

Both orbitals are primarily sulfur based, so that efficient overlap in the transition state is best achieved via addition at sulfur as opposed to nitrogen. The stereospecificity of the reaction has no ready explanation on symmetry grounds. Exo- α addition would give rise to a small but positive stabilization of the transition state by the second olefin π bond, but steric factors may well be more important.

Calculations on a Nonplanar $H_2PS_2N_3$ Model. In addition to studying the planar $H_2PS_2N_3$ system described above, we have carried out an analogous calculation using a nonplanar conformation (with C_s symmetry). In this second calculation, the PS_2N_3 ring geometry was identical with that observed for the $Ph_3PS_2N_3$ molecule, with the phosphorus atom displaced by 0.28 Å from the plane of the other five atoms. We find that this model is somewhat lower in energy (by 15 kcal/mol) than the planar structure, but the ordering and spacing of the energy levels remain essentially unchanged. The PN_a bonds have exactly the same net overlap population (of 0.230) but are slightly less polar ($q_P = 0.12$, $q_N = -0.41$) than in the planar conformation. Evidently, slight distortions from planarity lead to a more uniform charge distribution within the ring.

Conclusion

The phosphadithiatriazenes $R_2PS_2N_3$ **1** (R = Me, Ph, OPh) represent novel examples of a cyclic inorganic ring system possessing eight π electrons. SCF Hartree-Fock-Slater ab initio

(43) For a similar treatment of the S_4N_4 /norbornadiene reaction, see: Yanabe, T.; Tanaka, K.; Tachibana, A.; Fukui, K. *J. Phys. Chem.*, **1979**, *83*, 767.

calculations on the model compound $H_2PS_2N_3$ confirm the validity of the HMO method in describing the basic features of the PS_2N_3 ring system. The concept of σ/π separability has been shown to be a reasonable assumption, and the importance of 3d orbitals on phosphorus in stabilizing antibonding π levels has been demonstrated. The intense low-energy absorption which is characteristic of these molecules has been assigned to a $HOMO(\pi^*) \rightarrow LUMO(\pi^*)$ transition. The thermally allowed ($8_s + 2_s$) cycloaddition of norbornadiene to the phosphadithiatriazene ring suggests that other planar or near-planar sulfur-nitrogen heterocycles may also undergo thermally or photochemically initiated cycloaddition reactions.

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Registry No. **1** (R = Ph), 80326-52-9; **1** (R = Me), 80326-53-0; **1** (R = OPh), 80326-54-1; **2** (R = Ph), 80326-55-2; **2** (R = Me), 80339-90-8; **2** (R = OPh), 80326-56-3; tetrasulfur tetranitride, 28950-34-7; tetraphenyldiphosphine, 1101-41-3; tetramethyldiphosphine, 3676-91-3; triphenyl phosphite, 101-02-0; norbornadiene, 121-46-0.

Supplementary Material Available: A listing of structure factor amplitudes and tables of hydrogen atom positions (SI) and thermal parameters (SII) for **1** (R = Ph) and **2** (R = Ph) (19 pages). Ordering information is given on any current masthead page.

$Fe_2(\mu-E_2)(CO)_6$ (E = S, Se, and Te) as Reagents for the Preparation of Mixed-Metal Chalcogenide Clusters

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Abstract: The compounds $Fe_2(\mu-E_2)(CO)_6$, where E = S, Se, and Te, react efficiently with $Pt(PPh_3)_2C_2H_4$ to afford the new heterometallic clusters, $(CO)_6Fe_2(\mu_3-E)_2Pt(PPh_3)_2$. This reaction formally involves the homolytic cleavage of the E-E bond in the $\mu-E_2$ precursor complexes and represents a novel route to mixed-metal clusters. ³¹P NMR of $(PPh_3)(CO)_5Fe_2(\mu_3-S)_2Pt(PPh_3)_2$ (prepared from $Fe_2(\mu-S_2)(CO)_5(PPh_3)$) indicates that the plane of the Pt coordination sphere is perpendicular to the iron-iron vector. The structure of $(CO)_6Fe_2(\mu_3-Se)_2Pt(PPh_3)_2$ was determined by conventional X-ray crystallographic techniques. The crystals were monoclinic with $a = 10.944$ (2) Å, $b = 16.321$ (3) Å, $c = 23.135$ (4) Å, $\beta = 94.68$ (1)°, $Z = 4$; the space group is $P2_1/n$. Conventional full-matrix least-squares refinement with nonhydrogen atoms anisotropic and fixed hydrogen atoms isotropic gave $R_1 = 0.037$ and $R_2 = 0.040$ for 7119 reflections having 2θ Mo $K\alpha < 58.7^\circ$ and $I > 3\sigma(I)$. The structure consists of an isosceles triangle of metal atoms tethered by two capping μ_3 -Se moieties. The two $Fe(CO)_3$ units are mutually bonded, and this fragment closely resembles $Fe_2(\mu-Se_2)(CO)_6$ with an expanded Se-Se vector. We reconcile the reactivity of these $\mu-E_2$ compounds and the chemical dormancy of species such as Ph_2Te_2 and monometallic S_2 complexes as being both electronic and steric (ring strain) in origin.

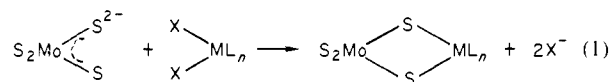
The chemistry of transition-metal chalcogenides is presently expanding at a rapid rate commensurate with the structural, spectroscopic, and chemical novelty of these compounds. Recognized goals in this area of inorganic chemistry include the synthesis of models for important biological² and industrial³ catalysts and the preparation of materials for energy storage and conversion.⁴ Of particularly topical interest is the prospect that

discrete metal chalcogenide clusters may prove to be functional analogues of the catalytic sites in nitrogenase⁵⁻⁷ and hydrodesulfurization catalysts.⁸

