(arene) distances in compound [W(OC$_6$HPh$_3$-η^6-C$_6$H$_5$)(OC$_6$HPh$_4$-2,3,5,6)(PMe$_3$)] and [W(OC$_6$HPh$_3$-η^6-C$_6$H$_5$)(OC$_6$HPh$_4$-2,3,5,6)(py-Bu^t-4)], **4**, and the W–C(cyclohexadienyl) distances in [W(OC$_6$HPh$_3$-η^5-C$_6$H$_6$)(OC$_6$HPh$_3$-η^1-C$_6$H$_4$)(OC$_6$HPh$_4$-2,3,5,6)][Cl], **5**. The coordination is exaggerated by using a plot scale of 2.0–2.4 Å from the metal center.

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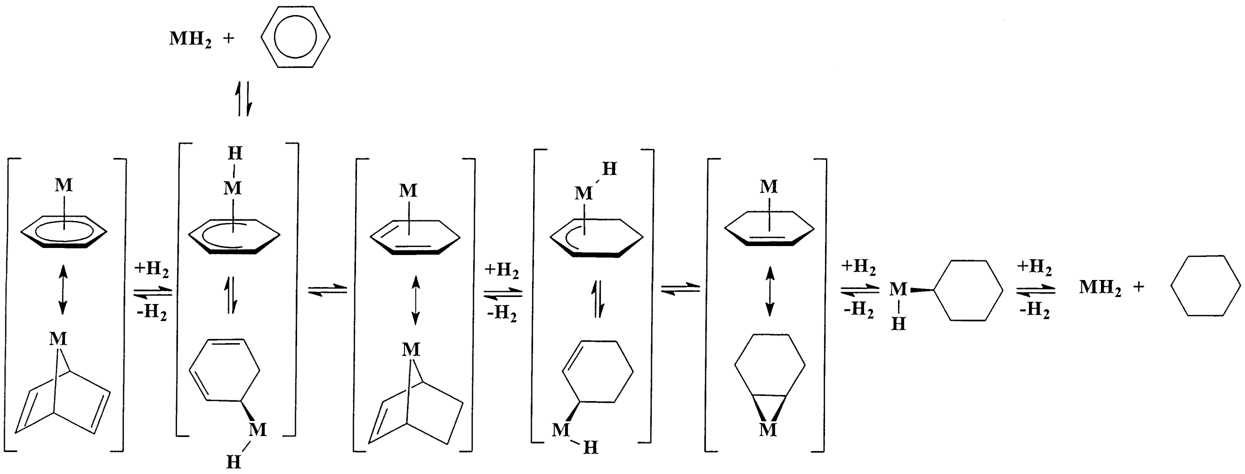
Scheme 4



initial attack has been discussed in terms of the stereochemical outcome,[27] particularly as it relates to deuterium incorporation.

Experimental Section

All operations were carried out under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab or by standard Schlenk techniques. The hydrocarbon solvents were distilled from sodium benzophenone and stored under nitrogen until use. All organic reagents were bought from Aldrich Chemical Co., Milwaukee, WI, and used as received. The compounds $[W(OC_6HPh_3\text{-}\eta^6\text{-}C_6H_5)(OC_6HPh_4\text{-}2,3,5,6)(PMe_3)]$, $W(OC_6HPh_3\text{-}\eta^6\text{-}C_6H_5)(OC_6HPh_4\text{-}2,3,5,6)(PEt_3)]$, and $[W(OC_6HPh_4\text{-}2,3,5,6)_2Cl_4]$ were obtained by previously reported procedures.[5] All ^1H NMR and DQF-COSY spectra were recorded on either a Varian Inova 300 or Varian Unity 600 spectrometer and referenced to protio impurities of commercial d_6-benzene or d_8-toluene. Dynamic NMR experiments were all preformed on a Varian Unity Inova 300 using a 5 mm, 4 nucleus probe. X-ray diffraction studies were preformed in-house at Purdue University.

