Organometallics **1984,** *3,* 1038–1044

exception of the dissymetrically substituted $Rh_2Cl_2(CO)_2(PR_3)_2$ isomer, and $[Rh(\mu\text{-}Cl)(CO)\{(CH_3)_2PC_6H_5\}]_2$ was even stable enough to allow an X-ray structural determination to be made.[9] A larger excess of ligand then results in bridge cleavage and formation of mononuclear $(CO)ClRh(PR_3)_2$ complexes. Chelating ligands either follow the same reaction pathway[2,12] or displace the chloride bridges by ligand bridges,[13] thus preserving the dinuclear doubly bridged character of the adducts. No example of a singly bridged dinuclear rhodium(I) complex appears to have been reported so far, but the influence of the stoichiometry of these ligands on the issue of the reaction has not been investigated.

The formation of **5a** from a Rh/ligand ratio of 2:1 extends the range of hitherto assumed reaction pathways, as shown in Scheme I. It leads to the proposal that an incoming phosphonite ligand such as Me_4-phoran should first form a monodentate, phosphorus only bound complex corresponding to structure B via a pentacoordinated intermediate A, according to the presently accepted scheme. However, it must be noted that, although several examples of monocoordination of the cyclic aminophosphanes at transition-metal centers through the phosphorus site only have been established,[14] no Rh complex in which these phosphanes behave as monodentate ligands has as yet been identified. The addition of the free nitrogen site could then take place at the same Rh atom to give intermediate C and then **5a** (Scheme Ib). The formation of **5a** may be favored by the constraint caused by the presence of two *gem*-dimethyl groups. It is noteworthy that no P–N bridged complex could be observed. An extension of this pathway to other phosphorus/nitrogen bidentate ligands should be possible, as exemplified by a comparative experiment with the unsubstituted parent compound $H(C_6H_5)P(OCH_2CH_2)_2N$, which, in addition to the mononuclear complex (CO)ClRh(phoran), gives the binuclear complex **5b** analogous to **5a**.

The novel character of this dirhodium species, with a single chlorine bridge, should open new prospects in reactivity and structures. Under the action of nucleophiles and small unsaturated molecules, for example, these reactions may proceed either via a halide bridge cleavage or via a stabilization of the dinuclear arrangement by means of the formation of new, additional, bridges. Preliminary results on the addition of CO, SO_2, and alkynes show indeed that both pathways may be operative; this will be the subject of further investigations.

Acknowledgment. J.W. is grateful to Prof. H. Brunner and F.J., G.L.B., and J.G.R. are grateful to CNRS for generous support of this work.

Registry No. 1a, 90132-09-5; 3a, 70415-00-8; 5a, 90108-65-9; $[Rh(CO)_2Cl]_2$, 14523-22-9.

Supplementary Material Available: Tables of positional and thermal parameters of hydrogen atoms, general temperature factor expressions, and structure factors (14 pages). Ordering information is given on any current masthead page.

---

(11) Gallay, J.; De Montanzon, D.; Poilblanc, R. *J. Organomet. Chem.* **1972,** *38,* 179.

(12) Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1974,** *96,* 3098.

(13) Haines, R. J.; Meintjies, E.; Laing, M. *Inorg. Chim. Acta* **1979,** *36,* L403; Farr, J. P.; Olmstead, M. M.; Hunt, C. H.; Balch, A. L. *Inorg. Chem.* **1981,** *20,* 1182. Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1982,** 387.

(14) Wachter, J.; Jeanneaux, F.; Riess, J. G. *Inorg. Chem.* **1980,** *19,* 2169. Wachter, J.; Mitschler, A.; Riess, J. G. *J. Am. Chem. Soc.* **1981,** *103,* 2121.

Molecular and Electronic Structure of $(CO)_2Co(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]Fe(\eta^5\text{-}C_5H_5)(CO)$

John R. Matachek,[1a] Robert J. Angelici,[1a] Kimberly A. Schugart,[1b] Kenneth J. Haller,[1b] and Richard F. Fenske*[1b]

Department of Chemistry and Ames Laboratory—U.S. DOE, Iowa State University, Ames, Iowa 50011, and Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

Received March 20, 1984

The reaction of $Co(CO)_4^-$ with the dithiocarbene complex $Cp(CO)(MeCN)Fe{=}C(SMe)_2^+$ yields the dinuclear $(CO)_2Co(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]Fe(Cp)(CO)$, which was originally formulated on the basis of spectroscopic results as a compound with the carbon of the $C(SMe)_2$ carbene ligand bridging the Co–Fe bond. An X-ray diffraction study now indicates a sulfur atom of the carbene is also bonded to the Co. The compound crystallizes in orthorhombic space group *Pbca* with eight formula units per unit cell. Cell dimensions are $a = 14.252$ (4), $b = 20.235$ (4), and $c = 10.353$ (2) Å. The structure has been refined to $R = 0.029$. The Co–Fe bond, 2.502 (1) Å, is bridged by a CO group and a carbene ligand, Co–C(carbene), 1.916 (2) Å, and Fe–C(carbene), 1.966 (2) Å. One sulfur atom of the bridging $C(SMe)_2$ unit coordinates to the Co giving a triangular Co–C–S grouping and a highly distorted bridging carbene carbon atom. A molecular orbital calculation provides insight into the bonding interactions that stabilize this unusual bridging carbene ligand.

Introduction

Recent interest in the synthesis and reactivity of bimetallic bridged carbene complexes evolves from the proposed or demonstrated involvement of these and similar species in carbon monoxide reduction chemistry[2] and olefin metathesis[3] along with a variety of other reactions.[4] While a plethora of carbene-bridged complexes exists, only a few

---

(1) (a) Department of Chemistry and Ames Laboratory—U.S. DOE, Iowa State University, Ames, IA. (b) Department of Chemistry, University of Wisconsin—Madison, Madison, WI.

(2) (a) Masters, C. *Adv. Organomet. Chem.* **1979,** *17,* 61. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979,** *79,* 479. (c) Dyke, A. F.; Guerchais, J. E.; Knox, S. A. R.; Roue, J.; Short, R. L.; Taylor, G. E.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981,** 537. (d) Brady, R. C., III; Pettit, R. *J. Am. Chem. Soc.* **1980,** *102,* 6181. (e) Steinmetz, G. R.; Geoffroy, G. L. *Ibid.* **1981,** *103,* 1278. (f) Cooke, M.; Davies, D. L.; Guerchais, J. E.; Knox, S. A. R. *J. Chem. Soc., Chem. Commun.* **1981,** 862. (g) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982,** *21,* 117.

