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Intra- vs Intermolecular α -Hydrogen Abstraction in the Generation of Multiple Imido Complexes: Synthesis, Reactivity, and Structural Studies of the d⁰ Tris(imido) **Functional Group of Tungsten**

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The synthesis, reactivity, and structural characterization of the d⁰ tris(imido) complex $[\text{Li}(\text{THF})_4][W(\text{NAr})_3\text{Cl}](2, \text{Ar} = 2,6-\text{C}_6\text{H}_3-i-\text{Pr}_2)$ are reported. When $W(\text{NAr})\text{Cl}_4(\text{THF})$ reacts with 2 equiv of Me₃SiNHAr in THF, the bis(imido) compound W(NAr)₂Cl₂(THF)₂ (1) is isolated. Reacting W(NAr)₂Cl₂(THF)₂ with 2 equiv of LiNHAr in THF affords the yellow, crystalline tris(imido) complex $[\text{Li}(\text{THF})_4][W(\text{NAr}_3)Cl]$ (2). Complex 2 is shown to be the kinetic product of this reaction since it reacts with byproduct H_2NAr to afford $W(NAr)_2$ - $(NHAr)_2$ (3). Experiments are described that support the d⁰ W(=NR)₂ functional group in $W(NAr)_2Cl_2(THF)_2$ (1) arising by an *intra*molecular α -H abstraction in $[W(NAr)(NHAr)_2 Cl_{2}(THF)_{n}$ (with loss of H₂NAr), while the formation of $[W(NAr)_{3}Cl]^{-}(2)$ from $W(NAr)_{2}Cl_{2}$ - $(THF)_2$ (1) most likely proceeds by an *intermolecular* deprotonation of nascent W(NAr)₂-(NHAr)Cl by the second equivalent of [NHAr]⁻. These experiments include synthesis and reactivity studies of W(NAr)₂Cl₂(NH₂Ar) (4), W(NAr)(NEt₂)Cl₃(THF) (5), and W(NAr)₂- $(NEt_2)Cl$ (6). The d⁰ metal center in $[W(NAr)_3Cl]^-$ (2) is susceptible to nucleophilic attack as seen in its reactions with PMePh₂, PMe₃, [n-Bu₄N]Br, MeLi, and LiCH₂SiMe₃ to afford the substitution products W(NAr)₃(PMePh₂) (7), W(NAr)₃(PMe₃) (8), [n-Bu₄N][W(NAr)₃Br] (9), $[\text{Li}(\text{THF})_4][W(\text{NAr})_3\text{Me}]$ (10), and $[\text{Li}(\text{THF})_4][W(\text{NAr})_3(\text{CH}_2\text{SiMe}_3)]$ (11), respectively. Kinetic and mechanistic evidence is presented that suggests these reactions proceed by a bimolecular, $S_N 2$ attack at the d⁰ tungsten center. [Li(THF)₄][W(NAr)₃Cl] (2) crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with a = 13.787(4), Å, b = 17.348(5) Å, c =22.781(8) Å, $\beta = 90.426(28)^{\circ}$, and V = 5448.5(30) Å³, with Z = 4 and D(calc) = 1.268 g cm⁻³. $W(NAr)_3(PMe_3)$ (8) crystallizes in the orthorhombic space group Pbca (No. 61) with a =18.572(3) Å, b = 25.966(4) Å, c = 16.819(3) Å, and V = 8111(4) Å³, with Z = 8 and D(calc)= 1.29 g cm⁻³. The tungsten atom of $[Li(THF)_4][W(NAr)_3Cl](2)$ is tetrahedrally coordinated with three virtually identical imido ligands with an average W-N bond length of 1.78 Å and an average W-N-Cipso bond angle of 171°. W(NAr)₃(PMe₃) (8) is also tetrahedrally coordinated and displays an average imido W-N bond length of 1.79 Å and slightly bent $W-N-C_{ipso}$ bond angles (av 167°), though one imido ligand is more strongly bent than the other two. The electronic structure of the C_{3v} W(NAr)₃L compounds suggests a ligand-based, nonbonding a₂ HOMO comprised of a $N(p\pi)$ orbital combination oriented perpendicular to the molecule's C_3 axis. Accordingly, an imido nitrogen is subject to electrophilic attack, as seen in the reactions of $W(NAr)_3(PMe_3)$ (8) with HOAr' (Ar' = 2,6-C₆H₃Me₂), Me₃SiI, MeI, and PhNCO that afford W(NAr)₂(NHAr)(OAr') (12), W(NAr)₂[N(SiMe₃)Ar]I (13), W(NAr)₂-

(NMeAr)I (14), and W[NArC(O)NPh](NAr)₂(PMe₃) (15), respectively. Similarly, the reaction of $[Li(THF)_4][W(NAr)_3Me]$ (10) with $[HNMe_3]BPh_4$ does not protonate the W-Me bond but rather attacks the imido nitrogen to afford W(NAr)₂(NHAr)Me (16). W(NAr)₂(NHAr)Me (16) does not eliminate CH_4 upon thermolysis to afford base-free [W(NAr)₃]; other attempts to generate this species are described.

Introduction

Transition metal organoimido complexes^{1,2} have been applied to catalytic and synthetic methodologies involv-

ing net [NR] transfer chemistry,³ as in the amination⁴ and aziridination⁵ of olefins or the ammoxidation of propylene.⁶ Organoimido ligands have also been implicated in nitrile reduction⁷ and have seen increasing utility as ancillary groups to support high oxidation

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state metals.⁸ Recent advances in metal imido chemistry include the generation of compounds containing reactive $L_n M = NR$ ligands that can activate the C-H bonds of methane⁹ or engage in cycloaddition chemistry.^{3d,10} Various strategies employed to activate imido ligands include coordinating these ligands to late transition elements or using mid- to low-valent metals in an effort to destabilize the strong $d\{\pi\} \leftarrow p\{\pi\}$ interactions that often make imido complexes inert. One aspect of many early transition metal compounds with reactive $L_n M = NR$ ligands is a coordination sphere containing multiple π donor ligands,^{11,12} a feature that has aroused interest in " π -loaded" multiple imido complexes as another potential means to activate M=NR bonds.¹²⁻¹⁷

We recently reported¹² the preparation and properties of d⁰ tris(imido) complexes of tungsten, thereby completing the series of $d^{\bar{0}} W(NR)_n$ imido-metal functional groups for n = 1,¹⁸ 2,¹⁹ 3,¹² and 4.²⁰ Prior to our initial report, tris(imido) complexes were restricted to select metals in groups 7 and $8.^1$ Given the potential utility

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of imido complexes such as Mn(N-t-Bu)₃X²¹ in oxidation chemistry and Tc(NAr)₃X²² in radiopharmaceutical applications, delineating the properties of this class of compound constitutes a significant goal. In this paper, we report the synthesis, reactivity, and structural properties of the d⁰ W(=NR)₃ functional group, describe experiments that address how multiple imido complexes arise, and demonstrate an electronic analogy of $W(=NR)_3$ to related $M(1\sigma, 2\pi)_3$ complexes.

Results

Formation of the d^0 W(=NR)₂ and d^0 W(=NR)₃ Functional Groups. Upon reacting W(NAr)Cl₄(THF)²³ with 2 equiv of Me₃SiNHAr in THF (Ar = $2,6-C_6H_3-i$ - Pr_2 , red-orange W(NAr)₂Cl₂(THF)₂ (1) is isolated in 81% yield. NMR data for 1 reveal equivalent imido and THF ligands; thus, a structure analogous to the chelate adducts $W(NR)_2Cl_2(L-L)$ is proposed, i.e., with *cis*-imido and trans-chloride ligands, as suggested in Scheme 1.^{19c,23,24} When W(NAr)₂Cl₂(THF)₂ is reacted with 2 equiv of LiNHAr in THF, the yellow, crystalline tris-(imido) complex [Li(THF)₄][W(NAr)₃Cl] (2) is obtained in \sim 75% yield. This formulation of **2** is consistent with the absence of a $\nu(N-H)$ mode in its IR spectrum, the lack of NH resonances in its ¹H NMR spectrum, its elemental analysis, and its X-ray structural determination (vide infra). Under prolonged vacuum, [Li-(THF)₄][W(NAr)₃Cl] slowly loses THF; thus, [Li(THF)₄]⁺ is considered the maximum THF coordination in this complex. The solid state structure of 2 reveals the plane of the imido phenyl rings oriented roughly parallel with the molecule's z axis (the W–Cl bond), but ¹H and ¹³C NMR spectra of the equivalent NAr ligands exhibit one $CHMe_2$ septet and a single $CHMe_2$ doublet, implying free rotation about the W-N-C_{ipso} bond and a threefold axis of symmetry.

