Reactions of Metal–Metal and Metal–Carbon Multiple Bonds with 2*H*-Azirines, 1,3-Dipolar Reagents. Structures of $Cp_2M_2(CO)_4(NC(Ar){=}CMe_2)$ (Ar = Aryl; M = Mo, W) and $(CO)_5W{-}N({=}CPh(OMe))(C(Ph){=}CMe_2)$

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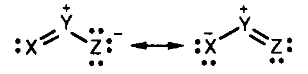
The reactions of compounds $(C_5R_5)_2M_2(CO)_4$(*M*≡*M*) (R = Me, H; M = Mo, W) and $W_2(OBu^t)_6$(*W*≡*W*) with 2,2-dimethyl-3-aryl-2*H*-azirines lead to the vinylimido adducts $Cp^*_2W_2(CO)_4(NC(Ar){=}CMe_2)$ (Ar = 4-*tert*-butylphenyl; **6**), $Cp^*_2Mo_2(CO)_4(NC(Ar){=}CMe_2)$ (Ar = 4-*tert*-butylphenyl, **8a**; Ar = phenyl, **8b**), $Cp_2Mo_2(CO)_4(NC(Ph){=}CMe_2)$ (**7**), and $W_2(O^tBu)_6(NC(Ar){=}CMe_2)_2$ (Ar = 4-*tert*-butylphenyl, **9b**; Ar = phenyl, **9a**). Complex **7** exists in two isomeric forms that are in dynamic equilibrium. With the carbene complexes $(CO)_5W{=}C(OMe)Ph$ and $[Cp(CO)_2Fe{=}C(OMe)Me]X$ (X = BF_4, PF_6), the vinylimidate complexes $(CO)_5WN({=}C(OMe)Ph)(C(Ph){=}CMe_2)$ (**11**) and $Cp(CO)_2FeN({=}C(OMe)Me)(C(Ar){=}CMe_2)$ (**13**) are produced. Air oxidation of **11** releases the imidate ligand. In these reactions, the 2*H*-azirine is behaving as a masked vinylnitrene rather than as a nitrile ylide. The structures of **6**, **8b**, and **11** are determined: **6**, a = 8.2120 (2) Å, b = 11.2370 (3) Å, c = 15.5170 (4) Å, α = 71.51 (2)°, β = 84.24 (2)°, γ = 81.71 (2)°, V = 1341.5 Å^3, Z = 2, space group $P\bar{1}$ (triclinic), R = 0.0360, R_w = 0.0399 based on 5050 reflections with $F_o \geq 3\sigma(F)$; **8b**, a = 17.490 (6) Å, b = 8.973 (3) Å, c = 22.023 (6) Å, β = 109.09 (2)°, V = 3266 (2) Å^3, Z = 4, space group Cc (monoclinic), R = 0.0280, R_w = 0.0214 based on 2455 reflections with $F_o \geq 3\sigma(F)$; **11**, a = 12.141 (9) Å, b = 11.770 (5) Å, c = 16.91 (2) Å, β = 107.02 (6)°, V = 2310 (3) Å^3, Z = 4, space group $P2_1/n$ (monoclinic), R = 0.0612, R_w = 0.0847 based on 2416 reflections with $F_o \geq 3\sigma(F)$. The structure of **6** is $Cp(CO)(NR)W{-}W(CO)_3Cp$ with CO semibridging, but **8b** has a structure with two nearly symmetrical CO bridges: $Cp^*(NR)Mo(\mu\text{-}CO)_2Mo(CO)_2Cp^*$(*Mo–Mo*) (R = C(Ar)CMe$_2$).

Introduction

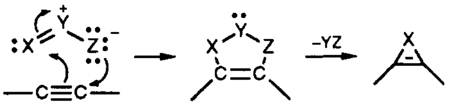
The 1,3-dipolar cycloaddition reaction as developed by Huisgen[1] and Padwa,[2] for example, is a powerful tool for the synthesis of organic heterocycles. The 1,3-dipolar reagents may be divided into two types, the propargyl–allenyl type (eq 1) and the allyl type (eq 2). The former are usually linear and the latter bent.

(1)



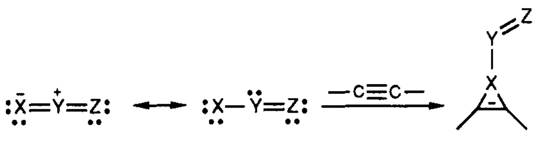
(2)

These reagents react with dipolarophiles, e.g., carbon–carbon multiple bonds, to give a [3 + 2 → 5] cycloaddition adduct via a concerted mechanism or, in some cases, via a high-energy zwitterionic intermediate (eq 3).[3] In some cases, the five-membered cycloadduct may expel a small stable molecule, e.g., N_2, and give the three-membered heterocycle.



(3)

The propargyl–allenyl reagents may be drawn with a sextet resonance form with no formal charges. Such a resonance structure may confer carbene- or nitrene-type character which may lead to 1,1-cycloaddition behavior (eq 4). In organic reactions, this type of behavior is rare for



(4)

intermolecular reactions but has been observed in certain intramolecular transformations.[4,5] The 1,1-addition pathway is apparently favored when the dipole and dipolarophile have difficulty approaching one another in parallel planes, as required for the 1,3-cycloaddition mode. The 1,1-cycloaddition product has not been observed to rearrange to a 1,3-adduct.

In contrast, the reactions of diazoalkanes and organic azides, both propargyl–allenic type 1,3-dipoles, with the metal–metal triple bond in $R_2M_2(CO)_4$ (R = C_5H_5 (Cp), C_5H_4Me (Cp′), C_5Me_5 (Cp*); M = Mo, W) seem to occur primarily via initial attack by the terminal N atom of the diazoalkane or azide on one metal center.[6-9] Such an attack creates an electrophilic center on the contiguous metal, as opposed to a neighboring nucleophilic center in the case of attack on carbon–carbon multiple bonds (see

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[1] Huisgen, R. *Angew Chem., Int. Ed. Engl.* **1963**, *2*, 565.

[2] Padwa, A., Ed. *1,3-Dipolar Cycloaddition Chemistry*; Wiley Interscience: New York, 1984; Vols 1 and 2.

[3] Chang, Y. M.; Sims, J.; Houk, K. N. *Tetrahedron Lett.* **1975**, 4445.

[4] Miyashi, T.; Mukai, T.; Nishzawa, Y. *J. Am. Chem. Soc.* **1980**, *102*, 1176.

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[6] Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Solis, H. E.; Barcelo, I. D.; Butler, W. M. *J. Am. Chem. Soc.* **1987**, *109*, 3603.

[7] Curtis, M. D.; D'Errico, J. J.; Butler, W. M. *Organometallics* **1987**, *6*, 2151.

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[9] Review: Curtis, M. D. *Polyhedron* **1987**, *6*, 759.

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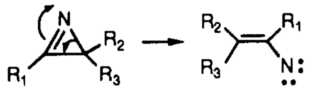
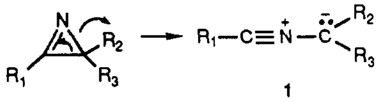
ref 9). Thus, rather than closing to form a 3 + 2 cycloadduct, the initial 1,1-adduct rearranges in a variety of ways.[9] In some cases, loss of N_2 is believed to occur by way of 3 + 2 cycloadduct intermediates and alkylidene or nitrene adducts are the final products.

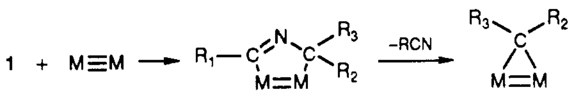
We desired to extend this work to other 1,3-dipolar reagents to compare the reactivity patterns of M–C and M–M multiple bonds with C–C multiple bonds and to develop new routes to novel metallacycles. Using only first-row elements, there are 18 possible types of 1,3-dipolar reagents.[1] Most of these are very reactive and must be generated in situ from reagents that are incompatible with low-valent metal carbonyls. From the list of stable reagents, we chose 2*H*-azirines for initial study. Azirines may behave as masked vinylnitrenes (eq 5) or as nitrile ylides (eq 6). The latter could be a valuable synthon for metal alkylidenes (eq 7).



(5)

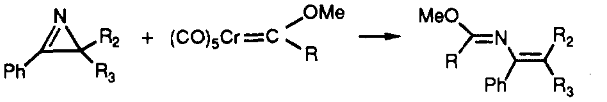


(6)



(7)

In a seminal series of papers, Alper et al. showed that metal carbonyls could catalyze the ring-opening dimerization of azirines,[10] ring expansion of substituted azirines to form five-membered heterocycles,[11] and condensations to indoles,[12] β-lactams,[13] and succinimides.[14] Hegedus et al. had shown that 2*H*-azirines react with Fischer carbenes to give vinylimidates (eq 8).[15] Metal-containing products were not isolated.

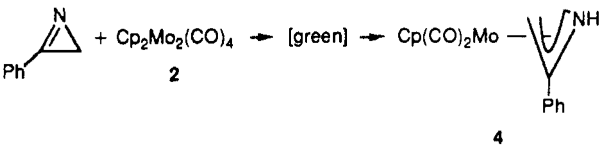


(8)

Here, we report the results obtained for the reactions of 3-aryl-2*H*-azirines with metal–metal triple bonds in the compounds $Cp_2M_2(CO)_4$ (M = Mo, W) and $W_2(OBu^t)_6$ and with metal–carbon multiple bonds in the complexes $(CO)_5W{=}C(OMe)Ph$ and $[Cp(CO)_2Fe{=}C(OMe)Me]X$ (X = BF_4^-, PF_6^-).

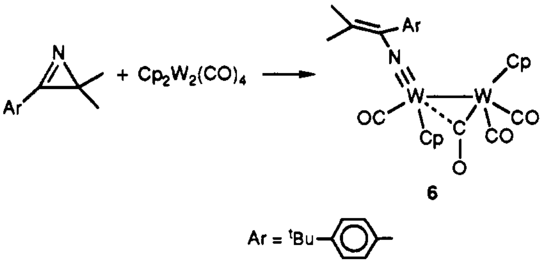
Results and Discussion

The reaction of 3-phenyl-2*H*-azirine with $Cp_2Mo_2(CO)_4$ (**2**) or $Cp_2{}^*Mo_2(CO)_4$ (**3**) at –20 °C produced a red, thermolabile complex which decomposed on warming to room temperature. During the course of our studies, a communication reported that 3-phenyl-2*H*-azirine reacted with **2** at room temperature to form a green compound that decomposed on attempted column chromatography to give the azaallyl complex **4**, in low yield.[16] Note that **4** has one more H atom than the starting materials.



