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Intramolecular C–H Bond Activation Promoted by the d^0 $[(\eta^5\text{-}C_5Me_5)W(=NR)_2]^+$ Functional Group

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The bis(imido) complex of tungsten, $W(=NAr)_2Cl_2(THF)_2$ (Ar = 2,6-$C_6H_3{}^iPr_2$) reacts with $Li[C_5Me_5]$ to provide burgundy $(\eta^5\text{-}C_5Me_5)W(=NAr)_2Cl$ (1) in high yield. Compound 1 may be functionalized using MeLi, PhLi, or $LiBEt_3H^*$ (H^* = H or D) to provide $(\eta^5\text{-}C_5Me_5)W(=NAr)_2$-Me (2), $(\eta^5\text{-}C_5Me_5)W(=NAr)_2Ph$ (3), $(\eta^5\text{-}C_5Me_5)W(=NAr)_2H$ (4), and $(\eta^5\text{-}C_5Me_5)W(=NAr)_2D$ (4-*d*) in moderate to high yields. $(\eta^5\text{-}C_5Me_5)W(=NAr)_2Cl$ (1) crystallizes in the monoclinic $P2_1/n$ (no. 14) with a = 11.880 (1) Å, b = 15.946 (1) Å, c = 17.703 (1) Å, β = 73.65 (15)°, and V = 3218.1 (17) Å^3 with Z = 4 and ρ_{calcd} = 1.46 g cm^{-3}. The molecular structure of 1 is characterized by nearly identical imido ligands with W–N–C_{ipso} angles averaging 169.3 (4)° and W–N bonds averaging 1.783 (4) Å. Upon reaction of $(\eta^5\text{-}C_5Me_5)W(=NAr)_2Cl$ (1) with LiNHAr, the "tucked-in" complex $(\eta^5,\eta^1\text{-}C_5Me_4CH_2)W(=NAr)_2$ (5) is formed in nearly quantitative yield. Experiments are presented which indicate the most likely mechanism of formation of 5 involves the intermediacy of the substituted complex, $(\eta^5\text{-}C_5Me_5)W(=NAr)_2(NHAr)$.

Introduction

Organoimido complexes of the transition metals[1] have been implicated in catalytic processes such as propylene ammoxidation[2] and nitrile reduction[3] and have been shown to function as imido transfer intermediates in the aziridination[4] and amination[5] of olefins.[6] Recent achievements in imido chemistry include the generation of reactive M=NR ligands which can serve as sites for C–H bond activation (e.g. $({}^tBu_3SiNH)_2Ti(=NSi{}^tBu_3)$[7] and $({}^tBu_3SiNH)_2Zr(=NSi{}^tBu_3)$[8]) or for cycloaddition chemistry (e.g. $(\eta^5\text{-}C_5Me_5)Ir(=NR)$,[9] $(\eta^6\text{-arene})Os(=NR)$,[10] and $(\eta^5\text{-}C_5H_5)_2Zr(=NR)$[6b,11]). One important aspect of these compounds is the metal's coordination by *multiple* π donors, a feature which may contribute to destabilizing strong metal–ligand $d\{\pi\} \leftarrow p\{\pi\}$ interactions and which has prompted our efforts in multiple imido chemistry.[12,13]

On the basis of the recently reported complex $[W(=NAr)_3Cl]^-$ (Ar = 2,6-$C_6H_3{}^iPr_2$)[13] we set out to substitute a $[\eta^5\text{-}C_5Me_5]^-$ ligand in place of one $[NAr]^{2-}$ to afford $(\eta^5\text{-}C_5Me_5)W(=NAr)_2Cl$, a neutral analog of the tris(imido) anion. The existence of such a compound is expected on the basis of the formal "$1\sigma,2\pi$" orbital analogy between $[NR]^{2-}$ and $[\eta^5\text{-}C_5R_5]^-$ ligands.[14] Herein, we report derivatives of the d^0 $W(=NR)_2$ functional group[15] of the form $(\eta^5\text{-}C_5Me_5)W(=NAr)_2X$, some of which undergo intramolecular C–H bond activation to afford a "tucked-in" $\eta^5,\eta^1\text{-}C_5Me_4CH_2$ complex.

Results

Preparation and Properties of $(\eta^5\text{-}C_5Me_5)W(=NAr)_2Cl$ and Its Derivatives. Upon reaction of $W(=NAr)_2Cl_2(THF)_2$[13] with $Li[C_5Me_5]$ in refluxing THF/toluene, burgundy crystals of compound 1 are obtained in high yield after workup (Scheme I). Spectroscopic data and elemental analyses for 1 are consistent with its formulation as $(\eta^5\text{-}C_5Me_5)W(=NAr)_2Cl$ (1). As expected, the ^1H and ^{13}C NMR spectra for 1 (probe temperature)

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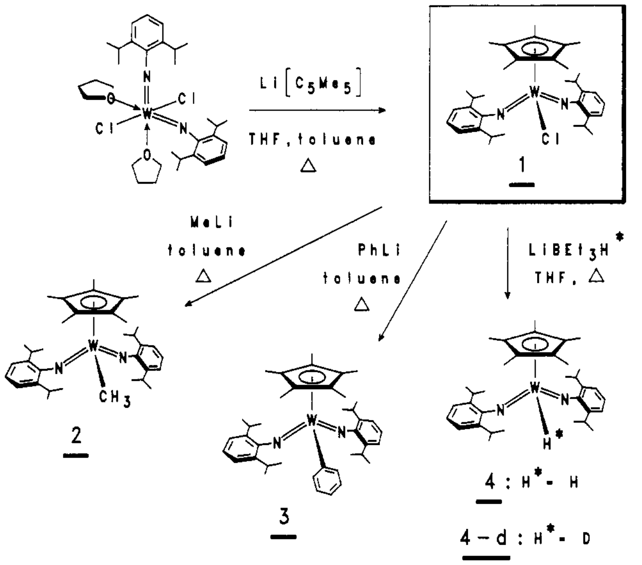
Scheme I



reveal a compound with a molecular plane of symmetry and free rotation about the W–N–C_{ipso} linkage as characterized by the single $C_5\mathit{Me}_5$ and $C\mathit{H}Me_2$ resonances but two $CH\mathit{Me}_2$ environments. (η^5-C_5Me_5)W(=NAr)$_2$Cl (1) is soluble in aromatic hydrocarbons, somewhat less soluble in alkanes, and is quite stable thermally as samples of 1 show no decomposition in refluxing C_6D_6 even after several days. Formally, 1 is related to the tris(imido) anion $[W(=NAr)_3Cl]^-$ in that this neutral analog maintains a coordination sphere of three $1\sigma,2\pi$ donor ligands.[13,14a] Tungsten tris(imido) complexes are susceptible to electrophilic attack at the imido nitrogens;[13,16] thus, the reactions of (η^5-C_5Me_5)W(=NAr)$_2$Cl (1) with MeI and OCNR (R = ^{t}Bu, Ph, 2,6-$C_6H_3Me_2$) were carried out. However, in no case was a reaction observed, even under severe conditions (refluxing C_6D_6, sealed tube, 5 days).

