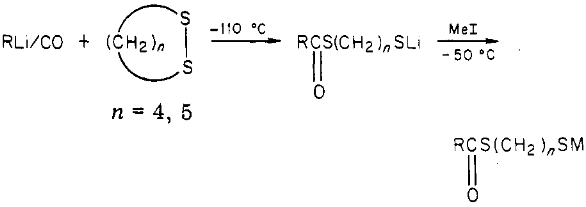
perature was 171% based on *t*-BuLi (or 85.5% based on *both* *n*-BuS units of the disulfide).

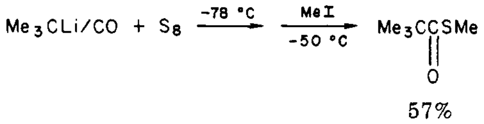
Such nucleophilic acylations of cyclic disulfides are of special interest in that the mercaptide leaving group (cf. eq 2) is retained in the acylation product (eq 5). In such



(5)

a reaction of the *t*-BuLi/CO reagent with 1,2-dithiane ($n = 4$) the methylated product $Me_3CC(O)S(CH_2)_4SMe$ was obtained in 63% yield. Similar reactions are listed in Table I.

In view of this facile nucleophilic acylation of organic disulfides, it was of interest to see if the acylation of elemental sulfur, *cyclo*-S_8, also could be effected. (Elemental sulfur, it is known,[5] reacts with alkyllithiums to give lithium alkyl mercaptides, RSLi.) Such a reaction does indeed occur (eq 6). The yield of thioester was lower (45%) when



$$Me_3CLi/CO + S_8 \xrightarrow{-78\ ^\circ C} \xrightarrow[-50\ ^\circ C]{MeI} Me_3CC(O)SMe \quad (6)$$

57%

the reaction was carried out at −110 °C. In both reactions the 1,2-diketone, *t*-BuC(O)C(O)Bu-*t*, was a minor byproduct. The *sec*-BuLi/CO reagent reacted with elemental sulfur at −78 °C, and after treatment of the reaction mixture with iodomethane the yield of *sec*-BuC(O)SMe was 51%. With *n*-butyllithium this chemistry was not successful in that at −78 °C the yield of *n*-BuC(O)SMe was only 5%, while the *n*-BuC(O)C(O)Bu-*n* yield was 32%. The provenance of the latter has not yet been established.

Direct nucleophilic acylation with in situ generated acyllithium reagents thus seems to be a rather generally applicable procedure. As noted, we have been able to acylate aldehydes, ketones, esters, lactones, and trialkylchlorosilanes, and now, organic disulfides, thioesters, and elemental sulfur have been added to this list. Further work in progress is aimed at the in situ nucleophilic acylation of still other organic, organometallic and inorganic electrophiles.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this work.

Synthesis, Crystal and Molecular Structure, and Reactions of the Bridging Vinylidenedicobalt Complex (μ-CCH_2)($CpCoCO$)$_2$. Reaction with Molybdenum Hydrides To Give a Heteronuclear Cluster Complex

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Summary: The first unsubstituted dicobalt μ-vinylidene complex (μ-CCH_2)($CpCoCO$)$_2$ (**1**) has been synthesized and characterized by X-ray diffraction. **1** is readily protonated by HBF_4 at the β-carbon to yield an isolable μ-ethylidyne salt, **2**, which in turn is reduced by $NaBH_4$ to give the corresponding μ-ethylidene complex **3**. Complex **3** is also formed on treatment of **1** with H_2 at 60 °C, but under these conditions competitive hydrogenolysis of **3** to ethane occurs. Reaction of **1** with $CpMo(CO)_2(L)H$ (L = CO, PPh_3) affords the mixed-metal cluster **4** in good yield, in a rational and potentially general route to μ-carbyne trinuclear systems. Possible mechanisms are briefly discussed.

As members of the important family of complexes containing a carbon bridging two or more metals, bridging vinylidene systems are particularly interesting in that the organic moiety is unsaturated. Therefore, in comparison with bridging alkylidene[1] and alkylidyne[2] complexes, they are expected to display unique reactivity at that site. Despite the fact that mono- and dinuclear vinylidene complexes of several transition-metal complexes are known,[3] no simple cobalt vinylidene complex has yet been reported.[4] In addition, aside from simple protonation reactions,[3,10] the chemistry of bridging vinylidene complexes remains virtually unexplored.

