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# Syntheses of Tungsten Imido Cyclohexylidene Complexes Using Perfluoro-*t*-butanol or Hexafluoro-*t*-butanol as Acids

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**Abstract:** The fluorinated alcohols, $(CF_3)_3COH$ ($R_{F9}OH$) and $(CF_3)_2MeCOH$, react with $W(NR)_2Cy_2$ (Cy = Cyclohexyl; R = 2,6-diisopropylphenyl or 1-adamantyl) in $C_6D_6$ at 55°C to give cyclohexylidene complexes through a double protonation of the imido ligand. Traditional routes to terminal alkylidene complexes (neopentylidene or neophylidene) have used strong acids, namely either triflic acid or HCl (rarely), but relatively weak fluorinated acids are sufficient and active catalysts are prepared directly. An $\alpha$ hydrogen abstraction reaction to give a cyclohexylidene complex from a biscyclohexyl appears to be as facile as $\alpha$ hydrogen abstraction to give a neopentylidene or neophylidene ligand, but isomerization of a cyclohexene formed through $\beta$ hydrogen abstraction may be a significant pathway also. The $OR_{F9}$ ligands can be replaced readily with dimethylpyrrolide ($Me_2Pyr$) or other more basic alkoxides. Single crystal X-ray studies were carried out on $W(NAr)_2Cy_2$, $W(NAr)(OR_{F9})_2(C_6H_{10})(ArNH_2)$, $W(NAr)(OR_{F6})_2(C_6H_{10})(ArNH_2)$, $W(NAd)(OR_{F9})_2(C_6H_{10})(AdNH_2)$, $W(NAr)(O\text{-}i\text{-}Pr_{F6})_3Cy$, and $W(NAd)(\eta^1\text{-}Me_2Pyr)_2(C_6H_{10})$.

Since the discovery in 1980[1] of tungsten catalysts for the olefin metathesis reaction,[2] a large number and variety of four-coordinate homogeneous Mo and W alkylidene complexes that catalyze that reaction have been prepared. Neutral complexes usually have the general formula $M(D)(CHR')(Y)(Z)$, where D is a dianionic imido or oxo ligand, Y and Z are monoanionic ligands such as an alkoxide, an aryloxide, or a pyrrolide, and CHR' is initially $CH\text{-}t\text{-}Bu$ or $CHCMe_2Ph$.[3] The initial alkylidene ligand usually is generated through some variation of the $\alpha$ hydrogen abstraction reaction[3c] in a dineopentyl or dineophyl intermediate, *e.g.*, through addition of triflic acid or (rarely) HCl to $M(NR)_2(CH_2R')_2$ to form $RNH_3X$ and a $M(NR)(CHR')(dme)X_2$ complex (X = OTf or Cl) in the presence of 1,2-dimethoxyethane (dme; eq 1). With the

$$M(NR)_2(CH_2R')_2 + 3\ HX + \text{dimethoxyethane} \longrightarrow$$

$$RNH_3X + M(NR)(CHR')(dme)X_2 + R'CH_3 \qquad (1)$$
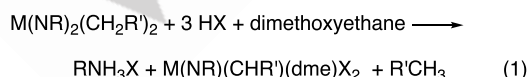
exception of 2-adamantylidene complexes,[4] disubstituted methylidene (internal alkylidene) complexes have been prepared in reactions between $CH_2=CR'R''$ and a M=CHR complex.[5] For decades, simpler and more direct syntheses of metathesis-active alkylidenes have been sought that do not require strong acids to remove the imido ligand and that give metathesis- active catalysts directly.

Some of the most active metathesis catalysts are those in which X is an alkoxide ligand, especially $OC(CF_3)_2Me$. This alkoxide (and also $OC(CF_3)_3$) are sufficiently electron-withdrawing and sterically demanding to accelerate formation of the metallacyclobutane intermediate formed in the reaction between a four-coordinate alkylidene, $M(NR)(CHR')X_2$, and an olefin. Their steric bulk also protects any alkylidene (except perhaps a methylidene) from decomposing through bimolecular coupling to give olefins. Because the $pK_a$ values are 9.8 for $Me(CF_3)_2COH$ and 5.4 for $(CF_3)_3COH$, it seems possible that the alcohols themselves might protonate an imido group and induce $\alpha$ hydrogen abstraction to give a four-coordinate alkylidene complex and bound or free $RNH_2$ or $[RNH_3][OR'']$.