(η^5-C_5Me_5)W(=NAr)$_2$Cl (1) is functionalized using MeLi or PhLi in toluene to provide moderate yields of orange red (η^5-C_5Me_5)W(=NAr)$_2$Me (2) and red brown (η^5-C_5Me_5)W(=NAr)$_2$Ph (3), respectively (Scheme I). These reactions require forcing conditions to proceed to completion (≥90 °C for days), which indicates the thermal stability of complexes 2 and 3 themselves. Attempts to prepare alkyl derivatives from Grignard reagents (under similar conditions) and attempts to prepare alkoxide and phenoxide compounds with LiOR provided no reaction. (η^5-C_5Me_5)W(=NAr)$_2$Cl (1) also reacts with $LiBEt_3H$ in refluxing THF to afford cherry red crystals of the hydride derivative (η^5-C_5Me_5)W(=NAr)$_2$H (4) in 88% yield (Scheme I). Complex 4 is characterized by a hydride resonance at δ 6.65 (C_6D_6) in its ^{1}H NMR spectrum ($^1J(^{183}W-^1H)$ = 269 Hz for 14.40% abundant ^{183}W) and a ν(W–H) at 1938 cm^{-1} in its infrared spectrum (CsI). This assignment is confirmed by the disappearance of the δ 6.65 signal from the ^{1}H NMR spectrum of the deuterated analog (η^5-C_5Me_5)W(=NAr)$_2$D (4-*d*; prepared from 1 and $LiBEt_3D$ in THF) and the isotopic shift observed in the infrared spectrum of 4-*d* where ν(W–D) appears at 1395 cm^{-1}.

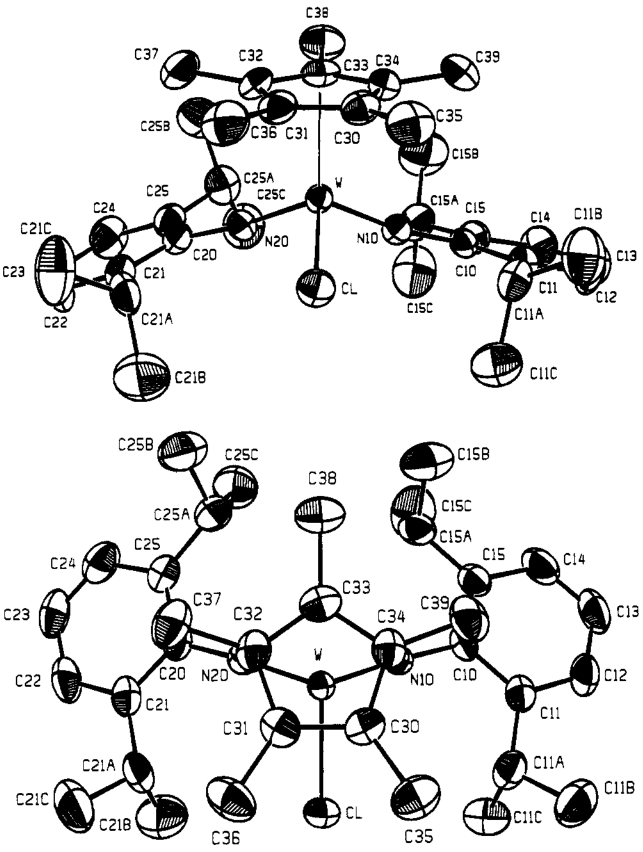


Figure 1. Molecular structure of (η^5-C_5Me_5)W(=NAr)$_2$Cl (1, Ar = 2,6-diisopropylphenyl) with atoms shown as 50% probability ellipsoids.

Table I. Details of the X-ray Diffraction Study for (η^5-C_5Me_5)W(=NAr)$_2$Cl (1)

molecular formula	$C_{34}H_{49}ClN_2W$
molecular weight	705.09
crystal color	burgundy
space group	$P2_1/n$ (no. 14)
unit cell volume, Å^3	3218.1 (17)
a, Å	11.880 (1)
b, Å	15.946 (1)
c, Å	17.703 (1)
β, deg	73.65 (15)
Z	4
calculated density, g cm^{-3}	1.46
crystal dimensions, mm	0.18 × 0.25 × 0.45
data collection temp, °C	20 ± 1
Mo Kα radiation, λ, Å	0.710 73
monochromator	graphite
absorption coefficient, cm^{-1}	37.7
2θ range, deg	2–50
total no. of reflns measd	6204 (5671 unique)
no. of reflns measd with $I > 3\sigma(I)$	4216
scan type	$\omega - 2\theta$
scan speed, deg min^{-1}	3
parameters refined	343
R	0.024
R_w	0.028

Structural Study of (η^5-C_5Me_5)W(=NAr)$_2$Cl. Burgundy red crystals of (η^5-C_5Me_5)W(=NAr)$_2$Cl (1) were obtained from a pentane solution at −35 °C. Figure 1 shows the approximately tetrahedral structure of (η^5-C_5Me_5)W(=NAr)$_2$Cl (1), and Tables I and II summarize crystal and structural data. As Figure 1 shows, the planes of the NAr phenyl rings are turned roughly parallel to the Cp* plane rather than perpendicular, presumably to minimize steric repulsion between the Cp* methyl and NAr isopropyl groups. This effect is also manifested in the distortions from the idealized 109° tetrahedral angles since the Cp*$_{cent}$–W–N angles (average 118.3 (1)°) are distended to further avoid this interaction which, in turn,

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Table II. Selected Bond Distances (Å) and Bond Angles (deg) in (η^5-C$_5$Me$_5$)W(=NAr)$_2$Cl (1)^{a,b}

Bond Distances

W-N(10)	1.785 (4)	W-Cp*$_{cent}$	2.1015 (2)
W-N(20)	1.781 (4)	N(10)-C(10)	1.394 (7)
W-Cl	2.359 (1)	N(20)-C(20)	1.394 (7)
W-C(30)	2.471 (6)	C(30)-C(31)	1.444 (8)
W-C(31)	2.462 (6)	C(31)-C(32)	1.401 (8)
W-C(32)	2.424 (5)	C(32)-C(33)	1.422 (8)
W-C(33)	2.334 (5)	C(33)-C(34)	1.431 (8)
W-C(34)	2.429 (6)	C(30)-C(34)	1.401 (8)

Bond Angles

Cl-W-N(10)	99.4 (1)	W-N(20)-C(20)	171.0 (4)
Cl-W-N(20)	100.4 (1)	C(30)-C(31)-C(32)	108.6 (5)
Cl-W-Cp*$_{cent}$	107.40 (3)	C(31)-C(32)-C(33)	106.7 (5)
N(10)-W-N(20)	109.6 (2)	C(32)-C(33)-C(34)	109.6 (5)
N(10)-W-Cp*$_{cent}$	118.8 (1)	C(33)-C(34)-C(30)	106.7 (5)
N(20)-W-Cp*$_{cent}$	117.8 (1)	C(34)-C(30)-C(31)	108.3 (5)
W-N(10)-C(10)	167.6 (4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Cp*$_{cent}$ represents the average of the *x*, *y*, and *z* coordinates of the η^5-C$_5$Me$_5$ ring carbons.

