ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

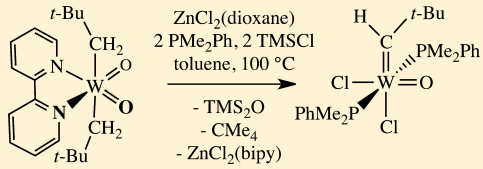
Synthesis of Tungsten Oxo Alkylidene Complexes

Dmitry V. Peryshkov and Richard R. Schrock*

Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Supporting Information

ABSTRACT: Reaction of $W(O)_2(CH_2\text{-}t\text{-}Bu)_2(bipy)$ with a mixture of $ZnCl_2(dioxane)$, PMe_2Ph, and trimethylsilyl chloride in toluene at 100 °C produced the known tungsten oxo alkylidene complex $W(O)(CH\text{-}t\text{-}Bu)Cl_2(PMe_2Ph)_2$ (**1a**) in 45% isolated yield. The neophylidene analogue $W(O)(CHCMe_2Ph)Cl_2(PMe_2Ph)_2$ was prepared similarly in 39% yield. The reaction between **1a** and LiOR (LiOR = LiOHIPT, LiOHMT) in benzene at 22 °C led to formation of the off-white $W(O)(CH\text{-}t\text{-}Bu)Cl(OR)(PMe_2Ph)$ complexes **4a** (OR = OHMT = 2,6-dimesitylphenoxide) and **4b** (OR = OHIPT = 2,6-(2,4,6-triisopropylphenyl)$_2$phenoxide). Compound **4a** serves as a starting material for the synthesis of $W(O)(CH\text{-}t\text{-}Bu)(OHMT)$(2,6-diphenylpyrrolide) (**6**), $W(O)(CH\text{-}t\text{-}Bu)[N(C_6F_5)_2](OHMT)(PMe_2Ph)$ (**7**), $W(O)(CH\text{-}t\text{-}Bu)[OSi(t\text{-}Bu)_3](OHMT)$ (**8**), and $W(O)(CH\text{-}t\text{-}Bu)(OHMT)_2$ (**10**). The reaction between **8** and ethylene was found to yield the square-pyramidal metallacyclobutane complex $W(O)(C_3H_6)[OSi(t\text{-}Bu)_3](OHMT)$ (**9**), while the reaction between **10** and ethylene was found to yield the square-pyramidal metallacyclobutane complex $W(O)(C_3H_6)(OHMT)_2$ (**11**). Compound **11** loses ethylene to yield isolable $W(O)(CH_2)(OHMT)_2$ (**12**). X-ray structures were determined for **6**, **7**, **9**, and **12**.



INTRODUCTION

Tungsten has figured prominently in the history of the olefin metathesis reaction, which is the only way to prepare olefins from olefins directly and catalytically.[1,2] Oxo alkylidene complexes were the first high-oxidation-state alkylidene complexes containing tungsten to be identified as olefin metathesis catalysts,[3] but attention soon shifted to imido alkylidene complexes of W, and ultimately Mo, in anticipation of slowing bimolecular decomposition of 14-electron four-coordinate $M(NR)(CHR')X_2$ catalysts, relative to hypothetical $M(O)(CHR')X_2$ catalysts, for steric reasons.[4] Unlike oxo ligands, imido ligands, along with X ligands (e.g., alkoxides), can be varied sterically and electronically and the chemistry of Mo and W imido alkylidene complexes in olefin metathesis reactions thereby controlled to a significant degree. For the last 25 years, imido alkylidene complexes have been the mainstay of high-oxidation-state olefin metathesis catalysts. In contrast, interest in oxo alkylidene complexes has been limited.[5,6] Oxo alkylidene complexes or oxo-free cationic complexes of the type discovered by Osborn[2] are likely to be the active catalysts in many of the "classical" olefin metathesis systems. Therefore, we thought it worthwhile to attempt to prepare oxo alkylidene complexes using recently proven methods that have been employed to slow bimolecular decomposition of imido alkylidene complexes.

The most recent advance in Mo and W imido alkylidene chemistry has been the discovery and development of $M(NR)(CHR')(OR'')$(Pyrrolide) (monoaryloxide pyrrolide or MAP) complexes.[7] One of the most interesting aspects of MAP catalysts is that they can be designed to promote *Z*-selective metathesis reactions as a consequence of the presence of a relatively "large" aryloxide (OR″) in combination with a "small" NR ligand.[8] The most successful OR″ ligands so far in *Z*-selective MAP catalysts have been O-2,6-(2,4,6-triisopropylphenyl)$_2$C$_6$H$_3$ (OHIPT)[9] and O-2,6-Mesityl$_2$C$_6$H$_3$ (OHMT).[10] It has been proposed that the high steric demands of these hexasubstituted 2,6-terphenoxide ligands force all substituents on the metallacyclobutane ring to point away from the bulky aryloxide ligand and therefore allow only *Z* products to form. Since an oxo ligand is smaller than any NR ligand, we wanted to know whether MAP versions of tungsten oxo alkylidene complexes would be useful *Z*-selective catalysts, to what degree the behavior of oxo alkylidene complexes as olefin metathesis catalysts might differ from the behavior of imido alkylidene complexes as olefin metathesis catalysts, and what ligands would be required to stabilize oxo alkylidene complexes against bimolecular decomposition reactions.

In 1996 we showed that $W(O)(CH\text{-}t\text{-}Bu)L_2Cl_2$ complexes (L = PMe_3 or other phosphines) would react with 2 equiv of $KO\text{-}2,6\text{-}Ph_2C_6H_3$ to yield $W(O)(CH\text{-}t\text{-}Bu)(O\text{-}2,6\text{-}Ph_2C_6H_3)_2(L)$ complexes, one of which was shown to be a trigonal-bipyramidal complex containing an equatorial oxo, an alkylidene, and one $O\text{-}2,6\text{-}Ph_2C_6H_3$ ligand.[6] More recently,[11] we showed that a similar approach could be employed in order to prepare W(O)(CH-*t*-Bu)(Cl)(OHIPT) and W(O)(CH-*t*-Bu)(Cl)(OHMT)(PMe_2Ph) and their 2,5-dimethylpyrrolide derivatives W(O)(CH-*t*-Bu)(Me_2Pyr)(OHIPT) and W(O)(CH-*t*-Bu)(Me_2Pyr)(OHMT)(PMe_2Ph). In line with the theory of *Z*-selectivity described above, W(O)(CH-*t*-Bu)(Me_2Pyr)(OHMT)(PMe_2Ph) was shown to be a highly effective catalyst for the *Z*-selective coupling of several terminal olefins (at 0.2% loading) to give product in >75% yield with >99% *Z* configuration. Addition of 2 equiv of $B(C_6F_5)_3$ to

Received: September 4, 2012
Published: October 2, 2012

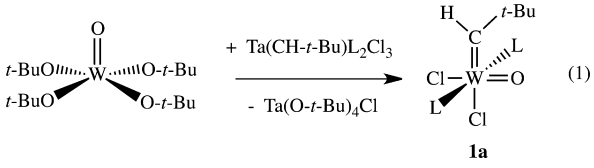
   dx.doi.org/10.1021/om3008579 | *Organometallics* 2012, 31, 7278−7286

W(O)(CH-*t*-Bu)(Me_2Pyr)(OHMT)(PMe_2Ph) led to formation of the adduct W[$OB(C_6F_5)_3$](CH-*t*-Bu)(Me_2Pyr)(OHMT), which was found to be highly active for olefin metathesis, but gave the *E*:*Z* mixture expected from thermodynamic control upon coupling terminal olefins. How oxo alkylidene complexes behave in the presence of Lewis acids, an issue that was explored by Osborn[2] to some degree and that remains unexplored as far as well-defined catalysts are concerned, is an important goal that is relevant to "classical" catalysts, as discussed above, and to new isolable oxo alkylidene complexes.

A simpler synthesis of tungsten oxo alkylidene starting materials would be beneficial to further studies of oxo alkylidene chemistry. In this paper we report a simplified synthesis of tungsten oxo alkylidene complexes that involves formation of the neopentylidene ligand on tungsten through α hydrogen atom abstraction in a dineopentyl precursor and elaborate the syntheses of tungsten oxo alkylidene complexes that are relevant to olefin metathesis. We also for the first time prepare and characterize oxo metallacyclobutane and oxo methylidene complexes.

RESULTS

New Synthesis of Oxo Alkylidene Complexes of Tungsten. The original synthesis of W(O)(CH-*t*-Bu)$Cl_2(PMe_2Ph)_2$ (**1a**) and related bis-phosphine complexes[3] was based on synthesis of a tantalum neopentylidene complex and transfer of the neopentylidene ligand from tantalum to tungsten, as shown in eq 1. Ta(CH-*t*-Bu)$Cl_2(PMe_2Ph)_2$ is



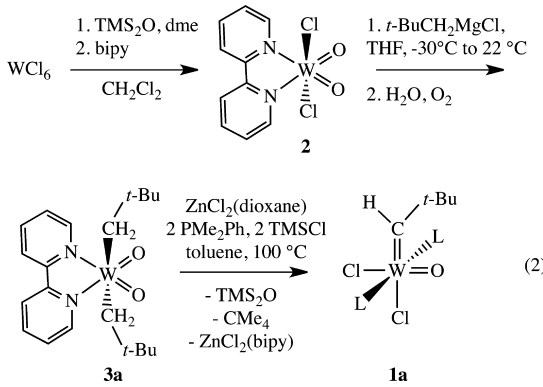
(1)

1a

formed readily upon addition of PMe_2Ph to a solution of $Ta(CH_2\text{-}t\text{-}Bu)_3Cl_2$ in pentane. The synthesis of $Ta(CH_2\text{-}t\text{-}Bu)_3Cl_2$ from $TaCl_5$ and $Zn(CH_2\text{-}t\text{-}Bu)_2$ in pentane is also straightforward, but $Zn(CH_2\text{-}t\text{-}Bu)_2$ must be prepared and purified for this purpose. W(O)(O-*t*-Bu)$_4$ can be synthesized in modest yield in a reaction between W(O)Cl_4 and LiO-*t*-Bu and isolated through sublimation. Therefore, synthesis of W(O)(CH-*t*-Bu)Cl_2L_2 complexes (L = a phosphine) is somewhat lengthy and "indirect": i.e., the alkylidene is not prepared on tungsten.

