

Facile Tungsten Alkylidene Synthesis: Alkylidene Transfer from a Phosphorane to a Tungsten Imido Complex¹

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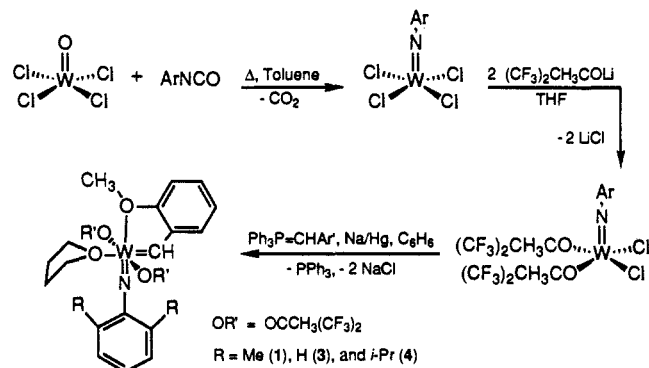
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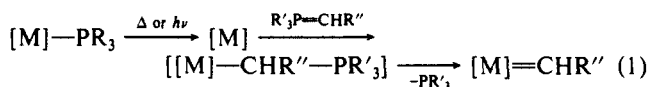
A number of transition-metal complexes catalyze the ring-opening metathesis polymerization (ROMP) of a variety of cyclic olefins.² Notable among these catalysts are the titanacyclobutane derivatives³ and certain alkylidene complexes of tungsten,⁴ molybdenum,⁵ tantalum,⁶ and rhenium.⁷ The highly reactive tungsten alkylidene complexes⁴ developed by Schrock, Osborn, and Basset are particularly useful for the synthesis of unsaturated polymers such as novel conducting polymers and soluble precursors and derivatives of polyacetylene.⁸ Recent applications of these catalytic systems involve the polymerization of acyclic alkynes and dienes.⁹ In addition, the use of tungsten alkylidene complexes as Wittig-type reagents in organic synthesis holds considerable promise.¹⁰

The incorporation of different alkylidene ligands into these tungsten metathesis catalysts is desirable as it allows the variation of the reactivity of the catalyst, the polymer end-group in ROMP, and the products synthesized in Wittig-type reactions.¹¹ To date, the synthesis of tungsten neopentylidene complexes has been achieved by α -hydride elimination.⁴ Other alkylidenes must be incorporated through the metathesis reaction.^{4a,c,11} One attractive route to alkylidene complexes involves alkylidene transfer from

Scheme I. Synthesis of W(CHAr')(NAr)[OCMe(CF₃)₂]₂(THF)



readily available phosphoranes. However, despite extensive study, few concrete examples of this reaction have been observed.^{12,13} In these examples, the sequential addition of phosphorane and loss of phosphine generates the metal alkylidene (eq 1).¹³ We report here a convenient synthesis of W(CHAr')(NAr)[OCMe(CF₃)₂]₂(THF) **1** (Ar = 2,6-Me₂C₆H₃ and Ar' = *o*-MeOC₆H₄) and related complexes in which alkylidene transfer from a phosphorane to tungsten is the key step (Scheme I).¹⁴



M = Ta, Zr

The synthesis of **1** involves the initial reaction of W(O)Cl₄¹⁵ with 2,6-dimethylphenyl isocyanate to give W(NAr)Cl₄(Et₂O).¹⁶ Subsequent chloride displacement with 2 equiv of (CF₃)₂MeCOLi produces W(NAr)Cl₂[OCMe(CF₃)₂]₂(THF). In the key step, sodium amalgam reduction of the tungsten imido complex in the presence of the phosphorane yields **1** as a mono-THF adduct in 64% yield based on W(O)Cl₄.^{16,17} A "one-pot" version of this

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(17) A representative procedure for the alkylidene transfer step is as follows: W(NAr)Cl₂[OCMe(CF₃)₂]₂(THF) (16.0 g, 19.8 mmol) and Ar'CH=PPh₃ (7.78 g, 20.3 mmol) were dissolved in 160 mL of benzene and 2.5 mL of THF, and the solution was added to a 1% sodium amalgam (3.59 g of Na, 7.90 equiv). After being stirred for 8 h at room temperature, the mixture was allowed to settle, and the orange-brown supernatant was added via cannula to 2.07 g of CuCl (20.9 mmol). The residual sodium amalgam was washed with a total of 120 mL of Et₂O, and the combined benzene/Et₂O solution was stirred with CuCl for 12 h before removal of the solvent in vacuo. The brown solid was then extracted with 260 mL of Et₂O. After addition of 2 mL of THF to the extract and filtering, the solution was slowly cooled to -50 °C to give 12.0 g (70.6%) of **1** as an olive-yellow powder: ¹H NMR (C₆D₆) δ 10.81 (s, 1, CHAr'), 6.96 (m, 1, H_{Ar}), 6.95 (d, 2, J = 8.06, Ar H_m), 6.75 (m, 1, H_{Ar}), 6.53 (d, 1, J = 7.32, Ar' H), 6.48 (m, 1, H_{Ar}), 6.26 (d, 1, J = 7.32, Ar' H), 3.93 (m, 4, THF), 3.59 (s, 3, OMe), 2.66 (s, 6, Ar Me), 1.37 (m, 4, THF), 1.19 [s, 6, OMe(CF₃)₂].