[Li(THF)₄][W(NAr)₃Cl] (2) is observed to be the kinetic product of the reaction between $W(NAr)_2Cl_2(THF)_2$ (1) and LiNHAr, since byproduct H₂NAr reacts with $[W(NAr)_3Cl]^-$ over a period of 1-2 days to convert it to the more stable $W(NAr)_2(NHAr)_2$ (3). This reactivity feature is confirmed by reacting isolated [Li(THF)₄]- $[W(NAr)_3Cl]$ with 1 equiv of H₂NAr, which affords yellow W(NAr)₂(NHAr)₂ in high yield; therefore, reaction time is important for the successful isolation of complex 2. A similar reactivity feature has been established in

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Scheme 1



the preparation of the molybdenum analog, $[Li(THF)_4]$ - $[Mo(NAr)_3Cl]$, except that $[Mo(NAr)_3Cl]^-$ reacts with H_2 -NAr even faster than $[W(NAr)_3Cl]^{-.25}$

The conversion of the d⁰ W=NR functional group in W(NAr)Cl₄(THF) to the d⁰ W(=NR)₂ functional group in W(NAr)₂Cl₂(THF)₂ (1) could conceivably proceed by two pathways: (i) the formation of intermediate W(NAr)-(NHAr)₂Cl₂(THF)_n that undergoes an *intra*molecular α -H transfer to afford W(NAr)₂Cl₂(NH₂Ar), followed by THF displacement of diisopropylaniline, or (ii) the intermediacy of W(NAr)(NHAr)Cl₃(THF) that undergoes an *inter*molecular deprotonation by the second equivalent of base (Me₃SiNHAr), followed by THF displacement of Cl⁻ from presumed [W(NAr)₂Cl₃(THF)]⁻. The formation of the d⁰ W(=NR)₂ group in W(NAr)₂Cl₂-(THF)₂ (1) is examined in the following experiments.

(i) When W(NAr)Cl₄(OEt₂)²³ reacts with 2 equiv of Me₃SiNHAr in a weakly coordinating solvent, viz. Et₂O, the five-coordinate adduct W(NAr)₂Cl₂(NH₂Ar) (4) is isolated as an orange solid in moderate yield, presumably via the unobserved bis(amide) [W(NAr)(NHAr)₂Cl₂]. Adding THF to 4 results in the rapid displacement of the coordinated aniline and formation of 1. The structure proposed for 4 is analogous to the related five-coordinate W(NSiMe₃)₂Cl₂(PMePh₂)²⁶ and Ta(NAr)₂Cl-(py)₂,²⁷ i.e., trigonal bipyramidal with two equatorial imides and an axial H₂NAr ligand. (Note that many imides of this stiochiometry are dimeric in the solid state.¹)

(ii) Orange, crystalline $W(NAr)(NEt_2)Cl_3(THF)$ (5) can be obtained in 77% yield from the reaction of W(NAr)- $Cl_4(THF)$ with Me_3SiNEt_2 in Et_2O . The structure of $W(NAr)(NEt_2)Cl_3(THF)$ presented in Scheme 1 allows for the maximum number of $M(d\pi) \leftarrow N(p\pi)$ interactions since the $[NAr]^{2-}$ ligand will engage the d_{xz} and d_{yz} orbitals (with the $M-N_{imido}$ linkage defining the z axis), leaving the d_{xy} orbital available for π bonding with the amido [NEt2]⁻ ligand. This notion is consistent with the NMR data that reveal inequivalent ethyl groups in the NEt₂ ligand. $W(NAr)_2Cl_2(THF)_2(1)$ is generated in quantitative yield upon reacting W(NAr)(NEt₂)Cl₃(THF) (5) with 1 equiv of LiNHAr (in THF), most likely via incipient $[W(NAr)(NHAr)(NEt_2)Cl_2(THF)_n]$. When this reaction is monitored in THF- d_8 (over 48 h, room temperature, ¹H NMR), exactly 1 equiv of $HNEt_2$ is produced per equiv of W(NAr)₂Cl₂(THF)₂ formed. Based on these experiments, the $d^0 W = NR_2$ group in $W(NAr)_2$ - $Cl_2(THF)_2$ (1) is proposed to arise through an *intra*molecular α -H abstraction sequence in an intermediate of the type $W(NAr)(NHAr)_2Cl_2(THF)_n$, with the concomitant loss of H₂NAr.

Similarly, the question of how the tris(imido) complex 2 arises from W(NAr)₂Cl₂(THF)₂ (1) and LiNHAr is also significant. One can envision the 1 + 2LiNHAr \rightarrow 2 reaction proceeding either by (i) the formation of intermediate W(NAr)₂(NHAr)₂ that transfers an amido α -H *intra*molecularly to afford W(NAr)₃(NH₂Ar), followed by displacement of aniline by Cl⁻, or (ii) the intermediacy of nascent W(NAr)₂(NHAr)Cl (cf. W(NAr)₂(NEt₂)Cl) that undergoes an *inter*molecular deprotonation by the second equivalent of [NHAr]⁻. The formation of the d⁰ W(=NR)₃ functional group in [W(NAr)₃Cl]⁻ is examined in the following experiments.

(i) $W(NAr)_2Cl_2(THF)_2$ is readily functionalized using excess Me_3SiNEt_2 (in Et_2O) to provide orange crystals of the base-free amido complex $W(NAr)_2(NEt_2)Cl$ (6). However, upon reacting $W(NAr)_2(NEt_2)Cl$ with LiNHAr, *no* [Li(THF)₄][$W(NAr)_3Cl$] could be identified in the reaction mixture.

(ii) As described above, by product H_2NAr (from the 1 + 2LiNHAr \rightarrow 2 reaction) is observed to react with

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 $[W(NAr)_3Cl]^-$ over a period of 1-2 days to convert it to more stable $W(NAr)_2(NHAr)_2$ (3) and LiCl. This reaction proceeds even in solvents in which LiCl is soluble, clearly demonstrating the thermodynamics of the $[W(NAr)_3Cl]^- + H_2NAr \rightleftharpoons W(NAr)_2(NHAr)_2 + Cl^$ system.

(iii) Accordingly, prolonged heating of solutions of $W(NAr)_2(NHAr)_2$ (3) in the presence of PMe_3 or $PMePh_2$ does not produce any detectable amount of either H_2 -NAr or the tris(imido) complexes $W(NAr)_3(PR_3)$ (¹H NMR, C_6D_6).

Thus, while the d⁰ W(=NR)₂ group in W(NAr)₂Cl₂-(THF)₂ (1) appears to arise by an *intra*molecular α -H abstraction in [W(NAr)(NHAr)₂Cl₂(THF)_n], the formation of [W(NAr)₃Cl]⁻ (2) from W(NAr)₂Cl₂(THF)₂ most likely proceeds by an *inter*molecular deprotonation of nascent W(NAr)₂(NHAr)Cl by the second equivalent of [NHAr]⁻. These results provide precedent for each step of the proposed sequence illustrated in eqs 1–7 for the sequential formation of the d⁰ W(=NR)₂ and d⁰ W(=NR)₃ functional groups, followed by conversion of the *kinetic* product of the W(NAr)₂Cl₂(THF)₂ + 2LiNHAr system, [W(NAr)₃Cl]⁻, to the *thermodynamic* product W(NAr)₂-(NHAr)₂. We note that the influence of a bulky aryl

 $W(=NR)Cl_4 + 2[NHR]^- \rightarrow W(=NR)(NHR)_2Cl_2 \quad (1)$

$$W(=NR)(NHR)_2Cl_2 \rightarrow W(=NR)_2(NH_2R)Cl_2 \quad (2)$$

$$W(=NR)_2(NH_2R)Cl_2 + nL \rightleftharpoons W(=NR)_2Cl_2L_n + H_2NR (3)$$

W(=NR)₂(NH₂R)Cl₂ or
W(=NR)₂Cl₂L_n + [NHR]⁻
$$\rightarrow$$

W(=NR)₂(NHR)Cl + Cl⁻ (4)

$$W(=NR)_{2}(NHR)Cl + [NHR]^{-} \rightarrow [W(=NR)_{3}Cl]^{-} + H_{2}NR (5)$$

$$[W(=NR)_{3}Cl]^{-} + H_{2}NR \rightarrow W(=NR)_{3}(NH_{2}R) + Cl^{-} (6)$$

$$W(=NR)_3(NH_2R) \rightarrow W(=NR)_2(NHR)_2$$
(7)

substituent such as $2,6-C_6H_3$ -*i*-Pr₂ is paramount in determining both the course of these reactions and the kinetic stability of **2**, since attempts to prepare stable $[W(NR)_3Cl]^-$ with less-hindered substituents have not yet proven fruitful.

Reactions of the d⁰ W(=NR)₃ Functional Group with Nucleophiles. [Li(THF)₄][W(NAr)₃Cl] (2) affords a convenient source of the d⁰ tris(imido) functional group of tungsten since the metal center in [W(NAr)₃Cl]⁻ is susceptible to attack by nucleophiles, Scheme 2. Upon adding excess PMePh₂ to a benzene solution of [Li(THF)₄-[W(NAr)₃Cl], red W(NAr)₃(PMePh₂) (7) readily forms in >90% yield. Similarly, the chloride ligand in [Li(THF)₄]-[W(NAr)₃Cl] is smoothly displaced by PMe₃ to afford red crystals of W(NAr)₃(PMe₃) (8) in high yield. ¹H and ¹³C NMR spectra for 7 and 8 reveal symmetric compounds in which all of the imido ligands are equivalent, consistent with free rotation around the W-N-C_{ipso} linkage and a three-fold axis of symmetry.

