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Syntheses of Tungsten *tert*-Butylimido and Adamantylimido Alkylidene Complexes Employing Pyridinium Chloride As the Acid

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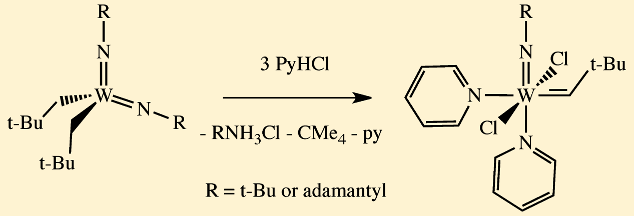
Supporting Information

ABSTRACT: Routes to new tungsten alkylidene complexes that contain *tert*-butylimido or adamantylimido ligands have been devised that begin with a reaction between WCl_6 and 4 equivalents of HNR(TMS) to give $[W(NR)_2Cl(\mu\text{-}Cl)(RNH_2)]_2$ (R = t-Bu or 1-adamantyl). Alkylation leads to $W(NR)_2(CH_2R')_2$ (R′ = t-Bu or CMe_2Ph), which upon treatment with pyridinium chloride yields $W(NR)(CHR')Cl_2(py)_2$ complexes, from which $W(NR)(CHR')(pyrrolide)_2$ and two W(N-t-Bu)(CHR′)(pyrrolide)(OAr) complexes (OAr = hexamethyl- or hexaisopropylterphenoxide) have been prepared.



Olefin metathesis catalyzed by well-defined Mo, W, and Ru catalysts is the only way to prepare olefins from olefins catalytically and with a high degree of control.[1] Arylimido ligands usually have been employed in high oxidation state imido alkylidene complexes of molybdenum and tungsten, especially aryls that are mono- or disubstituted in the *ortho* position(s).[2] However, it has become clear that (i) adamantylimido alkylidene complexes of molybdenum often are the catalysts of choice in some circumstances such as *Z*-selective ring-opening metathesis reactions[3] and (ii) tungsten arylimido alkylidene complexes are often more successful than molybdenum complexes for *Z*-selective reactions.[4] However, no *tungsten-based alkylimido* alkylidene complexes have been reported to our knowledge. Therefore, we were compelled to explore routes to tungsten *tert*-butylimido or adamantylimido alkylidene complexes.

A logical starting material for the synthesis of *tert*-butylimido alkylidene complexes of tungsten would be $W(N\text{-}t\text{-}Bu)_2Cl_2(DME)$. However, attempts to prepare $W(N\text{-}t\text{-}Bu)_2Cl_2(DME)$ through reactions between $WO_2Cl_2(DME)$, *tert*-butylamine, Me_3SiCl, and NEt_3 under conditions analogous to those employed to prepare $W(NAryl)_2Cl_2(DME)$ and $Mo(NAryl)_2Cl_2(DME)$ complexes[2] have failed so far in our hands; similar reactions to synthesize the 1-adamantyl analogue, including conditions in which an *N*-sulfinylamine is employed as the imido source,[5] were also unsuccessful. As far as we are aware, $W(N\text{-}t\text{-}Bu)_2Cl_2(DME)$ is still unknown, although adducts such as $W(N\text{-}t\text{-}Bu)_2Cl_2(pyridine)_2$ have been reported.[6]

In 1987 Nielson[7] reported that addition of 4 equivalents of t-BuNH(TMS) to WCl_6 gave a compound with the formula $W(N\text{-}t\text{-}Bu)_2(t\text{-}BuNH_2)Cl_2$.[8] This compound has also been prepared in 30% yield in a reaction between $WO_2Cl_2(DME)$ and t-BuNH(TMS) in heptane or dimethoxyethane.[9] By analogy with $\{W(N\text{-}t\text{-}Bu)(\mu\text{-}NPh)(t\text{-}BuNH_2)Cl_2\}_2$ and $\{W(N\text{-}t\text{-}Bu)(\mu\text{-}Ntolyl)(t\text{-}BuNH_2)Cl_2\}_2$,[10] $W(N\text{-}t\text{-}Bu)_2Cl_2(t\text{-}BuNH_2)$ was proposed to be a dimer that contains bridging *tert*-butylimido groups. We have confirmed that $W(N\text{-}t\text{-}Bu)_2(t\text{-}BuNH_2)Cl_2$ can be prepared conveniently on a 15 g scale as described by Nielson, but have found through XRD that it contains bridging chlorides, not bridging imido groups. The structure of $[W(N\text{-}t\text{-}Bu)_2Cl(\mu\text{-}Cl)(t\text{-}BuNH_2)]_2$ (**1a**, Figure 1) can be viewed as essentially two square pyramids with slightly bent imido groups in the apical positions (those that contain