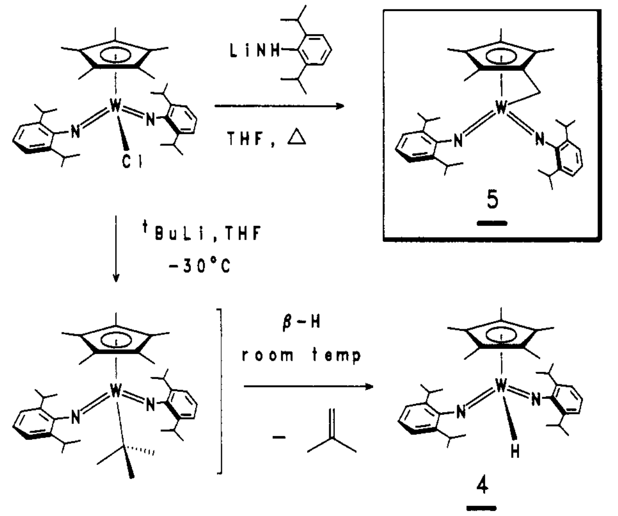
induces the Cl-W-N (imido) angles to decrease to an average 99.9 (1)°. (Note that N(10)-W-N(20) = 109.6 (2)°, which is not apparent from Figure 1.)

The nearly linear phenylimido linkages (W-N-C$_{ipso}$ = 167.6 (4)° and 171.0 (4)°) and the short W-N distances (1.785 (4) and 1.781 (4) Å) fall in the range of previously observed d^0 W-imide bonds[13,15] and are consistent with a W-N bond order somewhat greater than two. The view of 1 looking down the Cp* $_{cent}$-W axis highlights the Cp* rotational preference which places its methyl groups in pockets lined by the NAr isopropyl substituents. The differences between the imido ligands in 1 and its analog[13] [W(=NAr)$_3$Cl]$^-$ can largely be ascribed to the cone angle of the Cp* ligand inducing distortions from an idealized tetrahedron as described above. Thus, the imido ligands in both complexes are oriented similarly, viz. with the NAr planes roughly parallel to the W-Cl bond.

The W-Cp* ring carbon distances show an interesting variation (Table II) since W-C(33) is an abnormally short 2.334 (5) Å, while the other four W-Cp* ring carbon distances fall in a narrow range between 2.424 (5) and 2.471 (6) Å.[17] Additionally, the Cp* ring itself displays a small measure of π-electron localization of a 1,4-diene type in that C(31)-C(32) and C(30)-C(34) are both slightly shorter than the other ring carbons. This η^1,η^4-bonding mode has been noted by Bercaw and co-workers in the "η^5"-C$_5$Me$_5$ ligands of (η^5-C$_5$Me$_5$)W(O)$_2$(OC$_5$Me$_5$)[18] and (η^5-C$_5$Me$_5$)W(O)$_2$(η^1-C$_5$Me$_5$)[19] and has been attributed to the strong trans influence of the oxo ligands. Similarly, the orientation of the Cp* ligand in 5 (Figure 1) places the short W-C(33) bond trans to the W-Cl bond and therefore this feature may also be construed as evidence for the strong trans influence of the imido ligand.

Formation of the "Tucked-In" Complex (η^5,η^1-C$_5$Me$_4$CH$_2$)W(=NAr)$_2$. Reactions of (η^5-C$_5$Me$_5$)W(=NAr)$_2$Cl (1) with LiNHR reagents were investigated with a view to preparing an amido analog of the alkyl complexes described above. Upon reaction of (η^5-C$_5$Me$_5$)W(=NAr)$_2$Cl (1) with 1 equiv of LiNHAr (refluxing THF), orange crystalline 5 is obtained in high yield. The ^{1}H and ^{13}C NMR spectra of 5 reveal a structure with a molecular plane of symmetry, but *without* a coordinated NHAr ligand. The NMR data and elemental analysis all support the formulation of 5 as the "tucked-in" complex (η^5,η^1-C$_5$Me$_4$CH$_2$)W(=NAr)$_2$ (Scheme II). Thus, three Cp* ^{1}H NMR resonances are observed with the lowest field signal at δ 3.97 (C$_6$D$_6$) integrating for 2 protons and showing doublet satellites with $^2J(^{183}$W-^{1}H) = 11.0 Hz.

Scheme II

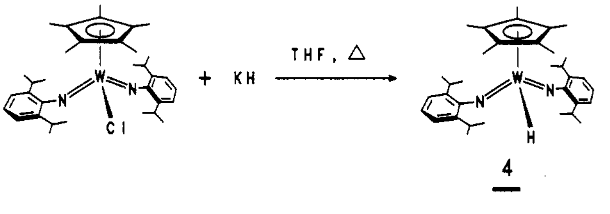


The formation of 5 proceeds quite slowly and, like the preparations of 2-4, requires forcing conditions. The reaction is extremely clean as examining solutions of 1 + LiNHAr at intermediate reaction times reveals only the presence of 1 and 5. Scheme III presents possible mechanisms for the formation of 5 which include: (i) chloride displacement by [NHAr]$^-$ to form A, followed by the deprotonation of a Cp* methyl by [NHAr]$^-$; (ii) *inter*molecular deprotonation of a η^5-C$_5$Me$_5$ methyl group by [NHAr]$^-$ to generate B, followed by chloride displacement by a formal η^5-C$_5$Me$_4$CH$_2$ carbanion; and (iii) intramolecular addition of a Cp* C—H bond across W=NR, generating (η^5,η^1-C$_5$Me$_4$CH$_2$)W(=NAr)(NHAr)Cl (C), followed by its (inter- or intramolecular) reaction with LiNHAr to remove "HCl".

The following experiments were carried out:

(1) Although deprotonation pathway ii seemed unlikely in view of the reactions of (η^5-C$_5$Me$_5$)W(=NAr)$_2$Cl (1) with lithium alkyls (vide supra), the reaction of (η^5-C$_5$Me$_5$)W(=NAr)$_2$Cl with a stronger base was carried out (Scheme II). Upon reaction of (η^5-C$_5$Me$_5$)W(=NAr)$_2$Cl with 1 equiv of ^{t}BuLi, the *hydride* derivative (η^5-C$_5$Me$_5$)W(=NAr)$_2$H (4) *only* is formed in high yield. The inferred intermediate, (η^5-C$_5$Me$_5$)W(=NAr)$_2$(CMe$_3$), is not observed (^{1}H NMR) and is presumed to undergo β-hydrogen elimination very rapidly.