In 1989 Osborn[6] reported that $Mo(N\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$ reacts with $(CF_3)_2HCOH$ ($i\text{-}Pr_{F6}OH$; $pK_a$ = 9.3) at room temperature in pentane in 10 min to give $Mo(N\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(O\text{-}i\text{-}Pr_{F6})_2(t\text{-}BuNH_2)$ and neopentane. It was stated that "unfortunately, reaction of $Mo(N\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$ with many other alcohols does not lead to carbene complexes" analogous to $Mo(N\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)[OCH(CF_3)_2]_2(t\text{-}BuNH_2)$. The alcohols mentioned were MeOH, $t\text{-}BuCH_2OH$, and $t\text{-}BuOH$, which have relatively high $pK_a$ values (*e.g.*, ~19 for $t$-butanol).

We now have found that alkylidene complexes of W that contain hexafluoro-*t*-butoxide ($OR_{F6}$) or perfluoro-*t*-butoxide ($OR_{F9}$) ligands can be prepared, most easily and interestingly, from dicyclohexyl complexes. These are more convenient routes to a variety of imido alkylidenes of W that avoid triflic acid and neopentyl or neophyl ligands, avoid intermediate bistriflate complexes, and yield products that are metathesis catalysts themselves and ~~that~~ can be converted readily into other catalyst variations.

$W(NAr)_2(dme)Cl_2$ reacts with two equivalents of CyMgCl (Ar = 2,6-diisopropylphenyl, Cy = cyclohexyl) in diethyl ether to give yellow crystalline $W(NAr)_2Cy_2$ (85% yield). A single crystal X-ray analysis confirmed the structure shown in Fig 1 in which each cyclohexyl ligand has a chair formation. Examples of transition metal cyclohexyl complexes in the literature include $[(t\text{-}Bu)_3SiO]_3M(Cy)$ (M = Nb or Ta),[7] $Mo[(Me_3SiNCH_2CH_2)_3N]Cy$,[8] $Fe(i\text{-}Pr_2PCH_2CH_2P\text{-}i\text{-}Pr_2)(Cl)Cy$,[9] $Mn_2Cy_2(\mu\text{-}Cy)_2(\mu\text{-}dmpe)$,[10] and a series of $MCy_4$ complexes where M = Ti,[11] Ru,[12] Os,[12-13] Cr,[12] or Fe.[14] The unusual stabilities of $MCy_4$ complexes have been ascribed to weak, attractive London dispersion forces (LDFs) between cyclohexyl ligands.[15],[16]
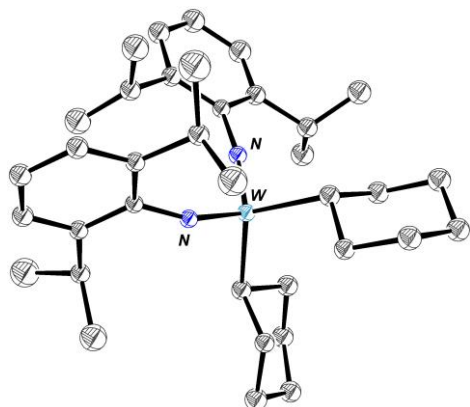
**Figure 1.** The structure of W(NAr)$_2$Cy$_2$.