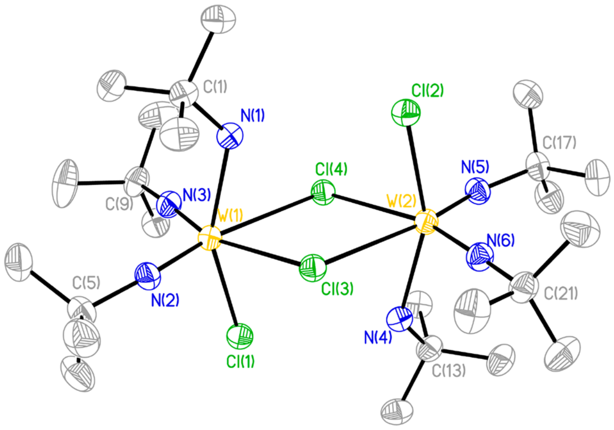


Figure 1. Thermal ellipsoid drawing (50%) of **1a**. Selected bond distances (Å) and angles (deg): W(1)−Cl(1) = 2.3942(6), W(1)−Cl(3) = 2.6104(6), W(1)−Cl(4) = 2.8063(6), W(1)−N(1) = 2.210(2), W(1)−N(2) = 1.754(2), W(1)−N(3) = 1.743(2), W(1)−N(1)−C(1) = 126.63(15), W(1)−N(2)−C(5) = 159.36(18), W(1)−N(3)−C(9) = 177.24(19), W(1)−Cl(3)−W(2) = 106.72(2), W(1)−Cl(4)−W(2) = 106.14(2).

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N(2) and N(5) in Figure 1) "joined" to create an octahedral geometry about tungsten through relatively long W−Cl bridges (e.g., W(1)−Cl(4) = 2.8063(6) Å). Interestingly, the N(1)···Cl(2) and N(4)···Cl(1) distances (3.34 Å) are in the range observed when a hydrogen bond is present between an NH proton and chloride (N···Cl = 3.30 Å).[11] Also, *one* of the two protons on each amine nitrogen points toward the terminal chloride on the neighboring tungsten (e.g., H···Cl(1) = 2.448 Å). Therefore, we propose that two hydrogen bonds stabilize the structure of **1a**. The fact that **1a** can be prepared in dimethoxyethane,[9] as noted earlier, attests to the integrity of the dimeric structure of **1a**, at least toward dimethoxyethane, although addition of nitrogen donors to **1a**, e.g., pyridine[6] or di-*tert*-butyl-1,4-diaza-1,3-butadiene,[9] leads to formation of monomeric complexes of the type $W(N\text{-}t\text{-}Bu)_2Cl_2L_2$. The 1-adamantylimido analogue of **1a** (**1b**) was prepared similarly and has a structure that is closely analogous to that of **1a** (see SI). Heating a solution of **1b** in DME at 120 °C for 24 h in a high-pressure vessel results in neither replacement of the amines by dimethoxyethane nor decomposition of **1b**.

In spite of the presence of *tert*-butylamine in **1a**, we find that **1a** reacts cleanly with 2 equivalents of $t\text{-}BuCH_2MgCl$ (per W) to give $W(N\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$ (**2a**) in 87% yield. $W(N\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$ so far has been obtained only as a light brown oil that becomes solid at ca. −20 °C. However, the analogous reaction between **1b** and Me_2PhCCH_2MgCl yielded crystalline $W(NAd)_2(CH_2CMe_2Ph)_2$ (**2b**), XRD of which revealed the expected pseudotetrahedral structure shown in Figure 2. The neopentyl analogue of **2b** (**2c**) has also been synthesized and can be isolated as a crystalline solid in 53% yield.