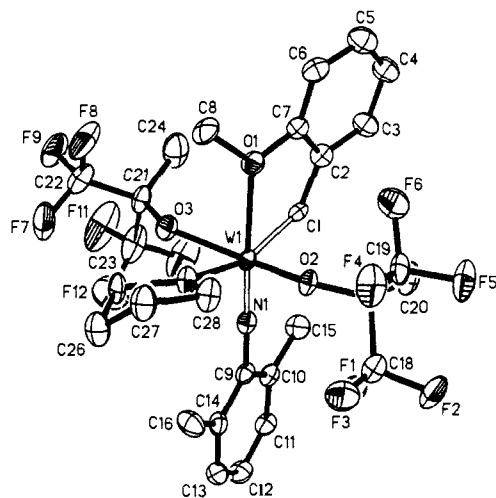


Figure 1. ORTEP diagram of **1**. Selected bond distances (Å) and angles (deg) are as follows: W–C(1), 1.943 (5); W–N(1), 1.737 (4); W–O(1), 2.346 (3); W–O(2), 1.995 (4); W–O(3), 1.995 (3); W–O(4), 2.294 (3); W–C(1)–C(2), 121.9 (4); W–N(1)–C(9), 174.6 (4); W–O(2)–C(17), 138.8 (3); W–O(3)–C(21), 138.4 (3); C(1)–W–O(2), 97.6 (2); O(2)–W–O(4), 75.2 (1); C(1)–W–O(3), 103.0 (2); O(3)–W–O(4), 75.1 (1); C(1)–W–O(1), 74.2 (2); O(1)–W–O(2), 82.0 (1); O(1)–W–O(3), 79.7 (1); O(1)–W–O(4), 79.8 (1); C(1)–W–N(1), 99.2 (2); N(1)–W–O(2), 101.2 (2); N(1)–W–O(3), 100.2 (2); N(1)–W–O(4), 107.0 (2).

reaction sequence involving the recrystallization of only the final product gave 20.7 g of **1** (32.2%, not optimized). Complex **1** resembles the arylimido tungsten alkylidene catalysts developed by Schrock and co-workers.^{4a} These catalysts are known to be deactivated by the coordination of Lewis bases such as THF and sterically nondemanding phosphines and amines.^{4a,8c,9a,15b} Fortunately, PPh₃, a reaction byproduct, does not coordinate to **1**. Therefore, phosphine-free **1** can readily be prepared by scavenging PPh₃ with CuCl.^{15b}

The structure of **1** has been determined by X-ray diffraction.¹⁸ An ORTEP diagram is included in Figure 1 along with selected bond distances and angles. The geometry about the metal center can best be described as a distorted octahedron with the imido and alkylidene ligands lying in the expected *cis* orientation.^{4a} The methoxy group of the benzylidene ligand occupies an axial site of the octahedron, and the 2.346 (3) Å W–O(1) bond distance is comparable to the 2.294 (3) Å W–O(4) (THF) bond distance.¹⁹ The W–C(1)–C(2) bond angle is approximately 23° smaller than the analogous angle reported for W(CHPh)(NAr)[OCMe(CF₃)₂]₂.^{4a} This smaller angle is reflected in the respective coupling constants of these two complexes: $J_{\text{CH}\alpha} = 151$ Hz for **1** and $J_{\text{CH}\alpha} = 121$ Hz for W(CHPh)(NAr)[OCMe(CF₃)₂]₂.^{4a}

The coordination of the methoxy group to the tungsten metal center of **1** in solution is implied by difference NOE experiments and reactivity studies. NOEs are not observed in either direction between the methoxy group and the carbene α -proton. Donation by the methoxy group is further suggested by the lack of PPh₃ coordination and by the stability of **1**. The analogous unsubstituted benzylidene complex W(CHPh)(NAr)[OCMe(CF₃)₂]₂ reversibly binds PPh₃ and largely decomposes within a day in solution in its absence.²⁰ Two imido methyl groups are observed in the ¹H

NMR spectrum of **1** at –70 °C, requiring that the aryl ring not lie in the RO–W(N)–OR plane. At room temperature, the arylimido ligand rotates freely, and deuteriotetrahydrofuran exchanges rapidly with coordinated THF.

