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Reaction of Dialkylamido and Alkylimido Derivatives of Molybdenum and Tungsten with *o*-Arylphenols: Intramolecular Activation of Aromatic CH Bonds by Mo–NR$_2$ Groups

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The reaction of the molybdenum tetrakis(dimethylamide), Mo(NMe$_2$)$_4$, with 2,6-diphenylphenol (HOAr-2,6-Ph$_2$; ≥3 equiv) in hydrocarbon solvents leads to the formation of deep red, paramagnetic Mo(OC$_6$H$_3$PhC$_6$H$_4$)(OAr-2,6-Ph$_2$)$_2$(HNMe$_2$) (**1a**). The presence of the cyclometalated 2,6-diphenylphenoxide ligand in **1a** was confirmed by a single-crystal X-ray diffraction study. The central MoO$_3$CN core in **1a** is found to form a square-pyramidal geometry about the metal with the carbon atom of the new metallacycle occupying the axial position, while the dimethylamine ligand is coordinated in the basal plane cis to the oxygen atom of the metallacycle ring. The open space trans to the axial Mo–C bond is found to be occupied by the ortho-CH bond of an aryl side group of one of the non-metalated OAr-2,6-Ph$_2$ ligands. The distances to this CH bond, Mo–H = 2.67 (5) Å and Mo–C = 2.814 (5) Å, are outside of the range of distances one would expect for an agostic interaction to be present. Compound **1a** reacts with pyridine (excess) to yield the complex Mo(OC$_6$H$_3$PhC$_6$H$_4$)(OAr-2,6-Ph)$_2$(py) (**1b**). No evidence for a bis(pyridine) adduct was obtained. Solid-state structural studies of **1b** show it to be closely related to **1a**, again with Mo–H = 2.72 (5) Å and Mo–C = 2.760 (6) Å contacts below the basal plane trans to the new Mo–C bond. In contrast to this facile activation of the aromatic CH bond by Mo–NMe$_2$ groups, treatment of the mixed amido, imido compound W(NBu^t)$_2$(NHBu^t)$_2$ with HOAr-2,6-Ph$_2$ or HOAr-2-Ph leads only to simple substitution products. Hence reaction with HOAr-2,6-Ph$_2$ (≥2 equiv) leads to the formation of the bis(imido), bis(aryloxide) W(NBu^t)$_2$(OAr-2,6-Ph$_2$)$_2$ (**2**) while the less bulky HOAr-2-Ph (≥4 equiv) yields the mixed imido, amine W(NBu^t)(H$_2$NBu^t)(OAr-2Ph)$_4$ (**3**). Structural studies confirmed these formulations with pseudotetrahedral and pseudooctahedral environments existing about the tungsten metal centers in **2** and **3**, respectively. In **3** the *tert*-butylamine ligand is located trans to the *tert*-butylimido group. The W═NBu^t distances are comparable in **2** and **3**. Crystal data for MoO$_3$NC$_{59}$H$_{48}$ (**1a**) at 22 °C: a = 13.431 (2) Å, b = 18.213 (5) Å, c = 10.262 (1) Å, α = 101.68 (2)°, β = 106.53 (1)°, γ = 77.93 (2)°, Z = 2, d_{calcd} = 1.306 g cm^{-3} in space group $P\bar{1}$. For MoO$_3$NC$_{59}$H$_{43}$ (**1b**) at −155 °C: a = 13.236 (3) Å, b = 22.034 (5) Å, c = 15.991 (3) Å, β = 109.63 (1)°, Z = 4, d_{calcd} = 1.376 g cm^{-3} in space group $P2_1/c$. For WO$_2$N$_2$C$_{44}$H$_{44}$ (**2**) at 19 °C: a = 11.455 (1) Å, b = 11.600 (1) Å, c = 16.003 (3) Å, α = 91.07 (1)°, β = 93.00 (1)°, γ = 117.20 (1)°, Z = 2, d_{calcd} = 1.438 g cm^{-3} in space group $P\bar{1}$. For WO$_4$N$_2$C$_{56}$H$_{56}$ (**3**) at 18 °C: a = 14.472 (1) Å, b = 12.146 (1) Å, c = 28.055 (4) Å, β = 92.115 (8)°, Z = 4, d_{calcd} = 1.354 g cm^{-3} in space group $P2_1/c$.