(2) The reaction of (η^5-C$_5$Me$_5$)W(=NAr)$_2$Cl (1) with KH, after appropriate workup, afforded a virtually quantitative yield of (η^5-C$_5$Me$_5$)W(=NAr)$_2$H (4) (reaction 1).



(1)

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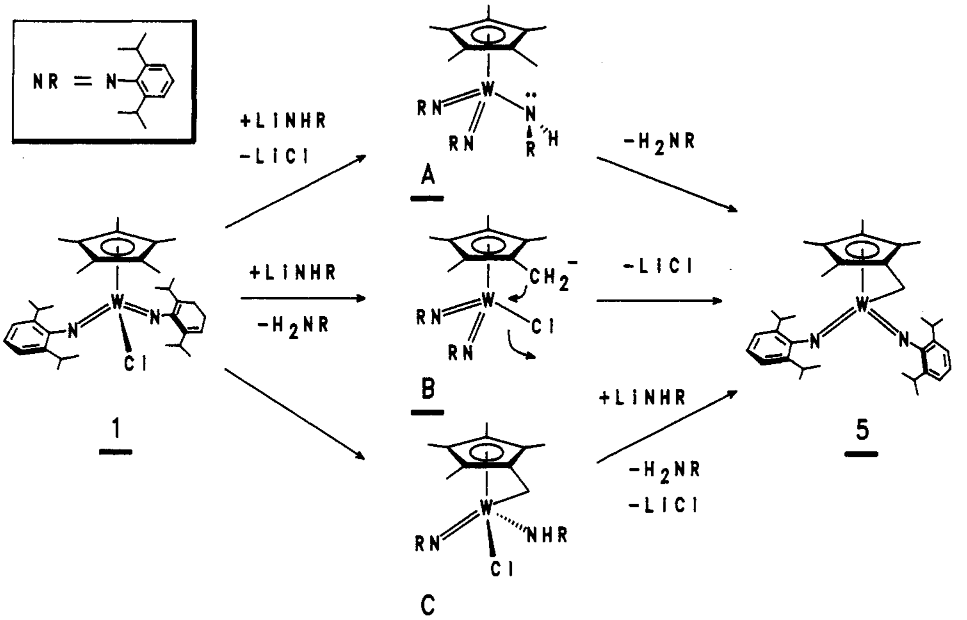
Scheme III



To test whether the tucked-in compound **5** was a kinetic product of this reaction, i.e. whether **1** + KH affords **5** + H_2 which then reacted to give (η^5-C_5Me_5)W(=NAr)$_2$H (**4**), we examined the reaction of (η^5,η^1-$C_5Me_4CH_2$)W(=NAr)$_2$ (**5**) with H_2. When a THF solution of (η^5,η^1-$C_5Me_4CH_2$)W(=NAr)$_2$ (**5**) was purged with dry H_2 and heated to reflux for two days, considerable decomposition was observed; however, *no* (η^5-C_5Me_5)W(=NAr)$_2$H was present in the reaction products (^{1}H NMR).

(3) Pathway **1** → **C** → **5** is difficult to rule out entirely; however, if intermediate **C** (η^5,η^1-$C_5Me_4CH_2$)W(=NAr)(NHAr)Cl reacts with LiNHAr to afford (η^5,η^1-C_5Me_4-CH_2)W(=NAr)(NHAr)$_2$, then *either* NHAr ligand should be susceptible to α-hydrogen abstraction by the other. When the reaction of (η^5-C_5Me_5)W(=NAr)$_2$Cl (**1**) with LiNHAr′(Ar′ = 2,6-$C_6H_3Me_2$) was carried out, the only tungsten complex formed was (η^5,η^1-$C_5Me_4CH_2$)W(=NAr)$_2$ (**5**), suggesting that (η^5,η^1-$C_5Me_4CH_2$)W(=NAr)(NHAr)(NHAr′) was *not* involved and most consistent with the intermediacy of (η^5-C_5Me_5)W(=NAr)$_2$(NHAr′), an analog of **A**. The same result was obtained in the reaction of **1** with LiNH^{t}Bu. We note, however, that this experiment does not exclude the *inter*molecular deprotonation of **C** with the external base, LiNHAr′ or LiNH^{t}Bu.

These results are most consistent with **5** arising via pathway i described above, i.e. pathway **1** → **A** → **5** of Scheme III is proposed as the major mechanistic route in forming tucked-in complex (η^5,η^1-$C_5Me_4CH_2$)W(=NAr)$_2$ (**5**) with LiNHAr. The reactions of **1** with ^{t}BuLi and KH to generate **4** appear to be examples of these reagents serving as nucleophiles to displace chloride at the metal. Although rare, we note that KH has been observed to exhibit nucleophilic behavior.[20]

Discussion

The cyclopentadienyl anion $[C_5R_5]^-$, imido dianion $[NAr]^{2-}$, and acetylene dianion $[RC = CR]^{2-}$, as well as oxo O^{2-}, nitrido N^{3-}, and alkylidyne $[CR]^{3-}$ ligands, may all be described as "1σ,2π" donors.[14] One might expect this formal electronic analogy to be reflected in the stoichiometries and structures of their compounds. Indeed, there are several examples where these ligands can be "interchanged" to afford congeners within or between groups. For example, the series Re(=NR)$_n$(RC≡CR)$_{3-n}$X has been reported for n = 3,[14b,15c,21] 2,[14c,22] 1,[14c] and 0.[23] This work compares (η^5-C_5Me_5)W(=NAr)$_2$Cl to $[W(=NAr)_3Cl]^-$, and we note that the related oxo complexes (η^5-C_5Me_5)W(=O)$_2$Cl and (η^5-C_5Me)W(=O)$_2$R have been reported.[24] We have also shown that (η^5-C_5Me_5)Zr(=NAr)Cl(pyridine)$_2$[12c] is formally isoelectronic (and isostructural) with Ta(=NAr)$_2$Cl(pyridine)$_2$.[12a]

However, this 1σ,2π orbital analogy is perhaps most dramatically illustrated in complexes with 3-fold symmetry. For example, the electronic similarities between the classic "20-electron" W(RC≡CR)$_3$L species[25,26] and imido complexes W(=NAr)$_3$L[13] and Os(=NR)$_3$[27] have been detailed. Each of these complexes is characterized by a ligand-based, nonbonding MO comprised of a set of ligand π orbitals oriented roughly perpendicular to the molecule's C_3 axis.[26,27b] Therefore while each of these compounds may be considered a 20-electron species if the