We describe here the synthesis of a new μ-vinylidene system (1) by a route that exploits the versatile reactivity[5,6] of the radical anion $[CpCo(CO)]_2^-$, and the structural characterization of 1 by X-ray diffraction. Preliminary studies on the chemistry of 1 are also reported, including its reaction with mononuclear metal hydrides to afford a rational and potentially general route to μ-carbyne trinuclear cluster systems.

Addition of 1,1-dibromoethylene[7] to a stirred suspension of $Na[CpCo(CO)]_2$ at ambient temperature results in the appearance of new absorbances at 1796 (due to neutral dimer $[CpCo(CO)]_2$) and at 1960 cm^{-1} in the IR spectrum of the solution. Purification by chromatography on neutral alumina II under air-free conditions affords the deep red (μ-vinylidene)bis[(η^5-cyclopentadienyl)carbonylcobalt] (1)[8] in 40% of the theoretical yield (Scheme I). Only a single, presumably trans isomer could be detected by NMR and

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[1] For reviews, see: (a) Herrmann, W. A. *Angew. Chem.* **1982**, *94*, 118. (b) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

[2] For reviews, see: (a) Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97. (b) Dickson, R. S.; Fraser, P. J. *Ibid.* **1974**, *12*, 323.

[3] Dinuclear μ-vinylidene complexes have been reported for the following metals. (a) Mn: Folting, K.; Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1979**, *18*, 3483. (b) Fe: Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911. Dawkins, G. M.; Green, M.; Jeffery, J. C.; Sambale, C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 499. (c) Ru: Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Plaas, D.; Taylor, G. E. *J. Organomet. Chem.* **1980**, C43. Cooke, M.; Davies, D. L.; Gherchais, J. E.; Knox, S. A. R.; Mead, K. A.; Roue, J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 862. (d) Rh: Al-Obaidi, Y. N.; Green, M.; White, N. D.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 319. (e) Fe–Mn: Kolobova, N. E.; Ivanov, L. L.; Zhivanko, O. S.; Aleksandrov, G. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1982**, *228*, 265.

[4] To our knowledge the only cobalt complexes in the μ-vinylidene class are the monohalo- and dihalo-substituted (μ-butenolido)(μ-vinylidene)hexacarbonyldicobalt complexes reported by: Horvath, I. T.; Palyi, G.; Marko, L.; Andreetti, G. D. *Inorg. Chem.* **1983**, *22*, 1049.

[5] Schore, N. E.; Ilenda, C. S.; Bergman, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 7436; **1977**, *99*, 1781.

[6] (a) White, M. A.; Bergman, R. G. *J. Chem. Soc., Chem. Commun.* **1979**, 1056. Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113. (b) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 5694; *Organometallics* **1982**, *1*, 1571. (c) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 464.

[7] Prepared by addition of $CHBr_2CH_2Br$ to a suspension of K_2CO_3 and KOAc in boiling ethanol. The dibromide is collected by distillation as an azeotrope with ethanol at 90 °C. Verhulst, J.; van Hemelrijck, F.; Jungers, J. C. *Natuurwet. Tijdschr. (Ghent)* **1943**, *25*, 203.

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Table I. Selected Distances (Å) and Angles (deg) for Complex 1

atom 1	atom 2	dist	atom 1	atom 2	atom 3	angle
Co1	Co2	2.500 (1)	Co2	Co1	C1	90.88 (5)
			Co2	Co1	C3	48.37 (4)
Co1	C1	1.726 (2)	C1	Co1	C3	92.89 (6)
Co1	C3	1.886 (1)	Co1	Co2	C2	90.94 (5)
Co1	CP1	1.716	Co1	Co2	C3	48.50 (4)
Co1	CP1	1.	C2	Co2	C3	90.43 (6)
Co2	C2	1.722 (1)	Co1	C3	Co2	83.13 (5)
Co2	C3	1.882 (1)	Co1	C3	C4	13[illegible].84 (11)
Co2	CP2	1.724	Co2	C3	C4	138.98 (11)
C3	C4	1.312 (2)	C3	C4	H4A	121.9 (10)
C4	H4A	1.03 (2)	C3	C4	H4B	121.9 (11)
C4	H4B	0.95 (2)	H4A	C4	H4B	115.9 (15)