Introduction

The activation of carbon–hydrogen bonds by early-transition-metal compounds has been the subject of intense research interest.[2–4] Two general mechanistic regimes for this type of reactivity have been outlined. The first, favored for low- and mid-valent derivatives involves CH bond breakage via oxidative addition to the metal center,[5] while for high-valent (typically d^0) metal substrates a heterolytic pathway is typically invoked.[6] In the oxidative-addition pathway a d^n ($n \geq 2$) configuration is a prerequisite, while in the heterolytic path a suitable leaving group (M$^{\delta+}$–X$^{\delta-}$ bond) is essential.[6] By far the most common leaving groups in the latter case for both intra- and intermolecular CH bond activation involve metal–alkyl, metal–aryl, or metal–hydride bonds,[2–4,6,7] while metal–alkylidene[8] and metal–benzyne (*o*-phenylene)[9] functions have also been shown to be able to activate certain types of CH bonds. Much less well documented are the activation of CH bonds by metal halide, alkoxide, or amido substrates.[10,11] This is despite the fact that these ligands contain lone pairs of electrons with which they can bond to the hydrogen atom being transferred, thus potentially stabilizing the expected transition state.[6]

We have recently shown that the ligand 2,6-diphenylphenoxide (OAr-2,6-Ph$_2$) has the ability to undergo the sometimes facile activation of one of the ortho-CH bonds of a side-chain aryl group resulting in the formation of a six-membered metallacycle ring.[12,13] Both oxidative ad-

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Scheme I

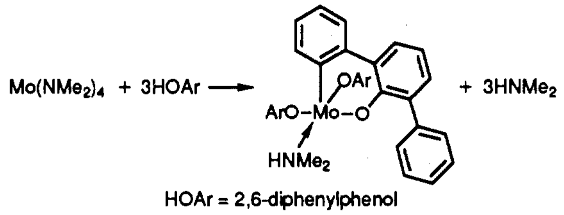

Table I. Selected Bond Distances (Å) and Angles (deg) for $Mo(OC_6H_3PhC_6H_4)(OAr\text{-}2,6\text{-}Ph_2)_2(NHMe_2)$ (1a)

Mo–O(10)	1.919 (2)	Mo–O(20)	1.976 (2)
Mo–O(30)	1.962 (3)	Mo–N(40)	2.288 (4)
Mo–C(122)	2.075 (4)	Mo–C(262)	2.814 (5)
Mo–H(262)	2.67 (5)	C(262)–H(262)	0.87 (5)
O(10)–Mo–O(20)	165.8 (1)	O(16)–Mo–O(30)	97.9 (1)
O(10)–Mo–N(40)	87.3 (1)	O(10)–Mo–C(122)	86.4 (1)
O(20)–Mo–O(30)	94.1 (1)	O(20)–Mo–N(40)	79.7 (1)
O(20)–Mo–C(122)	98.9 (1)		
O(30)–Mo–N(40)	88.3 (2)	O(30)–Mo–C(262)	174.5 (1)
O(30)–Mo–H(262)	164 (1)		
Mo–O(10)–C(11)	136.6 (3)	Mo–O(20)–C(21)	143.6 (3)
Mo–O(30)–C(31)	131.3 (2)	Mo–H(262)–C(262)	91 (3)

dition at W(II), d^4 or Ta(III), d^2 metal centers has been demonstrated[13] as well as activation by d^0 metal–alkyl and –hydride bonds.[12] In this paper we wish to report on the reaction of both 2-phenylphenol and 2,6-diphenylphenol with dialkylamido and alkylimido derivatives of Mo and W. Besides leading to a new series of group 6 metal aryloxide derivatives via simple protonolysis, in one instance very facile cyclometalation is shown to take place by an $Mo–NMe_2$ bond, converting a dimethylamido group into a dimethylamine ligand. Recent work by Bergman et al. and Wolczanski et al. has shown that intermolecular activation of CH bonds can take place by zirconium(IV) imido groups.[14] In this study we find that there is no evidence for intramolecular activation of aromatic CH bonds by tungsten(VI) imido groups.

Results and Discussion

In a previous study we have shown that reaction of the hexaamide compound $Mo_2(NMe_2)_6$(*Mo≡Mo*) with 2,6-diphenylphenol can lead to both bis- and tris(aryloxide) derivatives of the type $1,2\text{-}Mo_2(OAr\text{-}2,6\text{-}Ph_2)_2(NMe_2)_4$ and $1,1,2\text{-}Mo_2(OAr\text{-}2,6\text{-}Ph_2)_3(NMe_2)_3$.[15] Further substitution of the remaining dimethylamido groups is presumably sterically inhibited. The use of the smaller, asymmetric 2-phenylphenol (OAr-2-Ph) leads to complete substitution and formation of the bis(amine) adduct $Mo_2(OAr\text{-}2\text{-}Ph)_6(HNMe_2)_2$.[16] The deep purple, amide $Mo(NMe_2)_4$ has also been shown to be a valuable starting material for the preparation of molybdenum(IV) alkoxides[17] and aryloxides.[18] However, although treatment of $Mo(NMe_2)_4$ with $HOAr\text{-}2,6\text{-}Ph_2$ (≥3 equiv, 25 °C) rapidly leads to the formation of a deep red, paramagnetic product of stoichiometry "$Mo(OAr\text{-}2,6\text{-}Ph_2)_3(NMe_2)$" (**1a**), the spectroscopic properties of **1a** are inconsistent with a simple substitution compound. Specifically, the presence of a strong $\bar{\nu}$(N–H) stretch in the IR spectrum (Nujol mull) strongly indicated the presence of a dimethylamine ligand. A solid-state, X-ray diffraction analysis of **1a** confirmed the presence of an $Mo(NHMe_2)$ group (vide infra) accompanied by the formation of a six-membered metallacycle by cyclometalation of one of the $OAr\text{-}2,6\text{-}Ph_2$ ligands (Scheme I). An ORTEP view of **1a** is shown in Figure 1 while in Table I are collected some selected bond distances and angles. The treatment of **1a** with pyridine (excess) in toluene followed by addition of hexane yielded deep red blocks of the mono(pyridine) derivative $Mo(OC_6H_3PhC_6H_4)(OAr\text{-}2,6\text{-}Ph_2)_2(py)$ (**1b**). Again the molecular structure was confirmed by X-ray diffraction techniques (Figure 2). Some selected bond distances and