0276-7333/84/2303-1038$01.50/0

Table I. Selected Bond Lengths (Å) and Angles (deg)

Bond Lengths

Fe-Co	2.502 (1)	Co-C(1)	1.800 (2)	C(3)-O(3)	1.176 (3)
Fe-C(3)	1.952 (2)	Co-C(2)	1.761 (3)	C(4)-O(4)	1.143 (3)
Fe-C(6)	1.769 (2)	Co-C(3)	1.899 (2)	C(5)-C(6)	1.420 (3)
Fe-C(5)	2.117 (2)	Co-C(10)	1.916 (2)	C(6)-C(7)	1.424 (3)
Fe-C(6)	2.118 (2)	S(1)-C(10)	1.789 (2)	C(7)-C(8)	1.402 (4)
Fe-C(7)	2.122 (2)	S(1)-C(11)	1.810 (3)	C(8)-C(9)	1.427 (4)
Fe-C(8)	2.110 (2)	S(2)-C(10)	1.770 (2)	C(5)-C(9)	1.406 (3)
Fe-C(9)	2.087 (2)	S(2)-C(12)	1.810 (3)		
Fe-C(10)	1.966 (2)	C(1)-O(1)	1.139 (3)		
Co-S(1)	2.275 (1)	C(2)-O(2)	1.149 (3)		

Bond Angles

C(1)-Co-C(3)	97.74 (10)	Co-Fe-C(3)	48.56 (7)	S(2)-C(10)-Fe	127.41 (12)
C(1)-Co-Fe	50.75 (6)	Co-C(3)-Fe	81.04 (9)	Co-S(1)-C(10)	54.70 (7)
Fe-Co-C(3)	50.40 (7)	Co-C(10)-Fe	80.25 (8)	Co-S(1)-C(11)	108.30 (10)
C(10)-Co-S(1)	49.64 (6)	Co-C(10)-S(1)	75.66 (8)	C(10)-S(2)-C(11)	100.1 (1)
C(10)-Fe-Co	49.00 (6)	S(1)-C(10)-S(2)	117.69 (12)	C(10)-S(2)-C(12)	107.0 (1)
C(10)-Fe-C(3)	94.36 (9)				

theoretical studies have been reported;[5-7] these studies have dealt only with the μ-CH_2 group bridging two identical metal atoms. It was of interest to explore the bonding in a complex in which two different metal atoms were bridged by a carbene group containing sulfur atoms. Two of us had reported[8] such a complex $(CO)_3Co(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]Fe(\eta^5\text{-}C_5H_5)(CO)$, and an X-ray diffraction study was undertaken in order to obtain intermolecular distances and angles that were required for a molecular orbital calculation. To our surprise, the complex did not contain the originally postulated simple bridging carbene group but rather one of the S atoms also coordinated to the Co atom. Herein, we describe the synthesis, spectroscopic characterization, X-ray diffraction results, and molecular orbital calculations on this complex, $(CO)_2Co(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]Fe(\eta^5\text{-}C_5H_5)(CO)$, I, with an unusual bridging carbene group.

Experimental Section

Preparation of $(CO)_2Co(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]Fe(Cp)(CO)$ Where Cp = η^5-C_5H_5. A solution of $Na[Co(CO)_4]$ was prepared in situ by combining $Co_2(CO)_8$ (0.13 g, 0.38 mmol) with finely ground NaOH (1.30 g, 32.5 mmol) in THF (50 mL) under an N_2 atmosphere.[9] After 30 min with occasional shaking, the brown color of $Co_2(CO)_8$ disappeared. The resulting suspension was filtered through a medium glass frit into a Schlenk flask containing $\{Cp(CO)(MeCN)Fe[C(SMe)_2]\}PF_6$ (0.30 g, 0.68 mmol).[10] Upon mixing, the color changed from red to dark brown. After 30 min, the solvent was removed under vacuum, and the residue was extracted with hot hexanes until the extracts were clear. The hexane extracts were combined, filtered through Celite, and evaporated under vacuum to dryness. The resulting purple residue was dissolved in a minimum volume of boiling hexanes; slow cooling to −20 °C gave after 24 h 0.22 g (83%) of the air-stable, crystalline product: mp 103–104 °C; IR (cyclohexane) ν(CO) 2037 (m), 1988 (br s), 1836 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 4.70 (s, 5 H, Cp), 2.70 (s, 3 H, SCH_3), 2.23 (s, 3 H, SCH_3); ^{13}C NMR (CD_2Cl_2, −80 °C, $Cr(acac)_3$) δ 249.59 (s, μ-CO), 212.50 (s, FeCO), 208.77 (s, CoCo), 201.06 (s, CoCo), 176.44 (s, μ-carbene C), 83.27 (s, Cp), 29.97 (s, SCH_3), 24.85 (s, SCH_3); MS (20 eV), m/e 398 (M^+). Anal. Calcd for $C_{12}H_{11}O_4S_2FeCo$: C, 36.20; H, 2.79. Found: C, 36.60; H, 2.93.

X-ray Data Collection and Structure Solution. Crystals of $CoFeS_2C_{12}O_4H_{11}$ suitable for X-ray diffraction study were obtained by cooling a hexane solution of the complex to −20 °C. A single crystal of approximate dimensions 0.30 × 0.30 × 0.35 mm was mounted on a glass fiber for the X-ray study. Preliminary examination of the crystal on a syntex Nicolet P$\bar{1}$ diffractometer showed the crystal to be orthorhombic. The observed systematic absences $0kl$ ($k = 2n + 1$), $h0l = l = 2n + 1$), and $hk0$ ($h = 2n + 1$) uniquely define the space group as *Pbca* (No. 61). The unit cell parameters, determined by a least-squares refinement utilizing the setting angles of 60 reflections ($35° < 2\theta < 41°$) collected at $\pm 2\theta$, are $a = 14.252$ (4), $b = 20.235$ (4), and $c = 10.353$ (2) Å (at −60 (±5) °C; λ(Mo Kα) = 0.71073 Å). The unit cell volume of 2985.7 Å^3 led to a calculated density of 1.76 g/cm^3 for eight formula units of $CoFeS_2C_{12}O_4H_{11}$ per unit cell. The experimental density determined by flotation is 1.63 g/cm^3 (determined at 20 °C).