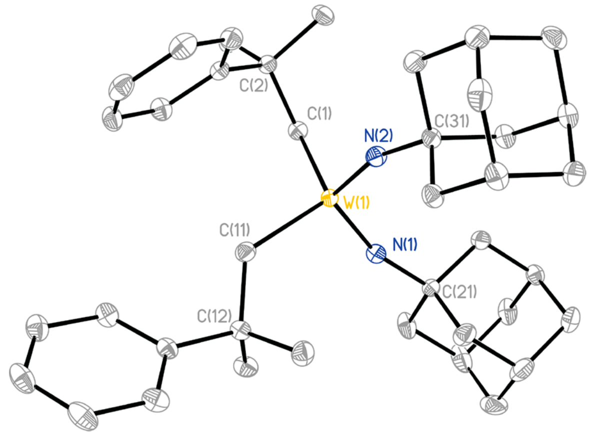
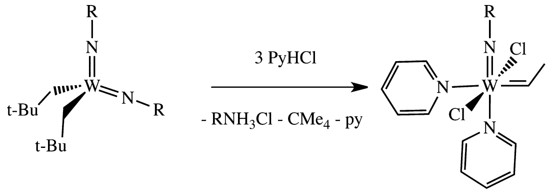


Figure 2. Thermal ellipsoid drawing (50%) of **2b**. Selected bond distances (Å) and angles (deg): W(1)−N(1) = 1.7520(15), W(1)−N(2) = 1.7564(16), W(1)−C(1) = 2.1467(18), W(1)−C(11) = 2.1256(19), W(1)−N(1)−C(21) = 159.84(13), W(1)−N(2)−C(31) = 162.84(13), W(1)−C(1)−C(2) = 119.70(12), W(1)−C(11)−C(12) = 127.92(12).

Addition of 3 equivalents of triflic acid to **2a**, **2b**, or **2c** in a mixture of 1,2-dimethoxyethane and ether, which is the method employed to form $M(NR)(CHR')(OTf)_2(DME)$ complexes of Mo and W,[2b] in our hands has not yet led to $W(NR)(CHR)(OTf)_2(DME)$ complexes (R = t-Bu or Ad). We also found that triflic acid could not be employed in order to remove the *tert*-butylimido group selectively from $Mo(NAr^*)(N\text{-}t\text{-}Bu)(CH_2CMe_2Ph)_2$ (Ar* = 2,6-dimesitylphenyl) to give $Mo(NAr^*)(CHCMe_2Ph)(OTf)_2(DME)$.[12] Instead, 3 equivalents of 3,5-lutidinium chloride was found to give $Mo(NAr^*)(CHCMe_2Ph)Cl_2(3,5\text{-lutidine})$ in good yield. Therefore we turned to reactions employing pyridinium chloride. Addition of 3 equivalents of pyridinium chloride to **2a** or **2c** led to formation of $W(NR)(CH\text{-}t\text{-}Bu)Cl_2(py)_2$ (R = t-Bu (**3a**) or 1-Ad (**3b**)) in good yield (eq 1).



(1)

R = t-Bu (**3a**, 64%) or adamantyl (**3b**, 75%)

An XRD of crystals obtained through recrystallization of **3a** from a mixture of methylene chloride and pentane showed the crystal to be $[W(NR)(CHR')Cl(\mu\text{-}Cl)(py)]_2$, formed through loss of one pyridine from **3a** (Figure 3). The W═N and W═C bond lengths and W−N−C and W−C−C angles are normal, as are the terminal, approximately equal, and longer bridging W−Cl bond lengths. The W(1)−N(2) bond length (2.207(5) Å) is also within the expected range. In contrast, there is no evidence for formation of a dimer analogous to **3a** through loss of pyridine from **3b**.

