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Preparation of Tungsten(VI) Phenylimido Alkyl and Alkylidene Complexes[1]

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Abstract: Phenylimido neopentylidene complexes of the type $W(NPh)(CHCMe_3)L_2Cl_2$ ($L = PMe_3$ or PEt_3) have been prepared by reacting $W(NPh)(OCMe_3)_4$ with $Ta(CHCMe_3)L_2Cl_3$. $[W(NPh)(CHCMe_3)L_2R]^+$ (R = Cl or Me), $W(NPh)(CHCMe_3)(OCMe_3)_2L$, and $W(NPh)(CHCMe_3)(L)Cl_2$ were prepared straightforwardly from $W(NPh)(CHCMe_3)L_2Cl_2$. $W(NPh)(Neo)_3Cl$ ($Neo = CH_2CMe_3$) was prepared from $W(NPh)Cl_4$ and (Neo)MgCl, and from it $W(NPh)(CHCMe_3)(Neo)_2$ and $WCp(NPh)(CHCMe_3)Neo$ were prepared by α-hydrogen abstraction reactions. $W(NPh)(Neo)_3Cl$ reacts with LHCl ($L = PMe_3$ or py) in the presence of excess L to give $W(NPh)(CHCMe_3)L_2Cl_2$, presumably via unobservable $W(NPh)(Neo)_2(L)Cl_2$. $W(NPh)(CH_2SiMe_3)_4$, which can be prepared from $W(NPh)(CH_2SiMe_3)_3Cl$ and $LiCH_2SiMe_3$, decomposes smoothly in a first-order reaction ($\Delta H^\ddagger = 22 \pm 2$ kcal mol^{-1}, $\Delta S^\ddagger = -8 \pm 4$ eu) to give $W(NPh)(CHSiMe_3)(CH_2SiMe_3)_2$ while $W(NPh)(CH_2SiMe_3)_2Cl_2$ reacts with $L = PMe_3$ or PEt_3 to give $W(NPh)(CHSiMe_3)L_2Cl_2$. We also report the preparation of several miscellaneous phenylimido alkyl complexes such as $W(NPh)R_3Cl$ (R = Me or Bz), $WCp(NPh)Me_3$, and $W(NPh)R_3(OCMe_3)$ (R = Me, Bz, Neo) and the product of decomposition of $[W(NPh)(CHCMe_3)(PMe_3)_2Me][AlMe_2Cl_2]$, $W(NPh)(CCMe_3)(PMe_3)_2Cl(AlMe_2Cl)$.

Introduction

The preparation of a large number of (primarily) neopentylidene complexes of niobium and tantalum in the past several years has depended largely on the α-hydrogen atom abstraction reaction.[2] Naturally, we have been interested in the extent to which the principles that govern Nb and Ta d^0 alkyl chemistry might extend to group 4 or group 6 metal alkyl chemistry. So far we have found that the principles of α-hydrogen abstraction do not appear to extend to the group 4 metals. Zirconium alkyls, for example, reduce by homolytic cleavage of the metal-carbon bond under conditions resembling those that result in formation of alkylidene complexes of Nb and Ta.[3] Testing the principles of α-hydrogen abstraction for group 6 alkyls has been hampered by a different problem, the relatively small number of Mo(VI) and W(VI) alkyl complexes.[4] Therefore, we have been looking for a new class of W(VI) alkyl complexes that might undergo α-H abstraction reactions to give stable alkylidene complexes.

The first W(VI) alkylidene complex to be prepared was $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)L_2$ ($L_2 = (PMe_3)_2$ or dmpe).[5] The reaction that gave it ($W(CCMe_3)(CH_2CMe_3)_3$ plus L) is a ligand-induced α-hydrogen abstraction reaction (if we assume the neopentylidyne ligand plays no direct role). Later we showed that oxo alkylidene complexes ($W(O)(CHCMe_3)L_2Cl_2$; $L = PR_3$) could be prepared by transferring a neopentylidene ligand from tantalum to tungsten in exchange for two *tert*-butoxide ligands.[6] The common feature of these two types of tungsten alkylidene complexes is the presence of a strong π-bonding ligand (a neopentylidyne ligand or an oxo ligand). Therefore, we considered preparing and studying tungsten alkyl complexes containing an ostensibly even better π-bonding ligand than the oxo ligand, the imido ligand.[7a] We report here the preparation of one type of phenylimido neopentylidene complex by neopentylidene ligand transfer from tantalum to tungsten, along with the preparation of several phenylimido alkyl complexes and how some of them can be converted into alkylidene complexes by α-hydrogen abstraction reactions. These results demonstrate that the principles of intramolecular α-hydrogen abstraction do extend to tungsten alkyls, at least if a strong π-donor ligand is present. As in Nb and Ta chemistry[2] more complex α-hydrogen abstraction reactions should be more common but more difficult to predict or control.[5]

Table I. Pertinent ^1H and ^{13}C NMR Data for Phenylimido Alkylidene Complexes[a]

compd	$^1H_\alpha$, ppm	$^{13}C_\alpha$, ppm	J_{CH_α}, Hz
$W(NPh)(CHCMe_3)(PMe_3)_2Cl_2$	10.92	307	123[b]
$W(NPh)(CHCMe_3)(PEt_3)_2Cl_2$	11.92	304	119[c]
$[W(NPh)(CHCMe_3)(PMe_3)_2Cl][AlCl_4]$	10.39	303	106
$[W(NPh)(CHCMe_3)(PEt_3)_2Cl][AlCl_4]$	9.6	301	106
$W(NPh)(CHCMe_3)(PMe_3)(OCMe_3)_2$	10.17	265	114
$W(NPh)(CHCMe_3)(PEt_3)(OCMe_3)_2$	10.27	266	111[d]
$[W(NPh)(CHCMe_3)(PMe_3)_2Me][AlMe_2Cl_2]$	8.40	303	106
$[W(NPh)(CHCMe_3)(PEt_3)_2Me][AlMe_2Cl_2]$	7.84	301	105
$W(NPh)(CHCMe_3)(PEt_3)Cl_2$	10.8	301	106[e]
$W(NPh)(CHCMe_3)(CH_2CMe_3)_2$	6.61	246	106
$W(NPh)(CHSiMe_3)(CH_2SiMe_3)_2$	7.79	230	108
$W(\eta^5\text{-}C_5H_5)(NPh)(CHCMe_3)(CH_2CMe_3)$	9.81	269	117
$W(NPh)(CHSiMe_3)(PMe_3)_2Cl_2$	12.75	293	119
$W(NPh)(CHCMe_3)(py)_2Cl_2$	11.3	303	121

[a] Full details can be found in the Experimental Section. [b] $J_{CH_\alpha} = 121$ Hz in the analogous oxo complex. [c] $J_{CH_\alpha} = 126$ Hz in the analogous oxo complex. [d] $J_{CH_\alpha} = 119$ Hz in the analogous oxo complex. [e] $J_{CH_\alpha} = 115$ Hz in the analogous oxo complex.

Results

Preparation of Imido Neopentylidene Complexes via Neopentylidene Ligand Transfer. The first task was to show that imido alkylidene complexes are stable species. We prepared one type by an alkylidene ligand transfer reaction (eq 1) that is entirely analogous to that used to prepare $W(O)(CHCMe_3)L_2Cl_2$ complexes.[6] The required $W(NPh)(OCMe_3)_4$ complex can be prepared straightforwardly and quantitatively from $[W(NPh)Cl_4]_n$, which in turn can be prepared in large quantities from $W(O)Cl_4$

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[1] Multiple Metal-Carbon bonds. 28. For part 27, see: Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.

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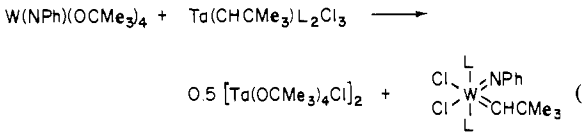


$$\mathrm{W(NPh)(OCMe_3)_4 + Ta(CHCMe_3)L_2Cl_3 \longrightarrow 0.5\,[Ta(OCMe_3)_4Cl]_2 + WCl_2(NPh)(CHCMe_3)L_2} \quad (1)$$

L = PMe_3, PEt_3

and phenyl isocyanate in refluxing octane (eq 2).[7b]

$$\mathrm{W(O)Cl_4 + PhNCO \xrightarrow{octane} [W(NPh)Cl_4]_n + CO_2} \quad (2)$$

The two $W(NPh)(CHCMe_3)L_2Cl_2$ complexes appear to be entirely analogous to their oxo analogues. The imido and neopentylidene ligands are cis to one another, and the phosphine ligands are trans to one another. The imido ligand should be linear,[7a] and the β-carbon atom of the neopentylidene ligand should lie in the same plane in which the imido nitrogen and the tungsten atoms lie. Therefore, two isomers are possible, depending on which way the alkylidene ligand is oriented. We only observe one isomer, we assume the one in which the *tert*-butyl group points toward the imido ligand (cf. $W(O)(CHCMe_3)L_2Cl_2$[8]). Pertinent ^1H and ^{13}C NMR data for these and other phenylimido complexes we will be discussing are listed in Table I.

Several other imido neopentylidene complexes can be prepared from $W(NPh)(CHCMe_3)L_2Cl_2$ (Figure 1). In each case the oxo analogue is known. The main difference between an oxo and an imido complex is the greater stability of the latter, in general. For example, $[W(O)(CHCMe_3)L_2Me][AlMe_2Cl_2]$ decomposes readily in solution at 25 °C ($t_{1/2} \approx 5$ min in $CDCl_3$) to unidentified products,[6] but the analogous phenylimido complex is stable in $CDCl_3$ at 25 °C.

When $[W(NPh)(CHCMe_3)(PMe_3)_2Me][AlMe_2Cl_2]$ does decompose (60 °C in toluene), methane is evolved steadily and a single product can be isolated in high yield (eq 3). This new complex is soluble in pentane and does not conduct in dichloromethane, two facts that suggest that it is no longer ionic. We observe signals for a pair of trans PMe_3 groups and two equivalent aluminum methyl groups in the ^1H NMR spectrum and, in the $^{13}C\{^1H\}$ NMR spectrum, a triplet resonance for C_α at 309.4 ppm ($^2J_{CP} = 12$ Hz), which does not split into a doublet in the gated proton-decoupled spectrum. Therefore, this product is most likely a phenylimido neopentylidyne complex. Two structures for $W(NPh)(CCMe_3)(PMe_3)_2Cl(AlMe_2Cl)$ consistent with the NMR data are shown in Figure 2. Although in one of these (A) the $AlMe_2Cl$ group is bound in a manner similar to the way it is bound in $W(CH)(PMe_3)_3Cl(AlMe_2Cl)$,[9] we favor the alternative (B) for three reasons. First, the imido ligand is not likely to be able to effectively donate its π-electron density to the metal in competition with the neopentylidyne ligand. Therefore, it should not be linear; i.e., its π-electron pair should be exposed and easily attacked by a Lewis acid. Second, the *tert*-butyl group should make coordination of the Lewis acid to the neopentylidyne ligand much more difficult for steric reasons than coordination of the Lewis acid to the methylidyne ligand. Third, $AlMe_2Cl$ cannot be removed by adding TMEDA or PMe_3 to $W(NPh)(CCMe_3)(PMe_3)_2Cl(AlMe_2Cl)$, whereas excess PMe_3 reacts with $W(CH)(PMe_3)_3Cl(AlMe_2Cl)$ to give $W(CH)(PMe_3)_4Cl$.[9]

$$\mathrm{[W(NPh)(CHCMe_3)(PMe_3)_2Me][AlMe_2Cl_2] \xrightarrow[60\ ^\circ C]{toluene} W(NPh)(CCMe_3)(PMe_3)_2Cl(AlMe_2Cl) + CH_4} \quad (3)$$

Preparation of Imido Neopentyl and Neopentylidene Complexes by Direct Methods. After demonstrating that phenylimido neopentylidene complexes are stable and isolable, we wanted to demonstrate that imido neopentyl complexes can be prepared and converted into neopentylidene complexes by α-hydrogen abstraction reactions.

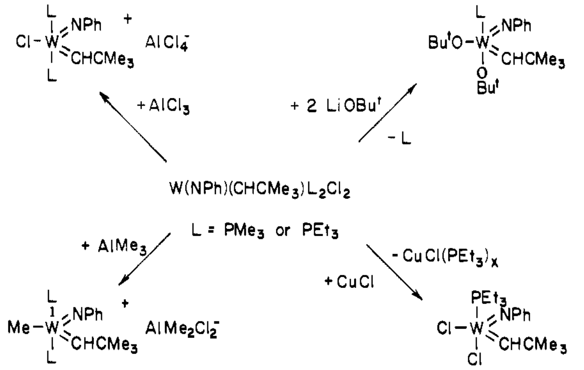


Figure 1. Preparation of some phenylimido alkylidene complexes from $W(NPh)(CHCMe_3)L_2Cl_2$.

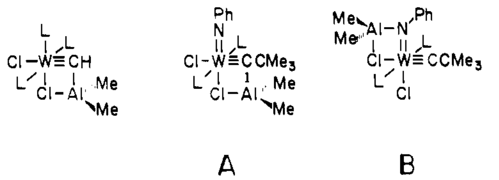


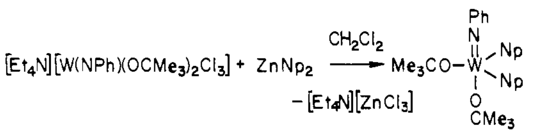
Figure 2. Structure of $W(CH)(PMe_3)_3Cl(AlMe_2Cl)$ and proposed structures for $W(NPh)(CCMe_3)(PMe_3)_2Cl(AlMe_2Cl)$.