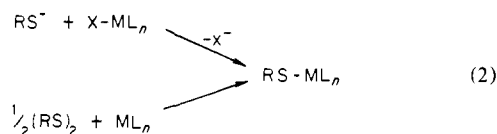
(1) (a) University of Nebraska. (b) University of Illinois.
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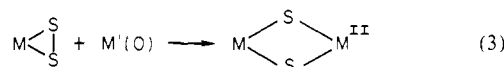
The development of rational syntheses for metal chalcogenide clusters must be predicated upon an understanding of the reactivity of the chalcogenide functional groups found in metal complexes. For example, the synthetic chemistry of tetrathiometalates as developed by Müller and co-workers⁹ (eq 1) has been heavily exploited for the preparation of iron-molybdenum aggregates.⁵⁻⁷



The reactivity of the thiometalates toward metal ions is comparable to the coordination chemistry of organic thiolates. Since synthetic methods employing organic disulfides often complement those for the thiolate anion¹⁰ (eq 2), it was logical to try to extend the



analogy to inorganic disulfides (eq 3).^{11,12} In view of the large



and growing numbers of S₂ complexes, this synthetic approach may prove to be of considerable preparative value. While the results outlined in this paper are primarily concerned with bridging dichalcogenide functionalities in diiron carbonyls, the same methodology should be applicable to other systems such as the μ-S₂ dimolybdenum complexes recently prepared and characterized by Green,¹³ Müller,¹⁴ and co-workers. Similarly, these results bear on a range of electronically equivalent bimetallic complexes which contain bridging R₂N₂,¹⁵ R₂C₂,¹⁶ As₂,¹⁷ and P₂¹⁸ ligands.

While metal sulfido clusters are numerous, there exist far fewer examples of clusters containing selenium or tellurium atoms. One reason for preparing clusters of these heavier chalcogenides is that they both have acceptably abundant (7.6% and 7.0%, respectively) NMR responsive isotopes whose receptivity relative to protons is 5.25 × 10⁻⁴ and 2.21 × 10⁻³, respectively.¹⁹ Thus, ⁷⁷Se and ¹²⁵Te NMR spectroscopy will likely evolve as a useful spectroscopic tool for the study of these chalcogenide clusters. A more obvious distinction for tellurium is that it is the largest naturally abundant chalcogenide (r_{cov}(Te) = 1.36 Å, r_{cov}(Se) = 1.16 Å, r_{cov}(S) = 1.02 Å). In another paper we show how this size effect can have significant structural and chemical ramifications.²⁰ A second

intriguing characteristic of tellurium is that it exhibits an extensive coordination chemistry in its own right;²¹ therefore, as a component in metal cluster systems, this element could function both as a tethering unit and as a binding site for catalytic substrates.

Experimental Section

¹H NMR spectra were obtained on a Varian EM-390 spectrometer using Me₄Si as an internal reference. Heteronuclear NMR spectra were obtained on a modified Varian XL-100 spectrometer using an external D₂O lock with 85% H₃PO₄, Me₂Se (neat), and Me₂Te (neat) as external references. All NMR samples were CDCl₃ solutions. IR spectra were obtained on a Perkin-Elmer 599B spectrophotometer on CH₂Cl₂ solutions. UV-vis spectra were recorded with a Varian Cary 219 spectrophotometer on toluene solutions. Field-desorption mass spectra were run on a Varian 731 spectrometer by Carter Cook. All cluster compounds showed molecular ions in their field desorption mass spectra. Microanalyses were performed by the School of Chemical Sciences analytical laboratory.

Reactions were performed under nitrogen in reagent grade solvents. Organic compounds were obtained from commercial sources and used without further purification. The use of Me₃NO·2H₂O²² and the preparations of Pd(PPh₃)₂C₂H₄,²³ [Ir(Ph₂PCH₂CH₂PPh₂)₂S₂]Cl,²⁴ (C₅H₅)₂Nb(S₂)Cl,²⁵ Fe₂S₂(CO)₆,²⁶ Fe₂Te₂(CO)₆,²⁷ and Fe₂S₂(CO)₅(PPh₃)²⁸ are described in the literature.

(CO)₆Fe₂(μ₃-S)₂Pt(PPh₃)₂. To a stirred C₆H₆ solution (50 mL) of Pt(PPh₃)₂(C₂H₄) (0.45 g, 0.60 mmol) was added Fe₂S₂(CO)₆ (0.21 g, 0.60 mmol). After 30 min the solution was evaporated to dryness and the residue was recrystallized from CH₂Cl₂-hexanes, affording 0.57 g (90%) of red needles: IR 2050 (s), 2009 (vs), 1975 (s), 1963 (s) cm⁻¹. Anal. Calcd for C₄₂H₃₀Fe₂O₆P₂PtS₂: C, 47.43; H, 2.84; Fe, 10.50; P, 5.82; S, 6.03. Found: C, 47.41; H, 2.91; Fe, 10.52; P, 6.00; S, 6.02.

Fe₂(μ-S)₂(CO)₅PPh₃. To a stirred solution of Fe₂S₂(CO)₆ (0.034 g, 0.10 mmol) in MeCN (30 mL) was added a solution Me₃NO·2H₂O (0.010 g, 10 mmol) in MeCN (25 mL). After 10 min a MeCN (20 mL) solution of PPh₃ (0.026 g, 0.10 mmol) was added, after an additional 10 min the solution was evaporated to dryness. The residue was chromatographed on a Bio-Beads SX-8 column eluting with CH₂Cl₂. The second red band was evaporated to dryness and identified by IR;²⁸ yield, 0.031 g (53%).

(PPh₃)(CO)₅Fe₂(μ₃-S)₂Pt(PPh₃)₂. To a stirred solution of Pt(PPh₃)₂C₂H₄ (0.040 g, 0.53 mmol) in C₆H₆ (15 mL) was added Fe₂S₂(CO)₅(PPh₃) (0.031 g, 0.053 mmol) in C₆H₆ (5 mL). After 30 min TLC indicated complete conversion. The solution was evaporated to dryness, and the residue was chromatographed on silica gel by eluting with CH₂Cl₂. The red product was collected and identified spectroscopically. IR 2044 (m), 2029 (m), 2003 (s), 1997 (s), 1950 (vs) cm⁻¹.