(9)

The more highly substituted 3-aryl-2,2-dimethyl-2*H*-azirines were then employed in the hope of obtaining more stable products. With $Cp_2W_2(CO)_4$ (**5**), complex **6** was isolated in 95% yield (aryl = 4-*tert*-butylphenyl) (eq 10). The vinylimido complex is quite stable in the solid state and can be handled in air for short periods. Solutions of **6** decompose slowly.



(10)

Complex **6** exhibits IR absorptions at 1953 (s), 1924 (s), and 1848 (s) cm^{-1}. The ^1H NMR spectrum shows two singlets for the Cp protons (δ 5.17, 4.79), two for the vinylic methyl groups (δ 1.59, 1.30), and a singlet for the *tert*-butyl protons at δ 1.16. The ^{13}C NMR spectrum has a broad singlet at δ 231.2 for the CO ligands at room temperature. The resonances for the vinyl and ipso phenyl carbons appear at δ 155.4, 133.4, and 130.7. The structure of **6** was confirmed by an X-ray study (see below).

With $Cp_2Mo_2(CO)_4$ (**2**) at 21 °C, 3-phenyl-2,2-dimethyl-2*H*-azirine reacted to form a red substance whose elemental analysis was consistent with the formula $Cp_2Mo_2(CO)_4(NC(Ph)CMe_2)$ (**7**). The NMR and IR spectra of **7** were too complex to be attributed to only one isomer, and the spectra changed with temperature or solvent polarity. The spectra were readily interpreted as arising from two isomers, **7A** and **7B**, in dynamic equilibrium. In C_6D_6, the ^1H NMR spectrum displayed two Cp resonances (δ 5.08, 4.83) and two methyl resonances (δ 1.76, 1.28) for **7A**. Isomer **7B** is fluxional on the NMR time scale and shows a broadened singlet at δ 4.99 for the Cp protons and two singlets for the methyl groups at δ 1.55 and 1.44. At 22 °C, the ratio of isomers **7A**:**7B** is 1.5:1 in C_6D_6, but in acetone-d_6 the ratio is 1:1.35. At room temperature, the **7A** ↔ **7B** interconversion is slow on the NMR time scale, but at 50 °C the Cp resonances have coalesced to a broad line at δ 5.09 and another of ca. half the intensity of the first at δ 4.89. The methyl resonances also start to merge at 50 °C. The high-temperature limit could not be reached due to sample decomposition.

The ν_{CO} regions of the IR spectra of **7** dissolved in acetone or CH_2Cl_2 and of $Cp_2W_2(CO)_4(NC(Ar)CMe_2)$ (**6**) in CH_2Cl_2 are displayed in Figure 1. The absorptions at 1960, 1930, and 1852 cm^{-1} of **7A**, the predominant isomer in CH_2Cl_2, closely resembles that of the tungsten complex **6**. The IR and NMR spectra taken together thus suggest that **7A** has the same structure as **6**.

In acetone solvent, isomer **7B** predominates and shows absorptions at 1990, 1913, and 1834 cm^{-1}. We believe the structure of **7B** is closely related to that of the adduct formed between **2** and diaryldiazomethanes. These

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(10) (a) Alper, H.; Wollowitz, *J. Am. Chem. Soc.* **1975**, *97*, 3541. (b) Alper, H.; Sakakibora, T. *Can. J. Chem.* **1979**, *57*, 1541.

(11) Alper, H.; Prickett, J. E.; Wollowitz, S. *J. Am. Chem. Soc.* **1977**, *99*, 4330.

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(13) Alper, H.; Mahatontilla, C. P. *Organometallics* **1982**, *1*, 70.

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(15) Hegedus, L. S.; Kramer, A.; Yijun, C. *Organometallics* **1985**, *4*, 1747.

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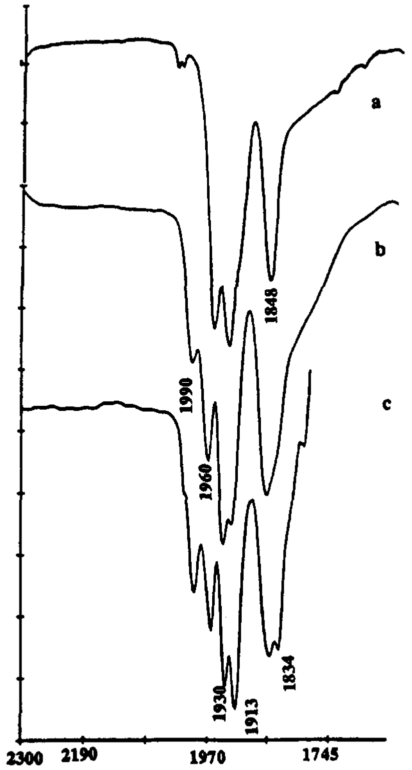
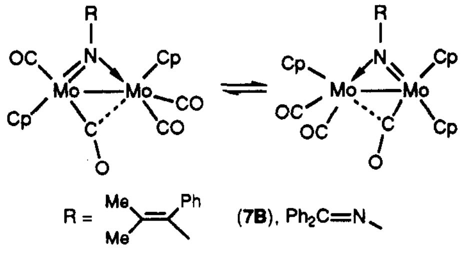
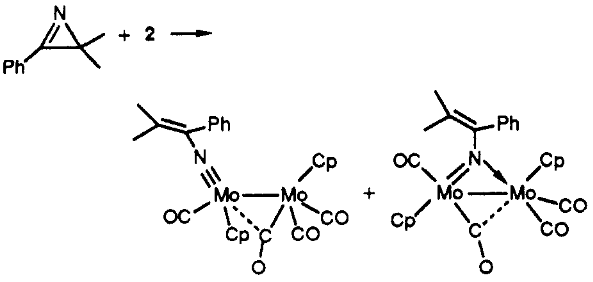


Figure 1. IR spectra of (a) $Cp_2W_2(CO)_4(NR)$ (6) in CH_2Cl_2, (b) $Cp_2Mo_2(CO)_2(NR)$ (7) in CH_2Cl_2, and (c) 7 in acetone.

structures (eq 11) have the terminal nitrogen bridging the Mo–Mo bond and the unsaturated portion of the diazomethane or azirine (the R group in eq 11) remains uncoordinated. The diazoalkane adducts are fluxional. Thus, the reaction of 2 with 3-phenyl-2,2-dimethyl-2*H*-azirine is summarized in eq 12.



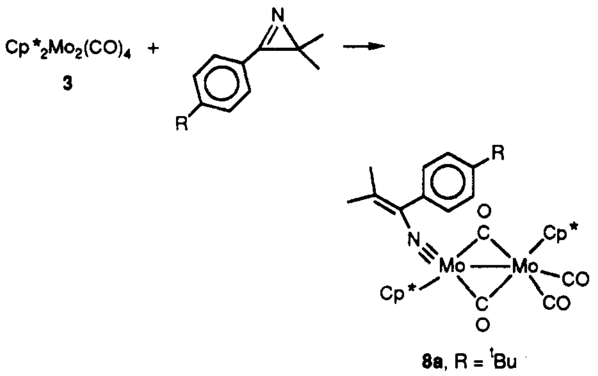
(11)



(12)

7A **7B**

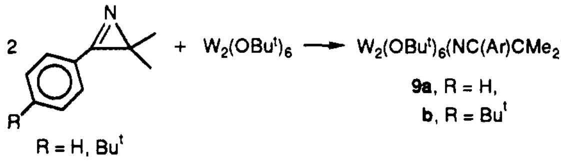
The permethylated analog of 2 is much less reactive toward azirines, but $Cp^*{}_2Mo_2(CO)_4$ (3) does react with 3-aryl-2,2-dimethyl-2*H*-azirines at 35 °C over the course of 48 h to give the 1:1 adducts 8 in high yield (eq 13). Adduct **8a** shows two singlets for the Cp* methyl protons (δ 1.73, 1.71) in the ^1H NMR spectrum. Two singlets for the vinyl methyl protons appear at δ 1.92 and 1.48. The ^{13}C NMR spectra of complexes **8a,b** are very similar to that of 6, but **8a,b** have a very low frequency ν_{CO} band near 1690 cm^{-1} in addition to bands near 1930 and 1865 cm^{-1}. An X-ray structure determination (see eq 13) of **8b** revealed two CO groups nearly symmetrically bridging the Mo–Mo bond. Compounds with CO groups symmetrically bridging Mo–Mo bonds are extremely rare.



(13)

8a, R = ᵗBu
b, R = H

The success of the experiments with $Cp_2M_2(CO)_4$ compounds suggested extension to other metal–metal multiply bonded complexes. $W_2(OBu^t)_6$ required 2 equiv of 3-aryl-2,2-dimethyl-2*H*-azirine for complete reaction when conducted at 0 °C. The bis(vinylimido) adducts, 9, were obtained in high yield (eq 14). Adducts 9 are extremely air-sensitive, and solutions of 9 decompose fairly rapidly at room temperature under an inert atmosphere. This thermolability has hampered our ability to grow X-ray-quality crystals.