Alternative methods of forming tungsten oxo alkylidene complexes have included oxidation of W(II) and W(IV) complexes and hydrolysis of W(VI) alkylidynes.[12,15] Although it would be most desirable to prepare oxo alkylidenes through alkylation of W(O)Cl_4, direct alkylation of W(O)Cl_4 with lithium, magnesium, and zinc alkyls has been found to lead to complex mixtures in which the oxo group has been removed from the metal and/or the metal has been reduced.[2,13] Several tungsten d^0 oxo alkyl complexes are known,[2,14,15] but they generally cannot be synthesized through direct alkylation for the reasons just stated. What could be called exceptions are reactions between W(O)$_2$Br$_2$(bipy) (bipy = 2,2′-bipyridine) and Grignard reagents developed and explored by Schrauzer's group.[15] Although alkylations of W(O)$_2$Br$_2$(bipy) with methyl, ethyl, propyl, and neopentyl Grignard reagents led to dark mixtures that probably contain reduced metal complexes, *aqueous workup in air* of the crude product led to air-stable W(O)$_2$R$_2$(bipy) complexes in good yields.

A starting material more convenient than W(O)$_2$Br$_2$ is W(O)$_2$Cl$_2$, which can be prepared on a large scale in a reaction between tungsten hexachloride and hexamethyldisiloxane in dichloromethane.[16] Pale yellow W(O)$_2$Cl$_2$(bipy) (**2**)[16a,b] can be prepared on a large scale in essentially one step from WCl_6 through addition of bipyridine to a dichloromethane solution of W(O)$_2$Cl$_2$(DME) (DME = dimethoxyethane) (eq 2). Addition



(2)

of 3.7 equiv of neopentylmagnesium chloride to a solution of **2** in THF results in the formation of dark red solutions. After aqueous aerobic workup analogous to that reported by Schrauzer,[15] yellow W(O)$_2$(CH_2-*t*-Bu)$_2$(bipy) (**3a**) can be isolated in 70% yield. Similar reactions employing $PhMe_2CH_2MgCl$ led to W(O)$_2$(CH_2CMe_2Ph)$_2$(bipy) (**3b**) in 70% yield. Proton NMR spectra are consistent with **3a**,**b** having C_{2v} symmetry with the two oxo ligands *cis* to each other and *trans* to bipy. All structurally characterized M(O)$_2$R$_2$(bipy) complexes (M = Mo, W) have this basic structure.[15,17]

Fürstner showed that bipy can be removed from molybdenum imido alkylidene or alkylidyne complexes through addition of zinc chloride and catalysts for olefin or acetylene metathesis thereby generated in situ.[18] Bipy complexes also can be useful intermediates in synthesis, as we have shown recently for some molybdenum-based MAP complexes.[19] Treatment of **3a** with a mixture containing 1 equiv of $ZnCl_2$(dioxane), slightly less than 2 equiv of of PMe_2Ph, and 2 equiv of trimethylsilyl chloride (TMSCl) in toluene at 100 °C for 2 h led to the formation of the tungsten oxo alkylidene complex W(O)(CH-*t*-Bu)$Cl_2(PMe_2Ph)_2$ (**1a**), hexamethyldisiloxane, neopentane, and $ZnCl_2$(bipy) (eq 2). Double recrystallization of the crude product from a mixture of diethyl ether and tetrahydrofuran gave **1a** in 45% isolated yield. The neophylidene analogue W(O)($CHCMe_2Ph$)$Cl_2(PMe_2Ph)_2$ (**1b**) was prepared in a similar manner and isolated in 39% yield as a yellow solid. Like **1a**, **1b** is a *syn* alkylidene on the basis of the J_{CH_α} value for the alkylidene (126 Hz). The two phosphine ligands are equivalent and remain bound to tungsten on the NMR time scale at 22 °C with J_{PW} = 333 Hz. The new synthesis of W(O)(CHR)$Cl_2(PMe_2Ph)_2$ complexes consists of three relatively simple steps starting from tungsten hexachloride, which is a significant improvement over the existing method shown in eq 1.

The mechanism of formation of the alkylidene in **1a**,**b** is proposed to involve attack on one of the oxo ligands in W(O)$_2$(CH_2R)$_2$(bipy) (R = *t*-Bu, CMe_2Ph) successively by 2 equiv of TMSCl to give TMS_2O and a W(O)Cl_2(CH_2R)$_2$(bipy) intermediate, from which CH_3R is lost to

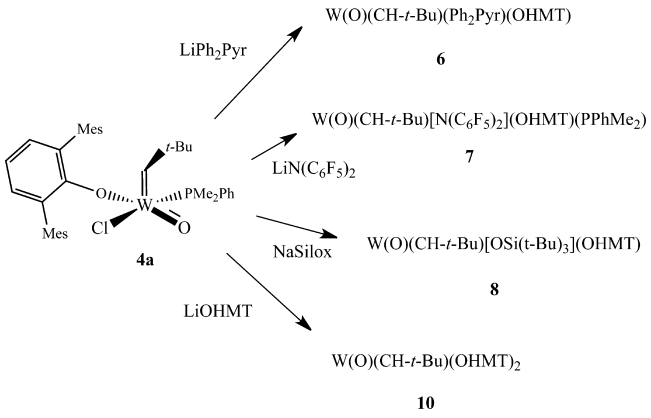
dx.doi.org/10.1021/om3008579 | *Organometallics* 2012, 31, 7278−7286

give W(O)(CHR)Cl_2(bipy). Intramolecular abstraction of an α proton in the alkyl group becomes possible after one oxo ligand is replaced by two chlorides,[4] especially in the presence of a ligand that could promote α abstraction in an 18-electron, seven-coordinate intermediate. We cannot exclude the possibility that α abstraction takes place in an intermediate W(O)Cl($OSiMe_3$)($CH_2R)_2$(bipy) species followed by replacement of the trimethylsiloxide with chloride upon further reaction with TMSCl. Although treatment of W(O)$_2$(CH_2-*t*-Bu)$_2$(bipy) with only 2 equiv of TMSCl leads to a product mixture whose NMR spectra are consistent with the major product being W(O)(CH-*t*-Bu)Cl_2(bipy), we have not been able to obtain this compound in pure form. The one-step conversion of **3a**,**b** to **1a**,**b** is more convenient in any case.

Synthesis of Oxo Alkylidene Derivatives. The reaction between **1a** and LiOR (LiOR = LiOHIPT, LiOHMT) in benzene at 22 °C led to formation of the off-white W(O)(CH-*t*-Bu)Cl(OR)(PMe_2Ph) complexes **4a** (OR = OHMT) and **4b** (OR = OHIPT), each as a mixture of two *syn* alkylidene isomers.[11] The phosphine remains bound to tungsten on the NMR time scale at 22 °C in both **4a** and **4b**. Addition of $LiMe_2Pyr$ to **4a**,**b** led to isolation of W(O)(CH-*t*-Bu)(η^1-Me_2Pyr)(OHMT)(PMe_2Ph) (**5a**) and W(O)(CH-*t*-Bu)(η^1-Me_2Pyr)(OHIPT) (**5b**), both of which were characterized through X-ray studies.[11] Phosphine-free **5b** is formed as a consequence of the greater steric demand of the OHIPT versus that of the OHMT ligand. The structure of **5a** is a square pyramid with a *syn* neopentylidene in the apical position and the phosphine bound *trans* to the pyrrolide.[11] The equilibrium constant for phosphine dissociation in **5a** was estimated to be 0.015 M at room temperature through NMR studies, a value that corresponds to 57% dissociation of phosphine-free W(O)(CH-*t*-Bu)(η^1-Me_2Pyr)(OHMT) being present in a 20 mM solution of **5a** in C_6D_6. The steric demand of the OHIPT ligand limits the reactivity of **5b** versus that of **5a** in the few reactions that were explored.[11]

We have found **4a** to be a suitable starting point for formation of several other oxo alkylidene species, in addition to **5a**, as shown in Scheme 1, most of which are obtained as 14e

Scheme 1



(phosphine-free) species. Addition of 1 equiv of lithium 2,5-diphenylpyrrolide to a toluene solution of W(O)(CH-*t*-Bu)(OHMT)Cl(PMe_2Ph) at room temperature led to the formation of yellow W(O)(CH-*t*-Bu)(Ph_2Pyr)(OHMT) (**6**) in 57% isolated yield. The α proton resonance for the alkylidene resonance in the ^{1}H NMR spectrum of **6** is found at 9.99 ppm (cf. 9.14 ppm in **5a**[11]) with J_{CH} = 124 Hz, which is characteristic of a *syn* orientation of the alkylidene. Although the alkylidene resonance is broadened slightly, the ^{183}W satellites are discernible (J_{HW} = 10 Hz). The resonances for the two protons on the pyrrolide ring are broad at room temperature, which suggests either hindered rotation of the diphenylpyrrolide ligand or an equilibrium between η^1 and η^5 coordination modes. Compound **6** apparently is too crowded to coordinate dimethylphenylphosphine to give an adduct analogous to **5a**.[11]