Treatment of **1** with PMe₃ gives yellow W(CHAr')(NAr)[OCMe(CF₃)₂]₂(PMe₃). Heating a toluene solution of **1** under vacuum generates THF-free W(CHAr')(NAr)[OCMe(CF₃)₂]₂ (**2**) as a bright red solid. The downfield chemical shift of the α -proton of the *o*-methoxybenzylidene ligand of **2** (10.94 ppm) can be compared with the downfield shifts reported for alkylidene complexes coordinated by Lewis bases,^{4a,15b} which suggests that in solution the methoxy group of **2** coordinates to the tungsten metal center.²¹ As expected, **1** and **2** are active metathesis catalysts, rapidly polymerizing cyclic olefins such as norbornene and cyclooctatetraene. The acyclic olefin *cis*-2-pentene is slowly metathesized by **2**.²² Complex **1** reacts in a Wittig-type fashion with carbonyl compounds, including esters and amides, in yields of 82–100% as measured by NMR spectroscopy.

The steric bulk of the imido ligand can be varied without greatly affecting the transfer of the *o*-methoxybenzylidene moiety from phosphorus to tungsten. For example, in addition to the (2,6-dimethylphenyl)imido complex **1**, the phenylimido (**3**) and (2,6-diisopropylphenyl)imido (**4**) complexes are obtained in good yields from the reaction sequence shown in Scheme I. To date, the transfer of other aryl carbenes in high yields has required the (2,6-dimethylphenyl)imido precursor. In all cases, the incorporation of electron-withdrawing alkoxides is necessary for successful reduction and alkylidene transfer.

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Supplementary Material Available: Experimental details and spectroscopic and analytical data for complexes **1**–**4** and precursors and derivatives of these complexes, additional information regarding the polymerizations, Wittig-type reactions, and crystal structure of **1**, and tables of crystal data, atomic coordinates, bond distances and angles, and thermal parameters for **1** (19 pages); listing of observed and calculated structure factors for **1** (19 pages). Ordering information is given on any current masthead page.

(20) Complex **2** has been isolated and characterized as its PMe₃ adduct W(CHPh)(NAr)[OCMe(CF₃)₂]₂(PMe₃).

(21) In the crystal structure of the THF-free alkylidene complex W(CHAr')[N-2,6-(*i*-Pr)₂C₆H₃][OCMe(CF₃)₂]₂, the methoxy group does coordinate to tungsten: Johnson, L. K.; Grubbs, R. H.; Ziller, J. W., unpublished results.

(22) The lower limit for the rate of metathesis of *cis*-2-pentene by a 3 mM toluene-*d*₈ solution of **2** is 1.4 equiv/min at room temperature.

Reaction Sequence Related to That of Carbon Monoxide Dehydrogenase (Acetyl Coenzyme A Synthase): Thioester Formation Mediated at Structurally Defined Nickel Centers

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The nickel-containing carbon monoxide dehydrogenases¹ (CODH) from certain bacteria such as *Clostridium thermo-*

(18) **1** crystallizes in space group $P2_1/c$ (C_2^2 ; No. 14) with $a = 12.606$ (3) Å, $b = 12.981$ (3) Å, $c = 18.998$ (5) Å, $\beta = 91.85$ (2)°, $V = 3108.0$ (13) Å³, and $D_{\text{calc}} = 1.830$ g cm⁻³ for $Z = 4$, $T = 173$ K. The structure was solved via an automatic Patterson method (SHELXTL PLUS). Refinement of positional and anisotropic thermal parameters led to convergence with $R_F = 3.8\%$, $R_{wF} = 4.4\%$, and $GOF = 1.39$ for 415 variables refined against all 5269 unique data with $|F_o| > 0$; [$R_F = 3.1\%$, $R_{wF} = 4.1\%$ for those 4576 data with $|F_o| > 6.0\sigma(|F_o|)$].

(19) (a) The methoxy group coordinates to chromium in the crystal structure of (OC)₂Cr[=C(OMe)(*o*-MeOC₆H₄)]. See: Dotz, K. H.; Sturm, W.; Popall, M.; Riede, J. *J. Organomet. Chem.* **1984**, *277*, 267–275. (b) For information on analogous tungsten complexes, see: Dotz, K. H.; Erben, H.-G.; Staudacher, W.; Harms, K.; Müller, G.; Riede, J. *J. Organomet. Chem.* **1988**, *355*, 177–191.