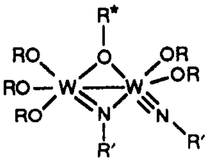


(14)

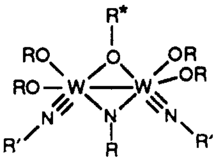
9a, R = H,
b, R = Buᵗ

R = H, Buᵗ

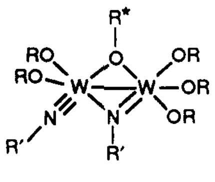
The ^1H NMR spectrum of **9b** shows a doublet of doublets at δ 7.40 for the phenyl protons and two singlets for the vinylic methyl groups (δ 2.82, 1.91), while the *tert*-butyl resonances appear as a sharp singlet at δ 1.85 and a broader singlet at δ 1.48 in an area ratio of 1:5. This spectrum is the result of a fluxional process. A variable-temperature study was inconclusive since the low-temperature limit was not reached at −80 °C, at which point the *tert*-butyl signal had broadened considerably and the phenyl protons were also showing signs of restricted rotation of the phenyl group. The ^{13}C NMR spectrum shows peaks for the vinylimido ligand which are nearly identical to those observed in the spectra of the $Cp_2M(CO)_4$ adducts. On the basis of the stoichiometry and spectra, a tentative structural assignment is given as follows:



9A

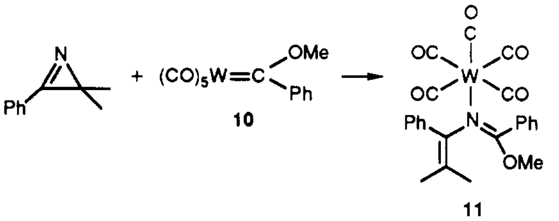


9B



In this scheme, all five terminal alkoxide ligands of **9A** are involved in the fluxional process and are equivalent at room temperature, but the unique alkoxide exchanges more slowly in this temperature range. Structure **9B** is similar to that of diaryldiazoalkane adducts of $Mo_2(OPr^i)_6$.[17]

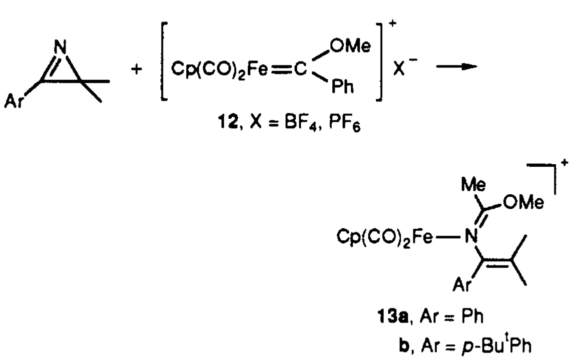
The metal–carbon double bonds in two Fischer type carbenes reacted with 2*H*-azirines under ring opening to give adducts derived from a vinylnitrene. Thus, $(CO)_5WC(OMe)Ph$ (**10**) reacts within 3 h at 21 °C as shown in eq 15. The adduct **11** shows IR absorptions at 2067, 1970, 1922, and 1893 cm^{-1} for the CO stretches. Absorptions for C=N and C=C occur at 1621 and 1595 cm^{-1}.



The ^1H NMR spectrum of **11** shows a singlet for O*Me* at δ 2.63 and two singlets for the vinylic methyl groups at δ 1.82 and 1.78. The ^{13}C NMR spectrum has peaks at δ 202.6 and 198.6 for the two types of CO groups. The resonance due to the "carbene" carbon atom has shifted upfield relative to its position in **10** and appears at δ 169.4. Other resonances are as expected. The structure was confirmed by a single-crystal X-ray study (see below).

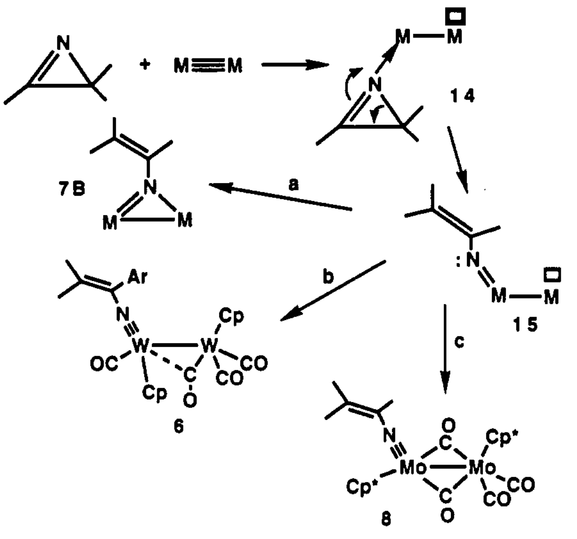
As a solid, compound **11** reacts only slowly with air, but in solution a rapid oxidation deposits a tan precipitate and releases the *N*-vinylimidate ligand which may be recovered from the solution (cf. eq 8). Thus, the reaction of chromium carbenes with azirines[15] most likely produces compounds analogous to **11** which are decomposed by air during workup.

The cationic carbene complexes, **12**, also react with the 2*H*-azirine shown in eq 16 to give cationic *N*-vinylimidate complexes similar to **11**. Good yields of **13** are only obtained if the azirine is used in a 2-fold excess. The ν_{CO} absorptions occur at 2054 and 2009 cm^{-1}. An absorption at 1607 cm^{-1} may be due to C=N or C=C stretching. The ^1H NMR spectrum of **11** shows a singlet (δ 5.05) for the Cp protons and singlets at δ 4.13 and 2.86 for the OMe and C*Me*(OMe) groups, respectively. Singlets at δ 1.78 and 1.54 are assigned to the vinylic methyl groups. The resonance of the formerly carbene carbon shifts upfield to δ 174.3. An attempt to exchange the BF_4^- counterion with BPh_4^- led to the zwitterionic complex $CpFe^+(\eta^6-C_6H_5BPh_3)^-$.[18] The iron *N*-vinylimidate complexes do not release the imidate ligand upon air oxidation. A yellow solid, insoluble in all common solvents, was formed.

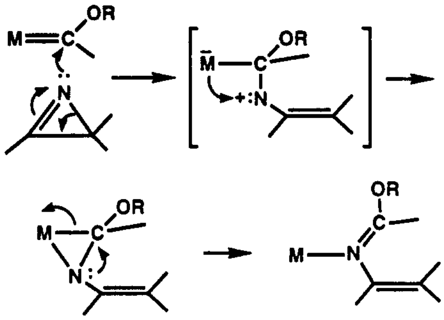


Thus, the 3-aryl-2,2-dimethyl-2*H*-azirines react with the M–M or M–C multiple bonds used in this study exclusively as a vinylnitrene; no evidence for nitrile ylide behavior was noted (cf. eqs 5 and 6). The metal complex-mediated ring-opening reactions occur at much lower temperatures than the purely thermal ring opening of these azirenes. Possible reaction pathways with M≡M or M=C bonds are shown in Schemes I and II.

Scheme I



Scheme II



Initial nucleophilic attack by the lone pair on the N-atom leads to intermediate **14**. The square over the metal signifies the vacant coordination site generated on the remote metal by disruption of the M–M triple bond. Electrocyclic ring opening can lead to **15**, which can then take several pathways. The N-lone pair can coordinate to the remote metal (path a), or the lone pair may displace a carbonyl which slides over to saturate the remote metal (path b). Path c may be an "arrested" version of path b. The bulky Cp* ligands push the carbonyl ligands toward the central region of the molecule where they form the more symmetrical bridging structure.

Reactions of the azirines with the carbene complexes are probably similar in the initial stages. Fischer carbenes are electrophilic, so the azirine may use the N-lone pair to initiate nucleophilic attack. Electrocyclic ring openings lead directly to the *N*-vinylimidate ligand as shown in Scheme II.

Various other reagent–substrate combinations were investigated. Reactions of nitrile *N*-oxides, e.g. mesitylnitrile *N*-oxide, with the triply-bonded complexes $(C_5R_5)_2M_2(CO)_4$ (R = H, Me; M = Mo, W), $W_2(OBu^t)_6$, and $(^tBuO)_3W{\equiv}CMe$ failed to give tractable products. The alkylidyne $(^tBuO)_3WCMe$ also failed to give isolable products when allowed to react with 2,2-dimethyl-3-phenyl-2*H*-azirine.

Structures: $Cp_2W_2(CO)_4(NC(Ar){=}CMe_2)$ (Ar = 4-*tert*-Butylphenyl) (6). Crystal and data statistics are listed in Table I. Table II contains the fractional atomic

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Table I. Crystallographic Data for Compounds 6, 8b, and 11

	6	8b	11
color	black	deep red	pale yellow
formula	$C_{28}H_{29}NO_4W_2$	$C_{34}H_{42}Mo_2NO_4$	$C_{23}H_{19}WNO_6$
MW	811.18	720.6	589.26
a (Å)	8.2120 (2)	17.490 (6)	12.141 (9)
b (Å)	11.2370 (3)	8.973 (3)	11.770 (5)
c (Å)	15.5170 (4)	22.023 (6)	16.91 (2)
α (deg)	71.51 (2)	90	90
β (deg)	84.24 (2)	109.09 (2)	107.02 (6)
γ (deg)	81.71 (2)	90	90
V (Å^3), Z	1341.5 (8), 2	3266 (2), 4	2310 (3), 4
space group	$P\bar{1}$	Cc	$P2_1/n$
radiation	Mo Kα monochromatized from a graphite crystal		
scan range	Kα_1 − 0.8 to Kα_2 + 0.8°	Kα_1 − 0.6 to Kα_2 + 0.6°	Kα_1 − 0.8 to Kα_2 + 0.8°
std rflns	3 stds/197 rflns	3 stds/100 rflns	3 stds/100 rflns
2θ range	4–56	5–50	5–50
no. of rflns ($>3\sigma(F)$)	6468 (5050)	2739 (2455)	4040 (2416)
N_o/N_v	16.0	6.7	8.6
GOF	1.01	3.20	4.64
R, R_w (%)	3.60, 3.99	2.80, 2.14	6.12, 8.47