Addition of two equivalents of (CF$_3$)$_3$COH (R$_{F9}$OH) to W(NAr)$_2$Cy$_2$ in C$_6$D$_6$ followed by heating the mixture to 55°C for 24 h led to formation of cyclohexane and the orange-yellow cyclohexylidene complex, W(NAr)(OR$_{F9}$)$_2$(C$_6$H$_{10}$)(ArNH$_2$), which was isolated in 79% yield (C$_6$H$_{10}$ = cyclohexylidene). The structure of W(NAr)(OR$_{F9}$)$_2$(C$_6$H$_{10}$)(ArNH$_2$) (Fig 2) was found to be a distorted SP (square pyramid; $\tau$[17] = 0.25) with the cyclohexylidene ligand bound in the axial position and *cis* alkoxides bound *trans* to the relatively donating NAr and H$_2$NAr ligands. According to NMR studies (Fig S41), addition of B(C$_6$F$_5$)$_3$ to a solution of W(NAr)(OR$_{F9}$)$_2$(C$_6$H$_{10}$)(ArNH$_2$) led to immediate formation of ((C$_6$F$_5$)$_3$B)(NH$_2$Ar), so ArNH$_2$ must be relatively labile in W(NAr)(OR$_{F9}$)(NH$_2$Ar). As one therefore would expect, W(NAr)(OR$_{F9}$)$_2$(C$_6$H$_{10}$)(ArNH$_2$) reacts readily with ethylene to give a TBP tungstacyclobutane complex, W(NAr)(OR$_{F9}$)$_2$(CH$_2$CH$_2$CH$_2$), and free ArNH$_2$ (Figs S46-47).
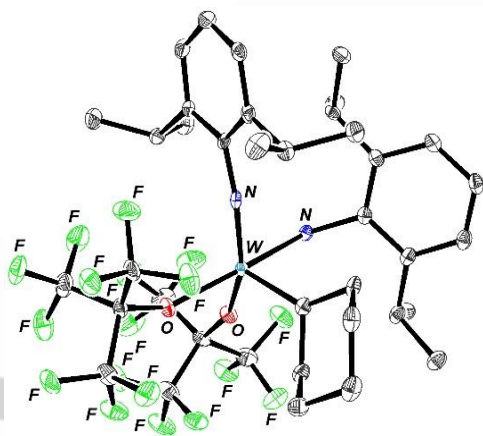


**Figure 2.** The structure of W(NAr)(OR$_{F9}$)$_2$(C$_6$H$_{10}$)(ArNH$_2$).

A plausible mechanism of forming an alkylidene from W(NR)$_2$Cy$_2$ and R'OH is shown in Scheme 1. In the reaction between W(NAr)$_2$Cy$_2$ and R$_{F9}$OH we propose that coordination of R$_{F9}$OH to the metal is the first step, followed by transfer of the first proton to one imido group to give W(NAr)(NHAr)(OR$_{F9}$)Cy$_2$; the cyclohexylidene ligand is generated through $\alpha$ abstraction in this five-coordinate and relatively sterically crowded 16e complex. A

second equivalent of R$_{F9}$OH coordinates to the four-coordinate metal and a proton then migrates from coordinated R$_{F9}$OH to the amido ligand to give W(NAr)(OR$_{F9}$)$_2$(C$_6$H$_{10}$)(ArNH$_2$). This proposal is consistent with the fact that when two equivalents of R$_{F9}$OD are added to W(NAr)$_2$Cy$_2$, the product is W(NAr)(OR$_{F9}$)$_2$(C$_6$H$_{10}$)(ArND$_2$), according to NMR spectra; the broad singlet at 3.32 ppm for ArNH$_2$ is not present (Fig S39). No facile reaction is observed between two equivalents of R$_{F9}$OH and W(NAr)$_2$(CH$_2$CMe$_2$Ph)$_2$ under analogous conditions, we presume primarily because R$_{F9}$OH cannot readily coordinate to the metal for steric reasons.
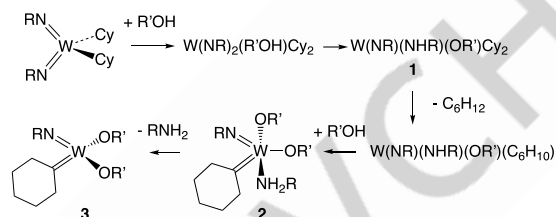


**Scheme 1.** The proposed mechanism of forming an alkylidene.

Formation of W(NAr)(OR$_{F9}$)$_2$(C$_6$H$_{10}$)(ArND$_2$) does not rule out formation of a cyclohexene complex through $\beta$ abstraction followed by an alcohol-catalyzed rearrangement[18] of cyclohexene to cyclohexylidene at some point; one possibility is shown in equation 2. (A related trisalkoxide cyclohexyl complex is described below.) Further exploration of this intriguing possibility will be required, as it could prove to be a more general mechanism for interconverting olefin and alkylidene complexes.



