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Olefin Metathesis Reactions Initiated by d^2 Molybdenum or Tungsten Complexes

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Summary: Dimeric or monomeric imido complexes of Mo(IV) or W(IV) will slowly catalyze some olefin metathesis reactions, although it is estimated that <2% of the d^2 species is "activated" by the olefin. An ethylene adduct of $\{W(NAr')[OCMe_2(CF_3)]_2\}_2$ can be isolated, which upon heating is transformed into a new dimeric species that contains an ethyl group and a CH activated ortho methyl group in the NAr′ ligand.

Formation of high-oxidation-state alkylidene complexes of Mo and W via α-hydrogen abstraction reactions in d^0 dialkyl complexes has given rise to a large class of catalysts for the metathesis of olefins of the type $M(NR)(CHR')(OR'')_2$.[1,2] There is now evidence that high-oxidation-state alkylidenes also can form in reactions between olefins and d^2 metal complexes, either by "rearrangement" of an olefin to an alkylidene (for Nb and Ta)[3−5] or by formation and contraction of a metallacyclopentane to a metallacyclobutane ring followed by a metathesis of the MC_3 ring (for Ta,[6] Re,[7] and Mo[8]). We have been drawn to the possibility that recently discovered d^2/d^2 dimeric species that contain unsupported M═M double bonds[9] might react with certain olefins to yield alkylidene complexes. This type of reaction could resemble that between d^3/d^3 dimeric species such as $(t\text{-BuO})_3W{\equiv}W(O\text{-}t\text{-Bu})_3$ and internal alkynes to yield $(t\text{-BuO})_3W{\equiv}CR$ complexes.[10−13] In this communication we present evidence that M═M (d^2/d^2) species, but also *monomeric* d^2 species, behave as olefin metathesis catalysts.

Recently we reported tungsten complexes that contain a W═W double bond unsupported by bridging ligands: e.g., centrosymmetric $[W(NAr)(CH_2\text{-}t\text{-Bu})(OC_6F_5)]_2$ (Ar = 2,6-diisopropylphenyl; W═W = 2.4445(3) Å).[9] The molybdenum analogue, $[Mo(NAr)(CH_2\text{-}t\text{-Bu})(OC_6F_5)]_2$, has been shown to be a C_2-symmetric species (Mo═Mo = 2.4104(8) Å).[14] An X-ray study has now shown[15] that $\{W(NAr')[OCMe_2(CF_3)]_2\}_2$ (Ar′ = 2,6-$Me_2C_6H_3$)[9] is a W═W dimer (W═W = 2.4905(3) Å) analogous to d^2/d^2 rhenium neopentylidyne complexes, $[Re(C\text{-}t\text{-Bu})(OR)_2]_2$ (OR = O-*t*-Bu or $OCMe(CF_3)_2$) (Re═Re = 2.3836(8) and 2.396(1) Å, respectively).[16] Therefore, d^2/d^2 M═M complexes that do not contain bridging ligands are now known for Mo, W, and Re. The Mo and W bis(alkoxide) dimers that contain terminal imido ligands are strikingly different from $[Mo(\mu\text{-NAr})(O\text{-}t\text{-Bu})_2]_2$, which contains a Mo_2N_2 core and a pseudotetrahedral arrangement about each Mo.[17]

The M═M species are formed through bimolecular decomposition of alkylidene complexes. Therefore, the reverse reaction is plausible. In fact, M═M species *will* slowly catalyze olefin metathesis reactions. For example, ring-closing metathesis of diallyl ether (22 °C, 20 h, 71%; 50 °C, 3 h, 86%) or diallyl tosylamine (55 °C, 1 h, 95%) is catalyzed by 5% $[Mo(NAr)(CH_2\text{-}t\text{-Bu})(OC_6F_5)]_2$ in C_6D_6, while addition of 10 equiv of norbornene to $\{W(NAr')[OCMe_2(CF_3)]_2\}_2$ in C_6D_6 led to formation of polynorbornene (87% cis) over a period of 24 h at 22 °C. The molecular weight of this sample is approximately 50 times that of a sample prepared using $W(NAr')(CH\text{-}t\text{-Bu})[OCMe_2(CF_3)]_2$ as the catalyst. Norbornene was polymerized in C_6D_6 at 22 °C with 5 mol % of $[Mo(NAr)(CH_2\text{-}t\text{-Bu})(OC_6F_5)]_2$ to give polynorbornene whose molecular weight ($M_n = 3.430 \times 10^5$, PDI = 1.25) was ~38 times than that obtained employing $Mo(NAr)(CH\text{-}t\text{-Bu})(CH_2\text{-}t\text{-Bu})(OC_6F_5)$ as a catalyst. No significant amount of catalyst (<5%) is consumed in any of the metathetical processes noted above. If we assume that the norbornene polymerization processes are living, then only 2−3% of a M═M species is "activated" by the olefin to yield a metathesis catalyst.

