

Electrophilic Tungsten(II) Methylene Carbene Complexes: Adduct Formation, Methylene Transfer, and Catalysis of Aziridine Formation from Imines and Ethyl Diazoacetate

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From Fischer's original heteroatom carbene synthesis¹ to use as carbene transfer mediators² and as ROMP³ and olefin metathesis catalysts,⁴ metal carbenes have been important exhibits in the organometallic showcase. Schrock's early methylene breakthrough riveted attention on the M=CH₂ entity,⁵ and during the ensuing two decades both nucleophilic^{6,7} and electrophilic^{8–10} M=CH₂ moieties have been generated. Most

(1) Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580.

(2) For metallocarbene reviews, see: (a) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994; p 151. (b) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (c) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121. (d) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919. (e) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (f) Dötz, K. H.; Fischer, H.; Hoffman, P.; Kreissl, F.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield, FL, 1983. (g) Schrock, R. R. *Science* **1983**, *219*, 13. (h) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, U.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733. (i) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (j) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545. (k) Cotton, F. A.; Lukehart, C. M. *Prog. Inorg. Chem.* **1972**, *16*, 487.

(3) For reviews of ROMP (ring opening metathesis polymerization), see refs 3–5 in Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039.

(4) For reviews of olefin metathesis, see: (a) Ivin, J. J. *Olefin Metathesis*; Academic Press: New York, 1983. (b) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449. (c) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G. W., Stone, A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, p 499. (d) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100 and references therein.

(5) (a) Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6577. (b) Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6578. (c) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

(6) For representative examples of other nucleophilic methylene carbenes, see: (a) Tour, J. M.; Bedworth, P. V.; Wu, R. *Tetrahedron Lett.* **1989**, *30*, 3927. (b) Cannizzo, L. F.; Grubbs, R. H. *J. Org. Chem.* **1985**, *50*, 2316. (c) Cannizzo, L. F.; Grubbs, R. H. *J. Org. Chem.* **1985**, *50*, 2386. (d) Schwartz, J.; Gell, K. I. *J. Organomet. Chem.* **1980**, *184*, C1. (e) Petasis, N. A.; Bzowej, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 6392. (f) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (g) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270. (h) Hartner, Jr., F. W.; Schwartz, J.; Clift, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 640.

(7) Numerous papers have been published concerning group VIII and group IX d⁶ and d⁸ carbenes that display nucleophilic behavior; see: Roper, W. R. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Norwell, MA, 1989; p 27 and references therein.

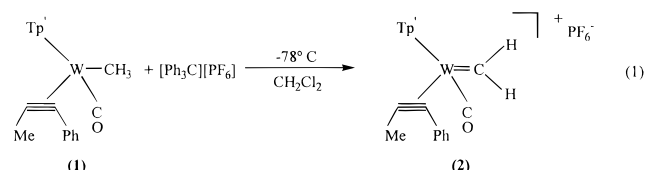
(8) (a) Brookhart, M.; Liu, Y. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Norwell, MA, 1989; p 251. (b) Kegley, S. E.; Brookhart, M. *Organometallics* **1982**, *1*, 760. (c) Studabaker, W. B.; Brookhart, M. *J. Organomet. Chem.* **1986**, *310*, C39. (d) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1980**, *102*, 1203. (e) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099.

(9) (a) Kiel, W. A.; Lin, G.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958. (b) Wang, Y.; Gladysz, J. A. *Chem. Ber.* **1995**, *128*, 213. (c) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804. (d) Merrifield, J. H.; Lin, G.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811. (e) Wong, W.; Tam, W. W.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5440. (f) Buhro, W. E.; Etter, M. C.; Georgiou, S.; Gladysz, J. A.; McCormick, F. B. *Organometallics* **1987**, *6*, 1150. (g) Buhro, W. E.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A.; McCormick, F. B.; Etter, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 1056.

germane here are the unusually robust methylene carbene complexes [Cp*(NO)(L)Re=CH₂][PF₆] (L = PPh₃ or P(OPh)₃) formed from a rhenium methyl precursor and triphenylcarbenium (trityl) hexafluorophosphate.^{9c}

We now report [Tp'(CO)(PhC₂Me)W=CH₂][PF₆] (**2**) (Tp' = hydridotris(3,5-dimethylpyrazolyl)borate), an electrophilic carbene complex that binds nucleophiles, transfers the methylene fragment to olefins to form cyclopropanes, and serves as a catalyst for aziridine formation from imines and EDA (ethyl diazoacetate).

Trityl cation reacts with Tp'(CO)(PhC₂Me)W–Me¹¹ (**1**) in CD₂Cl₂ at –78 °C to form methylene carbene complex **2** (eq 1). The NMR signature for a methylene complex includes two



doublets (12.33, 12.04 ppm; ²J_{HH} = 12 Hz) in the ¹H NMR spectrum and a low-field triplet for the carbene carbon (308.2 ppm, ¹J_{CH} = 140 Hz, ¹J_{WC} = 110 Hz, 14% ¹⁸³W, I = 1/2) in the ¹³C NMR spectrum. The absence of methylene rotation on the NMR time scale is compatible with optimal back-bonding from the metal d_π orbitals to the carbene, alkyne, and carbonyl, with the carbene orientation orthogonal to the W–CO axis. The IR spectrum exhibits a CO stretch at 2073 cm⁻¹ in CH₂Cl₂ (cf. 2073 cm⁻¹ for [Tp'(CO)W(PhC₂H₂)₂][BF₄]).¹² The cationic complex **2** shows no signs of decomposition in solution at room temperature over a period of several hours and persists for days in the solid state.