X-ray intensity data were collected by using a Syntex-Nicolet P$\bar{1}$ diffractometer equipped with a graphite-monochromated Mo Kα radiation source. A total of 3723 unique reflections with $(\sin\theta)/\lambda = 0.669$ Å^{-1} were collected by using a θ–2θ step-scan technique with a scan range of 0.55° below 2θ(Mo Kα_1) to 0.55° above 2θ(Mo Kα_2) and a variable scan rate (2.0–24.0°/min). Throughout data collection four standard reflections from diverse regions of reciprocal space were monitored every 50 reflections. The intensities of the standard reflections showed no systematic variations during the time required to collect the data. The data were reduced and standard deviations calculated by using methods similar to those described previously.[11] Psi scans showed minor intensity variations (~7%) and absorption corrections were not applied (μ = 22.1 cm^{-1}).

The structure was solved by direct methods using the MULTAN[12] package and the 250 reflections with he highest values of $|E|$. The mocel was refined by a full-matrix least-squares technique using the 3126 reflections with $F_o > 3\sigma(F_o)$ and standard values for atomic scattering factors including corrections for anomalous dispersion.[13] After anisotropic refinement of the non-hydrogen atoms a difference electron density map revealed the positions of all 11 hydrogen atoms. The hydrogen atoms were assumed to vibrate isotropically, and their position and thermal parameters were included in the parameters being refined. This final model refined to convergence with $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.029$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} = 0.036$. The final difference

---

(3) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 803.

(4) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

(5) Calabro, D. C.; Lichtenberger, D. L.; Herrmann, W. A. *J. Am. Chem. Soc.* **1981**, *103*, 6852 and references therein.

(6) Xiang, S. F.; Chen, H. W.; Eyermann, C. J.; Jolly, W. L.; Smit, S. P.; Theopold, K. H.; Bergman, R. G.; Herrmann, W. A.; Pettit, R. *Organometallics* **1982**, *1*, 1200.

(7) Clemente, D. A.; Biagini, M. C.; Rees, B.; Herrmann, W. A. *Inorg. Chem.* **1982**, *21*, 3741.

(8) Matachek, J. R.; Angelici, R. J. *Organometallics* **1982**, *1*, 1541.

(9) Edgell, W. F.; Lyford, J., IV *Inorg. Chem.* **1970**, *9*, 1932.

(10) McCormick, F. B.; Angelici, R. J. *J. Organomet. Chem.* **1981**, *205*, 79.

(11) Haller, K. J.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 3552.

(12) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

(13) Atomic form factors were from: Cromer, D. T.; Mann, J. B. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–101, Table 2.2B. Real and imaginary corrections for anomalous dispersion in the scattering factors of the cobalt, iron, and sulfur atoms were from: Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891. The hydrogen scattering factor is from: Stewart, R. F.; Davison, E. R.; Simpson, W. T. *Ibid.* **1965**, *47*, 3157.

Table II. Fractional Coordinates

atom	*x*	*y*	*z*	B_{iso}, Å^2
Fe	0.152 751 (21)	0.376 302 (14)	−0.002 552 (28)	1.32
Co	0.307 927 (21)	0.427 966 (14)	0.048 215 (28)	1.59
S(1)	0.354 07 (4)	0.358 851 (28)	−0.112 98 (5)	1.68
S(2)	0.309 12 (4)	0.267 609 (26)	0.112 70 (5)	1.77
C(1)	0.346 31 (21)	0.507 55 (14)	−0.008 87 (25)	2.77
O(1)	0.372 70 (22)	0.556 92 (11)	−0.047 13 (24)	4.17
C(2)	0.360 81 (19)	0.417 62 (12)	0.200 65 (27)	2.58
O(2)	0.390 87 (18)	0.409 63 (11)	0.302 44 (21)	3.77
C(3)	0.184 98 (17)	0.457 62 (11)	0.088 59 (23)	2.02
O(3)	0.148 64 (13)	0.502 63 (9)	0.140 14 (20)	2.77
C(4)	0.115 15 (16)	0.343 28 (11)	0.146 92 (21)	1.85
O(4)	0.087 02 (13)	0.322 31 (9)	0.241 82 (17)	2.63
C(5)	0.138 10 (16)	0.336 54 (12)	−0.190 62 (21)	1.78
C(6)	0.146 50 (17)	0.406 36 (12)	−0.198 30 (21)	1.84
C(7)	0.069 52 (18)	0.434 12 (13)	−0.129 49 (24)	2.13
C(8)	0.015 51 (17)	0.382 56 (12)	−0.078 04 (24)	2.03
C(9)	0.058 86 (17)	0.321 87 (12)	−0.114 93 (22)	1.98
C(10)	0.278 03 (15)	0.336 98 (10)	0.017 70 (20)	1.47
C(11)	0.469 38 (18)	0.327 30 (15)	−0.073 56 (28)	2.36
C(12)	0.263 57 (25)	0.201 75 (13)	0.012 42 (27)	2.73
H(5)	0.1792 (17)	0.3065 (14)	−0.2265 (26)	2.2 (5)
H(6)	0.1918 (18)	0.4304 (13)	−0.2437 (29)	2.7 (6)
H(7)	0.4473 (23)	0.5237 (16)	0.380 (3)	4.3 (8)
H(8)	0.4654 (22)	0.3881 (14)	0.5260 (28)	2.8 (6)
H(9)	0.0381 (20)	0.2791 (13)	−0.0924 (28)	3.0 (6)
H(11A)	0.4794 (22)	0.3276 (15)	0.019 (3)	3.7 (7)
H(11B)	0.5060 (25)	0.3548 (16)	−0.113 (3)	4.3 (8)
H(11C)	0.4757 (22)	0.2853 (16)	−0.106 (3)	4.2 (8)
H(12A)	0.2945 (20)	0.2030 (14)	−0.074 (3)	3.0 (6)
H(12B)	0.2792 (21)	0.1600 (15)	0.0574 (28)	3.2 (6)
H(12C)	0.2003 (24)	0.2070 (15)	0.004 (3)	3.3 (7)

[a] The estimated standard deviations of the least significant digits are given in parentheses. [b] Isotropic equivalents of the anisotropic thermal parameters are given for the atoms that were varied anisotropically.

map was featureless. The estimated error in an observation of unit weight was 1.18, and the final data to variable ratio was 13.9. A listing of the final observed and calculated structure factors (×10) is available as supplementary material. Table I presents selected interatomic distances and angles. Atomic coordinates are listed in Table II. (The anisotropic thermal parameters for the non-hydrogen atoms are included in the supplementary material).