Preparation of all-*trans*-$[W(OC_6HPh_4\text{-}2,3,5,6)_2Cl_2(py)_2]$ (1). A purple suspension of $[W(OC_6HPh_4\text{-}2,3,5,6)_2Cl_4]$ (2.00 g, 1.78 mmol) in benzene (75 mL) was added to a Na/Hg alloy (0.09 g, 3.91 mmol). To the suspension was added 2.2 equiv of pyridine (0.32 mL, 3.93 mmol). The reaction was allowed to stir for 14 h, after which the solution appeared red. The solution was filtered and dried in vacuo, affording a red solid. The crude material was recrystallized in hot toluene, yielding the pure product as small red needles (1.53 g, 71.6%). Anal. Calc for $C_{70}H_{52}Cl_2N_2O_2W$: C, 69.60; H, 4.34; Cl, 5.87; N, 2.32. Found: C, 69.69; H, 4.47; Cl, 5.48; N, 2.19. ^1H NMR (300 MHz, d_8-toluene, 25 °C): δ 12.15 (t, 4H, *meta*-H on pyridine), 8.67 (d, 8H, aromatics), 7.92 (d, 8H, aromatics), 6.92 (m, 12H, aromatics), 6.41 (t, 8H, aromatics), 5.86 (t, 4H, aromatics), 5.00 (s, 2H, aromatics), −23.71 (t, 2H, *para*-H on pyridine), −26.14 (d, 4H, *ortho*-H on pyridine).

Preparation of all-*trans*-$[W(OC_6HPh_4\text{-}2,3,5,6)_2Cl_2(py\text{-}Bu^t\text{-}4)_2]$ (2). A purple suspension of $[W(OC_6HPh_4\text{-}2,3,5,6)_2Cl_4]$ (2.00 g, 1.78 mmol) in benzene (75 mL) was added to a Na/Hg alloy (0.09 g, 3.91 mmol). To the suspension was added 2.2 equiv of 4-*tert*-butylpyridine (0.58 mL, 3.93 mmol). The reaction was allowed to stir for 20 h, after which the solution appeared red. The solution was filtered and dried in vacuo, affording a red solid. The crude material was recrystallized from hot toluene, yielding the pure product as small red needles (1.40 g, 59.4%). Anal. Calc for $C_{78}H_{68}Cl_2N_2O_2W$: C, 70.97; H, 5.19; Cl, 5.37; N, 2.12. Found: C, 70.99; H, 5.14; Cl, 5.49; N, 2.03. ^1H NMR (300 MHz, d_8-toluene, 25 °C): δ 13.96 (d, 4H, *meta*-H on 4-*tert*-butylpyridine), 9.26 (d, 8H, aromatics), 8.07 (d, 8H, aromatics), 7.24 (t, 8H, aromatics), 6.38 (t, 8H, aromatics), 5.75 (t, 8H, aromatics), 4.93 (s, 2H, aromatics), 0.09 (s, 18H, $-CH_3$ of 4-*tert*-butylpyridine), −34.92 (d, 4H, *ortho*-H on 4-*tert*-butylpyridine).

Preparation of $[W(OC_6HPh_4\text{-}2,3,5,6)_2(bipy)_2]$ (3). A sample of $[W(OC_6HPh_3\text{-}\eta^6\text{-}C_6H_5)(OC_6HPh_4\text{-}2,3,5,6)(PEt_3)]$ (80 mg, 0.073 mmol) was dissolved in 5 mL of benzene, and to this solution was added 2 equiv of 2,2′-bipyridine (25 mg, 0.160 mmol). After a few minutes of stirring, the solution went from emerald green to dark purple. The solution was layered with pentanes to induce crystal formation. The sample was analyzed by NMR spectrometry and X-ray diffraction study. Anal. Calc for $C_{80}H_{58}N_4O_2W$: C, 74.42; H, 4.53; N, 4.34. Calc for $C_{86}H_{64}N_4O_2W$ (benzene solvate): C, 75.43; H, 4.71; N, 4.09. Found: C, 74.88; H, 4.87; N, 4.08. ^1H NMR (600 MHz, C_6D_6, 25 °C): δ 8.70 (d, aromatics), 8.49 (d, aromatics), 7.37 (d, aromatics of bpy), 7.28 (s, aromatics), 7.19 (t, aromatics + bpy aromatics), 6.96 (m, aromatics), 6.89 (m, aromatics + bpy aromatic), 6.68 (s, aromatics), 6.64 (dd, aromatics), 5.08 (d, aromatics of bpy), 4.96 (t, aromatics of bpy), 4.93 (t, aromatics of bpy), 4.88 (t, aromatics of bpy), 4.65 (t, aromatics of bpy).