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ligands donate their full complement of electrons to the metal, it has been established[13,26,27b] (in 3-fold symmetry) that occupation of this nonbonding MO results in these compounds being more accurately described as 18-electron complexes. Other C_{3v} or D_{3h} complexes which are intimately related by analogous orbital descriptions include $Re(RC{\equiv}CR)_3X$ (X = I, Me, or $OSiMe_3$),[23] $[W(RC{\equiv}CR)_3]^{2-}$,[28] $Re({=}NR)_3X$,[14b,15c,21] $[Re({=}NR)_3]^-$,[14b] and $Tc({=}NAr)_3X$.[29]

There is now a body of collective evidence which suggests that the *3-fold orbital symmetry* of many $M(1\sigma,2\pi)_3$ complexes *results in the combination of three $1\sigma,2\pi$ ligands contributing 2 electrons less than the maximum possible.* We have termed such $M(1\sigma,2\pi)_3$ metal centers as "π-loaded". For example, "$(\eta^5-C_5R_5)_2Zr({=}NR)$" and "$[(\eta^5-C_5R_5)_2Ta({=}NR)]^+$" behave as 16-electron fragments, as seen in the chemistry of Bewcaw's $(\eta^5-C_5Me_5)_2Ta({=}NPh)H$[30] and Bergman's $(\eta^5-C_5H_5)_2Zr({=}NR)(THF)$ (R = ^tBu, 2,6-$C_6H_3Me_2$).[6b,9] Similarly, "$(\eta^5-C_5Me_5)W({=}O)_2$" binds a second C_5Me_5 ligand in an η^1 mode only,[19] and evidence for the "$[Re(O)(RC{\equiv}CR)_2]^+$" moiety constituting a 16-electron species has been presented.[31] In this paper, we propose that the "$[(\eta^5-C_5Me_5)W({=}NAr)_2]^+$" functional group is a formal 16-electron fragment, just like "$W({=}NAr)_3$"[3] and "$(\eta^5-C_5Me_5)Ta({=}NAr)_2$",[32] none of which has been isolated without an additional 2-electron donor. Obvious exceptions to this generalization include the "class b"[18,19] oxo compounds like $(\eta^5-C_5Me_5)_2W({=}O)$,[19] $(\eta^5-C_5Me_5)Re({=}O)_3$,[33] and $[(\eta^5-C_5Me_5)W({=}O)_3]^-$[34] in which oxygen lone-pair donation is not significant as supported by $\nu(M = O)$ frequencies.

Since the alkyl derivatives $(\eta^5-C_5Me_5)W({=}NAr)_2R$ (**3** and **4**) are so thermally stable, the instability of "$(\eta^5-C_5Me_5)W({=}NAr)_2(NHAr)$" must relate to availability of the amido lone pair, i.e. this lone pair is not engaging in bonding to the metal center. Such a notion is consistent with the orbital picture developed above for $M(1\sigma,2\pi)_3$ "π-loaded" metal centers. The orbital interactions which allow the "$[(\eta^5-C_5Me_5)W({=}NAr)_2]^+$" functional group to be described as a formal 16-electron fragment effectively restrict the metal from accepting *more than* 2 additional electrons from another ligand. Therefore the amido ligand in "$(\eta^5-C_5Me_5)W({=}NAr)_2(NHAr)$" does not appear to π donate to the already "π-loaded" metal center. The amide lone pair in such a species will be highly accessible for deprotonating a $\eta^5-C_5Me_5$ methyl group which is consistent with the instability of inferred "$(\eta^5-C_5Me_5)W({=}NAr)_2(NHAr)$" with respect to $(\eta^5,\eta^1-C_5Me_4CH_2)W({=}NAr)_2$ (**5**).

Intramolecular C–H bond activation in $\eta^5-C_5Me_5$ ligands has provided several isolable complexes containing the "tucked-in" $\eta^5,\eta^1-C_5Me_4CH_2$ moiety. The mechanistic pathways identified which may lead to these compounds include the following: C–H addition to an alkyl,[35] hydride,[36] and benzyne[37] ligand; C–H addition across a metal–carbon double bond;[35c,38] and C–H oxidative addition to a d^2 metal[39] or d^4 metal.[19] Additionally, the possible intramolecular C–H addition to an alkoxide ligand has been reported,[40] and the reaction to form tucked-in $(\eta^5,\eta^1-C_5Me_4CH_2)W({=}NAr)_2$ (**5**) from $(\eta^5-C_5Me_5)W({=}NAr)_2(NHAr)$ (**A**) would therefore constitute an intramolecular C–H addition across a metal–amide bond. The reactivity of these and related "π-loaded" metal centers are areas of our continued efforts.[48]

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere either by standard Schlenk techniques[41] or in a Vacuum Atmospheres HE-493 drybox at room temperature (unless otherwise indicated). Solvents were distilled under N_2 from an appropriate drying agent[42] and were transferred to the drybox without exposure to air. The "cold" solvents used to wash isolated solid products were typically cooled to ca. -30 °C before use. NMR solvents were passed down a short (5–6 cm) column of activated alumina prior to use. Abbreviations are as follows: Ar = 2,6-$C_6H_3{}^iPr_2$ and Cp* = $[C_5Me_5]^-$.

Starting Materials. $WOCl_4$ was obtained from Hermann C. Stark Berlin, sublimed (ca. 110 °C, 10^{-2} Torr) prior to use, and converted to $W({=}NAr)_2Cl_2(THF)_2$ by the literature procedure.[13] 2,6-Diisopropylaniline was obtained from Aldrich, vacuum distilled before use, and converted to LiNHAr, by the literature procedure.[43] Alkyl lithium and $LiBEt_3H^*$ (H^* = H and D) solutions were obtained from Aldrich and used as received. C_5Me_5H was prepared[44] and converted to $Li[C_5Me_5]$[39a,45] according to the literature procedures.

Physical Measurements. ^1H (250 MHz) and ^{13}C (62.9 MHz) NMR spectra were recorded at probe temperature (unless otherwise specified) on a Brucker WM-250 spectrometer in C_6D_6 solvent. Chemical shifts are referenced to protio impurities (δ 7.15) or the solvent ^{13}C resonance (δ 128.0) and are reported downfield of Me_4Si. Infrared spectra were recorded as CsI pellets between 4000 and 600 cm^{-1} using a Perkin-Elmer 1310 spectrophotometer. Microanalytical samples were stored cold, handled under N_2, and combusted with WO_3 (Texas Analytical Laboratories, Inc., Stafford, TX).