(2)
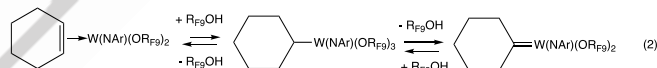
It should be noted that a dimethylanilinium-catalyzed interconversion of styrene and phenethylidene complexes of Mo through formation of an intermediate cationic alkyl complex has been observed[18-19] and that the pK$_a$ values (in water) of dimethylanilinium and R$_{F9}$OH are both ~5.5. No Mo or W cyclohexene complex analogous to Mo(NAr)(OSiPh$_3$)$_2$(olefin) complexes (olefin = styrene, ethylene, *trans*-3-hexene)[20] that would allow the proposal shown in eq 2 to be fully tested has yet to be reported.
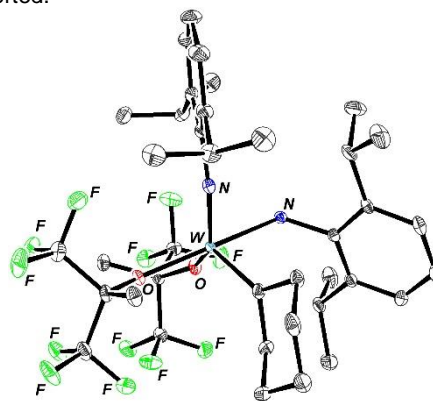


**Figure 3.** The structure of W(NAr)(OR$_{F6}$)$_2$(C$_6$H$_{10}$)(ArNH$_2$).

Addition of two equivalents of $(CF_3)_2MeCOH$ ($R_{F6}OH$) to $W(NAr)_2Cy_2$ in $C_6D_6$ followed by heating the mixture to 60°C for 24 h led to formation of $W(NAr)(OR_{F6})_2(C_6H_{10})(ArNH_2)$, which was isolated in 68% yield. The structure of $W(NAr)(OR_{F6})_2(C_6H_{10})(ArNH_2)$ (Fig 3) is approximately half-way between a TBP and a SP ($\tau = 0.40$). $R_{F6}OH$ is likely to coordinate to the metal more readily than $R_{F9}OH$ for electronic reasons, but in free form $R_{F6}OH$ is ~$10^3$ time less acidic than $R_{F9}OH$, as noted earlier.

$W(NAd)_2Cy_2$ (Ad = 2-Adamantyl) was prepared readily from $[W(NAd)_2Cl(\mu-Cl)(AdNH_2)]_2$[21] and two equivalents of CyMgBr per W; it was isolated in 55% yield. $W(NAd)_2Cy_2$ reacts with 2.2 equiv of $R_{F9}OH$ at 22 °C in toluene to give $W(NAd)(OR_{F9})_2(C_6H_{10})(AdNH_2)$ in 68 % yield. The structure of $W(NAd)(C_6H_{10})(OR_{F9})_2(AdNH_2)$ is analogous to the NAr analogs just described with the cyclohexylidene in the apical position of what is closest to a SP structure ($\tau = 0.17$; Fig S51).

Addition of ten equivalents of $R_{F9}OH$ to a suspension of $W(NAd)(C_6H_{10})(OR_{F9})_2(AdNH_2)$ in pentane yields a precipitate of $(AdNH_3)(OR_{F9})$ after 4 h at room temperature; it can be filtered off and $W(NAd)(C_6H_{10})(OR_{F9})_2$ recovered from the filtrate in 72 % yield. These results suggest that $AdNH_2$ is readily lost to solution and can be removed through protonation of free $AdNH_2$ by $R_{F9}OH$ to give $(AdNH_3)(OR_{F9})$ and $W(NAd)(C_6H_{10})(OR_{F9})_2$.

