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Preparation of Well-Defined, Metathetically Active Oxo Alkylidene Complexes of Tungsten

M. B. O'Donoghue, R. R. Schrock,* A. M. LaPointe, and W. M. Davis

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

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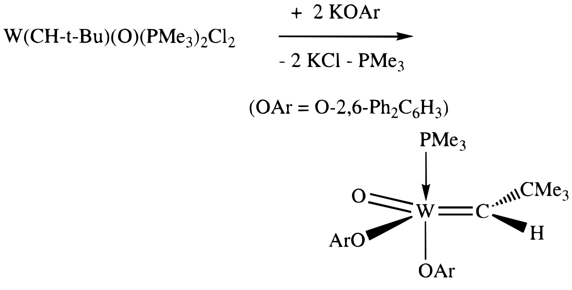
Summary: The reaction between $W(CH\text{-}t\text{-}Bu)(O)(PMe_3)_2Cl_2$ *and 2 equiv of* $KO\text{-}2,6\text{-}Ph_2C_6H_3$ *yields yellow crystalline syn-*$W(CH\text{-}t\text{-}Bu)(O)(OAr)_2(PMe_3)$ *(**1a**; Ar = 2,6-*$Ph_2C_6H_3$*) in which the* PMe_3 *is bound to tungsten on the NMR time scale. An analogous* PPh_2Me *complex, syn-*$W(CH\text{-}t\text{-}Bu)(O)(OAr)_2(PPh_2Me)$ *(**1b**), can be prepared. Both **1a** and **1b** react readily with 2,3-dicarbomethoxynorbornadiene (**2a**) and 2,3-bis(trifluoromethyl)norbornadiene (**2b**) in dichloromethane or toluene to give polymers that are >95% cis and >95% isotactic.*

The synthesis and olefin metathesis activity (especially for ROMP[1,2]) of pseudotetrahedral imido alkylidene complexes of the type $M(CHR)(NR')(OR'')_2$ (M = Mo, W)[3] have been investigated extensively in our laboratories. We believe there is a good possibility that many classical olefin metathesis catalysts[4] are related oxo alkylidene complexes (e.g., $M(CHR)(O)X_2$; X = Cl, OR, etc.), since if oxo ligands are not present initially, they could be formed readily from even traces of water, and at low catalyst concentrations bimolecular decomposition of oxo alkylidene complexes could be slow relative to metathesis activity. Oxo alkylidene complexes of the type $W(CH\text{-}t\text{-}Bu)(O)(PR_3)_2Cl_2$ and $W(CH\text{-}t\text{-}Bu)(O)(PR_3)Cl_2$ actually were the first well-defined group 6 alkylidene complexes to be prepared,[5−8] but their metathesis activity was found to be short-lived, and complexes such as "$W(CH\text{-}t\text{-}Bu)(O)(O\text{-}t\text{-}Bu)_2$" were found to be unstable. It would be desirable to prepare well-defined, metathetically active oxo alkylidene complexes[9,10] in order to compare them with analogousimido alkylidene catalysts, especially in terms of the proposed role of *syn* and *anti* alkylidene rotamers in determing ROMP polymer structure.[11] We report here the preparation and characterization of well-defined, metathetically active oxo alkylidene complexes of tungsten. [Note added in proof: Several tungsten oxo vinylalkylidene complexes have recently been synthesized using diphenylcyclopropene as the alkylidene source. See: de la Mata, F. J.; Grubbs, R. H. *Organometallics* **1996**, *15*, 577.]

The reaction between $W(CH\text{-}t\text{-}Bu)(O)(PMe_3)_2Cl_2$[7] and 2 equiv of $KO\text{-}2,6\text{-}Ph_2C_6H_3$ yields yellow crystalline **1a** (eq 1). The alkylidene H_α resonance in **1a** is found at 10.13 ppm ($^3J_{HP}$ = 3.5, $^2J_{HW}$ = 11 Hz) and the C_α resonance at 287.4 ppm ($^2J_{CP}$ = 11 Hz, $^1J_{CH}$ = 120 Hz). A J_{CH} value of 120 Hz suggests that the alkylidene has the *syn* orientation, as shown. ^{31}P NMR data (0.35 ppm, $^1J_{PW}$ = 333 Hz) suggest that the PMe_3 ligand is bound to tungsten on the NMR time scale. A strong absorbance at ~960 cm^{-1} in **1a** has been assigned to the metal−oxo stretch.



1a

(1)

An analogous PPh_2Me complex, $W(CH\text{-}t\text{-}Bu)(O)(OAr)_2(PPh_2Me)$ (**1b**), can be prepared by adding 2 equiv of KOAr to $W(CH\text{-}t\text{-}Bu)(O)(PPh_2Me)_xBr_2$ (a mixture in which x = 1, 2). Only a single broad ^{31}P NMR resonance is observed for **1b** at 11.6 ppm at 22 °C, but a sharp resonance is observed upon cooling the sample (J_{PW} = 305 Hz). The alkylidene H_α (10.37 ppm) and C_α (287.2 ppm) resonances also do not show coupling to ^{31}P at room temperature. A J_{CH} value of 118 Hz is consistent again with the *syn* rotamer being present. A neophylidene complex, $W(CHCMe_2Ph)(O)(OAr)_2(PPh_2Me)$ (**1b′**), has also been prepared.