(CO)₆Fe(μ₃-S)₂Pd(PPh₃)₂. This compound was prepared in a manner exactly analogous to (CO)₆Fe₂(μ₃-S)₂Pt(PPh₃)₂ in 82% yield: IR 2051 (s), 2009 (vs), 1974 (s), 1959 (s) cm⁻¹. Anal. Calcd for C₄₂H₃₀Fe₂O₆P₂PdS₂: C, 51.75; H, 3.10; Fe, 11.46; Pd, 10.91; S, 6.58. Found: C, 52.34; H, 2.93; Fe, 11.60; Pd, 10.59; S, 6.91.

(CO)₆Fe₂(μ₃-Se)₂Pt(PPh₃)₂. This compound was prepared in a manner exactly analogous to (CO)₆Fe₂(μ₃-S)₂Pt(PPh₃)₂ in 86% yield: IR 2044 (s), 2004 (vs), 1968 (s) cm⁻¹. Anal. Calcd for C₄₂H₃₀Fe₂O₆P₂PtSe₂: C, 43.59; H, 2.61; Fe, 9.65; P, 5.35. Found: C, 43.32; H, 2.69; Fe, 9.49; P, 5.36.

(CO)₆Fe₂(μ₃-Te)₂Pt(PPh₃)₂. This compound was prepared in a manner similar to (CO)₆Fe₂(μ₃-S)₂Pt(PPh₃)₂ using a stock solution of Fe₂Te₂(CO)₆.²⁷ Chromatography of the reaction mixture on silica gel (Merck) with CH₂Cl₂ as an eluent gave one red band which was diluted with hexanes and concentrated to afford the product as red needles: 0.25 g (70%); IR 2034 (s), 1995 (vs), 1960 (s) cm⁻¹. Anal. Calcd for C₄₂H₃₀Fe₂O₆P₂PtTe₂: C, 40.21; H, 2.41; Fe, 8.90; P, 4.94. Found: C, 40.17; H, 2.38; Fe, 8.98; P, ≤5.41.

Pt(SePh)₂(PPh₃)₂. To a stirred solution containing Pt(PPh₃)₂C₂H₄ (0.41 g, 0.55 mmol) in C₆H₆ (30 mL) was added Ph₂Se₂ (0.35 g, 1.1 mmol). After 8 h the solution was concentrated to a small volume and diluted with hexanes; yield, 0.43 g (76%) of yellow-orange crystals. Anal.

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Table I. NMR Data for New Compounds^a

compound	δ (³¹ P), ppm	¹ J(¹⁹⁵ Pt, ³¹ P), Hz	δ (E = ⁷⁷ Se, ¹²⁵ Te) ^b	² J(E = ³¹ P)	other
(CO) ₆ Fe ₂ (μ_3 -S) ₂ Pt(PPh ₃) ₂	20.4	2790.1			
(PPh ₃)(CO) ₅ Fe ₂ (μ_3 -S) ₂ Pt(PPh ₃) ₂	30.1	2825.9			6.8 (⁴ J(P,P'))
	111.1				84.1 (³ J(¹⁹⁵ Pt,P))
(CO) ₆ Fe ₂ (μ_3 -Se) ₂ Pt(PPh ₃) ₂	30.8	2854.0	-483	23.6	149 (¹ J(¹⁹⁵ Pt, ⁷⁷ Se))
(CO) ₆ Fe ₂ (μ_3 -Te) ₂ Pt(PPh ₃) ₂	19.3	2846.4	-861		561 (¹ J(¹⁹⁵ Pt, ¹²⁵ Te))
<i>cis</i> -Pt(SePh) ₂ (PPh ₃) ₂	27.2	3007.4	321	45.3	c
<i>trans</i> -Pt(SePh) ₂ (PPh ₃) ₂	30.6	2834.4	238	~27	c
Pt(SePh) ₂ (Ph ₂ P(CH ₂) ₃ PPh ₂)	-5.8	2798.4		~45	

^a Positive chemical shifts are downfield. ^b Data referenced to neat (CH₃)₂E (E = Se, Te). ^c ¹J(¹⁹⁵Pt, ⁷⁷Se) were not resolved.

Calcd for C₄₈H₄₀P₂PtSe₂: C, 55.88; H, 3.91; P, 6.00; Se, 15.30. Found: C, 55.92; H, 4.08; P, 5.74; Se, 15.13.

Pt(SePh)₂(Ph₂P(CH₂)₃PPh₂). A solution prepared from Ph₂Se₂ (0.47 g, 1.5 mmol) and NaBH₄ (0.12 g, 3.2 mmol) in EtOH (10 mL) was added to a stirred slurry of PtCl₂(dppp) (0.45 g, 0.66 mmol) in CH₂Cl₂. After 2 min the mixture was filtered, and the residue was extracted with CH₂Cl₂. The combined, yellow filtrate was diluted with 95% EtOH and concentrated to afford a yellow precipitate which was washed repeatedly with H₂O, EtOH, and Et₂O. The product was twice recrystallized from CH₂Cl₂ by the addition of 95% EtOH, affording fine yellow needles, 0.62 g (96%). Anal. Calcd for C₃₉H₃₆P₂PtSe₂: C, 50.92; H, 3.92; P, 6.75; Se, 17.2. Found: C, 50.68; H, 4.05; P, 6.86; Se, 16.85.

X-ray Crystallography. Red-brown single crystals of Fe₂PtSe₂(CO)₆(PPh₃)₂ were grown from CH₂Cl₂-hexanes. A spherically ground crystal of 0.46-mm diameter was mounted on a 0.15-mm diameter glass fiber. The crystals were monoclinic, *P*₂/n, an alternate setting of *P*₂/C—*C*_{2h} (No. 14),²⁹ with *a* = 10.944 (2) Å, *b* = 16.321 (3) Å, *c* = 23.135 (4) Å, β = 94.68 (1)°, and *Z* = 4 at 20 ± 1 °C. Intensity measurements were made on a computer-controlled four-circle Nicolet autodiffractometer using 0.90°-wide ω scans and graphite-monochromated Mo K α radiation. A total of 11 316 independent reflections having $2\theta < 58.7^\circ$ were measured in three concentric shells of increasing 2θ . A scanning rate of 4.0°/min was employed for those reflections having $3.0^\circ < 2\theta < 43.0^\circ$ and scanning rate of 3.0°/min was used for the remaining reflections. Six standard reflections measured every 300 reflections as monitor for possible disalignment and/or deterioration of the crystal gave no indication of either. A spherical absorption correction was applied ($\mu r = 1.45$)³⁰ to the intensity data before making standard Lorentz and polarization corrections.