Yellow, sublimable $W(NPh)(Neo)_3Cl$ (Neo = CH_2CMe_3) is best prepared by adding 3 equiv of NeoMgCl to $W(NPh)Cl_4(Et_2O)$ in ether at −78 °C. It is a monomer in dichloromethane. Its NMR spectra are consistent with it being a trigonal bipyramid in which the three alkyl ligands occupy the equatorial positions. An analogous reaction between $W(NPh)(OCMe_3)_4$ and NeoMgCl yields $W(NPh)(Neo)_3(OCMe_3)$. Interestingly, $W(NPh)(Neo)_3(OCMe_3)$ reacts in toluene with 1 equiv of HCl gas to give $W(NPh)(Neo)_3Cl$ quantitatively. Other derivatives can be prepared similarly (eq 4). This reaction appears to be quite general and should be applicable to the preparation of a variety of compounds with the general formula $W(NPh)R_3X$, starting from the appropriate *tert*-butoxy complex and HX.

$$\mathrm{W(NPh)(CH_2CMe_3)_3(OCMe_3) + HX \rightarrow W(NPh)(CH_2CMe_3)_3X} \quad (4)$$

$$\mathrm{X = Cl, Br, O_2CCF_3}$$

All attempts to prepare $W(NPh)(Neo)_2Cl_2$ have failed. However, a dineopentyl species can be prepared if one or two *tert*-butoxide ligands are present. $[Et_4N][W(NPh)(OCMe_3)_2Cl_3]$ (prepared by equilibrating $W(NPh)(OCMe_3)_4$ with $[Et_4N][W(NPh)Cl_5]$; see Experimental Section) reacts cleanly with $Zn(Neo)_2$ in CH_2Cl_2 to afford $W(NPh)(Neo)_2(OCMe_3)_2$ in high yield (eq 5). The ^1H NMR spectrum of this species at −10 °C is consistent with the structure shown. At higher temperatures the signals for the two *tert*-butoxy ligands broaden due to exchange of the axial and equatorial *tert*-butoxy groups. However, the AB patterns for the α protons in the neopentyl ligands do not change. Therefore, the intermediate in the exchange process does not contain a plane of symmetry that passes through the α-carbon atoms of the neopentyl ligands. The intermediate we favor is a cis tetragonal pyramid with the imido ligand at the apex.



$$\mathrm{[Et_4N][W(NPh)(OCMe_3)_2Cl_3] + ZnNp_2 \xrightarrow[-[Et_4N][ZnCl_3]]{CH_2Cl_2} Me_3CO-W(NPh)(Np)_2(OCMe_3)} \quad (5)$$

An analogous reaction between $[Et_4N][W(NPh)(OCMe_3)Cl_4]$ and $Zn(Neo)_2$ gave yellow $W(NPh)(Neo)_2(OCMe_3)Cl$. Only one isomer is observed. We suspect the *tert*-butoxide ligand is in an equatorial position, where it would not compete as a π-electron donor with the phenylimido ligand.

An attempt to prepare $W(NPh)(Neo)_4$ from $W(NPh)(Neo)_3Cl$ and LiNeo yields the complex shown in eq 6. W(NPh)-

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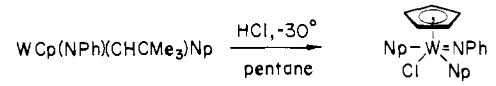
$$\mathrm{W(NPh)(Neo)_3Cl + LiNeo \xrightarrow[-CMe_4]{-LiCl} W(NPh)(CHCMe_3)(Neo)_2} \quad (6)$$

$(CHCMe_3)(Neo)_2$ is a red oil that can be purified by high-vacuum, short-path distillation. Pertinent ^1H and ^{13}C NMR data are given in Table I. A molecular weight determination confirmed that it is a monomer. It may also be prepared by reacting $W(NPh)(Neo)_3Cl$ with $Ph_3P{=}CH_2$ in ether. $W(NPh)(CHCMe_3)(Neo)_2$ resembles $Ta(CHCMe_3)(Neo)_3$ in some of its reactions. For example, it reacts with 1 equiv of HCl to give $W(NPh)(Neo)_3Cl$[10] and with an excess of dry acetone to yield 2,4,4-trimethyl-2-pentene (80%) and presumably $W(NPh)(O)(Neo)_2$.[11]

We wanted to prepare $WCp(NPh)(Neo)_2Cl$ ($Cp = \eta^5\text{-}C_5H_5$) in order to compare an α-hydrogen abstraction reaction in a W(VI) complex with that which is best studied for tantalum, decomposition of $TaCp(Neo)_2Cl_2$ to give $TaCp(CHCMe_3)Cl_2$.[12] Since we have not been able to prepare $W(NPh)(Neo)_2Cl_2$, we had to prepare $WCp(NPh)(Neo)_2Cl$ in a more circuitous manner. $W(NPh)(Neo)_3Cl$ reacts with NaC_5H_5 as shown in eq 7. We

$$\mathrm{W(NPh)(Neo)_3Cl + NaC_5H_5 \xrightarrow[-NaCl,\ -CMe_4]{THF,\ 36\ h} WCp(NPh)(CHCMe_3)Neo} \quad (7)$$

propose that $WCp(NPh)(CHCMe_3)Neo$ forms as a result of α-H abstraction in $WCp(NPh)(Neo)_3$ or as a result of a more complex dehydrohalogenation reaction (cf. preparation of $Ta(CHCMe_3)(Neo)_3$[10]). $WCp(NPh)(Neo)_2Cl$ can then be prepared as shown in eq 8. The ^1H NMR spectrum of $WCp(NPh)(Neo)_2Cl$ consists of a single cyclopentadienyl resonance, an AB quartet for the methylene protons of the neopentyl ligands, and a singlet for the *tert*-butyl groups. The spectrum does not change down to −50 °C. The structure shown in eq 8 is consistent with these data.



(8)

We were pleased to find that $WCp(NPh)(Neo)_2Cl$ does decompose in the dark in toluene to neopentane and $WCp(NPh)(CHCMe_3)Cl$ (H_α at 10.46 ppm). Unfortunately, however, the reaction appears to be as complex as some of those in the tantalum cyclopentadienyl system[12] (the light-induced reactions especially). Therefore, we do not expect it to be a viable preparative route to $WCp(NPh)(CHCMe_3)Cl$. We have not yet attempted to decompose $WCp(NPh)(Neo)_2Cl$ photochemically.

The unavailability of $W(NPh)(Neo)_2Cl_2$ prevented our examining a ligand-induced α-H abstraction reaction analogous to that between $M(Neo)_2X_3$ and phosphorus, nitrogen, or oxygen donor ligands (M = Nb or Ta; X = Cl or Br[13]). As we might now expect,[10,13] ligand-induced α-H abstraction is slow if two *tert*-butoxide ligands are present. An excess of PMe_3 (4 equiv) does not react with $W(NPh)(Neo)_2(OCMe_3)_2$ in benzene upon heating the mixture to 60 °C for 3.5 days. A noticeable change occurs when a benzene solution of $W(NPh)(Neo)_2(OCMe_3)_2$ containing PEt_3 is irradiated with 360-nm high-intensity light from a medium-pressure Hg lamp, but the reaction is obviously complex and was not investigated further.

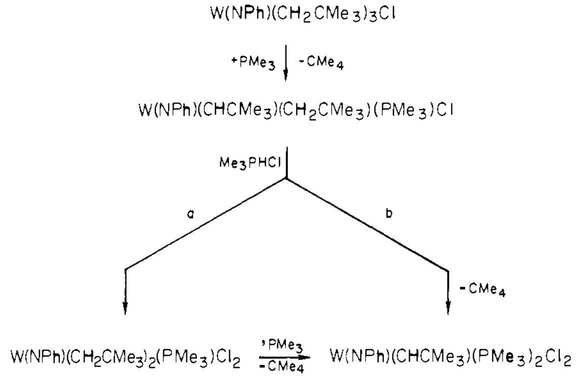
We overcame the problem of the unavailability of $W(NPh)(Neo)_2Cl_2$ and finally accomplished a direct synthesis of $W(NPh)(CHCMe_3)L_2Cl_2$ through the reaction shown in eq 9. We

$$\mathrm{W(NPh)(Neo)_3Cl + LHCl + L\ (excess) \xrightarrow[CHCl_3,\ 24\ h]{60\text{–}80\ °C} W(NPh)(CHCMe_3)L_2Cl_2 + 2CMe_4} \quad (9)$$

(e.g., L = PMe_3, pyridine)

have not examined this reaction in great detail but have made some observations that allow us to suggest a mechanism. First, in an attempt to prepare $W(NPh)(CHCMe_3)(L)Cl_2$ from $W(NPh)(Neo)_3Cl$ and Et_3PHCl (no excess PEt_3 present), we observed no reaction in $CHCl_3$ after 2 days at 70 °C. Apparently a free Lewis base is necessary to "activate" the tungsten complex. Indeed, PMe_3 alone reacts with $W(NPh)(Neo)_3Cl$ at 70 °C in C_6D_6 to give neopentane and 2,2,5,5-tetramethyl-3-hexene, the usual product of bimolecular decomposition of a neopentylidene complex.[2] Therefore, we believe that PMe_3 promotes an α-hydrogen abstraction reaction to form $W(NPh)(CHCMe_3)Neo(PMe_3)Cl$, which subsequently decomposes under these conditions. In the presence of Me_3PHCl, however, $W(NPh)(CHCMe_3)Neo(PMe_3)Cl$ reacts rapidly in one of the two ways shown in Scheme I. In one (a) the alkylidene ligand is protonated to give the dineopentyl complex, which should decompose and/or react rapidly with more PMe_3 to give the observed product. In the other (b) the neopentyl ligand itself is protonated. Since we have observed protonation of the neopentylidene ligand in $WCp(NPh)(CHCMe_3)(CH_2CMe_3)$ in preference to the neopentyl ligand (see above), we believe path a is the more likely.

Scheme I



Preparation of Imido (Trimethylsilyl)methyl and (Trimethylsilyl)methylidene Complexes. In tantalum chemistry (trimethylsilyl)methyl complexes almost always can be prepared more simply and prepared in higher yield than neopentyl complexes,[4] perhaps in part because the (trimethylsilyl)methyl ligand is less susceptible to α-H abstraction reactions.[2] Therefore, we hoped to be able to prepare (trimethylsilyl)methyl analogues of two of the neopentyl species we could not prepare, $W(NPh)(Neo)_2Cl_2$ and the supposed precursor to $W(NPh)(CHCMe_3)(Neo)_2$, $W(NPh)(CH_2CMe_3)_4$.

Trigonal-bipyramidal $W(NPh)(CH_2SiMe_3)_3Cl$ can be prepared from $W(NPh)Cl_4(Et_2O)$ and 1.5 equiv of $Zn(CH_2SiMe_3)_2$. Addition of $LiCH_2SiMe_3$ to $W(NPh)(CH_2SiMe_3)_3Cl$ in pentane yields yellow, crystalline $W(NPh)(CH_2SiMe_3)_4$. A 250-MHz ^1H NMR spectrum of $W(NPh)(CH_2SiMe_3)_4$ at −85 °C shows signals for two types of CH_2SiMe_3 groups in a ratio of 3:1, indicative of a trigonal-bipyramidal geometry with the NPh group occupying an axial position. At −40 °C the (trimethylsilyl)methyl groups begin to equilibrate on the ^1H NMR time scale. Similar fluxional behavior has been observed for $Ta(CH_2CMe_3)_4X$ (X = Cl[10] or $OCMe_3$[14]).

When $W(NPh)(CH_2SiMe_3)_4$ is heated to 60 °C in toluene, 1 equiv of tetramethylsilane is evolved and $W(NPh)(CHSiMe_3)(CH_2SiMe_3)_2$ can be isolated in high yield as a dark red oil (NMR data are listed in Table I). The conversion of $W(NPh)(CH_2SiMe_3)_4$ to $W(NPh)(CHSiMe_3)(CH_2SiMe_3)_2$ can be followed by ^1H NMR at 250 MHz. The rate was found to be first order and concentration independent, consistent with an intramolecular α-hydrogen abstraction reaction. Rate constants and activation parameters are given in Table II.

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Table II. Kinetic and Activation Parameters for Decomposition of $W(NPh)(CH_2SiMe_3)_4$ in Toluene-d_8[a]

T, K	10^3k, min^{-1}	$t_{1/2}$, min	T, K	10^3k, min^{-1}	$t_{1/2}$, min
347	74 ± 3	9 ± 0.3	335	25 ± 1	28 ± 1
322	5.7 ± 0.3	122 ± 6	330	12 ± 0.5	57 ± 2
341	45 ± 1	15 ± 0.4			

$\Delta H^{\ddagger} = 22 \pm 2$ kcal mol^{-1} $\Delta S^{\ddagger} = -8 \pm 4$ eu

[a] Data were obtained by ^{1}H NMR integration of the methylene resonances in starting material vs. product vs. time. The rate constant was determined by a linear least-squares fit of the data; correlation coefficients were always >0.98. Errors in k were determined by a standard statistical method based on standard deviations. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined by a least-squares fit of ln (k/T) vs. $1/T$. The errors were determined by a standard statistical method based on standard deviations.