Single crystals of **6** were grown from toluene/pentane solution at −30 °C. A thermal ellipsoid drawing of the structure is shown in Figure 1. The W═O distance (1.690(1) Å) is

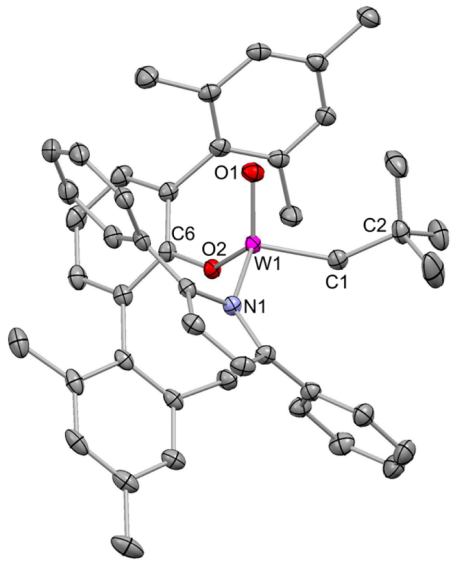


Figure 1. Thermal ellipsoid plot (50% probability) of W(O)(CH-*t*-Bu)(Ph_2Pyr)(OHMT) (**6**). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): W1−C1 = 1.895(2), W1−O1 = 1.690(1), W1−O2 = 1.894(1), W1−N1 = 2.037(2); W1−C1−C2 = 141.1(1), W1−O2−C6 = 143.1(1).

comparable to the W═O bond length in **5b** (1.695(3) Å).[11] The pyrrolide ligand is coordinated in η^1 fashion with an W−N_{pyr} distance of 2.037(2) Å, versus the W−N_{pyr} bond length in **5b** (2.001(2) Å). In Mo(NAr)(CH-*t*-Bu)(η^1-2,5-Ph_2Pyr)(η^5-2,5-Ph_2Pyr),[20] the Mo−N_{pyr} bond length for the η^1 pyrrolide is slightly longer (2.1145(10) Å) than in **5b**, as one might expect for an 18-electron complex. The W−N_{Pyr} vector in **6** does not lie in the plane of the pyrrolide ligand: i.e., the pyrrolide is tipped so that the angle between the W−N_{Pyr} vector and the plane is 161.7°. This phenomenon has been noticed in other high-oxidation-state pyrrolide complexes such as trigonal-bipyramidal unsubstituted metallacyclobutane complexes of Mo and W.[21]

Treatment of **4a** with $LiN(C_6F_5)_2$[22] in CH_2Cl_2 led to formation of W(O)(CH-*t*-Bu)[$N(C_6F_5)_2$](OHMT)(PMe_2Ph) (**7**) in 60% isolated yield. The X-ray structure of **7** showed it to be essentially a square pyramid with the *syn* alkylidene ligand in the apical position and the phosphine ligand *trans* to the amide (Figure 2). The amido nitrogen atom is not planar (the three angles sum to 349.7(2)°), and one of the ortho fluorides (F1) could be interacting weakly with the metal *trans* to the alkylidene (W−F1 = 2.758(1) Å), which is not unusual in compounds that contain the perfluorodiphenylamido ligand.[22]

dx.doi.org/10.1021/om3008579 | *Organometallics* 2012, 31, 7278−7286

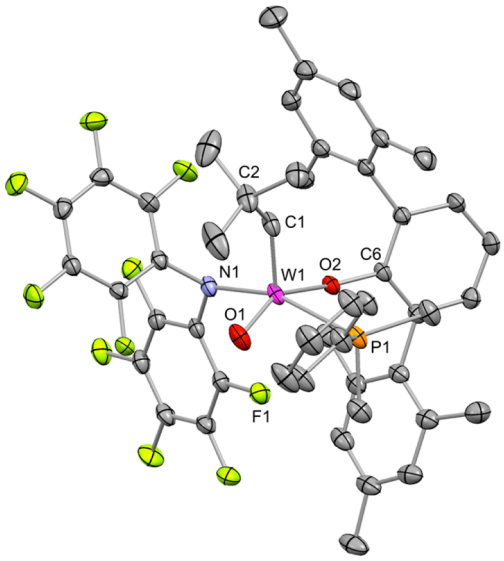
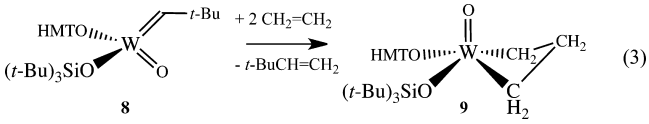


Figure 2. Thermal ellipsoid plot (50% probability) of W(O)(CH-*t*-Bu)[N(C_6F_5)$_2$](OHMT)(PMe_2Ph) (**7**). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): W1−C1 = 1.898(2), W1−O1 = 1.710(2), W1−O2 = 1.965(1), W1−N1 = 2.127(2), W1−P1 = 2.564(1); W1−C1−C2 = 141(2), W1−O2−C6 = 154.0(1).

The amido ligand could also be said to be "tipped" out of planarity, as found for the diphenylpyrrolide in **6**. The broad alkylidene resonance in **7** results from the phosphine dissociating in solution at room temperature. A variable-temperature ^{1}H and ^{31}P NMR study of a 74 mM solution of **7** in toluene-d_8 showed that the phosphine is bound on the NMR time scale below −20 °C (a sharp resonance is found at 2.69 ppm with J_{PW} = 347 Hz), but in toluene at 22 °C K_{eq} is ∼0.002 M, i.e., ∼50% of **7** is converted into W(O)(CH-*t*-Bu)[N(C_6F_5)$_2$](OHMT) at 74 mM concentration. A K_{eq} value of 0.002 should be compared with that for **5a** (0.015 M) noted earlier. At −20 °C, 10 broadened ^{19}F resonances are observed for **7**, which suggests that the N(C_6F_5)$_2$ ligand is not rotating freely at −20 °C on the NMR time scale.

Addition of 1 equiv of NaSilox to **4a** at room temperature resulted in formation of phosphine-free W(O)(CH-*t*-Bu)(OHMT)(Silox) (**8**) as essentially the only product, according to ^{1}H and ^{31}P NMR data. However, **8** was too soluble in pentane to isolate on the small scale employed (150 mg). Therefore, **8** was prepared from 250 mg of **4a** and a solution of it in pentane was exposed to 1 atm of ethylene; the metallacyclobutane complex W(O)($CH_2CH_2CH_2$)(OHMT)(Silox) (**9**) crystallized out as light yellow crystals in 25% isolated yield (eq 3). A 0.018 M solution of **9** in C_6D_6 under



(3)

dinitrogen was found to consist of 98% **9** and 2% of what is proposed to be the methylidene complex W(O)(CH_2)(OHMT)(Silox) (δ(CH_2) at 7.77 and 8.93 ppm), formed through loss of ethylene from **9**. Heating a solution of **9** in C_6D_6 to 70 °C led to broadening of the metallacycle proton resonances and the appearance of free ethylene and broadened methylidene resonances, consistent with facile exchange of ethylene in the WC_3 ring on the NMR time scale. Only three metallacycle resonances are observed for W(O)(C_3H_6)(OHMT)(Silox) in C_6D_6 (4.10, 2.54, and 1.93 ppm, 1:1:1 ratio); presumably three other resonances are obscured. Three ^{13}C resonances can be attributed to the metallacycle at 43.8, 41.5, and 22.3 ppm. The range of chemical shifts of metallacycle protons and carbons is indicative of square-pyramidal (SP) coordination of the metal center found for W(NAr)[CH_2CH(*t*-Bu)CH_2](O-*t*-Bu)$_2$.[23]

Single crystals of **9** were grown from a mixture of toluene and pentane at −30 °C. An X-ray structural study confirmed the proposed SP configuration of **9**, in which the oxo ligand is in the apical position (Figure 3). To our knowledge, **9** is the first

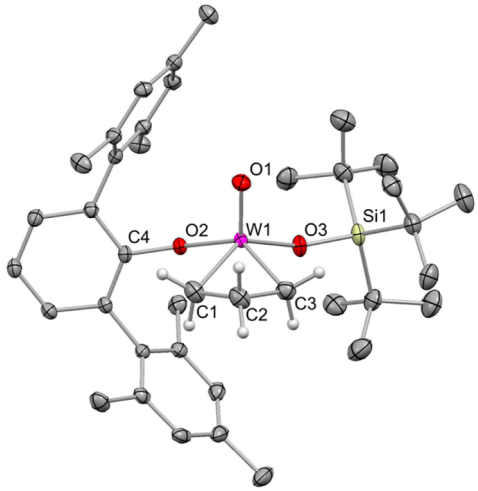
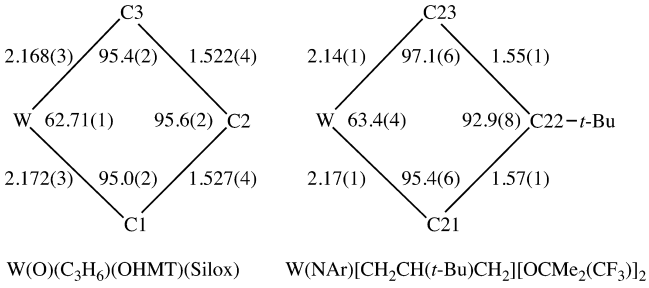