Treatment of 2 with $[n-Bu_4N]Br$ also results in the loss of LiCl and the formation of [*n*-Bu₄N][W(NAr)₃Br] (9) as an orange solid in 90% yield, Scheme 2. Alkylation reactions also proceed smoothly at low temperatures; reacting 2 with MeLi in THF at -35 °C cleanly yields [Li(THF)₄][W(NAr)₃Me] (10) as a yellow solid in good yield. Complex 10 exhibits coupling of the methyl resonance to ¹⁸³W [14% abundance, ${}^{2}J({}^{183}W-{}^{1}H) = 11$ Hz] in its ¹H NMR spectrum. The analogous reaction between 2 and $LiCH_2SiMe_3$ affords $[Li(THF)_4]$ - $[W(NAr)_3(CH_2SiMe_3)](11)$ as a yellow solid in moderate yield. One significant question concerning these nucleophilic displacements is whether they proceed via a binuclear, $S_N 2$ attack on $[W(NAr)_3Cl]^-$ or via an $S_N 1$ loss of chloride ion and generation of the short-lived intermediate [W(NAr)₃]. The displacement reactions described above are observed to proceed at rates that are nucleophile dependent, suggesting the former, bimolecular pathway. Attempts to form base-free [W(NAr)₃] are described below.

Molecular and Electronic Structures of Complexes Containing the d⁰ W(=NR)₃ Functional **Group.** Yellow single crystals of [Li(THF)₄][W(NAr)₃Cl] suitable for a structural determination were grown from THF/pentane solution at -35 °C. A summary of the crystal data and the structural analysis is given in Table 1, and relevant bond distances and angles are given in Table 2. Figure 1 presents the molecular structure of the [W(NAr)₃Cl]⁻ anion in [Li(THF)₄][W(NAr)₃Cl], in which the tungsten atom is tetrahedrally coordinated with three virtually identical imido ligands. The W-N- C_{ipso} bond angles are close to linear at 171° (av), and the average W-N bond length is 1.78 Å. Some tilting of the phenyl rings in a propeller arrangement is evident since a more favorable orientation of the isopropyl groups about the metal-chloride bond is attained.

Red single crystals of $W(NAr)_3(PMe_3)$ (8) suitable for a structural determination were grown from toluene/ pentane solution at -35 °C. A summary of the crystal data and the structural analysis is given in Table 1, and key bond distances and angles are given in Table 3. Figure 2 presents the molecular structure W(NAr)₃-(PMe₃) and reveals a tetrahedrally coordinated tungsten atom with the P-C bonds of PMe₃ staggering the W-N bonds of the $W(NAr)_3$ moiety. Also evident are some slight differences in the local coordination geometry as compared to $[W(NAr)_3Cl]^-$. The average imido W-Nbond length is 1.79 Å, and the W-N-C_{ipso} bond angles are slightly bent (av 167°), though one imido ligand is more strongly bent than the other two. Thus, the W-N(2)-C(21) angle of $161.4(9)^\circ$ is roughly 10° more acute than the other two imido bond angles. It seems likely that solid state effects are responsible for the slight distortion of this one imido ligand, as well as the resultant deviation from C_{3v} symmetry, since there appears to be no electronic constraints that might induce such a bend (vide infra).

Table 4 compares average bond angles and lengths for the imido ligands in 2 and 8, as well as their local tetrahedral geometries, and includes the results of Cundari's ab initio calculations on hypothetical $[W(NH)_3Cl]^{-.13,28}$ Aside from the somewhat bent W-N(2)-C(21) angle in $W(NAr)_3(PMe_3)$ (8), the imido ligand geometries in the two structurally characterized complexes are nearly identical. However, an examinaScheme 2



Table 1. Details of the X-ray Diffraction Studies for [Li(THF)₄][W(NAr)₃Cl] (2) and W(NAr)₃(PMe₃) (8)

parameter	[Li(THF)4][W(NAr)3Cl]	$W(NAr)_3(PMe_3)$				
Crystal Parameters						
molecular formula	$C_{52}H_{83}ClLiN_3O_4W$	$C_{39}H_{60}N_3PW$				
molecular weight	1040.49	785.76				
<i>F</i> (000)	2168	3232				
crystal color	yellow	red				
space group	monoclinic $P2_1/n$ (No. 14)	orthorhombic Pbca (No. 61)				
unit cell volume, Å ³	5449(3)	8111(4)				
a, Å	13.787(4)	18.572(3)				
b, Å	17.348(5)	25.966(4)				
c, Å	22.781(8)	16.819(3)				
β , deg	90.43(3)					
Z	4	8				
$D(\text{calc}), \text{g cm}^{-3}$	1.27	1.29				
crystal dimens, mm	0.46 imes 0.32 imes 0.06	0.23 imes 0.23 imes 0.47				
absorpt coeff, cm ⁻¹	23.3	29.7				
data collctn temp, °C	23 ± 1	19 ± 1				
	Data Collection					
diffractometer	Nicolet R3m	Syntex P2 ₁ , Crystal Logics				
monochromator	graphite crystal	graphite crystal, incident beam				
Mo Ka radiation, λ , Å	0.710 73	0.710 73				
2θ range, deg	4-45	2-50				
octants collected	$\pm h \pm k \pm 1$	+h+k+l				
scan type	$\omega - 2\theta$	$\omega - 2\theta$				
scan speed, deg min ^{-1}	5.0-20.0	3.0				
total no. of refins measd	6967 (6532 unique)	7839 (7141 unique)				
corrections	Lorentz-polarization. Ψ -scan absorption	Lorentz-polarization, Ψ -scan absorption				
	Solution and Bafinement	FF				
solution	Patterson method	Patterson method				
refinement	blocked-matrix least-squares	full-matrix least-squares				
refine used in refinement	2938 with $F > 5\sigma(F)$	2907 with $I > 3\sigma(I)$				
noromotors refined	2550 WILLI F 50(F)	2007 (1011 - 50(1))				
P	0.068	0.036				
R	0.064	0.030				
n_{w}	1 99	1 92				
$\Delta/\sigma(max) = -1/\Lambda^3$	1.20	0.65(10)				
$\Delta/\sigma(min) = -1/Å^3$	0.022	-0.30(10)				
computer hardware	Data Conoral Falinza S-20	VAV				
computer naruware	CHET VTI (A 9)	MalEN (Enrof Nanius)				
computer software	Shelall (4.2)	MOLETA (EULAI-INOUIUS)				

tion of the local tetrahedral geometries is instructive. As indicated in Table 4, the tetrahedron of the PMe₃ adduct W(NAr)₃(PMe₃) (8) is more "flattened" toward a trigonal pyramidal structure as compared to the more nearly tetrahedral [W(NAr)₃Cl]⁻ (2). Thus, the tungsten atom in [W(NAr)₃Cl]⁻ lies 0.72 Å out of the imido N₃ plane, while the tungsten atom in W(NAr)₃(PMe₃) is only 0.39 Å out of this molecule's N₃ plane. Bryan and co-workers^{22b} have taken such parameters to indicate increased imido ligand π donation in the flattened, more pyramidal complexes in comparing technetium tris-(imido) complexes. Indeed, in the molecular π framework, the chloride ion can engage in π bonding, whereas PMe₃ cannot; however, we hasten to add that the structural differences deliberated by this possible effect are slight. We note that in both complexes, the X–W–N angles are all less than 109° and the N–W–N angles are all greater than 109°.

In describing the electronic structure of C_{3v} M(NR)₃L complexes, as well as their D_{3h} M(NR)₃ relatives such as Os(NAr)₃,²⁹ it is convenient to consider these species

⁽²⁸⁾ For an analysis of methane binding by base-free W(=NH)₃, see: Cundari, T. R. Organometallics **1993**, *12*, 1998.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) in [Li(THF)₄][W(NAr)₃Cl] (2)^a

Bond Distances						
W-Cl	2.342(6)	N(1) - C(16)	1.398(25)			
W-N(1)	1.777(15)	N(2) - C(36)	1.415(26)			
W-N(2)	1.763(15)	N(3)-C(56)	1.430(29)			
W - N(3)	1.805(18)					
Bond Angles						
Cl-W-N(1)	106.0(6)	N(2) - W - N(3)	112.1(7)			
Cl-W-N(2)	104.7(5)	W-N(1)-C(16)	173.4(16)			
Cl-W-N(3)	107.2(6)	W-N(2)-C(36)	167.7(14)			
N(1) - W - N(2)	112.5(7)	W-N(3)-C(56)	171.4(15)			
N(1) - W - N(3)	113.5(7)					

 a Numbers in parentheses are estimated standard deviations in the least significant digits.



Figure 1. Molecular structure of the $[W(NAr)_3Cl]^-$ anion in $[Li(THF)_4][W(NAr)_3Cl]$ (2) with atoms represented as 35% ellipsoids.