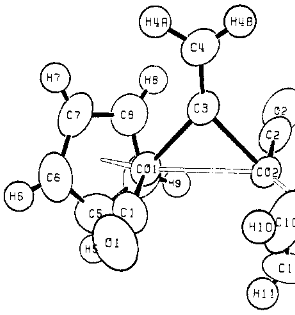
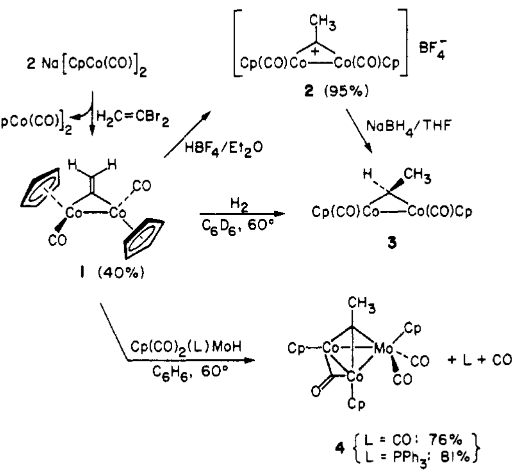


Figure 1. ORTEP drawing of one molecule of 1 showing the atomic labeling scheme. Thermal ellipsoids are scaled to represent the 50% probability surface.

Scheme I



by IR of the crude reaction mixtures.

Large black polyhedral crystals of 1 suitable for an X-ray diffraction study were grown by slow cooling of a hexane solution. An ORTEP diagram of the structure appears in Figure 1.[9] The molecule has approximate twofold rotational symmetry, strongly resembling the analogous bridging methylene complex[6c] in its geometry about the cobalt centers. The vinylic hydrogens are nearly coplanar with the metal atoms (3° twist angle). The vinylidene double bond is rather short, and the average distance from the bridging carbon to the cobalt atoms of 1.885 Å is approximately 0.03 Å shorter than the corresponding bonds in the sp^3-hybridized bridging methylene complex.

Consistent with studies performed on the other known μ-vinylidene complexes,[3b–d,10] 1 is readily protonated by HBF$_4$ in ether solution. The resulting air sensitive blue black precipitate is analytically pure and is formulated to be 2 based on its low temperature ^{1}H NMR spectrum and on elemental analysis data.[11] Protonation at the β-carbon of the vinylidene has also been observed in the analogous Fe, Mn, and Ru systems,[3b,c,10] whereas the Rh complex is initially protonated at the metal–metal bond.[3d] Salt 2 is indefinitely stable under nitrogen in the solid state, but it decomposes completely in CH$_2$Cl$_2$ solutions within a few hours at −78 °C and within seconds in CH$_3$CN, Me$_2$SO, and other highly polar donor solvents. Further evidence for the structure of 2 is provided by its heterogeneous reaction with sodium borohydride in THF to yield the new bridging ethylidene complex **3**. **3** was fully characterized after purification by chromatography on alumina II and sublimation under vacuum at 40 °C.[12]

Direct conversion of 1 into 3 may be detected by ^{1}H NMR in the reaction of 1 with 3–4 atm of H$_2$ in C$_6$D$_6$ at 60 °C. Under these conditions, however, 3 is slowly hydrogenated to give ethane, and the maximum buildup of the ethylidene complex never exceeds 43%.

At moderate temperatures in benzene solution, vinylidene complex 1 reacts with 1 equiv of Cp(CO)$_3$MoH to form heteronuclear cluster complex 4[13] and traces of CpCo(CO)$_2$ and [CpMo(CO)$_3$]$_2$. Purification by chromatography on silica followed by crystallization by vapor diffusion of hexane into a saturated benzene solution at room temperature yields black crystals of 4 in 76% isolated yield.[14] The phosphine-substituted complex CpMo(CO)$_2$(PPh$_3$)H also reacts with 1 under the same conditions to afford 4 in similar yield (by ^{1}H NMR).

The IR spectrum of a Nujol mull of 4 shows three low-frequency absorbances in the carbonyl region, consistent with a structure in which there is one bridging carbonyl

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(8) 1: mp 73–74 °C; ^{1}H NMR (C$_6$D$_6$) δ 6.10 (s, 1 H), 4.69 (s, 5 H); ^{13}C NMR (C$_6$D$_6$) δ 247.84 (μ-C=CH$_2$), 206.76 (CO), 125.71 (μ-C=CH$_2$), 87.52 (C$_5$H$_5$); MS (15 eV), *m/e* 330 (M$^+$); IR (KBr pellet) 1960 (s), 1990 (s) cm^{-1}. Anal. Calcd for C$_{14}$H$_{12}$Co$_2$O$_2$: C, 50.94; H, 3.66; Co, 35.70. Found: C, 51.07; H, 3.81; Co, 35.2.