Details of MO Calculations

The Fenske–Hall SCF method, an approximation to Hartree–Fock–Roothaan LCAO MO technique, has been described elsewhere,[14] and its applications have been reviewed.[15] Since the method is devoid of empirical parameters, the result of calculations, eigenvectors and eigenvalues, is completely determined by the geometry of the molecule as well as by the size and nature of the atomic basis set. Clementi's double-ζ functions[16] were used for C, O, and S. However, only the valence shell p functions were kept as double-ζ and all other functions were curve fit to single-ζ forms.[16,17] Fe and Co functions were taken from the tables of Richardson et al. Separate calculations were first carried out on ligands CO, μ-CO, C_5H_5, and $C(SCH_3)_2$. The resulting molecular orbitals of the free ligand were used in the calculation of the complex to facilitate interpretation of the ligand contribution to orbitals of the complex.

Results and Discussion

Synthesis of $(CO)_2Co(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]Fe(Cp)(CO)$, I. The reaction of the terminal dithiocarbene complex $(Cp)Fe(CO)(NCMe)[{=}C(SMe)_2]^+$ with $Co(CO)_4^-$ at room temperature gives an 83% yield of the unusual bridging carbene complex I as air-stable purple crystals according to 1. The same product is obtained although

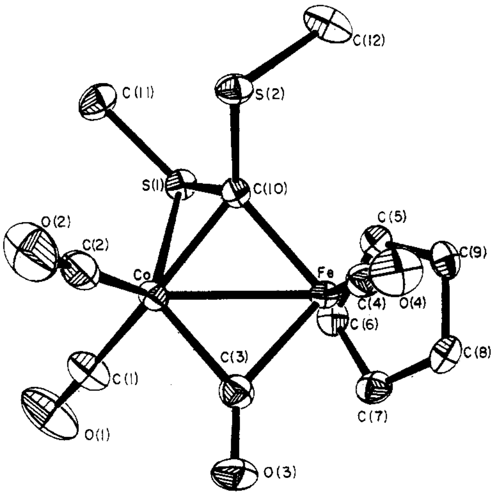
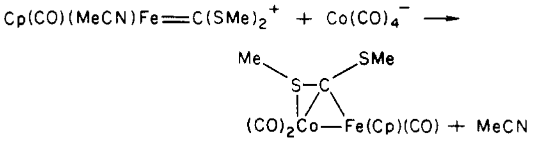


Figure 1. ORTEP of bridged dithiocarbene compound.



$$Cp(CO)(MeCN)Fe{=}C(SMe)_2^+ + Co(CO)_4^- \longrightarrow (CO)_2Co(\mu\text{-}C(SMe)(SMe))Fe(Cp)(CO) + MeCN + CO \quad (1)$$

I

in somewheat lower yield (~60%) when $Cp(CO)_2Fe{=}C(SMe)_2^+$[18] is used as the carbene reactant. There is no IR

---

(14) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

(15) Fenske, R. F. *Prog. Inorg. Chem.* **1976**, *21*, 179.

(16) Clementi, E. *J. Chem. Phys.* **1964**, *40*, 1944.

(17) Radtke, D. D. Ph.D. Dissertation, University of Wisconsin—Madison, Madison, WI, 1966.

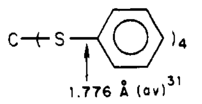
(18) McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1979**, *18*, 1231.

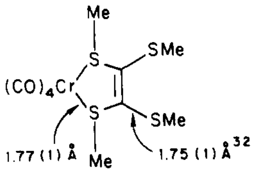
evidence for a simple bridging carbene complex intermediate, $(CO)_3Co(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]Fe(Cp)(CO)$, in which an S atom is not coordinated to the Co.

Molecular Structure of $(CO)_2Co(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]Fe(Cp)(CO)$, I. The atom labeling scheme and molecular geometry of the bridged dithiocarbene are shown in Figure 1. Important bond lengths and angles are given in Table I, and atomic coordinates for the atoms are listed in Table II. The crystallographically determined structure structure differs from that originally proposed[8] in that the bridging carbene group $C(SMe)_2$ not only bonds to the Fe and Co atoms through the carbene carbon, but in addition, one of the S atoms coordinates to the Co in place of a CO group. The Fe–Co distance of 2.502 (1) Å is somewhat shorter than corresponding distances in $(CO)_3Co(\mu\text{-}CO)_2Fe(Cp)(CO)$, 2.545 (1) Å,[19] and the indenyl analogue $(CO)_3Co(\mu\text{-}CO)_2Fe(\eta\text{-}C_9H_7)(CO)$, 2.552 (2) Å.[20] The bridging system in I is nonplanar with the angle between te Co–C(10)–Fe and C–C(3)–Fe planes being 154.4°, which compares with 143.5° and 148.0° in the carbonyl derivatives.[19,20]

The geometry around the bridging carbene carbon C(10) is unusual in the sense that C(10), S(1), S(2), and Fe are nearly coplanar; the sum of the angles around C(10) to S(1), S(2), and Fe are 356.8°. The Fe–C(10) bond distance of 1.966 (2) Å is very similar to those observed in other Fe(Cp)(CO) carbene-bridged compounds: $(\mu\text{-}CO)(\mu\text{-}CHCH_3)[Fe(Cp)(CO)]_2$, 1.987 (1) Å;[21] $(\mu\text{-}CO)(\mu\text{-}CHCO_2\text{-}t\text{-}Bu)[Fe(Cp)(CO)]_2$, 1.97 (3), 2.00 (2) Å.[22] It is, however, longer than the average distance of 1.921 Å observed in the disordered structure $(CO)_4Mn(\mu\text{-}CO)(\mu\text{-}CH_2)Fe(Cp)(CO)$.[23] The Co–C(10) bond length of 1.916 (2) Å compares with the following values in other cobalt bridging carbene complexes: $(\mu\text{-}CO)[m\text{-}\overline{CCH{=}CHC({=}O)O}][Co(CO)_3]_2$, 1.93 Å (av);[24] $(\mu\text{-}CHCo_2Et)[Co(Cp)(CO)]_2$, 1.95 Å (av);[25] $[\mu\text{-}\overline{CC({=}O)C_6H_4C}({=}O)][Co(Cp)(CO)]_2$, 1.916 (4), 1.973 (4) Å;[26] $(\mu\text{-}CO)(\mu\text{-}CH_2)[Co(Me_5Cp)]_2$, 1.909 (9) Å;[27] and $(\mu\text{-}CH_2)[Co(Me_5Cp)(CO)]_2$, 1.907 (10), 1.943 (8) Å.[28] The Co–C(10)–Fe angle, 80.25 (8) Å, is in the range (76–81°) that is typical[4] of μ-carbene compounds.