Table	3.	Sele	cted	Bond	l Dist	ances	(A)	and	Bond
	An	gles	(deg)) in V	V(NA)	r)3(PM	e ₃)	(8)a	

Bond Distances						
W-P	2.466(4)	N(1) - C(11)	1.40(1)			
W-N(1)	1.78(1)	N(2) - C(21)	1.38(1)			
W-N(2)	1.80(1)	N(3) - C(31)	1.38(1)			
W-N(3)	1.79(1)					
Bond Angles						
P - W - N(1)	97.3(3)	N(2) - W - N(3)	112.8(4)			
P-W-N(2)	104.8(3)	W - N(1) - C(11)	172.5(8)			
P - W - N(3)	105.9(3)	W-N(2)-C(21)	161.4(9)			
N(1) - W - N(2)	117.3(5)	W - N(3) - C(31)	169 (1)			
N(1) - W - N(3)	115.9(4)					

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

as " $M(1\sigma,2\pi)_3$ " complexes, characterizing the symmetries of the $[NAr]^{2-}$ donor orbitals. Thus, tris(imido) complexes such as $W(NAr)_3L$ ($L = X^-$ or PR₃) and Os-(NAr)₃ have been characterized by a ligand-based, nonbonding a₂ (C_{3v}) or a₂' (D_{3h}) MO comprised of a set of ligand π orbitals oriented perpendicular to the molecule's C₃ axis, Figure 3. Therefore, while each of these compounds may be considered a 20 electron species if the ligands donate their full complement of electrons to the metal, it has been established^{11c,12,29} (in three-fold symmetry) that occupation of this nonbonding MO results in these compounds being more accurately



Figure 2. Molecular structure of $W(NAr)_3(PMe_3)(8)$ with atoms represented as 20% ellipsoids.

Table 4. Comparison of Structural Data^a for [W(NAr)₃Cl]⁻ (2) and W(NAr)₃(PMe₃) (8)

	[W(NAr) ₃ Cl] ⁻	$W(NAr)_3(PMe_3)$	$[W(NH)C1]^{-b}$
W=N (Å)	1.78	1.79	1.79
$\angle W - N - C_{ipso} (deg)$	170.8	167.6	
∠X-W-N (deg)	106.0	102.7	
$\angle N - W - N \;(deg)$	112.7	115.3	112

^{*a*} Average values. ^{*b*} Ab initio calculations from ref 13.

described as 18 electron complexes.³⁰ There is now a significant number of d⁰ tris(imido) species characterized by this same orbital description, including Re-(NR)₃X,³¹ Tc(NAr)₃X,^{14,22} Mo(NAr)₃(PMe₃),²⁵ and Mn(N-t-Bu)₃X.²¹ A simple, qualitative orbital interaction diagram for complexes of the form W(NAr)₃L (L = X⁻ or PR₃) is presented in Figure 3. The bonding description in C_{3v} symmetry of complexes of the type M(NR)₃L (where L is a σ donor only) is illustrated by ligand and metal orbitals of the following symmetries: ligand σ (2a₁ + e), ligand π (a₁ + 2e + a₂), metal s + p (2a₁ + e), and

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Figure 3. Qualitative orbital interaction diagram for $W(NAr)_{3L}$ complexes ($L = \sigma$ donor only) in $C_{3\nu}$ symmetry.

metal d $(a_1 + 2e)$.^{1,32} Thus, one of the ligand π orbitals, the a_2 , is necessarily nonbonding. An analogous electronic structure also appears to describe certain d¹ complexes, such as Tc₂(NAr)₆.³³

Reactions of the d⁰ W(=NR)₃ Functional Group with Electrophiles. The presence of a nonbonding a₂ MO situated on the imido nitrogens in W(NR)₃L, which appears to be the HOMO of these complexes, suggests that this orbital might be subject to electrophilic attack. Thus, the reaction of W(NAr)₃(PMe₃) (8) with 1 equiv of HOAr' $(Ar' = 2,6-C_6H_3Me_2)$ affords yellow crystals of W(NAr)₂(NHAr)(OAr') (12) in low to moderate yield, Scheme 3. The low yield of this complex can be attributed in part to its extreme solubility. Other electrophiles also attack the imido nitrogens with formation of a compound of the form W(NAr)₂(NEAr)X. For example, excess Me₃SiI can be added to a pentane solution of W(NAr)₃(PMe₃) to provide a moderate yield of W(NAr)₂[N(SiMe₃)Ar]I (13). Similarly, excess methyl iodide reacts with W(NAr)₃(PMe₃) in benzene, forming yellow W(NAr)₂(NMeAr)I (14) and byproduct [Me₄P]I. The broad resonances observed in the ¹H NMR spectra of these species at room temperature are consistent with rotation about the $W-N_{amide}$ bond on the order of the NMR time scale. However, at lower temperatures, rotation about W-N_{amide} is slowed, and spectra consistent with the structures presented in Scheme 3 are observed. A cycloaddition reaction occurs between PhNCO and a W=NAr bond in W(NAr)₃(PMe₃) to afford

the metallacyclic complex $\dot{W}[NArC(O)\dot{N}Ph](NAr)_2(PMe_3)$ (15). ¹H and ¹³C NMR data for 15 indicate that only one imido ligand has reacted with isocyanate, even though excess PhNCO is present. The proposed regiochemistry is that expected from the polarity of the $W^{\delta+}-N^{\delta-}$ bond and the highly electropositive carbon in PhNCO and is consistent with the strong mode at 1654 cm⁻¹ (Nujol mull) in the IR spectrum of 15 that is assigned as ν (C=O), Scheme 3. Accordingly, similar metallacyclic structures have been reported with this same regiochemistry.³⁴

Since metal-carbon bonds in early metal alkyl complexes are typically subject to electrophilic attack, the question arises whether $[Li(THF)_4][W(NAr)_3R]$ compounds will be protonated at the alkyl or the imido ligand. Thus, $[Li(THF)_4][W(NAr)_3Me]$ (10) is found to react with $[HNMe_3]BPh_4$ in Et₂O to form yellow crystals of $W(NAr)_2(NHAr)Me$ (16), as indicated in eq 8.



Attempts To Generate Base-Free [W(NAr)₃]. W-(NAr)₃L derivatives are characterized as saturated compounds, and highly polar $W^{\delta+}-N^{\delta-}$ bonds are a feature of this π -loaded system; therefore, we considered whether generating base-free, 16 electron $[W(NAr)_3]$ would provide a highly reactive species that might be capable of, inter alia, activating C-H bonds. Such a notion is supported by Cundari's ab initio calculations on base-free [W(NH)₃] that suggest a pyramidal ground state, a highly distended dz² LUMO, and extremely polar $W^{\delta+}-N^{\delta-}$ bonds.¹³ These features have led to calculations of hypothetical [W(NH)₃] that coordinates methane [as the adduct $W(NH)_3(\eta^2-CH_4)$] with the highest binding energy of all the imido complexes examined²⁸ and suggest that C-H activation by base-free [W(NAr)₃] should be facile. In the event that base-free, nascent $[W(NAr)_3]$ could be generated, either a solvent C-H bond activation product, a stable dinuclear species, or some other product that arises from [W(NAr)₃] might be isolated. The following experiments were carried out in attempts to form transient [W(NAr)₃].

(i) Attempts to precipitate chloride ion from solutions of $[W(NAr)_3Cl]^-$ by addition of AgBPh₄ in THF resulted in no reaction, even under forcing conditions.

(ii) Attempts to remove PMe_3 from $W(NAr)_3(PMe_3)$ under high-vacuum and high-temperature conditions (e.g., 10^{-6} Torr and >100 °C) resulted in no reaction; starting material was recovered.

(iii) The gradual (over several days) precipitation of LiCl is observed from solutions of $[\text{Li}(\text{THF})_4][W(\text{NAr})_3\text{Cl}]$ (2) in benzene, and the formation of a complex formulated as $W(\text{NAr})_3(\text{THF})\cdot n\text{THF}$ (n = 2-3) by ¹H NMR is observed. Attempts to remove THF from $W(\text{NAr})_3$ -

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(THF) *n*THF under high-vacuum and high-temperature conditions resulted in the loss of some THF, with the analysis of the residue approaching a minimum THF component of W(NAr)₃(THF) THF (i.e., n = 1). NMR data for this compound reveal equivalent though broad THF resonances, suggesting exchange between free and bound THF. (W(NAr)₃(THF) *n*THF has rarely been induced to crystallize.) In no case was evidence for basefree [W(NAr)₃] or the solvent C-H activation product W(NAr)₂(NHAr)Ph observed.

(iv) Extended thermolysis of $W(NAr)_2(NHAr)Me$ (16) (vide supra) in refluxing benzene affords no evidence for the elimination of CH_4 and the formation of either a C-H bond activation product $W(NAr)_2(NHAr)Ph$ that might arise via the formation of base-free $[W(NAr)_3]$ or any other product that might arise from $[W(NAr)_3]$ under these conditions.

These experiments are consistent with the mechanistic studies described above, suggesting that ligand dissociation from $W(NAr)_3L$ ($L = X^-$ or PR₃) to generate [$W(NAr)_3$] in the absence of a nucleophile is unlikely. Furthermore, the fact that $W(NAr)_2(NHAr)Me$ does not eliminate methane is most likely a reflection of the thermodynamic differences between [$W(NAr)_3$] + CH₄ and $W(NAr)_2(NHAr)(CH_3)$ as predicted from the high-energy, *pyramidal* ground state calculated for [$W(NAr)_3$].¹³

Discussion

When the reaction of $W(NAr)_2Cl_2(THF)_2$ with LiNHAr is allowed to proceed for more than several hours, significant amounts of $W(NAr)_2(NHAr)_2$ are isolated from the reaction mixture. After prolonged reaction time, most of the kinetic product [Li(THF)₄][W(NAr)₃Cl] has converted to the more stable $W(NAr)_2(NHAr)_2$. This feature is also established by reacting isolated [Li-(THF)₄][W(NAr)₃Cl] with H₂NAr, which affords $W(NAr)_2$ -(NHAr)₂ in near quantitative yield; therefore, reaction time is crucial for the successful isolation of [Li(THF)₄]-[W(NAr)₃Cl]. This reaction probably proceeds through the intermediacy of unstable [W(NAr)₃(NH₂Ar)], as suggested in Scheme 4, and, consistent with the experiments described above, clearly demonstrates the thermodynamic preferences of this system.



