zophenone ketyl in toluene was used to drive purged, thermostated H_2 gas saturated with toluene vapor through the Calvet cell. The enthalpy of reaction 3, −10.2 ± 1.0 kcal/mol, can be used to calculate the solution-phase Cr–H bond strength in this complex of 62.3 ± 1.0 kcal/mol.

Relative Cr–H bond strengths in solution can be determined to within ±0.2 kcal/mol by solution calorimetric measurement of radical/hydride reactions.[10] For example, reaction 4 is rapid at room temperature. The enthalpy of reaction 4, −2.5 ± 0.2

$$^{\bullet}Cr(CO)_3(C_5Me_5) + H\text{-}Cr(CO)_2(PPh_3)(C_5H_5) \rightarrow HCr(CO)_3(C_5Me_5) + {^{\bullet}Cr(CO)_2(PPh_3)(C_5H_5)} \quad (4)$$

kcal/mol, is a direct measure of the difference in solution-phase bond strengths between the two complexes and leads to a Cr–H bond strength of 59.8 kcal/mol for the PPh_3-substituted complex. In analogous fashion, the Cr–H bond strength estimates for the PEt_3, CO, and $P(OMe)_3$ complexes shown in Table I have been determined.

The value for the $H\text{-}Cr(CO)_3(C_5H_5)$ bond strength is in agreement with our earlier work[11] on the heat of hydrogenation of the Cr–Cr dimer shown in eq 5. At that time, no accurate

$$[Cr(CO)_3(C_5H_5)]_2(s) + H_2(g) \rightarrow 2\,H\text{-}Cr(CO)_3(C_5H_5)(s) \quad (5)$$

value was available for the Cr–Cr bond strength. Use of the recent value[8] of 14.8 kcal/mol for the Cr–Cr bond strength and $\Delta H_{rxn} = -3 \pm 1$ kcal/mol[11] leads to a Cr–H bond strength estimate of 61 kcal/mol, in agreement with the present work. These data are also in agreement with the work of Tilset and Parker based on electrochemical and pK_a data.[12]

The Cr–H bond strengths shown in Table I represent some of the first data to demonstrate the role of ligand substituents on single M–X bond strengths in solution. The range of values is on the order of 3 kcal/mol. In view of the fact that radical/hydride transfer reactions are rapid, as discussed below, this data may be useful in understanding concurrent reactions with several metal species present. The lowest value, 59.8 kcal/mol, is close to the estimated limit for thermodynamic stability for M–H complexes of 56 kcal/mol.[13]

In view of the importance of hydrogen atom transfer in catalytic reactions, we have studied the kinetics of reaction 4 using stopped-flow techniques. The hydride abstraction is first order in both reactants: rate = $k[^{\bullet}Cr(CO)_3(C_5Me_5)][H\text{-}Cr(CO)_2(PPh_3)(C_5H_5)]$, with values for the second-order rate constant k = 1040, 910, and 768 $M^{-1}\,s^{-1}$ at 35, 25, and 15 °C, respectively. The low enthalpy of activation ($\Delta H^{\ddagger} = 2.1 \pm 0.2$ kcal/mol) and high negative entropy of activation ($\Delta S^{\ddagger} = -38.2 \pm 3.8$ cal mol^{-1} deg^{-1}) are consistent with direct H atom transfer through a $Cr\cdots H\cdots Cr'$ intermediate. Additional work is in progress to map out the thermodynamic and kinetic factors controlling stability in these and related hydride/radical reactions.

Acknowledgment. Support of this work by the National Science Foundation, Grant CHE-8618753 (C.D.H.), and by the Komaromi Koolajipari Vallalat, Komarom, Hungary (G.K.), is gratefully acknowledged. We also thank Dr. M. C. Baird, Queen's University, for helpful discussions.

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(10) In studies of the radical/hydride reactions, a large excess of one reagent was used to drive the equilibrium quantitatively to products. Enthalpies of reaction based on the use of hydride as limiting reagent were in agreement with those done with radical as limiting reagent.

(11) Landrum, J. T.; Hoff, C. D. *J. Organomet. Chem.* **1985**, *282*, 215.