$W(NPh)(CH_2SiMe_3)_2Cl_2$ may be synthesized as shown in eq 10 (see discussion of the preparation and use of anionic starting materials in the Experimental Section).

$$[Et_4N][W(NPh)Cl_5] + Zn(CH_2SiMe_3)_2 \xrightarrow{CH_2Cl_2} W(NPh)(CH_2SiMe_3)_2Cl_2 + [Et_4N][ZnCl_3] \quad (10)$$

An excess of $[Et_4N][W(NPh)Cl_5]$ is required to avoid forming a large amount of $W(NPh)(CH_2SiMe_3)_3Cl$. An AB pattern for the methylene protons in the ^{1}H NMR spectrum of $W(NPh)(CH_2SiMe_3)_2Cl_2$ suggests that the molecule is a trigonal bipyramid with the phenylimido group occupying an axial position, but we cannot rule out a square-pyramidal structure on the basis of these NMR data alone.

We are now in a position to test whether $W(NPh)R_2Cl_2$ complexes can be induced to lose RH on addition of donor ligands, a reaction that we could only infer for R = CH_2CMe_3. $W(NPh)(CH_2SiMe_3)_2Cl_2$ reacts with 2 equiv of PMe_3 or PEt_3 in methylene chloride to give $W(NPh)(CHSiMe_3)(PR_3)_2Cl_2$ and Me_4Si. Addition of 1 equiv of PEt_3 yields a mixture of $W(NPh)(CHSiMe_3)(PEt_3)_2Cl_2$ and $W(NPh)(CH_2SiMe_3)_2Cl_2$, which remains unchanged after heating for 2 days at 60 °C. The reason, we propose, is first that α-H abstraction occurs in seven-coordinate $W(NPh)(CH_2SiMe_3)_2(PEt_3)_2Cl_2$ and second that PEt_3 in $W(NPh)(CHSiMe_3)(PEt_3)_2Cl_2$ is not labile. These results contrast sharply with those found for related tantalum species. For example, a mixture of $Ta(CHCMe_3)(PMe_3)_2Cl_3$ and $Ta(CH_2CMe_3)_2Cl_3$ soon yields $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ quantitatively.[13] The PMe_3 ligands in $Ta(CHCMe_3)(PMe_3)_2Cl_3$ are observed to be quite labile.

Preparation of Some Methyl and Benzyl Complexes. On the basis of the apparent similarities between tungsten phenylimido alkyl chemistry and tantalum alkyl chemistry that we have seen so far, we would expect tungsten phenylimido methyl and benzyl complexes to be more difficult to prepare, less stable toward bimolecular decomposition processes, and less likely to undergo clean intramolecular α-hydrogen abstraction reactions.[15] We report several methyl and benzyl complexes here for the sake of completeness. We did not pursue their chemistry in any detail because we felt that our suspicions were correct and that no new principles would be forthcoming.

Preparation of phenylimido methyl and benzyl complexes sometimes requires unique methods. An example of a typical problem is that $W(NPh)Cl_4$ reacts with $ZnMe_2$ to give predominantly an insoluble, uncharacterized precipitate. We speculated that $ZnCl_2$ was the cause of a secondary reaction and therefore devised a method of removing it from the reaction as quickly as possible (eq 11). The tetraethylammonium salt of $ZnCl_3^-$ forms rapidly and is relatively insoluble in dichloromethane.

$$[Et_4N][W(NPh)Cl_5] + 1.5ZnMe_2 + 0.5NEt_4Cl \xrightarrow[-30\ ^\circ C]{CH_2Cl_2} W(NPh)Me_3Cl + 1.5[NEt_4][ZnCl_3] \quad (11)$$

Similarly, $W(NPh)Me_3(OCMe_3)$, a yellow oil, can be prepared best by reacting $[Et_4N][W(NPh)(OCMe_3)Cl_4]$ with $ZnMe_2$ in dichloromethane. Although there may be a problem associated with a secondary reaction involving $ZnCl_2$ in this case also, the main problem is that $W(NPh)(OCMe_3)Cl_3$ is not stable enough to use as a starting material (see Experimental Section). Both $W(NPh)Me_3Cl$ and $W(NPh)Me_3(OCMe_3)$ appear to be trigonal-bipyramidal molecules analogous to the neopentyl and (trimethylsilyl)methyl complexes.

The only facile route into benzyl chemistry that we have found is via $W(NPh)Bz_3(OCMe_3)$, prepared from $[Et_4N][W(NPh)(OCMe_3)Cl_4]$ and BzMgCl in THF at 0 °C. $W(NPh)Bz_3Cl$ can then be prepared by treating $W(NPh)Bz_3(OCMe_3)$ with HCl gas.

$W(NPh)Me_3Cl$ reacts readily with LiMe in ether to give LiCl and an unstable yellow product. We propose that the product is $W(NPh)Me_4$, but it could not be isolated without extensive decomposition. $W(NPh)Me_3Cl$ also reacts with NaC_5H_5 to give yellow crystalline $WCp(NPh)Me_3$. The fact that two types of methyl ligands are observed by NMR at 25 °C suggests that $WCp(NPh)Me_3$ is probably a tetragonal pyramid.

Discussion

It is worthwhile noting that in a general sense the preparative methods and properties of alkyl and alkylidene complexes in the W=NPh system often closely resemble the preparative methods and properties of alkyl and alkylidene complexes in an isoelectronic TaX (X = chloride or alkyl) system.[2] In particular, we note that, as in tantalum chemistry, tungsten neopentyl complexes seem most susceptible to intramolecular α-H abstraction reactions, alkoxide ligands in place of chloride ligands slow down α-H abstraction reactions markedly, and α-H abstraction can be induced by adding donor ligands. A more specific example of the similarity between tungsten imido chemistry and tantalum chemistry is that tungsten complexes of the type $W(NPh)R_3X$ (X = halide or alkoxide; R = Neo or CH_2SiMe_3) are especially stable compared to complexes of the type $W(NPh)R_4$ (cf. $Ta(Neo)_3Cl_2$ vs. $Ta(Neo)_4Cl$[10]). These results are consistent with the proposal that a bond between the metal and an axial alkyl ligand in a tetraalkyl complex is weaker than a bond between the metal and an equatorial alkyl ligand; i.e., an axial alkyl group is the leaving group in an α-H abstraction process.[10] Of course, many differences in detail between the tantalum and tungsten systems would become apparent if we were to examine the tungsten system in as much detail as the tantalum systems, but that was not our purpose here.

One potentially important preparative trick that we have discovered is the use of anions as starting materials. One advantage of anions is that they are more stable toward intermolecular decomposition reactions. For example, $W(NPh)(OCMe_3)_2Cl_2$ can be prepared in situ by mixing 1 equiv of $W(NPh)Cl_4(Et_2O)$ with $W(NPh)(OCMe_3)_4$ in dichloromethane, but it decomposes readily to give isobutylene, *tert*-butyl chloride, and tungsten oxo complexes. Such decomposition reactions (generally resulting in the formation of oxo-containing compounds) are not uncommon for alkoxy–halide species of early transition metals in high oxidation states.[16] In contrast, $[Et_4N][W(NPh)(OCMe_3)_2Cl_3]$ is a stable, yellow crystalline species that can be prepared quantitatively.

A second important advantage of using anions is that in reactions with zinc reagents $ZnCl_2$ is removed effectively as $ZnCl_3^-$. Removing the metal chloride product of other alkylation reactions (e.g., $MgCl_2$) might also be useful in certain situations. We believe that some of the tricks we have used will be useful in preparing analogous tungsten oxo complexes, e.g. $W(O)Me_3Cl$.

Several methyl imido complexes of the type $W(NMe)(Neo)_3X$ (X = Cl, Br, or OR) have been mentioned in a recent communication.[4c] $W(NMe)(Neo)_3X$ forms an adduct with Lewis acids in which it is believed that the Lewis acid binds to the nitrogen of the imido ligand. When X = Cl or Br, this species decomposes

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to give neopentane and a complex that will catalytically metathesize olefins. The authors implied that the catalyst is an imido neopentylidene species, possibly $W(NMe\text{–}acid)(CHCMe_3)(CH_2CMe_3)X$. This postulate is reasonable since several representative imido alkylidene complexes we describe here are the products of α-H abstraction reactions and since several of them will metathesize olefins, albeit slowly.[17]

An interesting question is whether oxo alkyl complexes will also be successful precursors to oxo alkylidene complexes. (Oxo alkylidene complexes are believed to be one important type of olefin metathesis catalyst.[4c,18,19]) Oxo complexes of the type $W(O)(Neo)_3X$ (X = halide or alkoxide) have been prepared and were found to decompose in the presence of light or Lewis acids to give observable, but as yet unisolated, oxo alkylidene complexes.[4c] Therefore, α-H abstraction reactions do occur in oxo alkyl complexes and there is a good possibility that they can be controlled. A potentially complicating feature of oxo chemistry that should make it more difficult to control than imido chemistry is the relative accessibility of the oxo ligand to Lewis acids, including another metal (to give μ-oxo complexes). Primarily for steric reasons, imido ligands, especially *tert*-butylimido ligands, should not bind Lewis acids or bridge two tungsten centers as readily as oxo ligands. A recent structural determination of $W(NCMe_3)_2Me_2$ demonstrates that a *tert*-butylimido ligand *may* bridge between tungsten centers.[4f] Note, however, that the basicity of this imido ligand is significantly increased (i.e., it is bent) as a result of the presence of the other. An imido ligand in an imido alkylidene complex should still be able to donate its π electrons to the metal without competition from the alkylidene ligand for the three d orbitals of π-type symmetry.

The low values for J_{CH_α} (105–115 Hz) listed in Table I are indicative of some distortion of the neopentylidene ligand toward a large $W{=}C_\alpha{-}C_\beta$ angle.[2] Although no imido alkylidene complex has been studied by single-crystal X-ray diffraction, we can propose that the correlation of $\angle W{=}C_\alpha{-}C_\beta$ with J_{CH_α} in the imido alkylidene complex is similar to what it is in $W(O)(CHCMe_3)(PMe_3)_2Cl_2$, where $J_{CH_\alpha} = 121$ Hz and $\angle W{=}C_\alpha{-}C_\beta = 140°$.[8] The fact that the values for J_{CH_α} in several oxo complexes are, in three out of the four cases noted in Table I, slightly higher than the values for J_{CH_α} in the analogous imido complexes could be taken as evidence that the neopentylidene ligand is slightly more distorted in the imido complexes than in the oxo complexes. Unfortunately, it is not yet known to what extent relatively small differences in the degree of distortion of the alkylidene ligand might correlate with rates and/or selectivities of reactions of alkylidene complexes, e.g., in the olefin metathesis reaction.

Experimental Section

All experiments were done under nitrogen either by standard Schlenk techniques or in a Vacuum Atmospheres HE 43-2 drybox. Solvents were rigorously purified and dried under N_2 by standard techniques and transferred into the drybox without exposure to air. $WOCl_4$ was prepared either by the reaction of WO_3 with S_2Cl_2[6] or by the method described below. $Ta(CHCMe_3)L_2Cl_3$ (L = PMe_3, PEt_3[13]), PMe_3,[20] $LiCH_2CMe_3$,[10] $ZnMe_2$,[21] and $Zn(CH_2CMe_3)_2$[10] were prepared by published methods. $Zn(CH_2SiMe_3)_2$ and $LiCH_2SiMe_3$ were prepared in a manner analogous to that described for $Zn(CH_2CMe_3)_2$ and $LiCH_2CMe_3$, respectively. Tetraethylammonium chloride was purchased from standard sources and dried in vacuo (50 μm) at 90–100 °C for at least 24 h.

^{13}C NMR spectra are reported in the proton-gated decoupled mode (unless otherwise noted). If coupling to phosphorus and/or tungsten can be observed in the proton broad-band decoupled spectrum, than it is reported as part of the data for the ^1H-gated decoupled spectrum even though in this mode long-range C–H coupling usually obscures small C–P couplings. All ^{31}P NMR spectra were run at ~30 °C and 36.2 MHz. All chemical shifts are reported in ppm downfield from Me_4Si (^1H or ^{13}C) or 30% H_3PO_4 (^{31}P).

Preparation of $WOCl_4$. Finely ground WCl_6 (54.5 g, 0.14 mol) was suspended in dichloromethane (350 mL), and the mixture was stirred vigorously while a dichloromethane solution (40 mL) of Me_3SiOMe (14.3 g, 0.14 mol) was added dropwise over a 4-h period. The mixture was filtered, and the orange precipitate was washed with pentane and dried in vacuo. The dichloromethane was removed from the filtrate in vacuo, leaving a red-orange solid. This material along with the above orange precipitate was sublimed at 80 °C (<0.1 μm) to give 42.7 g (91%) of pure, crystalline $WOCl_4$. This preparation is the scaled-up version of an observation made by Handy *et al.*[16a]

Preparation of $W(NPh)Cl_4(Et_2O)$. Freshly distilled phenyl isocyanate (7.0 g, 58.8 mmol) was added to an octane suspension (250 mL) of finely ground $WOCl_4$ (20.0 g, 58.5 mmol). The mixture was heated to reflux while it was stirred until CO_2 evolution had ceased. A green powder was filtered off, washed with pentane (50 mL), and dried in vacuo to give 23.2 g of crude $[W(NPh)Cl_4]_x$. This material was dissolved in ether (200 mL), and the solution was filtered off and concentrated in vacuo to give green crystals (25.9 g, 90%): ^1H NMR ($CDCl_3$, 60 MHz) δ 7.95–7.38 (m, 5, NPh), 5.28 (q, 4, $J_{HH} \approx 7$ Hz, $O(C\mathit{H}_2CH_3)_2$), 1.55 (t, 6, $J_{HH} \approx 7$ Hz, $O(CH_2C\mathit{H}_3)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22.5 MHz), δ 149.6 (NPh ipso), 134.6, 131.4, and 127.2 (NPh), 66.2 ($\mathit{C}H_2CH_3$), 13.2 ($CH_2\mathit{C}H_3$).