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 6

	x	y	z	U^a
W(1)	1124.9 (4)	1404.9 (3)	1511.6 (2)	35.9 (1)
W(2)	−1367.7 (4)	910.5 (3)	3119.6 (2)	33.6 (1)
O(1)	−256 (9)	−830 (7)	1164 (5)	67 (3)
O(2)	4550 (10)	−177 (7)	1513 (7)	91 (4)
O(3)	2364 (8)	341 (6)	3488 (4)	59 (3)
O(4)	−3700 (9)	2199 (7)	1513 (5)	75 (3)
N	−1312 (7)	2247 (6)	3497 (4)	35 (2)
C(1)	255 (11)	−19 (8)	1330 (6)	46 (3)
C(2)	3245 (11)	380 (8)	1512 (7)	55 (4)
C(3)	1643 (10)	740 (7)	2803 (5)	42 (3)
C(4)	−2778 (12)	1729 (8)	2075 (7)	52 (3)
C(5)	−1261 (9)	3265 (7)	3806 (5)	35 (2)
C(6)	−2340 (10)	3497 (8)	4459 (5)	41 (3)
C(7)	−3722 (10)	2697 (9)	4859 (6)	53 (4)
C(8)	−2220 (14)	4512 (9)	4875 (6)	61 (4)
C(9)	151 (10)	3993 (7)	3393 (5)	38 (3)
C(10)	−93 (10)	5246 (7)	2868 (6)	46 (3)
C(11)	1222 (10)	5915 (7)	2437 (6)	44 (3)
C(12)	2834 (19)	5345 (7)	2530 (5)	37 (3)
C(13)	3055 (10)	4082 (8)	3068 (6)	46 (3)
C(14)	1774 (10)	3428 (8)	3486 (6)	44 (3)
C(15)	4302 (10)	6075 (7)	2062 (6)	42 (3)
C(16)	4860 (14)	6674 (11)	2729 (7)	74 (5)
C(17)	3842 (12)	7091 (10)	1196 (7)	65 (4)
C(18)	5775 (12)	5168 (10)	1830 (8)	70 (4)
C(21)	1402 (14)	3607 (8)	1112 (6)	59 (4)
C(22)	2437 (12)	3073 (9)	530 (6)	57 (4)
C(23)	1483 (14)	2655 (10)	6 (6)	66 (4)
C(24)	−136 (13)	2925 (10)	268 (7)	66 (4)
C(25)	−235 (13)	3519 (8)	947 (7)	66 (4)
C(31)	−3429 (12)	−409 (10)	3689 (7)	66 (4)
C(32)	−2368 (14)	−989 (9)	3096 (7)	63 (4)
C(33)	−804 (14)	−1369 (8)	3430 (7)	61 (4)
C(34)	−843 (12)	−1064 (8)	4233 (7)	58 (4)
C(35)	−2423 (13)	−498 (9)	4406 (7)	62 (4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Distances (Å) and Angles (deg) for 6

Distances			
W(1)–W(2)	3.024 (1)	W(1)–C(1)	1.950 (10)
W(1)–C(2)	1.944 (9)	W(1)–C(3)	1.972 (8)
W(1)–C(21)	2.392 (9)	W(1)–C(22)	2.331 (9)
W(1)–C(23)	2.327 (9)	W(1)–C(24)	2.348 (9)
W(1)–C(25)	2.402 (8)	W(2)–N	1.785 (7)
W(2)–C(3)	2.463 (8)	W(2)–C(4)	1.984 (9)
W(2)–C(31)	2.331 (11)	W(2)–C(32)	2.406 (11)
W(2)–C(33)	2.435 (9)	W(2)–C(34)	2.353 (8)
W(2)–C(35)	2.299 (9)	O(1)–C(1)	1.164 (14)
O(2)–C(2)	1.161 (12)	O(3)–C(3)	1.195 (10)
O(4)–C(4)	1.157 (12)	N–C(5)	1.379 (11)
C(5)–C(6)	1.342 (11)	C(5)–C(9)	1.489 (11)
C(6)–C(7)	1.510 (12)	C(6)–C(8)	1.497 (15)
Angles			
W(2)–W(1)–C(1)	81.8 (2)	W(2)–W(1)–C(2)	122.9 (3)
C(1)–W(1)–C(2)	84.4 (4)	W(2)–W(1)–C(3)	54.3 (2)
C(1)–W(1)–C(3)	102.0 (3)	C(2)–W(1)–C(3)	75.5 (4)
W(1)–W(2)–N	101.4 (2)	W(1)–W(2)–C(3)	40.5 (2)
N–W(2)–C(3)	90.7 (3)	W(1)–W(2)–C(4)	77.4 (3)
N–W(2)–C(4)	98.8 (3)	C(6)–C(5)–C(9)	124.8 (8)
W(2)–N–C(5)	178.9 (5)	W(1)–C(1)–O(1)	175.8 (7)
W(1)–C(2)–O(2)	176.4 (10)	W(1)–C(3)–W(2)	85.2 (3)
W(1)–C(3)–O(3)	163.0 (7)	W(2)–C(3)–O(3)	111.8 (6)
W(2)–C(4)–O(4)	174.9 (8)	N–C(5)–C(6)	121.6 (7)
N–C(5)–C(9)	113.5 (7)	C(10)–C(9)–C(14)	117.0 (7)
C(5)–C(6)–C(7)	121.7 (9)	C(5)–C(6)–C(8)	123.0 (8)
C(7)–C(6)–C(8)	115.2 (8)	C(5)–C(9)–C(10)	121.5 (7)
C(5)–C(9)–C(14)	121.4 (6)		

coordinates, and Table III presents selected bond distances and angles. Figure 2 shows an ORTEP plot of the structure with the atom-numbering scheme.

The W–W triple bond in the starting dimer, $Cp_2W_2(CO)_4$, has been transformed into a W–W single bond (d(W–W) = 3.024 (1) Å) in molecule 6. This indicates that the vinylnitrene ligand has donated a total of four electrons to the dimetal fragment.[9] The W–N distance, 1.785 (7) Å, is consistent with a bond order of ca. 2.8.[19] The nearly linear (178.9 (5)°) W(2)–N–C(5) angle is consistent with sp-hybridization at nitrogen, and the N–C(5) distance, 1.38 (1) Å, is commensurate with an N(sp)–C(sp^2) single bond.

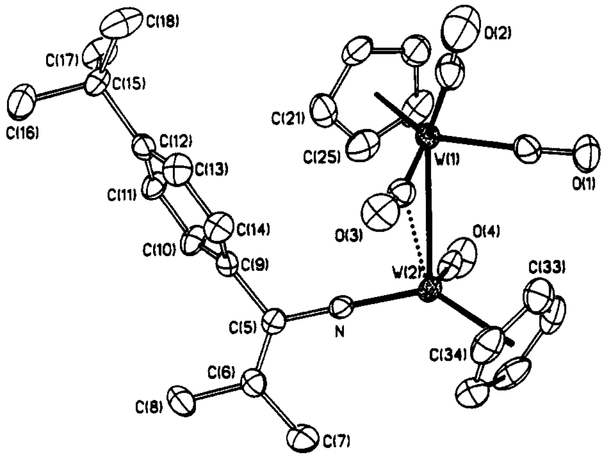

Figure 2. ORTEP plot of Cp(CO)$_3$WW(CO)(NR)Cp (6), where R = C(Ar)CMe$_2$. Thermal ellipsoids are at the 50% level.

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(19) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

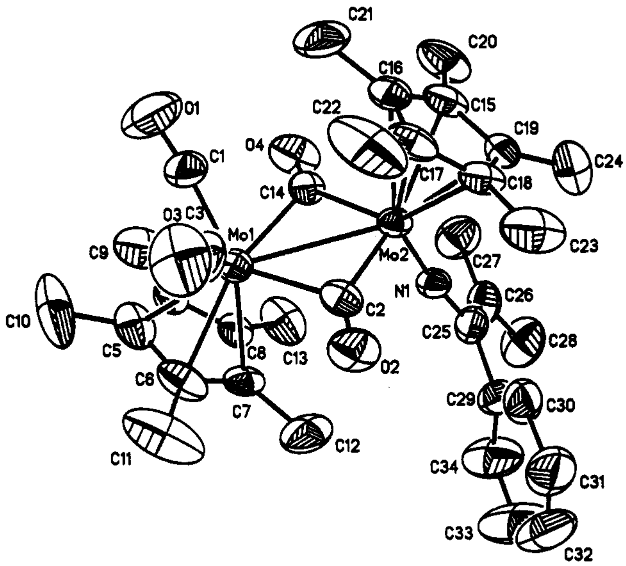
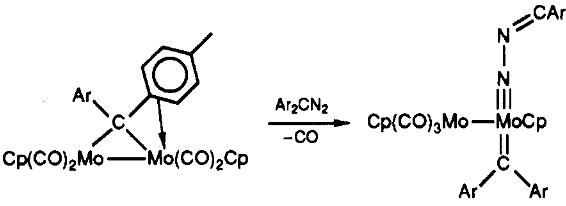


Figure 3. ORTEP plot (50% thermal ellipsoids) of Cp*(CO)$_2$Mo(μ-CO)$_2$Mo(NR)Cp* (**8b**, R = C(Ph)CMe$_2$).

Thus, the W-N bond is well represented by the formalism shown as follows:

$$R{-}N{\equiv}W$$

The addition of the nitrene or imido ligand has also caused one carbonyl to shift from W(2) to W(1). This ligand migration, and the resulting structural parameters, are very similar to those in complex **16** (eq 17), formed by a shift of a bridging alkylidene to a terminal position.[20] The Mo-N distance in **16** is 1.74 (1) Å.



(17)

16

The C(3)-O(3) carbonyl group is slightly semibridging as indicated by the relatively close C(3)···W(2) approach (2.463 (8) Å), the acute W(2)-W(1)-C(3) angle (54.3 (2)°), and W(1)-C(3)-O(3) bending (163.0 (7)°).[21,22] This semibridging may be in response to π-donation to W(2) from the imido ligand.[23]

Cp*$_2$Mo$_2$(CO)$_4$(NC(Ph)=CMe$_2$) (8b). An ORTEP plot of this molecule with atom-labelling scheme is shown in Figure 3. Crystallographic statistics are in Table I, while Tables IV and V have the atomic coordinates and selected bond distances and angles, respectively.