(12) (a) Bond-strength estimates based on electrochemical data have recently been corrected by 8.0 kcal/mol.[12b] The reported bond strength for $H\text{-}Cr(CO)_3(C_5H_5)$ of 54 ± 1.0 kcal/mol[4] would then be 62 ± 1.0 kcal/mol, in agreement with our value of 61.5 kcal/mol. (b) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2843.

(13) For the reaction $2M^{\bullet} + H_2 \rightarrow 2M\text{-}H$, entropic factors (on the order of 8 kcal/mol at room temperature) will favor loss of H_2. If the M–H bond strength = 56 kcal/mol, the free energy of H_2 addition will be 0 at room temperature. Metal complexes with bond strengths lower than this will be thermodynamically unstable with respect to loss of H_2.

Stannadesulfurization of a Bis(dimethyldithiocarbamato)tungsten(II) Complex: Formation of a Coordinated $Me_2NCCNMe_2$ Complex

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Received December 18, 1989

Reactions leading to C–C bond formation may often be effected via organometallic intermediates.[1] Many C–S bond-cleavage reactions are likewise metal assisted.[2] We now report the exhaustive desulfurization of two bis(dithiocarbamato) ligands $[\eta^2\text{-}S_2CNMe_2]^-$ at a tungsten center with concomitant production of the coordinated alkyne $\mu^2\text{-}Me_2NC{\equiv}CNMe_2$ by a reaction involving both these processes.

Numerous metal complexes containing a terminally coordinated stannylene ligand SnX_2 are known but, with the exception of a single Sc(III) and several Cr(0), Mo(0), and W(0) complexes, there are no reports of such derivatives of an early transition metal in a higher oxidation state.[3]

Yellow plates of $[W(CO)_2(\eta^2\text{-}S_2CNMe_2)_2(SnR_2)]$ [R = $CH(SiMe_3)_2$] (**1**) were obtained from $[W(CO)_3(\eta^2\text{-}S_2CNMe_2)_2]$[4] and an equimolar portion of SnR_2[5] in benzene at ambient temperature. Spectroscopic data for **1**[6] are consistent with the illustrated monocapped trigonal prismatic structure, having a cis arrangement of the CO's and a plane of symmetry bisecting the SnR_2 unit and one $[\eta^2\text{-}S_2CNMe_2]^-$ ligand but containing the other. Surprisingly the ligand arrangement in **1** was stereochemically rigid (−80 to +60 °C, ^1H NMR), an unusual feature for a seven-coordinate metal complex,[7] attributed to the bulky SnR_2 moiety. The SnR_2 unit was readily (24–72 h) displaced by a nucleophile L; e.g., reaction with Ph_2C_2 yielded $[W(CO)(\eta^2\text{-}PhC{\equiv}CPh)(\eta^2\text{-}S_2CNMe_2)_2]$.[8]

Thermolysis of $[W(CO)_2(\eta^2\text{-}S_2CNMe_2)_2(SnR_2)]$ (**1**) in benzene for 4 h generated $[SnR_2(\mu\text{-}S)]_n$ (**2**)[9] and emerald crystals of $[\{W(\eta^2\text{-}SCNMe_2)(\eta^2\text{-}S_2CNMe_2)\}\{W(S)(\eta^2\text{-}S_2SnR_2)\}(\mu\text{-}$

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† Present address: Olin Chemicals Research, 350 Knotter Drive, P.O. Box 586, Cheshire, CT 06410-0586.

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(6) $[W(CO)_2(\eta^2\text{-}S_2CNMe_2)_2(SnR_2)]$ (**1**) (75%, after column chromatography on a Florisil support and elution with $n\text{-}C_6H_{14}$): IR (Nujol) ν(CO) 1984 (s) and 1887 (s), ν(C–N) 1504 (m), ρ(Si–C–Si) 841 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 3.57 and 3.56 (s, 3 H each, NCH_3), 3.18 (s, 6 H, NCH_3), 0.50 [s, 2 H, $C(H)Si_2$], 0.19 [br s, 36 H, $Si(CH_3)_3$]; ^{13}C NMR (C_6D_6) δ 223.9 ($^1J_{WC}$ 134 Hz, CO), 210.4 and 205.4 ($S_2CN<$), 45.3, 44.7, and 38.1 (NCH_3), 18.1 [$C(H)Si_2$], 5.3 and 4.9 [$Si(CH_3)_3$]; ^{119}Sn NMR (C_6D_6) δ 188.3. Mass spectrum (FAB), m/z (assign) 862 $(M - 2CO)^+$. Anal. Calcd for $C_{22}H_{50}N_2O_2S_4Si_4SnW$: C, 28.8; H, 5.50; N, 3.05. Found: C, 28.6; H, 4.96; N, 2.81.