Pure $[W(NPh)Cl_4]_x$ can be prepared by removing the ether from $W(NPh)Cl_4(Et_2O)$ in vacuo (0.1 μm, 25 °C, 24 h).

Preparation of $W(NPh)(OCMe_3)_4$. An ether solution (200 mL) of $W(NPh)Cl_4(Et_2O)$ (12.68 g, 25.8 mmol) was cooled to 0 °C, and $LiOCMe_3$ (8.27 g, 103.3 mmol) in 120 mL of ether was added rapidly (2 min). The reaction mixture was stirred for 12 h and filtered through Celite. The salts were washed with 100 mL of pentane. The solvent was removed in vacuo, leaving yellow crystals, which were recrystallized from pentane (total yield 13.67 g, 93%): ^1H NMR ($CDCl_3$, 250 MHz) δ 7.37–6.93 (m, 5, NPh), 1.40 (s, 36, $OCMe_3$); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 154.6 (br s, NPh ipso), 127.9, 126.3, and 125.2 (NPh), 81.4 (br s, $O\mathit{C}Me_3$), 31.4 (q, $J_{CH} = 126$ Hz, $OC\mathit{Me}_3$); mass spectrum parent ion at *m/e* 567; mol wt (CH_2Cl_2, differential vapor pressure) calcd 567, found 546. The product may be sublimed (125 °C, <1 μm), but yields are typically 20% lower.

Preparation of $[Et_4N][W(NPh)Cl_5]$. Et_4NCl (2.04 g, 12.3 mmol) was added to a well-stirred solution of $W(NPh)Cl_4(Et_2O)$ (6.0 g, 12.2 mmol) in 40 mL of dichloromethane. Some product crystallized out immediately. After 5 min the solution was cooled to −30 °C. Two crops of lime green flakes were collected by filtration, washed with pentane, and dried in vacuo (7.10 g, 100%).

Preparation of $[Et_4N][W(NPh)(OCMe_3)_2Cl_3]$ and $[Et_4N][W(NPh)(OCMe_3)Cl_4]$. $W(NPh)Cl_4(Et_2O)$ (2.0 g, 4.1 mmol) and Et_4NCl (1.35 g, 8.2 mmol) were codissolved in 40 mL of dichloromethane, and after a few minutes $W(NPh)(OCMe_3)_4$ (2.31 g, 4.1 mmol) was added. After 8 h the orange solution was filtered and concentated in vacuo. Addition of pentane and cooling to −30 °C afforded four crops of yellow microcrystals of $[Et_4N][W(NPh)(OCMe_3)_2Cl_3]$ (5.1 g, 95%): ^1H NMR ($CDCl_3$, 60 MHz) δ 7.5–7.1 (m, 5, NPh), 3.3 (br m, 8, $N(C\mathit{H}_2CH_3)_4$), 1.5 (s, 18, $OC\mathit{Me}_3$), 1.3 (br m, 12, $N(CH_2C\mathit{H}_3)_4$).

A similar procedure employing 0.63 g (3.8 mmol) of Et_4NCl, 1.4 g (2.9 mmol) of $W(NPh)Cl_4(Et_2O)$, 0.54 g (0.95 mmol) of $W(NPh)(OCMe_3)_4$ in 40 mL of dichloromethane gave 2.35 g (100%) of brick red $[Et_4N][W(NPh)(OCMe_3)Cl_4]$ upon removing the solvent from the reaction mixture in vacuo: ^1H NMR ($CDCl_3$, 60 MHz) δ 7.7–6.8 (m, 5, NPh), 3.2 (br, 8, $N(C\mathit{H}_2CH_3)_4$), 1.6 (s, 9, $OC\mathit{Me}_3$), 1.2 (br, 12, $N(CH_2C\mathit{H}_3)_4$). $[Et_4N][W(NPh)(OCMe_3)Cl_4]$ can be recrystallized at −30 °C from a saturated CH_2Cl_2 solution.

Preparation of $W(NPh)(CHCMe_3)(PMe_3)_2Cl_2$. $W(NPh)(OCMe_3)_4$ (9.4 g, 16.6 mmol) and $Ta(CHCMe_3)(PMe_3)_2Cl_3$ (8.4 g, 16.6 mmol) were dissolved in 75 mL of ether. After 12 h pale orange crystals were collected by filtration, washed with pentane, and dried in vacuo (5.5 g). Addition of the washings to the mother liquor precipitated another 1.92 g of product, which may be recrystallized from minimal toluene by adding pentane and cooling to −30 °C (total yield 7.42 g, 79%): ^1H NMR ($CDCl_3$, 250 MHz) δ 10.92 (t, 1, $^3J_{HP} = 4.4$ Hz, $C\mathit{H}CMe_3$), 7.51–7.12 (m, 5, NPh), 1.68 (t, 18, $^2J_{HP} = 4.6$ Hz, PMe_3), 1.30 (s, 9, $CHC\mathit{Me}_3$); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 307.0 (d, $J_{CH} = 123$ Hz, $^2J_{CP} = 11$ Hz, $\mathit{C}HCMe_3$), 154.8 (s, NPh ipso), 128.2, 127.2, and 126.4 (NPh), 46.4 (s, $CH\mathit{C}Me_3$), 34.3 (q, $J_{CH} = 125$ Hz, $CHC\mathit{Me}_3$), 16.2 (q t, $J_{CH} = 130$ Hz, $J_{CP} = 15$ Hz, PMe_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −8.1 (s, $J_{PW} = 288$ Hz). Anal. Calcd for $WC_{17}H_{33}Cl_2NP_2$: C, 35.94; H, 5.85. Found: C, 36.25; H, 5.95.

The solvent from the above mother liquors was removed in vacuo, leaving a sticky orange solid. Sublimation of this material (80 °C, 1 μm)

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gave 5 g (60%) of pale yellow, crystalline [Ta(OCMe$_3$)$_4$Cl]$_2$.[22]

Preparation of W(NPh)(CHCMe$_3$)(PEt$_3$)$_2$Cl$_2$. The procedure is the same as that for W(NPh)(CHCMe$_3$)(PMe$_3$)$_2$Cl$_2$ starting with Ta(CHCMe$_3$)(PEt$_3$)$_2$Cl$_3$. This derivative does not crystallize from the reaction mixture until the solution is concentrated and cooled to −30 °C: ^{1}H NMR (C$_6$D$_6$, 90 MHz) δ 11.92 (t, 1, $^3J_{HP}$ = 3.9 Hz, C*H*CMe$_3$), 7.90–6.91 (m, 5, NPh), 1.99 (m, 12, P(C*H*$_2$CH$_3$)$_3$), 1.35 (s, 9, CHC*Me*$_3$), 0.93 (m, 18, P(CH$_2$C*H*$_3$)$_3$); ^{13}C NMR (C$_6$D$_6$, 22.5 MHz) δ 303.8 (d, J_{CH} = 119 Hz, $^2J_{CP}$ = 11 Hz, *C*HCMe$_3$), 155.3 (s, NPh ipso), 128.3, 126.2, and 125.6 (NPh), 46.2 (s, CH*C*Me$_3$), 34.7 (q, J_{CH} = 126 Hz, CHC*Me*$_3$), 17.4 (tt, J_{CH} = 127 Hz, J_{CP} = 13 Hz, P(*C*H$_2$CH$_3$)$_3$), 7.9 (q, J_{CH} = 127 Hz, P(CH$_2$*C*H$_3$)$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 15.7 (s, J_{PW} = 273 Hz). Anal. Calcd for WC$_{23}$H$_{45}$Cl$_2$NP$_2$: C, 42.35; H, 6.95. Found: C, 41.97; H, 7.08.

Preparation of [W(NPh)(CHCMe$_3$)(PMe$_3$)$_2$Cl][AlCl$_4$]. W(NPh)(CHCMe$_3$)(PMe$_3$)$_2$Cl$_2$ (1.0 g, 1.8 mmol) was dissolved in 15 mL of dichloromethane, and AlCl$_3$ (0.24 g, 1.8 mmol) was added. The mixture was stirred for 0.5 h and filtered through Celite. Decreasing the volume in vacuo and cooling to −30 °C gave 1.18 g (95%) of bright yellow crystals: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 10.39 (br s, 1, C*H*CMe$_3$), 7.46–7.34 (m, 5, NPh), 1.72 (t, 18, $^2J_{HP}$ = 4.8 Hz, PMe$_3$), 1.32 (s, 9, CHC*Me*$_3$); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 303.4 (d, J_{CH} = 106 Hz, $^2J_{CP}$ = 8 Hz, *C*HCMe$_3$), 153.3 (s, NPh ipso), 129.7, 129.5, and 126.8 (NPh), 48.6 (s, CH*C*Me$_3$), 31.4, (q, J_{CH} = 127 Hz, CHC*Me*$_3$), 14.9 (qt, J_{CH} = 132 Hz, J_{CP} = 15 Hz, PMe$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 6.5 (s, J_{PW} = 273 Hz); conductivity (CH$_2$Cl$_2$, 1.13 × 10^{-3} M) 48 cm^{-1} M^{-1} Ω^{-1}. Anal. Calcd for WC$_{17}$H$_{33}$AlCl$_5$NP$_2$: C, 29.11; H, 4.74. Found: C, 28.99; H, 5.05.

Preparation of [W(NPh)(CHCMe$_3$)(PEt$_3$)$_2$Cl][AlCl$_4$]. This product was prepared from W(NPh)(CHCMe$_3$)(PEt$_3$)$_2$Cl$_2$ by a procedure similar to that described above: ^{1}H NMR (CDCl$_3$, 60 MHz) δ 9.6 (s, 1, C*H*CMe$_3$), 7.2 (br s, 5, NPh), 2.0 (m, 12, P(C*H*$_2$CH$_3$)$_3$), 1.4 (s, 9, CHC*Me*$_3$), 1.1 (m, 18, P(CH$_2$C*H*$_3$)$_3$); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 300.5 (d, J_{CH} = 106 Hz, $^2J_{CP}$ = 8 Hz, *C*HCMe$_3$), 153.8 (s, NPh ipso), 129.3, 128.4, and 126.9 (NPh), 48.6 (s, CH*C*Me$_3$), 31.8 (q, J_{CH} = 126 Hz, CHC*Me*$_3$), 16.4 (tt, J_{CH} = 127 Hz, J_{CP} = 13 Hz, P(*C*H$_2$CH$_3$)$_3$), 8.0 (q, J_{CH} = 125 Hz, P(CH$_2$*C*H$_3$)$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 37.2 (s, J_{PW} = 264 Hz).

Preparation of [W(NPh)(CHCMe$_3$)(PMe$_3$)$_2$Me][AlMe$_2$Cl$_2$]. AlMe$_3$ (640 μL, 6.7 mmol) was added to a stirred toluene/pentane solution (30 mL/5 mL) of W(NPh)(CHCMe$_3$)(PMe$_3$)$_2$Cl$_2$ (3.48 g, 6.1 mmol). An orange solid precipitated immediately, and the mixture was cooled to 30 °C. Pale orange crystals were isolated by filtration and washed with toluene (20 mL) and pentane (3.66 g, 93%): ^{1}H NMR (CDCl$_3$, 250 MHz) δ 8.40 (br s, 1, C*H*CMe$_3$), 7.36–7.16 (m, 5, NPh), 1.68 (t, 18, $^2J_{HP}$ = 4.0 Hz, PMe$_3$), 1.28 (s, 9, CHC*Me*$_3$), 0.85 (t, 3, $^3J_{HP}$ = 16.5 Hz, WMe), −0.68 (s, 6, AlMe$_2$Cl$_2$); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 302.8 (d, J_{CH} = 106 Hz, J_{CP} = 9 Hz, *C*HCMe$_3$), 154.3 (s, NPh ipso), 129.2, 127.9, and 126.2 (NPh), 47.7 (s, CH*C*Me$_3$), 38.0 (qt, J_{CH} = 119 Hz, $^2J_{CP}$ = 9 Hz, WMe), 31.1 (q, J_{CH} = 125 Hz, CHC*Me*$_3$), 15.0 (qt, J_{CH} = 132 Hz, J_{CP} = 15 Hz, PMe$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$) δ −8.3 (s, J_{PW} = 286 Hz); conductivity (CH$_2$Cl$_2$, 8.93 × 10^{-4} M) 45 cm^{-1} M^{-1} Ω^{-1}. Anal. Calcd for WC$_{20}$H$_{42}$AlCl$_2$NP$_2$: C, 37.52; H, 6.61. Found: C, 37.06;, H, 6.74.

