Synthesis and Reactivity of Tungsten(II) Methylene Complexes

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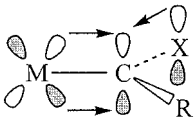
Treatment of the methyl complex Tp′(CO)(PhC_2Me)W−Me **(1)** or Tp(CO)(PhC_2Ph)W−Me **(2)** with trityl cation yields the corresponding methylene complex [Tp′(CO)(PhC_2Me)W=CH_2]-[PF_6] **(3)** (Tp′ = hydridotris-(3,5-dimethylpyrazolyl)borate) or [Tp(CO)(PhC_2Ph)W=CH_2][PF_6] **(4)** (Tp = hydridotris(pyrazolyl)borate). The carbene complex **(3)** is unusually persistent for a methylene complex. Complexes **3** and **4** display electrophilic behavior, as evidenced both by addition of nucleophiles and by methylene transfer to electron rich olefins. When bound to either carbene **3** or **4**, arylimines are activated toward nucleophilic attack by ethyl diazoacetate (EDA). The net result of the addition of excess arylimine followed by excess EDA to a solution of either **3** or **4** is catalytic aziridine formation. X-ray diffraction studies have revealed the structures of [Tp′(CO)(PhC_2Me)W−CH_2PMe_3][PF_6] **(7)** and [Tp′(CO)(PhC_2-Me)W−CH_2N(Me)=C(H)(Ph)][PF_6] **(15)**. The relative stabilities of **3** and **4** are discussed as well as the mechanism of aziridine catalysis.

Introduction

Since Fischer's formulation of a metal−carbon double bond in $(CO)_5W$=C(OMe)(Me), transition metal carbene complexes have been utilized in a wide variety of synthetic chemistry.[1,2] In particular, carbene complexes have been utilized as carbene transfer mediators[2] and as ROMP[3] and olefin metathesis catalysts.[4]

Early reports of transition metal carbenes focused on complexes in which the carbene moiety was stabilized via π-bonding to both the metal center and a heteroatom substituent (Scheme 1). The presence of a heteroatom substituent proved vital to the stability of electrophilic carbene complexes, as evidenced by Casey's early work with non-heteroatom carbene complexes.[5]

Scheme 1. Bonding in Fischer Carbene Complexes



Pettit and Jolly observed that treatment of $Cp(CO)_2$-$Fe(CH_2OMe)$ with acid in the presence of cyclohexene produced norcarane.[6] The methylene complex [$Cp(CO)_2$-Fe=CH_2]$^+$ was postulated as a reactive intermediate, although no direct observation of this complex was made. Additional speculation of methylene carbene intermediates in cyclopropanation reactions has been reported.[7]

Schrock's seminal report of the synthesis of the persistent tantalum methylene $Cp_2(Me)Ta$=CH_2 focused attention on methylene complexes.[8] This group V carbene, synthesized by deprotonation of the precursor dimethyl complex, decomposes only slowly in solution. Since Schrock's discovery, both nucleophilic[9,10] and electrophilic[11−13] M=CH_2 moieties have been gener-

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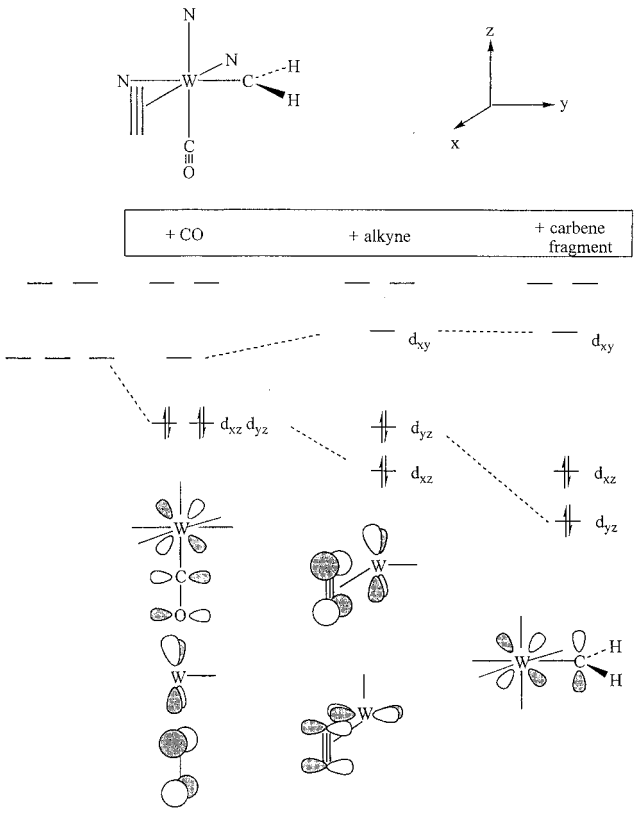
Scheme 2. Qualitative Molecular Orbital Diagram for [Tp^x(CO)(PhC≡CR)W=CH$_2$][PF$_6$] (3) and (4) (R = Ph, Me; Tp^x = Tp, Tp′)



ated. However, reports of stable methylene complexes remain rare.

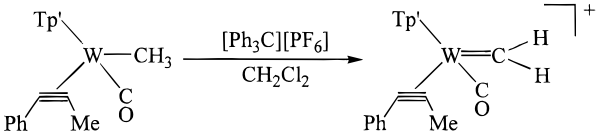
Although attempts to observe the putative [Cp(CO)$_2$Fe=CH$_2$]$^+$ complex proposed by Pettit and Jolly were unsuccessful, Brookhart *et al.* were able to spectroscopically observe the methylene complex [Cp(Ph$_2$PCH$_2$CH$_2$PPh$_2$)Fe=CH$_2$]$^+$.[11d] The ruthenium analog has also been spectroscopically identified as have the group VI carbenes [Cp(CO)$_2$(L)M=CH$_2$]$^+$ (L = PPh$_3$, PEt$_3$; M = Mo, W).[11b]

Gladysz *et al.* have reported the extraordinarily robust methylene complexes [Cp*(NO)(L)Re=CH$_2$][PF$_6$] (L = PPh$_3$, P(OPh)$_3$; Cp* = pentamethylcyclopentadienyl).[12c] The rhenium methylene carbenes are formed from a methyl precursor and triphenylcarbenium hexafluorophosphate.

We have previously communicated the conversion of the methyl complex Tp′(CO)(PhC≡Me)W−Me **(1)** (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) to a methylene complex via net hydride abstraction from the methyl moiety.[14] We now report the complementary carbene complex [Tp(PhC≡CPh)(CO)W=CH$_2$][PF$_6$] **(4)** (Tp = hydridotris(pyrazolyl)borate) as well as details of the reactivity of both methylene complexes. These carbene complexes bind nucleophiles, act as methylene transfer reagents to form cyclopropanes, and catalyze aziridine formation from imines and EDA (ethyl diazoacetate). The focus of this report is centered upon elucidation of the nature of the methylene fragment, the stability of the Tp′ carbene **3** compared to the facile decomposition of the Tp carbene **4**, and the mechanism by which **3** or **4** catalyzes the formation of aziridines from *N*-arylimines and EDA.

Results and Discussion

Synthesis and Stability of Methylene Carbenes. Trityl cation reacts with Tp′(CO)(PhC≡CMe)W−Me **(1)** at −78 °C in methylene chloride to form the corresponding methylene complex, [Tp′(CO)(PhC≡CMe)W=CH$_2$][PF$_6$] **(3)** (eq 1). A color change from blue to reddish-



(1) (3) (1)

brown accompanies the formation of **3**. The IR spectrum exhibits a high-energy CO stretching frequency at 2073 cm^{-1} in methylene chloride (cf. 2073 cm^{-1} for [Tp′(CO)(PhC≡CH)$_2$W][BF$_4$]).[15] The ^{13}C and ^{1}H NMR spectra display classical methylene carbene features, including low-field chemical shifts for the protons and carbon of the [W]=CH$_2$ unit. Thus, two doublets (12.33, 12.04 ppm, $^2J_{HH}$ = 12 Hz, $^2J_{WH}$ = 7 Hz, ^{183}W (14% abundance), $I = {}^1/_2$) are observed in the ^{1}H NMR spectrum, while a low-field triplet (308.2 ppm, $^1J_{CH}$ = 140 Hz, $^1J_{WC}$ = 110 Hz) is revealed in the ^{13}C NMR spectrum. In order to achieve an 18-electron count, the alkyne must serve as a four-electron donor, consistent with the downfield chemical shifts in the ^{13}C NMR spectrum (213.8, 211.5 ppm). The absence of methylene rotation on the NMR time scale is compatible with optimal back-bonding from the metal dπ orbitals to the carbene, alkyne, and carbonyl. It is expected that the plane of the CH$_2$ fragment will be orthogonal to the W−CO axis (Scheme 2).