(7) (a) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 3743 and references therein. (b) Examples of rigid seven-coordinate complexes are known; see, for example: Hawthorne, S. L.; Fay, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 5268 and references therein.

(8) Identified by comparison of IR and ^1H NMR spectra with those reported in the following: Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532.

(9) $[SnR_2(\mu\text{-}S)]_n$ (**2**): IR (Nujol) ρ(Si–C–Si) 841 (s) cm^{-1}; ^1H NMR (C_7D_8) δ 1.13 [s, $C(H)Si_2$], 0.32 [s, $Si(CH_3)_3$]; ^{13}C NMR (C_7D_8) δ 4.6 [$Si(CH_3)_3$], $C(H)Si_2$ carbon signal was obscured by solvent resonances; ^{119}Sn NMR (C_7D_8) δ 121.4.

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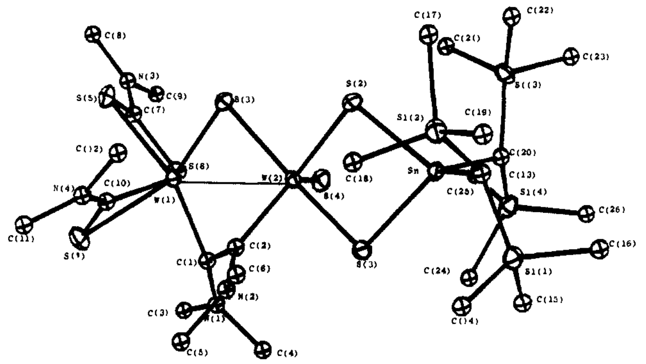
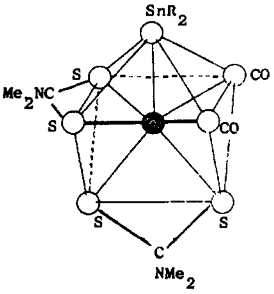


Figure 1. An ORTEP drawing of $[\{W(\eta^2\text{-SCNMe}_2)(\eta^2\text{-S}_2\text{CNMe}_2)\}\{W(S)(\eta^2\text{-S}_2\text{SnR}_2)\}(\mu\text{-Me}_2\text{NCCNMe}_2)(\mu\text{-S})](W,W)$ (3). Selected bond distances (Å): W(1)–S(1) 2.24 (2); W(1)–S(5) 2.58 (2); W(1)–S(6) 2.46 (2); W(1)–S(7) 2.52 (1); W(1)–C(1) 2.04 (5); W(2)–S(1) 2.35 (2); W(2)–S(2) 2.40 (2); W(2)–S(3) 2.43 (2); W(2)–S(4) 2.14 (2); W(2)–C(2) 2.03 (4); W(1)–W(2) 2.819 (3); Sn–S(2) 2.39 (2); Sn–S(3) 2.38 (1); Sn–C(13) 2.21 (5); Sn–C(20) 2.10 (4). Selected bond angles (deg): W(1)–S(1)–W(2) 75.8 (5); W(2)–S(2)–Sn 92.2 (5), W(2)–S(3)–Sn 92.0 (5), N(1)–C(1)–C(2) 131 (5), C(1)–C(2)–N(2) 115 (4); W(1)–C(1)–C(2) 84 (3); C(1)–C(2)–W(2) 103 (3).

$\text{Me}_2\text{NCCNMe}_2)(\mu\text{-S})](W,W)$ (3),[10] consistent with the following equation: 2(**1**) → 1/*n*(**2**) + (**3**) + 4CO.