Preparation of $[W(OC_6HPh_3\text{-}\eta^6\text{-}C_6H_5)(OC_6HPh_4\text{-}2,3,5,6)(py\text{-}Bu^t\text{-}4)]$ (4) and $[W(OC_6HPh_3\text{-}\eta^5\text{-}C_6H_6)(OC_6HPh_3\text{-}\eta^1\text{-}C_6H_4)(OC_6HPh_4\text{-}2,3,5,6)][Cl]$ (5). A purple suspension of $[W(OC_6HPh_4\text{-}2,3,5,6)_2Cl_4]$ (2.00 g, 1.78 mmol) in benzene (75 mL) was added to a Na/Hg alloy (0.20 g, 8.0 mmol). To the suspension was added 2.2 equiv of 4-*tert*-butylpyridine (0.58 mL, 3.93 mmol). The reaction was allowed to stir for 24 h, after which the solution appeared almost black. The solution was filtered, evaporated to dryness, and taken up in toluene. Addition of a small amount of pentane intially yielded red crystals of **2**. Further addition of pentane gave a few dark green crystals identified as containing a mixture of **4** and **5** in a 1:1 ratio.

X-ray Data Collection and Reduction. Crystal data and data collection parameters are contained in Table 5. A suitable crystal was mounted on a glass fiber in a random orientation

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[27] (a) Steffey, B. D.; Chesnut, R. W.; Kerschner, J. L.; Pellechia, P.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1989**, *111*, 378. (b) Steffey, B. D.; Rothwell, I. P. *J. Chem Soc., Chem. Commun.* **1990**, 213. (c) Lockwood, M. A.; Potyen, M. C.; Steffey, B. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1995**, *14*, 3293. (d) Visciglio, V. M.; Clark, J. R.; Nguyen, M. T.; Mulford, D. R.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 3490.

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Table 5. Crystal Data and Data Collection Parameters

	3·C_6H_6	**4/5**
formula	$C_{86}H_{64}N_4O_2W$	$C_{159}H_{118}ClNO_5W_2$
fw	1369.34	2525.87
space group	*P* (No. 2)	*P* (No. 2)
a, Å	12.9675(2)	11.7261(1)
b, Å	14.2048(2)	19.1182(2)
c, Å	18.0995(3)	29.6646(3)
α, deg	76.783(1)	87.8455(5)
β, deg	82.922(1)	79.6683(5)
γ, deg	86.671(1)	72.8854(5)
V, Å	3219.4(1)	6251.9(2)
Z	2	2
ρ_{calc}, g cm^{-3}	1.413	1. 342
temperature, K	150	150
radiation (wavelength)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
R	0.032	0.052
R_w	0.077	0.138

under a cold stream of dry nitrogen. Preliminary examination and final data collection were performed with Mo Kα radiation (λ = 0.71073 Å) on a Nonius Kappa CCD. Lorentz and polarization corrections were applied to the data.[31] An empirical absorption correction using SCALEPACK was applied.[32] Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIRDIF92.[33] The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares where the function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ and the weight *w* is defined as $w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 1.4064P]$ where $P = (F_o^2 + 2F_c^2)/3$. Scattering factors were taken from the International Tables for Crystallography.[34] Refinement was performed on a AlphaServer 2100 using SHELX-97.[35] Crystallographic drawings were done using the programs ORTEP.[36]

Acknowledgment. We thank the National Science Foundation (Grant CHE-0078405) for financial support of this research.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM030054S

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