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Preparations. (η^5-C$_5$Me$_5$)W(=NAr)$_2$Cl (1). An ampule (Teflon stopcock) was charged with 4.00 g (5.34 mmol) of W(=NAr)$_2$Cl$_2$(THF)$_2$, 0.76 g (5.34 mmol) of LiCp*, and ca. 80 mL of THF/toluene (1:1, v/v). The reaction vessel was closed, placed in an oil bath maintained at ca. 100 °C, and allowed to stir at reflux for 2 days. Over this time the reaction slowly proceeded as noted by the slow dissolution of the suspended LiCp* and the gradual darkening of the solution from red to burgundy. The reaction volatiles were then removed in vacuo and the product extracted with toluene. The toluene extract was filtered through Celite and the solvent removed from the filtrate in vacuo to afford the product as a dark purple or burgundy microcrystalline solid. The product was washed with minimal pentane and dried in vacuo to afford 3.65 g (5.18 mmol, 97%) crude yield. (η^5-C$_5$Me$_5$)W(=NAr)$_2$Cl obtained in this fashion was analytically pure, but recrystallization could be effected from pentane at −35 °C. The product was also obtained in somewhat lower yields by extracting with Et$_2$O rather than toluene. ^{1}H NMR (C$_6$D$_6$): δ 7.07–6.85 (A$_2$B mult, 6 H, H$_{aryl}$), 3.70 (spt, 4 H, C*H*Me$_2$), 1.91 (s, 15 H, C$_5$*Me*$_5$), 1.23 and 1.18 (d, 12 H each, CH*Me*$_2$). ^{13}C NMR (C$_6$D$_6$): δ 151.4 (C$_{ipso}$), 141.5 (C$_o$), 124.5 (C$_m$), 122.8 (*C*$_5$Me$_5$), 118.7 (C$_p$), 27.4 (*C*HMe$_2$), 25.4 and 24.2 (CH*Me*$_2$), 11.1 (C$_5$*Me*$_5$). Anal. Calcd for C$_{34}$H$_{49}$ClN$_2$W: C, 57.92; H, 7.00; N, 3.97. Found: C, 56.85; H, 6.75; N, 3.47.

(η^5-C$_5$Me$_5$)W(=NAr)$_2$Me (2). A solution of 0.50 g (0.71 mmol) of (η^5-C$_5$Me$_5$)W(=NAr)$_2$Cl (1) in ca. 25 mL of toluene was prepared in an ampule (Teflon stopcock). A MeLi solution (0.50 mL of 1.4 M MeLi in Et$_2$O, 0.71 mmol) was added, the ampule was sealed, and this mixture was stirred at ca. 95 °C for 5 days. During this time the solution color changed from burgundy red to red orange. The resulting solution was cooled and filtered through Celite, and the solvent was removed from the filtrate in vacuo. The red solid which remained was collected on a frit, washed with cold pentane, and dried in vacuo, yield 0.37 g (0.54 mmol, 76%). Analytically pure samples were obtained by recrystallization from Et$_2$O/pentane solutions at −35 °C. ^{1}H NMR (C$_6$D$_6$): δ 7.07–6.86 (A$_2$B mult, 6 H, H$_{aryl}$), 3.64 (spt, 4 H, C*H*Me$_2$), 1.79 (s, 15 H, C$_5$Me$_5$), 1.31 (s, 3 H, WCH$_3$), 1.24 and 1.21 (d, 12 H each, CH*Me*$_2$). ^{13}C NMR (C$_6$D$_6$): δ 151.3 (C$_{ipso}$), 140.3 (C$_o$), 122.9 (C$_p$), 122.6 (C$_m$), 114.7 (*C*$_5$Me$_5$), 27.3 (*C*HMe$_2$), 25.0 and 24.2 (CH*Me*$_2$), 13.2 (WCH$_3$), 10.6 (C$_5$*Me*$_5$). Anal. Calcd for C$_{35}$H$_{52}$N$_2$W: C, 61.40; H, 7.66; N, 4.09. Found: C, 61.08; H, 7.61; N, 4.02.

(η^5-C$_5$Me$_5$)W(=NAr)$_2$Ph (3). A solution of 0.25 g (0.35 mmol) of (η^5-C$_5$Me$_5$)W(=NAr)$_2$Cl (1) in ca. 30 mL of toluene was prepared in an ampule (Teflon stopcock). A PhLi solution (0.30 mL of 1.8 M PhLi in Et$_2$O, 0.5 mmol) was added, the ampule was sealed, and this mixture was stirred at ca. 90 °C for 48 h. The resulting red-brown solution was cooled and filtered through Celite, and the volatiles were removed from the filtrate in vacuo. The red brown solid which remained was collected on a frit, washed with cold pentane, and dried in vacuo, yield 0.16 g (0.21 mmol, 61%). Analytically pure samples were obtained by recrystallization from Et$_2$O/pentane solutions at −35 °C. ^{1}H NMR (C$_6$D$_6$): δ 7.75 (d, 2 H, H$_o$, C$_6$H$_5$), 7.21–6.84 (overlapping mult, 9 H total, H$_m$ and H$_p$ (C$_6$H$_5$) and H$_{aryl}$ (NAr)), 3.83 (spt, 4 H, C*H*Me$_2$), 1.82 (s, 15 H, C$_5$Me$_5$), 1.15 and 1.07 (d, 12 H each, CH*Me*$_2$). ^{13}C NMR (C$_6$D$_6$): δ 168.2 (C$_{ipso}$, C$_6$H$_5$), 152.2 (C$_{ipso}$, NAr), 141.6 (C$_o$, C$_6$H$_5$), 141.3 (C$_o$, NAr), 128.6 (C$_m$, C$_6$H$_5$), 125.7 (C$_p$, C$_6$H$_5$), 123.7 (C$_m$, NAr), 123.1 (*C*$_5$Me$_5$), 116.4 (C$_p$, NAr), 27.5 (*C*HMe$_2$), 24.9 and 24.4 (CH*Me*$_2$), 10.9 (C$_5$*Me*$_5$). Anal. Calcd for C$_{40}$H$_{54}$N$_2$W: C, 64.34; H, 7.29; N, 3.75. Found: C, 64.21, H, 7.23; N, 3.68.

(η^5-C$_5$Me$_5$)W(=NAr)$_2$H (4). A 1.00-g (1.42 mmol) sample of (η^5-C$_5$Me$_5$)W(=NAr)$_2$Cl (1) was dissolved in 40 mL of THF in an ampule (Teflon stopcock). A solution of LiBEt$_3$H (1.70 mL of 1 M LiBEt$_3$H in THF, 1.70 mmol) was added, the reaction vessel was closed, and the mixture was maintained at reflux in an 80 °C oil bath for 2 days with stirring. Over this time the solution's burgundy color slowly changed to cherry red. Solvent was then removed in vacuo to provide an orange solid which was extracted with toluene. The extract was filtered through Celite and the solvent removed from the filtrate in vacuo to afford red orange microcrystals of product which were collected on a frit, washed with cold heptane, and dried in vacuo, yield 0.83 g (1.24 mmol, 87%). Samples of (η^5-C$_5$Me$_5$)W(=NAr)$_2$H obtained in this fashion were analytically pure. ^{1}H NMR (C$_6$D$_6$): δ 7.13–6.96 (A$_2$B mult, 6 H, H$_{aryl}$), 6.65 (s, 1 H, W*H*), 3.78 (spt, 4 H, C*H*Me$_2$), 1.96 (s, 15 H, C$_5$Me$_5$), 1.31 and 1.27 (d, 12 H each, CH*Me*$_2$). ^{13}C NMR (C$_6$D$_6$): δ 152.6 (C$_{ipso}$), 137.6 (C$_o$), 122.3 (C$_m$), 122.1 (C$_p$), 114.2 (*C*$_5$Me$_5$), 27.5 (*C*HMe$_2$), 24.3 and 23.9 (CH*Me*$_2$), 11.1 (C$_5$*Me*$_5$). IR (CsI): ν(W–H) = 1938 cm^{-1}. Anal. Calcd for C$_{34}$H$_{50}$N$_2$W: C, 60.89; H, 7.52; N, 4.18. Found: C, 60.73; H, 7.63, N, 4.19.