This adduct has a vinylimido ligand virtually identical with the one in complex **6** described above. The metal-metal and molybdenum-nitrogen distances are 2.9904 (5) and 1.752 (5) Å, again indicative of Mo—Mo and and Mo≡N single and triple bonds, respectively. The most striking difference between the structures of **6** and **8** is in the presence of nearly symmetrically bridging carbonyl groups in the latter. The carbonyl carbon atoms are approximately 0.2 Å closer to the molybdenum atom bearing the imido substituent; the average distances are Mo(2)-CO(br) = 2.06 (1) Å and Mo(1)-CO(br) = 2.28 (1) Å. It is certainly reasonable to suppose that Mo(2) with the π-donor imido ligand is more electron rich than Mo(1) with

Table IV. Fractional Atomic Coordinates and Isotropic Temperature Factors (Å^2) for Cp*$_2$Mo$_2$(CO)$_4$(NC(Ph)=CMe$_2$) (8b)

atom	*x*	*y*	*z*	*U*(eq)
Mo(1)	0.00000	0.12787 (8)	0.00000	0.0420 (3)
Mo(2)	0.05488 (4)	0.03124 (7)	−0.10900 (3)	0.0359 (2)
C(1)	0.1011 (5)	0.195 (1)	0.0623 (4)	0.079 (4)
O(1)	0.1567 (4)	0.244 (1)	0.1014 (4)	0.147 (5)
C(2)	−0.0134 (4)	−0.081 (1)	−0.0635 (4)	0.045 (3)
O(2)	−0.0544 (3)	−0.1880 (7)	−0.0685 (3)	0.065 (3)
C(3)	0.0297 (5)	−0.046 (1)	0.0578 (4)	0.070 (4)
O(3)	0.0394 (4)	−0.1451 (8)	0.0932 (3)	0.106 (4)
O(4)	0.1044 (3)	0.3466 (7)	−0.0549 (3)	0.072 (3)
C(4)	0.0760 (4)	0.227 (1)	−0.0557 (4)	0.044 (3)
C(5)	−0.0791 (5)	0.241 (1)	0.0494 (4)	0.061 (4)
C(6)	−0.1275 (5)	0.128 (1)	0.0081 (6)	0.060 (5)
C(7)	−0.1378 (4)	0.171 (1)	−0.0545 (4)	0.048 (4)
C(8)	−0.0981 (4)	0.307 (1)	−0.0540 (4)	0.042 (3)
C(9)	−0.0618 (4)	0.352 (1)	0.0090 (4)	0.045 (3)
C(10)	−0.0608 (6)	0.251 (1)	0.1209 (4)	0.117 (6)
C(11)	−0.1659 (6)	−0.001 (1)	0.0302 (5)	0.118 (6)
C(12)	−0.1906 (5)	0.096 (1)	−0.1151 (4)	0.089 (5)
C(13)	−0.1018 (5)	0.396 (1)	−0.1130 (4)	0.076 (4)
C(14)	−0.0192 (5)	0.495 (1)	0.0314 (5)	0.084 (5)
C(15)	0.1884 (5)	0.041 (1)	−0.1151 (5)	0.053 (4)
C(16)	0.1992 (4)	−0.014 (1)	−0.0523 (4)	0.054 (4)
C(17)	0.1590 (4)	−0.151 (1)	−0.0587 (4)	0.055 (4)
C(18)	0.1230 (4)	−0.184 (1)	−0.1234 (5)	0.056 (4)
C(19)	0.1420 (4)	−0.066 (1)	−0.1591 (4)	0.051 (4)
C(20)	0.2231 (5)	0.186 (1)	−0.1302 (4)	0.085 (5)
C(21)	0.2508 (5)	0.056 (1)	0.0102 (5)	0.100 (6)
C(22)	0.1607 (5)	−0.249 (1)	−0.0038 (5)	0.112 (6)
C(23)	0.0825 (5)	−0.328 (1)	−0.1498 (5)	0.104 (6)
C(24)	0.1222 (6)	−0.057 (1)	−0.2322 (4)	0.100 (6)
N(1)	−0.0219 (3)	0.0872 (7)	−0.1788 (3)	0.041 (2)
C(25)	−0.0770 (4)	0.121 (1)	−0.2386 (3)	0.049 (3)
C(26)	−0.0672 (4)	0.239 (1)	−0.2715 (3)	0.056 (3)
C(27)	0.0019 (4)	0.344 (1)	−0.2445 (3)	0.078 (4)
C(28)	−0.1241 (5)	0.281 (1)	−0.3384 (3)	0.087 (4)
C(29)	−0.1456 (4)	0.002 (1)	−0.2612 (3)	0.055 (3)
C(30)	−0.1273 (5)	−0.144 (1)	−0.2485 (4)	0.066 (4)
C(31)	−0.1880 (7)	−0.252 (1)	−0.2701 (4)	0.099 (6)
C(32)	−0.2649 (8)	−0.206 (2)	−0.3014 (5)	0.120 (7)
C(33)	−0.2847 (7)	−0.060 (2)	−0.3117 (5)	0.134 (7)
C(34)	−0.2249 (5)	0.048 (1)	−0.2915 (4)	0.098 (5)

Table V. Selected Bond Distances (Å) and Angles (deg) for Cp*$_2$Mo$_2$(CO)$_4$(NC(Ph)=CMe$_2$) (8b)[a]

	Distances		
Mo(1)-Mo(2)	2.9904 (5)	Mo(2)-N(1)	1.752 (5)
Mo(1)-C(1)	1.947 (8)	Mo(1)-C(3)	1.973 (9)
Mo(1)-C(2)	2.301 (9)	Mo(2)-C(2)	2.054 (7)
Mo(1)-C(4)	2.266 (7)	Mo(2)-C(4)	2.081 (9)
C(1)-O(1)	1.15 (1)	C(2)-O(2)	1.19 (1)
C(3)-O(3)	1.16 (1)	C(4)-O(4)	1.18 (1)
N(1)-C(25)	1.387 (7)	C(25)-C(29)	1.56 (1)
C(25)-C(26)	1.32 (1)	C(Cp)-C(Me)	1.50 (2)*
Mo(1)-C(Cp)	2.32 (4)*	Mo(2)-C(Cp)	2.39 (6)*
C-C(Cp)	1.41 (2)*	C-C(Ph)	1.37 (2)*
	Angles		
Mo(1)-Mo(2)-C(2)	50.2 (2)	Mo(1)-C(2)-Mo(2)	86.5 (3)
Mo(1)-Mo(2)-C(4)	49.2 (2)	Mo(1)-C(4)-Mo(2)	86.8 (3)
Mo(1)-Mo(2)-N(1)	105.4 (2)	Mo(1)-C(2)-O(2)	131.0 (5)
Mo(2)-Mo(1)-C(2)	43.3 (2)	Mo(1)-C(4)-O(4)	132.1 (6)
Mo(2)-Mo(1)-C(4)	44.0 (2)	Mo(2)-C(2)-O(2)	141.5 (5)
Mo(2)-Mo(1)-C(1)	101.5 (2)	Mo(2)-C(4)-O(4)	140.6 (5)
Mo(2)-Mo(1)-C(3)	101.7 (2)	Mo(1)-C(1)-O(1)	173.5 (8)
Mo(2)-N(1)-C(25)	172.3 (5)	Mo(1)-C(3)-O(3)	172.4 (7)
N(1)-C(25)-C(26)	121.3 (7)	C(29)-C(25)-C(26)	126.5 (6)
N(1)-C(25)-C(29)	112.1 (6)	C(25)-C(26)-C(27)	121.3 (6)
C(25)-C(26)-C(28)	124.5 (7)	C(27)-C(26)-C(28)	114.2 (6)

[a] Asterisks indicate average values.

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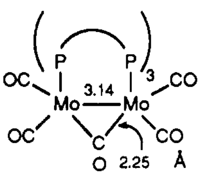
Table VI. Fractional Atomic Coordinates and Isotropic Temperature Factors (Å^2) for $(CO)_5WN({=}C(Ph)OCH_3)C(Ph){=}C(CH_3)_2$ (11)

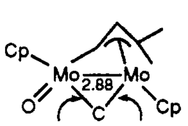
atom	*x*	*y*	*z*	*U*
W(1)	0.1997 (1)	−0.1050 (0)	0.4462 (0)	0.038
N(1)	0.2419 (11)	−0.2937 (10)	0.4340 (8)	0.057
C(1)	0.3603 (16)	−0.0843 (13)	0.5245 (11)	0.049
O(1)	0.4516 (11)	−0.0679 (10)	0.5726 (8)	0.039
C(2)	0.1779 (15)	0.0598 (18)	0.4590 (11)	0.055
O(2)	0.1651 (14)	0.1531 (11)	0.4716 (11)	0.061
C(3)	0.2635 (17)	−0.0659 (14)	0.3517 (10)	0.055
O(3)	0.2857 (15)	−0.0344 (14)	0.2984 (9)	0.066
C(4)	0.0349 (23)	−0.1050 (14)	0.3648 (12)	0.066
O(4)	−0.0563 (15)	−0.0952 (14)	0.3237 (11)	0.067
C(5)	0.1363 (16)	−0.1402 (14)	0.5437 (11)	0.047
O(5)	0.1057 (14)	−0.1537 (15)	0.5980 (9)	0.065
O(6)	0.2267 (11)	−0.4833 (9)	0.4100 (9)	0.043
C(6)	0.1746 (17)	−0.3815 (14)	0.4081 (11)	0.045
C(7)	0.0451 (14)	−0.3724 (13)	0.3734 (11)	0.046
C(8)	−0.0201 (16)	−0.3606 (17)	0.4245 (13)	0.062
C(9)	−0.1395 (21)	−0.3641 (22)	0.3876 (15)	0.090
C(10)	−0.1908 (19)	−0.3826 (18)	0.3046 (15)	0.074
C(11)	−0.1194 (15)	−0.3879 (19)	0.2587 (12)	0.068
C(12)	0.0022 (17)	−0.3859 (18)	0.2904 (11)	0.066
C(13)	0.1564 (20)	−0.5844 (13)	0.3853 (12)	0.063
C(14)	0.3645 (14)	−0.3199 (13)	0.4626 (11)	0.047
C(15)	0.4246 (13)	−0.2904 (12)	0.4019 (10)	0.044
C(16)	0.5243 (14)	−0.2247 (14)	0.4174 (13)	0.058
C(17)	0.5796 (20)	−0.2022 (17)	0.3591 (15)	0.079
C(18)	0.5339 (15)	−0.2434 (17)	0.2810 (14)	0.070
C(19)	0.4308 (17)	−0.3066 (16)	0.2626 (12)	0.062
C(20)	0.3793 (16)	−0.3337 (15)	0.3225 (12)	0.060
C(21)	0.4112 (15)	−0.3560 (12)	0.5420 (11)	0.041
C(22)	0.5379 (18)	−0.3765 (20)	0.5760 (15)	0.078
C(23)	0.3466 (25)	−0.3757 (15)	0.5987 (14)	0.082

two π-acceptor carbonyl groups. It is then understandable that the bridging carbonyls, which drain off excess charge,[23] bond more strongly to Mo(2).