The plane described by Co, C(10), and S(1) triangle makes an angle of 115.5° with the plane defined by Co, C(10), and Fe. The unusual $\overline{\text{Co, C(10), S(1)}}$ triangle is reminiscent of mononuclear $\overline{M\text{–}CH_2S}Me$ complexes in which the following CS bond distances in the three-membered ring are known: $(Ph_3P)_2Pd(\eta^2\text{-}CH_2SMe)^+$, 1.77 (4) Å, 1.678 (14) Å;[29e] $(Ph_3P)(Cl)Pd(\eta^2\text{-}CH_2SMe)$, 1.756 (6) Å;[29g] $Cp(CO)_2Mo(\eta^2\text{-}CH_2SMe)$, 1.78 (1) Å;[29b] $[Me_2Ga(N_2C_3H_3)(OCH_2CH_2NMe_2)]Mo(CO)_2(\eta^2\text{-}CH_2SMe)$, 1.744 (3) Å.[29d] Although the C(10)–S distance, 1.789 (2) Å, in I is comparable to these values, it is shorter than C–S single bonds in ethylene sulfide (1.819 (1) Å)[30] and tetrahydrothiophene (1.839 (1) Å).[30] It is however, similar to C(sp²)–S distances in the molecules It is evident, even from this





limited comparison, that C–S bond distances in triangular metal–C–S units result in an ambiguous interpretation of the bonding between the C and S atoms and the C and S bonding interactions with the metal. For this reason, the molecular orbital calculations were of particular interest. It should be noted that the sulfur distances, 1.810 (3) Å, to the methyl groups are longer than either of the C(10)–S distances and the C–S–C angles around S(1), 100.1 (1)°, and S(2), 107.0 (1)°, differ considerably.

Originally, the IR, ^1H and ^{13}C NMR, and mass spectra were interpreted in terms of a structure in which the $C(SMe)_2$ ligand was bonded to the Co and Fe atoms only through the bridging carbene carbon atom. These spectroscopic results (see Experimental Section) are even more consistent with the S-coordinated structure established by X-ray diffraction. The mass spectrum shows a parent ion for the complex. In the ^1H and ^{13}C NMR spectra, the two types of methyl groups give separate resonances. In the ^{13}C NMR spectrum, resonances for the terminal CO groups, the bridging CO, and the bridging carbene carbon are all readily assigned. The infrared spectrum shows ν(CO) absorptions for both the terminal (2037 (m), 1988 (br, s) cm^{-1}) and bridging (1836 (m) cm^{-1}) carbonyl groups.

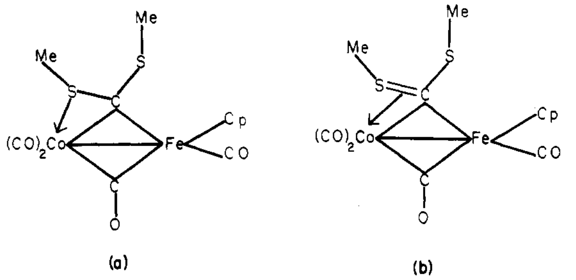


Figure 2. Valence bond description of two possible bonding modes.

Molecular Orbital Investigation of $(CO)_2Co(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]Fe(Cp)(CO)$, I. A valence bond description of two modes of bonding in the complex is depicted in Figure 2. Figure 2a depicts an entirely σ-bonding framework between the cobalt, carbene carbon, and sulfur that compose a triangular ring. Figure 2b shows a π-bonding system in which the metal atom acts as a π acceptor. While a and b are completely different from each

---

[19] Campbell, I. L. C.; Stephens, F. S. *J. Chem. Soc., Dalton Trans.* **1975**, 22.

[20] Stephens, F. S. *J. Chem. Soc., Dalton Trans.* **1974**, 13.

[21] (a) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1980**, 441. (b) Meyer, B. B.; Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1981**, *20*, 3024.

[22] Herrmann, W. A.; Plank, J.; Bernal, I.; Creswick, M. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35*, 680.

[23] Gadol, S. M.; Davis, R. E. *Organometallics* **1982**, *1*, 1607.

[24] Mills, O. S.; Robinson, G. *Inorg. Chim. Acta* **1967**, *1*, 61.

[25] Herrmann, W. A.; Schweizer, I.; Creswick, M.; Bernal, I. *J. Organomet. Chem.* **1979**, *165*, C17.

[26] Creswick, M.; Bernal, I.; Herrmann, W. A.; Steffl, I. *Chem. Ber.* **1980**, *113*, 1377.

[27] Halbert, T. R.; Leonowicz, M. E.; Maydonovitch, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 5102.

[28] Herrmann, W. A.; Huggins, J. M.; Bauer, C.; Smischek, M.; Pfisterer, H.; Ziegler, M. L. *J. Organomet. Chem.* **1982**, *226*, C59.

[29] (a) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1965**, *4*, 486. (b) deGil, E. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 3751. (c) Yoshida, G.; Kurosawa, H.; Okawara, R. *J. Organomet. Chem.* **1977**, *131*, 309. (d) Chong, K. S.; Retting, S. J.; Storr, A.; Trotter, S. *Can. J. Chem.* **1980**, *58*, 1080. (e) Mikl, K.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3639. (f) McPherson, H. M.; Wardell, J. L. *Inorg. Chim. Acta* **1983**, *75*, 37. (g) Miki, K.; Kai, Y.; Yasuoka, N.; Kasai, N. *J. Organomet. Chem.* **1979**, *165*, 79.

[30] Oae, S. "Organic Chemistry of Sulfur"; Plenum Press: New York, 1977.

[31] Kato, K. *Acta Crystallogr., Sect. B* **1972**, *B28*, 606.

[32] Lappert, M. F.; Shaw, D. B.; McLaughlin, G. M. *J. Chem. Soc., Dalton Trans.* **1979**, 427. Collins, R. C.; Davis, R. E. *Acta Crystallogr., Sect. B* **1978**, *B34*, 283.