Rapid decomposition is common among methylene complexes. Decomposition often occurs through a bimolecular route that results in the coupling of two methylene units to form ethylene. However, carbene **3** decomposes slowly in methylene chloride at room tem-

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perature ($t_{1/2} \approx 3700$ min) and persists for days in the solid state. While the presence of the electron-rich Tp′ ligand should provide electronic stabilization to the carbene moiety, the presence of other π-acids (CO, PhC≡CMe) in the coordination sphere likely compromises this electronic contribution. If a bimolecular decomposition pathway is operative, the steric bulk of the borate ligand could serve to deter degradation and account for the kinetic stability of **3**. Synthesis of the Tp analogue of **3** provides an opportunity to investigate the relative roles of electronic and steric factors. In comparison to Tp′, the unsubstituted Tp ligand provides less electron density and is sterically less bulky (cone angle = 224° for Tp′, 184° for Tp).[16]

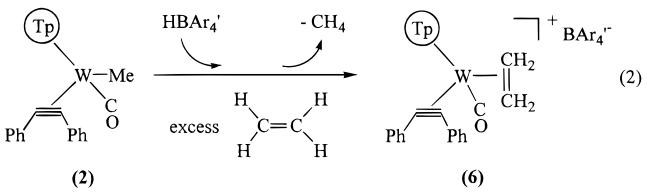
Reaction of Tp(CO)(PhC≡CPh)W−Me **(2)** with trityl cation in CD_2Cl_2 at −78 °C yields the corresponding methylene complex, [Tp(CO)(PhC≡CPh)W=CH_2][PF_6] **(4)**. A CO stretching absorption at 2100 cm^{-1}, the appearance of two low field doublets (12.4 and 12.1 ppm; $^2J_{HH}$ = 12 Hz) in the ^{1}H NMR, and a color change from dark green to bright yellow characterize the formation of **4**. Between −50 and −40 °C, carbene **4** undergoes rapid decomposition.

We tentatively attribute the stability of the Tp′ carbene **3** relative to the Tp carbene **4** to the steric bulk of the substituted borate. The electronic difference between the two borate ligands may play some role in the stability of **3**. However, given the large difference in steric factors between Tp and Tp′, the electronic contribution is probably secondary.

Decomposition of [Tp(CO)(PhC≡CPh)W=CH_2][PF_6] (4). Decomposition of **4** initially forms two products, as indicated by ^{1}H NMR and IR spectroscopies. ^{1}H NMR spectroscopy indicates that the Tp ligand and alkyne remain intact, while IR spectroscopy reveals two carbonyl stretching frequencies (1937 and 2043 cm^{-1}). On the basis of literature precedents[11b,e,12d] and spectroscopic data, we propose that the two products are Tp(CO)(PhC≡CPh)W−FPF_5 **(5)** and [Tp(CO)(PhC≡CPh)W(CH_2=CH_2)][PF_6] **(6)**.

The ^{1}H NMR spectrum of the decomposition products of **4** exhibits four broad multiplets with approximate triplet character (4.7, 4.0, 2.4, and 1.8 ppm). This pattern is consistent with the formation of ethylene complex **6** in which olefin rotation is slow on the NMR time scale. Hindered rotation of ethylene would result in four non-equivalent olefinic protons and could yield the four observed resonances. The high-energy CO stretching frequency at 2043 cm^{-1} is congruous with a cationic complex with three π-acids in the coordination sphere (CO, alkyne, and olefin).

Efforts were made to independently synthesize ethylene complex **6**. In the presence of excess ethylene (−78 °C), Tp(CO)(PhC≡CPh)W−Me **(2)** was treated with $HBAr_4'$ (BAr_4' = tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate). Elimination of methane[17] should generate an open coordination site suitable for binding ethylene (eq 2). The result was the formation of a complex which exhibited a CO stretching frequency at 2043 cm^{-1}.[18] Evaporation of the solvent and dissolution

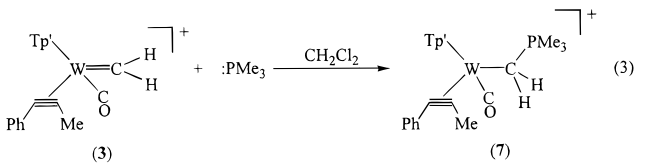


(2) (6) (2)

of the green oil in CD_2Cl_2 allowed observation of the ^{1}H NMR spectrum, which displayed the four multiplets we have assigned above to the ethylene complex **6**. Consistent with earlier observations, this complex decomposes over a period of hours.

What is the identity of the second decomposition product? Decomposition via transfer of a methylene fragment between two metal carbene centers to form the ethylene complex **6** would open a coordination site at the metal. We have previously found that fluorinated anions (PF_6^- and BF_4^-) are willing σ-donor ligands for W(II) d^4 metal fragments of the type [Tp^x(CO)(RC≡CR′)W]$^+$.[19] Therefore, a likely product is Tp(CO)(PhC≡CPh)W−FPF_5 **(5)**. The CO stretching frequency of 1937 cm^{-1} is consistent with previously reported Tp′ species (for example, Tp′(CO)(PhC≡CMe)W−FBF_3, ν_{CO} = 1917 cm^{-1}).[19] Unfortunately, as with the ethylene complex **6**, complex **5** decomposes to intractable products.

Reactions with PMe_3. Addition of PMe_3 to a CH_2Cl_2 solution of [Tp′(CO)(PhC≡CMe)W=CH_2][PF_6] **(3)** yields the phosphine adduct [Tp′(CO)(PhC≡CMe)W−CH_2PMe_3][PF_6] **(7)** (eq 3). Attack of PMe_3 on carbene



(3) (7) (3)

complex **3** demonstrates the electrophilic nature of the carbene fragment. Formation of **7** is accompanied by a vivid color change to purple and the appearance of a CO stretch at 1893 cm^{-1} (CH_2Cl_2) in the IR spectrum. The ^{1}H NMR spectrum of **7** reveals a doublet of doublets for one of the diastereotopic methylene protons (0.79 ppm, $^2J_{HH}$ = 14 Hz, $^2J_{PH}$ = 22 Hz), a doublet for the PMe_3 methyl groups (1.57 ppm, $^2J_{PH}$ = 13 Hz), and signature features for the ancillary ligands. 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. The ^{13}C NMR reveals a definitive triplet of doublets ($^1J_{CH}$ = 125 Hz, $^1J_{PC}$ = 33 Hz) for the methylene carbon and a quartet of doublets ($^1J_{CH}$ = 130 Hz, $^1J_{PC}$ = 55 Hz) for the phosphine moiety.

Reaction of the Tp carbene **4** with PMe_3 forms the complex [Tp(CO)(PhC≡CPh)W−CH_2PMe_3][PF_6] **(8)**. A triplet (2.01 ppm, $^2J_{HH}$ = 14, $^2J_{PH}$ = 14 Hz), a doublets of doublets (1.19 ppm, $^2J_{HH}$ = 14 Hz, $^2J_{PH}$ = 20 Hz), and a doublet (1.59 ppm, $^2J_{PH}$ = 13 Hz) are observed in the ^{1}H NMR spectrum for the diastereotopic methylene protons and the phosphine methyl groups. The ^{13}C NMR of **8** reveals a triplet of doublets centered at 23.2 ppm ($^1J_{CH}$ = 120 Hz, $^1J_{PC}$ = 38 Hz) and a quartet and

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(18) In addition to the putative ethylene complex, other products are observed for this reaction.
(19) Caldarelli, J. L. Optical Resolution and Reactivity of Chiral Tungsten(II) Alkyne Complexes. Ph.D. Dissertation, University of North Carolina at Chapel Hill, Chapel Hill, NC, 1993.

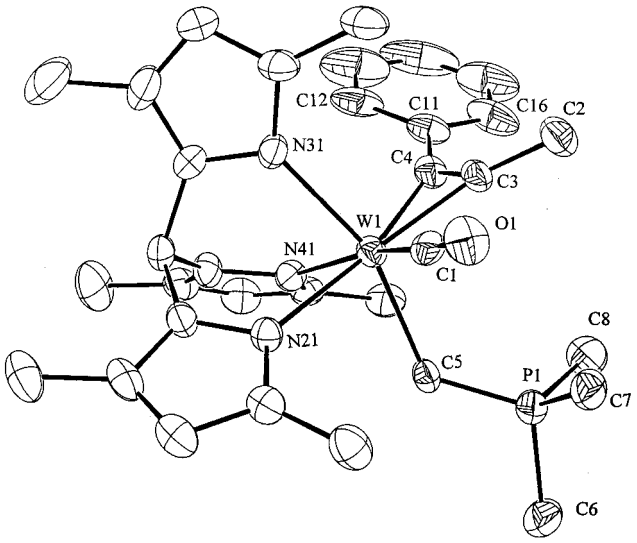


Figure 1. ORTEP diagram for [Tp′(CO)(PhC≡CMe)W−CH_2PMe_3][PF_6] (**7**).