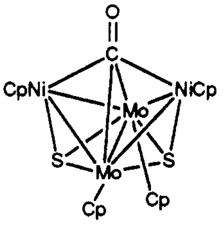
Carbonyl groups bridging a Mo–Mo bond are exceedingly rare. At one time, it was believed that the typical Mo–Mo single bond distance of ca. 3.0 Å was too long to support bridging carbonyls. A search of the Cambridge Crystallographic Data Base revealed just three other compounds, 17–19, with Mo–Mo bonds symmetrically (or nearly so) bridged by CO.[24-27]



17, ν_{CO} = 1787 cm^{-1}



18, ν_{CO} = 1675 cm^{-1}



19, ν_{CO} = 1654 cm^{-1}

$\widehat{P\;\;P}$ = $(F_2P)_2NR$

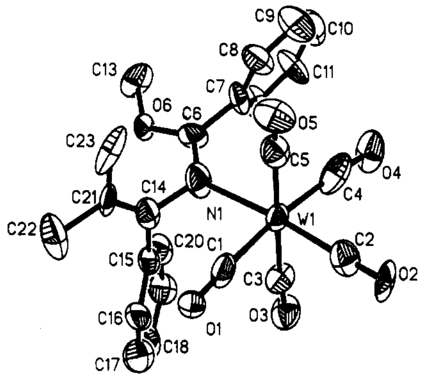


Figure 4. ORTEP plot (50% thermal ellipsoids) of $(CO)_5WN(C(OMe)Ph(R)$ (11), where R = $C(Ph)CMe_2$.

Table VII. Selected Bond Distances (Å) and Angles (deg) for $(CO)_5WN({=}C(Ph)OCH_3)C(Ph){=}C(CH_3)_2$ (11)

Distances			
W(1)–N(1)	2.302 (12)	C(7)–C(8)	1.338 (26)
W(1)–C(1)	2.026 (18)	C(7)–C(12)	1.356 (25)
W(1)–C(2)	1.978 (20)	C(8)–C(9)	1.402 (30)
W(1)–C(3)	2.023 (16)	C(9)–C(10)	1.375 (31)
W(1)–C(4)	2.070 (24)	C(10)–C(11)	1.325 (31)
W(1)–C(5)	2.055 (20)	C(11)–C(12)	1.416 (25)
N(1)–C(6)	1.310 (19)	C(14)–C(15)	1.465 (24)
N(1)–C(14)	1.457 (19)	C(14)–C(21)	1.363 (23)
C(1)–O(1)	1.182 (21)	C(15)–C(16)	1.396 (23)
C(2)–O(2)	1.138 (24)	C(15)–C(20)	1.389 (23)
C(3)–O(3)	1.144 (21)	C(16)–C(17)	1.371 (27)
C(4)–O(4)	1.127 (27)	C(17)–C(18)	1.363 (29)
C(5)–O(5)	1.098 (22)	C(18)–C(19)	1.410 (26)
C(6)–O(6)	1.350 (20)	C(19)–C(20)	1.375 (26)
C(13)–O(6)	1.453 (19)	C(21)–C(22)	1.496 (25)
C(6)–C(7)	1.513 (22)	C(21)–C(23)	1.424 (32)
Angles			
N(1)–W(1)–C(1)	88.7 (5)	N(1)–C(6)–C(7)	123 (2)
N(1)–W(1)–C(2)	175.0 (6)	O(6)–C(6)–C(7)	120 (1)
C(1)–W(1)–C(2)	86.8 (7)	C(6)–C(7)–C(8)	120 (2)
N(1)–W(1)–C(3)	90.1 (6)	C(6)–C(7)–C(12)	116 (2)
C(1)–W(1)–C(3)	88.4 (8)	C(8)–C(7)–C(12)	124 (2)
C(2)–W(1)–C(3)	87.6 (7)	C(7)–C(8)–C(9)	116 (2)
N(1)–W(1)–C(4)	97.9 (5)	C(8)–C(9)–C(10)	124 (2)
C(1)–W(1)–C(4)	173.1 (6)	C(9)–C(10)–C(11)	115 (2)
C(2)–W(1)–C(4)	86.5 (7)	C(10)–C(11)–C(12)	124 (2)
C(3)–W(1)–C(4)	89.6 (9)	C(7)–C(12)–C(11)	116 (2)
N(1)–W(1)–C(5)	91.3 (6)	N(1)–C(14)–C(15)	113 (1)
C(1)–W(1)–C(5)	90.8 (7)	N(1)–C(14)–C(21)	119 (2)
C(2)–W(1)–C(5)	90.9 (7)	C(15)–C(14)–C(21)	128 (2)
C(3)–W(1)–C(5)	178.4 (6)	C(14)–C(15)–C(16)	126 (2)
C(4)–W(1)–C(5)	91.0 (8)	C(14)–C(15)–C(20)	117 (2)
W(1)–N(1)–C(6)	131 (1)	C(16)–C(15)–C(20)	117 (2)
W(1)–N(1)–C(14)	114.0 (9)	C(15)–C(16)–C(17)	124 (2)
C(6)–N(1)–C(14)	115 (1)	C(16)–C(17)–C(18)	119 (2)
W(1)–C(1)–O(1)	176 (2)	C(17)–C(18)–C(19)	119 (2)
W(1)–C(2)–O(2)	175 (2)	C(18)–C(19)–C(20)	122 (2)
W(1)–C(3)–O(3)	174 (2)	C(15)–C(20)–C(19)	119 (2)
W(1)–C(4)–O(4)	173 (2)	C(14)–C(21)–C(22)	121 (2)
W(1)–C(5)–O(5)	176 (2)	C(14)–C(21)–C(23)	124 (2)
C(6)–O(6)–C(13)	119 (1)	C(22)–C(21)–C(23)	115 (2)
N(1)–C(6)–O(6)	117 (1)		

The structural parameters associated with the bridging carbonyl in **8b** most closely resemble those in **18**. Both **8b** and **18** have one C–Mo distance of ca. 2.06 Å, this being to the Mo-atom with the π-donor substituent (oxo or imido), and one longer C–Mo distance, 2.28 Å (**8b**) and 2.16 Å (**18**). The CO distances (ca. 1.18 (1) Å) in these complexes are significantly longer than the terminal C–O bonds (ca. 1.15 (1) Å). The CO stretching frequencies in these complexes are over 100 cm^{-1} lower than what might be expected for a μ_2-carbonyl (cf ν_{CO} of **17**) and approach that of the μ_4-carbonyl in **19**. This reduction in CO stretching frequency is most likely connected to the high electron density on Mo due to the π-donor groups.

The Cp ligand in **8b** shows a considerable "tilt". The Mo–C distances transoid to the imido ligand (Mo–C-

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(16),C(17)) average about 2.44 (2) Å, while the Mo–C(19) distance is only 2.32 (1) Å. This tilt presumably reflects the high trans influence of the imido ligand. A large tilt of the Cp ligand in carbonyl complexes with strong π-donor ligands has been seen previously.[31-33]

$(CO)_5W{-}N({=}C(OMe)Ph)({-}C(Ph){=}CMe_2)$ (11). Crystallographic statistics are in Table I, fractional atomic coordinates are in Table VI, and selected bond distances and angles are in Table VII. Figure 4 shows the ORTEP plot with numbering scheme.

The ring-opened azirine has inserted into the tungsten–carbene bond to form an *N*-vinylimidate ligand, bonded to the tungsten through the nitrogen atom. The W–N distance, 2.30 (1) Å, is longer than the W–N distance in amine complexes, e.g. $(CO)_5W(NH_2Me)$ (W–N = 2.24 (1) Å).[34] The increased length may simply reflect the steric crowding in the highly substituted imidate ligand and its lower basicity.

The overall coordination about W is very nearly octahedral, but some significant distortions are present arising from steric interactions. The N–W–C(4) angle, 97.9 (5)°, shows the largest distortion and appears to result from the carbonyl group clashing with the C(7)–phenyl group. All the CO(eq)–W–CO(ax) angles are less than the complementary CO(eq)–W–N angles, so the equatorial carbonyls bend toward the axial carbonyl and away from the imidate ligand.

The (C(Ph)═CMe$_2$) portion of the imidate ligand is essentially identical to this group in **6** and **8b**. The metrical values averaged over all three structures are C═C = 1.34 (2), C–Me = 1.50 (4), and C–Ph = 1.50 (4) Å, respectively. The "internal" angles of the vinyl group average 122 (2)°, while the "external" angles, i.e. Me–C–Me and N–C–Ph, average 114 (1)°.

The former carbene group is doubly bonded to nitrogen (C(6)–N(1) = 1.31 (2) Å). The C(6)–O(6) length of 1.35 (2) Å is significantly shorter than the O(6)–C(13) distance, 1.45 (2) Å. The shortness of the former bond may be ascribed to conjugation with the N═C double bond and to the decreased radius of the sp^2-hybridized C(6).

Experimental Section

All reactions and manipulations were carried out in a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were carefully dried and distilled under nitrogen prior to use. Toluene, diethyl ether, and tetrahydrofuran were distilled from sodium benzophenone ketyl. Hexane and methylene chloride were distilled from calcium hydride. All reagents were purchased from Aldrich Chemical Co. or prepared using published procedures.

The NMR data were collected on a Bruker AM-300 or Bruker WM-360 spectrometer. The IR data were collected on a Nicolet 5-DX or a Perkin-Elmer 1330 spectrometer. Elemental analyses were carried out by the Microanalysis Laboratory, University of Michigan.

$(C_5H_5)_2W_2(CO)_4(NC(C_6H_4C(CH_3)_3){=}C(CH_3)_2)$ (6). A solution of 0.28 g (0.46 mmol) of $(C_5H_5)_2W_2(CO)_4$ in 20 mL of CH_2Cl_2 was cooled to 0 °C in an ice-bath. To this solution was added 0.10 g (0.49 mmol) of 2,2-dimethyl-3-(4-*tert*-butylphenyl)-2*H*-azirine.[35] The solution was stirred at 0 °C for $^1/_2$ h and then allowed to warm to room temperature. After $^1/_2$ h at room temperature, the solution IR spectrum showed the reaction to be complete as evidenced by new absorbtion bands at 1953 (s), 1924 (s), and 1848 (s, br) cm^{-1}. After the addition of 10 mL of hexane, the solution was concentrated and cooled yielding dark red crystals of the product. A second crop of crystals was obtained by concentration of the mother liquor. Yield: 0.35 g (95%). IR (cm^{-1}) (CH_2Cl_2): ν_{CO} 1953 (s), 1924 (s), 1848 (s). ^{1}H NMR (C_6D_6): δ 7.25 (s, 4 H, $(CH_3)_3CC_6\mathit{H}_4$), 5.17 (s, 5 H, C_5H_5), 4.79 (s, 5 H, C_5H_5), 1.59 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 1.16 (s, 9 H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 231.2 (CO); 155.4, 150.9, 129.0, 125.5 (Ph); 133.4, 130.7 ($-\mathit{C}{=}\mathit{C}(CH_3)_2$); 96.1, 88.9 ($C_5H_5$); 34.6 ($-\mathit{C}(CH_3)_3$); 31.3 ($-C(\mathit{C}H_3)_3$); 21.8, 21.1 ($-C{=}C(\mathit{C}H_3)_2$). Anal. Found (calc for $C_{28}H_{29}NO_4W_2$): C, 41.45 (41.45); H, 3.51 (3.61); N, 1.75 (1.73).