Preparation of [W(NPh)(CHCMe$_3$)(PEt$_3$)$_2$Me][AlMe$_2$Cl$_2$]. A toluene solution (15 mL) of W(NPh)(CHCMe$_3$)(PEt$_3$)$_2$Cl$_2$ (2.0 g, 3.1 mmol) was treated with AlMe$_3$ (295 μL, 3.1 mmol). An orange oil formed immediately. Pentane was added (6 mL), and the solution was shaken until the oil crystallized. The solution was cooled to −30 °C, and the pale orange crystals were filtered off, washed with pentane, and dried in vacuo (2.12 g, 95%): ^{1}H NMR (CDCl$_3$, 250 MHz) δ 7.84 (s, 1, C*H*CMe$_3$), 7.38–7.22 (m, 5, NPh), 1.99 (m, 12, P(C*H*$_2$CH$_3$)$_3$), 1.31 (s, 9, CHC*Me*$_3$), 1.13 (m, 18, P(CH$_2$C*H*$_3$)$_3$), 0.76 (t, 3, $^3J_{HP}$ = 15.0 Hz, WMe), −0.65 (s, 6, AlMe$_2$Cl$_2$); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 300.8 (d, J_{CH} = 105 Hz, $^2J_{CP}$ = 8 Hz, *C*HCMe$_3$), 154.9 (s, NPh ipso), 129.0, 128.1, and 126.9 (NPh), 48.3 (s, CH*C*Me$_3$), 35.5 (qt, J_{CH} = 119 Hz, $^2J_{CP}$ = 9 Hz, WMe), 31.7 (q, J_{CH} = 125 Hz, CHC*Me*$_3$), 16.9 (tt, J_{CH} = 130 Hz, J_{CP} = 14 Hz, P(*C*H$_2$CH$_3$)$_3$), 8.1 (q, J_{CH} = 125 Hz, P(CH$_2$*C*H$_3$)$_3$), −5.7 (br, AlMe$_2$Cl$_2$); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 32.4 (s, J_{PW} = 254 Hz).

Preparation of W(NPh)(CHCMe$_3$)(PMe$_3$)(OCMe$_3$)$_2$. LiOCMe$_3$ (0.35 g, 4.4 mmol) was added to a stirred solution of W(NPh)(CHCMe$_3$)(PMe$_3$)$_2$Cl$_2$ (1.25 g, 2.2 mmol) in 10 mL of THF. After 24 h the THF was removed in vacuo, leaving a yellow solid, which was extracted with pentane (40 mL). The mixture was filtered, and the pentane was removed in vacuo. The yellow solid was dissolved in ether, and the solution was concentrated in vacuo until crystallization began. At this point the sample was stored at −30 °C for 12 h to give 0.9 g of product. The mother liquor was further concentrated to give another 0.1 g (total 1.0 g, 79%): ^{1}H NMR (toluene-*d*$_8$, 250 MHz, 0 °C) δ 10.17 (d, 1, $^3J_{HP}$ = 3.4 Hz, C*H*CMe$_3$), 7.08–6.77 (m, 5, NPh), 1.64 (s, 9, OCMe$_3$), 1.47 (s, 9, OCMe$_3$), 1.31 (s, 9, CHC*Me*$_3$), 0.51 (d, 9, $^2J_{HP}$ = 8.3 Hz, PMe$_3$); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 265.3 (d, J_{CH} = 114 Hz, *C*HCMe$_3$), 156.9 (s, NPh ipso), 128.2, 125.6, and 122.6 (NPh), 76 (br s, O*C*Me$_3$), 43.8 (s, CH*C*Me$_3$), 34.0 (q, J_{CH} = 125 Hz, CHC*Me*$_3$), 32.5 (q, J_{CH} = 125 Hz, OC*Me*$_3$), 16.2 (qd, J_{CH} = 130 Hz, J_{CP} = 24 Hz, PMe$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 1.2 (s, J_{PW} = 269 Hz). Anal. Calcd for WC$_{22}$H$_{42}$NO$_2$P: C, 46.57; H, 7.46. Found: C, 46.67; H, 7.48.

Preparation of W(NPh)(CHCMe$_3$)(PEt$_3$)(OCMe$_3$)$_2$. W(NPh)(CHCMe$_3$)(PEt$_3$)$_2$Cl$_2$ (1.58 g, 2.4 mmol) was dissolved in ether, and the solution was cooled to −30 °C. LiOCMe$_3$ (0.39 g, 4.8 mmol) was added in one portion and the temperature allowed to rise to ambient. After 16 h the reaction mixture was filtered and the ether was removed in vacuo. The resulting sticky solid was extracted with pentane. The mixture was filtered, concentrated, and cooled to −30 °C to give orange crystals (1.20 g, 81%): ^{1}H NMR (toluene-*d*$_8$, 250 MHz, −30 °C) δ 10.27 (br s, 1, C*H*CMe$_3$), 7.25–6.78 (m, 5, NPh), 1.69 (s, 9, OCMe$_3$), 1.53 (s, 9, OCMe$_3$), 1.47–1.36 (m under singlet at 1.43, 15, P(C*H*$_2$CH$_3$)$_3$ and CHC*Me*$_3$), 0.81 (m, 9, P(CH$_2$C*H*$_3$)$_3$); ^{13}C NMR (toluene-*d*$_8$, 62.83 MHz) δ 265.87 (d, J_{CH} ≈ 111 Hz, *C*HCMe$_3$), 157.72 (br s, NPh ipso), 130.1–123.3 (overlapping resonances of NPh and toluene-*d*$_8$), 76.85 (s, O*C*Me$_3$), 76.11 (s, O*C*Me$_3$), 43.55 (s, CH*C*Me$_3$), 34.71 (q, J_{CH} = 119.2 Hz, CHC*Me*$_3$), 32.91 (q, J_{CH} = 122.1 Hz, OC*Me*$_3$), 17.20 (td, J_{CH} = 127.9 Hz, J_{CP} = 20.3 Hz, P(*C*H$_2$CH$_3$)$_3$), 8.72 (q, J_{CH} = 127.9 Hz, P(CH$_2$*C*H$_3$)$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 32.1 (s, J_{PW} = 261 Hz).

Preparation of W(NPh)(CHCMe$_3$)(PEt$_3$)Cl$_2$. CuCl (80 mg, 0.8 mmol) was added to a vigorously stirred solution of W(NPh)(CHCMe$_3$)(PEt$_3$)$_2$Cl$_2$ (0.50 g, 0.77 mmol) in 10 mL of toluene. After 6 h the solvent was removed in vacuo until a large fraction of white CuCl(PEt$_3$)$_x$ precipitated. The CuCl(PEt$_3$)$_x$ was then filtered off, and pentane was added to the filtrate just short of cloudiness. Cooling to −30 °C yielded 0.35 g (85%) of orange crystals: ^{1}H NMR (C$_6$D$_6$, 60 MHz) δ 10.8 (d, 1, $^3J_{HP}$ = 3 Hz, C*H*CMe$_3$), 7.2 (br, 5, NPh), 2.1 (m, 6, P(C*H*$_2$CH$_3$)$_3$), 1.3 (s, 9, CHC*Me*$_3$), 1.1 (m, 9, P(CH$_2$C*H*$_3$)$_3$); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 300.5 (d, J_{CH} = 106 Hz, $^2J_{CP}$ = 8 Hz, *C*HCMe$_3$), 153.7 (s, NPh ipso), 129.3, 128.4, and 126.9 (NPh), 48.6 (s, CH*C*Me$_3$), 31.8 (q, J_{CH} = 127 Hz, CHC*Me*$_3$), 16.4 (td, J_{CH} = 127 Hz, J_{CP} = 14 Hz, P(*C*H$_2$CH$_3$)$_3$), 8.0 (q, J_{CH} = 125 Hz, P(CH$_2$*C*H$_3$)$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 37.2 (s, J_{PW} = 264 Hz).

Preparation of W(NPh)(CCMe$_3$)(AlMe$_2$Cl)(PMe$_3$)$_2$Cl. [W(NPh)(CHCMe$_3$)(PMe$_3$)$_2$Me][AlMe$_2$Cl$_2$] (3.62 g, 5.65 mmol) was suspended in toluene (40 mL), and the mixture was heated to 50 °C. Gas evolved steadily. After 14 h at 50 °C the now homogeneous, dark orange solution was filtered and the toluene filtrate was concentrated in vacuo until crystallization began. Cooling to −30 °C gave 2.1 g of orange crystals. The mother liquor was further concentrated. Pentane was added, and the solution was cooled to −30 °C to give another 1.1 g of product (total yield 91%): ^{1}H NMR (C$_6$D$_6$, 250 MHz) δ 7.26–6.86 (m, 5, NPh), 1.42 (t, 18, $^2J_{HP}$ = 4.4 Hz, PMe$_3$), 0.83 (s, 9, CCMe$_3$), −0.27 (s, 6, AlMe$_2$); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 309.4 (s, $^2J_{CP}$ = 12 Hz, *C*CMe$_3$), 163.7 (s, NPh ipso), 127.4, 123.2, and 120.6 (NPh), 50.9 (s, C*C*Me$_3$), 31.6 (q, J_{CH} = 125 Hz, CC*Me*$_3$), 16.5 (qt, J_{CH} = 132 Hz, J_{CP} = 15 Hz, PMe$_3$), −6.9 (q, J_{CH} = 116 Hz, AlMe$_2$); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 14.1 (s, J_{PW} = 298 Hz). Anal. Calcd for WC$_{19}$H$_{38}$AlCl$_2$NP$_2$: C, 36.56; H, 6.14. Found: C, 36.68; H, 6.06.

Preparation of W(NPh)(CH$_2$CMe$_3$)$_3$Cl. A solution of W(NPh)Cl$_4$(Et$_2$O) (8.95 g, 18.2 mmol) in 200 mL of ether was cooled to −78 °C and stirred vigorously while 3 equiv of NeoMgCl (1.34 M in ether) was added rapidly. The reaction was warmed to room temperature slowly. After 24 h at room temperature the mixture was filtered through Celite and the magnesium salts were washed thoroughly with ether. The solvent was removed from the filtrate in vacuo. The resulting dark oily solid was dissolved in pentane and the solution treated with activated charcoal. Filtration and removal of the pentane in vacuo left a dark solid that was sublimed at 80–90 °C (1 μm) to give 4.32 g (45%) of pale yellow crystals: ^{1}H NMR (C$_6$D$_6$, 250 MHz) δ 7.56–6.88 (m, 5, NPh), 2.42 (s, 6, $^2J_{HW}$ = 9.6 Hz, C*H*$_2$CMe$_3$), 1.13 (s, 27, CH$_2$C*Me*$_3$); ^{13}C NMR (C$_6$D$_6$, 22.5 MHz) δ 153.7 (s, NPh ipso), 128.8, 128.0, and 127.5 (NPh), 92.9 (t, J_{CH} = 121 Hz, J_{CW} = 79.1 Hz, *C*H$_2$CMe$_3$), 36.2 (s, CH$_2$*C*Me$_3$), 34.3 (q, J_{CH} = 125.2 Hz, CH$_2$C*Me*$_3$); mol wt (CH$_2$Cl$_2$, differential vapor pressure) calcd 524, found 522. Anal. Calcd for WC$_{21}$H$_{38}$ClN: C, 48.15; H, 7.31. Found: C, 48.37; H, 7.20.

Preparation of W(NPh)(CH$_2$CMe$_3$)$_3$Br. A solution of W(NPh)(CH$_2$CMe$_3$)$_3$(OCMe$_3$) (1.0 g, 1.8 mmol; see later preparation) in toluene (20 mL) was cooled to 0 °C. HBr gas (50 mL, 2.2 mmol) was added above it in a closed system. After the reaction mixture was stirred for 0.5 h, the toluene was removed in vacuo. The resulting orange oil was extracted with pentane. Activated charcoal was added, and the mixture

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[22] Kapoor, R. N.; Prakash, S.; Kapoor, P. N. *Indian J. Chem.* **1967**, *5*, 442–443.

was filtered. Pure $W(NPh)(CH_2CMe_3)_3Br$ (0.95 g, 94%) was obtained as a tan solid after filtration and removal of the pentane in vacuo. $W(NPh)(CH_2CMe_3)_3Br$ may be recrystallized from ether by adding acetonitrile and cooling to -30 °C. ^1H NMR (C_6D_6, 250 MHz) δ 7.53 (d, 2, $^3J_{H_oH_m}$ = 8.8 Hz, NPh ortho), 7.03 (t, 2, $J_{H_{obsd}}$ = 7.8 Hz, NPh meta), 6.88 (t, 1, $^3J_{H_pH_m}$ = 7.3 Hz, NPh para), 2.51 (s, 6, $^2J_{HW}$ = 9.8 Hz, CH_2CMe_3), 1.13 (s, 27, CH_2CMe_3); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 153.2 (s, NPh ipso), 128.8, 128.4, and 127.9 (NPh), 95.8 (t, J_{CH} = 125.2 Hz, J_{CW} = 79.1 Hz, CH_2CMe_3), 36.6 (s, CH_2CMe_3), 34.5 (q, J_{CH} = 125.2 Hz, CH_2CMe_3).

Preparation of $W(NPh)(CH_2CMe_3)_3(O_2CCF_3)$. $W(NPh)(CH_2CMe_3)_3(O_2CCF_3)$ is prepared by a procedure analogous to that used to prepare $W(NPh)(CH_2CMe_3)_3Br$ above, with use of neat CF_3CO_2H: ^1H NMR (C_6D_6, 60 MHz) δ 7.5–6.9 (m, 5, NPh), 2.34 (s, 6, $^2J_{HW} \approx 9$ Hz, CH_2CMe_3), 1.18 (s, 27, CH_2CMe_3); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 160.4 (q, J_{CF} = 40 Hz, O_2CCF_3), 154.5 (s, NPh ipso), 129.0–127.0 (NPh), 95.9 (t, J_{CH} = 122 Hz, J_{CW} = 81.3 Hz, CH_2CMe_3), 36.8 (s, CH_2CMe_3), 33.7 (q, J_{CH} = 125 Hz, CH_2CMe_3).