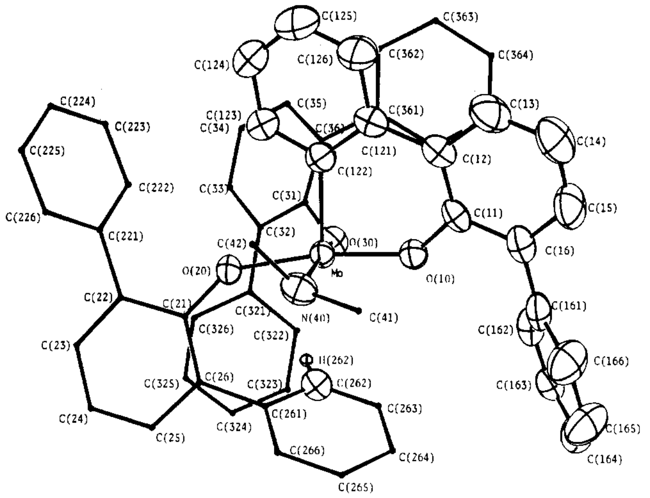

Figure 1. ORTEP view emphasizing the central coordination sphere in $Mo(OC_6H_3PhC_6H_4)(OAr\text{-}2,6\text{-}Ph_2)_2(NHMe_2)$ (**1a**).

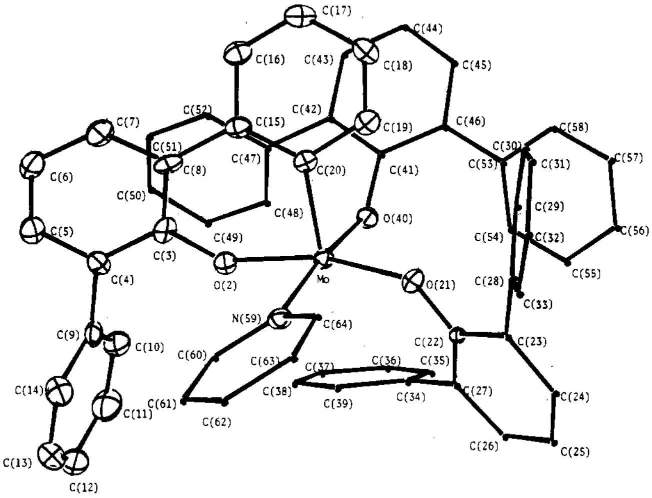

Figure 2. ORTEP view of $Mo(OC_6H_3PhC_6H_4)(OAr\text{-}2,6\text{-}Ph_2)_2(py)$ (**1b**) emphasizing the central coordination sphere.

Table II. Selected Bond Distances (Å) and Angles (deg) for $Mo(OC_6H_3PhC_6H_4)(OAr\text{-}2,6\text{-}Ph_2)_2(py)$ (1b)

Mo–O(2)	1.946 (3)	Mo–O(21)	1.964 (3)
Mo–O(4)	1.939 (3)	Mo–N(59)	2.306 (3)
Mo–C(20)	2.081 (4)	Mo–C(39)	2.760 (6)
Mo–H(25)	2.72 (5)	C(39)–H(25)	0.87 (4)
O(2)–Mo–O(21)	160.2 (1)	O(2)–Mo–O(40)	103.4 (1)
O(2)–Mo–N(59)	82.3 (1)	O(2)–Mo–C(20)	87.6 (1)
O(21)–Mo–O(40)	94.9 (1)	O(21)–Mo–N(59)	79.0 (1)
O(21)–Mo–C(20)	99.4 (1)		
O(40)–Mo–N(59)	173.6 (1)	O(40)–Mo–C(20)	99.4 (1)
N(59)–Mo–C(20)	91.8 (1)		
Mo–O(2)–C(3)	133.9 (2)	Mo–O(21)–C(22)	138.7 (3)
Mo–O(40)–C(41)	134.9 (2)		