$(C_5H_5)_2Mo_2(CO)_4(NC(Ar){=}C(CH_3)_2)$ (7). To a solution of 0.35 g (0.8 mmol) of $(C_5H_5)_2Mo_2(CO)_4$ dissolved in 15 mL of toluene was added 0.16 g (1.1 mmol) of 2,2-dimethyl-3-phenyl-2*H*-azirine. The reaction mixture was stirred at room temperature for 1 h. The toluene was removed under vacuum leaving a black oily residue which was extracted with 35 mL of hexane. The extracts were filtered through a fritted glass funnel and concentrated to ~10 mL. Cooling of the hexane solution to 0 °C produced a dark red microcrystalline solid which was a mixture of two isomers of $(C_5H_5)_2Mo_2(CO)_4(NC(C_6H_5){=}C(CH_3)_2)$. Yield: 0.24 g (53%). IR (cm^{-1}) (CH_2Cl_2): ν_{CO} 1990 (s), 1960 (s), 1925 (s), 1850 (s, br). ^{1}H NMR (C_6D_6): δ 7.05 (m, 5 H, C_6H_5); *5.08*, 4.99, *4.83* (s, 10 H, C_5H_5); *1.76*, 1.55, 1.44, *1.28* (s, 6 H, CH_3) (peaks due to isomer A are italicized). Anal. Found (calc for $C_{24}H_{21}Mo_2NO_4$): C, 49.98 (49.76); H, 3.65 (3.65); N, 2.40 (2.42).

$(C_5Me_5)_2Mo_2(CO)_4(NC(Ar){=}C(CH_3)_2)$ (8). To a solution of 1.44 g (2.5 mmol) of $(C_5Me_5)_2Mo_2(CO)_4$ in 20 mL of toluene was added 0.56 g (2.9 mmol) of 2,2-dimethyl-3-phenyl-2*H*-azirine.[3] The solution was heated to 35 °C and stirred for 2 days. After addition of 10 mL of hexane, the solution was concentrated and cooled to 0 °C, yielding dark red crystals of the product. Yield: 1.56 g (81%). Similar yields were obtained using 2,2-dimethyl-3-(4-*tert*-butylphenyl)-2*H*-azirine.

$(C_5Me_5)_2Mo_2(CO)_4(NC(C_6H_4C(CH_3)_3){=}C(CH_3)_2)$ (8a). IR (cm^{-1}) (CH_2Cl_2): ν_{CO} 1930 (s), 1867 (s), 1693 (m). ^{1}H NMR (C_6D_6): δ 7.32 (dd, 4 H, $(CH_3)_3CC_6\mathit{H}_4$, J = 8 Hz); 1.92 (s, 3 H, CH_3); 1.73, 1.71 (s, 15 H, $C_5(CH_3)_5$); 1.48 (s, 3 H, CH_3); 1.24 (s, 9 H, $(CH_3)_3C-$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 234.0 (CO); 152.3, 150.2, 129.1, 125.5 ($(CH_3)_3C\mathit{C}_6H_4$); 135.4, 130.6 ($\mathit{C}{=}\mathit{C}(CH_3)_2$); 109.9, 103.7 ($\mathit{C}_5Me_5$); 34.6 ($-\mathit{C}(CH_3)_3$); 31.4 ($-C(\mathit{C}H_3)_3$); 21.7, 21.4 ($C{=}C(\mathit{C}H_3)_2$); 10.4, 10.0 ($C_5(\mathit{C}H_3)_5$). Anal. Found (calc for $C_{38}H_{49}Mo_2NO_4$): C, 58.58 (58.84); H, 6.11 (6.37); N, 2.10 (1.891).

$(C_5Me_5)_2Mo_2(CO)_4(NC(C_6H_5){=}C(CH_3)_2)$ (8b). IR (cm^{-1}) (CH_2Cl_2): ν_{CO} 1925 (s), 1865 (s), 1690 (m). ^{1}H NMR (C_6D_6): δ 7.10 (m, 5 H, C_6H_5); 1.83, 1.34 (s, 3 H, CH_3); 1.63, 1.62 (s, 15 H, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 235.0 (CO); 152.3, 129.4, 128.2, 127.7 (C_6H_5); 137.9, 132.4 ($-\mathit{C}{=}\mathit{C}(CH_3)_2$); 110.3, 104.0 ($\mathit{C}_5Me_5$); 21.9, 21.3 ($-C{=}C(\mathit{C}H_3)_2$); 10.6, 10.0 ($C_5(\mathit{C}H_3)_5$). Anal. Found (calc for $C_{34}H_{41}Mo_2NO_4$): C, 57.06 (56.75); H, 5.47 (5.74); N, 2.13 (1.95).

$((CH_3)_3CO)_6W_2(NC(Ar){=}C(CH_3)_2)_2$ (9). A solution of 1.5 g (1.86 mmol) of $W_2(OC(CH_3)_3)_6$[36] dissolved in 30 mL of toluene was cooled to 0 °C in an ice bath. To this solution was added 0.76 g (3.8 mmol) of 2,2-dimethyl-3-(4-*tert*-butylphenyl)-2*H*-azirine and the mixture stirred for 15 min. The reaction mixture was allowed to warm to room temperature and stirred for an additional 45 min. The toluene was removed under vacuum, and the residue was redissolved in 40 mL of hexane. The hexane solution was filtered through a fritted glass funnel and then concentrated to 20 mL. On cooling, dark red crystals of the product formed. Another crop of crystals was recovered by concentration and cooling of the mother liquor. Yield: 1.75 g (78%). Similar yields were obtained using 2,2-dimethyl-3-phenyl-2*H*-azirine.

$((CH_3)_3CO)_6W_2(NC((CH_3)_3CC_6H_4){=}C(CH_3)_2)_2$ (9b). ^{1}H NMR (C_6D_6): δ 7.40 (dd, 8 H, $(CH_3)_3CC_6\mathit{H}_4$, J = 8 Hz); 2.82 (s, 6 H, CH_3); 1.91 (s, 6 H, CH_3); 1.85 (s, 9 H, $OC(CH_3)_3$); 1.48 (s, br , 45 H, $OC(CH_3)_3$; 1.26 (s, 18 H, $(C\mathit{H}_3)_3CC_6H_4$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 151.9, 149.9, 130.0, 125.0 ($(CH_3)_3C\mathit{C}_6H_4$); 139.2, 130.5 ($-\mathit{C}{=}\mathit{C}(CH_3)_2$); 81.4, 78.8 ($O\mathit{C}(CH_3)_3$); 34.6 ($(CH_3)_3\mathit{C}C_6H_4$); 33.3, 32.9 ($OC(\mathit{C}H_3)_3$); 31.4 ($(\mathit{C}H_3)_3CC_6H_4$); 22.8, 21.2 ($-C{=}C(\mathit{C}H_3)_2$).

$((CH_3)_3CO)_6W_2(NC(C_6H_5){=}C(CH_3)_2)_2$ (9a). ^{1}H NMR (C_6D_6): δ 7.0–7.5 (m, 10 H, C_6H_5); 2.75 (s, 6 H, CH_3); 1.83 (s, 15 H, CH_3

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and $\mathrm{OC(CH_3)_3}$); 1.45 (s, 45 H, $\mathrm{OC(CH_3)_3}$). Anal. Found (calc for $\mathrm{C_{44}H_{76}N_2O_6W_2}$): C, 46.89 (48.18); H, 6.89 (6.98); N, 2.60 (2.55). (A satisfactory analysis could not be obtained due to the air sensitivity and thermolability of the compound.)

$\mathbf{(CO)_5WN(C(OCH_3)C_6H_5)(C(C_6H_5){=}C(CH_3)_2)}$ (11). To a solution of 0.5 g (1.13 mmol) of $\mathrm{(CO)_5W{=}C(OCH_3)(C_6H_5)}$[37] in 20 mL of hexane was added 0.18 g (1.28 mmol) of 2,2-dimethyl-3-phenyl-2*H*-azirine. After the mixture was stirred at room temperature for 3 h, a yellow crystalline solid precipitated from the reaction mixture. The yellow solid was collected by filtration through a fritted glass funnel and washed with 3 × 3 mL of hexane. The product was analytically pure. Yield: 0.56 g (84%). IR ($\mathrm{cm^{-1}}$) (toluene): ν_{CO} 2067 (s), 1970 (s), 1922 (s), 1893 (s), 1621 (m), 1595 (m). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 7.45 (m, 2 H, $\mathrm{C_6H_5}$); 7.20 (m, 2 H, $\mathrm{C_6H_5}$); 7.17 (m, 2 H, $\mathrm{C_6H_5}$); 7.05 (s, 4 H, $\mathrm{C_6H_5}$); 2.63 (s, 3 H, $\mathrm{OCH_3}$); 1.82 (s, 3 H, $\mathrm{CH_3}$); 1.78 (s, 3 H, $\mathrm{CH_3}$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 202.6, 198.6 (CO, $J_{\mathrm{W-C}}$ = 60 Hz); 169.4 ($C\mathrm{(OCH_3)C_6H_5}$); 136.6, 119.2 ($C{=}C\mathrm{(CH_3)_2}$); 142.4, 131.6, 131.2, 130.8, 129.7, 129.5, 128.6, 127.1 ($\mathrm{C_6H_5}$); 59.1 ($\mathrm{C(O}C\mathrm{H_3)C_6H_5}$); 20.4, 20.2 ($\mathrm{C{=}C(}C\mathrm{H_3)_2}$. Anal. Found (cald for $\mathrm{C_{23}H_{19}NO_6W}$): C, 46.94 (46.88); H, 2.89 (3.25); N, 2.05 (2.38).