Table 1. Crystallographic Data and Collection Parameters for [Tp′(CO)(PhC≡CMe)W−CH_2PMe_3][PF_6] (7)

formula	$C_{29}H_{41}BF_6ON_6P_2W$
mol wt	860.27
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	17.005(4)
b, Å	13.3937(25)
c, Å	17.704(3)
β, deg	96.458(23)
V, Å^3	4006.6(13)
Z	4
D_{calcd}, g cm^{-3}	1.426
F(000)	1711.70
cryst dimens, mm	0.15 × 0.20 × 0.40
temp, °C	20
radiation (λ, Å)	Mo Kα (0.710 73)
2θ range, deg	5.00 < θ < 46.00
μ, mm^{-1}	3.02
scan mode	ω
total no. of data	6630
total no. of unique data	5571
no. of obsd data ($I > 2.5\sigma(I)$)	3528
R_F	0.042
R_w	0.048
GOF	1.71

doublets at 13.6 ppm ($^1J_{CH}$ = 130 Hz, $^1J_{PC}$ = 53 Hz). The IR spectrum of **8** shows a CO absorption at 1914 cm^{-1} (KBr). Complex **8** could not be obtained in analytically pure form.

Recrystallization upon layering a methylene chloride solution of **7** with hexanes at room temperature provided a suitable single crystal (0.15 × 0.20 × 0.40 mm) for an X-ray diffraction study. A labeled ORTEP diagram of **7** is shown in Figure 1, while crystallographic data and collection parameters are given in Table 1. Selected bond distances and angles for **7** are presented in Table 2. The alkyne is aligned parallel to the W−CO axis with the alkyne phenyl substituent *syn* to Tp′, both typical structural features for d^4 metal complexes of this class.[20] The PMe_3 moiety is bound to the former carbene carbon. The W−C(5) bond distance of 2.232(11) Å is typical for tungsten−carbon single bonds.[21] The carbon−phosphorus bond length is 1.744(10) Å, and the W−C−P bond angle is 125.9(6)°.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Tp′(CO)(PhC≡CMe)W−CH_2PMe_3][PF_6] (7)

W(1)−C(1)	1.938(14)	C(2)−C(3)	1.494(17)
W(1)−C(3)	2.055(11)	C(3)−C(4)	1.301(18)
W(1)−C(4)	2.041(11)	C(4)−C(11)	1.432(17)
W(1)−C(5)	2.232(11)	C(11)−C(12)	1.39(2)
W(1)−N(21)	2.257(8)	P(1)−C(5)	1.744(10)
W(1)−N(31)	2.202(8)	P(1)−C(6)	1.763(13)
W(1)−N(41)	2.249(9)	P(1)−C(7)	1.783(12)
C(1)−O(1)	1.168(16)	P(1)−C(8)	1.779(12)
C(1)−W(1)−C(3)	72.7(5)	N(21)−W(1)−N(31)	79.3(3)
C(1)−W(1)−C(4)	109.3(5)	N(21)−W(1)−N(41)	80.7(3)
C(1)−W(1)−C(5)	94.6(4)	N(31)−W(1)−N(41)	84.8(3)
C(1)−W(1)−N(21)	84.8(4)	C(5)−P(1)−C(6)	110.8(6)
C(1)−W(1)−N(31)	93.4(4)	C(5)−P(1)−C(7)	114.3(5)
C(1)−W(1)−N(41)	165.5(4)	C(5)−P(1)−C(8)	111.3(6)
C(3)−W(1)−C(4)	37.0(5)	C(6)−P(1)−C(7)	105.6(6)
C(3)−W(1)−C(5)	101.0(4)	C(6)−P(1)−C(8)	106.2(6)
C(3)−W(1)−N(21)	157.4(4)	C(7)−P(1)−C(8)	108.2(6)
C(3)−W(1)−N(31)	99.0(4)	W(1)−C(1)−O(1)	176.0(9)
C(3)−W(1)−N(41)	121.7(4)	W(1)−C(3)−C(2)	149.6(9)
C(4)−W(1)−C(5)	103.6(4)	W(1)−C(3)−C(4)	70.9(7)
C(4)−W(1)−N(21)	163.5(4)	C(2)−C(3)−C(4)	139.4(11)
C(4)−W(1)−N(31)	91.0(4)	W(1)−C(4)−C(3)	72.1(7)
C(4)−W(1)−N(41)	85.1(4)	W(1)−C(4)−C(11)	148.8(10)
C(5)−W(1)−N(21)	83.1(3)	C(3)−C(4)−C(11)	138.7(11)
C(5)−W(1)−N(31)	159.9(4)	W(1)−C(5)−P(1)	125.9(6)
C(5)−W(1)−N(41)	82.9(3)		

Cyclopropane Synthesis. Transition metal mediated carbene transfer to olefins to form cyclopropanes is a well-established synthetic methodology.[2,22−25] Enantioselective cyclopropane formation with substituted carbene entities, CHR, has been achieved both catalytically and stoichiometrically. However, transfer of the parent CH_2 methylene fragment from a transition metal complex to a prochiral olefin with high enantioselectivity has not been achieved.

In order to explore the possible use of chiral tungsten carbenes [Tp^x(CO)(PhC≡CR)W=CH_2]$^+$ (R = Ph, Me) for enantioselective cyclopropane synthesis, we investigated reactions of the racemic carbene complexes **3** and **4** with olefins. Cyclopropane yields for a range of olefins are presented in Table 3.

Initially, CH_2 transfer to the monosubstituted olefins styrene and 4-methylstyrene was explored. In each reaction, the corresponding carbene complex was reacted with 10 equiv of olefin. Cyclopropane yields, particularly for disubstituted olefins (*vide infra*), decreased with a decrease in the ratio of olefin to metal complex. Methylene transfer from either **3** or **4** to styrene occurred with almost identical yield. In addition, production of norcarane from cyclohexene was achieved in 51% yield with either **3** or **4**. The Tp carbene **4** is significantly more reactive than **3**, as manifested by its rapid reaction with olefins.[26]

(20) (a) Feng, S. G.; Philipp, C. C.; Gamble, A. S.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 3504. (b) Feng, S. G.; White, P. S.; Templeton, J. L. *Organometallics* **1993**, *12*, 2131.

(21) See, for example: (a) Schrock, R. R.; Kolodziej, R. M.; Liu, A. H.; Davis, W. M.; Vale, M. G. *J. Am. Chem. Soc.* **1990**, *112*, 4338. (b) O'Regan, M. B.; Liu, A. H.; Finch, W. C.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 4331. (c) Schrock, R. R.; Glassman, T. E.; Vale, M. G.; Kol, M. *J. Am. Chem. Soc.* **1993**, *115*, 1760. (d) Liu, A. H.; Murray, R. C.; Dewan, J. C.; Santarsiero, B. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 4282.

(22) Brookhart, M.; Humphrey, M. B.; Kratzer, H. J.; Nelson, G. O. *J. Am. Chem. Soc.* **1980**, *102*, 7802.

(23) Friedrich, E. C.; Lunetta, S. E.; Lewis, E. J. *J. Org. Chem.* **1989**, *54*, 2388.

(24) Du, H.; Yang, F.; Hossain, M. M. *Synth. Commun.* **1996**, *26*, 1371.

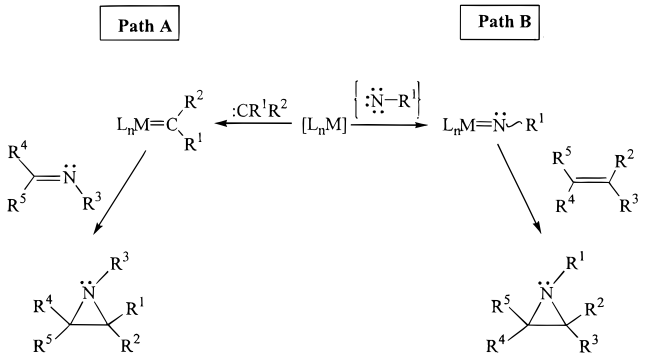
(25) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282.

Table 3. Yields for Cyclopropanation Reactions

metal complex	olefin	% yield	ref[a]
Tp′ **3**	styrene	73%	22
Tp **4**	styrene	74%	22
Tp′ **3**	cyclohexene	51%	23
Tp **4**	cyclohexene	51%	23
Tp′ **3**	4-methylstyrene	57%	24
Tp **4**	4-methylstyrene	85%	24
Tp′ **3**	*cis*-β-methylstyrene	32%	25
Tp **4**	*cis*-β-methylstyrene	44%	25
Tp′ **3**	*trans*-β-methylstyrene	19%	25
Tp **4**	*trans*-β-methylstyrene	54%	25

[a] References give ^{1}H NMR data for the resulting cyclopropane.