The polarity of the $W^{\delta+}-N^{\delta-}$ bonds of the imido ligands in the d⁰ tris(imido) complexes make them subject to both nucleophilic and electrophilic attack, as described above. Reactions with electrophiles underscore the stability of four-coordinate bis(imido) complexes of W^{VI} of the form $W(NAr)_2X_2$ and five-coordinate bis(imido) metallacyclic compounds, relative to the higher energy $W(NAr)_3L$ derivatives.

Since the cyclopentadienyl anion $[C_5R_5]^-$, the acetylene dianion $[RC=CR]^{2-}$, and oxo O^{2-} , nitrido N^{3-} , and alkylidyne $[CR]^{3-}$ ligands may all be described as $1\sigma,2\pi$ donors, ^{11a,c,16,35} one might expect analogies in the stoichiometries and structures of their compounds. Therefore, other C_{3v} or D_{3h} compounds that are intimately related by analogous orbital descriptions include tris-(alkyne) compounds, such as $Re(RC=CR)_3X$ (X = I, Me, or OSiMe₃),³⁶ [W(RC=CR)_3]²⁻,^{30a} and W(RC=CR)_3L.^{30b,c} An argument has been made regarding the application of such an orbital description to mixed-ligand species

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with $1\sigma_{,2}\pi$ orbital symmetry, such as Re(RC=CR)₂(NR)-X^{11a} and $(\eta^5-C_5Me_5)W(NAr)_2Cl.^{11c}$

These experiments reported here suggest one way to attain reactive imido ligands: π -loading appears to encourage highly polar $M^{\delta+}-N^{\delta-}$ linkages and renders the imido ligand especially susceptible to electrophilic attack. Since factors that favor C-H bond activation by imido ligands include (i) an imido nitrogen bearing a large negative charge and (ii) an empty metal orbital of σ symmetry,^{9,28} ligand loss from W(NAr)₃L to generate transient, 16 electron W(NAr)3 would presumably form a species capable of such reactivity. However, we have found no indication that a ligand coordinated to $[W(NAr)_3]$ is labile, nor have attempts to eliminate alkane RH upon thermolyzing W(NAr)₂(NHAr)R been successful. Since base-free $[W(NAr)_3]$ is not required for any of the reactions reported here, we conclude that it is highly energetic and does not form if a lower energy pathway is accessible. The preparation and reactivity of such species are areas of our continued interest.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere either by standard Schlenk techniques³⁷ or in a Vacuum Atmospheres HE-493 drybox at room temperature (unless otherwise indicated). Solvents were distilled under N₂ from an appropriate drying agent³⁸ and were transferred to the drybox without exposure to air. The "cold" solvents used to wash isolated solid products were typically cooled to \sim -35 °C before use. NMR solvents were passed down a short (5–6 cm) column of activated alumina prior to use. In all preparations, Ar = 2,6-C₆H₃-*i*-Pr₂ and Ar' = 2,6-C₆H₃Me₂.

Starting Materials. WOCl4 was obtained from Hermann C. Stark (Berlin), sublimed (~80 °C, 10⁻² Torr) prior to use, and converted to W(NAr)Cl₄ and then to W(=NAr)Cl₄(THF) or W(=NAr)Cl₄(Et₂O) according to the literature procedures.²³ 2,6-Diisopropylaniline was obtained from Aldrich, vacuum distilled before use, and converted to LiNHAr³⁹ according to the literature procedure. Me₃SiNHAr was prepared from LiNHAr and Me₃SiCl as previously described.³⁹ Me₃SiI and Me₃SiNEt₂ were obtained from Petrarch and used as received. Methyl iodide was obtained from EM Sciences and distilled prior to use. Alkyllithium solutions (used as received), [HNMe₃]-BPh4 (used as received), phenyl isocyanate (distilled), and HO-2,6-C₆H₃Me₂ (sublimed) were obtained from Aldrich. Trimethylphosphine was prepared and purified according to the literature procedure,⁴⁰ with the modification of using MeMgI rather than MeMgBr in the preparation. PMePh₂ was obtained from Strem and used as received. Tetraalkylammonium bromide was dried by heating to ~ 120 °C under high vacuum (> 10^{-6} Torr), followed by recrystallization from minimal THF at -35 °C. AgBPh₄ was prepared according to the literature procedure.⁴¹

Physical Measurements. ¹H (250 MHz) and ¹³C (62.9 MHz) NMR spectra were recorded at probe temperature (unless otherwise specified) on a Brucker WM-250 or AM-250 spectrometer in C₆D₆, CDCl₃, CD₂Cl₂, or toluene- d_8 solvent. Chemical shifts are referenced to protio impurities (δ 7.15, C₆D₆; 7.24, CDCl₃; 5.32, CD₂Cl₂; 2.09, toluene- d_8) or solvent

 $^{13}\mathrm{C}$ resonances (δ 128.0, C₆D₆; 77.0, CDCl₃; 53.8, CD₂Cl₂; 20.4, toluene-d₈) and are reported downfield of Me₄Si. $^{13}\mathrm{C}$ NMR assignments were assisted by APT spectra. Infrared spectra were recorded as Nujol mulls (NaCl plates) between 4000 and 600 cm⁻¹ using a Perkin-Elmer 1310 spectrometer. Microanalytical samples were stored cold, handled under N₂, and combusted with WO₃ (Texas Analytical Laboratories, Inc., Stafford, TX, or Desert Analytics, Tucson, AZ).

Preparations. W(NAr)₂Cl₂(THF)₂ (1). Neat Me₃SiNHAr (4.33 g, 17.4 mmol) was added dropwise to a stirred solution of 5.00 g (8.69 mmol) of W(NAr)Cl₄(OEt₂) in \sim 85 mL of THF. (The solution of W(NAr)Cl₄(OEt₂) in THF immediately forms W(NAr)Cl₄(THF).) This mixture was heated to 60 °C for 48 h, over which time its color changed from dark green to bright red. The reaction volatiles were then removed in vacuo to provide the product as a microcrystalline, red solid. This solid was washed with cold heptane, collected by filtration, and dried in vacuo. Additional product was obtained upon concentrating the heptane filtrate and cooling to -35 °C; yield (two crops) 5.28 g (7.04 mmol, 81%). Analytically pure samples were obtained from pentane/Et₂O solutions at -35 °C. Either W(NAr)Cl₄ or (isolated) W(NAr)Cl₄(THF) can also be used in this preparation, although $W(NAr)CL_4(OEt_2)$ is preferred since it can be obtained purer than $W(NAr)Cl_4$. If this reaction is run under more dilute conditions, the product is contaminated with varying amounts of W(NAr)₂Cl₂(NH₂Ar), and heating must be prolonged for several more days for W(NAr)₂Cl₂(THF)₂ to form completely. ¹H NMR (C₆D₆): δ 7.13–6.81 (A₂B mult, 6 H, H_{aryl}), 4.09 (spt, 4 H, CHMe₂), 3.87 (br, 8 H, $C_{\alpha}H$, THF), 1.34 (br, 8 H, C_{β} H, THF), 1.26 (d, 24 H, CHMe₂). ¹³C NMR $(C_6D_6): \delta 151.2 (C_{ipso}), 144.9 (C_o), 126.6 (C_p), 122.5 (C_m), 71.2$ (C_{α}, THF) , 27.8 (CHMe₂), 25.6 (C_{β}, THF) , 24.7 (CHMe₂). Anal. Calcd for C₃₂H₅₀Cl₂N₂O₂W: C, 51.28; H, 6.72; N, 3.74. Found: C, 51.68; H, 6.95; N, 3.97.