Decomposition of 11. A solution of 0.2 g (0.34 mmol) of **11** in 20 mL of hexane was stirred at 21 °C in contact with air. After 6 h a large amount of a light colored precipitate had formed, which was removed by filtration. The solvent was removed from the filtrate leaving a yellow oil which was found to be the *N*-vinylimidate, $\mathrm{Ph(MeO)C{=}NC(Ph){=}C(CH_3)_2}$, identified by comparison of its ^{1}H NMR spectrum with that reported in the literature.[15]

$\mathbf{[(C_5H_5)(CO)_2FeN(C(OCH_3)CH_3)C(Ar){=}C(CH_3)_2]BF_4}$ (13). To a solution of 0.5 g (1.5 mmol) of $\mathrm{[(C_5H_5)(CO)_2Fe{=}C(OMe)Me]BF_4}$[38] in 20 mL of $\mathrm{CH_2Cl_2}$ was added 0.45 g (3.1 mmol) of 2,2-dimethyl-3-phenyl-2*H*-azirine. The reaction mixture was stirred at room temperature for 4 h. The solution was concentrated to ~5 mL and hexane added dropwise until a yellow-orange precipitate started to form. The precipitate was removed by filtration and subsequently shown by IR spectroscopy to be contaminated with unreacted $\mathrm{[(C_5H_5)(CO)_2Fe{=}C(OMe)Me]BF_4}$. The solvent was removed from the filtrate and the residue washed with 3 × 5 mL of hexane yielding an orange powder. After drying under vacuum, the orange powder was redissolved in 15 mL of $\mathrm{CH_2Cl_2}$. This solution was filtered through a fritted glass funnel, and toluene was added dropwise until the solution appeared cloudy. Upon standing at room temperature, orange crystals of the product formed which were isolated by careful removal of the solvent via cannula. A second crop of crystals were isolated by concentration and cooling of the mother liquid. Yield: 0.41 g (58%). The same procedure was followed to prepare the 2,2-dimethyl-3-(4-*tert*-butylphenyl)-2*H*-azirine derivative. The $\mathrm{PF_6^-}$ salts can be prepared by the same method as above using $\mathrm{[(C_5H_5)(CO)_2Fe{=}C(OMe)Me]PF_6}$.

$\mathbf{[(C_5H_5)(CO)_2FeN(C(OCH_3)CH_3)C(CH_3)_2]BF_4}$ (13a). IR ($\mathrm{cm^{-1}}$) ($\mathrm{CH_2Cl_2}$): ν_{CO} 2054 (s), 2009 (s), 1607 (m). ^{1}H NMR (acetone-d_6): δ 7.50 (m, 5 H, $\mathrm{C_6H_5}$); 5.05 (s, 5 H, $\mathrm{C_5H_5}$); 4.13 (s, 3 H, $\mathrm{OCH_3}$); 2.86 (s, 3 H, $\mathrm{CH_3}$); 1.78 (s, 3 H, $\mathrm{CH_3}$); 1.54 (s, 3 H, $\mathrm{CH_3}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 212.1, 210.0 (CO); 174.3 ($C\mathrm{(OCH_3)CH_3}$); 143.9, 130.0, 129.1, 128.9 ($\mathrm{C_6H_5}$); 135.9, 122.2 ($C{=}C\mathrm{(CH_3)_2}$); 86.9 ($\mathrm{C_5H_5}$); 59.9 ($\mathrm{C(O}C\mathrm{H_3)}$); 20.5 ($\mathrm{C(OCH_3)}C\mathrm{H_3}$); 20.2, 19.8 ($C{=}C\mathrm{(CH_3)_2}$. Anal. Found (calc for $\mathrm{C_{20}H_{22}BF_4FeNO_3}$): C, 51.48 (51.44); H, 4.67 (4.75); N, 2.81 (3.00).

$\mathbf{[(C_5H_5)(CO)_2FeN(C(OCH_3)CH_3)(C((CH_3)_3CC_6H_4){=}C(CH_3)_2)]BF_4}$ (13b). IR ($\mathrm{cm^{-1}}$) ($\mathrm{CH_2Cl_2}$): ν_{CO} 2054 (s), 2009 (s), 1606 (m). ^{1}H NMR (DMSO-d_6): δ 7.32 (dd, 4 H, $\mathrm{(CH_3)_3CC_6}H_4$, J = 8 Hz); 4.95 (s, 5 H, $\mathrm{C_5H_5}$); 3.94 (s, 3 H, $\mathrm{OCH_3}$); 2.60 (s, 3 H, $\mathrm{CH_3}$); 1.70 (s, 3 H, $\mathrm{CH_3}$); 1.41 (s, 3 H, $\mathrm{CH_3}$); 1.31 (s, 9 H, $\mathrm{(C}H_3\mathrm{)_3CC_6H_4}$). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 211.1, 209.2 (CO); 173.1 ($C\mathrm{(OCH_3)CH_3}$); 149.8, 142.1, 128.1, 123.9 ($\mathrm{(CH_3)_3C}C_6\mathrm{H_4}$); 131.4, 119.1 ($C{=}C\mathrm{(CH_3)_2}$); 87.7 ($\mathrm{OCH_3}$); 85.9 ($\mathrm{C_5H_5}$); 58.2 ($\mathrm{C(OCH_3)}C\mathrm{H_3}$); 33.4 ($\mathrm{(CH_3)_3}C$); 30.7 ($\mathrm{(}C\mathrm{H_3)_3C}$); 18.9, 18.3 ($\mathrm{C{=}C(}C\mathrm{H_3)_2}$).

$\mathbf{[(C_5H_5)(CO)_2FeN(C(OCH_3)CH_3)(C((CH_3)_3CC_6H_4){=}C(CH_3)_2)]PF_6}$. IR ($\mathrm{cm^{-1}}$) ($\mathrm{CH_2Cl_2}$): ν_{CO} 2056 (s), 2012 (s), 1606 (m). ^{1}H NMR (acetone-d_6): δ 7.47 (dd, 4 H, $\mathrm{(CH_3)_3CC_6}H_4$, J = 8 Hz); 5.01 (s, 5 H, $\mathrm{C_5H_5}$); 4.09 (s, 3 H, $\mathrm{OCH_3}$); 2.83 (s, 3 H, $\mathrm{CH_3}$); 1.81 (s, 3 H, CH3); 1.33 (s, 9 H, $\mathrm{(C}H_3\mathrm{)_3CC_6H_4}$).

Reaction of 13b with $\mathbf{NaBPh_4}$. In a 100-mL Schlenk flask were placed 0.58 g (1.1 mmol) of **13b** and 1.0 g (3.0 mmol) of $\mathrm{NaBPh_4}$. The reactants were dissolved in 20 mL of THF, and the solution was stirred at 21 °C for 1 h and then filtered through a fritted funnel containing a small amount of Celite to remove the fine white precipitate which had formed. The filtrate was stripped to dryness under vacuum and the residue extracted with 20 mL of $\mathrm{CH_2Cl_2}$. The $\mathrm{CH_2Cl_2}$ solution was filtered to remove the unreacted $\mathrm{NaBPh_4}$, leaving a clear orange solution. Diethyl ether was added slowly to precipitate the product as a yellow powder. The yellow powder was recrystallized from the slow concentration of a $\mathrm{CH_2Cl_2}$ solution yielding large yellow crystals of the known compound $\mathrm{[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_5BPh_3]}$,[18] as determined by X-ray crystallography.

Crystal Structure Determinations. $\mathbf{(CO)_5WN(C(OCH_3)Ph)C(Ph){=}C(CH_3)_2}$ (11). Crystals of **11** were grown from cooling a $\mathrm{CH_2Cl_2}$ solution to 0 °C. The crystal was mounted in a capillary on a Syntex P2$_1$ diffractometer. Lattice parameters were determined by least-squares analysis of 15 reflections distributed in reciprocal space. Intensity data were collected at ambient temperature with standard reflections monitored every 100 reflections. The structure was solved using direct methods contained in the SHELX package.[39] Positions for all H atoms were calculated but were not refined.

$\mathbf{(C_5H_5)_2W_2(CO)_4(NC(C_6H_4(CH_3)_3C){=}C(CH_3)_2)}$ (6). Crystals of **6** were grown from the cooling of a hexane solution to 0 °C. The crystals were mounted in a capillary on a Nicolet R3m diffractometer. Lattice parameters were determined from the least-squares analysis of 25 reflections distributed in reciprocal space. Standard reflections were measured every 197 reflections. The structure was solved using the direct methods contained in the SHELXTL (1.5) program library.[39]

$\mathbf{(C_5Me_5)_2Mo_2(CO)_2(\mu\text{-}CO)_2(NC(Ph){=}CMe_2)}$ (8b). Crystals of **8b** were grown from a $\mathrm{Et_2O}$ solution at 0 °C. The crystals were mounted in a capillary on a Siemens R3m/v diffractometer. Lattice parameters were determined by least-squares analysis of 25 reflections distributed in reciprocal space. Intensity data were collected at ambient temperature with three standard reflections monitored every 100 reflections, and empirical absorption corrections (ψ scans) were applied to the data. The structure was solved using direct methods contained in the SHELXTL program library. The final structure was also solved with enantiomorphic coordinates in order to choose the correct absolute configuration. The coordinates reported here gave the lower *R*-value.

For all structure determinations, the agreement indices R and R_{w} are defined as $R = \sum[|F_{\mathrm{o}}| - |F_{\mathrm{c}}|]/\sum|F_{\mathrm{o}}|$ and $R_{\mathrm{w}} = (\sum w[F_{\mathrm{o}}| - |F_{\mathrm{c}}|]^2)^{1/2}/(\sum w|F_{\mathrm{o}}|^2)^{1/2}$, with $w = 1/(\sigma^2 F_{\mathrm{o}} + PF_{\mathrm{o}}^2)$ ($P = 0.0001$). The "goodness of fit" for the refinement is defined as $(w[|F_{\mathrm{o}}| - |F_{\mathrm{c}}]^2)^{1/2}/(N_{\mathrm{o}} - N_{\mathrm{v}})^{1/2}$, where N_{o} is the number of observed reflections and N_{v} is the number of parameters varied. The scattering factors were taken from ref 40.

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Supplementary Material Available: Tables of temperature factors, hydrogen atom positions, and complete bond lengths and angles for **6**, **8b**, and **11** (17 pages). Ordering information is given on any current masthead page.

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