Scheme 3. Two Methodologies for Aziridine Synthesis[a]



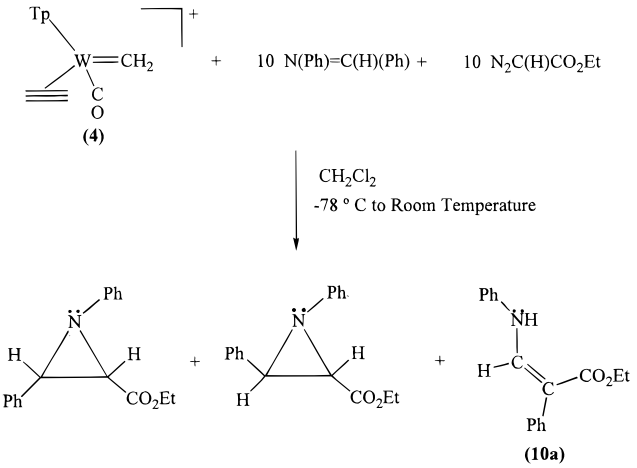
[a] Path A: carbene transfer to an imine. Path B: nitrene transfer to an alkene.

The disparate yields between reaction of the Tp carbene **4** and the Tp′ carbene **3** with 4-methylstyrene were unexpected (85% vs 57% yield, respectively). At the completion of reaction of the Tp′ carbene with 4-methylstyrene, only a small amount of starting olefin is observed in the GC analysis. Given 4-methylstyrene's proclivity to undergo electrophilic polymerization, polymerization of 4-methylstyrene may be responsible for consumption of this olefin and the reduced cyclopropane yields. The higher yield of cyclopropane incurred with the Tp carbene **4** can be explained by the high reactivity of this complex. In this case, the kinetics of methylene transfer presumably compete favorably with electrophilic polymerization.

Reaction of carbene **3** or **4** with *cis*- or *trans*-β-methylstyrene proceeded to form cyclopropanes in varying yields. In either case, the Tp′ carbene **3** produced cyclopropane in lower yields than Tp carbene **4**. This can be rationalized by steric inhibition between the Tp′ ligand and the disubstituted olefins. In each reaction, the original stereochemistry of the olefin is conserved in the cyclopropane products, i.e., *cis*-olefin yields *cis*-cyclopropane.

Aziridine Catalysis. A recently discovered route to aziridine synthesis is metal-mediated nitrene transfer to olefins (Scheme 3, Path B).[27] A new development in aziridine synthesis is an extension of the nitrene-to-olefin transfer methodology to metal-catalyzed carbene transfer to imines (Scheme 3, Path A).[28−30] In preliminary reports, the source of the carbene fragment is ethyl diazoacetate (EDA) to give dinitrogen and C(H)(CO_2Et).

Scheme 4. Catalytic Aziridine Formation



Jørgensen and Rasmussen have reported that the addition of EDA to a solution of an imine and a catalytic amount of Cu(OTf)$_2$ results in aziridine formation.[28] The addition of EDA to arylimines in the presence of a catalytic amount of Cu(I) and chiral bis(dihydrooxazole) ligands yields aziridines along with low yields of a pyrrolidine.[29] Mechanistic speculation included initial formation of a Cu(I) carbene complex (via reaction with EDA) followed by nucleophilic attack of the imine on the carbene fragment. At this stage, ring closure and copper−carbon bond cleavage would yield aziridine.

Methylrhenium trioxide catalyzes the production of aziridines from alkyl, or arylimines and EDA.[30] Mechanistic consideration again invokes a metal−carbenoid intermediate in the catalytic cycle.

EDA can attack imines which are activated by simple Lewis acids (BF_3, $TiCl_4$, or $AlCl_3$).[31] Two major products are typically observed for these systems: aziridines and enamines. The ratio of these products was found to be dependent on both the Lewis acid and the identity of the arylimine.

Addition of 10 equiv of *N*-benzylideneaniline and EDA to the Tp carbene **4** at −78 °C followed by allowing the solution to reach room temperature resulted in the observation of gas evolution (presumably dinitrogen). ^{1}H NMR analysis of the reaction mixture indicated the formation of three major organic products: *cis* and *trans* aziridine and enamine **(10a)** (60%, 6% and 25% yield, respectively) (Scheme 4).

Both **3** and **4** were found to catalyze aziridine formation from imines and EDA. Yields for aziridine and enamine production for a range of imines are shown in Table 4. Three trends are noteworthy. For reasons that we have not been able to elucidate, the catalytic synthesis of aziridines in these systems works only with *N*-arylimines. Use of the Tp carbene **4** as the catalyst results in higher overall yields of aziridine and enamine.

(26) Reaction of the Tp′ carbene complex **3** with olefins typically requires several hours at room temperature, while the Tp carbene complex **4** reacts in ≤1 h at room temperature.

(27) See, for example: (a) Evans, D. A.; Faul, M. M.; Bilodeau, M. T.; Anderson, B. A.; Barnes, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 5328. (b) Li, Z.; Conser, K. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1993**, *115*, 5326.

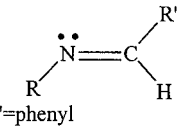
(28) Rasmussen, K. G.; Jørgensen, K. A. *J. Chem. Soc., Chem. Commun.* **1995**, 1401.

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

(30) (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.

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

Table 4. Yields and Ratios for Aziridine Catalysis

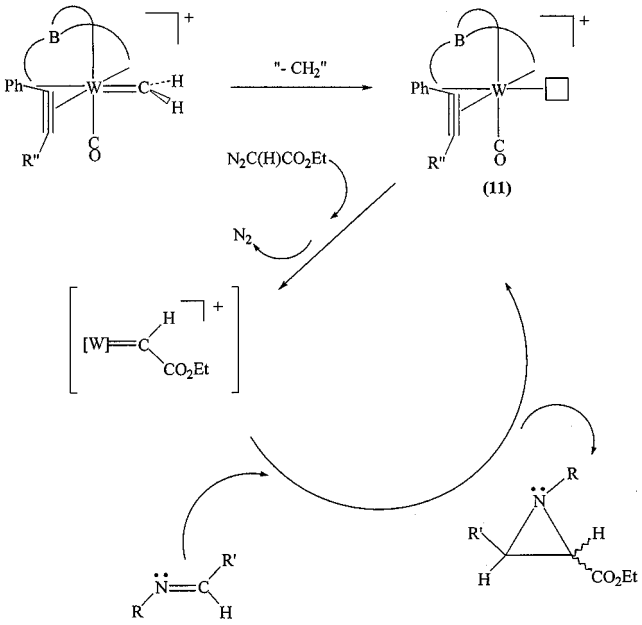


(12a) R=R'=phenyl
(12b) R=phenyl; R'=*p*-nitrophenyl
(12c) R=*p*-methoxyphenyl; R'=phenyl
(12d) R=phenyl; R'=*t*-butyl

catalyst	imine	total yield[a]	*cis*	*trans*	enamine
4	**12a**	91.0%	60.0	6.0	25.0
4	**12b**	93.4%	62.0	17.3	14.1
4	**12c**	90.5%	71.7		18.8
4	**12d**	89.8%	32.9	43.7	13.2
3	**12a**	67.5%	45.0	4.5	18.0
3	**12b**	64.6%	41.3	14.4	8.9
3	**12c**	87.5%	65.0		22.5
3	**12d**	71.2%[b]	27.7	30.1	13.4

[a] As determined by integration (versus an internal standard) of well-resolved peaks in the ^{1}H NMR. [b] Isolated yield: reaction performed in CH_2Cl_2 with products purified by chromatography on silica gel (10:1 hexanes:ethyl acetate).

Scheme 5. Possible Mechanism for Aziridine Catalysis



The *cis*/*trans* ratios of aziridine and aziridine/enamine ratios seem to be more dependent upon the identity of the imine than the catalyst.

Two plausible mechanisms deserve consideration in the catalytic formation of aziridines described above. One possibility is that the carbene complexes **3** and **4** initially lose the methylene fragment, regardless of mechanistic details, resulting in the formation of a transient five-coordinate intermediate of the type $[Tp^x(CO)(PhC{\equiv}CR)W]^+$ **(11)** (Scheme 5). Fragment **11** could combine with EDA to form a highly reactive carbene complex with elimination of dinitrogen. Nucleophilic attack of the imine upon the carbene carbon would yield a transient intermediate, which could ring close to form aziridine and regenerate **11**. This mechanism is reminiscent of that reported for a Cu(I) complex.[29]

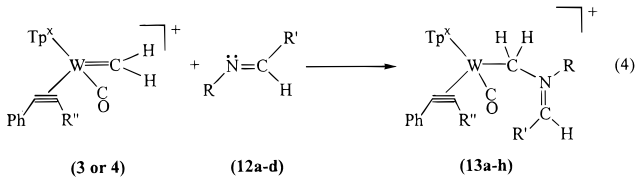
The discovery of Lewis-acid-catalyzed aziridine formation from EDA and imines prompted us to consider a second possible mechanism. The tungsten carbene complexes could be acting as Lewis acids to bind and activate the imine toward attack by EDA. Subsequent loss of dinitrogen and formation of aziridine would regenerate the carbene catalyst.