Preparation of $W(NPh)(CH_2CMe_3)_3(OCMe_3)$. A 1.19 M solution of Me_3CCH_2MgCl (19 mL) was added dropwise to a stirred solution of $W(NPh)(OCMe_3)_4$ (4.18 g, 7.4 mmol) in 150 mL of ether at 0 °C. After 12 h the reaction was filtered and the salts were washed with pentane until the washings were colorless. The solvent was removed from the filtrate in vacuo, and the tan-colored residue was sublimed at 85 °C and ~0.1 μm to give 3.0 g (73%) of yellow crystals in two crops: ^1H NMR (C_6D_6, 250 MHz) δ 7.60 (d, 2, $^3J_{H_oH_m}$ = 8.6 Hz, NPh ortho), 7.24 (t, 2, $J_{H_{obsd}}$ = 7.3 Hz, NPh meta), 6.90 (t, 1, $^3J_{H_oH_m}$ = 7.3 Hz, NPh para), 1.94 (s, 6, $^2J_{HW}$ = 9.9 Hz, CH_2CMe_3), 1.58 (s, 9, $OCMe_3$), 1.17 (s, 27, CH_2CMe_3); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 157.3 (s, NPh ipso), 128.0, 127.2, and 123.7 (NPh), 80.9 (s, $OCMe_3$), 78.0 (t, J_{CH} = 124 Hz, J_{CW} = 85.0 Hz, CH_2CMe_3), 34.8 (s, CH_2CMe_3), 34.3 (q, J_{CH} = 124 Hz, CH_2CMe_3), 31.4 (q, J_{CH} = 125 Hz, $OCMe_3$). Anal. Calcd for $WC_{25}H_{47}NO$: C, 53.48; H, 8.44. Found: C, 53.41; H, 8.55.

Preparation of $W(NPh)(CH_2CMe_3)_2(OCMe_3)_2$. A solution of $[Et_4N][W(NPh)(OCMe_3)_2Cl_3]$ (2.0 g, 3.0 mmol) in dichloromethane (40 mL) was cooled to -30 °C, and a pentane solution (8 mL) of $Zn(Neo)_2$ (0.63 g, 3.0 mmol) was added dropwise with stirring. The reaction mixture was warmed to room temperature, stirred for 2 h, and filtered. The solvent was removed in vacuo. The residue was extracted with pentane, the mixture was filtered, and the pentane was removed in vacuo to give pure (by ^1H NMR) $W(NPh)(CH_2CMe_3)_2(OCMe_3)_2$ as a waxy yellow solid (1.48 g, 86%): ^1H NMR (toluene-d_8, 250 MHz, 0 °C) δ 7.43–6.82 (m, 5, NPh), 2.33 (d, 2, $^2J_{H_AH_B}$ = 8.8 Hz, $CH_AH_BCMe_3$), 2.02 (d, 2, $^2J_{H_AH_B}$ = 8.8 Hz, $CH_AH_BCMe_3$), 1.64 (s, 9, $OCMe_3$), 1.33 (s, 9, $OCMe_3$), 1.19 (s, 18, CH_2CMe_3); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 156.5 (s, NPh ipso), 128.4, 128.0, and 124.8 (NPh), 84.1 (t, J_{CH} = 127.5 Hz, J_{CW} = 90.1 Hz, CH_2CMe_3), 82.9 (br s, $OCMe_3$), 35.8 (s, CH_2CMe_3), 35.1 (q, J_{CH} = 125 Hz, CH_2CMe_3), 32.1 (q, J_{CH} = 125 Hz, $OCMe_3$). An analytical sample was obtained by recrystallization from ether by adding acetonitrile and cooling to -30 °C. Anal. Calcd for $WC_{24}H_{45}NO_2$: C, 51.16; H, 8.05. Found: C, 50.92; H, 7.78.

Preparation of $W(NPh)(CH_2CMe_3)_2(OCMe_3)Cl$. A solution of $[NEt_4][W(NPh)(OCMe_3)Cl_4]$ (1.0 g, 1.6 mmol) in 40 mL of dichloromethane was cooled to -30 °C, and $Zn(CH_2CMe_3)_2$ (0.32 g, 1.5 mmol) in pentane (5 mL) was added dropwise. After the reaction mixture was warmed to room temperature and stirred for 4 h, pentane (10 mL) was added and the mixture was filtered. The volatiles were then removed in vacuo. The oily residue was dissolved in pentane (10 mL), and this solution was treated with activated charcoal and filtered. The pentane was removed from the filtrate in vacuo, leaving a sticky yellow solid after drying in vacuo for several hours (0.61 g, 72%, pure by ^1H and ^{13}C NMR): ^1H NMR (C_6D_6, 270 MHz) δ 7.30 (d, 2, $^3J_{H_oH_m}$ = 8.8 Hz, NPh ortho), 7.09 (t, 2, $J_{H_{obsd}}$ = 7.8 Hz, NPh meta), 6.86 (t, 1, $^3J_{H_pH_m}$ = 7.3 Hz, NPh para), 3.23 (d, 2, $^2J_{H_AH_B}$ = 9.8 Hz, $^2J_{HW}$ = 10.3 Hz, $CH_AH_BCMe_3$), 2.27 (d, 2, $^2J_{H_AH_B}$ = 9.8 Hz, $^2J_{HW}$ = 9.5 Hz, $CH_AH_BCMe_3$), 1.27 (s, 9, $OCMe_3$), 1.15 (s, 18, CH_2CMe_3); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 153.7 (s, NPh ipso), 129.0, 128.3, and 128.0 (NPh), 92.5 (t, J_{CH} = 124 Hz, J_{CW} = 81.1 Hz, CH_2CMe_3), 88.4 (s, $OCMe_3$), 37.1 (s, CH_2CMe_3), 34.9 (q, J_{CH} = 125 Hz, CH_2CMe_3), 31.3 (q, J_{CH} = 127 Hz, $OCMe_3$).

Preparation of $W(NPh)(CHCMe_3)(CH_2CMe_3)_2$. (a) From $W(NPh)(Neo)_3Cl$ and Ph_3PCH_2. A solution of $W(NPh)(CH_2CMe_3)_3Cl$ (1.94 g, 3.7 mmol) in ether (40 mL) was cooled to -30 °C. Ph_3PCH_2 (1.07 g, 3.89 mmol) dissolved in 25 mL of ether was added dropwise to the stirred solution. After addition was complete, the reaction mixture was warmed to room temperature and stirred for 24 h. The mixture was filtered, and the $Ph_3PCH_3^+Cl^-$ was washed with pentane and dried in vacuo; yield 1.1 g (95%). The solvent was removed from the filtrate in vacuo, leaving a dark oil, which was distilled at 100–110 °C (0.1 μm) in a short-path apparatus to give 1.1 g (61%) of pure product as an orange-red oil: ^1H NMR (toluene-d_8, 250 MHz) δ 7.35–6.87 (m, 5, NPh), 6.61 (br s, 1, $^2J_{HW}$ = 9.3 Hz, $CHCMe_3$), 1.33 (br s, 4, $^2J_{HW}$ = 9.3 Hz, CH_2CMe_3), 1.21 (s, 9, $CHCMe_3$), 1.14 (s, 18, CH_2CMe_3) (the ^1H NMR spectrum was identical at -20 °C); ^{13}C NMR (toluene-d_8, 62.83 MHz) δ 246.1 (d, J_{CH} = 106 Hz, J_{CW} = 163 Hz, $CHCMe_3$), 157.5 (t, $^2J_{CH_o}$ = 9.0 Hz, $^2J_{CW}$ = 45 Hz, NPh ipso), 129.3–124.9 (overlapping resonances of NPh and toluene-d_8), 88.5 (t, J_{CH} = 112 Hz, J_{CW} = 95 Hz, CH_2CMe_3), 46.2 (s, $CHCMe_3$), 36.1 (s, CH_2CMe_3), 35.1 (q, J_{CH} = 124 Hz, CH_2CMe_3), 33.4 (q, $J_{CH} \approx$ 126 Hz, $CHCMe_3$); mol wt (differential vapor pressure, ether, 0 °C) calcd 487, found 413 at 4.6 × 10^{-2} M.

(b) From $W(NPh)(Neo)_3Cl$ and LiNeo. A pentane solution (30 mL) of $W(NPh)(CH_2CMe_3)_3Cl$ (1.52 g, 2.9 mmol) was cooled to -30 °C, and $LiCH_2CMe_3$ (0.23 g, 2.9 mmol) was added in solid portions while the mixture was stirred. The solution turned orange, and LiCl precipitated. The reaction was warmed to room temperature. After 8 h of stirring, the mixture was filtered and the pentane was removed in vacuo, leaving a red oil, which was 95% pure $W(NPh)(CHCMe_3)(CH_2CMe_3)_2$ by ^1H NMR.

Preparation of $W(\eta^5\text{-}C_5H_5)(NPh)(CHCMe_3)(CH_2CMe_3)$. A solution of $W(NPh)(CH_2CMe_3)_3Cl$ (3.0 g, 5.7 mmol) in THF (40 mL) was cooled to -30 °C. NaC_5H_5 (0.56 g, 6.3 mmol) was added as a solid, and the solution was warmed to room temperature. After 36 h of stirring, the reaction mixture was filtered and the THF removed from the filtrate in vacuo. The resulting dark oil was extracted with pentane, and activated charcoal was added. The mixture was filtered, and the orange filtrate was concentrated and cooled to -30 °C to give 2.2 g of yellow crystals (80%): ^1H NMR (C_6D_6, 250 MHz) δ 9.81 (s, 1, $CHCMe_3$), 7.12–6.85 (m, 5, NPh), 5.37 (s, 5, C_5H_5), 2.21 (d, 1, $^2J_{H_AH_B}$ = 13.6 Hz, $^2J_{HW}$ = 9.6 Hz, $CH_AH_BCMe_3$), 2.03 (d, 1, $^2J_{H_BH_A}$ = 13.6 Hz, $^2J_{HW}$ = 9.6 Hz, $CH_AH_BCMe_3$), 1.36 (s, 9, CMe_3), 1.19 (s, 9, CMe_3); ^{13}C NMR (C_6D_6, 62.83 MHz) δ 268.7 (d, J_{CH} = 117.4 Hz, $CHCMe_3$), 157.9 (s, NPh ipso), 128.6, 125.5, and 124.5 (NPh), 101.8 (d, J_{CH} = 178.4 Hz, C_5H_5), 46.5 (s, $CHCMe_3$), 36.7 (s, CH_2CMe_3), 34.3 (q, J_{CH} = 124.4 Hz, CMe_3), 33.8 (q, J_{CH} = 124.4 Hz, CMe_3) (the CH_2CMe_3 resonance, which was never observed in the ^{13}C NMR spectra, is believed to lie under the CMe_3 resonances). Anal. Calcd for $WC_{21}H_{31}N$: C, 52.40; H, 6.49. Found: C, 52.67; H, 6.74.

Preparation of $W(\eta^5\text{-}C_5H_5)(NPh)(CH_2CMe_3)_2Cl$. A pentane solution (40 mL) of $W(\eta^5\text{-}C_5H_5)(NPh)(CHCMe_3)(CH_2CMe_3)$ (0.74 g, 1.5 mmol) was cooled to -30 °C, and HCl gas (34 mL, 15 mmol) was added by syringe. A yellow powder precipitated immediately. After 15 min the yellow powder was filtered off and dissolved in 10 mL of toluene. Addition of pentane followed by cooling to -30 °C gave orange, flaky crystals (0.64 g, 80%): ^1H NMR ($CDCl_3$, 250 MHz, -40 °C) δ 7.35–7.11 (m, 5, NPh), 6.16 (s, 5, C_5H_5), 2.95 (d, 2, $^2J_{H_AH_B}$ = 12.9 Hz, $CH_AH_BCMe_3$), 2.19 (d, 2, $^2J_{H_BH_A}$ = 12.9 Hz, $^2J_{HW}$ = 10.3 Hz, $CH_AH_BCMe_3$), 1.26 (s, 18, CH_2CMe_3); $^{13}C\{^1H\}$ NMR (toluene-d_8, 22.5 Hz, -10 °C) δ 158.2 (NPh ipso), 130–124 (NPh), 106.1 (C_5H_5), 67.9 (CH_2CMe_3), 38.8 (CH_2CMe_3), 35.7 (CH_2CMe_3). Anal. Calcd for $WC_{21}H_{33}NCl$: C, 48.71; H, 6.42. Found: C, 46.56; H, 5.51. The analysis value is presumably low because the product is not stable at room temperature. It should be stored at ca. -30 °C.

Preparation of $W(NPh)(CHCMe_3)(PMe_3)_2Cl_2$ from $W(NPh)(CH_2CMe_3)_3Cl$ and Me_3PHCl. Me_3PHCl (0.11 g, 0.95 mmol) and PMe_3 (0.27 mL, 2.8 mmol) were added to a chloroform solution (8 mL) of $W(NPh)(CH_2CMe_3)_3Cl$ (0.50 g, 0.95 mmol). The mixture was stirred and heated to 60 °C in a glass bomb for 24 h. Filtration, followed by removal of the solvent in vacuo left an orange solid, which was recrystallized from toluene at -30 °C (0.35 g, 65%).

Preparation of $W(NPh)(CHCMe_3)(py)_2Cl_2$. A solution containing $W(NPh)(CH_2CMe_3)_3Cl$ (0.50 g, 0.95 mmol), py·HCl (0.11 g, 0.95 mmol), and pyridine (0.54 mL, 6.7 mmol) in chloroform (6 mL) was heated at 60 °C for 48 h. The volatiles were then removed in vacuo. The red residue was extracted with a 1:1 mixture of toluene and dichloromethane, and the extract was filtered and concentrated in vacuo. Pentane was added, and the mixture was cooled to -30 °C to give 0.40 g of yellow crystals (73%): ^1H NMR ($CDCl_3$, 60 MHz) δ 11.3 (s, 1, $CHCMe_3$), 9.1 (br, 10, py), 7.1 (br, 5, NPh), 1.0 (s, 9, $CHCMe_3$); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 303.2 (d, J_{CH} = 121 Hz, $CHCMe_3$), 154.8, 152.2, and 138.5 (py), 128.0, 126.4, and 124.3 (NPh), 45.8 ($CHCMe_3$), 33.3 (q, J_{CH} = 125 Hz, $CHCMe_3$).