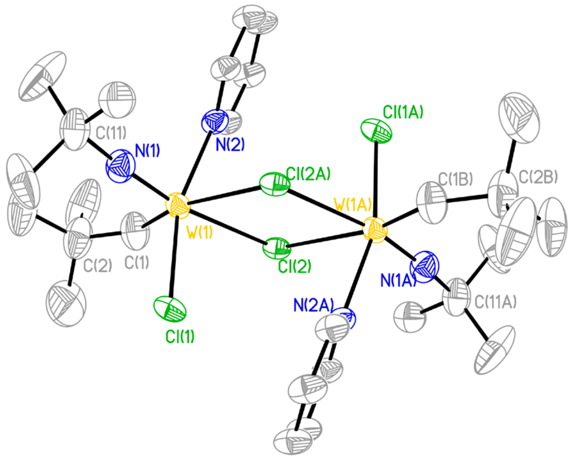
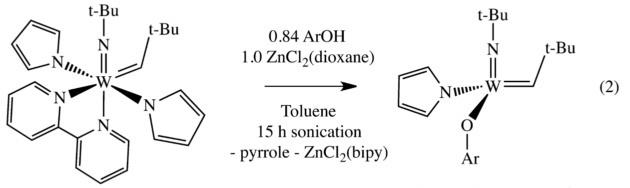


Figure 3. Thermal ellipsoid drawing (50%) of **3a**. Selected bond distances (Å) and angles (deg): W(1)−Cl(1) = 2.4056(13), W(1)−Cl(2) = 2.6085(13), W(1)-Cl(2A) = 2.6781(13), W(1)−N(1) = 1.687(6), W(1)−N(2) = 2.207(5), W(1)−C(1) = 1.928(8), W(1)−Cl(2)−W(1A) = 105.28(4), W(1)−N(1)−C(11) = 169.8(5), W(1)−C(1)−C(2) = 145.1(7).

The reaction between **3a** and 2 equivalents of lithium 2,5-dimethylpyrrolide led to formation of $W(N\text{-}t\text{-}Bu)(CHCMe_3)(2,5\text{-}Me_2pyr)_2$ (**4a**) in 58% isolated yield. We propose that the one pyrrolide is bound to the metal in **4a** in an η^1 fashion, while the other is bound in an η^5 fashion, as found in bispyrrolide complexes of Mo or W of this general type that do not contain donor ligands,[13] unless the pyrrolide cannot bind readily in an η^5 fashion, as in the case of 2-mesitylpyrrolide.[14] Compound **4a** was treated with 1 equivalent of HMTOH ($2,6\text{-}(2,4,6\text{-}Me_3C_6H_2)_2C_6H_3OH$) in benzene to generate the MAP complex $W(N\text{-}t\text{-}Bu)(CHCMe_3)(2,5\text{-}Me_2pyr)(OHMT)$ (MAP = monoaryloxide pyrrolide; **5a**).

An attempted synthesis of $W(N\text{-}t\text{-}Bu)(CHCMe_3)(pyr)_2$ (where pyr is the parent pyrrolide) in a manner similar to that described for **4a** was not successful. Isolation and storage of bis(parent)pyrrolide complexes of Mo has also been problematic, but a solution to their synthesis and use was provided through formation of 2,2′-bipyridine adducts as intermediates.[15] As in Mo chemistry, we find that W(N-t-Bu)($CHCMe_3$)$(pyr)_2$(bipy) (**6a**) can be prepared in 83% yield. The ^1H NMR spectrum of **6a** obtained in CD_2Cl_2 showed four alkylidene resonances at room temperature. However, after the sample was heated to 100 °C overnight in CD_2Cl_2 in a sealed tube the ^1H NMR spectrum at room temperature showed just one isomer to be present. Limited solubility of **6a** prevents the determination of whether the alkylidene is the *syn* or *anti* isomer.

Compound **6a** was treated with 1 equivalent of $ZnCl_2$(dioxane) (in order to remove 2,2′-bipyridine[16]) and 0.84 equivalent of HIPTOH (2,6-(2,4,6-i-$Pr_3C_6H_2)_2C_6H_3OH$) in toluene, and the mixture was placed in an ultrasonic sonicator for 15 h. The yellow-brown mixture was filtered through a pad of Celite, and W(N-*t*-Bu)($CHCMe_3$)(pyr)(OHIPT) (**7a**) isolated in good yield from the filtrate (eq 2). Exchange of the pyrrolide ligand with chloride is minimal during formation of **7a**. W(N-*t*-Bu)($CHCMe_3$)(pyr)(OHMT) (**8a**) can be synthesized in an analogous manner.