Figure 3. Thermal ellipsoid plot (50% probability) of square-pyramidal W(O)(C_3H_6)(OHMT)(Silox) (**9**). Hydrogen atoms, except for those on the metallacycle, have been omitted for clarity. Only the major component of disorder is shown. Selected bond distances (Å) and angles (deg): W1−C1 = 2.172(3), W1−C3 = 2.168(3), W1−O1 = 1.690(2), W1−O2 = 1.896(2), W1−O3 = 1.875(3), C1−C2 =1.527(4), C2−C3 = 1.522(4); W1−C1−C2 = 95.0(2), W1−C3−C2 = 95.4(2), C1−C2−C3 = 95.6(2), C1−W1−C3 = 62.7(1), O2−W1−O3 = 103.3(1), O1−W1−O2 = 113.6(1), O1−W1−O3 = 113.4(1), W1−O2−C4 = 148.0(1), W1−O3−Si1 = 161.9(4).

structurally characterized metallacyclobutane derived from an oxo alkylidene and the first *unsubstituted* high-oxidation-state molybdacyclobutane or tungstacyclobutane that has a square-pyramidal geometry. (All unsubstituted Mo or W imido metallacyclobutane complexes have TBP geometries.[23]) The bond lengths and bond angles in the WC_3 ring in **9** are identical with those in W(NAr)[CH_2CH(*t*-Bu)CH_2][$OCMe_2(CF_3)$]$_2$ (within 3σ), as shown in Figure 4.[23] The WC_3 ring in **9** is bent with a 33.8° dihedral angle between the C1−W−C3 and C1−C2−C3 planes, in comparison to a 33.4° angle in W(NAr)[CH_2CH(*t*-Bu)CH_2][$OCMe_2(CF_3)$]$_2$.[23] Relatively long W−C_β distances in SP metallacyclobutane complexes of W (W···C2 = 2.762(3) Å in **9**) have led to the proposal that SP metallacyclobutane complexes are further from the transition state for loss of olefin to give an alkylidene than are TBP metallacycles.[24]

Addition of 1 equiv of LiOHMT to W(O)(CH-*t*-Bu)(OHMT)Cl(PMe_2Ph) (100 °C, toluene) leads to formation of W(O)(CH-*t*-Bu)(OHMT)$_2$ (**10**) in good yield, but **10** is prepared most conveniently in 41% isolated yield by treating

dx.doi.org/10.1021/om3008579 | *Organometallics* 2012, 31, 7278−7286

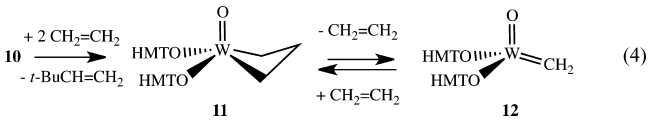


$W(O)(C_3H_6)(OHMT)(Silox)$ $W(NAr)[CH_2CH(t\text{-}Bu)CH_2][OCMe_2(CF_3)]_2$

Figure 4. Comparison of bond distances and angles in two SP metallacyclobutane complexes.

$W(O)(CH\text{-}t\text{-}Bu)Cl_2(PMe_2Ph)_2$ with 2 equiv of LiOHMT at 100 °C in toluene for 48 h. The resonance for the alkylidene proton in the proton NMR spectrum of **10** is found at 7.34 ppm with $^1J_{CH}$ = 122 Hz and $^2J_{HW}$ = 14 Hz. Three mesityl methyl resonances were observed for the OHMT ligands in the proton NMR spectrum at 22 °C, consistent with the OHMT ligands being equivalent, free rotation about the W−O bonds, and (as one would expect) no rotation about the C−C bonds to the central phenyl ring. The *two* sets of *ortho* mesityl methyl groups arise from the fact that no symmetry plane bisects the C═W═O angle in **10**. Two other bis-2,6-terphenoxide alkylidene complexes, $M(NC_6F_5)(CHR)(ODFT)_2$ (M = Mo, W; ODFT = O-2,6-$(C_6F_5)_2C_6H_3$), have been reported in the literature.[25] The fluorine NMR spectra of $M(NC_6F_5)(CHR)(ODFT)_2$ complexes show one *para*, two *meta*, and two *ortho* fluorine resonances between 22 and 100 °C, which is consistent with the proposals with respect to **10** discussed above.

When a pentane solution of **10** was placed under 1 atm of ethylene, a yellow precipitate can be isolated whose proton NMR spectrum in C_6D_6 shows that a mixture of $W(O)(C_3H_6)(OHMT)_2$ (**11**) and $W(O)(CH_2)(OHMT)_2$ (**12**) in a 3:1 ratio is present. We propose that the precipitate is pure **11**, but upon dissolution in benzene some ethylene is lost from **11** to give the mixture of **11** and **12** in solution. Theoretical values for % C and % H are too similar for **11** (68.00 and 6.27) and **12** (67.43 and 6.01) to confirm that the precipitate is pure **11** (found: C, 67.82; H, 6.29) through elemental analysis; therefore, we have to rely on the fact that only **11** is sufficiently insoluble to precipitate in the manner described. Compound **12** can be isolated in pure form through repeated dissolution of mixtures of **11** and **12** in toluene followed by slow removal of the solvent in vacuo (eq 4). Two methylidene doublet



(4)

resonances are observed in ^{1}H NMR spectra of **12** in C_6D_6 at 8.90 ppm (H_{syn}, $^1J_{CH}$ = 160 Hz, $^2J_{HH}$ = 10 Hz) and 7.85 ppm (H_{anti}, $^1J_{CH}$ = 140 Hz). The lower J_{CH} value for H_{anti} is consistent with a C−H_{anti} agostic interaction with the metal center. Three mesityl methyl resonances are found in the proton NMR spectrum at 22 °C, as noted above for **10**. Compound **12** was found to be stable in solution for at least 24 h at room temperature at a concentration of ∼20 mM.

An X-ray structural determination of **12** confirms that it is a monomeric tetrahedral 14-electron species in the solid state (Figure 5). To our knowledge, this is the first X-ray structural study of an oxo methylidene complex. The oxo and

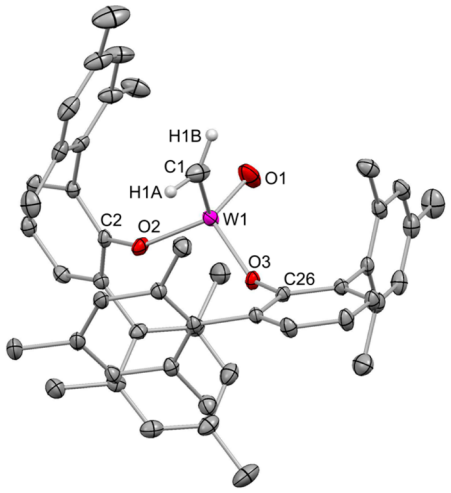


Figure 5. Thermal ellipsoid plot (50% probability) of tetrahedral $W(O)(CH_2)(OHMT)_2$ (**12**). Hydrogen atoms, except for those on the methylidene, have been omitted for clarity. Only the major component of disorder is shown. Selected bond distances (Å) and angles (deg): W1−C1 = 1.895(8), W1−O1 = 1.694(5), W1−O2 = 1.881(2), W1−O3 = 1.917(2); W1−C1−H1A = 109(3), W1−C1−H1B = 127(3), H1A−C1−H1B = 123(4), O1−W1−C1 = 103.1(3), W1−O2−C2 = 136.3(2), W1−O3−C26 = 138.6(2).

methylidene ligands were found to be mutually disordered in a ratio of 71:29. The disorder could be resolved and the methylidene protons located in the major component; they were refined semifreely with appropriate bond length restraints (see the Supporting Information). The W═C bond length (1.895(8) Å) is similar to the M═C distances in two structurally characterized 14e imido methylidene MAP complexes of Mo (1.892(5) Å) and W (1.908(4) Å).[26] The CH_2 plane is tipped ∼9° relative to the O═W═C plane, as is also found in the two Mo and W imido methylidene complexes (by 8°). The W═C1−H1a (H_{anti}) angle (109(3)°) is smaller than the W═C1−H1b (H_{syn}) angle (127(3)°), consistent with an agostic interaction between the CH_{anti} bond and the metal center and with the lower $^2J_{CH_{anti}}$ values relative to $^2J_{CH_{syn}}$ values. The W═O bond length (1.694(5) Å) is comparable to that in $W(O)(CH\text{-}t\text{-}Bu)(Me_2Pyr)(HIPTO)$ (1.695(3) Å).[11] The planes of two phenolate rings of the terphenoxides intersect at an angle of 81.5° with respect to each other. This nearly "perpendicular" relationship of the two OHMT ligands resembles a baseball cover and must hinder formation of the bis-μ-methylidene intermediate required for bimolecular decomposition yet not block access of ethylene to the metal and formation of the square-pyramidal metallacyclobutane complex **11**.