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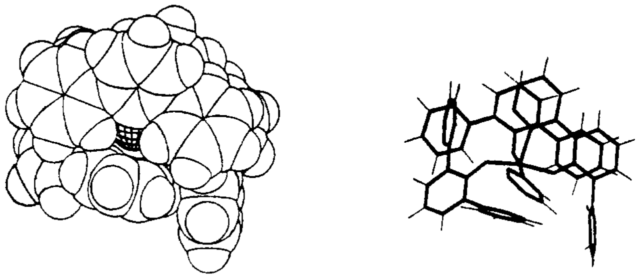


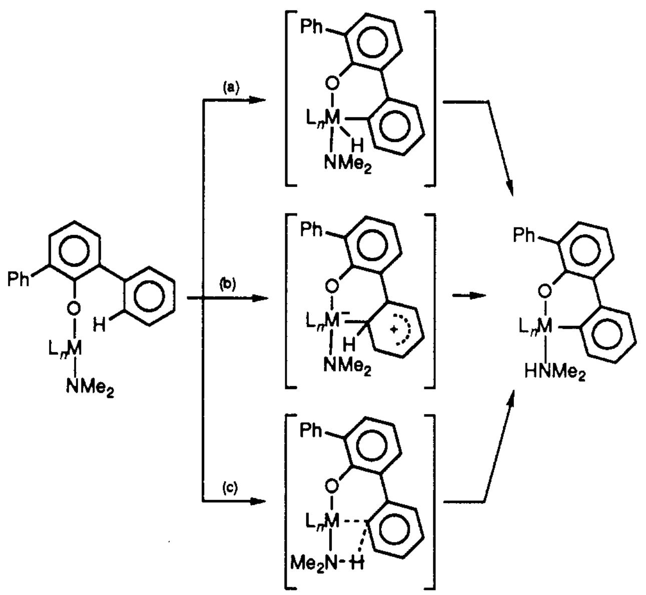
Figure 3. Space-filling model of **1b** showing the lack of contact between the metal atom and the aryl group below the basal plane.

angles for **1b** are collected in Table II.

The molecular structures of **1a** and **1b** can be seen to be closely related. In both there is present a square-pyramidal MO_3CN core in which the axial position consists of the new metal–carbon bond (Figures 1 and 2). The six-membered metallacycle ring appears to be only slightly puckered in both cases, maintaining a bite of 86.4 (1)° and 87.6 (1)° at the metal for **1a** and **1b**, respectively. The nitrogen atom of the neutral donor ligand is located in the basal plane in a cis orientation to the oxygen atom of the metallacycle ring. The distances to these nitrogen atoms are the largest in the coordination sphere, and in the case of **1a**, 2.288 (4) Å, are consistent with the presence of a molybdenum–dimethylamine bond and not a molybdenum–dimethylamido group (typically 1.9–2.0 Å).[19] In both the metalated compounds **1a** and **1b** the Mo–O–C angles lie in a very narrow range of 131–144° for **1a** and 134–139° for **1b**. These numbers indicate that the formation of the six-membered metallacycle with an ~90° bite at the metal does not cause a significant bending of the Mo–O–Ar linkage.

An interesting feature of both **1a** and **1b** concerns the vacant site below the basal plane trans to the Mo–C bond. Searching out from the metal in this direction shows the closest contact to be between the metal center and a particular aromatic CH bond. This CH bond in both compounds represents one of the ortho-CH bonds of a phenyl substituent of the aryloxide ligand located trans to the oxygen atom of the metallacycle ring. In both compounds this aryloxide is oriented so that this CH bond occupies a position almost exactly trans to the new Mo–C bond. The CH bond does not point directly at the metal center but instead lies in a sideways fashion with Mo–H–C angles close to 90°. The Mo–C distances of 2.814 (5) Å and 2.760 (6) Å for **1a** and **1b**, respectively, are long, being considerably longer than the 2.2–2.4 Å distance typically found for molybdenum–η^6-arene interactions.[20] Furthermore, the Mo–H distances of 2.67 (5) and 2.72 (5) Å are outside the range typically found for agostic interactions between molybdenum metal centers and CH bonds.[21] We, therefore, conclude on the basis of this data that efficient packing of the molecular units results in this particular arene ring's moving into the gap below the square-pyramidal base, hence bringing one of the ortho-CH bonds close to the metal. The lack of any bonding interaction with this ring in **1b** is also confirmed by space-filling diagrams of the molecule (Figure 3).