Since dimeric M═M species are formed via decomposition of M═CHR species, a nagging question is whether a tiny residual amount of some monomeric alkylidene complex is present in samples of dimeric species, even though none can be observed in NMR spectra and even

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though the much less soluble dimeric species were recrystallized several times in order to free them of any monomeric alkylidene species. Therefore, it was important to prepare and test M=M dimers prepared through a route that does not involve alkylidenes.

Addition of 2 equiv of $LiOCMe_2(CF_3)$ to $W(NAr')Cl_4(THF)$ yields yellow $W(NAr')[OCMe_2(CF_3)]_2Cl_2$, which is analogous to known $W(NAr)(O\text{-}t\text{-}Bu)_2Cl_2$[18] and $W(N\text{-}t\text{-}Bu)[OSi(t\text{-}Bu)_3]_2Cl_2$.[19] Reduction of $W(NAr')[OCMe_2(CF_3)]_2Cl_2$ with 2.1 equiv of 5% sodium amalgam in ether, or with KC_8, leads to $\{W(NAr')[OCMe_2(CF_3)]_2\}_2$ in good yield, a sample of which is identical in all respects with a sample prepared via decomposition of an alkylidene complex.[20] A sample of $\{W(NAr')[OCMe_2(CF_3)]_2\}_2$ prepared via reduction of $W(NAr')[OCMe_2(CF_3)]_2Cl_2$ also will metathesize olefins as described above. Therefore, metathesis activity by $\{W(NAr')[OCMe_2(CF_3)]_2\}_2$ cannot be ascribed solely to the presence of any residual $W(NAr')(CHR)[OCMe_2(CF_3)]_2$ complex. It should be noted that reduction of $W(N\text{-}t\text{-}Bu)[OSi(t\text{-}Bu)_3]_2Cl_2$ with Mg in ether yielded three-coordinate $W(N\text{-}t\text{-}Bu)[OSi(t\text{-}Bu)_3]_2$,[19] while reduction of $Mo(N\text{-}t\text{-}Bu)[OSi(t\text{-}Bu)_3]_2Cl_2$ with Na amalgam led to formation of $\{Mo(N\text{-}t\text{-}Bu)[OSi(t\text{-}Bu)_3]_2\}_2(\mu\text{-}Hg)$.[21]

Monoadducts can be observed by NMR upon addition of PMe_3, 2-butyne, ethylene, or norbornene to $\{W(NAr')[OCMe_2(CF_3)]_2\}_2$. All are unsymmetric; i.e., they have four different CF_3 resonances and two sets of Ar′ resonances. The PMe_3, 2-butyne, and ethylene adducts can be isolated. The norbornene complex is not stable enough to be isolated; it loses norbornene (as polynorbornene is formed) to regenerate $\{W(NAr')[OCMe_2(CF_3)]_2\}_2$, although small quantities of unidentified side products are also formed. The ethylene adduct also loses ethylene slowly in the solid state, especially in vacuo, a fact that could account for attempted elemental analyses to be low in C.

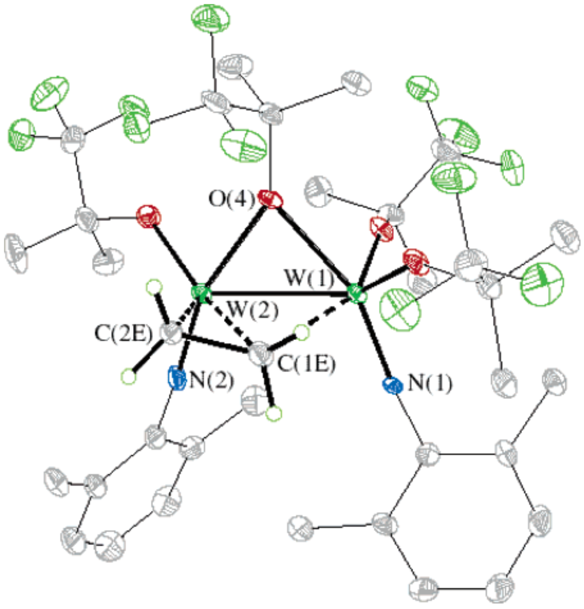
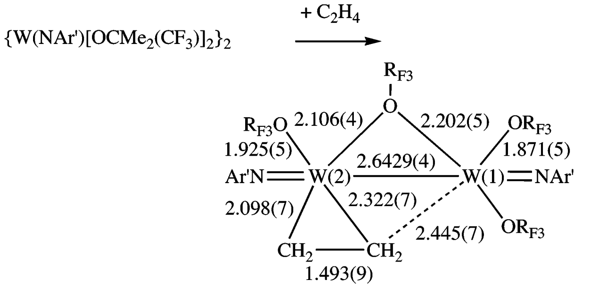