Addition of three equiv of $R_{F9}OH$ to $W(NAd)_2(CH_2CMe_2Ph)_2$ in the presence of one equivalent of pyridine yields $W(NAd)(CHCMe_2Ph)(OR_{F9})_2(py)$ in 76% yield at room temperature in 48 h (eq 3). In the absence of pyridine at 70°C, mixtures of $W(NAd)(NHAd)(OR_{F9})(CH_2CMe_2Ph)_2$, $W(NAd)_2(OR_{F9})(CH_2CMe_2Ph)$, and $W(NAd)(CHCMe_2Ph)(OR_{F9})_2(AdNH_2)$, are formed, according to NMR studies. We propose that pyridine can move a proton through a deprotonation/protonation sequence. Therefore, in any of the reactions described so far, any *free* aniline or amine also could be involved in moving the proton. Some of the first W imido alkylidene complexes were made by transferring a proton from an amido ligand to an alkylidyne ligand to give imido alkylidene complexes, a reaction that is related to proton transfer from a coordinated alcohol to an imido ligand reported here.[22] In that case, a weakly binding external base ($NEt_3$) appeared to be required to move the proton readily.

$$W(NAd)_2(CH_2CMe_2Ph)_2 + 2\ R_{F9}OH \xrightarrow[+\ py]{-\ PhCMe_3} W(NAd)(OR_{F9})_2(CHCMe_2Ph)(py) \quad (3)$$
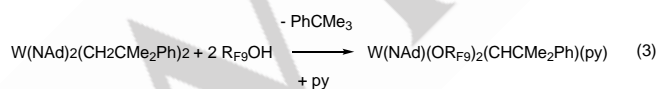
No reaction was observed when a solution of $W(NAr)_2(CH_2CMe_2Ph)_2$ (~0.01 M in $C_6D_6$) and hexafluoroisopropanol ($i$-$Pr_{F6}OH$) (4 eq) was heated for 12 h at 80 °C (Fig S43). However, heating a mixture of $W(NAr)_2Cy_2$ and $i$-$Pr_{F6}OH$ (5 eq) at 60 °C, led to formation of $W(NAr)(O$-$i$-$Pr_{F6})_3Cy$ and cyclohexane. An X-ray structural study shows that $W(NAr)(O$-$i$-$Pr_{F6})_3Cy$ has essentially a square pyramidal geometry with the imido ligand in the apical position (Fig 4; $\tau = 0.18$). The $^{19}F$ NMR spectrum confirms that two similar, but inequivalent, $CF_3$ groups are present on the two mutually trans $O$-$i$-$Pr_{F6}$ ligands in $W(NAr)(O$-$i$-$Pr_{F6})_3Cy$. At room temperature $^1H$ and $^{13}C$ carbon NMR spectra show that the $O$-$i$-$Pr_{F6}$ ligands begin to exchange on the NMR time scale (Fig S20), probably through formation of a

trigonal bipyramidal intermediate with a plane of symmetry that passes through a $O$-$i$-$Pr_{F6}$ ligand. At the $W(NAr)(NHAr)(OR)Cy_2$ stage the choices (for a forward reaction) are formation of either
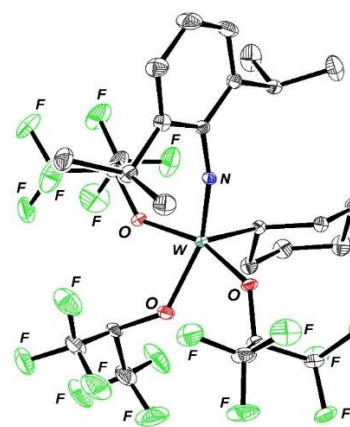