[Li(THF)₄[W(NAr)₃Cl] (2). A solution of LiNHAr (0.977 g, 5.33 mmol) in 15 mL of THF was added dropwise to a rapidly stirred solution of W(NAr)₂Cl₂(THF)₂ (1) (2.00 g, 2.67 mmol) in \sim 50 mL of THF. The reaction was allowed to stir at room temperature for 2 h, over which time its color changed from red to yellow. The reaction volatiles were then removed in vacuo to provide a yellow oil. The product was extracted from the oil with Et_2O (~20 mL), the extract was filtered through Celite, and the solvent was removed from the filtrate in vacuo to yield a waxy, yellow solid. This solid was transferred to a frit, pumped on for ~ 1 h to remove H₂NAr, washed with cold pentane $(3 \times 10 \text{ mL})$, and dried in vacuo, yielding a yellow, microcrystalline solid. Additional product was obtained by concentrating the pentane wash and cooling to -35 °C; yield (two crops) 2.074 g (1.99 mmol, 75%). Analytically pure samples were obtained by recrystallization from THF/pentane solutions at -35 °C. ¹H NMR (CD₂Cl₂): δ 6.97-6.65 (A₂B mult, 9 H, H_{aryl}), 3.71 (m, 16 H, $C_{\alpha}H$, THF), 3.57 (spt, 6 H, $CHMe_2$, 1.90 (m, 16 H, C_β H, THF), 1.06 (d, 36 H, $CHMe_2$). ¹H NMR (C₆D₆): δ 7.17–6.91 (A₂B mult, 9 H, H_{aryl}), 3.81 (spt, 6 H, CHMe₂), 3.35 (m, 16 H, C_aH, THF), ~1.3 (obscured m, 16 H, C_{β}H, THF), 1.26 (d, 36 H, CHMe₂). ¹³C NMR (CD₂Cl₂): δ 140.4 (C₀), 125.1 (C_{ipso}), 122.0 (overlapping C_m and C_p), 68.7 $(C_{\alpha}, \text{THF}), 28.3 (CHMe_2), 25.8 (C_{\beta}, \text{THF}), 23.8 (CHMe_2).$ ¹³C $NMR~(C_{6}D_{6}):~\delta~154.7~(C_{ipso}),~140.3~(C_{o}),~122.9~(C_{p}),~122.4~(C_{m}),$ 68.4 (C_{α} , THF), 28.3 (CHMe₂), 25.4 (C_{β} , THF), 24.2 (CHMe₂). Anal. Calcd for C₅₂H₈₃ClLiN₃O₄W: C, 60.03; H, 8.04; N, 4.04; Cl, 3.41. Found: C, 59.54; H, 8.44; N, 4.15; Cl, 2.81. This complex loses THF under prolonged vacuum.

 $W(NAr)_2(NHAr)_2$ (3). To a solution of 0.20 g (0.192 mmol) of [Li(THF)₄][W(NAr)₃Cl] (2) in 20 mL of benzene was added a solution of 1 equiv of H₂NAr (0.034 g, 0.192 mmol) in 5 mL of benzene. This mixture was stirred at room temperature for 36 h, over which time a white solid (presumably LiCl) precipitated, but little change in solution color was observed. The solution was then filtered through Celite, and the volatile components were removed from the filtrate in vacuo to afford a sticky, yellow solid. This solid was washed with cold

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pentane, collected on a frit, and dried in vacuo; yield 0.12 g (1.37) mmol, 71%). Analytically pure samples were obtained by recrystallization from minimal Et₂O/pentane solutions at -35 °C. ¹H NMR (C₆D₆): δ 7.44 (s, 2 H, NHAr), 7.12–6.87 (overlapping A₂B mult, 12 H total, H_{aryl}, NAr and NHAr), 3.82 and 3.37 (spt, 4 H each, CHMe₂, NAr and NHAr), 1.27 and 1.03 (d, 24 H each, CHMe₂, NAr and NHAr), 1.27 and 1.03 (d, 24 H each, CHMe₂, NAr and NHAr), 142.8 and 141.5 (C₆, NAr and NHAr), 125.2 and 124.9 (C_p, NAr and NHAr), 123.7 and 122.3 (C_m, NAr and NHAr), 29.1 and 28.3 (CHMe₂, NAr and NHAr), 24.4 and 23.6 (CHMe₂, NAr and NHAr). Anal. Calcd for C₄₈H₇₀N₄W: C, 65.00; H, 7.95. Found: C, 64.82; H, 8.07.

W(NAr)₂Cl₂(NH₂Ar) (4). A solution of 0.31 g (1.21 mmol) of Me₃SiNHAr in 5 mL of Et₂O was added to a stirred solution of 0.35 g (0.608 mmol) of $W(NAr)Cl_4(OEt_2)$ in 15 mL of Et_2O . This mixture was stirred at room temperature for 24 h, during which time the solution color slowly changed to red. The reaction volatiles were then removed in vacuo to afford an orange oil. Upon trituration of the oil with cold pentane, an orange, fluffy solid was obtained which was filtered off and dried in vacuo; yield 0.28 g (0.34 mmol, 56%). Analytically pure samples were obtained by recrystallization from pentane at -35 °C. ¹H NMR (C₆D₆): δ 7.10-6.82 (m, 9 H, H_{arvl}), 5.28 (br, 2 H, NH₂Ar), 3.92 (spt, 4 H, CHMe₂, NAr), 3.20 (spt, 2 H, CHMe₂, NH₂Ar), 1.195 (d, 24 H, CHMe₂, NAr), 1.17 (d, 12 H, CHMe2, NH2Ar). ¹³C NMR (CDCl3): δ 150.5, 145.4, 138.5, and 135.1 (C_{ipso} and C_o , NH₂Ar and NAr), 127.4, 125.3, 123.2, and 121.9 (C_m and C_p, NAr and NH₂Ar), 28.7 (CHMe₂, NH₂Ar), 27.9 (CHMe₂, NAr), 23.9 (CHMe₂, NH₂Ar), 23.2 (CHMe₂, NAr). Anal. Calcd for C₃₆H₅₃Cl₂N₃W: C, 55.25; H, 6.83; N, 5.37. Found: C, 55.54; H, 7.10; N, 5.24.

W(NAr)(NEt₂)Cl₃(THF) (5). To a stirred solution of 0.66 g (1.14 mmol) of W(NAr)Cl₄(THF) in 10 mL of diethyl ether was added 0.35 g (2.29 mmol) of Me₃SiNEt₂ (neat). After the solution was stirred at room temperature for 16 h, the volatile components were removed from the resulting orange solution in vacuo to afford an orange solid. Redissolving this solid in minimal Et₂O (\sim 2 mL) and cooling the solution to -30 °C provided orange crystals of product which were filtered off and dried in vacuo; yield 0.54 g (0.88 mmol, 77%). Analytically pure compound was obtained by recrystallization from Et₂O solutions at -35 °C. ¹H NMR (C₆D₆): δ 7.12-6.74 (A₂B mult, 3 H, H_{arvl}), 4.94 and 4.83 (q, 2 H each, NCH₂CH₃), 4.75 (spt, 2 H, CHMe₂), 4.06 (br, 4 H, $C_{\alpha}H$, THF), 1.34 (d, 12 H, CHMe₂), 1.14 (br, 4 H, $C_{\beta}H$, THF), 1.26 and 1.00 (t, 3 H each, NCH_2CH_3). ¹³C NMR (C₆D₆): δ 153.4 (C₀), 145.8 (C_{ipso}), 130.6 (C_p) , 123.6 (C_m) , 72.5 (C_{α}, THF) , 66.1 and 59.0 (NCH_2CH_3) , 27.9 (CHMe₂), 25.3 (CHMe₂), 15.7 and 14.0 (NCH₂CH₃). The C_{β} THF peak was not observed and is presumably coincident with another resonance. Anal. Calcd for C₂₀H₃₅Cl₃N₂OW: C, 39.40; H, 5.79; N, 4.59. Found: C, 39.58; H, 5.87; N, 4.58.

W(NAr)₂(NEt₂)Cl (6). To a solution of 0.58 g (0.77 mmol) of W(NAr)₂Cl₂(THF)₂ (1) in 15 mL of Et₂O was added 0.14 g (0.91 mmol) of neat Me₃SiNEt₂. This mixture was allowed to stir with gentle heating (\sim 35 °C) for 7 days, over which time the solution color changed from red to yellow-orange. The volatile components were then removed from the reaction in vacuo, and the yellow orange solid which remained was redissolved in minimal Et₂O. Upon cooling of this ether solution to -35 °C for 2 days, orange crystals of product formed. The crystals were filtered off and dried in vacuo; yield 0.26 g (0.40 mmol, 52%). Analytically pure samples were obtained by recrystallization from Et_2O solution at -35 °C. ¹H NMR (C₆D₆): δ 7.12–6.83 (A₂B mult, 6 H, H_{aryl}), 4.04 (spt, 4 H, CHMe₂), 3.21 and 2.60 (mult, 2 H each, NCH₂CH₃), 1.23 (d, 24 H, CHMe₂) 0.98 (t, 6 H, NCH₂CH₃). ¹³C NMR (C₆D₆): δ 151.0 (C_{ipso}), 146.1 (C_o), 127.9 (C_m), 122.5 (C_p), 46.4 (NCH₂- CH_3), 28.3 ($CHMe_2$), 24.6 ($CHMe_2$), 14.5 (NCH_2CH_3). Anal. Calcd for C₂₈H₄₄ClN₃W: C, 52.39; H, 6.91; N, 6.55. Found: C, 52.23; H, 6.95; N, 6.53.