(9) Crystal data for 1 (25 °C): triclinic crystals; space group $P\bar{1}$ with a = 8.2535 (6) Å, b = 9.0316 (8) Å, c = 9.1980 (11) A, α = 74.427 (8)°, β = 76.745 (8)°, γ = 84.514 (7)°; M = 330.12 amu; Z = 2; d = 1.71 g/cm^3; μ = 25.07 cm^{-1}. The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques; the hydrogen atoms were included in the refinement with isotropic thermal parameters. Of the 2936 unique reflections, 2522 were used in least-squares analysis. The final residuals for 212 variables refined against the 2522 data for which $F^2 > 3\sigma(F^2)$ were R = 2.32%, wR = 3.57%, and GOF = 2.399. The R value for all 2936 data was 3.01%.

(10) Lewis, L. N.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 403.

(11) **2**: ^{1}H NMR (CD$_2$Cl$_2$, −30 °C) δ 5.43 (s, 10 H), 4.37 (s, 3 H). Anal. Calcd for C$_{14}$H$_{13}$BCo$_2$F$_4$O$_2$: C, 40.24; H, 3.14; Co, 28.20. Found: C, 40.11; H, 3.10; Co, 28.1.

(12) Data for **3**: mp 63–64 °C ^{1}H NMR (C$_6$D$_6$) δ 8.28 (q, 1 H, J = 7.4 Hz), 4.61 (s, 10 H), 2.35 (d, 3 H, J = 7.4 Hz); MS (15 eV), *m/e* 332 (M$^+$); IR (C$_6$H$_6$) 1951 (s) cm^{-1}. For closely related complexes and a discussion of the type of fluxional process which results in a single ^{1}H NMR Cp resonance for **3**, see ref 6c. Anal. Calcd for C$_{14}$H$_{14}$Co$_2$O$_2$: C, 50.63; H, 4.25. Found: C, 50.79; H, 4.40.

(13) We know of only one similar reaction, involving the reaction of the trinuclear metal hydride [Mn$_3$(μ-H)$_3$(CO)$_{12}$] with a diiron μ-vinylidene complex: Brun, P.; Dawkins, G. M.; Green, M.; Mils, R. M.; Saaun, J.-Y.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 966.

(1778 cm^{-1}) and two terminal carbonyls (1874, 1830 cm^{-1}).[15] In solution, however, the spectrum of 4 becomes more complicated, and it seems likely that the carbonyl ligands undergo some type of fluctional behavior. There is only a single carbonyl resonance in the ^{13}C NMR spectrum, suggesting that interconversion of all the CO ligands in solution is rapid on the NMR time scale.[16]

Preliminary mechanistic studies of the cluster forming reaction show that no significant rate inhibition occurs upon addition of free CO to the reaction of 1 with $CpMo(CO)_3H$ or of free PPh_3 in the $CpMo(CO)_2(PPh_3)H$ reaction. It therefore appears unlikely that the reaction is initiated by reversible loss of a ligand from either the hydride or the vinylidene complex. Other mechanistic alternatives for the first steps of the reaction include direct, irreversible displacement of L from the molybdenum center by the vinylidene group, followed by insertion of this group into the M–H bond, or transfer of a hydrogen atom from Mo to the β-carbon of the vinylidene, leading to a radical pair, in a process analogous to that which occurs in the hydrogenation of α-methylstyrene by $Cp(CO)_3MoH$[17] or by $HMn(CO)_5$.[18,19] Kinetic and isotope effect studies aimed at distinguishing these possibilities are in progress.

Acknowledgment. We are grateful for financial support of this work by the National Science Foundation (Grant No. CHE-79-26291). The crystal structure analysis was performed by Dr. F. J. Hollander, staff crystallographer at the U.C. Berkeley X-ray crystallographic Facility (CHEXRAY). Funds for the analysis were provided by the above NSF grant; partial funding for the equipment in the facility was provided by the NSF through Grant No. CHE 79-07027. R.G.B. acknowledges a research professorship (1982–1983) from the Miller Institute for Basic Research at U.C. Berkeley.

Registry No. 1, 88336-67-8; 2, 88336-69-0; 3, 88336-70-3; 4, 88343-62-8; $Na[CpCo(CO)]_2$, 62602-00-0; $Cp(CO)_3MoH$, 12176-06-6; $CpMo(CO)_2(PPh_3)H$, 33519-69-6; $H_2C{=}CBr_2$, 593-92-0.