Table 5. Infrared and ^{1}H NMR Data for Iminium Complexes

metal complex	imine	^{1}H NMR (ppm)[a]	infrared (cm^{-1})	iminium complex
3	**12a**	4.43, 3.98 (13Hz)[b]	1894	**13a**
3	**12b**		1894	**13b**
3	**12c**	4.41 (14 Hz)[b]	1894	**13c**
3	**12d**			**13d**
4	**12a**	4.60, 4.00 (13 Hz)[b]	1929	**13e**
4	**12b**	4.85, 4.03 (13 Hz)[b]	1927	**13f**
4	**12c**	4.50, 4.10 (13 Hz)	1925	**13g**
4	**12d**	4.66, 3.71 (14 Hz)	1916	**13h**

[a] ^{1}H NMR data for the methylene protons. [b] NMR data for the major isomer of two observed isomers (at room temperature).

Reaction of the carbene complexes **3** and **4** with *N*-arylimines in the absence of EDA results in the spectroscopic observation of iminium complexes **(13a−h)** (eq 4). No aziridine products are observed in these



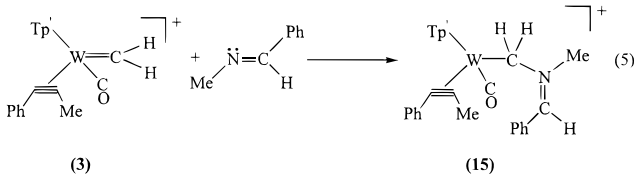
(3 or 4) (12a-d) (13a-h) (4)

reactions. The formation of Tp complexes **(13e−h)** results in a decrease in the CO stretching frequency from 2100 to 1916−1929 cm^{-1} (Table 5). For the Tp′ carbene, the corresponding CO stretching frequency is reduced from 2073 to 1894 cm^{-1}. Diagnostic doublets can be observed for diastereotopic methylene protons for most iminium complexes in the ^{1}H NMR (Table 5). Only $[Tp(CO)(PhC{\equiv}CPh)W{-}CH_2{-}N(Ph){=}C(H)(Ph)][PF_6]$ **(13e)** could be isolated in the solid state.

Reaction of 1 equiv of EDA with the iminium complex **13e** results in the production of *cis* and *trans* aziridine in a 10:1 ratio. In addition, formation of the enamine product is noted with an aziridine/enamine ratio consistent with the aziridine catalysis performed with the Tp methylene carbene **4**.

On the basis of these observations, we propose that the methylene carbene complexes **3** and **4** are acting as Lewis acids for the activation of imines (Scheme 6). When bound to the carbene fragment, the imine becomes susceptible to nucleophilic attack by EDA. The formation of enamine is rationalized by migration of the R′ group on the imine carbon to form a bound imine, which could undergo facile tautomerization to the observed enamine. As an alternate route, carbon−nitrogen bond formation from the putative complex **14** would yield aziridine and re-form the carbene catalyst.

As already mentioned, of the *N*-arylimine adducts **(13a−h)** only $[Tp(CO)(PhC{\equiv}CPh)W{-}CH_2{-}N(Ph){=}C(H)(Ph)][PF_6]$ **(13e)** could be isolated in the solid state. Attempts to produce X-ray quality crystals of **13e** were ineffectual. Reaction of $[Tp'(CO)(PhC{\equiv}CMe)W{=}CH_2][PF_6]$ **(3)** with excess *N*-benzylidenemethylamine yields the iminium complex $[Tp'(CO)(PhC{\equiv}CMe)W{-}CH_2{-}N(Me){=}C(H)(Ph)][PF_6]$ **(15)** (eq 5). ^{1}H NMR data for **15** 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 ^{13}C NMR. The infrared spectrum exhibits a CO stretching frequency at 1886 cm^{-1}.

Recrystallization of **15** was achieved by layering a CH_2Cl_2 solution with hexanes at room temperature. X-ray data were collected as outlined in Table 6. Selected bond distances and angles are presented in Table 7. Figure 2 depicts an ORTEP diagram of **15**.

The W−C(5) bond length of 2.237(13) Å is typical of tungsten−carbon single bonds.[21] The imine fragment is bound to the former carbene carbon with a bond length of 1.468(17) Å. The imine N=C bond length is 1.318(19) Å. Phenyl rings demonstrate a propensity for juxtaposition between two pyrazolyl rings of the borate ligand (see, for example, the phenyl ring of Tp′−phenyl alkyne complexes).[20] In agreement with this observation, the phenyl ring of *N*-benzylidenemethylamine is positioned proximal to the pyrazolyl rings of the Tp′ ligand, a counterintuitive location based on steric considerations.

The tungsten carbene [Tp′(CO)(PhC≡CMe)W=CH_2]-[PF_6] **(3)** possesses a chiral metal center. With the ultimate goal of metal-mediated enantioselective cyclopropane and aziridine synthesis, we attempted resolution of the methyl complex **1** into single enantiomers.

The immediate precursor to the methyl complex **1**, Tp′(CO)(PhC≡CMe)W-I **(16)**, has been isolated as a single enantiomer.[32] Reaction of **16** with $LiMe_2Cu$ yields the methyl complex **1**, and HPLC on a chiral column provides a convenient means to assay the enantiomeric purity of the product. Figure 3 shows the results of HPLC of racemic **1** and of complex **1** produced from opposite enantiomers of the iodide complex **16**.

Conversion of a single enantiomer of **16** to the methyl complex **1** reproducibly yields a 4:1 ratio of enantiomers. Further enantiomeric enrichment of **1** can be achieved by recrystallization from CH_2Cl_2/hexanes. Collection of the supernatant from a single recrystallization yields two enantiomers of **1** in a 9:1 ratio, but loss of the racemic precipitate is costly in time and effort.

An alternate route to the methyl complex **1** was sought. To date, the only other route to **1** from **16** is reaction with Me_2Mg. However, this reaction results in racemization of the metal center.

Although the current methodology for the preparation of enantiomerically enriched **1** is tedious, we were able to isolate enough enriched **1** to probe enantioselective aziridine synthesis. The aziridine was formed from *N*-benzylideneaniline and EDA, and the enantiomeric ratio of products was determined by enantiomorph separation on a chiral HPLC column.

The tungsten carbene complex **3** was generated at low temperature (−78 °C). The imine was added to this solution followed by addition of EDA. The solution was then allowed to come to room temperature and stirred for 30 min. Purification of the aziridine products was performed by chromatography on a silica gel column (20:1 hexanes/ethyl acetate), and the enantioselectivity was assayed by HPLC. Unexpectedly, a 1:1 ratio of the two enantiomers of *cis*-aziridine was observed.

Investigation of this unanticipated and disappointing result is in progress. One possible explanation involves

Scheme 6. Proposed Mechanism for Aziridine Catalysis

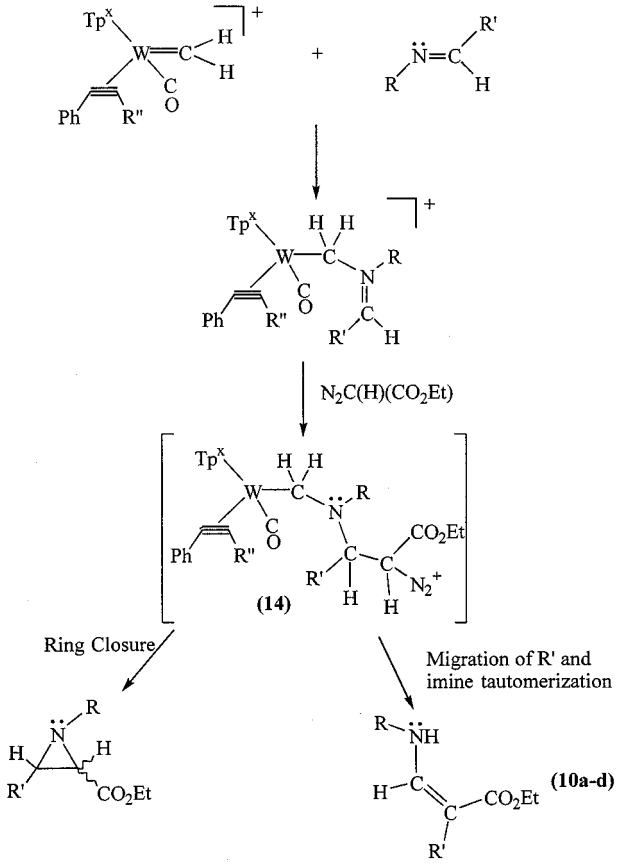


Table 6. Crystallographic Data and Collection Parameters for [Tp′(CO)(PhC≡CMe)W−CH_2−N-(Me)=C(H)(Ph)][PF_6] (15)

formula	$C_{37}H_{47}BCl_6F_6ON_7PW$
mol wt	1158.16
cryst syst	triclinic
space group	*P*1̄
a, Å	13.026(6)
b, Å	14.770(9)
c, Å	15.012(8)
α, deg	64.26(5)
β, deg	88.38(4)
γ, deg	66.93(4)
V, Å^3	2358.2(22)
Z	2
D_{calcd}, g cm^{-3}	1.631
F(000)	1151.97
cryst dimens, mm	0.40 × 0.30 × 0.15
temp, °C	−120
radiation (*λ*, Å)	Mo Kα (0.710 73)
2*θ* range, deg	5.00 < *θ* < 46.00
μ, mm^{-1}	2.94
scan mode	*ω*
total no. of data	6712
total no. of unique data	6586
no. of obsd data ($I > 2.5\sigma(I)$)	4842
R_F	0.062
R_w	0.065
GOF	1.79

(32) Separation of the two diastereomers resulting from coordination of optically pure (*S*)-(−)-α-methylbenzylamine to the racemic fragment [Tp′(CO)(PhC≡CMe)W]$^+$ allows access to enantiomerically enriched Tp′(CO)(PhC≡CMe)W−I, see: Caldarelli, J. L.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*,10097.