W(NAr)₃(PMePh₂) (7). A 0.053 g (0.526 mmol) sample of $PMePh_2$ was added directly (neat) to a solution of 0.25 g (0.245 mmol) of $[Li(THF)_4][W(NAr)_3Cl](2)$ in ~15 mL of benzene. The reaction was stirred at room temperature for 4 h, during which time the yellow solution developed a dark red color. The reaction volatiles were removed in vacuo to afford a red solid. The product was extracted with pentane, the extract filtered through Celite, and the filtrate concentrated in vacuo and cooled to -35 °C. The analytically pure, red crystals which formed overnight were filtered off and dried in vacuo; yield 0.198 g (0.218 mmol, 91%). ¹H NMR (C₆D₆): δ 7.69 (dd, 4 H, H_{o} , PMePh₂), 7.18-6.95 (A₂B mult, 9 H, H_{aryl}, NAr), 6.87 (m, 6 H, H_m and H_p, PMePh₂), 3.87 (spt, 6 H, CHMe₂), 2.04 (d, ${}^{2}J_{H-P} = 9.8 \text{ Hz}, 3 \text{ H}, PMePh_{2}), 1.12 (d, 36 \text{ H}, CHMe_{2}).$ ¹³C NMR $(C_6D_6): \delta 154.9 (C_{ipso}, NAr), 140.8 (C_o, NAr), 133.6 (d, C_{ipso}, C_{ipso})$ PMePh₂), 132.0, 129.6, and 129.4 (PMePh₂), 123.0 (C_p, NAr), 122.2 (Cm, NAr), 28.3 (CHMe₂), 23.9 (CHMe₂), 16.6 (d, PMe-Ph₂). Anal. Calcd for $C_{49}H_{64}N_3PW$: C, 64.68; H, 7.09; N, 4.62. Found: C, 64.37; H, 7.18; N, 4.60.

W(NAr)₃(PMe₃) (8). A solution of 2.00 g (1.92 mmol) of $[Li(THF)_4][W(NAr)_3Cl]$ (2) in ~50 mL of benzene was prepared and cooled to -78 °C. A 0.44 g (5.80 mmol) sample of PMe_3 was then added dropwise (neat) to the stirred [Li(THF)₄]- $[W((NAr)_3Cl]$ solution. The reaction was allowed to warm to room temperature over several hours, during which time the yellow solution developed a cherry red color. After the solution was stirred for 15 h, the reaction volatiles were removed in vacuo to afford a red oil. The product was extracted with Et_2O , the extract filtered through Celite, and the solvent removed from the filtrate in vacuo to afford a red solid. The product was washed with cold pentane and dried in vacuo; yield 1.40 g (1.78 mmol, 92%) of W(NAr)₃(PMe₃) sufficiently pure for further reactions. Analytically pure compound was obtained by recrystallization from pentane solutions at -35 °C. ¹H NMR (C₆D₆): δ 7.18–6.94 (A₂B mult, 9 H, H_{aryl}, NAr), 3.95 (spt, 6 H, CHMe₂), 1.24 (d, 36 H, CHMe₂), 1.21 (d, overlapping with δ 1.24 signal, 9 H, PMe₃). ¹³C NMR (C₆D₆): δ 155.0 (C_{ipso}, NAr), 140.4 (Co, NAr), 122.9 (Cp, NAr), 122.1 (Cm, NAr), 28.2 (CHMe₂), 23.9 (CHMe₂), 16.7 (d, PMe₃). Anal. Calcd for C₃₉H₆₀N₃PW: C, 59.62; H, 7.70. Found: C, 59.54; H, 7.61.

[n-Bu₄N][W(NAr)₃Br] (9). A 0.309 g (0.96 mmol) sample of solid [n-Bu₄N]Br was added directly to a solution of 1.00 g $(0.96 \text{ mmol}) \text{ of } [\text{Li}(\text{THF})_4][W(\text{NAr})_3\text{Cl}] (2) \text{ in } 20 \text{ mL of benzene.}$ This mixture was stirred at room temperature for 15 h, over which time an orange color developed and a white precipitate formed. The reaction solution was filtered through Celite, and the volatile components were removed from the filtrate in vacuo to afford an orange solid. This product was washed with cold pentane, collected by filtration, and dried in vacuo; yield 0.89 g (0.87 mmol, 90%). Analytically pure compound was obtained by recrystallization from Et_2O solution at -35 °C. ¹H NMR (C₆D₆): δ 7.21-6.85 (A₂B mult, 9 H, H_{aryl}), 4.19 (spt, 6 H, CHMe₂), 2.31 (br m, 8 H, NCH₂CH₂CH₂CH₃), 1.42 (d, 36 H, CHMe₂), 1.09-0.93 (br m, 16 H total, NCH₂CH₂CH₂CH₃), 0.80 (pseudo t, 12 H, NCH₂CH₂CH₂CH₃). ¹³C NMR (C₆D₆): δ 156.6 (C_{ipso}), 140.0 (C_o), 121.5 (C_m), 119.6 (C_p), 58.4 (NCH₂-CH₂CH₂CH₃), 28.5 (CHMe₂), 24.1 (CHMe₂), 23.8 and 19.7 (NCH₂CH₂CH₂CH₃), 13.8 (NCH₂CH₂CH₂CH₃). Anal. Calcd for C₅₂H₈₇BrN₄W: C, 60.52; H, 8.50; N, 5.43. Found: C, 60.44 (60.61); H, 9.02 (8.87); N, 5.28 (5.15). (Duplicate analyses reported.)

[Li(THF)4][W(NAr)3Me] (10). To a cold $(-35 \,^{\circ}\text{C})$ solution of 1.00 g (0.96 mmol) of [Li(THF)4][W(NAr)3Cl] in 30 mL of THF was added 1 equiv of MeLi (0.68 mL of a 1.4 M Et₂O solution) dropwise. This reaction mixture was stirred at room temperature for 18 h, after which the solvent was removed in vacuo to afford a yellow, oily residue. The product was extracted with Et₂O, the ether extract filtered through Celite, and the solvent removed from the filtrate in vacuo to provide a yellow solid. The solid was washed with minimal cold

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pentane, collected on a frit, and dried in vacuo; yield 0.60 g (0.59 mmol, 61%). Analytically pure compound was obtained by recrystallization from THF/pentane solutions at -35 °C. ¹H NMR (C₆D₆): δ 7.17–6.92 (A₂B mult, 9 H, H_{aryl}), 3.79 (spt, 6 H, CHMe₂), 3.22 (m, C_aH, THF), 1.20 (m, C_βH, THF), 1.51 (s, 3 H, WMe), 1.27 (d, 36 H, CHMe₂). ¹³C NMR (C₆D₆): δ 155.3 (C_{ipso}), 139.3 (C_o), 122.3 (C_m), 121.6 (C_p), 68.4 (C_a, THF), 28.3 (CHMe₂), 25.3 (C_β, THF), 24.1 (CHMe₂), 15.2 (WMe). Anal. Calcd for C₈₃H₈₆N₃O₄W: C, 62.40; H, 8.50; N, 4.12. Found: C, 62.24; H, 8.71; N, 4.01.

[Li(THF)₄][W(NAr)₃(CH₂SiMe₃)] (11). To a cold (-35 °C) solution of 0.127 g (0.12 mmol) of [Li(THF)4][W(NAr)3Cl] in 25 mL of THF was added 1 equiv of solid LiCH₂SiMe₃ (0.011 g, 0.12 mmol). This reaction mixture was allowed to stir at room temperature for 15 h, after which the solvent was removed in vacuo to afford a yellow, oily residue. The product was extracted with Et₂O, the ether extract filtered through Celite, and the solvent removed from the filtrate in vacuo to provide an oily, yellow solid. This solid was dissolved in ~ 10 mL of pentane and cooled to -35 °C for 24 h, whereupon a yellow solid precipitated. This solid was filtered off and dried in vacuo; yield 0.058 g (0.053 mmol, 44%). Analytically pure compound was obtained by recrystallization from THF/pentane solutions at -35 °C. ¹H NMR (C₆D₆): δ 7.15-6.90 (A₂B mult, 9 H, H_{arvl}), 3.83 (spt, 6 H, CHMe₂), 3.19 (m, 16 H, C_aH, THF), 1.44 (br, 2 H, CH₂SiMe₃), 1.26 (d, 36 H, CHMe₂), 1.14 (m, 16 H, C_{β}H, THF), 0.31 (s, 9 H, CH₂SiMe₃). ¹³C NMR (C₆D₆): δ 122.5 (C_m), 122.2 (C_p), 68.2 (C_{α}, THF), 28.2 (CHMe₂), 25.3 (C_{β}, THF), 24.2 (CHM e_2), 3.0 (CH $_2$ Si Me_3). Several attempts were made to locate the signals for C_{ipso} (NAr), C_o (NAr), and CH_2 - $SiMe_3$; C_0 (NAr) is possibly obscured by the C_6D_6 signal. Anal. Calcd for C₅₆H₉₄N₃O₄LiSiW: C, 61.58; H, 8.68; N, 3.85. Found: C, 61.40; H, 8.72; N, 3.81.