Scheme II



The facile, room-temperature, intramolecular activation of the arene CH bonds in OAr-2,6-Ph_2 ligands by the Mo(IV)–NMe_2 bond has significant mechanistic ramifications. The fact that the metal center in these reactions is Mo(IV) (d^2) means that an oxidative addition/reductive elimination sequence cannot be dismissed out of hand. Although feasible, there appears to be no evidence in the reaction chemistry of Mo(IV) amido, alkoxy, or aryloxy compounds for facile oxidative addition of even OH or NH bonds which one would expect to be even more reactive than the CH bonds in OAr-2,6-Ph_2.[17,18,22] Hence on this precedent an initial oxidative addition process for CH bond activation seems unlikely. Two alternative pathways for the formation of **1a** involve more heterolytic/electrophilic mechanisms (Scheme II). In pathway b a "classical" electrophilic substitution process is envisaged involving deprotonation of the "metallo-Wheland" intermediate by the dimethylamido ligand. The second pathway, c, proceeds through a multicenter transition state formed between the CH bond and the Mo–NMe_2 group with no loss of aromaticity of the arene ring during the reaction. Mechanistic studies of the activation of arene CH bonds by d^0 high-valent metal alkyl and hydride substrates implicate the latter pathway b as operative.[23] However, Lewis acidic main-group metal centers (e.g. Hg^{2+}) are know to definitely favor an electrophilic substitution pathway.[24] In this context it is interesting to note the facile cyclometalation of two OAr-2,6-Ph_2 ligands by the tin(IV) substrate $Sn(NMe_2)_4$.[25] Hence, whether an electrophilic substitution or multicenter transition-state pathway is operative for the formation of **1a** is unknown. Unfortunately the paramagnetic nature of the Mo(IV) metal center renders these reactions not very amenable to routine methods of study.

The initially surprising ability of the metal–dialkylamido groups in $Mo(NMe_2)_4$ to activate aromatic CH bonds has led us to evaluate the ability of the related metal–alkyl-

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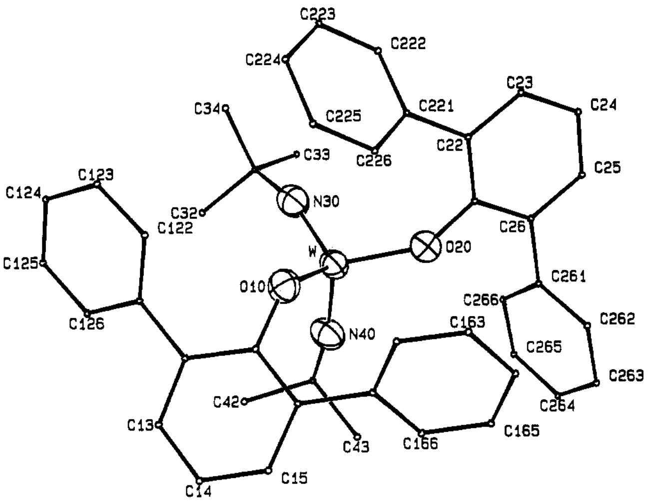

Figure 4. ORTEP view of $W(NBu^t)_2(OAr\text{-}2,6\text{-}Ph_2)_2$ (2) emphasizing the central coordination sphere.

Table III. Selected Bond Distances (Å) and Angles (deg) for $W(NBu^t)_2(OAr\text{-}2,6\text{-}Ph_2)_2$ (2)

W-O(10)	1.920 (2)	W-O(20)	1.906 (2)
W-N(30)	1.743 (3)	W-N(40)	1.730 (3)
O(10)-W-O(20)	117.3 (1)	O(20)-W-N(30)	111.8 (1)
O(10)-W-N(30)	107.1 (1)	O(20)-W-N(40)	106.7 (1)
O(10)-W-N(40)	103.5 (1)	N(30)-W-N(40)	110.0 (1)
W-O(10)-C(11)	126.3 (2)	W-N(30)-C(31)	159.2 (3)
W-O(20)-C(21)	147.5 (2)	W-N(40)-C(41)	166.5 (3)