Ar = OHIPT (**7a**, 67%) or OHMT (**8a**, 99%)

The solid-state structure of **8a** was determined in an X-ray study (Figure 4). It is interesting to note that the distance between tungsten and the imido nitrogen is relatively short compared with W–N distances in MAP complexes of arylimido tungsten species. Compound **8a** has a W=N distance 1.670 Å, whereas several 2,6-diisopropylimido and 3,5-dimethylphenylimido MAP compounds have W=N distances of ~1.75–1.77 Å.[3,17] We attribute this difference to the greater electron-donating ability of the *tert*-butylimido ligand compared to arylimido ligands.

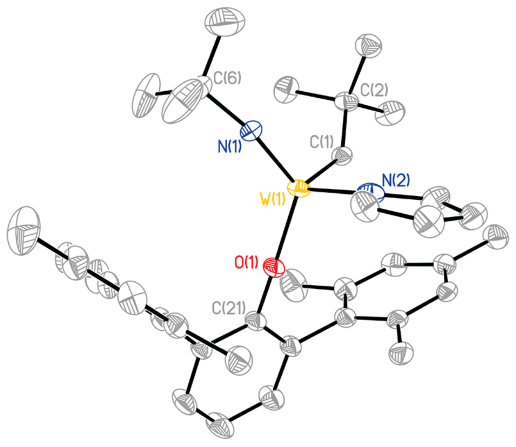
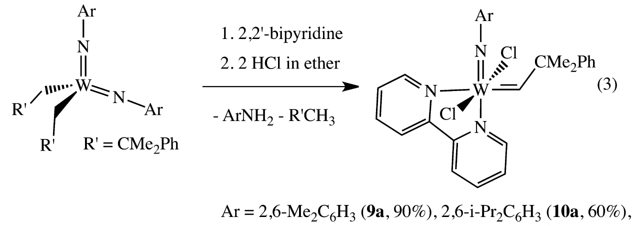


Figure 4. Thermal ellipsoid drawing (50%) of **8a**. Selected bond distances (Å) and angles (deg): W(1)–N(1) = 1.670(3), W(1)–N(2) = 2.0214(16), W(1)–C(1) = 1.916(3), W(1)–O(1) = 1.8691(12), W(1)–N(1)–C(6) = 169.5(5), W(1)–C(1)–C(2) = 141.9(3), W(1)–O(1)–C(21) = 173.81(13), N(1)–W(1)–C(1) = 105.63(14), O(1)–W(1)–C(1) = 108.10(10), N(2)–W(1)–N(1) = 105.42(10), O(1)–W(1)–N(2) = 109.29(6), C(1)–W(1)–N(2) = 100.62(10), N(1)–W(1)–O(1) = 125.10(12).

The use of pyridinium chloride as shown in eq 1 would be of significant benefit for the syntheses of the chloride analogues of known *arylimido* alkylidene bistriflate complexes. Although use of pyridinium chloride has not looked promising so far, we have found that the addition of 1 equivalent of 2,2′-bipyridine to $W(NAr)_2(CH_2CMe_2Ph)_2$ (Ar = 2,6-$Me_2C_6H_3$, 2,6-i-$Pr_2C_6H_3$, 2,6-$Cl_2C_6H_3$, or 2-i-PrC_6H_4) complexes followed by 2 equivalents of HCl in diethyl ether leads to formation of W(NAr)($CHCMe_2Ph$)Cl_2(bipy) complexes **9a–12a** (eq 3).



Ar = 2,6-$Me_2C_6H_3$ (**9a**, 90%), 2,6-i-$Pr_2C_6H_3$ (**10a**, 60%), 2,6-$Cl_2C_6H_3$ (**11a**, 54%), 2-i-PrC_6H_4 (**12a**, 57%)

Compounds **9a–12a** are essentially insoluble and therefore isolated readily in good yields and high purity simply through filtration. The aniline ($ArNH_2$) and alkane ($R'CH_3$) were the only byproducts observed (in high yields versus an internal standard) in ^1H NMR spectra of the filtrates of the reaction mixtures from which ether had been removed *in vacuo*. Proton NMR spectra of **9a–12a** (in CD_2Cl_2) are consistent with the presence of two isomers, one that contains *trans* chlorides and another (out of two possible) that contains *cis* chlorides. A spectrum of W(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)Cl_2(bipy), for example, has alkylidene α-proton resonances at 11.29 and 10.48 ppm for *cis* and *trans* isomers, respectively, the ratio of which varies with reaction conditions. Limited solubility of **9a–12a** in CD_2Cl_2 prevented confirmation (by either ^1H or ^{13}C NMR studies) of the proposal that the alkylidene in each case is the *syn* isomer.