Addition of a nucleophile is classic behavior for an electrophilic Fischer carbene. Here addition of 1 equiv of PMe₃ to a CH₂Cl₂ solution of **2** results in the formation of [Tp'(CO)(PhC₂Me)W–CH₂–PMe₃][PF₆] (**3**), characterized by a CO stretch at 1888 cm⁻¹ in CH₂Cl₂ (Scheme 1). In the ¹H NMR one of the diastereotopic CH₂ protons appears as a doublet of doublets (1H, 0.79 ppm, ²J_{HH} = 14 Hz, ²J_{PH} = 22 Hz). The second methylene proton lies between 1.5 and 1.6 ppm and is obscured by methyl peaks. A COSY was used to assign the resonances of the second methylene proton. A definitive triplet of doublets (20.1 ppm, ¹J_{CH} = 125 Hz; ¹J_{PC} = 33 Hz) is observed for the methylene carbon in the ¹³C NMR.

The carbene complex reacts with a variety of electron rich olefins to form cyclopropanes (Scheme 1). For example, addition of styrene, 4-methylstyrene, or cyclohexene results in stoichiometric CH₂ transfer to form cyclopropane products in 73%, 57%, and 51% yield, respectively.¹³

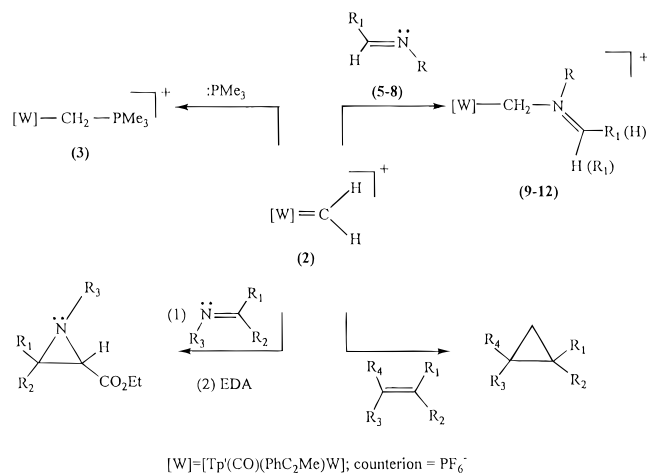
A new development in aziridine synthesis is metal-catalyzed carbene transfer to imines. Addition of EDA to imines in the presence of a catalytic amount of Cu(OTf)₂ results in aziridine

(10) Some representative examples of electrophilic methylene carbenes: (a) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044. (b) Guerschais, V.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1985**, 835. (c) Barefield, E. K.; McCarten, P.; Hillhouse, M. C. *Organometallics* **1985**, *4*, 1682. (d) Davison, A.; Krusell, W. C.; Michaelson, R. C. *J. Organomet. Chem.* **1974**, *72*, C7. (e) Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1979**, *101*, 6473. (f) O'Connor, E. J.; Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1987**, *109*, 3739. (g) Mattson, M. N.; Bays, J. P.; Zakutansky, J.; Stolarski, V.; Helquist, P. *J. Org. Chem.* **1989**, *54*, 2467. (h) Riley, P. E.; Capshaw, C. E.; Pettit, R.; Davies, R. E. *Inorg. Chem.* **1978**, *17*, 408. (i) Flood, T. C.; DiSanti, F. J.; Miles, D. L. *Inorg. Chem.* **1976**, *15*, 1910.

(11) Complex **1** was synthesized according to a published procedure: Caldarelli, J. L.; Wagner, L. E.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 2878.

(12) Feng, S. G.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 2951.

(13) Yields for cyclopropanation reactions were determined by isolation of the cyclopropane on an alumina column, followed by GC analysis with a known amount of the internal standard undecane.

Scheme 1. Reactions of the Methylene Carbene 2

formation.¹⁴ Copper(I) catalysts with chiral bis(dihydrooxazole) ligands¹⁵ and methylrhodium trioxide¹⁶ have also been used to produce aziridines from imines and EDA. Mechanistic speculation for the copper(I) system postulates the formation of a copper carbene complex followed by nucleophilic attack of the imine on the carbene fragment.