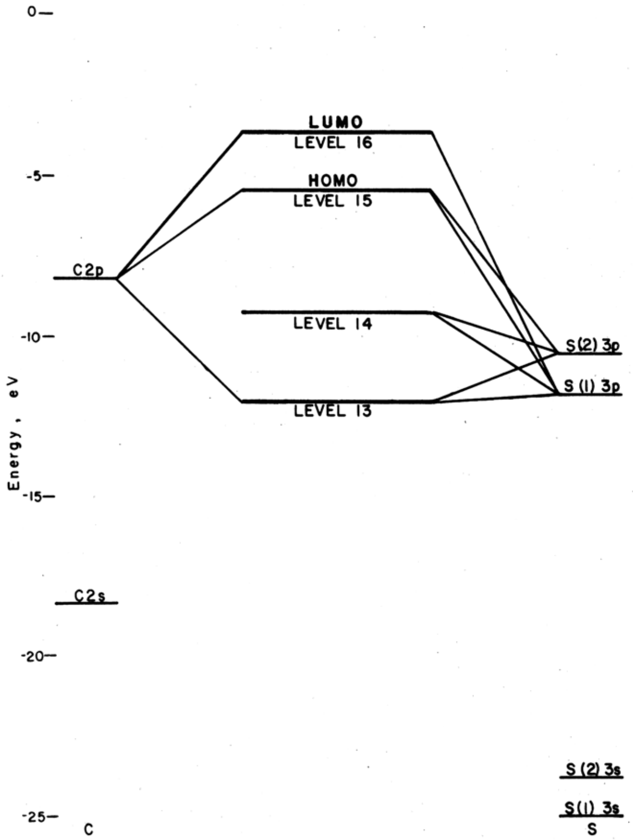


Figure 3. Molecular orbital diagram depicting frontier levels of the dithiocarbene ligand.

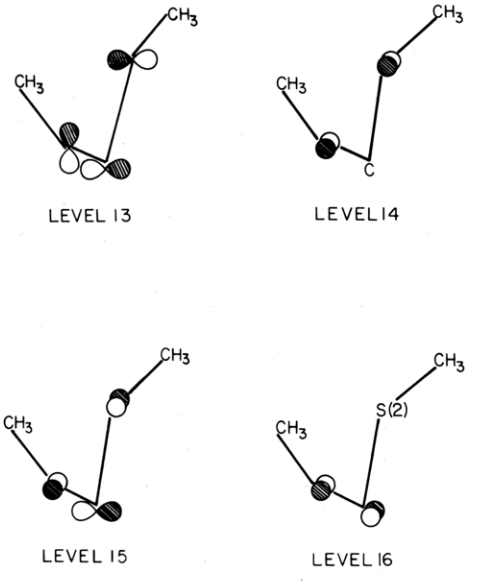


Figure 4. Arrangement of the atomic orbitals of the dithiocarbene compound.

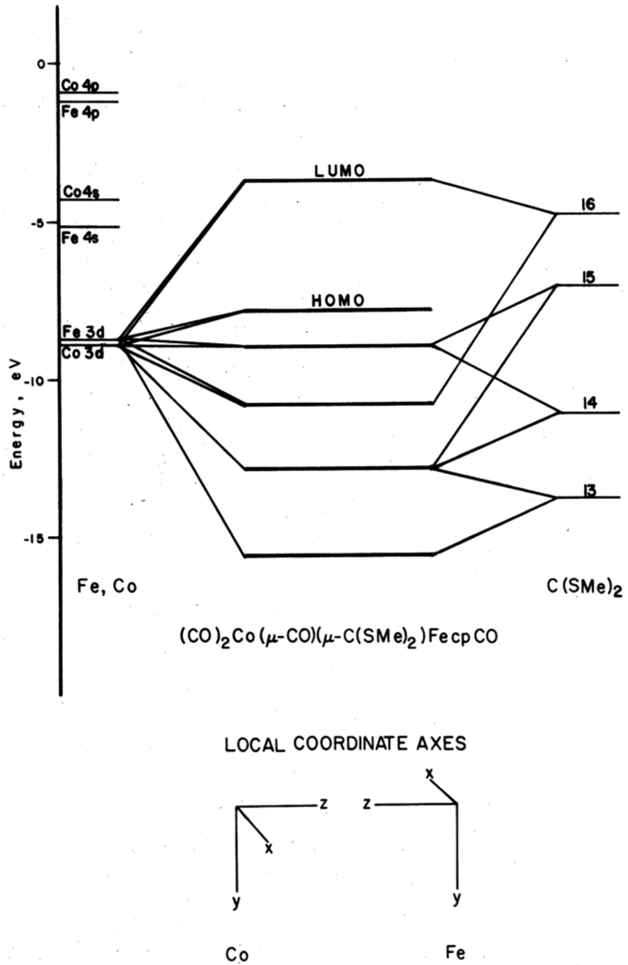


Figure 5. Molecular orbital diagram showing only dithiocarbene interactions with the metals.

other, it must be remembered that these two pictures are extremes and a third mode of bonding, a hybridization of a and b, could also occur.

To elucidate the type of bonding in the three-membered ring, it is easiest to first examine the dithiocarbene ligand as a separate entity. A molecular orbital diagram of the frontier orbitals of the dithiocarbene ligand is shown in Figure 3, and the arrangement of atomic orbitals in each of the energy levels is shown in Figure 4. From the molecular orbital diagram and orbital sketches of Figures 3 and 4, it is apparent that the p orbitals are responsible for interactions of the ligand atoms at the level of the frontier orbitals. Level 13 consists of p orbitals on all three atoms but is located primarily on sulfur 1, the sulfur atom that is part of the three-membered ring. Level 14 is a nonbonding level that consists only of two sulfur atoms that interact minimally due to the distance that separates them. This level is located primarily on sulfur 2, the sulfur atom that does not participate in the ring formation. Level 15 is the HOMO of the dithiocarbene ligand and consists of the orbitals located on all three atoms. This level is located primarily on the carbene carbon atom, and the p orbitals of the sulfur atoms contribute equal amounts of character but much less character than the carbon. Level 16, the LUMO, is an antiboding orbital and is the most significant ligand orbital. This level consists essentially of the carbene carbon atom and the sulfur atom that participate in the ring structure.