Table 7. Selected Bond Distances (Å) and Angles (deg) for [Tp′(CO)(PhC≡CMe)W−CH_2−N(Me)=C(H)(Ph)][PF_6] (15)

W(1)−C(1)	1.943(16)	C(2)−C(3)	1.460(19)
W(1)−C(3)	2.076(13)	C(3)−C(4)	1.304(19)
W(1)−C(4)	2.032(12)	C(4)−C(11)	1.483(18)
W(1)−C(5)	2.237(13)	C(5)−N(6)	1.468(17)
W(1)−N(31)	2.198(11)	N(6)−C(7)	1.318(19)
W(1)−N(41)	2.270(11)	N(6)−C(8)	1.495(20)
W(1)−N(51)	2.255(11)	C(7)−C(21)	1.403(23)
C(1)−O(1)	1.183(19)		
C(1)−W(1)−C(3)	68.4(6)	C(5)−W(1)−N(51)	90.1(4)
C(1)−W(1)−C(4)	104.7(5)	N(31)−W(1)−N(41)	84.2(4)
C(1)−W(1)−C(5)	96.0(5)	N(31)−W(1)−N(51)	75.1(4)
C(1)−W(1)−N(31)	97.0(5)	N(41)−W(1)−N(51)	83.3(4)
C(1)−W(1)−N(41)	169.9(5)	W(1)−C(1)−O(1)	178.3(11)
C(1)−W(1)−N(51)	87.3(5)	W(1)−C(3)−C(2)	149.0(11)
C(3)−W(1)−C(4)	37.0(5)	W(1)−C(3)−C(4)	69.7(8)
C(3)−W(1)−C(5)	97.6(5)	C(2)−C(3)−C(4)	141.3(13)
C(3)−W(1)−N(31)	101.6(5)	W(1)−C(4)−C(3)	73.3(8)
C(3)−W(1)−N(41)	121.2(5)	W(1)−C(4)−C(11)	145.4(10)
C(3)−W(1)−N(51)	155.1(5)	C(3)−C(4)−C(11)	138.8(13)
C(4)−W(1)−C(5)	101.3(5)	W(1)−C(5)−N(6)	125.3(9)
C(4)−W(1)−N(31)	90.3(4)	C(5)−N(6)−C(7)	127.0(12)
C(4)−W(1)−N(41)	85.3(5)	C(5)−N(6)−C(8)	112.9(11)
C(4)−W(1)−N(51)	162.3(5)	C(7)−N(6)−C(8)	119.7(12)
C(5)−W(1)−N(31)	159.8(4)	N(6)−C(7)−C(21)	127.2(12)
C(5)−W(1)−N(41)	80.4(4)		

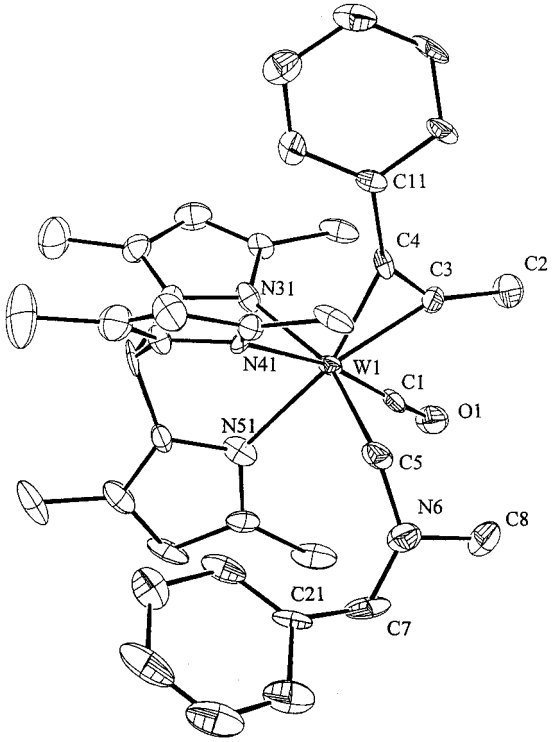
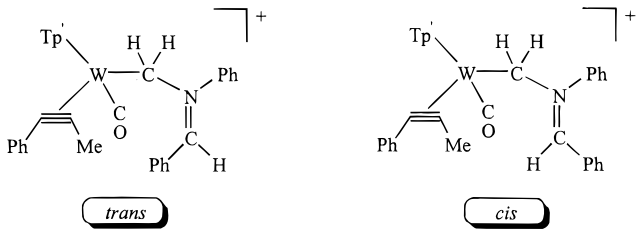


Figure 2. ORTEP diagram for [Tp′(CO)(PhC≡CMe)-W−CH_2−N(Me)=C(H)(Ph)][PF_6] (**15**).

the stereochemistry of the imine upon binding to the carbene fragment. Addition of *N*-benzylideneaniline to an NMR tube sample of **3** at −78 °C yields two isomers of the iminium complex **13a**, as evidenced by observation of two sets of doublets for the diastereotopic methylene protons. We assign these two isomers to *cis* and *trans* geometries around the iminic double bond (Scheme 7).

After approximately 45 min at room temperature, the ^{1}H NMR of **13a** reflects the thermodynamic preference for one of the stereoisomers, i.e., one of the isomers becomes dominant. However, if nucleophilic attack of EDA is rapid (as suggested by the fast reaction time),

Scheme 7. Two Proposed Isomers for the Iminium Complex 13a



the kinetic tendency to form a nearly 1:1 ratio of *cis* and *trans* isomers around the bound imine could explain the racemic mixture of aziridine produced with enriched metal.

Large quantities of enantiomerically enriched **1** would be required for the exploration of stoichiometric enantioselective CH_2 transfer to disubstituted olefins.

Summary

Hydride abstraction from the methyl complex Tp′(CO)(PhC≡CMe)W−Me **(1)** quantitatively yields the methylene carbene [Tp′(CO)(PhC≡CMe)W=CH_2][PF_6] **(3)**. The carbene complex **3** exhibits unusual stability, showing only slow decomposition in solution at room temperature. We attribute this kinetic stabilization to the bulky Tp′ ligand. In agreement with this assessment, the Tp analogue of **3** decomposes rapidly between −50 and −40 °C.

Methylene carbene complexes **3** and **4** display electrophilic reactivity at the carbene carbon, as evidenced by the binding of PMe_3 and methylene transfer to electron-rich olefins to form cyclopropanes. In addition, **3** and **4** catalyze the formation of aziridines from *N*-arylimines and EDA. Mechanistic investigations indicate that binding of the *N*-arylimine to the carbene moiety activates the iminic carbon toward nucleophilic attack by EDA. Subsequent ring closure forms the aziridine product and regenerates the carbene catalyst. The development of enantioselective variants of stoichiometric cyclopropane synthesis and catalytic aziridine formation have been frustrated by the circuitous procedure currently necessary for the resolution of the methyl complex **1** and by the apparent kinetic tendency for the formation of two isomers upon binding *N*-benzylideneaniline to the carbene **3**.

Experimental Section

General Considerations. All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Infrared spectra were recorded on a Mattson Polaris FT-IR spectrometer. Routine ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-400 spectrometer or a Bruker WM250 spectrometer with ^{1}H and ^{13}C NMR shifts referenced to residual ^{1}H signals and to the ^{13}C signals of the deuterated solvents. GC analysis was performed with a Hewlett Packard 5890A gas chromatograph using a J&W Scientific DB-5 capillary column (30 M, 0.25-mm i.d., 0.25-mm film thickness) and flame ionization detection (temperature program 30 °C for 4 min; 30−200 °C at 4 deg min^{-1}). Enantiomeric separation was performed utilizing HPLC on a chiral polysaccharide OD-type column purchased from Chiral Technologies, Inc. Detection of enantiomers of Tp′(CO)(PhC_2Me)WMe **(1)** using HPLC was performed with a mobile phase consisting of 99.7% hexanes and 0.3% *i*-PrOH at a flow rate of 0.4 mL/min. Analysis of the enantiomers of the *cis*-aziridine produced from