**Figure 4.** The structure of $W(NAr)(O$-$i$-$Pr_{F6})_3Cy$.
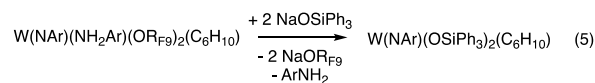
$W(NAr)_2(OR)Cy$ (eq 4) or $W(NAr)(NHAr)(OR)(C_6H_{10})$ (Scheme 1) and cyclohexane. When OR = $O$-$i$-$Pr_{F6}$, the former is faster under conditions used so far. Either $\alpha$ abstraction is slower in the $O$-$i$-$Pr_{F6}$ intermediate than in analogous $OR_{F9}$ or $OR_{F6}$ complexes, or protonation of a cyclohexyl group is faster with $O$-$i$-$Pr_{F6}OH$ than with $R_{F9}OH$ or $R_{F6}OH$, or both. Note that $W(NAr)(O$-$i$-$Pr_{F6})_3Cy$ is analogous to the type of intermediate that we propose is formed in an $R_{F9}OH$-catalyzed isomerization of a cyclohexene complex to a cyclohexylidene complex (eq 2).

$$W(NAr)(NHAr)(OR)Cy_2 \xrightarrow{-\ C_6H_{12}} W(NAr)_2(OR)Cy \quad (4)$$
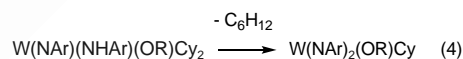
Nonafluoro-t-butoxide ligands can be replaced readily by more electron-donating ligands. Examples are syntheses of $W(NAr)(OSiPh_3)_2(C_6H_{10})$[23] (eq 5) and $W(NAd)(Me_2Pyr)_2(C_6H_{10})$ (eq 6; $Me_2Pyr$ = 2,6-dimethylpyrrolide). A single crystal X-ray

$$W(NAr)(NH_2Ar)(OR_{F9})_2(C_6H_{10}) \xrightarrow[-\ 2\ NaOR_{F9}]{\ +\ 2\ NaOSiPh_3\ } W(NAr)(OSiPh_3)_2(C_6H_{10}) \quad (5)$$
$$-\ ArNH_2$$

$$W(NAd)(OR_{F9})_2(C_6H_{10}) \xrightarrow[-\ 2\ LiOR_{F9}]{\ +\ 2\ LiMe_2Pyr\ } W(NAd)(Me_2Pyr)_2(C_6H_{10}) \quad (6)$$
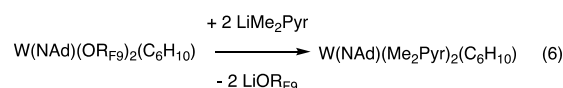
study of $W(NAd)(C_6H_{10})(Me_2Pyr)_2$ shows that it contains two $\eta^1$-$Me_2Pyr$ ligands (Fig 5), not one $\eta^1$-$Me_2Pyr$ and one $\eta^5$-$Me_2Py$, an arrangement that is often found for bis-2,5-dimethylpyrrolide complexes.[6] Another example of a bis-$\eta^1$-$Me_2Pyr$ complex is $W(O)(2$-adamantylidene)$(\eta^1$-$Me_2Pyr)_2$.[23-24] In four-coordinate $\eta^1$-pyrrolide/$\eta^5$-pyrrolide complexes of this general type, the two pyrrolides often interconvert on the NMR time scale, presumably via the formation of a bis-$\eta^1$-pyrrolide intermediate. The 14e bis($\eta^1$-pyrrolide) isomers are likely to be much more reactive toward olefins than 18e $\eta^1/\eta^5$ isomers.
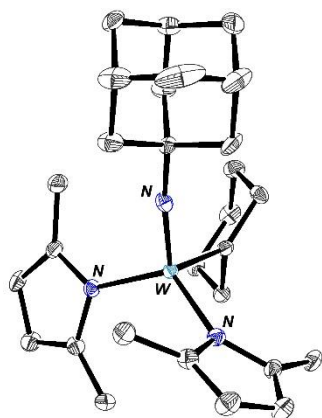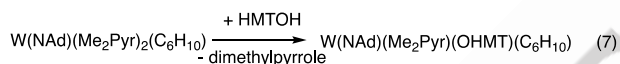
**Figure 5.** The structure of W(NAd)(C$_6$H$_{10}$)($\eta^1$-Me$_2$Pyr)$_2$.