The platinum, iron, selenium, and phosphorus atoms were located by direct methods, and the remaining nonhydrogen atoms were located by using the standard difference Fourier techniques. Isotropic unit-weighted³¹ full-matrix least-squares refinement for the nonhydrogen atoms gave *R*₁ (unweighted, based on *F*) = 0.069³² and *R*₂ (weighted) = 0.074; the anisotropic refinement converged to *R*₁ = 0.036³² and *R*₂ = 0.040³³ for 3707 reflections having 2θ Mo K $\alpha < 33^\circ$ and *I* < 3 σ (*I*). These and all other structure-factor calculations employed an anomalous dispersion correction³⁴ to the scattering factors of the iron, platinum, selenium, and phosphorus atoms.

Atomic positions were then calculated for all (phenyl) hydrogen atoms, assuming trigonal geometry and a C—H bond length of 0.95 Å; these atoms were assigned isotropic thermal coefficients of *B* = 5.0 Å² and included in the final structure-factor calculation. Hydrogen parameters were not varied. The final cycles of (empirically weighted) full-matrix refinement which included anisotropic thermal parameters for all nonhydrogen atoms³⁵ and isotropic thermal parameters for the fixed hydrogen atoms converged to *R*₁ = 0.037 and *R*₂ = 0.040 for 7119 independent reflections having 2θ Mo K $\alpha < 58.7^\circ$ and *I* > 3 σ (*I*). During the final cycle of refinement, no parameter shifted by more than 0.18 σ_p , with an average shift of 0.03 σ_p , where σ_p is the estimated standard deviation of the parameter. A detailed crystal analysis report is included in the supplementary material.

(29) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1967; Vol. I.

(30) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1976; Vol. II, pp 302–305.

(31) The weighting scheme used in the least-squares minimization of the function $\sum w(|F_o| - |F_c|)^2$ is defined as $w = 1/\sigma F^2$.

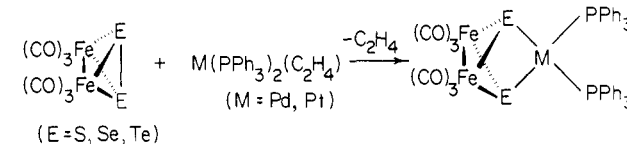
(32) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

(33) $R_2 = \{ \sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV}) \}^{1/2}$ where NO is the number of observations and NV is the number of variables.

(34) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1967; Vol. IV, 149–150.

(35) The anisotropic thermal parameter is of the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Scheme I



Results and Discussion

Synthesis. X-ray diffraction studies have previously shown that the S—S distances in the compounds (C₅H₅)₂Nb(S₂)Cl³⁶ and [Ir(dppe)₂S₂]Cl³⁷ are ~2.05 Å and thus considerably elongated relative to molecular S₂, whose internuclear distance is 1.88 Å. The S—S distance in these metal S₂ complexes is indicative of a single bond and as such is comparable to the intersulfur distances in Ph₂S₂ (2.08 Å)³⁸ and cyclo-S₈ (2.06 Å).^{39,40} Although both Ph₂S₂ and S₈ are well-known to be reactive toward low-valent metal compounds,^{41,42} the aforementioned niobium and iridium S₂ complexes proved to be unreactive toward Pt(PPh₃)₂C₂H₄, **1**. These negative results demonstrated that the S—S bond distance alone is an insufficient criterion for reactivity of metal disulfides toward metallic nucleophiles. Pursuant to the disulfide paradigm (eq 2 and 3), we recognized that the aptitude of an organic disulfide toward oxidative addition is very dependent on the nature of its substituents, and with this in mind, we examined the reactivity of a bimetallic S₂ complex.

The X-ray structures of the compounds Fe₂(μ -E₂)(CO)₆ (E = S⁴³ and Se⁴⁴) have established the presence of a single E—E bond which represents one edge of the tetrahedral cluster core. The fragile tellurium compound Fe₂(μ -Te₂)(CO)₆ is spectroscopically and presumably structurally similar to the S₂ and Se₂ compounds.²⁷ In keeping with the 18-electron rule, the μ -E₂ moiety functions as a net 6e⁻ donor to the diiron fragment, while the S₂ and Se₂ ligands in monometallic complexes only as 2e⁻ donors. Therefore the bimetallic dichalcogenide complexes should display reactivity toward nucleophiles which is significantly enhanced relative to the monometallic derivatives.

Consistent with the above rationale, we found that Fe₂(μ -S₂)(CO)₆ reacted cleanly and quickly with **1** to afford a new

(36) The structure of (C₅H₅)₂Nb(S₂)X (X = I and CN) as solved by Dahl and co-workers is discussed in a review: Vergamini, P. E.; Kubas, G. J. *Prog. Inorg. Chem.* **1976**, *21*, 261. According to Professor Dahl (private communication), a crystallographic disorder problem was not recognized initially; therefore early comments about its S—S distance, e.g., ref 25, are wrong.

(37) Bonds, W. D.; Ibers, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 3413.

(38) Dawson, I. M.; Mathieson, A. M.; Robertson, J. M. *J. Chem. Soc.* **1948**, 322.

(39) Abrahams, S. C.; Copper, A. S.; Bond, W. L. *Acta Crystallogr.* **1961**, *14*, 1008, and references therein.

(40) For a recent discussion of sulfur rings, see: Chivers, T. in "Homoatomic Rings, Chains, and Macromolecules of the Main Group Elements"; Rheingold, A., Ed.; Elsevier: Amsterdam, 1977; p 499.

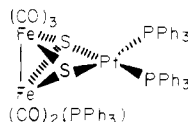
(41) For representative examples of the reactivity of organic disulfides toward low-valent metal complexes, see Tang, S. C.; Koch, S.; Papaefthymiou, G. C.; Foner, S.; Frankel, R. B.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 2414.