W(NAr)₂(NHAr)(OAr') (12). A solution of 2,6-dimethylphenol (0.081 g, 0.67 mmol) in 10 mL of pentane was added dropwise to a stirred solution of W(NAr)₃(PMe₃) (8, 0.52, 0.66 mmol) in 40 mL of pentane. The reaction was stirred at room temperature for 15 h, over which time the solution color had changed from red to yellow-orange. After this time, the solvent was removed in vacuo to afford a clear, pale orange oil which was dissolved in minimal pentane and stored at -35 °C for \sim 24 h. The yellow block crystals which had formed were filtered off and dried in vacuo; yield 0.230 g (0.28 mmol, 42%). Analytically pure samples were obtained by recrystallization from a minimal volume of pentane at -35 °C. ¹H NMR (C₆D₆): δ 7.88 (s, 1 H, NHAr), 7.10-6.74 (overlapping mult, 12 H total, Haryl; NAr, NHAr, and OAr'), 3.76 (spt, 2 H, CHMe₂, NHAr), 3.45 (spt, 4 H, CHMe₂, NAr), 2.44 (s, 6 H, Me, OAr'), 1.17, 1.05, and 0.98 (d, 12 H each, CHMe2, NAr and NHAr). $^{13}\mathrm{C}$ NMR (C₆D₆): δ 160.6, 151.4, and 145.0 (C_{ipso}, NAr, NHAr, and OAr'), 143.2 and 142.9 (C_o, NAr and NHAr), 128.8, 127.3, 126.4, 125.6, 123.8, 122.4, and 122.2 (C_o , OAr'; C_p and C_m , NAr, NHAr, and OAr'), 28.9 (CHMe2, NHAr), 28.4 (CHMe2, NAr), 24.1, 23.8, and 23.5 (CHMe2, NAr and NHAr), 17.3 (Me, OAr'). Anal. Calcd for C44H61N3OW: C, 63.53; H, 7.39; N, 5.05. Found: C, 63.48; H, 7.42; N, 5.02.

W(NAr)₂[N(SiMe₃)Ar]I (13). Neat Me₃SiI (0.224 g, 1.11 mmol, ~ 0.16 mL) was added dropwise to a stirred solution of 0.15 g (0.19 mmol) of W(NAr)₃(PMe₃) (8) in 20 mL of pentane. This mixture was stirred at room temperature for 24 h, over which time the solution had become cloudy, red-orange in color. The reaction mixture was filtered (fine porosity frit), and the volatile components were removed from the filtrate in vacuo to afford an orange oil which, upon trituration with cold pentane, formed an orange powder. This powder was collected by filtration and dried in vacuo; yield 0.09 g (0.0989 mmol), 52%). Analytically pure compound was obtained by recrystallization from pentane solution at -35 °C. ¹H NMR (C₆D₆): δ 7.06-6.91 (overlapping A₂B m, 9 H total, H_{arvl}), 3.63 and 3.47 (overlapping br, 6 H total, CHMe₂, NAr and N(SiMe₃)-Ar), 1.30 (br, 6 H, CHMe2, Ar), 1.18-1.06 (br, 30 H, CHMe2, NAr and N(SiMe₃)Ar), 0.35 (s, 9 H, N (SiMe₃)Ar). ¹³C NMR $(C_6D_6): \delta$ 151.9, 148.5, and 142.0 $(C_{ipso} \ and \ C_o, \ NAr \ and \ N(SiMe_3)Ar; one signal not observed), 126.8 <math display="inline">(C_p, \ NAr)$, 126.5 $(C_p, \ N(SiMe_3)Ar)$, 124.8 $(C_m, \ NAr)$, 122.8 $(C_m, \ N(SiMe_3)Ar)$, 29.0 and 28.2 $(CHMe_2, \ NAr \ and \ N(SiMe_3)Ar)$, 26.2, 25.2, 24.7, and 24.2 $(CHMe_2, \ NAr \ and \ N(SiMe_3)Ar)$, 26.6 $(N(SiMe_3)Ar)$. Anal. Calcd for $C_{39}H_{60}N_3ISiW$: C, 51.49; H, 6.65. Found: C, 51.36; H, 6.73.

W(NAr)2(NMeAr)I (14). An ampule (Teflon stopcock) was charged with 0.25 g (0.319 mmol) of W(NAr)₃(PMe₃), 20 mL of benzene, and excess MeI (0.50 g, 3.50 mmol). The reaction vessel was closed, placed in an oil bath maintained at ~ 70 °C, and allowed to stir for 15 h. Over this time, the solution's red color turned to pale yellow, and a white precipitate ([Me₄P]I by ¹H NMR) formed. The reaction mixture was filtered through Celite, concentrated in vacuo, and filtered again, and the solution was further stripped to afford the product as a yellow powder. Analytically pure samples of W(NAr)₂(NMeAr)I, obtained by recrystallization from pentane at -35 °C, were collected by filtration and dried in vacuo: vield 0.20 g (0.247 mmol, 77%). ¹H NMR (C₆D₆): δ 7.07-6.93 (overlapping A₂B mult, 9 H total, H_{aryl}), 3.83 (s, 3 H, NMeAr), 3.58 (br, overlapping spt, 6 H total, CHMe₂, NAr and NMeAr), 1.20-1.05 (overlapping br, 36 H total, CHMe2, NAr and NMeAr). Anal. Calcd for C37H59N3IW: C, 52.18; H, 6.39. Found: C, 52.13; H, 6.48.

W[**NArC(O)**NPh](**NAr**)₂(**PMe**₃) (15). Neat phenyl isocyanate (0.192 g, 1.61 mmol, ~0.17 mL) was added dropwise to a stirred solution of 0.15 g (0.19 mmol) of W(NAr)₃(PMe₃) (8) in 15 mL of pentane at room temperature. Reaction occurred quickly as this mixture was stirred for 15-20 min, over which time an orange powder precipitated. The powder was collected by filtration, washed with minimal cold pentane, and dried in vacuo; yield 0.15 g (0.16 mmol, 82%). Analytically pure compound was obtained by recrystallization from a pentane solution at -35 °C. ¹H NMR (C_6D_6): δ 8.01 (d, 2 H, H_o, C_6H_5), $7.20{-}6.72~(m,\,12$ H total, $H_{\text{aryl}}),\,3.733$ and 3.725~(overlappingspt, 6 H total, CHMe₂, NAr and WNArC(O)NPh), 1.60 and 1.27 (d, 6 H each, CHMe2, WNArC(O)NPh), 1.17 and 1.03 (d, 12 H each, CHMe₂, NAr), 0.86 (d, 9 H, PMe₃). ¹³C NMR (C₆D₆): δ 152.6, 146.7, 145.0, 140.4, 133.3, 133.1, 129.3, 129.2, 126.8, 126.7, 123.7, and 122.9 (Carvi, CO, and C₆H₅), 28.8, 28.0, 25.3, 25.0, and 23.9 (CHMe2 and CHMe2, imide and amide), 13.5 (PMe₃). One resonance from the $CHMe_2$ and $CHMe_2$ set was not located. Anal. Calcd for C46H65N4OPW: C, 61.06; H, 7.24; N, 6.19. Found: C, 61.53; H, 7.52; N, 5.77. IR (Nujol mull), cm⁻¹: 1654 s [ν (C=O)].

W(NAr)₂(NHAr)Me (16). A slurry of 0.18 g (0.47 mmol) of [HNMe₃]BPh₄ in \sim 20 mL of Et₂O was added to a stirred solution of 0.50 g (0.47 mmol) of $[Li(THF)_4][W(NAr)_3Me]$ in 20 mL of Et_2O . This mixture was stirred at room temperature for 12 h, after which the solution was filtered through Celite and the solvent removed under reduced pressure to afford a yellow to brown oil. This oil was dissolved in a minimal volume of pentane and cooled to -35 °C to provide yellow crystals, which were collected by filtration and dried in vacuo. Additional product was obtained from the pentane filtrate (-35)°C), for a total yield of 0.14 g (0.21 mmol, 45%). Analytically pure product was obtained from Et_2O /pentane solutions at -35°C. ¹H NMR (C₆D₆): δ 8.36 (s, 1 H, NHAr), 7.08–6.91 (m, 9 H total, H_{arvl}), 3.63-3.50 (overlapping spt, 6 H total, CHMe₂, NAr and NHAr), 1.73 (s, 3 H, WCH₃), 1.17, 1.13, and 1.10 (overlapping d, 12 H each, CHMe₂, NAr and NHAr). ¹³C NMR (C₆D₆): δ 152.4 (C_{ipso}, NAr), 146.0 (C_{ipso}, NHAr), 142.7 (C_o, NAr), 141.1 (Co, NHAr), 125.1 and 123.6 (Cp, NAr and Cm, NHAr), 125.7 (C_p, NHAr), 122.4 (C_m, NAr), 29.2, 28.6, 23.8, 23.7, and 23.4 (CHMe2 and CHMe2, NAr and NHAr; WCH3). Anal. Calcd for C₃₇H₅₅N₃W: C, 61.23; H, 7.64; N, 5.79. Found: C, 61.15; H, 7.71; N, 5.73.

Structural Determinations. [Li(THF)₄][W(NAr)₃Cl] (2). Crystallographic data for 2 are collected in Table 1. Data were collected on a specimen sealed in a Lindemann capillary.

Photographic evidence and systematic absences in the diffraction data uniquely identified the space group. The structure was solved by direct methods. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were treated as idealized contributions.

 $W(NAr)_{3}(PMe_{3})$ (8). Crystallographic data for 8 are collected in Table 1. A red, irregular block crystal of 8 was mounted in a glass capillary in a random orientation. The space group was determined from the systematic absences and the subsequent least-squares refinement, and the structure was solved by the Patterson method. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in idealized positions and were included in the refinement. Methyl group hydrogens were initially located from a difference map and then idealized.

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Supplementary Material Available: Details of the structure solution and refinement, including tables of crystal data and data collection parameters, atomic positional and thermal parameters, bond distances, bond angles, least-squares planes, and ORTEP figures for [Li(THF)₄][W(NAr)₃Cl] and W(NAr)₃-(PMe₃) (19 pages). Ordering information is given on any current masthead page.

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