DISCUSSION

The most interesting synthetic aspect of this work is the preparation of relatively stable 14e or 16e tungsten oxo alkylidene complexes with some variety. Bimolecular decomposition must be discouraged primarily by the two anionic ligands present, where at least one is a 2,6-terphenoxide (OHMT in this work). Dimethylphenylphosphine is sometimes retained in the product (as in **7**) but is partially dissociated in solution. All 14e tungsten oxo neopentylidene complexes have been found to be the *syn* isomer, which is not surprising from a steric point of view. It is interesting to note that reactions of the type shown in Scheme 1 do not appear to suffer from

dx.doi.org/10.1021/om3008579 | *Organometallics* 2012, 31, 7278−7286

competitive deprotonation of the alkylidene ligand by the added nucleophile, a problem that has been encountered in the synthesis of certain stereogenic-at-metal imido alkylidene complexes of molybdenum recently that contain sterically demanding ligands.[27]

Another interesting feature of this work is that we have seen no evidence for intermediate trigonal-bipyramidal metallacyclobutane complexes, even unsubstituted metallacycles. Therefore, it appears that square-pyramidal oxo metallacyclobutane complexes are significantly more stable than the TBP versions, in contrast to the case for many tungsten imido analogues. This fact could have major implications in terms of the ease of turnover in metathesis reactions, since SP metallacycles are further from the transition state for loss of olefin than TBP metallacycles, as noted earlier. Extensive calculations on oxo alkylidene and metallacyclobutane complexes have been reported recently.[34]

There are many aspects of oxo alkylidene chemistry that will be explored in due course. One of the most interesting is the role of Lewis acids in oxo alkylidene chemistry. In the preliminary communication[11] it was noted that W[OB-(C_6F_5)$_3$](CH-*t*-Bu)(Me_2Pyr)(OHMT), which is in equilibrium with W(O)(CH-*t*-Bu)(Me_2Pyr)(OHMT) and B(C_6F_5)$_3$ in solution, could be structurally characterized and that it was highly active for olefin metathesis. Therefore, we now have an opportunity to move toward an understanding of the consequence of Lewis acids being present in oxo alkylidene systems. We anticipate being able to determine (inter alia) whether the general intolerance of classical catalysts, which are often prepared in the presence of Lewis acids, toward organic electron donor functionalities is a consequence of basic functionalities competing for the Lewis acid and thereby deactivating the catalyst. Studies concerned with the role of Lewis acids in oxo alkylidene chemistry are in progress.

EXPERIMENTAL SECTION

General Comments. All manipulations were done either in a nitrogen-filled drybox or on an air-free dual-manifold Schlenk line. The solvents were sparged with nitrogen, passed through activated alumina, and stored over activated 4 Å Linde-type molecular sieves. Methylene chloride-d_2, benzene-d_6, and toluene-d_8 were distilled from calcium hydride (CD_2Cl_2) or sodium ketyl (C_6D_6, C_7D_8) and stored over activated 4 Å Linde-type molecular sieves. NMR spectra were recorded using Varian spectrometers at 500 (^{1}H), 125 (^{13}C), and 121 (^{31}P) MHz, reported in δ (parts per million) relative to tetramethylsilane (^{1}H, ^{13}C) or 85% phosphoric acid (^{31}P), and referenced to the residual ^{1}H/^{13}C resonances of the deuterated solvent (^{1}H (δ), benzene 7.16, methylene chloride 5.32, chloroform 7.26, toluene 7.09, 7.01, 6.97, 2.08; ^{13}C (δ), benzene 128.06, methylene chloride 53.84, chloroform 77.16, toluene 20.43) or external 85% phosphoric acid standard (^{31}P (δ), 0) and hexafluorobenzene (^{19}F (δ), −164.9). Midwest Microlab, Indianapolis, IN, provided the elemental analysis results.

W(O)(CH-*t*-Bu)Cl(HMTO)(PMe_2Ph),[11] 2,5-diphenylpyrrolide,[28] and NH(C_6F_5)$_2$[29] were prepared according to reported procedures. H(Silox) was received as a generous gift from Professor Pete Wolczanski. NaSilox was prepared in the reaction of H(Silox) and NaH in THF. All other reagents were used as received unless noted otherwise.

Synthesis of W(O)$_2$Cl$_2$(bipy) (2). Compound **2** was prepared by a modification of the published procedure.[16] A solution of hexamethyldisiloxane (21.49 g, 132 mmol, 2.1 equiv) was added dropwise to the solution of tungsten hexachloride (25.00 g, 63.0 mmol) in 250 mL of dichloromethane. A solution of dimethoxyethane (13.06 g, 145 mmol, 2.3 equiv) was added. The mixture was stirred for 2 h at room temperature, during which time it became dark blue and contained a suspended precipitate. A pale blue solution was obtained after filtration of the mixture through Celite. A solution of 2,2′-bipyridine (10.33 g, 66.1 mmol, 1.05 equiv) in 30 mL of dichloromethane was added, and the mixture was stirred for 30 min. The precipitate was isolated by filtration, washed twice with 50 mL of dichloromethane, and dried under vacuum. The pale yellow powder was collected (25.83 g, 58.3 mmol, 92% yield). Anal. Calcd for $C_{10}H_8Cl_2N_2O_2W$: C, 27.10; H, 1.82; N, 6.32. Found: C, 26.27; H, 1.86; N, 5.97.

Synthesis of W(O)$_2$(CH$_2$-*t*-Bu)$_2$(bipy) (3a). Compound **3a** was prepared in a manner similar to the published procedure[15] using W(O)$_2$Cl$_2$(bipy) instead of W(O)$_2$Br$_2$(bipy) as a starting material. A cold (−30 °C) solution of *t*-BuCH$_2$MgCl in ether (40 mL, 1.66 M, 3.7 equiv) was added to a cold (−30 °C) suspension of W(O)$_2$Cl$_2$(bipy) (8.00 g, 18.06 mmol) in 150 mL of THF. The reaction mixture was stirred at room temperature for 1 h. Volatiles were removed under vacuum, leaving a dark red residue. After addition of water (300 mL) the mixture was periodically shaken with CH_2Cl_2 (200 mL) in air. The organic fraction gradually changed color from green to yellow to orange. The mixture was filtered through Celite. The aqueous layer was separated and discarded. The organic layer was washed five times with portions of water (150 mL), dried with anhydrous $MgSO_4$, and concentrated to 20 mL volume, causing formation of a yellow solid. A portion of hexane (200 mL) was added, and the mixture was filtered. The precipitate was recrystallized from dichloromethane/hexane. The solid product was isolated by filtration and dried under vacuum (6.47 g, 12.57 mmol, 70% yield): ^{1}H NMR (CD_2Cl_2) δ 9.55 (m, 2, bipy *H*), 8.39 (m, 2, bipy *H*), 8.15 (m, 2, bipy *H*), 7.58 (m, 2, bipy *H*), 0.94 (s, 18, CH_2CMe_3), 0.81 (s, 4, CH_2CMe_3, J_{WH} = 8 Hz); ^{13}C NMR (CD_2Cl_2) δ 196.3, 152.0, 150.4, 139.2, 125.8, 123.6, 68.1, 34.9, 33.5. Anal. Calcd for $C_{20}H_{30}N_2O_2W$: C, 46.71; H, 5.88; N, 5.45. Found: C, 46.79; H, 5.91; N, 5.47.

Synthesis of W(O)$_2$(CH$_2$CMe$_2$Ph)$_2$(bipy) (3b). The compound was prepared in a manner analogous to that employed to prepare **3a**. A cold (−30 °C) solution of $(CH_3)_2$PhCCH$_2$MgCl in ether (100 mL, 0.5 M, 3.7 equiv) was added to a cold (−30 °C) suspension of W(O)$_2$Cl$_2$(bipy) (6.000 g, 13.55 mmol) in 80 mL of THF. The reaction mixture was stirred at room temperature for 1 h. Volatiles were removed under vacuum, leaving a dark red residue. After addition of water (300 mL) the mixture was periodically shaken with CH_2Cl_2 (200 mL) in air. The organic fraction gradually changed color from green to yellow. The mixture was filtered through Celite. The aqueous layer was separated and discarded. The organic layer was washed five times with portions of water (150 mL), dried with anhydrous $MgSO_4$, and concentrated to 20 mL volume, causing formation of a pale yellow solid. A portion of hexane (150 mL) was added, and the mixture was filtered. The precipitate was recrystallized from chloroform/hexane. The solid product was isolated by filtration and dried under vacuum (5.85 g, 9.16 mmol, 67% yield): ^{1}H NMR (CD_2Cl_2) δ 8.95 (m, 2, bipy *H*), 8.24 (m, 2, bipy *H*), 8.03 (m, 2, bipy *H*), 7.35 (m, 2, bipy *H*), 7.05 (m, 10, CH_2CMe_2Ph), 1.38 (s, 12, CH_2CMe_2Ph), 1.06 (s, 4, CH_2CMe_2Ph, J_{WH} = 8 Hz); ^{13}C NMR (CD_2Cl_2) δ 154.1, 152.0, 149.9, 138.9, 127.7, 126.0, 125.8, 124.8, 123.6, 68.2, 41.3, 32.2. Anal. Calcd for $C_{30}H_{34}N_2O_2W$: C, 56.44; H, 5.37; N, 4.39. Found: C, 56.42; H, 5.44; N, 4.35.

Synthesis of W(O)(CH-*t*-Bu)Cl$_2$(PMe$_2$Ph)$_2$ (1a). Compound **3a** (3.80 g, 7.39 mmol) was mixed with ZnCl$_2$(dioxane) (1.74 g, 7.76 mmol, 1.05 equiv) and PMe_2Ph (1.94 g, 14.04 mmol, 1.9 equiv) in 40 mL of toluene. The mixture was cooled to −30 °C, and TMSCl (1.77 g, 16.26 mmol, 2.2 equiv) was added. The mixture was stirred at room temperature for 30 min and then heated to 100 °C for 2 h, during which time the color darkened and a precipitate formed. All the volatiles were removed under vacuum at 50 °C. Benzene (40 mL) was added to the dark residue, and the mixture was filtered through Celite. Solvent was evaporated from the filtrate in vacuo, leaving a yellow solid and a brown oil. The residue was stirred with 40 mL of ether for 3 h, during which time the oil disappeared and a yellow solid remained. The solid was recrystallized twice from a mixture of ether and tetrahydrofuran at −30 °C to produce a yellow crystalline solid (2.03 g, 45% yield). The ^{1}H NMR spectrum of the product is identical with that reported: ^{1}H NMR (C_6D_6) δ 12.10 (t, 1, WC*H*CMe$_3$, $^1J_{CH}$ = 125 Hz, $^3J_{PH}$ = 4 Hz), 7.65 (m, 4), 6.97 (m, 6), 1.92 (m, 12, P*Me*$_2$Ph),

dx.doi.org/10.1021/om3008579 | *Organometallics* 2012, 31, 7278−7286

0.82 (s, 9, WCHCMe_3). Anal. Calcd for $C_{21}H_{32}Cl_2OP_2W$: C, 40.87; H, 5.23. Found: C, 40.90; H, 5.12.