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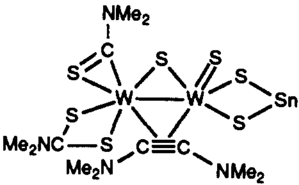
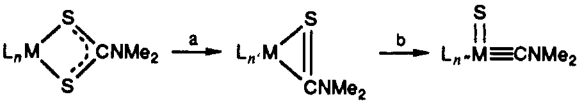


3

An X-ray diffraction structure determination of **3**[11] revealed a W_2Sn cluster with a sulfide and an alkyne bridge between W(1) and W(2) and two sulfide bridges linking W(2) to tin (Figure 1). The short W(1)–W(2) separation, 2.819 (3) Å, is appropriate for a tungsten–tungsten single bond[12] and the diamagnetism of this mixed-valence $W^{III}(d^3)\text{–}W^{V}(d^1)$ assembly. The metrical parameters associated with the $W_2\text{–}(\text{Me}_2\text{NCCNMe}_2)$ core indicate a mode of attachment rarely observed for an alkyne bridging two metals:[13] (i) the C–C vector is rotated 55° relative to the W(1)–W(2), an orientation intermediate between the two commonly observed extreme dispositions; (ii) the large N–C–C–N torsion angle, 63 (7)°, and long C(1)–C(2) bond distance, 1.51 (8) Å, show that CC multiple bonding is severely attenuated; and (iii) the CC atoms are bound strongly but unsymmetrically to the W_2 framework. The W(1)–C(1) and W(2)–C(2) contacts, average 2.03 (5) Å, are indicative of some WC double bond character;[14] an additional attraction exists between C(2) and W(1), 2.41 (5) Å, that is not found between C(1) and W(2), 2.80 (5) Å.

The formation of complex **3** from **1** involves inter alia CC bond formation and CS bond rupture. There is literature support for the notion that the coordinated $\text{Me}_2\text{NCCNMe}_2$ moiety might have originated from coupling of two aminocarbyne ligands, $C(\text{NMe}_2)$.[15] Since the dithiocarbamato ligand is the only source of $C(\text{NMe}_2)$ and sulfide fragments, multiple exhaustive C–S bond cleavages must have occurred along the reaction coordinate. Ample precedent exists for internal oxidative addition of *one* such C–S bond to tungsten (eq 1a),[16] and the $[\eta^2\text{-SCNMe}_2]^-$ ligand (cf. ref 17) is even featured in **3**. Cleavage of the remaining C–S



(1)

bond (eq 1b) to generate an aminocarbyne has not been unambiguously demonstrated previously.[18] Subsequent to the present study, we have isolated and structurally characterized the bridging aminocarbyne complex $[\{W(\eta^2\text{-S}_2\text{CNEt}_2)\}_2(\mu\text{-CNEt}_2)(\mu\text{-S})(\mu\text{-S}_2\text{CNEt}_2)(\mu\text{-S}_2\text{SnR}_2)](W,W)$ from the thermolysis of $[W(\text{CO})_2(\eta^2\text{-S}_2\text{CNEt}_2)_2(\text{SnR}_2)]$ in benzene.[19]

It is evident that there is a redox component in the formation of 1 mol of **3** $[W^{V}W^{III}Sn^{IV}]$ and an equivalent of **2** $[Sn^{IV}]$ from 2 mol of **1** $[W^{II}Sn^{II}]$. The presence in **3** of the $[\eta^2\text{-S}_2\text{SnR}_2)]^{2-}$ ligand, a novel tin equivalent of the dianion of a *gem*-dithiol, is noteworthy. Whereas several types of oxidative addition reactions of SnR_2 are known,[20] those involving Sn–S bond formation or C–S bond cleavage are unprecedented.

In conclusion, facile stannadesulfurization of $[W(\text{CO})_2(\eta^2\text{-S}_2\text{CNMe}_2)_2(\text{SnR}_2)]$ has been demonstrated. Early transition-metal–stannylene complexes warrant further investigation as potential homogeneous models for Chevrel phase hydrodesulfurization catalysts.[21]