Preparation of $W(NPh)(CH_2SiMe_3)_3Cl$. $Zn(CH_2SiMe_3)_2$ (3.67 g, 15.3 mmol) in 10 mL of pentane was added dropwise to a vigorously stirred suspension of $W(NPh)Cl_4(Et_2O)$ (5.0 g, 10.2 mmol) in pentane. After 1 h the mixture was filtered and the zinc salts were washed with pentane (20 mL). The combined filtrates were concentrated in vacuo until crystallization began. The solution was cooled to -30 °C for 12 h, and beige, powdery $W(NPh)(CH_2SiMe_3)_3Cl$ was collected by filtration and dried in vacuo (4.03 g). The mother liquor was concentrated further and cooled to −30 °C again. Two more crops were obtained for a total of 4.93 g (85%): ^{1}H NMR ($\mathrm{C_6D_6}$, 250 MHz) δ 7.48–7.04 (m, 5, NPh), 2.18 (s, 6, $^2J_{\mathrm{HW}}$ = 8.1 Hz, $\mathrm{C\mathit{H}_2SiMe_3}$), 0.25 (s, 27, $\mathrm{CH_2Si\mathit{Me}_3}$); ^{13}C NMR ($\mathrm{C_6D_6}$, 22.5 MHz) δ 153.0 (s, NPh ipso), 129.0, 128.8 and 127.4 (NPh), 72.4 (t, J_{CH} = 118.8 Hz, J_{CW} = 74.7 Hz, $\mathrm{\mathit{C}H_2SiMe_3}$), 2.9 (q, J_{CH} = 118.7 Hz, $\mathrm{CH_2Si\mathit{Me}_3}$). Anal. Calcd for $\mathrm{WC_{18}H_{38}ClNSi_3}$: C, 37.79; H, 6.70. Found: C, 38.11; H, 6.63.

Preparation of $\mathbf{W(NPh)(CH_2SiMe_3)_2Cl_2}$. $\mathrm{[Et_4N][W(NPh)Cl_5]}$ (2.50 g, 4.29 mmol) was suspended in 75 mL of dichloromethane, and $\mathrm{Zn(CH_2SiMe_3)_2}$ (0.71 g, 2.96 mmol) in 5 mL of dichloromethane was added dropwise to the well-stirred solution over a 0.5-h period. After 2 h pentane (20 mL) was added to aid in precipitation of the Zn salts and the mixture was filtered. The insolubles were washed with ether, and the solvent was removed in vacuo from the combined filtrates. The residue was extracted with pentane (20 mL). The mixture was filtered, and the filtrate was concentrated in vacuo. Cooling to −30 °C gave orange crystals, which were isolated by filtration and dried in vacuo (0.92 g, 60% based on $\mathrm{Zn(CH_2SiMe_3)_2}$): ^{1}H NMR ($\mathrm{C_6D_6}$, 250 MHz) δ 7.31–7.02 (m, 5, NPh), 2.96 (d, 2, $^2J_{\mathrm{H_AH_B}}$ = 6.25 Hz, $^2J_{\mathrm{HW}} \approx$ 10 Hz, $\mathrm{C\mathit{H}_AH_BSiMe_3}$), 2.82 (d, 2, $^2J_{\mathrm{H_BH_A}}$ = 6.25 Hz, $^2J_{\mathrm{HW}} \approx$ 10 Hz, $\mathrm{CH_A\mathit{H}_BSiMe_3}$), 0.16 (s, 18, $\mathrm{CH_2Si\mathit{Me}_3}$); ^{13}C NMR ($\mathrm{C_6D_6}$, 22.5 MHz) δ 151.0 (s, NPh ipso), 129–127 (NPh), 86.9 (t, J_{CH} = 125.2 Hz, $J_{\mathrm{CW}} \approx$ 78 Hz, $\mathrm{\mathit{C}H_2SiMe_3}$), 2.1 (q, J_{CH} = 118.6 Hz, $\mathrm{CH_2Si\mathit{Me}_3}$); mol wt (cyclohexane, cryoscopic) calcd 520, found 468.

Preparation of $\mathbf{W(NPh)(CH_2SiMe_3)_4}$. (a) From $\mathbf{W(NPh)(CH_2SiMe_3)_3Cl}$ and $\mathbf{LiCH_2SiMe_3}$. $\mathrm{LiCH_2SiMe_3}$ (0.12 g, 1.3 mmol) was added in one portion to a stirred solution of $\mathrm{W(NPh)(CH_2SiMe_3)_3Cl}$ (0.75 g, 1.3 mmol) in pentane (40 mL) that had been cooled to −30 °C. The solution became orange, and LiCl precipitated as the reaction mixture warmed to room temperature. After 4 h the reaction mixture was filtered and the pentane was removed from the filtrate in vacuo, leaving red-orange crystals. These were dissolved in a minimum of ether. One volume of acetonitrile was added. Yellow crystals (0.38 g) were collected after 24 h at −30 °C, washed with $\mathrm{CH_3CN}$, and dried in vacuo. The other liquor was further concentrated and cooled to −30 °C to give another 0.24 g of product (total yield 0.62 g, 76%): ^{1}H NMR (toluene-d_8, 0.1 M, −85 °C, 250 MHz) δ 7.4–6.8 (m, 5, NPh), 1.92 (br s, 6, equatorial $\mathrm{C\mathit{H}_2SiMe_3}$), 1.11 (br s, 2, axial $\mathrm{C\mathit{H}_2SiMe_3}$), 0.58 (br s, 9, axial $\mathrm{CH_2Si\mathit{Me}_3}$), 0.23 (br s, 27, equatorial $\mathrm{CH_2Si\mathit{Me}_3}$); ^{1}H NMR (25 °C) δ 7.4–6.8 (m, 5, NPh), 1.57 (s, 8, $^2J_{\mathrm{HW}}$ = 7.6 Hz, $\mathrm{C\mathit{H}_2SiMe_3}$), 0.23 (s, 36, $\mathrm{CH_2Si\mathit{Me}_3}$); ^{13}C NMR ($\mathrm{C_6D_6}$, 22.5 MHz) δ 154.0 (s, NPh ipso), 128.6, 127.5, and 126.6 (NPh), 79.9 (t, J_{CH} = 115 Hz, J_{CW} = 61.5 Hz, $\mathrm{\mathit{C}H_2SiMe_3}$), 3.0 (q, J_{CH} = 119 Hz, $\mathrm{CH_2Si\mathit{Me}_3}$). Anal. Calcd for $\mathrm{WC_{22}H_{49}NSi_4}$: C, 42.36; H, 7.92. Found: C, 39.98; H, 7.27. (The values found compare quite favorably with those calculated for loss of one $\mathrm{Me_4Si}$: C, 40.29; H, 6.95.) This product decomposes noticeably in the solid state at room temperature in ~1 day and therefore should be stored at ca. −30 °C.

(b) From $\mathbf{W(NPh)Cl_4(Et_2O)}$ and $\mathbf{Me_3SiCH_2MgCl}$. A solution of $\mathrm{W(NPh)Cl_4(Et_2O)}$ (2.0 g, 4.1 mmol) in 50 mL of ether was added dropwise to $\mathrm{Me_3SiCH_2MgCl}$ in ether (80 mL, 16.5 mmol) that was kept at −78 °C. After the addition was complete, the mixture was allowed to warm to room temperature and was stirred for 16 h. The magnesium salts were filtered off and washed with ether. The solvent was removed from the combined filtrates in vacuo, leaving a solid that was isolated and purified as above (1.02 g, 40%).

Preparation of $\mathbf{W(NPh)(CHSiMe_3)(CH_2SiMe_3)_2}$. A solution of $\mathrm{W(NPh)(CH_2SiMe_3)_4}$ (1.0 g, 1.6 mmol) in toluene (30 mL) was heated at 60 °C for 5 h. Removing all volatiles in vacuo left a dark red oil, which was pure by ^{1}H and ^{13}C NMR: ^{1}H NMR (toluene-d_8, 250 MHz, 25 °C) δ 7.79 (s, 1, $\mathrm{C\mathit{H}SiMe_3}$), 7.29–6.98 (m, 5, NPh), 0.63 (s, 4, $^2J_{\mathrm{HW}}$ = 9.8 Hz, $\mathrm{C\mathit{H}_2SiMe_3}$), 0.22 (s, 9, $\mathrm{CHSi\mathit{Me}_3}$), 0.14 (s, 18, $\mathrm{CH_2Si\mathit{Me}_3}$); ^{1}H NMR (70 °C) δ 7.89 (s, 1, $^2J_{\mathrm{HW}}$ = 8.8 Hz, $\mathrm{C\mathit{H}SiMe_3}$), 7.29–6.98 (m, 5, NPh), 0.70 (d, 2, $^2J_{\mathrm{H_AH_B}}$ = 10.7 Hz, $\mathrm{C\mathit{H}_AH_BSiMe_3}$), 0.62 (d, 2, $^2J_{\mathrm{H_BH_A}}$ = 10.7 Hz, $\mathrm{CH_A\mathit{H}_BSiMe_3}$), 0.21 (s, 9, $\mathrm{CHSi\mathit{Me}_3}$), 0.13 (s, 18, $\mathrm{CH_2Si\mathit{Me}_3}$) (we believe that the equivalence of the (trimethylsilyl)methyl α-protons in the 25 °C ^{1}H NMR spectrum is accidental); ^{13}C NMR ($\mathrm{C_6D_6}$, 22.5 MHz): 230.4 (d, J_{CH} = 108 Hz, J_{CW} = 127 Hz, $\mathrm{\mathit{C}HSiMe_3}$), 157.4 (s, NPh ipso), 128.8, 125.0, and 124.7 (NPh), 60.8 (t, J_{CH} = 110 Hz, J_{CW} = 83.5 Hz, $\mathrm{\mathit{C}H_2SiMe_3}$), 2.6 (q, J_{CH} = 119 Hz, $\mathrm{CHSi\mathit{Me}_3}$ and $\mathrm{CH_2Si\mathit{Me}_3}$).

Preparation of $\mathbf{W(NPh)(CHSiMe_3)(PMe_3)_2Cl_2}$. $\mathrm{PMe_3}$ (0.12 mL, 2.1 mmol) was added to 12 mL of dichloromethane containing 0.45 g (0.86 mmol) of $\mathrm{W(NPh)(CH_2SiMe_3)_2Cl_2}$. After 18 h the dichloromethane was removed in vacuo. The residue was extracted with toluene (20 mL). The extract was filtered and concentrated in vacuo to ~10 mL. Pentane was added, and the solution was cooled to −30 °C to give orange crystals (0.44 g, 88%): ^{1}H NMR ($\mathrm{CDCl_3}$, 270 MHz) δ 12.75 (t, 1, $^3J_{\mathrm{HP}}$ = 4.6 Hz, $\mathrm{C\mathit{H}SiMe_3}$), 7.45 (d, 2, $^2J_{\mathrm{H_oH_m}}$ = 7.3 Hz, NPh ortho), m.28 (t, 2, $J_{\mathrm{H_{obsd}}}$ = 7.4 Hz, NPh meta), 7.12 (t, 1, $^3J_{\mathrm{H_pH_m}}$ = 7.3 Hz, NPh para), 1.60 (t, 18, $^2J_{\mathrm{HP}}$ = 4.7 Hz, $\mathrm{PMe_3}$), 0.17 (s, 9, $\mathrm{CHSi\mathit{Me}_3}$); ^{13}C NMR ($\mathrm{C_6D_6}$, 22.5 MHz) δ 293.1 (d, J_{CH} = 119 Hz, $^2J_{\mathrm{CP}}$ = 9 Hz, $\mathrm{\mathit{C}HCMe_3}$), 154.7 (s, NPh ipso), 128.4 and 126.9 (NPh), 16.1 (qt, J_{CH} = 132 Hz, J_{CP} = 15 Hz, $\mathrm{PMe_3}$), 3.0 (q, J_{CH} = 119 Hz, $\mathrm{CHSi\mathit{Me}_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$) δ −7.0 (s, J_{PW} = 288 Hz).

Preparation of $\mathbf{W(NPh)(CH_3)_3Cl}$. $\mathrm{[Et_4N][W(NPh)Cl_5]}$ (6.6 g, 11.2 mmol) was suspended in 150 mL of dichloromethane along with $\mathrm{Et_4NCl}$ (0.93 g, 5.6 mmol). After the mixture was cooled to 0 °C, $\mathrm{ZnMe_2}$ (1.2 mL, 16.9 mmol) in 10 mL of pentane was added rapidly (1 min) while the suspension was stirred. After 17 h the reaction mixture was filtered and the solids were washed with toluene. The solvent was removed from the filtrate in vacuo, leaving a tan solid, which was extracted with ether (75 mL). The extract was filtered and concentrated in vacuo until crystallizaiton began. Cooling to −30 °C gave 2.41 g of a tan powder. Concentrating the mother liquor further gave another 0.65 g of product (total yield 3.06 g, 77%). The product may be recrystallized at −30 °C from dilute ether solutions to give golden needles: ^{1}H NMR ($\mathrm{C_6D_6}$, 250 MHz) δ 7.06–6.89 (m, 5, NPh), 1.28 (s, 9, $^2J_{\mathrm{HW}}$ = 8.1 Hz, $\mathrm{CH_3}$); ^{13}C NMR ($\mathrm{CDCl_3}$, 22.5 MHz) δ 151.8 (s, NPh ipso), 128.6, 128.0, and 127.2 (NPh), 53.8 (q, J_{CH} = 128 Hz, J_{CW} = 75.2 Hz, $\mathrm{CH_3}$). Anal. Calcd for $\mathrm{WC_9H_{14}ClN}$: C, 30.41; H, 3.97. Found: C, 30.70; H, 4.05.