Synthesis of W(O)(CHCMe$_2$Ph)Cl$_2$(PMe$_2$Ph)$_2$ (1b). The compound was prepared in a manner analogous to that described for **1a**. Compound **3b** (2.99 g, 4.68 mmol) was mixed with $ZnCl_2$(dioxane) (1.10 g, 4.91 mmol, 1.05 equiv) and PMe_2Ph (1.22 g, 8.85 mmol, 1.8 equiv) in 40 mL of toluene. The mixture was cooled to −30 °C, and TMSCl (1.17 g, 10.76 mmol, 2.3 equiv) was added. The mixture was stirred at room temperature for 30 min and was heated at 100 °C for 2 h, during which time the color darkened and a precipitate formed. The solvent volume was reduced to approximately 30 mL in vacuo, and 10 mL of pentane was added. The solution was filtered through Celite, and the volatiles were removed in vacuo, leaving a brown oil. The residue was recrystallized twice from a mixture of ether and tetrahydrofuran at −30 °C to give a yellow crystalline solid (1.24 g, 39% yield): ^{1}H NMR (C_6D_6) δ 12.01 (t, 1, WC*H*CMe$_2$Ph, $^1J_{CH}$ = 126 Hz, $^3J_{PH}$ = 4 Hz), 7.68 (m, 4), 7.03 (m, 8), 6.96 (m, 3), 1.94 (t, 6, P*Me*$_2$Ph), 1.58 (t, 6, P*Me*$_2$Ph), 1.27 (s, 6, WCHC*Me*$_2$Ph); ^{13}C NMR (C_6D_6) δ 315.8 (t, WCHCMe$_2$Ph, J_{PC} = 11 Hz), 150.6, 135.1 (t), 131.4 (t), 130.6, 128.75, 128.70, 128.65, 126.8, 126.1, 51.9, 30.9, 14.7 (td); ^{31}P NMR (C_6D_6) δ 4.02 (J_{PW} = 333 Hz). Anal. Calcd for $C_{26}H_{34}Cl_2OP_2W$: C, 45.97; H, 5.05. Found: C, 46.23; H, 4.99.

Synthesis of W(O)(CH-*t*-Bu)(Ph$_2$Pyr)(OHMT) (6). A solution of W(O)(CH-*t*-Bu)Cl(OHMT)(PMe$_2$Ph) (300 mg, 0.388 mmol) in 10 mL of benzene was added to a portion of solid Li(Ph$_2$Pyr) (105 mg, 0.466 mmol, 1.2 equiv). The cloudy reaction mixture was stirred at room temperature for 24 h. The solvent was removed in vacuo to give a brown oil. The product was extracted into toluene (5 mL), and the solution was filtered through a bed of Celite. Toluene was removed in vacuo to produce a brown oil. Yellow solid precipitated upon addition of pentane (4 mL), and the resulting suspension was filtered and washed with 5 mL of pentane. The yellow product was recrystallized from a mixture of toluene and pentane at −30 °C: yield 182 mg, 57%; ^{1}H NMR (C_6D_6) δ 9.99 (s, 1, WC*H*-*t*-Bu, $^1J_{CH}$ = 124 Hz, $^2J_{WH}$ = 11 Hz), 7.24−6.94 (m, 12), 6.89 (s, 2), 6.65 (s, 2), 6.61 (d, 1), 6.46−6.14 (br., 2), 2.22 (s, 6, Ar *Me*), 2.18 (s, 6, Ar *Me*), 2.04 (s, 6, Ar *Me*), 0.71 (s, 9, WCH-*t*-*Bu*); ^{13}C NMR (C_6D_6) δ 279.7 (WCH-*t*-Bu, $^1J_{CW}$ = 201 Hz), 157.4, 137.8, 137.5, 137.3, 136.2, 133.8, 133.5, 133.1, 131.5, 130.7, 129.4, 129.2, 129.1, 127.1, 126.4, 124.3, 123.1, 113.1, 111.4, 108.6, 42.9, 32.1, 21.4, 21.2, 21.1. Anal. Calcd for $C_{45}H_{47}NO_2W$: C, 66.10; H, 5.79; N, 1.71. Found: C, 65.93; H, 5.90; N, 1.76.

Synthesis of W(O)(CH-*t*-Bu)[N(C$_6$F$_5$)$_2$](OHMT)(PMe$_2$Ph) (7). A solution of W(O)(CH-*t*-Bu)Cl(OHMT)(PMe$_2$Ph) (252 mg, 0.326 mmol) in 10 mL of dichloromethane was added to a portion of solid LiN(C$_6$F$_5$)$_2$ (127 mg, 0.358 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature for 8 h, during which time a white precipitate formed. The solvent was removed in vacuo to give a brown oil. The product was extracted into toluene (5 mL), and the solvent was filtered through a bed of Celite. Toluene was removed in vacuo to produce a yellow oil. The oil was dissolved in a 1/4 mixture of ether and pentane and cooled to −30 °C. The product was collected as an off-white solid: yield 230 mg, 65%; ^{1}H NMR (74 mM in $C_6D_5CD_3$, 22 °C) δ 10.21 (br, 1, WC*H*-*t*-Bu), 7.25 (m, 2), 7.00 (m, 3), 6.82 (m, 6), 6.64 (br, 2), 2.23 (br, 6, Ar *Me*), 2.10 (br, 6, Ar *Me*), 2.04 (br, 6, Ar *Me*), 1.20 (br, 6, P*Me*$_2$Ph) 0.60 (br, 9, WCH-*t*-*Bu*); ^{31}P NMR (74 mM in $C_6D_5CD_3$, 22 °C) δ 2.44 (br); ^{1}H NMR (74 mM in $C_6D_5CD_3$, −20 °C) δ 10.37 (br, 1, WC*H*-*t*-Bu), 7.20 (m, 2), 6.95 (m, 3), 6.81 (m, 6), 6.72 (br, 1), 6.54 (br, 1), 2.35 (br, 3, Ar *Me*), 2.22 (br, 3, Ar *Me*), 2.17 (br, 6, Ar *Me*) 2.03 (br, 3, Ar *Me*), 2.00 (br, 3, Ar *Me*), 1.17 (d, 6, P*Me*$_2$Ph) 0.52 (br, 9, WCH-*t*-*Bu*); ^{13}C NMR (74 mM in $C_6D_5CD_3$, −20 °C, *C*−F are expected to be weak) δ 297.3 (WCH-*t*-Bu), 160.1, 139.1, 138.5, 138.0, 137.6, 137.1, 136.8, 136.5, 135.0, 134.7, 133.8, 133.4, 133.0, 132.7, 131.9, 130.9, 130.8, 130.6, 129.7, 128.5, 128.4, 128.2, 120.9, 44.3, 29.8, 22.1, 21.8, 21.4, 21.1, 21.0, 20.9, 14.3 (d), 11.4 (d); ^{31}P NMR (74 mM in $C_6D_5CD_3$, −20 °C) δ 2.69 (s, J_{PW} = 347 Hz); ^{19}F NMR (74 mM in $C_6D_5CD_3$, −20 °C) δ −146.18 (br, 1), −146.62 (br, 1), −152.04 (br, 1), −160.78 (br, 1), −165.66 (br, 1), −167.58 (br, 2), −168.91 (br, 1), −169.09 (br, 1), −174.82 (br, 1). Anal. Calcd for $C_{49}H_{46}F_{10}NO_2PW$: C, 54.21; H, 4.27; N, 1.29. Found: C, 54.50; H, 4.32; N, 1.59.

Synthesis of W(O)(C$_3$H$_6$)(OHMT)(Silox) (9). A cold (−30 °C) solution of W(O)(CH-*t*-Bu)(OHMT)Cl(PMe$_2$Ph) (250 mg, 0.323 mmol) in 10 mL of toluene was added to a portion of solid NaSilox (85 mg, 0.357 mmol, 1.1 equiv). The brown reaction mixture was stirred at room temperature for 3 h. The solvent was removed in vacuo to give a brown oil. The product was extracted to toluene (5 mL), and the mixture was filtered through a bed of Celite. Toluene was removed in vacuo to produce a brown oil. Pentane (3 mL) was added to the oil. The solution was degassed by three successive freeze−pump−thaw cycles, and 1 atm of ethylene was added. The mixture was stirred at 0 °C for 1 h, during which time a yellow crystalline precipitate formed. The precipitate was filtered off, washed with 0.5 mL of cold pentane, and collected: yield 64 mg, 25%. A 0.018 M solution in C_6D_6 contained 98% of **4** and 2% of the corresponding methylidene along with the equivalent amount of ethylene: ^{1}H NMR (C_6D_6) δ 7.02−6.90 (m, 7, Ar *H*), 4.10 (m, 1, WC$_3H_6$), 2.54 (m, 1, WC$_3H_6$), 2.26 (br s, 12, Ar *Me*), 2.20 (s, 6, Ar *Me*), 1.93 (m, 1, WC$_3H_6$), 1.05 (s, 27, SiC*Me*$_3$); ^{13}C NMR (C_6D_6) δ 156.6, 136.8 (br), 136.4 (br), 135.0 (br), 134.4 (br), 130.6, 129.2, 128.7, 124.0, 43.8 (WC$_3$H$_6$), 41.4 (WC$_3$H$_6$), 30.0 (SiC*Me*$_3$), 23.9 (SiC*Me*$_3$), 22.3 (WC$_3$H$_6$), 21.4 (br, Ar *Me*), 21.2 (Ar *Me*). Anal. Calcd for $C_{39}H_{58}O_3SiW$: C, 59.42; H, 7.43. Found: C, 59.20; H, 7.11.