imido group for similar reactivity. As mentioned previously, work by our group and others[8] has shown that early transition metal alkylidene ($M{=}CR_2$) functional groups are more potent than their alkyl ($M{-}CR_3$) counterparts. One might, therefore, extrapolate a similar relationship between $M{=}NR$ and $M{-}NR_2$ bonds. Indeed the recent work of Bergman and Wolczanski has shown that it is possible for zirconium(IV) imido groups to activate benzene and even methane.[14] Previously we have shown that the tantalum and niobium imido compounds $M({=}NMe)(OAr\text{-}2,6\text{-}Ph_2)_3(HNMe_2)$ do not undergo facile intramolecular CH bond activation.[26] Although the compound $[W(NMe_2)_4]$ is not reported, the mixed imido, amido substrate $W(NBu^t)_2(NHBu^t)_2$ is easily obtained.[27] The reaction of $HOAr\text{-}2,6\text{-}Ph_2$ (≥2 equiv) with $W(NBu^t)_2(NHBu^t)_2$ takes place in hydrocarbon solvents at 125 °C to yield the pale yellow bis(aryloxide) $W(NBu^t)_2(OAr\text{-}2,6\text{-}Ph_2)_2$ (2). Spectroscopic studies of 2 showed the complete absence of any $\bar{\nu}$(NH) stretch in the infrared spectrum along with ^1H and ^{13}C NMR resonances consistent with the presence of non-metalated $OAr\text{-}2,6\text{-}Ph_2$ ligands. A solid-state structural study of 2 (Figure 4, Tables III and V) confirmed the presence of a pseudotetrahedral WO_2N_2 core. The short W–N distances and large W–N–Bu^t angles are also consistent with the retention of two *tert*-butylimido linkages in 2 (Table III). Compound 2 is closely related to the bis(*tert*-butoxy) compound $W(NBu^t)_2(OBu^t)_2$ reported by Nugent et al.[27] Attempts to thermally induce cyclometalation in 2 proved unproductive. The compound exhibits great thermal stability in the melt for extended periods at temperatures up to 300 °C. Attempts to induce metalation by increasing the coordination number about the metal center led us to exploring the reactivity of 2-phenylphenol (HOAr-2-Ph) with $W(NBu^t)_2(NHBu^t)_2$. In this case reaction with 4 equiv took place to produce

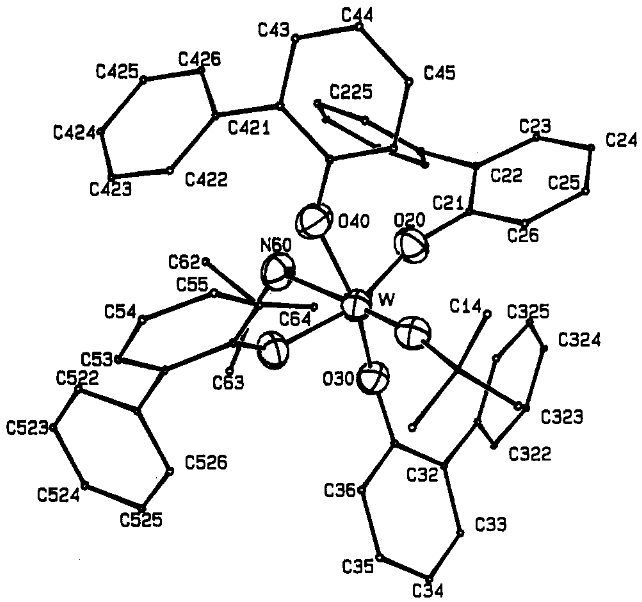

Figure 5. ORTEP view of $W(NBu^t)(NH_2Bu^t)(OAr\text{-}2\text{-}Ph)_4$ (3) emphasizing the central coordination sphere.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $W(NBu^t)(NH_2Bu^t)(OAr\text{-}2\text{-}Ph)_4$ (3)

W-O(20)	1.921 (3)	W-O(30)	1.920 (3)
W-O(40)	1.964 (3)	W-O(50)	1.973 (3)
W-N(10)	1.733 (3)	W-N(60)	2.380 (3)
O(20)-W-O(30)	91.9 (1)	O(40)-W-N(60)	75.5 (1)
O(20)-W-O(40)	85.6 (1)	O(50)-W-N(10)	96.4 (1)
O(20)-W-O(50)	159.7 (1)	O(50)-W-N(60)	80.4 (1)
O(20)-W-N(10)	102.7 (1)	N(10)-W-N(60)	176.7 (1)
O(20)-W-N(60)	80.4 (1)	W-O(20)-C(21)	146.0 (2)
O(30)-W-O(40)	159.3 (1)	W-O(30)-C(31)	136.3 (2)
O(30)-W-O(50)	92.6 (1)	W-O(40)-C(41)	142.1 (3)
O(30)-W-N(10)	97.0 (1)	W-O(50)-C(51)	133.5 (2)
O(30)-W-N(60)	83.9 (1)	W-N(10)-C(11)	170.2 (3)
O(40)-W-N(50)	83.2 (1)	W-N(60)-C(61)	132.5 (3)
O(40)-W-N(10)	103.6 (1)		

$W(NBu^t)(NH_2Bu^t)(OAr\text{-}2\text{-}Ph)_4$ (3) as a bright yellow material. Two, nonequivalent Bu^t resonances and a broad NH_2 peak in the ^1H NMR spectra of 3 along with a simple, unmetallated OAr-2-Ph pattern support this formulation which was confirmed by a single-crystal X-ray diffraction analysis (Figure 5; Table IV). Again no evidence for cyclometallation taking place upon thermolysis of 3 has been found.