(42) Sulfur reacts with practically all low-valent metal complexes; for a synopsis of a few of these derivatives, see: Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322.

(43) Dahl, L. F.; Wei, C. H. *Inorg. Chem.* **1965**, *4*, 493.

(44) Campana, C. F.; Lo, F. Y.-K.; Dahl, L. F. *Inorg. Chem.* **1979**, *18*, 3060, and references therein.

compound which we formulate as $(\text{CO})_6\text{Fe}_2(\mu_3\text{-S})_2\text{Pt}(\text{PPh}_3)_2$ ^{12,45} (Scheme I). The description of this product as containing the $(\mu_3\text{-S})_2$ unit serves to emphasize that the disulfide linkage ($\mu\text{-S}_2$) has been cleaved by the platinum(0) reagent. The $\text{Fe}_2\text{S}_2\text{Pt}$ cluster was extensively characterized spectroscopically, and some of these results are collected in Table I. Importantly, the ³¹P NMR spectrum of this cluster was consistent with this compound being a cis Pt(II) complex, as judged by both the chemical shift and the value of $^1J(^{195}\text{Pt}, ^{31}\text{P})$.⁴⁶ More structurally informative was the ³¹P NMR spectrum of $(\text{PPh}_3)(\text{CO})_5\text{Fe}_2(\mu_3\text{-S})_2\text{Pt}(\text{PPh}_3)_2$, which was prepared from the reaction of $\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_5\text{PPh}_3$ with **1**. The spectrum of this compound shows two sets of resonances, each of which shows the ¹⁹⁵Pt coupling. The iron-bound phosphine appears as a 1:4:1 triplet of triplets with $^4J(^{31}\text{P}, ^{31}\text{P}) = 6.8$ Hz and $^3J(^{195}\text{Pt}, ^{31}\text{P}) = 84.1$ Hz. The platinum-bound phosphines are equivalent with respect to the unique phosphine, as required by a structure where the iron-bound PPh_3 is in the Fe_2Pt plane.



$\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_6$ also reacted readily with $\text{Pd}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ to afford $(\text{CO})_6\text{Fe}_2(\mu_3\text{-S})_2\text{Pd}(\text{PPh}_3)_2$, which was completely analogous to the platinum derivative.

We have found that the other dichalcogenide complexes react similarly: in this way $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Se})_2\text{Pt}(\text{PPh}_3)_2$ was prepared and isolated as an orange microcrystalline derivative.^{12,45} IR and ³¹P NMR spectral data are similar to those found for the S_2 complexes. The ⁷⁷Se NMR spectrum of this compound consisted of a complex multiplet centered at 483 ppm upfield of $(\text{CH}_3)_2\text{Se}$, 300 ppm upfield of $\text{Fe}_2(\mu\text{-Se}_2)(\text{CO})_6$. The center envelope of three peaks is flanked by ¹⁹⁵Pt satellites where $^1J(^{195}\text{Pt}, ^{77}\text{Se})$ is 149 Hz.

Our first samples of $\text{Fe}_2(\mu\text{-Te}_2)(\text{CO})_6$ were invariably heavily contaminated with the well-known $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$.¹² We found, however, that treatment of this impure mixture with excess **1** selectively derivatized the $\text{Fe}_2(\mu\text{-Te}_2)(\text{CO})_6$, affording the robust $\text{Fe}_2\text{Te}_2\text{Pt}$ cluster which could be readily separated from the unreacted **1** and $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$ by thick-layer chromatography on silica gel. Subsequently, gel-permeation chromatography proved to be an effective means of separating $\text{Fe}_2(\mu\text{-Te}_2)(\text{CO})_6$ and $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$, thus allowing us to perform the platinum addition reaction on pure solutions of $\text{Fe}_2(\mu\text{-Te}_2)(\text{CO})_6$.²⁷ The ¹²⁵Te NMR spectrum of $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Te})_2\text{Pt}(\text{PPh}_3)_2$ reveals a chemical shift of 861 ppm upfield of $(\text{CH}_3)_2\text{Te}$. This shift is similar to that reported for $\text{Fe}_2(\mu\text{-Te}_2)(\text{CO})_6$ (-733 ppm vs. $(\text{CH}_3)_2\text{Te}$) but 1984 ppm higher field than the superficially similar derivative $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$.²⁷

For purposes of comparison, we have surveyed the reactivity of **1** toward the diphenyl dichalcogenides, Ph_2E_2 (E = Se and Te). It has previously been shown that **1** reacts with diphenyl disulfide.⁴⁷ We find that **1** also reacts with Ph_2Se_2 but *not* with Ph_2Te_2 . The addition of Ph_2Se_2 to **1** is slow, and ³¹P NMR spectroscopy indicated that the initial product slowly isomerized in solution. On the basis of the values measured for $^2J(^{77}\text{Se}, ^{31}\text{P})$, we deduce that the kinetic product is *cis*- $\text{Pt}(\text{SePh})_2(\text{PPh}_3)_2$,⁴⁸ which reverts to the trans isomer. As a reference compound we prepared $\text{Pt}(\text{SePh})_2(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)$: its ³¹P NMR spectrum revealed a $^2J(^{77}\text{Se}, ^{31}\text{P})$ which was similar to that measured for the kinetic isomer of $\text{Pt}(\text{SePh})_2(\text{PPh}_3)_2$. The dependence of $^2J(^{77}\text{Se}, ^{31}\text{P})$ on the geometry (cis or trans) of metal phosphine complexes has previously been noted by Pan and Fackler.⁴⁹