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(10) $[\{W(\eta^2\text{-SCNMe}_2)(\eta^2\text{-S}_2\text{CNMe}_2)\}\{W(S)(\eta^2\text{-S}_2\text{SnR}_2)\}(\mu\text{-Me}_2\text{NCCNMe}_2)(\mu\text{-S})](W,W)$ (3) [60%; compounds **2** and **3** after column chromatography (Florisil) and elution with successively $n\text{-C}_6\text{H}_{14}$ and C_6H_6:THF (1:1) yielding **2** and **3**, respectively]: IR (Nujol) ν(C–N) 1565 (m) and 1538 (m), ρ(Si–C–Si) 841 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 3.88, 3.79, 3.36, 3.26, 3.20, 2.88, 2.81, and 2.25 (s, 3 H each, NCH_3), 1.27 and 0.88 [s, 1 H each, C(H)Si_2], 0.29, 0.27, 0.18, and 0.16 [s, 9 H each, $\text{Si(CH}_3)_3$]; ^{13}C NMR (CD_2Cl_2) δ 254.6 (SCN<), 215.0 (S_2CN<), 206.9 and 173.3 (>NCCN<), 49.6, 47.9, 46.9, 46.5, 46.4, 42.6, 40.8, and 39.3 (NCH_3), 23.2 and 16.5 [C(H)Si_2], 4.1 and 3.5 [$\text{Si(CH}_3)_3$]; ^{119}Sn NMR (CD_2Cl_2) δ 316.2. Mass spectra (FAB), *m/z* (assign) 1252 (M)$^+$, 1093 (M – R)$^+$.

(11) Crystal data for $[\{W(\eta^2\text{-SCNMe}_2)(\eta^2\text{-S}_2\text{CNMe}_2)\}\{W(S)(\eta^2\text{-S}_2\text{SnR}_2)\}(\mu\text{-Me}_2\text{NCCNMe}_2)(\mu\text{-S})](W,W)$ (3): triclinic, space group $P\bar{1}$, a = 12.179 (15) Å, b = 13.808 (10) Å, c = 15.912 (26) Å, α = 90.64 (10)°, β = 96.47 (12)°, γ = 107.62 (8)°, U = 2531.2 Å^3, Z = 2, D_c = 1.65 g cm^{-3}, $F(000)$ = 1224. Monochromated Mo Kα radiation, λ = 0.71069 Å, μ = 55.2 cm^{-1}. Refinement of 2183 reflections with $|F^2| > \sigma(F^2)$ [where $\sigma(F^2) = \{\sigma^2(I) + (0.041)^2\}^{1/2}/\text{Lp}$] converged with final residuals R = 0.07 and R' = 0.100. Because of limited data, only the W, S, Sn, and Si atoms were refined anisotropically. Residual electron density up to 2.0 e Å^{-3} near the inversion center at 0,0,0 is probably due to toluene solvent included at partial occupancy and very disordered. Attempts to include solvent atoms in the refinement were unsuccessful and were abandoned.

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(18) Such a transformation has been proposed to account for the photochemical reaction of $[W(\eta^2\text{-PhCCH})_2(\eta^2\text{-S}_2\text{CNMe}_2)_2]$ with PhCCH to yield a complex containing the $[\eta^5\text{-C}_5\text{H}_2\text{Ph}_2(\text{NMe}_2)]^-$ ligand: Morrow, J. R.; Templeton, J. L.; Bandy, J. A.; Bannister, C.; Prout, C. K. *Inorg. Chem.* **1986**, *25*, 1923.

(19) Synthesis and structure of $[\{W(\eta^2\text{-S}_2\text{CNEt}_2)\}_2(\mu\text{-CNEt}_2)(\mu\text{-S})(\mu\text{-S}_2\text{CNEt}_2)(\mu\text{-S}_2\text{SnR}_2)]$, to be published.

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Registry No. 1, 127594-76-7; **2**, 127594-78-9; **3**, 127594-79-0; Ph_2C_2, 501-65-5; $[W(CO)(\eta^2\text{-}PhC{\equiv}CPh)(\eta^2\text{-}S_2CNMe_2)_2]$, 98735-58-1; $Sn[CH(SiMe_3)_2]_2$, 41823-72-7; $[W(CO)_3(\eta^2\text{-}S_2CNMe_2)_2]$, 72881-01-7.