Preparation of $\mathbf{W(NPh)(CH_3)_3(OCMe_3)}$. $\mathrm{[Et_4N][W(NPh)(OCMe_3)Cl_4]}$ (2.17 g, 3.50 mmol) was dissolved in 60 mL of dichloromethane, and the solution was cooled to −30 °C. A pentane solution (5 mL) of $\mathrm{ZnMe_2}$ (360 μL) was added dropwise to the stirred solution. The reaction mixture became bright yellow, and a white precipitate formed. After 1 h pentane (20 mL) was added to aid precipitation of the zinc salts and the salts were filtered off. The volatiles were removed from the filtrate in vacuo, leaving an oily orange solid. Extraction of this material with pentane followed by filtration and removal of the pentane in vacuo gave a yellow-orange oil that is pure $\mathrm{W(NPh)(CH_3)_3(OCMe_3)}$ by ^{1}H NMR (0.96 g, 70%): ^{1}H NMR ($\mathrm{C_6D_6}$, 60 MHz) δ 7.3–6.8 (m, 5, NPh), 1.4 (s, 9, $\mathrm{OCMe_3}$), 1.0 (s, 9, $^2J_{\mathrm{HW}} \approx$ 9 Hz, $\mathrm{CH_3}$); ^{13}C NMR ($\mathrm{C_6D_6}$, 22.5 MHz) δ 156.3 (br s, NPh, ipso), 128.5, 126.9, and 124.7 (NPh), 79.8 (br s, $\mathrm{O\mathit{C}Me_3}$), 40.8 (q, J_{CH} = 127.4 Hz, J_{CW} = 81.3 Hz, $\mathrm{CH_3}$), 31.76 (q, J_{CH} = 125 Hz, $\mathrm{OC\mathit{Me}_3}$).

Preparation of $\mathbf{W(\eta^5\text{-}C_5H_5)(NPh)(CH_3)_3}$. $\mathrm{NaC_5H_5}$ (0.12 g, 1.4 mmol) was added to a THF solution (15 mL) of $\mathrm{W(NPh)(CH_3)_3Cl}$ (0.41 g, 1.2 mmol) that had been cooled to −30 °C. The reaction mixture was warmed to room temperature and stirred for 8 h. The THF was removed in vacuo, and the residue was extracted with pentane. The pentane extract was filtered, and the filtrate was concentrated in vacuo and cooled to −30 °C to give yellow crystals (0.41 g, 92%): ^{1}H NMR ($\mathrm{C_6D_6}$, 270 MHz) δ 7.04–6.83 (m, 5, NPh), 5.09 (s, 5, $\mathrm{C_5H_5}$), 1.28 (s, 6, $^2J_{\mathrm{HW}} \approx$ 6 Hz, $\mathrm{CH_3}$), 0.92 (s, 3, $^2J_{\mathrm{HW}} \approx$ 6 Hz, $\mathrm{CH_3}$); ^{13}C NMR ($\mathrm{C_6D_6}$, 22.5 MHz) δ 158.0 (s, NPh ipso), 128.4–122.3 (NPh), 103.3 (d, J_{CH} = 178 Hz, $\mathrm{C_5H_5}$), 23.6 (q, J_{CH} = 127 Hz, $J_{\mathrm{CW}} \approx$ 62 Hz, $\mathrm{CH_3}$ trans to NPh), 17.6 (q, J_{CH} = 129 Hz, $J_{\mathrm{CW}} \approx$ 51 Hz, $\mathrm{CH_3}$ cis to NPh).

Preparation of $\mathbf{W(NPh)(CH_2Ph)_3Cl}$. $\mathrm{[Et_4N][W(NPh)(OCMe_3)Cl_4]}$ (2.41 g, 3.9 mmol) was suspended in THF that was kept at 0 °C while $\mathrm{PhCH_2MgCl}$ (11 mL, 0.94 M in ether) was added dropwise. After 24 h of stirring at 25 °C the solvent was removed from the reaction mixture in vacuo. Extraction of the dark residue with ether followed by filtration and removal of the ether in vacuo gave a dark orange oil, which was dissolved in toluene (50 mL). After this solution was cooled to 0 °C, HCl gas (96 mL, 4.3 mmol) was added by syringe. After 0.5 h all volatiles were removed in vacuo. The residue was extracted with ether, the extract was filtered, and the filtrate was concentrated in vacuo until crystallization began. Cooling the solution to −30 °C gave a total of 1.2 g (three crops) of yellow crystals (53%): ^{1}H NMR ($\mathrm{CDCl_3}$, 270 MHz) δ 7.53–7.24 (m, 20, $\mathrm{CH_2\mathit{Ph}}$ and NPh), 3.24 (s, 6, $^2J_{\mathrm{HW}}$ = 9.8 Hz, $\mathrm{C\mathit{H}_2Ph}$); ^{13}C NMR ($\mathrm{CDCl_3}$, 67.9 MHz) δ 151.9 (br s, NPh ipso), 135.4–126.9 ($\mathrm{CH_2\mathit{Ph}}$ and NPh), 66.4 (t, J_{CH} = 142 Hz, J_{CW} = 77.7 Hz, $\mathrm{\mathit{C}H_2Ph}$). Anal. Calcd for $\mathrm{WC_{27}H_{26}NCl}$: C, 55.55; H, 4.49. Found: C, 55.99; H, 4.71.

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Registry No. $\mathrm{WOCl_4}$, 13520-78-0; $\mathrm{WCl_6}$, 13283-01-7; $\mathrm{Me_3SiOMe}$, 1825-61-2; $\mathrm{W(NPh)Cl_4(Et_2O)}$, 83634-25-7; $\mathrm{[W(NPh)Cl_4]_\mathit{x}}$, 83634-49-5; $\mathrm{W(NPh)(OCMe_3)_4}$, 83634-50-8; $\mathrm{LiOCMe_3}$, 1907-33-1; $\mathrm{[Et_4N][W(NPh)Cl_5]}$, 83634-27-9; $\mathrm{Et_4NCl}$, 56-34-8; $\mathrm{W(NPh)(CHCMe_3)(PEt_3)_2Cl_2}$, 83634-28-0; $\mathrm{[Et_4N][W(NPh)(OCMe_3)_2Cl_3]}$, 83634-30-4; $\mathrm{[Et_4N][W(NPh)(OCMe_3)Cl_4]}$, 83634-32-6; $\mathrm{W(NPh)(CHCMe_3)(PMe_3)_2Cl_2}$, 83634-33-7; $\mathrm{Ta(CHCMe_3)(PMe_3)_2Cl_3}$, 70083-62-4; $\mathrm{Ta(CHCMe_3)(PEt_3)_2Cl_3}$, 77126-35-3; $\mathrm{[W(NPh)(CHCMe_3)(PMe_3)_2Cl]}$-

$[AlCl_4]$, 83634-35-9; $AlCl_3$, 7446-70-0; $[W(NPh)(CHCMe_3)(PEt_3)_2Cl][AlCl_4]$, 83634-37-1; $[W(NPh)(CHCMe_3)(PMe_3)_2Me][AlMe_2Cl_2]$, 83634-39-3; $AlMe_3$, 75-24-1; $[W(NPh)(CHCMe_3)(PEt_3)_2Me][AlMe_2Cl_2]$, 83634-41-7; $W(NPh)(CHCMe_3)(PMe_3)(OCMe_3)_2$, 83634-42-8; $W(NPh)(CHCMe_3)(PEt_3)(OCMe_3)_2$, 83634-43-9; $W(NPh)(CHCMe_3)(PEt_3)Cl_2$, 83634-44-0; CuCl, 7758-89-6; $W(NPh)(CCMe_3)(AlMe_2Cl)(PMe_3)_2Cl$, 83649-38-1; $W(NPh)(CH_2CMe_3)_3Cl$, 83634-51-9; NeoCl, 753-89-9; $W(NPh)(CH_2CMe_3)_3Br$, 83634-52-0; $W(NPh)(CH_2CMe_3)_3(OCMe_3)$, 83634-53-1; HBr, 10035-10-6; $W(NPh)(CH_2CMe_3)_3(O_2CCF_3)$, 83634-54-2; CF_3CO_2H, 76-05-1; $W(NPh)(CH_2CMe_3)_2(OCMe_3)_2$, 83649-39-2; $W(NPh)(CH_2CMe_3)_2(OCMe_3)Cl$, 83634-55-3; $Zn(Neo)_2$, 54773-23-8; $W(NPh)(CHCMe_3)(CH_2CMe_3)_2$, 83634-56-4; Ph_3PCH_2, 3487-44-3; LiNeo, 7412-67-1; $W(\eta^5\text{-}C_5H_5)(NPh)(CHCMe_3)(CH_2CMe_3)$, 83634-45-1; NaC_5H_5, 4984-82-1; $W(\eta^5\text{-}C_5H_5)(NPh)(CH_2CMe_3)_2Cl$, 83634-46-2; Me_3PHCl, 55903-13-4; $W(NPh)(CHCMe_3)(py)_2Cl_2$, 83664-23-7; $W(NPh)(CH_2SiMe_3)_3Cl$, 83634-57-5; $W(NPh)(CH_2SiMe_3)_2Cl_2$, 83634-58-6; $Zn(CH_2SiMe_3)_2$, 41924-26-9; $W(NPh)(CH_2SiMe_3)_4$, 83634-59-7; $LiCH_2SiMe_3$, 1822-00-0; Me_3SiCH_2Cl, 2344-80-1; $W(NPh)(CHSiMe_3)(CH_2SiMe_3)_2$, 83634-60-0; $W(NPh)(CHSiMe_3)(PMe_3)_2Cl_2$, 83634-47-3; $W(NPh)Me_3Cl$, 83634-61-1; PMe_3, 594-09-2; $ZnMe_2$, 544-97-8; $W(NPh)Me_3(OCMe_3)$, 83634-62-2; $W(\eta^5\text{-}C_5H_5)(NPh)Me_3$, 83634-48-4; $W(NPh)(CH_2Ph)_3Cl$, 83634-63-3; $PhCH_2Cl$, 100-44-7; phenyl isocyanate, 103-71-9; py·HCl, 628-13-7; py, 110-86-1.

Kinetics and Stereochemistry of the Titanacyclobutane–Titanamethylene Interconversion. Investigation of a Degenerate Olefin Metathesis Reaction

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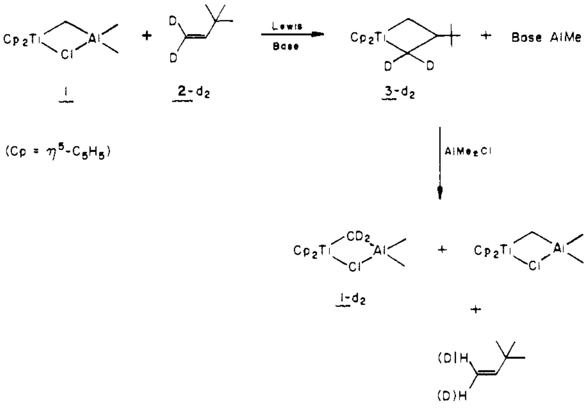
Abstract: Analysis of the kinetics of the reaction of dicyclopentadienyltitanacyclobutane **3** with diphenylacetylene to produce the dicyclopentadienyltitanacyclobutene **7** indicated that the exchange is first order in **3** and zeroth order in Ph—C≡C—Ph over a wide range of concentrations. The kinetics and stereochemistry of olefin exchange along with a large secondary isotope effect are consonant with the reaction proceeding via rate-limiting ring opening of **3** to $Cp_2Ti{=}CH_2$ and olefin (free or complexed), followed by rapid trapping by incoming olefin or acetylene. The complex **3** and its analogues are effective catalysts for the olefin metathesis reaction of terminal olefins.

Introduction

The mechanism of the metal-catalyzed olefin metathesis reaction[1] has been intensively studied for many years, and a consensus has emerged that metal alkylidenes and metallacyclobutanes are plausible intermediates in this reaction. The syntheses and isolation of metal alkylidene complexes and studies of their reactions with olefins have convincingly demonstrated the intermediacy of such species in metathesis.[2] In contrast, the evidence for the involvement of the metallacyclobutane intermediates has not been as well documented and is largely indirect. To date, examples of well-characterized complexes in this class are rare, being limited to only a few transition metals.[3] Recently, we reported the isolation of a titanacyclobutane[4] from an olefin metathesis system.[2a] In this paper we present detailed studies of the reactions of this class of metallacyclobutanes that are related to the mechanism and stereoselectivity of the olefin metathesis reaction.

Results and Discussion

Titanacyclobutane **3**, synthesized from the well-defined metathesis catalyst **1**, undergoes the reactions required of a metathesis intermediate. When **3**-d_2 was treated with $AlMe_2Cl$ (eq 1), deuterium was incorporated into **1** in a second-order reaction.[5]



(1)

Equation 1 represents a reasonable mechanism for the Lewis-acid-catalyzed route for metathesis involving **1** as the chain-carrying species. We now have found that complex **3** is also an

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[1] For recent reviews on the olefin metathesis reaction, see: Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449. Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1. Katz, T. J. *Adv. Organomet. Chem.* **1977**, *16*, 283.

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