We conclude that *tert*-butylimido and adamantylimido alkylidene complexes of tungsten are now readily accessible from tungsten hexachloride, that pyridinium chloride can be employed to initiate an α-abstraction reaction that generates the alkylidene, and that HCl can be employed in the presence of 2,2′-bipyridine to make several tungsten arylimido alkylidene complexes. Therefore, the use of WCl_6 and HCl in some form (in place of triflic acid) in order to prepare tungsten imido alkylidene complexes seems promising. We also are in the process of exploring the chemistry of *tert*-butylimido and adamantylimido alkylidene complexes of tungsten from a fundamental perspective and in terms of various applications that involve olefin metathesis reactions, especially metathesis reactions that are likely to be *Z*-selective.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details for the synthesis of all compounds and details of the X-ray structural studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003; Vols. *1*−*3*.

(2) (a) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. R., Ed.; Plenum: New York, 1986. (b) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (c) Schrock, R. R. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003; pp 8−46. (d) Schrock, R. R. *Chem. Rev.* **2009**, *109*, 3211.

(3) (a) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962.

(4) (a) Townsend, E. M.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2012**, *134*, 11334. (b) Yu, M.; Wang, C.; Kyle, A. F.; Jakubec, P.; Dixon, D. J.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2011**, *479*, 88.

(5) Rufanov, K. A.; Kipke, J.; Sundermeyer, J. *Dalton Trans.* **2011**, *40*, 1990.

(6) (a) Sundermeyer, J. *Chem. Ber.* **1991**, *124*, 1977. (b) Becker, J. S.; Suh, S.; Wang, S.; Gordon, R. G. *Chem. Mater.* **2003**, *15*, 2969. (c) Rische, D.; Baunemann, A.; Winter, M.; Fischer, R. A. *Inorg. Chem.* **2006**, *45*, 269.

(7) Nielson, A. J. *Polyhedron* **1987**, *6*, 1657.

(8) For leading references to organoimido complexes see: (a) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123. (b) Clegg, W.; Errington, R. J.; Hockless, D. C. R.; Redshaw, C. *J. Chem. Soc., Dalton Trans.* **1993**, 1965. (c) Nugent, W. A. *Inorg. Chem.* **1983**, *22*, 965. (d) Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1980**, *19*, 777. (e) Nugent, W. A. *Inorg. Chem.* **1983**, *22*, 965. (f) Sundermeyer, J. *Chem. Ber.* **1991**, *124*, 1977. (g) Dehnicke, K.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 413. (h) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239. (i) Zarubin, D. N.; Ustynyuk, N. A. *Russ. Chem. Rev.* **2006**, *75*, 671.

(9) Dreisch, K.; Andersson, C.; Stalhandske, C. *Polyhedron* **1993**, *12*, 1335.

(10) Ashcroft, B. R.; Nielson, A. J. *J. Chem. Soc., Dalton Trans.* **1987**, 2059.

(11) Steiner, T. *Acta Crystallogr.* **1998**, *B54*, 456.

(12) Gerber, L. C. H.; Schrock, R. R.; Müller, P.; Takase, M. K. *J. Am. Chem. Soc.* **2011**, *133*, 18142.

(13) (a) Marinescu, S. C.; Singh, R.; Hock, A. S.; Wampler, K. M.; Schrock, R. R.; Müller, P. *Organometallics* **2008**, *27*, 6570. (b) Kreickmann, T.; Arndt, S.; Schrock, R. R.; Müller, P. *Organometallics* **2007**, *26*, 5702.

(14) Jiang, A. J.; Schrock, R. R.; Müller, P. *Organometallics* **2008**, *27*, 4428.

(15) Lichtscheidl, A. G.; Ng, V. W.; Müller, P.; Takase, M. K.; Schrock, R. R. *Organometallics* **2012**, *31*, 2388.

(16) (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.

(17) Marinescu, S. C.; Schrock, R. R.; Müller, P.; Takase, M. K.; Hoveyda, A. H. *Organometallics* **2011**, *30*, 1780.