Table II. Atomic Coordinates for Nonhydrogen Atoms in Crystalline $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Se})_2\text{Pt}(\text{P}(\text{C}_6\text{H}_5)_3)_2$ ^a

atom type ^b	10 ⁴ x	10 ⁴ y	10 ⁴ z
Pt	904.8 (2)	2161.6 (2)	581.5 (1)
Se _a	-341.5 (5)	2214.0 (5)	-343.4 (2)
Se _b	2410.7 (5)	1992.6 (4)	-143.4 (3)
Fe ₁	1271.3 (9)	2917.2 (7)	-790.4 (4)
Fe ₂	996.5 (9)	1379.0 (6)	-864.0 (4)
P _a	697 (1)	2527 (1)	1103 (1)
P _b	2444 (1)	2014 (1)	1313 (1)
O ₁₁	-367 (6)	3164 (4)	-1838 (2)
O ₁₂	3520 (7)	3319 (7)	-1322 (3)
O ₁₃	1160 (9)	4476 (4)	-179 (3)
O ₂₁	-1059 (6)	1064 (5)	-1728 (3)
O ₂₂	2826 (7)	1300 (5)	-1705 (3)
O ₂₃	1180 (8)	-261 (4)	-356 (3)
C ₁₁	278 (7)	3076 (4)	-1428 (3)
C ₁₂	2634 (8)	3152 (7)	-1123 (4)
C ₁₃	1199 (9)	3856 (5)	-414 (3)
C ₂₁	-249 (7)	1186 (5)	-1392 (3)
C ₂₂	2128 (8)	1317 (6)	-1369 (4)
C ₂₃	1078 (8)	379 (5)	-547 (3)
C _{a11}	-314 (6)	3444 (4)	1522 (3)
C _{a12}	356 (7)	4050 (5)	1266 (3)
C _{a13}	694 (8)	4759 (5)	1558 (4)
C _{a14}	381 (8)	4873 (5)	2110 (4)
C _{a15}	-267 (7)	4281 (5)	2382 (3)
C _{a16}	-622 (6)	3571 (5)	2086 (3)
C _{a21}	-1310 (5)	1789 (4)	1595 (3)
C _{a22}	-2370 (6)	1970 (5)	1870 (3)
C _{a23}	-2799 (7)	1420 (6)	2263 (3)
C _{a24}	-2192 (8)	702 (5)	2378 (3)
C _{a25}	-1154 (8)	511 (5)	2101 (3)
C _{a26}	-726 (6)	1053 (4)	1708 (3)
C _{a31}	-2062 (6)	8219 (5)	643 (2)
C _{a32}	-2909 (7)	2222 (6)	451 (3)
C _{a33}	-3923 (8)	2431 (7)	86 (4)
C _{a34}	-4082 (9)	3192 (8)	-103 (4)
C _{a35}	-3254 (11)	3786 (7)	62 (5)
C _{a36}	-2230 (8)	3595 (6)	445 (4)
C _{b11}	3502 (5)	2879 (4)	1376 (3)
C _{b12}	3459 (7)	3481 (5)	958 (3)
C _{b13}	4268 (9)	4131 (6)	1006 (4)
C _{b14}	5120 (9)	4187 (6)	1475 (5)
C _{b15}	5189 (7)	3597 (6)	1894 (4)
C _{b16}	4377 (7)	2952 (5)	1851 (3)
C _{b21}	2096 (6)	1843 (5)	2068 (3)
C _{b22}	1847 (7)	2503 (7)	2408 (3)
C _{b23}	1532 (10)	2358 (9)	2972 (4)
C _{b24}	1451 (9)	1568 (10)	3181 (4)
C _{b25}	1736 (9)	936 (8)	2853 (4)
C _{b26}	2044 (7)	1051 (6)	2283 (3)
C _{b31}	3343 (6)	1118 (4)	1140 (3)
C _{b32}	2738 (7)	426 (5)	926 (4)
C _{b33}	3376 (9)	-272 (6)	797 (4)
C _{b34}	4635 (9)	-269 (6)	865 (4)
C _{b35}	5257 (7)	415 (6)	1070 (4)
C _{b36}	4621 (7)	1100 (5)	1200 (3)

^a Numbers in parentheses are the estimated standard deviation in the last significant digit. ^b Atoms are labeled in agreement with Figures 1 and 2.

The Structure of $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Se})_2\text{Pt}(\text{PPh}_3)_2$. The structure of $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Se})_2\text{Pt}(\text{PPh}_3)_2$ (Figure 1) was elucidated by single-crystal X-ray diffraction techniques. Final atomic coordinates are given with standard deviations in Table II. Tables III and IV of the supplementary material list the thermal parameters and calculated hydrogen positions. Bond lengths and angles are given in Tables V and VI. The metallic framework of this cluster is an isosceles triangle, the base of which is defined by a 2.533 (2) Å Fe-Fe bonding edge and the two sides by the long (>3.45 Å) nonbonding Fe...Pt vectors. Each iron is pseudooctahedral, the coordination sphere being comprised of three carbonyls, two selenium atoms, and one Fe-Fe bond. The platinum atom is in a square-planar environment containing cis selenium atoms and phosphine phosphorus atoms; these five atoms are all coplanar within 0.12 Å.

(45) The reactivity of $\text{Fe}_2(\mu\text{-E}_2)(\text{CO})_6$ (E = S, Se) toward low-valent metal complexes has been independently described by Seyferth and coworkers: Seyferth, D.; Henderson, R. S.; *J. Organomet. Chem.* **1981**, *204*, 333.

(46) Pergosin, P. S. ³¹P and ¹³C NMR of Transition Metal Phosphine Complexes; Springer-Verlag: Berlin, 1979.

(47) Zanella, R.; Ros, R.; Graziani, M. *Inorg. Chem.* **1973**, *12*, 2736.

(48) Kawakami, K.; Ozaki, Z.; Tanaka, T. *J. Organomet. Chem.* **1974**, *69*, 151.

(49) Pan, W.-H.; Fackler, J. P., Jr.; Chen, W.-H. *Inorg. Chem.* **1981**, *20*, 856.