Synthesis of W(O)(CH-*t*-Bu)(OHMT)$_2$ (10). A solution of W(O)(CH-*t*-Bu)Cl$_2$(PMe$_2$Ph) (200 mg, 0.324 mmol) in 10 mL of toluene was added to a solution of LiOHMT (262 mg, 0.778 mmol, 2.4 equiv). The reaction mixture was stirred at 100 °C for 48 h, and the volatiles were removed in vacuo to give a brown oil. The product was extracted into toluene (5 mL), and the mixture was filtered through a bed of Celite. The toluene was removed in vacuo to give a brown oil. Addition of 4 mL of pentane caused a yellow solid to precipitate. The solid was filtered off and washed with 3 mL of cold pentane: yield 124 mg, 41%; ^{1}H NMR (C_6D_6) δ 7.34 (s, 1, WC*H*-*t*-Bu, $^1J_{CH}$ = 122 Hz, $^2J_{WH}$ = 14 Hz), 6.90 (br s, 4, Ar *H*), 6.87−6.85 (m, 8, Ar *H*), 6.83−6.80 (m, 2, Ar *H*), 2.26 (s, 12, Ar *Me*), 2.08 (s, 12, Ar *Me*), 2.03 (s, 12, Ar *Me*), 0.92 (s, 9, WCH-*t*-*Bu*); ^{13}C NMR (C_6D_6) δ 253.6 (WCH-*t*-Bu), 158.5, 137.0, 136.7, 136.5, 134.9, 131.7, 130.7, 128.9, 128.8, 123.0, 41.1, 33.2, 21.6, 21.3, 20.8. Anal. Calcd for $C_{53}H_{60}O_3W$: C, 68.53; H, 6.51. Found: C, 68.22; H, 6.53.

Synthesis of W(O)(C$_3$H$_6$)(OHMT)$_2$ (11). A degassed solution of **10** (324 mg, 0.348 mmol) in 8 mL of pentane was exposed to 1 atm of ethylene at 0 °C for 2 h. The yellow precipitate that formed was filtered off and washed with 0.5 mL of cold pentane: yield 150 mg, 0.167 mmol, 48%. An ^{1}H NMR spectrum of **11** in C_6D_6 shows it to contain ∼25% of **12** (vide infra): ^{1}H NMR (C_6D_6) δ 6.89 (br s, 14, Ar *H*), 3.72 (m, 1, WCH$_2$C*H*$_2$CH$_2$), 2.28 (s, 12, Ar *Me*), 2.08 (s, 12, Ar *Me*), 2.05 (s, 12, Ar *Me*), 1.73 (m, 2, WC*H*$_2$CH$_2$C*H*$_2$), 0.54 (m, 2, WC*H*$_2$CH$_2$C*H*$_2$) (one of the metallacycle resonances is obscured by two Ar *Me* peaks at 2.08 and 2.05 ppm); ^{13}C NMR (C_6D_6) δ 156.7, 137.0, 136.8, 136.7, 135.0, 131.0, 130.0, 128.9, 128.8, 123.8, 42.4 (WCH$_2$CH$_2$CH$_2$, J_{CH} = 135 Hz), 22.2 (WCH$_2$CH$_2$CH$_2$, J_{CH} = 132 Hz), 21.5, 21.0, 20.8. Anal. Calcd for $C_{51}H_{56}O_3W$: C, 68.00; H, 6.27. Found: C, 67.82; H, 6.29.

Synthesis of W(O)(CH$_2$)(OHMT)$_2$ (12). A sample of **11** (60 mg, 0.067 mmol) was dissolved in 1 mL of toluene, and the solvent was removed in vacuo at room temperature. After two additional dissolution/evacuation cycles, a brown oil was obtained. Toluene (0.1−0.2 mL) and pentane (0.3−0.5 mL) were added, and the sample was placed in a freezer at −30 °C for 2 days. Yellow crystals formed and were separated from the brown mother liquor by decantation: yield 32 mg, 55%; ^{1}H NMR (C_6D_6) δ 8.90 (d, 1, WCH_{syn}, $^2J_{HH}$ = 10 Hz, $^1J_{CH}$ = 160 Hz), 7.85 (d, 1, WCH_{anti}, $^2J_{HH}$ = 10 Hz, $^1J_{CH}$ = 140 Hz), 6.90 (br s, 4, Ar *H*), 6.89−6.85 (m, 8, Ar *H*), 6.84−6.80 (m, 2, Ar *H*), 2.22 (s, 12, Ar *Me*), 2.00 (s, 12, Ar *Me*), 1.96 (s, 12, Ar *Me*); ^{13}C NMR (C_6D_6) δ 225.8 (WCH$_2$), 158.1, 137.2, 136.9, 136.7, 134.4, 131.5, 130.0, 128.3, 123.4, 123.0, 21.3, 20.9, 20.8. Anal. Calcd for $C_{49}H_{52}O_3W$: C, 67.43; H, 6.01. Found: C, 67.74; H, 6.12.

X-ray Crystal Structure Determination Details. Low-temperature diffraction data (φ and ω scans) were collected on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart APEX 2 CCD detector with Mo Kα radiation (λ = 0.710 73 Å) from an IμS

dx.doi.org/10.1021/om3008579 | *Organometallics* 2012, 31, 7278−7286

microsource. Absorption and other corrections were applied using SADABS.[30] All structures were solved by direct methods using SHELXS[31] and refined against F^2 on all data by full-matrix least squares with SHELXL-97[32] using established refinement approaches.[33] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the models at geometrically calculated positions and refined using a riding model, except for alkylidene, metallacycle, and methylidene protons. Coordinates for these hydrogen atoms were taken from the difference Fourier synthesis, and the hydrogen atoms were subsequently refined semifreely with the help of distance restraints. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U_{eq} value of the atoms they are linked to (1.5 times for methyl groups). All disordered atoms were refined with the help of similarity restraints on the 1,2- and 1,3-distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters.

W(O)(CH-*t*-Bu)(Ph_2Pyr)(OHMT) (**6**) crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit. Coordinates for the hydrogen atom bound to C1 were taken from the difference Fourier synthesis as noted above.

W(O)(CH-*t*-Bu)($N(C_6F_5)_2$)(OHMT)(PMe_2Ph) (**7**) crystallizes in monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. Coordinates for the hydrogen atom bound to C1 were taken from the difference Fourier synthesis as noted above.

W(O)(C_3H_6)(OHMT)(Silox) (**9**) crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit. The tungsten atom and oxo ligand were modeled as a two-component disorder, and the ratio of the occupancies was refined to 0.9687(6):0.0313(6). The Silox ligand was also found to be disordered over two positions, and the ratio of occupancies was refined to 0.521(8):0.479(8). The anisotropic displacement parameters for silicon and carbon atoms of the Silox group were constrained to be equivalent, pairwise.

W(O)(CH_2)$(OHMT)_2$ (**12**) crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. The tungsten atom, oxo, and methylidene ligand were modeled as a two-component disorder, and the ratio of the occupancies was refined to 0.711(1):0.289(1). The anisotropic displacement parameters for the tungsten (W1, W1A), oxo, and chloride ligands (C1, O1A and C1A, O1) were constrained to be equivalent, pairwise. Coordinates of the hydrogen atoms bound to C1 were taken from the difference Fourier synthesis as noted above. The hydrogen atoms bound to C1A, the minor component of the disorder, could not be found in the difference Fourier synthesis and were not included in the model.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables and CIF files giving crystallographic details and data. This material is available free of charge via the Internet at http://pubs.acs.org. Data for the X-ray structures are also available to the public at http://www.reciprocalnet.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rrs@mit.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

R.R.S. thanks the National Science Foundation (CHE-1111133) for research support. The Department of Chemistry thanks the NSF (CHE-9808061) for funds to purchase a Varian 500 NMR instrument.

■ REFERENCES

(1) (a) Ivin, K. J.; Mol, J. C., *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, CA, 1997. (b) Calderon, N.; Ofstead, E. A.; Ward, J. P.; Judy, W. A.; Scott, K. W. *J. Am. Chem. Soc.* **1968**, *90*, 4133. (c) Basset, J. M.; Coudurier, G.; Praliaud, H. *J. Catal.* **1974**, *34*, 152. (d) Mocella, M. T.; Rovner, R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 4689. (e) Burwell, R. L., Jr.; Brenner, A. *J. Mol. Catal.* **1976**, *1*, 77. (f) Muetterties, E. L.; Band, E. *J. Am. Chem. Soc.* **1980**, *102*, 6572.

(2) (a) Kress, J. R. M.; Russell, M. J. M.; Wesolek, M. G.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1980**, 431. (b) Kress, J. R. M.; Wesolek, M. G.; Le Ny, J.-P.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1981**, 1039. (c) Kress, J. R. M.; Wesolek, M. G.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 514.