(η^5-C$_5$Me$_5$)W(=NAr)$_2$D (4-*d*). This compound was prepared by a procedure analogous to that described for (η^5-C$_5$Me$_5$)W(=NAr)$_2$H (4), except that LiBEt$_3$D was substituted for LiBEt$_3$H. ^{1}H NMR (C$_6$D$_6$): The ^{1}H NMR spectrum for 4-*d* was identical to that for 4, except that the δ 6.65 singlet in the spectrum for 4 (1 H, W*H*) was absent in the spectrum of 4-*d*. IR (CsI): ν(W–D) = 1395 cm^{-1}.

(η^5,η^1-C$_5$Me$_4$CH$_2$)W(=NAr)$_2$ (5). An ampule (Teflon stopcock) was charged with 1.40 g (1.98 mmol) of (η^5-C$_5$Me$_5$)W(=NAr)$_2$Cl (1), 30 mL of THF, and 0.36 g (1.98 mmol) of LiNHAr. A stir bar was added, the reaction vessel was closed, and the mixture was maintained at reflux in an oil bath (at ca. 95 °C) for 24 h with stirring. Over this time the solution's burgundy color lightened to red-orange. The solvent was then removed in vacuo to provide an orange solid which was extracted with pentane, the extract was filtered through Celite, and the solvent was removed from the filtrate in vacuo to afford the product as an orange solid. This solid was washed with small portions of cold heptane, collected on a frit, and dried in vacuo to yield 0.90 g (1.35 mmol, 68%) of shiny orange, microcrystals. Samples obtained in this fashion were analytically pure; however, recrystallization could be effected from Et$_2$O/pentane solutions at −35 °C. The isolated yield is attributed to the extreme solubility of this complex, as examining the entire reaction solution reveals essentially quantitative conversion to 5. ^{1}H NMR (C$_6$D$_6$): δ 7.11–6.89 (A$_2$B mult, 6 H, H$_{aryl}$), 3.97 (s, 2 H, C$_5$Me$_4$C*H*$_2$; doublet satellites $^2J(^{183}\mathrm{W}\text{–}^1\mathrm{H})$ = 11.0 Hz), 3.64 (spt, 4 H, C*H*Me$_2$), 1.86 (s, 6 H, C$_5$*Me*$_4$CH$_2$), 1.32 (s, 6 H, C$_5$*Me*$_4$CH$_2$), 1.29 and 1.27 (overlapping d, 12 H each, CH*Me*$_2$). The 1.32 (s), 1.29 (d) and 1.27 (d) signals overlap and appear as 5, equally intense, closely spaced lines at 250 MHz. ^{13}C NMR (C$_6$D$_6$): δ 153.4 (C$_{ipso}$, NAr), 137.4 (C$_o$), 123.9 and 121.7 (*C*$_5$Me$_4$CH$_2$), 122.3 (C$_m$), 121.5 (C$_p$), 103.5 (C$_{ipso}$, *C*$_5$Me$_4$CH$_2$), 58.04 (t, C$_5$Me$_4$*C*H$_2$), 27.9 (*C*HMe$_2$), 24.3 and 23.8 (CH*Me*$_2$), 11.6 and 10.2 (C$_5$*Me*$_4$CH$_2$). Anal. Calcd for C$_{34}$H$_{48}$N$_2$W: C, 61.02; H, 7.24. Found: C, 60.71; H, 7.33.

Reactivity Studies. Reaction of (η^5-C$_5$Me$_5$)W(=NAr)$_2$Cl (1) with ^{t}BuLi. To a −35 °C solution of 0.25 g (0.35 mmol) of (η^5-C$_5$Me$_5$)W(=NAr)$_2$Cl (1) in 20 mL of toluene was added 0.21 mL of a ^{t}BuLi solution (1.7 M in pentane, 0.35 mmol). After being stirred at room temperature for 24 h, the reaction mixture was filtered through Celite and the solvent removed from the filtrate in vacuo. The resulting orange solid was washed with cold heptane, collected on a frit, and dried in vacuo. The filtrate was concentrated and cooled to −35 °C for an additional crop of product, shown by ^{1}H NMR to be (η^5-C$_5$Me$_5$)W(=NAr)$_2$H (4), yield 66%.

Reaction of (η^5-C$_5$Me$_5$)W(=NAr)$_2$Cl (1) with KH. An ampule (Teflon stopcock) was charged with 0.50 g (0.71 mmol) of (η^5-C$_5$Me$_5$)W(=NAr)$_2$Cl (1), 30 mL of THF, and 0.031 g (0.78 mmol) of KH. The mixture was heated to reflux in an oil bath at ca. 100 °C for 2 days with stirring. The solvent was then removed in vacuo, the residue was extracted with a toluene/pentane mixture (ca. 50:50, v/v) and filtered through Celite, and the solvent was removed from the filtrate in vacuo to afford a solid which was dried in vacuo. A C$_6$D$_6$ solution was made directly from the entire residue which was shown by ^{1}H NMR to be (η^5-C$_5$Me$_5$)W(=NAr)$_2$H (4).