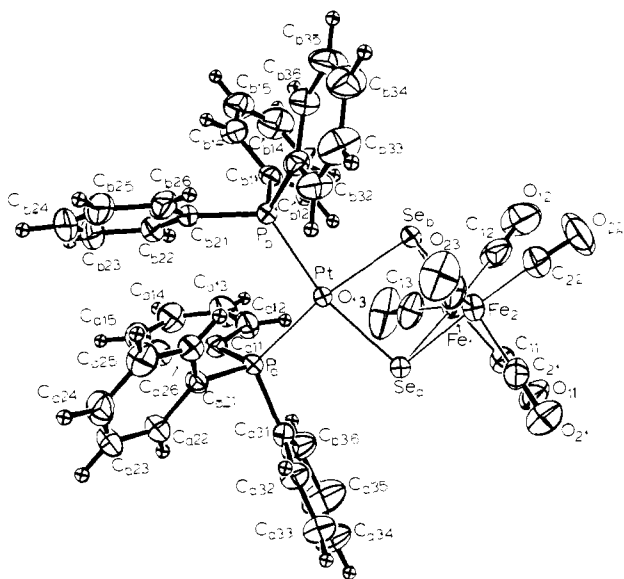


Figure 1. ORTEP plot of the $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Se})_2\text{Pt}(\text{PPh}_3)_2$ molecules. All nonhydrogen atoms are represented by thermal ellipsoids drawn at the 50% probability level; hydrogen atoms are represented by arbitrarily small spheres for purposes of clarity.

Table V. Bond Lengths Involving Nonhydrogen Atoms in Crystalline $(\text{CO})_6\text{Fe}_2\text{Se}_2\text{Pt}(\text{P}(\text{C}_6\text{H}_5)_3)_2^a$

type ^b	length, Å	type ^b	length, Å
Pt-Se _a	2.444 (1)	Pt-Se _b	2.461 (1)
Pt-P _a	2.286 (2)	Pt-P _b	2.300 (1)
Fe ₁ -Se _a	2.408 (1)	Fe ₁ -Se _b	2.402 (1)
Fe ₂ -Se _a	2.396 (1)	Fe ₂ -Se _b	2.399 (1)
Fe ₁ -Fe ₂	2.533 (2)	Se _a ...Se _b	3.032 (1)
Fe ₁ -C ₁₁	1.779 (7)	Fe ₂ -C ₂₁	1.782 (8)
Fe ₁ -C ₁₂	1.775 (9)	Fe ₂ -C ₂₂	1.773 (8)
Fe ₁ -C ₁₃	1.767 (8)	Fe ₂ -C ₂₃	1.788 (8)
P _a -C _{a11}	1.813 (7)	P _b -C _{b11}	1.825 (7)
P _a -C _{a21}	1.823 (6)	P _b -C _{b21}	1.840 (6)
P _a -C _{a31}	1.826 (6)	P _b -C _{b31}	1.825 (7)
O ₁₁ -C ₁₁	1.144 (9)	O ₂₁ -C ₂₁	1.148 (10)
O ₁₂ -C ₁₂	1.139 (12)	O ₂₂ -C ₂₂	1.135 (11)
O ₁₃ -C ₁₃	1.151 (11)	O ₂₃ -C ₂₃	1.137 (10)
C _{a11} -C _{a12}	1.391 (10)	C _{b11} -C _{b12}	1.377 (10)
C _{a11} -C _{a16}	1.391 (9)	C _{b11} -C _{b16}	1.401 (9)
C _{a12} -C _{a13}	1.375 (11)	C _{b12} -C _{b13}	1.381 (13)
C _{a13} -C _{a14}	1.362 (12)	C _{b13} -C _{b14}	1.374 (14)
C _{a14} -C _{a15}	1.380 (12)	C _{b14} -C _{b15}	1.364 (14)
C _{a15} -C _{a16}	1.385 (11)	C _{b15} -C _{b16}	1.376 (12)
C _{a21} -C _{a22}	1.399 (9)	C _{b21} -C _{b22}	1.375 (13)
C _{a21} -C _{a26}	1.376 (10)	C _{b21} -C _{b26}	1.388 (13)
C _{a22} -C _{a23}	1.387 (11)	C _{b22} -C _{b23}	1.397 (12)
C _{a23} -C _{a24}	1.362 (12)	C _{b23} -C _{b24}	1.381 (21)
C _{a24} -C _{a25}	1.386 (12)	C _{b24} -C _{b25}	1.332 (18)
C _{a25} -C _{a26}	1.377 (11)	C _{b25} -C _{b26}	1.400 (12)
C _{a31} -C _{a32}	1.392 (11)	C _{b31} -C _{b32}	1.381 (11)
C _{a31} -C _{a36}	1.354 (12)	C _{b31} -C _{b36}	1.395 (10)
C _{a32} -C _{a33}	1.382 (12)	C _{b32} -C _{b33}	1.382 (13)
C _{a33} -C _{a34}	1.324 (17)	C _{b33} -C _{b34}	1.374 (14)
C _{a34} -C _{a35}	1.360 (16)	C _{b34} -C _{b35}	1.373 (13)
C _{a35} -C _{a36}	1.405 (15)	C _{b35} -C _{b36}	1.363 (12)

^a The numbers in parentheses are the estimated standard deviations in the last significant digit. ^b Atoms are labeled in agreement with Figure 1 and Tables III-V.

One significant difference between $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Se})_2\text{Pt}(\text{PPh}_3)_2$ and $\text{Fe}_3(\mu_3\text{-Se})_2(\text{CO})_9$ ⁵⁰ is that in the Fe_2Pt case, each selenium atom functions as a formal three-electron donor to the mutually bonded iron atoms. A valence bond representation for $\text{Fe}_3(\mu_3\text{-$

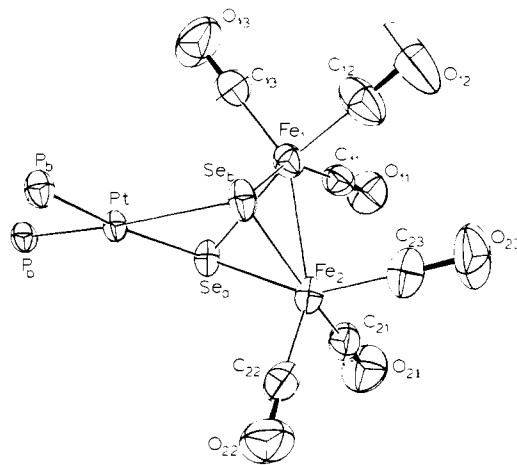


Figure 2. ORTEP plot of the nonhydrogen atoms of the metal coordination spheres of the $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Se})_2\text{Pt}(\text{PPh}_3)_2$ molecule with thermal ellipsoids drawn at the 50% probability level.