Supplementary Material Available: Details of the crystal structure analysis and tables of complete bond angles and distances, anisotropic and isotropic thermal parameters, and fractional atomic coordinates (6 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

Cyclopropanation with Acyloxy Chromium Carbene Complexes. A Synthesis of (±)-Prostaglandin E_2 Methyl Ester

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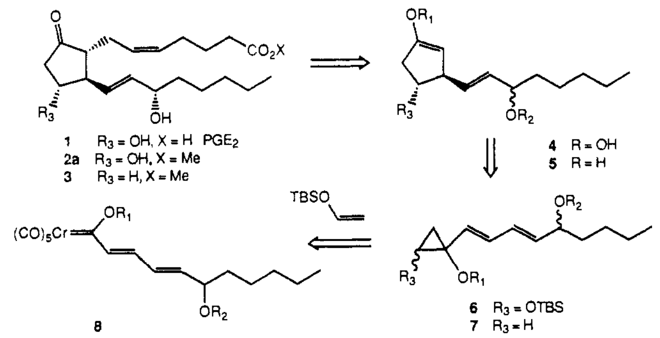
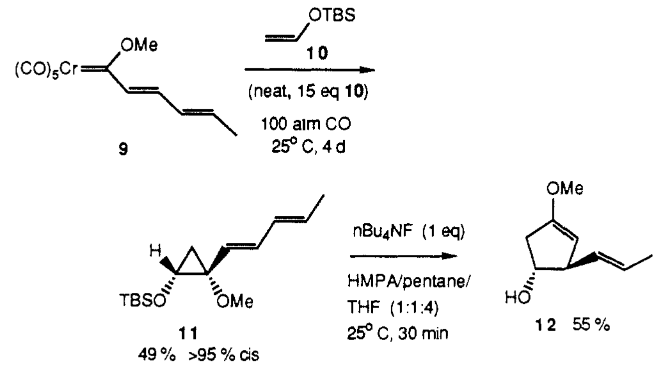
The first reaction of Fischer carbene complexes[2] that was examined for its potential in organic synthesis was the cyclopropanation of olefins; however, the utility of this reaction has yet to be demonstrated in a synthetic application.[3-5] The general strategy for prostaglandin synthesis[7,8] involving a ring expansion of a dienyl cyclopropanone of the type **7** (Scheme I) has only been employed in the synthesis of the C-11 deoxyprostaglandin **3**.[6] Presumably, this approach has been limited due to the lack of methods for the preparation of 1,2-dioxygenated cyclopropanes. We herein report the realization of this strategy for a fully functionalized prostaglandin, a strategy that is highlighted by the development of the cyclopropanation reactions of acyloxy carbene complexes.

Scheme I



In a model study for the synthesis of PGE_2 (**1**), the reaction of the pentadienyl complex **9**[9] and the silyl enol ether **10**[4h] was found to give the cis diastereomer of the cyclopropane **11**.[10] An anionic ring expansion was attempted with the conditions perfected by Danheiser,[11] and it realization for **11** to give *trans*-**12** establishes an alternative to the thermal protocol developed by Salaün[6] for the key ring expansion of **7** to **5** in the synthesis of C-11 deoxy PGE_2 methyl ester **3**.



All attempts to convert the methyl enol ether in **12** to the corresponding enolate met with disappointment (TMSI destroyed the molecule), and this generated significant concern since all of the cyclopropanation reactions with Fischer carbene complexes that have been reported in the literature with oxygen as the heteroatom have been with alkoxy complexes (R_1 in **8** is alkyl).[3,4] We turned to the investigation of the cyclopropanation of enol ethers with acyloxy carbene complexes (R_1 in **8** is acyl), since according to the synthetic approach outlined in Scheme I, this would deliver the enol acetate **4** and recourse could be made to the standard protocol for its conversion to the corresponding enolate. Acyloxy complexes of the type **15** are thermally unstable but can be generated cleanly[12] at low temperatures from tetraalkylammonium metal acylates of the type **13**[13,14] and acyl halides. The development of the chemistry of acyloxy complexes has been limited to reactions with heteroatomic nucleophiles.[4n,12a,15] As indicated by the data in Table I, a variety of 1,2-dioxygenated cyclopropanes can be obtained from the reactions of enol ethers with in situ generated acyloxy carbene complexes and without high pressures of CO. In a direct comparison to the reaction in entry 1, the methoxyl complex derived from **13a** has been reported to

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(1) National Institutes of Health Predoctoral Fellow.

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