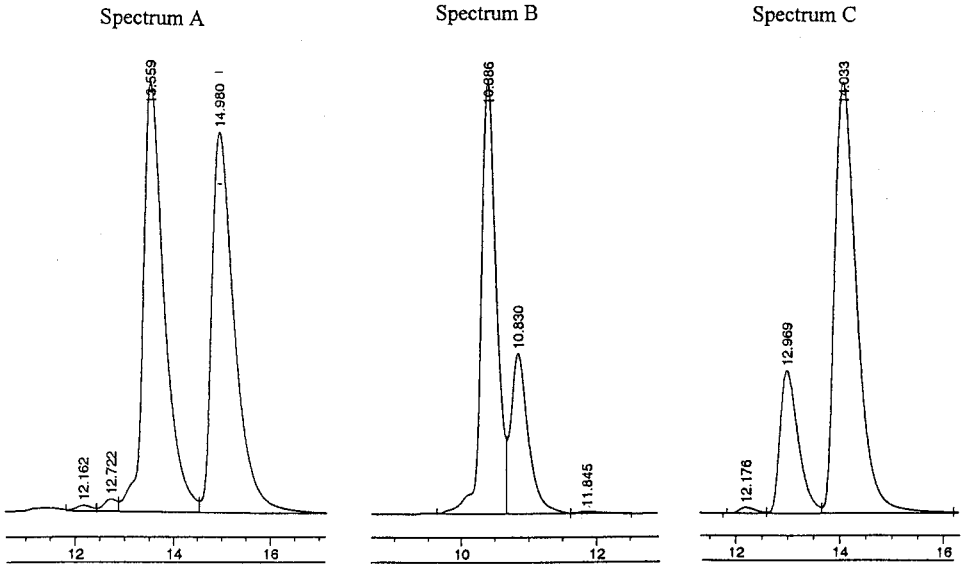


Figure 3. Determination of % ee for enriched Tp′(CO)(PhC≡CMe)W−Me (**1**) Using Chiral HPLC: spectrum A, racemic mixture; spectrum B, produced from *RS*-amine; spectrum C, produced from *SS*-amine (configuration at metal center given first, see ref 32).

EDA and *N*-benzylideneaniline was performed with a 99:1 hexanes/*i*-PrOH mixture at a flow rate of 0.5 mL/min. The injection volume for both experiments was 0.3 μL.

Tp′(CO)(PhC_2Me)WMe **(1)** and Tp(CO)(PhC_2Ph)WMe **(2)** were prepared according to literature methods.[17,33] Methylene chloride and hexanes were purified under a dry argon atmosphere by passage through a column packed with activated alumina.[34] Ethyl acetate was purged with nitrogen prior to use. Deuterated methylene chloride was deoxygenated by several freeze−pump−thaw cycles and stored in a nitrogen atmosphere over 4 Å (8−12 mesh) molecular sieves. All solvents were purged with nitrogen prior to use. Triphenylcarbenium hexafluorophosphate, *N*-benzylideneaniline, and *N*-benzylidenemethylamine were used as purchased from Aldrich Chemical Co. Trimethylphosphine was dried over sodium and transferred to a Kontes tube and stored under a dry nitrogen atmosphere. Imines **(12b−d)** were synthesized by reaction of the corresponding aldehyde with 1 equiv of aniline and excess $MgSO_4$ in CH_2Cl_2. The solution was stirred for approximately 24 h and filtered, and the solvent was removed under reduced pressure.

[Tp′(CO)(PhC_2Me)W=CH_2][PF_6] (3). In a solution of cold (−78° C) methylene chloride, 1 equiv of triphenylcarbenium hexafluorophosphate was added to a known amount of the tungsten methyl complex **2**. Upon addition of the trityl cation, the solution turned from deep blue to reddish-brown in color. Solvent removal under reduced pressure allowed isolation of the methylene carbene **3**; however, complex **3** slowly decomposes in the solid state. ^{1}H NMR experiments showed quantitative conversion of the methyl complex **2** to the methylene carbene complex **3**. IR (KBr): ν_{CO} 2066 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 12.33, 12.04 (each a d, $^2J_{HH}$ = 12 Hz, $^2J_{WH}$ = 7 Hz, 14% ^{183}W, I = $^1/_2$, [W]=CH_2), 7.29, 6.85 (5 H, 3:2 ratio, phenyl *H*s), 6.25, 5.99, 5.78 (3H, Tp′ C*H*), 4.14 (3H, PhC_2CH_3), 2.80, 2.63, 2.51, 2.48, 1.32, 1.24 (18 H, Tp′ CH_3). ^{13}C NMR (CD_2Cl_2, δ): 308.2 (t, $^1J_{CH}$ = 140 Hz, $^1J_{WC}$ = 110 Hz, 14% ^{183}W, I = $^1/_2$, [W]=*C*H_2), 205.2 (*C*O), 213.8, 211.5 (Ph*C*$_2$Me), 155.0, 154.2, 151.4, 148.8, 147.9, 147.3 (Tp′ *C*CH_3), 134.3, 132.9, 131.0, 129.7 (phenyl *C*s), 110.3, 109.3, 108.6 (Tp′ *C*H), 17.5, 17.0, 14.9, 14.2, 13.2, 13.0, 12.6 (Tp′ C*C*H_3 and alkyne *C*H_3).

Decomposition of [Tp′(CO)(PhC_2Me)W=CH_2][PF_6] (3). An attempt was made to quantitatively follow the decomposition of methylene carbene **3**. To an NMR tube was added 0.0390 g of the methyl complex **2**. Complex **2** was dissolved in 0.75 mL of CD_2Cl_2 and cooled to −78 °C, and tetramethylsilane was added as an internal standard. One equivalent of [Ph_3C][PF_6] was added to the solution, and the NMR tube was warmed to room temperature. Quantitative conversion of **2** to [Tp′(CO)(PhC≡CMe)W=CH_2][PF_6] **(3)** was noted by ^{1}H NMR. The decomposition of carbene **3** was monitored by ^{1}H NMR over a period of several days. Unfortunately, reliable kinetic data was difficult to obtain due to the length of time for decomposition. However, a rough estimate of $t_{1/2}$ for **3** could be obtained (3700 min).

[Tp(CO)(PhC_2Ph)W=CH_2][PF_6] (4). The methylene carbene [Tp(CO)(PhC_2Ph)W=CH_2][PF_6] **(4)** was generated at low temperature (−78 °C) in an NMR tube in a manner similar to the synthesis of methylene carbene **3**. Upon addition of trityl cation to a solution of the methyl complex **1**, a rapid color change from dark green to bright yellow was noted. ^{1}H NMR spectra at low temperature displayed characteristic features for a methylene carbene. Between −50 and −40 °C, rapid decomposition of **4** occurred (minutes). Attempts to isolate **4** in the solid state were thwarted by decomposition. IR (CH_2Cl_2): ν_{CO} 2100 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 12.4, 12.1 (1H each, each a d, $^2J_{HH}$ = 12 Hz, [W]=CH_2).

[Tp′(CO)(PhC_2Me)WCH_2PMe_3][PF_6] (7). A Schlenk flask was charged with Tp′(CO)(PhC_2Me)WCH_3 **(2)** (0.101 g, 0.16 mmol) and approximately 30 mL of CH_2Cl_2. The resulting solution was cooled to −78 °C, and 0.061 g (0.16 mmol) of [Ph_3C][PF_6] was added. To the reddish-brown solution was added 0.016 mL (0.16 mmol) of PMe_3. Solvent removal under reduced pressure yielded a purple oil. The oil was washed with hexanes, then washed with ethyl acetate, and finally abstracted with CH_2Cl_2. Purple crystals (81% yield) were isolated after slow diffusion of hexanes into the CH_2Cl_2 solution. IR (KBr): ν_{CO} 1888 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.31, 6.68 (5 H, 3:2 ratio, phenyl *H*s), 6.01, 5.99, 5.71 (3H, Tp′ C*H*), 3.58 (3H, PhC_2CH_3), 0.79, 1.50−1.60 (2H, each a d of d, $^2J_{HH}$ = 14 Hz, $^2J_{PH}$ = 22 Hz, [W]−CH_2PMe_3), 1.57 (9H, d, $^2J_{PH}$ = 13 Hz, [W]−CH_2P(CH_3)$_3$), 2.75, 2.58, 2.45, 2.39, 1.53, 1.35 (18H, Tp′ CH_3). ^{13}C NMR (CD_2Cl_2, δ): 238.7 (*C*O), 218.1, 211.6 (Ph*C*$_2$Me), 152.6, 152.2, 150.5, 146.5, 146.1, 145.5 (Tp′ *C*CH_3), 137.0, 130.0, 129.3, 128.7 (phenyl *C*s), 109.1, 108.9, 107.6 (Tp′ *C*H), 20.1 (t of d, $^1J_{CH}$ = 125 Hz, $^1J_{PC}$ = 33 Hz, [W]−*C*H_2PMe_3), 23.1, 17.0, 15.9, 15.8, 13.0, 12.8 (1:1:1:1:2:1; Tp′ C*C*H_3 and

(33) Schuster, D. M. Chiral Molybdenum(II) and Tungsten(II) Aldehyde and Ketone Complexes. Ph.D. Dissertation, University of North Carolina at Chapel Hill, Chapel Hill, NC, 1996.