Analogous 2,6-di-*tert*-butyl-4-methylphenoxide complexes in theory might contain more labile phosphine ligands, or none at all, but attempts to prepare them have led only to metallacycles (according to NMR data and elemental analysis) that are related to a structurally characterized metallacycle prepared by adding 2 equiv of $LiOC(CF_3)_2(p\text{-}C_6H_4Me)$ to $W(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}$

⊗ Abstract published in *Advance ACS Abstracts*, February 15, 1996.

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[9] Pseudooctahedral oxo alkylidene complexes have been prepared that contain a tris(pyrazolyl)borate ligand and that are "air-stable, moisture-stable, and thermally-stable".[10] However, when catalytic activity *is* observed (e.g., upon addition of $AlCl_3$) the nature of the catalytically active species could not be determined.

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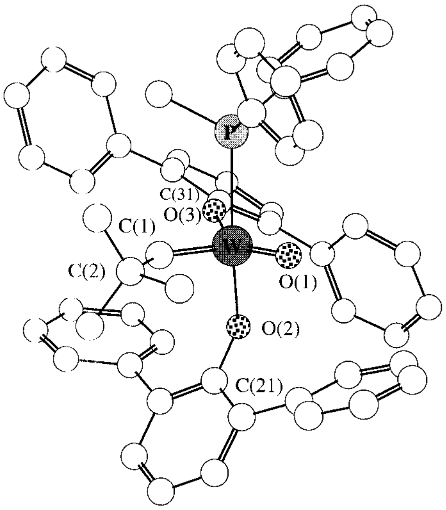
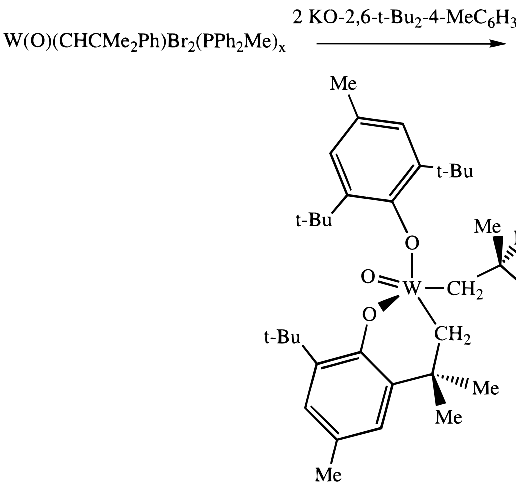


Figure 1. Chem 3D view of the structure of W(CH-*t*-Bu)(O)(O-2,6-$Ph_2C_6H_3)_2(PPh_2Me)$ (**1b**). Selected distances (Å) and angles (deg) are as follows: W−O(1) = 1.689(6); W−O(3) = 1.957(6); W−C(1) = 1.88(1); W−P = 2.590(2); W−O(2) = 1.993(5); W−C(1)−C(2) = 147.8(9); W−O(2)−C(21) = 129.0(5); W−O(3)−O(31) = 157.2(6); P−W−O(2) = 167.2(2); P−W−O(3) = 80.9(2); O(1)−W−C(1) = 105.5(4); O(1)−W−O(3) = 143.0(3); O(1)−W−O(2) = 98.1(3); O(3)−W−C(1) = 109.2(4); O(3)−W−O(2) = 87.7(2); O(2)−W−C(1) = 101.0(3).

i-$Pr_2C_6H_3$)(dme)Cl_2.[12] An example is shown in eq 2. So



(2)

far we have seen no evidence of CH activation in an ortho phenyl ring of the O-2,6-$Ph_2C_6H_3$ ligand related to what has been found in tungsten systems discovered by Basset.[13]

X-ray quality-crystals of **1b** were grown at room temperature from a mixture of dichloromethane and pentane. An X-ray study[14] (Figure 1) showed the molecule to be a distorted trigonal bipyramid in which the oxo ligand, C(1) and C(2) of the *syn* neopentylidene ligand, and O(3) of one phenoxide ligand all lie in the equatorial plane. The phosphine ligand is found in an axial position, as had been expected on the basis of the structures of five-coordinate adducts of imido alkylidene complexes[3] and the structure of W(CH-*t*-Bu)(O)(PEt_3)Cl_2.[15] The W=O(1) (1.689(6) Å) and W=C(1) bond lengths (1.88(1) Å) and the W=C(1)−C(2) bond angle (147.8(9)°) are similar to what has been found in other tungsten oxo alkylidene complexes.[3,5,6,10,15,16] A surprising feature is the significant difference between the axial W−O(2)−C(21) bond angle (129.0(5)°) and the equatorial W−O(3)−C(31) bond angle (157.2(6)°), even though for steric reasons one might expect the opposite result. The ortho phenyl rings of the phenoxide ligands approximately encircle the neopentylidene and oxo ligands and therefore should provide a significant degree of protection against bimolecular decomposition of the base-free form.