The structural parameters for four-coordinate (2) and six-coordinate (3) show the tungsten–imido bond lengths, 1.73–1.74 Å, to be comparable. In the case of 3 the imido group is located trans to the *tert*-butylamine ligand, which has a much longer, 2.38 Å, W–N distance.

Experimental Section

General experimental procedures have been described previously.[19] The starting materials $Mo(NMe_2)_4$[17] and $(Bu^tNH)_2W(NBu^t)_2$[27] were prepared by literature methods. The ^1H and ^{13}C NMR spectra were obtained on a Varian Associates XL-200 spectrometer, while the infrared spectra were obtained by using a Perkin-Elmer 1800 Fourier transform infrared spectrometer. Microanalysis were obtained from the Purdue Microanalysis Labs. The ESR spectra were recorded in the nonaqueous cavity of a Varian E-line Century Series spectrometer.

$Mo(OC_6H_3PhC_6H_4)(OAr\text{-}2,6\text{-}Ph_2)_2(HNMe_2)$ (1a). To a solution of $Mo(NMe_2)_4$ (1.00 g, 3.7 mmol) in benzene (25 mL) was added $HOAr\text{-}2,6\text{-}Ph_2$ (2.80 g, 11.4 mmol). The mixture was stirred at room temperature for 12 h. Removal of solvent under vacuum followed by recrystallization from hot benzene gave the product as dark red crystals. Typical yield: 75%. Anal. Calcd for

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[26] Chesnut, R. W.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* 1988, *27*, 752.

[27] Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* 1980, *19*, 777.

Table V. Crystallographic Parameters

	1a	**1b**	**2**	**3**
formula	$MoO_3NC_{56}H_{45}$	$MoC_{59}H_{43}NO_3$	$WO_2N_2C_{44}H_{44}$	$WO_4N_2C_{56}H_{56}$
fw	914.99	909.93	816.70	1004.93
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a, Å	13.431 (2)	13.236 (3)	11.455 (1)	14.472 (1)
b, Å	18.213 (5)	22.034 (5)	11.600 (1)	12.146 (1)
c, Å	10.262 (1)	15.991 (3)	16.003 (3)	28.055 (4)
α, deg	101.68 (2)	90.00	91.07 (1)	90
β, deg	106.53 (1)	109.63 (1)	93.00 (1)	92.115 (8)
γ, deg	77.93 (2)	90.00	117.20 (1)	90
Z	2	4	2	4
V, Å^3	2326 (1)	4392.65	1886.6 (9)	4928 (1)
d_{calcd}, g/cm^3	1.306	1.376	1.438	1.354
cryst size, mm	0.52 × 0.25 × 0.20	0.25 × 0.25 × 0.30	0.63 × 0.57 × 0.50	0.65 × 0.50 × 0.44
cryst color	red	orange	yellow	orange
radiatn	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	MoK$_\alpha$(0.71073 Å)
linear abs coeff, cm^{-1}	3.19	3.373	31.63	24.38
temp, °C	22.0	−155 °C	+19	+18
detector aperature, mm	(1.5 + tan θ) mm × 4.00	3.0 × 4.0	(1.5 + tan θ) mm × 4.00	(1.5 + tan θ) mm + 4.00
takeoff angle, deg	1.90	2.0	2.80	1.90
scan speed, deg/min	variable	4.0	variable	variable
scan width, deg	0.75 + 0.35 tan θ	2.0 + dispersion	0.48 + 0.35 tan θ	0.42 + 0.35 tan θ
bkgd counts, s	50% of scan	6	50% of scan	50% of scan
2θ range, deg	4.00–45.00	6–45	4.00–45.00	4.00–45.00
unique data	6113	5756	4879	6808
unique data with $F_o > 3.00\sigma(F)$	1625	4739	4610	5103
$R(F)$	0.038	0.0410	0.024	0.022
$R_w(F)$	0.054	0.0434	0.036	0.030
goodness of fit	1.174	0.838	1.587	1.036
largest Δ/σ	0.47	0.05	0.21	0.00

$MoC_{56}H_{45}NO_3$: C, 76.77; H, 5.18; N, 1.59. Found: C, 77.40; H, 5.24; N, 1.90. EPR (toluene): $g = 1.960$ (broad). Infrared (Nujol mull): $\bar{\nu}$(N–H) = 3250 cm^{-1}.

Mo(OC$_6$H$_3$PhC$_6$H$_4$)(OAr-2,6-Ph$_2$)$_2$(py) (1b). To a solution of Mo(OC$_6$H$_3$PhC$_6$H$_4$)(OAr-2,6-Ph$_2$)$_2$(HNMe$_2$) (0.20 g, 0.28 mmol) in toluene (20 mL) was added pyridine (py) (0.50 g, 0.63 mmol). The solution was stirred at room temperature for 6 h. Concentration of the toluene solution followed by addition of hexane (1:1) slowly produced well-formed red crystals. Typical yield: 70%. Anal. Calcd for $MoC_{59}H_{43}NO_3$: C, 77.88; H, 4.76; N, 1.58. Found: C, 77.74; H, 4.74; N, 1.38. EPR (toluene): $g = 1.959$ (broad).