(34) For further information concerning the purification of solvents using activated alumina, see: Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

alkyne CH_3), 13.4 (q of d, $^1J_{CH}$ = 130 Hz, $^1J_{PC}$ = 55 Hz, [W]−CH_2P(CH_3)$_3$). Anal. Calcd for [Tp′(CO)(PhC_2Me)WCH_2-PMe_3][PF_6]·0.5C_6H_{14}, ($C_{32}H_{48}N_6BF_6OP_2W$): C, 42.55; H, 5.36; N 9.30. Found: C, 42.55; H, 5.10; N, 9.10.

[Tp(CO)(PhC_2Ph)WCH_2PMe_3][PF_6] (8). A Schlenk flask was charged with Tp(CO)(PhC_2Ph)WCH_3 **(1)** (0.496 mmol) and approximately 30 mL of CH_2Cl_2. The resulting solution was cooled to −78 °C, and 0.496 mmol of [Ph_3C][PF_6] was added. To the bright yellow solution was added 1 equiv of PMe_3. Solvent removal under reduced pressure yielded a dark green oil. The oil was washed with hexanes, then dissolved in ethyl acetate, and filtered through Celite. The green solid was extracted with approximately 10 mL of methanol at −78 °C. Solvent removal from the filtrate yielded a green oil, which was washed with pentane and dried under vacuum. A green powder (45% yield) was isolated. IR (KBr): ν_{CO} 1914 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.8−7.0 (10H, phenyl protons), 8.08, 7.95, 7.80, 7.75, 6.79 (6H, each a d, Tp C*H*), 6.40, 6.35, 6.10 (3H, each a t, Tp C*H*), 2.01 (1H, d of d, $^2J_{HH}$ = 14 Hz, $^2J_{PH}$ = 14 Hz, [W]−C(*H*)(H)PMe_3), 1.59 (9H, d, $^2J_{PH}$ = 13 Hz, [W]−CH_2P-(CH_3)), 1.19 (1H, d of d, $^2J_{HH}$ = 14 Hz, $^2J_{PH}$ = 20 Hz, [W]−C(H)-(*H*)PMe_3). ^{13}C NMR (CD_2Cl_2, δ): 241.2 (*C*O,$^1J_{WC}$ = 130 Hz), 227.2, 211.8 (PhC_2Me), 146.3, 144.4, 142.8, 136.9, 136.5, 136.4 (Tp *C*H), 138.7, 137.8 (*ipso* phenyl), 131.0, 129.8, 129.3, 128.9, 128.8, 127.3 (phenyl *C*s), 107.6, 107.5, 107.2 (Tp′ *C*H), 23.2 (t of d, $^1J_{CH}$ = 120 Hz, $^1J_{PC}$ = 38 Hz, [W]−*C*$H_2$$PMe_3$), 13.5 (q of d, $^1J_{CH}$ = 130 Hz, $^1J_{PC}$ = 55 Hz, [W]−CH_2P(CH_3)$_3$).

[Tp′(CO)(PhC_2Me)WCH_2N(Me)═C(H)(Ph)][PF_6] (15). In a representative synthesis, 0.201 g (0.31 mmol) of **2** was dissolved in CH_2Cl_2 and the resulting solution cooled to −78° C. A CH_2Cl_2 solution of trityl cation (0.1221 g, 0.31 mmol) was added to the solution of **2** via cannula. Next, an excess (0.19 mL, 1.6 mmol) of *N*-benzylidenemethylamine was added to the reaction solution. Upon addition of the imine, the solution color changed from reddish-brown to wine red. After approximately 15 min, the solution was warmed to room temperature and the solvent was removed under reduced pressure. The remaining red oil was washed with hexanes and then extracted with CH_2Cl_2. Slow diffusion of hexanes into the CH_2Cl_2 solution of the red oil yielded deep red crystals (0.187 g, 66% yield). IR (KBr): ν_{CO} 1886 cm^{-1}. ^{1}H NMR (CD_2-Cl_2, δ): 8.13 (1H, [W]−CH_2−N(Me)═C(Ph)(*H*)), 7.44, 7.29, 7.07, 6.84, 6.76 (10H, each a m, phenyl *H*s), 6.04, 5.71, 5.47 (3H, Tp′ C*H*), 4.05 (3H, [W]−CH_2−N(CH_3)═C(Ph)(H)), 4.45, 2.00 (2H, each a d, $^2J_{HH}$ = 12 Hz, [W]−CH_2−N(Me)═C(Ph)(H)), 3.62 (3H, PhC_2CH_3), 2.73, 2.48, 2.46, 2.28, 1.39, 1.33 (18 H, Tp′ CH_3). ^{13}C NMR (CD_2Cl_2, δ): 237.0 (*C*O), 210.9, 207.3 (PhC_2-Me), 161.6 (d, $^1J_{CH}$ = 170 Hz, [W]−CH_2−N(Me)═C(H)(Ph)), 154.4, 153.0, 149.9, 147.2, 146.2, 145.1 (Tp′ *C*CH_3), 137.0, 134.3, 132.0, 129.7, 129.0, 128.9, 128.0 (1:1:1:1:2:1:1, phenyl *C*s), 109.7, 109.0, 107.4 (Tp′ *C*H), 66.4 (t, $^1J_{CH}$ = 135 Hz, $^1J_{WC}$ = 86 Hz, [W]−*C*H_2−N(Me)═C(Ph)(H)), 22.4 ([W]−CH_2−N(*C*H_3)═C(Ph)(H)), 16.7, 16.2, 15.7, 14.8, 12.9, 12.8 (1:1:1:1:2:1, Tp′ C*C*H_3 and alkyne *C*H_3). Anal. Calcd for [Tp′(CO)(PhC_2-Me)WCH_2N(Me)═C(H)(Ph)][PF_6], ($C_{34}H_{41}N_7BF_6OPW$): C, 45.21; H, 4.57; N, 10.85. Found: C, 45.32; H, 4.62; N, 10.75.

Cyclopropane Synthesis. A general reaction scheme involved dissolution of the starting methyl complex **(1** or **2)** in cold methylene chloride (−78 °C). To this solution was added 1 equiv of trityl cation, and the resulting solution was stirred for about 15 min. An excess of olefin (10 equiv) was syringed into the cold solution and stirred for approximately 30 min. Next, the solution was slowly allowed to warm to room temperature and was stirred for different times for different samples (approximately 30 min for the Tp complexes and several hours for the Tp′ complexes). Addition of pentane (∼50 mL) resulted in precipitation of metal decomposition products. The supernatant was filtered via cannula onto either a column of alumina or silica gel and washed with additional pentane. Concentration of the organic products upon removal of pentane under reduced pressure (0 °C) was performed, and the resulting solution was analyzed using GC (undecane added as an internal standard).

Catalytic Aziridination Reactions. Unless otherwise noted in Table 4, the following procedure was used in the aziridination of imines **12a**−**d**: In an NMR tube the tungsten methyl complex **1** or **2** was dissolved in CD_2Cl_2. To this solution was added 5 equiv of imine and an arbitrary amount of tetramethylsilane (internal standard). The ^{1}H NMR of this sample was obtained prior to cooling the solution to −78 °C. Triphenylcarbenium hexafluorophosphate (0.5 equiv, dissolved in CD_2Cl_2 at −78 °C) was added to the tungsten methyl complex/imine solution. An NMR spectrum was taken to confirm complete conversion of the trityl cation to triphenylmethane. Via syringe, 5 equiv of EDA (10:1 EDA:catalyst ratio) was added to the NMR tube, and the solution was slowly warmed to room temperature. Upon cessation of gas evolution (20−45 min), another ^{1}H NMR spectrum was recorded and product ratios and percent yields (utilizing internal standard) were determined by integration of well-resolved peaks.

Control Reactions. While we suggest that the [W]═CH_2^+ fragments play the role of catalyst in these reactions, other possibilities exist. In a series of control reactions, trityl cation was found to catalyze the conversion of imines and EDA to aziridines. However, when compared to carbene-complex-catalyzed reactions, the syntheses utilizing trityl as catalyst yield different *cis*/*trans* azirdine ratios, as well as different aziridine:enamine ratios. In addition, all reactions were performed with 0.5 equiv of trityl cation, assuring that all of the carbenium is converted to triphenylmethane prior to EDA addition. The triphenylmethane peak could be observed and integrated versus internal standard in the ^{1}H NMR prior to EDA addition.

Addition of EDA and *N*-benzylideneaniline to a CD_2Cl_2 solution of the tungsten methyl complex **2** showed no reaction. Treatment of the tungsten−imine complexes[35] with direct tungsten−nitrogen bonds with EDA showed no reaction after 48 h.

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Supporting Information Available: Labeled ORTEP diagrams and tables of crystallographic data and collection parameters, atomic positional parameters, complete bond lengths and angles, and anisotropic temperature factors for **7** and **15** (14 pages). Ordering information is given on any current masthead page.

OM970470A

(35) Francisco, L. W.; White, P. S.; Templeton, J. L. *Organometallics* **1996**, *15*, 5127.