Supplementary Material Available: Data collection and refinement parameters, least-squares positional parameters, positional parameters and their esd's, general temperature factor expressions and their esd's, and raw interatomic distances and angles for 1 (31 pages). Supplied with the archival edition of the journal, available in many libraries; alternatively, ordering information is given on any current masthead page.

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(14) 4: mp, no detectable melting or decomposition below 220 °C; ^1H NMR (C_6D_6) δ 4.74 (s, 5 H), 4.69 (s, 3 H), 4.44 (s, 10 H); ^{13}C NMR (CD_2Cl_2, gated spectrum) δ 341.2 (s, μ-CCH_3), 238.8 (s, CO), 92.4 (d, C_5H_5, J = 12.8 Hz), 89.7 (d, C_5H_5, J = 11.6 Hz), 55.3 (q, μ-CCH_3, J = 13.1 Hz, one line obscured by solvent resonances), 129.0 (very small resonance, not assignable); MS (15 eV), *m/e* 518, 519, 520, 521, 522, 524 (M^+ for each of the naturally occurring isotopes of Mo); IR (Nujol mull) 1874 (s), 1830 (s), 1778 (s) cm^{-1}; IR (C_6H_6) 1909 (s), 1840 (m), 1815 (sh), 1792 (m), 1747 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{18}Co_2MoO_3$: C, 46.18; H, 3.49. Found: C, 46.13; H, 3.60.

(15) This assignment has been confirmed by a single-crystal X-ray diffraction study. The details of this study will appear elsewhere.

(16) Quadrupolar broadening of the bridging CO may also explain this result. We thank a reviewer for suggesting this possibility.

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(19) An analogous proton-transfer mechanism seems unlikely. The reaction of 1 with $CpMo(CO)_3H$ is not accelerated in THF. Furthermore, the rate of formation of 4 is qualitatively similar in the reaction of 1 with both $CpMo(CO)_3H$ and $CpMo(CO)_2(PPh_3)H$, despite the very different acidities of the two Mo hydrides. Cf. Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255.

(Tropone)- and (Tropothione)iron Complexes from Ring Expansion Reactions

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Summary: The benzene ring in the η^6-phenoxide ion–, *o*-chlorophenoxide ion–, or thiophenoxide ion–(η^5-cyclopentadienyl)iron complex, which may be formulated as a neutral complexed cyclic ketone or thioketone, undergoes a ring expansion upon reaction with diazomethane to give, respectively, the (η-tropone)-, (2-chlorotropone)-, or (tropothione)(η^5-cyclopentadienyl)iron cation, isolated as the hexafluorophosphate. The bonding in these complexes appears to be different from that established for the (η^4-tropone)iron tricarbonyl complex.

We wish to report a novel ring expansion reaction of certain complexed phenoxide or thiophenoxide ions to give tropone or tropothione complexes of iron. Most of the known (tropone)metal carbonyl complexes have been prepared directly from tropone,[2] although a (tetraphenyltropone)iron tricarbonyl has been obtained from a rearrangement process.[3] There are very few known ring expansion reactions involving aromatic rings in organometallic chemistry, an example has been reported by Fischer and Breitschaft[4] in the Friedel–Crafts acylation of (η^6-benzene)(η^5-cyclopentadienyl)metal complexes (metal = Cr or Mn) to give low yields of products containing a substituted seven-membered ring as a ligand. reactions of cyclic ketones with CH_2N_2 are known to give ring expansion resulting in the formation of cyclic ketones with one more C atom in the ring.[5] Helling and Hendrickson[6] have reported that the (η^6-phenol)- or (thiophenol)(η^5-cyclopentadienyl)iron cation upon deprotonation in base gave the phenoxide or thiophenoxide complex (**1a,b**) which may be formulated as the neutral complexed cyclic ketone or thioketone (**2a,b**). In the present work, we have investigated the possibility of ring expansion upon reaction of complexes such as **2a,b** with CH_2N_2.

The complex **2a** or **2b** was prepared from reaction of (η^6-chlorobenzene)(η^5-cyclopentadienyl)iron hexafluorophosphate (4) with NaOH or NaSH,[6] and upon treatment with CH_2N_2, the tropone or tropothione complex, **3a** or **3b**,

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[1] Post-doctoral fellow from the Institute of Chemistry, Silesian University, Katowice, Poland.

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