W(NBu^t)$_2$(OAr-2,6-Ph$_2$)$_2$ (2). To a solution of (Bu^{t}N)$_2$W(NHBu^t)$_2$ (2.98 g, 6.24 mmol) in hexane (30 mL) was added HOAr-2,6-Ph$_2$ (3.30 g, 13.38 mmol). The mixture was heated in an oil bath (125 °C) for 7 h in a closed flask. The pale yellow crystalline product was obtained after slow cooling of the hot hexane solution. Yield: 3.21 g (63%). Anal. Calcd for $WC_{44}H_{44}N_2O_2$: C, 64.71; H, 5.43; N, 3.43. Found: C, 64.52; H, 5.57; N, 3.45. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 0.62 (s, *Me*$_3$CN), 6.8–7.6 (m, aromatics). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 31.8 ((*C*H$_3$)$_3$CN), 66.0 ((CH$_3$)$_3$*C*N).

W(NBu^t)(NH$_2$Bu^t)(OAr-2-Ph)$_4$ (3). To a solution of (Bu^{t}N)$_2$W(NHBu^t)$_2$ (3.00 g, 6.37 mmol) in hexane (60 mL) was added HOAr-2-Ph (4.45 g, 26.12 mmol). The mixture was heated in an oil bath (125 °C) for 5 h in a sealed flask. The bright orange crystalline product was obtained upon slow cooling of the hot hexane solution. Yield: 3.50 g (56%). Anal. Calcd for $WC_{56}H_{56}N_2O_4$: C, 66.93; H, 5.62; N, 2.79. Found: C, 66.49; H, 5.58; N, 2.21. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 0.20 (br, *Me*$_3$CNH$_2$), 1.36 (s, *Me*$_3$CN), 1.82 (br s, Bu^{t}N*H*$_2$), 6.7–7.4 (m, aromatics). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 29.4 ((*C*H$_3$)$_3$CNH$_2$), 34.0 ((*C*H$_3$)$_3$CN), 48.6 ((CH$_3$)$_3$*C*NH$_2$), 70.3 ((CH$_3$)$_3$*C*N). Infrared (Nujol mull): $\bar{\nu}$(N–H) = 3318 cm^{-1} and 3258 cm^{-1}.

Crystallographic Studies

Three of the X-ray diffraction studies were completed at Purdue, while the fourth, that of **1b**, was obtained through the Indiana University Molecular Structure Center.[28] Some selected crystallographic data are collected in Table V.

Mo(OC$_6$H$_3$PhC$_6$H$_4$)(OAr-2,6-Ph$_2$)$_2$(HNMe$_2$) (1a), W(OAr-2,6-Ph$_2$)$_2$(NBu^t)$_2$ (2), and W(OAr-2-Ph)$_4$(NBu^t)(H$_2$NBu^t) (3). Suitable crystals of the three compounds were examined under deoxygenated Nujol and mounted in an appropiate sized glass capillary surrounded by epoxy resin. The hydrogen atom positions were calculated after several cycles of anisotropic refinement assuming idealized geometries and a carbon–hydrogen bond distance of 0.95 Å. For the methyl groups, one hydrogen position was located in a difference Fourier map, this position idealized and the other two hydrogen positions calculated. Linear decay correction was applied with an overall decay of 44% (**1a**), 4.5% (**2**), and 12.8% (**3**). Hydrogens were not refined, and no correction for extinction was applied. Compound **1a** crystallized with half a molecule of benzene in the unit cell.

Mo(OC$_6$H$_3$PhC$_6$H$_4$)(OAr-2,6-Ph$_2$)$_2$(py) (1b). A suitable crystal was located and transferred to the goniostat by using standard inert-atmosphere handling techniques employed by the IUMSC and cooled to −155 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/c$. Subsequent solution and refinement of the structure confirmed this choice.

Data were collected in the usual manner by using a continuous θ–2θ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated σ's in the usual manner. No absorption correction was applied.

The structure was solved by a combination of direct methods (MULTAN 78) and Fourier techniques. The positions of all hydrogen atoms were clearly visible in a difference Fourier phased on the non-hydrogen atoms, and the coordinates and isotropic thermal parameters for hydrogens were varied in the final cycles of refinement. A final difference Fourier was essentially featureless, with the largest peak being 0.53 e/A^3.

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Supplementary Material Available: Tables of fractional coordinates, anisotropic thermal parameters, and full bond distances and angles for 1, 2, and 3 (55 pages); listings of observed and calculated structure factor tables for **1a**, **1b**, **2**, and **3** (102 pages). Ordering information is given on any current masthead page.

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