A molecular orbital diagram depicting metal–dithiocarbene interactions is shown in Figure 5. Table III describes all valence and frontier level molecular orbitals. The lowest level of energy at which the metal center interacts with the frontier orbitals of the dithiocarbene ligand is in orbital 33 at −15.62 eV. Dithiocarbene ligand level 13 interacts in a stabilizing manner with a linear combination of d orbitals on the iron atom that hybridize to accomodate the ligand orbital. The primary interaction in this orbital is the formation of a σ bond between the iron and the carbene carbon. Although orbitals on both sulfur atoms are available for bonding, they are too distant to interact with the iron. The level above this one, orbital 37, at −12.92 eV is more complicated in composition and interaction. Here, dithiocarbene ligand levels 13, 14, and 15 linearly combine to produce a rehybridized ligand orbital that interacts with an appropriately hybridized linear combination of cobalt d functions. This interaction of

Table III. Contributions to Frontier Molecular Orbitals[a,b]

orbital	orbital energy, eV	Co	Fe	μ-C(SCH$_3$)$_2$	μ-CO	$C_5H_5^-$	terminal COs
48	−1.81		11.21 $x^2 - y^2$ 7.67 xy 18.86 xz 9.92 4p$_x$	4.78 (16)		18.22 (e_1'') 4.17 (e_1'')	
47[c]	−3.54	11.48 z^2 4.80 4p$_z$	34.43 z^2	5.44 (16)	6.03 (5σ)		
46[c]	−7.85	5.27 $x^2 - y^2$ 4.28 xy 37.17 yz 5.21 4p$_y$	5.65 z^2 6.53 $x^2 - y^2$ 8.24 yz				
45	−8.81	11.96 z^2 4.22 xy 19.31 xz	24.95 yz				6.54 (2π cobalt)
44	−8.97	16.17 $x^2 - y^2$ 4.63 xy 7.49 yz	4.59 z^2 4.78 $x^2 - y^2$	16.81 (14) 25.53 (15)			
43	−9.27	13.53 $x^2 - y^2$ 4.57 xy 10.05 yz	25.90 xy	9.47 (15)			4.17 (2π cobalt) 4.52 (2π iron)
42	−9.42	22.75 xy	9.35 $x^2 - y^2$ 8.50 xy 4.20 xz 7.17 yz		10.12 (2π) 5.24 (2π)		
41	−9.43	20.58 xz	9.18 $x^2 - y^2$ 18.19 xz 12.38 yz		7.63 (5σ)		
40	−9.87	45.97 z^2 7.26 $x^2 - y^2$ 6.35 xy	6.18 z^2	8.13 (14)			
39	−9.99	13.38 $x^2 - y^2$ 8.51 yz	12.87 xy 9.0 xz 11.72 yz	6.46 (15)			
38	−10.80	5.89 $x^2 - y^2$ 11.10 xy 6.09 xz	6.60 z^2 8.77 $x^2 - y^2$ 3.42 xy	5.2312 29.69 (16)			
37	−12.92	4.64 z^2 4.01 xy		5.23 (11) 27.01 (13) 33.44 (14) 8.19 (15)			
36	−13.95		4.43 $x^2 - y^2$	16.11 (12) 9.83 (13)		13.02 (e_1'') 30.74 (e_1'')	
35	−14.52		6.87 z^2 7.68 xy 6.04 4p$_z$			49.75 (e_1'') 17.44 (e_1'')	
34	−15.14			38.79 (11) 24.76 (12)		17.92 (e_1'')	
33	−15.62		4.69 $x^2 - y^2$ 12.36 xz	39.34 (13) 4.67 (14) 5.40 (15)			

[a] Contributions greater than 4% for any orbital. Numbers in parentheses refer to a thiocarbene fragment orbital number. [b] Coordinate system designated in molecular orbital diagram (Figure 6). [c] Horizontal broken line separates HOMO (46) and LUMO (47).

ligand and metal levels forms one of the delocalized σ bonds that compose the basic triangular framework among the cobalt, sulfur, and carbene carbon atoms.

Dithiocarbene ligand level 16, the LUMO of the dithiocarbene fragment, interacts with the metal centers in a slightly different manner than levels 13, 14, and 15. In orbital 38, iron and cobalt character are present in allmost equal amounts. Their interaction with dithiocarbene ligand level 16 can be described as follows. The iron d functions overlap with the carbon p orbital alone since the sulfur orbital is too distant. The cobalt, however, can overlap with both the carbene carbon and the sulfur atom that compose the triangular ring, forming a π bond between the metal and the ligand. The interaction of both metal atoms with the dithiocarbene ligand in this molecular orbital results in a net flow of electrons from filled metal orbitals into an empty ligand orbital. The extent of this interaction is quite large; Mulliken population analysis shows 0.809 electron reside in the formerly empty ligand LUMO.

Orbital 44 at −8.97 eV is composed of iron and cobalt d orbitals and dithiocarbene ligand levels 14 and 15. Ligand levels 14 and 15 have rehybridized forming a symmetry equivalent complement to the available combination of metal d orbitals. The result of this last metal–ligand interaction is a σ bond between the carbene carbon and each metal atom.

The crystal structure and molecular orbital calculation show the loss of a terminal carbonyl from the cobalt atom in the expected product $(CO)_3Co(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]Fe(Cp)(CO)$ can be attributed to the ability of the dithiocarbene sulfur to bond to the cobalt. The consequent transfer of bonding density in both directions augments the valence bond description of Figure 3 and suggests a more complex mode of metal–ligand interaction, viz., a σ framework among the three atoms and a back-bond from the cobalt to the ligand. Stone and co-workers[33] had

---

(33) Howard, J. A. K.; Mead, K. A.; Moss, J. R.; Navarro, R.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, 743.

previously observed that the replacement of a tungsten CO group in the bridging carbene complex $(CO)_5W[\mu\text{-}C(OMe)(aryl)]Pt(PMe_3)_2$ with a PMe_3 ligand shortens the W–C(carbene) bond from 2.48 (1) to 2.37 (1) Å. This shortening may be understood in terms of increased π bonding from the W to the carbene carbon, which stabilizes the compound. Such a π bonding must also be responsible in part for the stability of I.

One other interesting aspect of the molecular orbital calculations on this compound is the extensive interaction of both iron and cobalt d functions in a single molecular orbital. This admixture is apparent in levels 38 and 44 and can be traced to the near degeneracy of cobalt and iron d functions. Since sizable percentages of iron and cobalt character are found together, we predict that experimental measurements such as photoelectron spectroscopy would reflect this admixture.