Reaction of (η^5,η^1-C$_5$Me$_4$CH$_2$)W(=NAr)$_2$ (5) with H$_2$. An ampule (Teflon stopcock) was charged with 0.030 g (0.045 mmol) of (η^5,η^1-C$_5$Me$_4$CH$_2$)W(=NAr)$_2$ (5) and 20 mL of THF, and the

Table III. Table of Positional Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*, Å^2
W	0.96397 (2)	0.75830 (1)	0.09840 (1)	2.072 (3)
Cl	1.0692 (1)	0.83750 (9)	−0.01132 (8)	3.33 (3)
N10	0.8842 (4)	0.6915 (3)	0.0513 (2)	2.46 (9)
C10	0.8041 (4)	0.6533 (3)	0.0178 (3)	2.6 (1)
C11	0.7613 (5)	0.6980 (4)	−0.0379 (3)	3.2 (1)
C12	0.6782 (5)	0.6602 (4)	−0.0673 (4)	4.2 (1)
C13	0.6356 (5)	0.5811 (5)	−0.0439 (4)	4.8 (2)
C14	0.6784 (5)	0.5377 (4)	0.0076 (4)	4.4 (1)
C15	0.7646 (5)	0.5704 (4)	0.0391 (3)	3.2 (1)
C11A	0.8113 (5)	0.7826 (4)	−0.0696 (3)	3.7 (1)
C11B	0.7222 (6)	0.8428 (5)	−0.0862 (4)	5.8 (2)
C11C	0.9155 (6)	0.7708 (4)	−0.1418 (4)	5.0 (2)
C15A	0.8123 (6)	0.5182 (4)	0.0945 (4)	3.8 (1)
C15B	0.7207 (8)	0.5082 (6)	0.1725 (4)	6.9 (2)
C15C	0.8540 (8)	0.4328 (5)	0.0596 (5)	6.9 (2)
N20	1.0809 (4)	0.7008 (3)	0.1190 (2)	2.52 (9)
C20	1.1744 (5)	0.6669 (3)	0.1419 (3)	2.8 (1)
C21	1.2847 (5)	0.7069 (4)	0.1179 (3)	3.5 (1)
C22	1.3794 (5)	0.6693 (5)	0.1360 (4)	4.6 (2)
C23	1.3653 (6)	0.5966 (5)	0.1801 (4)	5.1 (2)
C24	1.2573 (6)	0.5606 (4)	0.2055 (4)	4.7 (2)
C25	1.1592 (5)	0.5928 (4)	0.1875 (3)	3.3 (1)
C21A	1.3015 (5)	0.7880 (4)	0.0718 (4)	4.2 (1)
C21B	1.3581 (7)	0.7725 (6)	−0.0142 (4)	7.0 (2)
C21C	1.3656 (7)	0.8540 (5)	0.1039 (5)	7.3 (2)
C25A	1.0444 (6)	0.5492 (4)	0.2174 (4)	3.9 (1)
C25B	1.0009 (7)	0.5490 (5)	0.3066 (4)	5.6 (2)
C25C	1.0491 (7)	0.4601 (4)	0.1858 (5)	5.7 (2)
C30	0.8498 (5)	0.8889 (3)	0.1356 (3)	3.1 (1)
C31	0.9489 (5)	0.8936 (4)	0.1675 (3)	3.2 (1)
C32	0.9389 (5)	0.8294 (4)	0.2230 (3)	3.2 (1)
C33	0.8367 (5)	0.7828 (3)	0.2233 (3)	3.1 (1)
C34	0.7792 (5)	0.8124 (4)	0.1713 (3)	3.0 (1)
C35	0.8235 (6)	0.9521 (4)	0.0800 (4)	4.6 (2)
C36	1.0386 (6)	0.9617 (4)	0.1495 (4)	4.8 (2)
C37	1.0161 (6)	0.8152 (5)	0.2749 (3)	4.6 (2)
C38	0.7838 (6)	0.7109 (4)	0.2809 (4)	4.5 (2)
C39	0.6645 (5)	0.7954 (4)	0.1607 (4)	4.3 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2B(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

solution was purged with H_2 (which was passed through two liquid N_2 traps) for several minutes. The ampule was placed in an oil bath at ca. 95 °C. After being stirred for 2 days, the solvent was removed from the solution in vacuo, and the resulting oily residue was dried in vacuo. A C_6D_6 solution was made directly from the entire residue which was shown by ^{1}H NMR to contain *no* (η^5-C_5Me_5)W(=NAr)$_2$H (**4**). Reaction had occurred however to give decomposition products of which H_2NAr was the principal component.

Reaction of (η^5-C_5Me_5)W(=NAr)$_2$Cl (1) with LiNH-2,6-$C_6H_3Me_2$. This reaction was carried out in an analogous fashion to the reaction of (η^5-C_5Me_5)W(=NAr)$_2$Cl (**1**) with LiNHAr, which constituted the preparative method for the formation of (η^5,η^1-$C_5Me_4CH_2$)W(=NAr)$_2$ (**5**). Similarly, workup of this reaction afforded only **5** as determined by ^{1}H NMR.

Structural Determination of (η^5-C_5Me_5)W(=NAr)$_2$Cl (1). A burgundy, block crystal of **1** crystallized from pentane (−35 °C) and was mounted in a glass capillary in a random orientation. Preliminary examinations and data collection were performed at ambient temperature with Mo Kα radiation (λ = 0.710 73 Å) on a Syntex $P2_1$ diffractometer equipped with a Crystal Logics data collection control system and with a graphite cyrstal incident beam monochromator. Crystal color and dimensions are recorded in Table I. From the systematic absences of $h0l$ ($h+l = 2n+1$) and $0k0$ ($k = 2n + 1$) and from the subsequent least squares refinement, the space group was determined to be monoclinic $P2_1/n$ (no. 14). A total of 6204 reflections were collected in the $+h$, $+k$, $\pm l$ octants (5671 unique) in the range $2° \leq \theta \leq 50°$, with 4216 reflections having $I \geq 3\sigma(I)$. Three representative check reflection standards were measured after every 98 data reflections and remained constant within experimental error throughout data collection, so no decay correction was required. Only those reflections having intensities $I \geq 3\sigma(I)$ were used in the refinements. Hydrogen atoms were placed in calculated positions and included in the refinement. A Lorentz-polarization correction and empirical absorption[46] correction based on a ψ scan were applied to the data. The agreement factors for the 474 observed and accepted reflections was 1.4% based upon I and 1.1% based on F_0. The structure was solved using direct methods and refined in full-matrix least-squares techniques for a final R = 0.024 and R_w = 0.028. The largest peak in the final difference Fourier was 1.06 (9) e^{-1}/Å^3. All calculations were performed on a VAX computer using MolEN/VAX.[47] Positional parameters are listed in Table III.

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Supplementary Material Available: Full details of the structure solution and refinement, including tables of crystal data, data collection parameters, atomic positional and thermal parameters, bond distances, bond angles, least-squares planes, and ORTEP figures for (η^5-C_5Me_5)W(=NAr)$_2$Cl (1) (Ar = 2,6-diisopropylphenyl) (15 pages). Ordering information is given on any current masthead page.

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(46) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 159.

(47) *MolEN, An Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.

(48) Note Added in Proof: Since the submission of this paper, the related complex Cp*W(=NC_6H_4-*p*-Me)$_2$(CH_2SiMe_3) has been reported from the reaction of Cp*W(O)$_2$(CH_2SiMe_3) with tolyl isocyanate; see: Legzdins, P.; Phillips, E. C.; Rettig, S. J.; Trotter, J.; Veltheer, J. E.; Yee, V. C. *Organometallics* **1992**, *11*, 3104.