Is carbene transfer to an imine possible in this system? Reaction of [Tp'(CO)(PhC₂Me)W=CH₂][PF₆] (2) with *N*-benzylidenemethylamine results in formation of the isolable imine adduct [Tp'(CO)(PhC₂Me)W-CH₂N(Me)=C(H)(Ph)][PF₆] (4) ($\nu_{\text{CO}} = 1886 \text{ cm}^{-1}$). ¹H NMR data include two doublets (4.45, 2.00 ppm, ²J_{HH} = 12 Hz) assigned to the diastereotopic methylene protons. The iminic carbon resonates as a doublet at 161.6 ppm (¹J_{CH} = 170 Hz) while the methylene carbon is observed as a triplet at 66.4 ppm (¹J_{CH} = 135 Hz) in the ¹³C NMR. A low-temperature (-120 °C) single-crystal X-ray structure study provided metric details of 4 as shown in Figure 1.

The addition of benzylideneaniline to [Tp'(CO)(PhC₂Me)W=CH₂][PF₆] (2) yields the imine adduct [Tp'(CO)(PhC₂Me)W-CH₂N(Ph)=C(H)(Ph)][PF₆]. Reaction of additional arylimines 5–8¹⁷ with the carbene complex 2 yielded similar results (Scheme 1). These arylimine adducts 9–12 are not stable enough to permit isolation. No aziridine products have been detected in these reactions.

A recent report notes that EDA can attack imines which have been activated by simple Lewis acids (BF₃, TiCl₄, or AlCl₃).¹⁸ The two major products observed for these systems are aziridines and enamines. In a similar fashion, we have found that the methylene carbene complex 2 catalyzes the production

(14) Rasmussen, K. G.; Jørgensen, K. A. *J. Chem. Soc., Chem. Commun.* **1995**, 1401.

(15) Hansen, K. B.; Finney, N. S.; Jacobsen, E. N. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 676.

(16) (a) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1995**, *60*, 7090. (b) Zhu, Z.; Espenson, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 9901.

(17) For imines 5–8, (R)N=C(R₁)(H): **5**, R = R₁ = phenyl; **6**, R = phenyl, R₁ = *p*-nitrophenyl; **7**, R = *p*-methoxyphenyl, R₁ = phenyl; **8**, R = phenyl, R₁ = *tert*-butyl.

(18) Casarubios, L.; Pérez, J. A.; Brookhart, M.; Templeton, J. L. *J. Org. Chem.* **1996**, *61*, 8358.

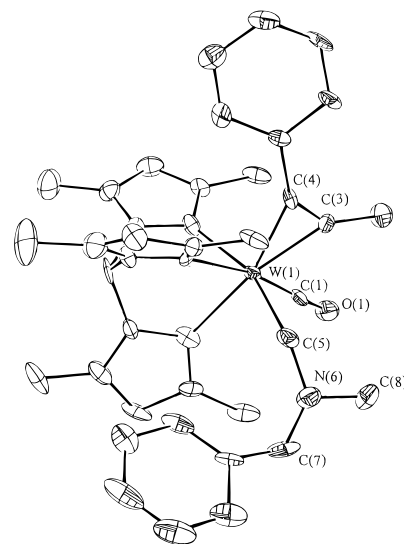


Figure 1. ORTEP diagram for [Tp'(CO)(PhC₂Me)W-CH₂N(Me)=C(H)(Ph)][PF₆] (4). Selected bond distances (Å) and angles (deg): W(1)–C(1), 1.943(16); W(1)–C(3), 2.076(13); W(1)–C(4), 2.032(12); W(1)–C(5), 2.237(13); C(5)–N(6), 1.468(17); C(1)–O(1), 1.183(19); W(1)–C(1)–O(1), 178.3(11); W(1)–C(5)–N(6), 125.3(9); C(5)–N(6)–C(8), 112.9(11); C(5)–N(6)–C(7), 127.0(12).

Table 1. Yields and Product Ratios for Aziridine Catalysis

imine	total yield, ^a %	% <i>cis</i>	% <i>trans</i>	% enamine	azir:enamine	<i>cis:trans</i>
5	67.5	45.0	4.5	18.0	2.8:1	10:1
6	64.6	41.3	14.4	8.9	6.3:1	2.9:1
7	87.5	65.0		22.5	2.9:1	
8	71.2 ^b	27.7	30.1	13.4	4.3:1	1:1.1

^a As determined by integration (versus an internal standard) of well-resolved peaks in the ¹H NMR. ^b Isolated yield: reaction performed in CH₂Cl₂ with products purified by chromatography on silica gel (10:1 hexanes/ethyl acetate).

of aziridines from imines and EDA (Scheme 1). Yields and ratios for *cis* and *trans* aziridines as well as for the formation of enamine products are given in Table 1.

We believe that these catalytic reactions utilize a reactive, electrophilic carbene complex simply as a Lewis acid to activate imines toward nucleophilic attack by EDA. The discovery of this catalytic sequence suggests another plausible mechanistic pathway in other transition metal mediated carbene transfer reactions.

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Supporting Information Available: Experimental procedures, analytical data, and discussion of control reactions with [Ph₃C][PF₆], X-ray and crystal structure information for 4, including a labeled ORTEP diagram, and tables showing crystallographic data and collection parameters, atomic positional parameters, complete bond lengths and angles, and anisotropic temperature factors (13 pages). See any current masthead page for ordering and Internet access instructions.

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