Addition of 2,6-Mesityl$_2$C$_6$H$_3$OH (hexamethylterphenol or HMTOH) to W(NAd)(C$_6$H$_{10}$)(Me$_2$Pyr)$_2$ in toluene leads to formation of W(NAd)(C$_6$H$_{10}$)(Me$_2$Pyr)(OHMT), a Monoaryloxide Pyrrolide (MAP) complex, after heating the reaction at 70 °C for 24h (eq 7). MAP complexes have been the catalysts of choice in a variety of challenging catalytic metathesis reactions.[25] The fact that MAPs are asymmetric raises questions about the role of that asymmetry at the metal in terms of the formation and reformation of alkylidenes and the efficiency of MAPs as metathesis catalysts.

$$\text{W(NAd)(Me}_2\text{Pyr)}_2\text{(C}_6\text{H}_{10}) \xrightarrow[\text{- dimethylpyrrole}]{\text{+ HMTOH}} \text{W(NAd)(Me}_2\text{Pyr)(OHMT)(C}_6\text{H}_{10}) \quad (7)$$

We conclude that imido ligands can be doubly protonated by hexafluoro- or perfluoro-$t$-butanols and W cyclohexylidenes (in particular) thereby accessed through relatively short syntheses without using strong acids. The bisnonafluoro-$t$-butoxide alkylidene complexes can be converted into others (*e.g.*, bisalkoxide, bispyrrolide, and MAP complexes). W(NR)(C$_6$H$_{10}$)(OR$_{F9}$)$_2$ complexes are available from tungsten oxo complexes in three steps (*e.g.*, WO$_2$Cl$_2$ -> W(NR)$_2$Cl$_2$ -> W(NR)$_2$Cy$_2$ -> W(NR)(C$_6$H$_{10}$)(OR$_{F9}$)$_2$). Alkylidene formation depends sharply upon the size and pK$_a$ of the alcohol. It is surprising to us that cyclohexylidene complexes appear to be prepared more readily than neopentylidene or neophylidene analogs, perhaps in part because any cyclohexene complex is catalytically isomerized to a cyclohexylidene complex in the presence of R$_{F9}$OH. It is important to note that cyclohexylidene complexes are relatively resistant to bimolecular decomposition and cannot form an alkylidyne complex through removal of an $\alpha$ proton.[26]

## Supporting Information

CCDC 2293446, 2293446, 2293448, 2357723, 2357724, and 2358851. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. The supporting information includes synthetic details of all complexes, NMR spectra, mechanistic experiments, and X-ray crystallographic details. Additional references have been cited within the Supporting Information.[28]

## Conflict of Interest

The authors declare no conflict of interest.

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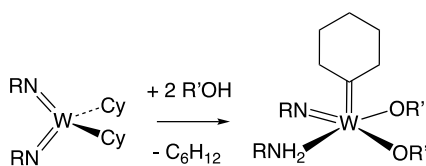


Cy = cyclohexyl; R'OH = $(CF_3)_3COH$ or $Me(CF_3)_2COH$;
R = 1-adamantyl or 2,6-diisopropylphenyl

The metathesis-active $W(NR)(C_6H_{10})(OR_{F9})_2$ ($C_6H_{10}$ = cyclohexylidene) complexes are available in three steps (tungsten oxides -> $W(NR)_2Cl_2$ -> $W(NR)_2Cy_2$ -> $W(NR)(C_6H_{10})(OR_{F9})_2$) without making alkylidene intermediates using strong acids. The bisnonafluoro-*t*-butoxide alkylidene complexes can be converted readily into bisalkoxide, bispyrrolide, and MAP complexes through nucleophilic substitutions. Cyclohexylidene complexes appear to be more readily prepared than neophylidene complexes, perhaps in part because any cyclohexene complex is isomerized to a cyclohexylidene complex by $R_{F9}OH$. This mild acid-catalyzed approach is an attractive alternative to established syntheses of tungsten neopentylidene or neophylidene imido complexes.