(3) (a) Schrock, R. R.; Rocklage, S. M.; Wengrovius, J. H.; Rupprecht, G.; Fellmann, J. *J. Mol. Catal.* **1980**, *8*, 73. (b) Churchill, M. R.; Rheingold, A. L.; Youngs, W. J.; Schrock, R. R.; Wengrovius, J. H. *J. Organomet. Chem.* **1981**, *204*, C17. (c) Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148. (d) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515.

(4) (a) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. R., Ed.; Plenum: New York, 1986; p 221. (b) (b) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (c) Schrock, R. R. In *Handbook of Metathesis*,; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003; Vol. *1*.

(5) (a) Bryan, J. C.; Mayer, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 2298. (b) Blosch, L. L.; Abboud, K.; Boncella, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7066. (c) Ahn, S.; Mayr, A. *J. Am. Chem. Soc.* **1996**, *118*, 7408. (d) De la Mata, F. J.; Grubbs, R. H. *Organometallics* **1996**, *15*, 577. (e) Crane, T. W.; White, P. S.; Templeton, J. L. *Organometallics* **1999**, *18*, 1897.

(6) O'Donoghue, M. B.; Schrock, R. R.; LaPointe, A. M.; Davis., W. M. *Organometallics* **1996**, *15*, 1334.

(7) Schrock, R. R. *Chem. Rev.* **2009**, *109*, 3211.

(8) (a) Ibrahem, I.; Yu, M.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 3844. (b) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962. (c) Flook, M. M.; Gerber, L. C. H.; Debelouchina, G. T.; Schrock, R. R. *Macromolecules* **2010**, *43*, 7515. (d) Flook, M. M.; Ng, V. W. L.; Schrock, R. R. *J. Am. Chem. Soc.* **2011**, *133*, 1784. (e) Jiang, A. J.; Zhao, Y.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 16630. (f) Marinescu, S. C; Schrock, R. R.; Müller, P.; Takase, M. K.; Hoveyda, A. H. *Organometallics* **2011**, *30*, 1780. (g) Marinescu, S. C.; Levine, D. S.; Zhao, Y.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2011**, *133*, 11512. (h) Malcolmson, S. J.; Meek, S. J.; Sattely, E. S.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2008**, *456*, 933. (i) Meek, S. J.; O'Brien, R. V.; Llaveria, J.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2011**, *471*, 461. (j) Yu, M.; Wang, C.; Kyle, A. F.; Jakubec, P.; Dixon, D. J.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2011**, *479*, 88.

(9) Stanciu, C.; Olmstead, M. M.; Phillips, A. D.; Stender, M.; Power, P. P. *Eur. J. Inorg. Chem.* **2003**, 3495.

(10) Dickie, D. A.; MacIntosh, I. S.; Ino, D. D.; He, Q.; Labeodan, O. A; Jennings, M. C.; Schatte, G.; Walsby, C. J.; Clyburne, J. A. C. *Can. J. Chem.* **2008**, *86*, 20.

(11) Peryshkov, D. V.; Schrock, R. R.; Takase, M. K.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2011**, *133*, 20754.

(12) Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1982**, *1*, 1332.

(13) Stavropoulos, P.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *Polyhedron* **1987**, *6*, 1081.

(14) (a) Feinstein-Jaffe, I.; Pedersen, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 7176. (b) Feinstein-Jaffe, I.; Gibson, D.; Lippard, S. J.; Schrock, R. R.; Spool, A. *J. Am. Chem. Soc.* **1984**, *106*, 6305. (c) Rosenfeld, D. C.; Kuiper, D. S.; Lobkovsky, E. B.; Wolczanski, P. T. *Polyhedron* **2006**, *25*, 251. (d) Lehtonen, A.; Sillanpaa, R. *Organometallics* **2005**, *24*, 2795.

(15) Zhang, C.; Schlemper, E. O.; Schrauzer, G. N. *Organometallics* **1990**, *9*, 1016.

(16) (a) Gibson, V. C.; Kee, T. P.; Shaw., A. *Polyhedron* **1988**, *7*, 579. (b) Herrman, W. A.; Theil, W. R.; Herdweck, E. *Chem. Ber.* **1990**, *123*, 271. (c) Kuhn, F. E.; Xue, W.-M.; Al-Ajlouni, A.; Santos, A. M.; Zang, S.; Romão, C. C.; Eickerling, G.; Herdtweck, E. *Inorg. Chem.* **2002**, *41*,

4468. (d) Dreisch, K.; Andersson, C.; Stalhandske, C. *Polyhedron* **1991**, *10*, 2417.
(17) (a) Schrauzer, G. N.; Hughes, L. A.; Strampach, N.; Robinson, P. R.; Schlemper, E. O. *Organometallics* **1982**, *1*, 44. (b) Schrauzer, G. N.; Hughes, L. A.; Therien, M. J.; Schlemper, E. O.; Ross, F.; Ross, D. *Organometallics* **1983**, *2*, 1163. (c) Schrauzer, G. N.; Hughes, L. A.; Strampach, N.; Ross, F.; Ross, D.; Schlemper, E. O. *Organometallics* **1983**, *2*, 481. (d) Schrauzer, G. N.; Schlemper, E. O.; Hui, L. N.; Rubin, K.; Zhang, X.; Long, X.; Chin, C. S. *Organometallics* **1986**, *5*, 2452. (e) Schrauzer, G. N.; Zhang, X.; Liu, N.; Schlemper, E. O. *Organometallics* **1988**, *7*, 279. (f) Zhang, C.; Zhang, X.; Liu, N. H.; Schrauzer, G. N.; Schlemper, E. O. *Organometallics* **1990**, *9*, 1307.
(18) (a) Heppekausen, J.; Fürstner, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 7829. (b) Heppekausen, J.; Stade, R.; Goddard, A.; Fürstner, A. *J. Am. Chem. Soc.* **2010**, *132*, 11045.
(19) Lichtscheidl, A. G.; Ng, V. W. L.; Müller, P.; Takase, K.; Schrock, R. R.; Malcolmson, S. J.; Meek, S. J.; Li, B.; Kiesewetter, E. T.; Hoveyda, A. H. *Organometallics* **2012**, *31*, 4558.
(20) Marinescu, S. C.; Singh, R.; Hock, A. S.; Wampler, K. M.; Schrock, R. R.; Müller, P. *Organometallics* **2008**, *27*, 6570.
(21) (a) Jiang, A. J.; Simpson, J. H.; Müller, P.; Schrock, R. R. *J. Am. Chem. Soc.* **2009**, *131*, 7770. (b) Marinescu, S. C.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 10840.
(22) (a) Cornelissen, C.; Chan, G.; Masuda, J. D.; Stephan, D. W. *Can. J. Chem.* **2007**, *85*, 135. (b) Click, D. R.; Scott, B. L.; Watkin, J. G. *Chem. Commun.* **1999**, 633. (c) Shutov, P. L.; Karlov, S. S.; Harms, K.; Sundermeyer, J.; Lorberth, J.; Zaitseva, G. S. *J. Fluor. Chem.* **2009**, *130*, 1017. (d) Yao, S.; Zhang, X.; Xiong, Y.; Schwarz, H.; Driess, M. *Organometallics* **2010**, *29*, 5353. (e) Khvorost, A.; Shutov, P. L.; Harms, K.; Lorberth, J.; Sundermeyer, J.; Karlov, S. S.; Zaitseva, G. S. *Z. Anorg. Allg. Chem.* **2004**, *630*, 885. (f) Giesbrecht, G. R.; Gordon, J. C.; Clark, D. L.; Hijar, C. A.; Scott, B. L.; Watkin, J. G. *Polyhedron* **2003**, *22*, 153. (g) Weber, K.; Korn, K.; Schorm, A.; Kipke, J.; Lemke, M.; Khvorost, A.; Harms, K.; Sundermeyer, J. *Z. Anorg. Allg. Chem.* **2003**, *629*, 744.
(23) (a) Feldman, J.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 2266. (b) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535. (c) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.
(24) (a) Poater, A.; Solans-Monfort, X.; Clot, E.; Copéret, C.; Eisenstein, O. *J. Am. Chem. Soc.* **2007**, *129*, 8207. (b) Solans-Monfort, X.; Copéret, C.; Eisenstein, O. *J. Am. Chem. Soc.* **2010**, *132*, 7750.
(25) Yuan, J.; Schrock, R. R.; Müller, P.; Axtell, J. C.; Dobereiner, G. E. *Organometallics* **2012**, *31*, 4650.
(26) Schrock, R. R.; King, A. J.; Marinescu, S. C.; Simpson, J. H.; Müller, P. *Organometallics* **2010**, *29*, 5241.
(27) Marinescu, S. C.; Ng, V. W. L.; Lichtscheidl, A. G.; Schrock, R. R.; Müller, P.; Takase, M. K. *Organometallics* **2012**, *31*, 6336.
(28) Patterson, J. M.; Soedigdo, S. *J. Org. Chem.* **1968**, *33*, 2057.
(29) Koppang, R. *Acta Chem. Scand.* **1971**, *25*, 3067.
(30) Sheldrick, G. M. *SADABS, v. 2.10-A program for area detector absorption corrections*; Bruker AXS, Madison, WI, 2003.
(31) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
(32) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.
(33) Müller, P. *Crystallogr. Rev.* **2009**, *15*, 57.
(34) Solans-Monfort, X.; Copéret, C.; Eisensein, O. *Organometallics*, published online September 26, 2012 http://dx.doi.org/10.1021/om300576r.