Figure 1. Thermal ellipsoid drawing of the structure of $\{W(NAr')[OCMe_2(CF_3)]_2\}_2(C_2H_4)$.

An X-ray structure of the ethylene adduct shows it to be an unsymmetric species with a bridging alkoxide and a "semibridging" ethylene (eq 1 and Figure 1). The



(1)

W−C bonds to W(2) are relatively short (2.098(7) Å) and long (2.322(7) Å), respectively, for a W−C single bond (typically 2.2 Å), while interaction between one methylene carbon (C(1E)) and W(1) is marginal (2.445(7) Å). The W(1)−W(2) bond is lengthened by ~0.15 Å from what it is in the parent compound (W=W = 2.4905(3) Å), which is more consistent with a W−W single bond. All four protons on the ethylene fragment were located, and there is no evidence for any interaction of an ethylene CH bond with tungsten. All ethylene protons are magnetically inequivalent on the ^1H NMR time scale at room temperature and appear as distinct resonances at 4.31 (m, $J_{CH} = 158$ Hz), 3.11 (m, $J_{CH} = 150$ Hz), 1.84 (m, $J_{CH} = 150$ Hz), and 1.62 ppm (m, $J_{CH} = 153$ Hz). The ethylene carbons were observed at 66.18 ($J_{CW} = 60$ Hz) and 33.97 ppm ($J_{CW} = 22$ Hz) in the ^{13}C NMR spectrum (toluene-d_8), with $^1J_{CC} = 26$ Hz. It should be noted that the "short" W−C distance of 2.098(7) Å is similar to the W−C$_\alpha$ distances in WC_3 rings in imido bis(alkoxide) tungstacyclobutane species.[22] Therefore, there is some justification for proposing that $\{W(NAr')[OCMe_2(CF_3)]_2\}_2(C_2H_4)$ contains a slightly bent "ditungstenacyclobutane" ring. The ethylene complex will polymerize norbornene at approximately the same rate as $\{W(NAr')[OCMe_2(CF_3)]_2\}_2$ itself (10 equiv in 12 h in C_6D_6).

When $\{W(NAr')[OCMe_2(CF_3)]_2\}_2(C_2H_4)$ is heated in toluene to 80 °C, it loses ethylene to yield $\{W(NAr')[OCMe_2(CF_3)]_2\}_2$ but also is transformed into a new species that has C_1 symmetry and that contains an ethyl group as a consequence of activation of an ortho methyl group in the NAr′ ligand. A useful signature resonance for this compound is a doublet ($J_{CH} = 18$ Hz) at 4.45 ppm for one of the methylene protons in the activated former NAr′ methyl group. An X-ray structure confirms that this is the case (eq 2, Figure 2, and Supporting Information) and that the metal is symmetrically bridged by two imido groups, one of them being CH activated. No bonds or angles in $(OR_{F3})_2(Et)W(\mu\text{-}NAr')(\mu\text{-}N\text{-}2\text{-}CH_2\text{-}$

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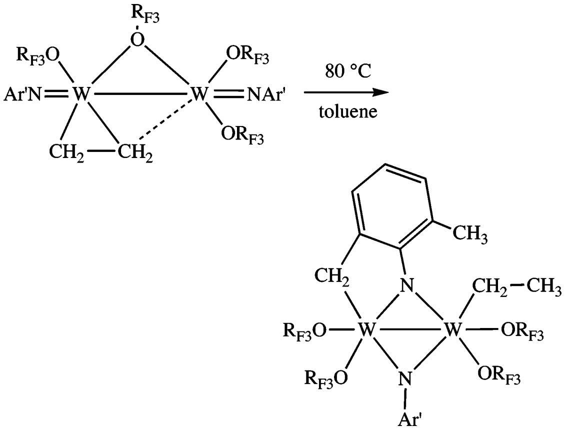

(2)