Acknowledgment. This research was supported by the National Science Foundation, Grant No. CHE-8207434 (R.F.F.), and the U.S. DOE (R.J.A.).

Registry No. I, 83043-22-5; $Na[Co(CO)_4]$, 14878-28-5; $\{Cp(CO)(MeCN)Fe[C(SMe)_2]\}PF_6$, 77781-29-4; Co, 7440-48-4; Fe, 7439-89-6.

Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms and calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

Reactivity of Diphosphenes, Phospharsenes, and Diarsenes toward Transition-Metal Carbonyls

A. H. Cowley,* J. E. Kilduff, J. G. Lasch, N. C. Norman, M. Pakulski, F. Ando, and T. C. Wright

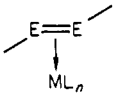
Department of Chemistry, University of Texas at Austin, Austin, Texas 78712

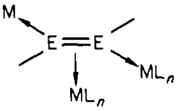
Received December 27, 1983

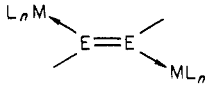
The reactivity of stable diphosphenes, phospharsenes, and diarsenes toward transition-metal carbonyls has been explored. The diphosphene $(2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2P_2$, **2**, forms adducts with one $Fe(CO)_4$ and one $Ni(CO)_3$ group from reactions with $Fe_2(CO)_9$ and $Ni(CO)_4$, respectively. The iron complex $(2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2P_2Fe(CO)_4$, **3**, has been structurally characterized by X-ray diffraction. Compound **3** crystallizes in the monoclinic space group $P2_1/c$, with a = 21.251 (6) Å, b = 9.793 (2) Å, c = 20.99 (2) Å, and β = 108.73 (6)°. The structure reveals that the diphosphene **2** is η^1 bonded to the $Fe(CO)_4$ group through a phosphorus lone pair. The phospharsene $2,4,6\text{-}t\text{-}Bu_3C_6H_2As{=}PCH(SiMe_3)_2$, **8**, reacts with $Fe_2(CO)_9$ to give complexes with an $Fe(CO)_4$ group attached to As, **9**, or P, **10**. Treatment of the diarsene $2,4,6\text{-}t\text{-}Bu_3C_6H_2As{=}AsCH(SiMe_3)_2$, **11**, with $Cr(CO)_5(THF)$ affords the complex $2,4,6\text{-}t\text{-}Bu_3C_6H_2As{=}AsCH(SiMe_3)_2Cr(CO)_5$, **12**, with the $Cr(CO)_5$ unit η^1 bonded to the $(Me_3Si)_2CH$-substituted arsenic. This was determined by an X-ray diffraction study. Compound **12** crystallizes in the monoclinic space group $P2_1/n$ with a = 10.710 (3) Å, b = 29.770 (3) Å, c = 11.984 (1) Å, and β = 98.02 (1)°. The structures of and bonding in these complexes are discussed.

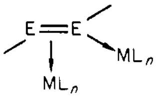
Introduction

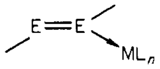
The coordination chemistry of compounds featuring double bonds between the heavier group 5A elements existed prior to the isolation of stable uncomplexed systems. Examples of diphosphene complexes include $[(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}P_2H_2)]$,[1] $[Pd(\eta^2\text{-}Ph_2P_2)(Ph_2PCH_2PPh_2)]$,[2] $[Ni(\eta^2\text{-}(Me_3Si)_2P_2)(Et_3P)_2]$,[3] and $[Pt(\eta^2\text{-}(C_6F_5)_2P_2)(Ph_3P)_2]$.[4] In all these complexes and the arsenic analogues $[Fe(\eta^2\text{-}(C_6F_5)_2As_2)(CO)_4]$[5] and $[Pt(\eta^2\text{-}(C_6F_5)_2As_2)(Ph_3P)_2]$,[5] the ligands adopt a trans conformation and the η^2-bonding mode A. Another bonding mode, B, has been observed in complexes of composition $(PhE{=}EPh)(M(CO)_5)_3$ (E = As,[6] Sb;[7], M = Cr,[6] W[7]). Six-electron donation on the part of the diarsene or distibene ligand is achieved by η^2 bonding to one $M(CO)_5$ moiety and η^1 bonding to the other two. The phenyl groups are trans in both cases.


A


B


C


D


E


F

Recent work by Power et al. has resulted in two new modes of ligation, C and D. Thus, treatment of $(Me_3Si)_2CHPCl_2$ with $[Fe(CO)_4]^{2-}$ afforded $[trans\text{-}\{[Fe(CO)_4]_2[PCH(SiMe_3)_2]_2\}]$,[8] an example of a type C complex in which each phosphorus lone pair bonds to an $Fe(CO)_4$ group in an η^1 fashion. This is the first example of a diphosphene complex containing an unsupported P=P double bond. A similar complex of the isoelectronic ligand $(Me_3Si)_2NP{=}PN(SiMe_3)_2$ has also been described.[9] On the other hand, the reaction of $(2,4,6\text{-}t\text{-}Bu_3C_6H_2O)PCl_2$ with $[Fe(CO)_4]^{2-}$ resulted in a type D complex featuring one η^1- and one η^2-bonded $Fe(CO)_4$ group.[10]

---

[1] (a) Green, J. C.; Green, M. L. H.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1974**, 212. (b) Cannillo, E.; Coda, A.; Prout, K.; Daran, J.-C. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2608.

[2] Chatt, J.; Hitchcock, P. B.; Pidcock, A.; Warrens, C. P.; Dixon, K. R. *J. Chem. Soc., Chem. Commun.* **1982**, 932.

[3] (a) Deppisch, B.; Schäfer, H. *Acta Crystallogr., Sect. B* **1982**, *B38*, 748. (b) Schafer, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 1358.

[4] Elmes, P. S.; Scudder, M. L.; West, B. O. *J. Organomet. Chem.* **1976**, *122*, 281.

[5] Elmes, P. S.; Leverett, P.; West, B. O. *J. Chem. Soc., Chem. Commun.* **1971**, 747.

[6] Huttner, G.; Schmid, H.-G.; Frank, A.; Orama, O. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 234.

[7] Huttner, G.; Weber, U.; Sigwarth, B.; Scheidsteger, O. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 215.

[8] Flynn, K. M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 2085.

[9] Flynn, K. M.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 7460.

0276-7333/84/2303-1044$01.50/0