Table 1. All−Cis, Isotactic Poly(2,3-dicarbomethoxynorbornadiene) Prepared Using Initiator 1a[a]

amount of substrate, equiv	M_n(calcd)	M_n(found)	PDI
22	4741	7934	1.03
43	9113	14280 (14590)	1.02 (1.01)
65	13694	19240	1.02
86	18067	27430 (27070)	1.01 (1.02)
129	27020	37530	1.03
166	34724	49050 (47160)	1.04 (1.04)
256	53463	63350 (53860)	1.05 (1.11)

[a] Molecular weights were determined by GPC using a light scattering detector set at 690 nm. The values for d_n/d_c were determined on samples weighed on a microbalance, assuming that all of the sample elutes from the column and that the refractive index does not change to any significant degree throughout the sample. The resulting average d_n/d_c value was 0.096, and the range was ±0.005. Numbers within parentheses are duplicate runs on the same sample.

Both **1a** and **1b** (or the neophylidene analog, **1b′**) react readily with 2,3-dicarbomethoxynorbornadiene (**2a**) in dichloromethane to give polymers whose molecular weights are directly proportional to the number of monomers added and that have low polydispersities, characteristic of living polymerizations (Table 1). Surprisingly, polymerization of ~100 equiv of **2a** with **1b** is complete in less than 15 min, and no change is observed in the PDI of the polymer after an additional 45 min. The apparent high reactivity of the oxo species might be expected in view of the oxo's small size and high electronegativity. We presume at this stage that phosphine dissociation is a requirement for reaction of the oxo alkylidene complex with an olefin and therefore that the phosphines in these catalysts must be labile on the polymerization time scale for steric reasons.[17] Interestingly, poly(**2a**) prepared from **1a** is >95% cis (according to proton NMR).[18−21] The high cis content is consistent with the proposal that cis polymers of this

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(14) Crystal data: space group $P2_1/n$, $a = 12.027(2)$ Å, $b = 19.486(3)$ Å, $c = 19.442(3)$ Å, $\beta = 100.12(1)°$, $V = 4486(2)$ Å^3, $Z = 4$, fw = 960.80, ρ(calcd) = 1.432 g/cm^3, $R = 0.041$, $R_w = 0.035$. Further details can be found in the Supporting Information.

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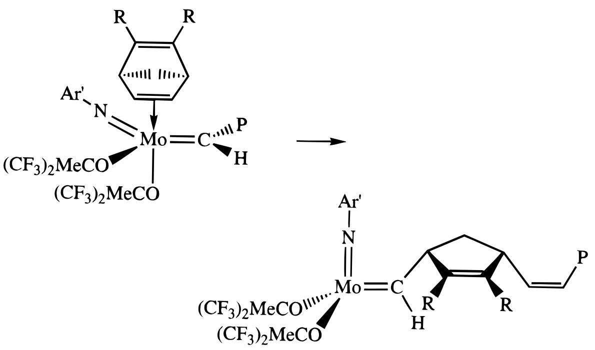
type arise from *syn*-propagating alkylidenes, as shown (for example) in eq 3 (P = polymer; Ar′ = 2,6-*i*-$Pr_2C_6H_3$;



(3)

R = CO_2Me),[11] and that the oxo ligand presents minimal steric hindrance toward approach of the monomer in this manner. Even more surprising is the finding that these polymers are >95% isotactic (according to carbon NMR).[18−21] Tacticity in the oxo alkylidene systems described here can arise solely by *chain end* control. Cis isotactic polymers of this type previously have been prepared only through enantiomorphic site control using molybdenum imido alkylidene catalysts that contain chiral chelating dialkoxide ligands,[20,21] a process that presumably is inherently more efficient than chain end control. Polymers prepared from 2,3-bis(trifluoromethyl)norbornadiene (**2b**) appear to be analogous to samples of poly(**2a**), according to NMR spectra,[20,21] although the fact that they are soluble only in acetone has prevented our characterizing them by gel permeation chromatography, as we have found to be the case in other circumstances.[20]

Future work will be aimed toward synthesizing W and Mo oxo alkylidene complexes and studying their metathesis activity toward a variety of substrates. Of particular interest will be the features of the oxo catalysts that can be traced directly to the influence of the small, relatively electronegative oxo ligand compared to relatively bulky imido ligands that have been employed most often to date.

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Supporting Information Available: Text giving experimental details for the synthesis of compounds reported here and a labeled ORTEP diagram, text giving a detailed description of X-ray data collection and structure solution and refinement, and tables of experimental details, final positional parameters, and final thermal parameters for **1b** (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm edition of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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