6-$MeC_6H_3)W(OR_{F3})_2$ are unusual. For example, W(1)–C(1) = 2.145(3) Å, W(2)–C(17) = 2.156(3) Å, W(1)–W(2) = 2.61757(14) Å, W(1)–N(1) = 1.964(2) Å, W(2)–N(1) = 1.962(2) Å, and W(1)–C(1)–C(2) = 110.95(18)°. The ethyl complex polymerizes norbornene more slowly than the ethylene complex (10 equiv in 48 h in C_6D_6). This result suggests that an alkylidene could form via α-hydrogen abstraction from the ethyl ligand, a method of rearranging an olefin to an alkylidene that is related to that found by Wolczanski in Nb and Ta systems.[5] However, formation of an alkylidene directly from $(OR_{F3})_2(Et)W(\mu\text{-}NAr')(\mu\text{-}N\text{-}2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)W(OR_{F3})_2$ appears to be slow compared to another mechanism of alkylidene formation.

Interestingly, it does not appear that M=M (d^2/d^2) species are necessary to generate catalytically active species. ROMP of norbornene by 1 mol % of $Mo(NAr_{Cl})$(*rac*-biphen)$(H_2C{=}CH_2)$(ether)[23] (biphen = 6,6′-dimethyl-3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diolate; Ar_{Cl} = 2,6-$Cl_2C_6H_3$) yielded polynorbornene (83% isolated yield in 10 min) whose molecular weight ($M_n = 8.158 \times 10^5$, PDI = 1.47) was found to be twice that of a sample prepared from $Mo(NAr_{Cl})$(*rac*-biphen)(CH-*t*-Bu) under the same conditions. Although $Mo(NAr_{Cl})$(*rac*-biphen)$(H_2C{=}CH_2)$(ether) is inactive for ring closing of diallyl ether over a period of 10 days at 22 °C, when 10 equiv of norbornene is added to a benzene solution of 5 mol % $Mo(NAr_{Cl})$(*rac*-biphen)$(H_2C{=}CH_2)$(ether)[23] and diallyl ether, a 56% yield of 2,4-dihydrofuran is obtained in 10 days. The ring-closing experiments in particular suggest that an alkylidene species can be generated in the presence of norbornene. It should be noted that $Mo(NAr_{Cl})$(*rac*-biphen)$(H_2C{=}CH_2)$(ether) was one of the catalysts that promoted the homologation (with ethylene) of vinyltin to allyltin species[8] and that CH activation within the $Mo{=}NAr_{Cl}$ group, at least, seems unlikely.

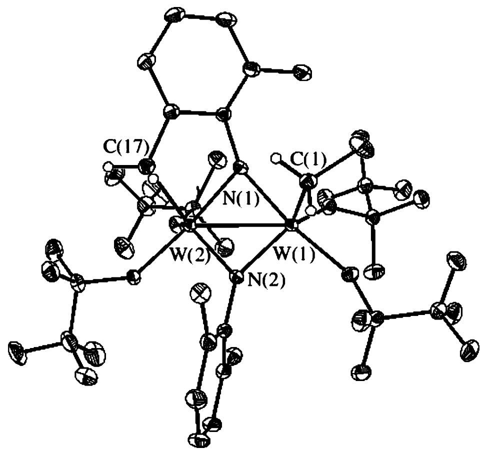

Figure 2. Thermal ellipsoid drawing of the structure of $(OR_{F3})_2W(\mu\text{-}N\text{-}2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)(\mu\text{-}NAr')W(Et)(OR_{F3})_2$.

At this stage we assume that alkylidenes are responsible for the observed metathesis activity and that they are of the type $M(NR)(CHR')(OR'')_2$. However, we have no proof. It also is possible that dimeric species in fact are not directly involved in forming the alkylidene but serve only as precursors to monomeric species (e.g., olefin complexes). In any case it appears that norbornene is in fact one of the olefins most susceptible to being converted into an alkylidene. We hope that further studies of reactions between olefins and d^2 Mo and W complexes (monomers or dimers) will lead to some firmer conclusions.

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Supporting Information Available: Text giving experimental details, a labeled thermal ellipsoid drawing, and tables giving crystal data and structure refinement details, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for $\{W(NAr')[OCMe_2(CF_3)]_2\}_2(C_2H_4)$ and $(OR_{F3})_2W(\mu\text{-}N\text{-}2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)(\mu\text{-}NAr')W(Et)(OR_{F3})_2$. This material is available free of charge via the Internet at http://pubs.acs.org. Data for the structures are also available to the public at http://www.reciprocalnet.org/ (numbers 04299 and 05121, respectively).

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