$\text{Se}_2(\text{CO})_9$, however, suggests that the $3e^-$ donation by each Se atom is directed to the pair of irons which are *not* mutually bonded, and furthermore, no reasonable structure can be drawn which involves a selenium atom functioning as an electron-pair donor to the unique iron atom. That this apparently minor difference in the electronic structures of these structurally similar compounds is significant is supported by the differences in the electronic absorption spectra for $\text{Fe}_3(\mu_3\text{-Se})_2(\text{CO})_9$ (λ_{max} 366 (6700), 462 (2900), 528 nm ($2500 \text{ cm}^{-1} \text{ M}^{-1}$)) and $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Se})_2\text{Pt}(\text{PPh}_3)_2$ (λ_{max} 473 nm ($2000 \text{ cm}^{-1} \text{ M}^{-1}$)). The selenium environment in the $\text{Fe}_2\text{Se}_2\text{Pt}$ cluster is more reminiscent of that in $\text{Fe}_2(\mu\text{-Se}_2)(\text{CO})_6$, and pursuant to this analogy, we note that in both cases the selenium atoms may be considered as triply bridging, be it to two iron atoms and a platinum *or* to two iron atoms and another selenium atom, respectively. This suggested similarity in the electronic structure of the bridging nonmetal atom is corroborated by ⁷⁷Se and ¹²⁵Te NMR.⁵¹

An interesting aspect of the present structure is its relationship to that of $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9(\text{PPh}_3)_2$.²⁰ The remarkable similarity of the two compounds can be seen by comparing Figures 2 and 3. The preparations of these two compounds employed completely different strategies. However, the description of the triiron cluster as $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Te})_2\text{Fe}(\text{CO})_3\text{PPh}_3$ suggests, conceptually at least, that it could be assembled by the reaction of $\text{Fe}_2(\mu\text{-Te}_2)(\text{CO})_6$ with " $\text{Fe}(\text{CO})_3\text{PPh}_3$ ".⁵²

The Basis for the Reactivity of the $\mu\text{-E}_2$ Group. It is interesting that the $\mu\text{-E}_2$ complexes are significantly more reactive than the monometallic S_2 complexes which we tried initially. Also significant is the fact that the bimetallic dichalcogenide compounds are more reactive than diorganodichalcogenides, as demonstrated by the observation that Ph_2Se_2 reacts only slowly with **1** and Ph_2Te_2 is completely inert under the same conditions.

We suggest that the reactivity of the diiron reagents is induced by two factors: the electrophilicity of the $\mu\text{-E}_2$ unit and the strain inherent in the heterotetrahedrane ring. As previously described, the $\mu\text{-E}_2$ unit functions as a $6e^-$ donor while in monometallic complexes the $\eta^2\text{-E}_2$ unit is (formally) a 2-electron donor. It is well recognized that the organic disulfides which serve best in the oxidative addition process are those which bear the most electronegative substituents,⁴¹ e.g., $(\text{CF}_3)_2\text{S}_2$. Similar arguments apparently hold in the case of inorganic disulfides.

We have previously indicated that $\text{Fe}_2(\mu\text{-Te}_2)(\text{CO})_6$ is a thermally fragile compound.²⁷ Schmid et al. have advanced arguments that closed transition-metal-nonmetal cluster compounds are not stable for relatively large nonmetals.⁵³ Thus, it is rea-

(51) Lesch, D. A.; Rauchfuss, T. B.; Weatherill, T. D., manuscript in preparation.

(52) In fact $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_{10}$ can be prepared from $\text{Fe}_2(\mu\text{-Te}_2)(\text{CO})_6$ and sources of $\text{Fe}(\text{CO})_4$.²⁷

(53) Schmid, G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 92.

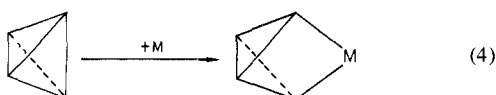
(50) Dahl, L. F.; Sutton, P. W. *Inorg. Chem.* **1963**, *2*, 1067.

Table VI. Bond Angles Involving Nonhydrogen Atoms in Crystalline $(\text{CO})_6\text{Fe}_2\text{Se}_2\text{Pt}(\text{P}(\text{C}_6\text{H}_5)_3)_2^a$

type ^b	angle, deg	type ^b	angle, deg
Se_aPtSe_b	76.36 (2)	P_aPtP_b	100.74 (6)
Se_aPtP_a	93.19 (4)	Se_bPtP_b	89.91 (4)
Se_aPtP_b	166.07 (4)	Se_bPtP_a	166.80 (4)
$\text{Se}_a\text{Fe}_1\text{Fe}_2$	57.95 (3)	$\text{Se}_a\text{Fe}_2\text{Fe}_1$	58.42 (3)
$\text{Se}_b\text{Fe}_1\text{Fe}_2$	58.12 (3)	$\text{Se}_b\text{Fe}_2\text{Fe}_1$	58.21 (3)
$\text{Se}_a\text{Fe}_1\text{Se}_b$	78.14 (4)	$\text{Se}_a\text{Fe}_2\text{Se}_b$	78.42 (4)
$\text{Fe}_2\text{Fe}_1\text{C}_{11}$	91.6 (2)	$\text{Fe}_1\text{Fe}_2\text{C}_{21}$	107.5 (3)
$\text{Fe}_2\text{Fe}_1\text{C}_{12}$	106.5 (2)	$\text{Fe}_1\text{Fe}_2\text{C}_{22}$	90.9 (3)
$\text{Fe}_2\text{Fe}_1\text{C}_{13}$	152.0 (3)	$\text{Fe}_1\text{Fe}_2\text{C}_{23}$	151.1 (3)
$\text{Se}_a\text{Fe}_1\text{C}_{11}$	90.3 (2)	$\text{Se}_a\text{Fe}_2\text{C}_{21}$	88.9 (3)
$\text{Se}_a\text{Fe}_1\text{C}_{12}$	163.8 (3)	$\text{Se}_a\text{Fe}_2\text{C}_{22}$	148.4 (3)
$\text{Se}_a\text{Fe}_1\text{C}_{13}$	97.9 (3)	$\text{Se}_a\text{Fe}_2\text{C}_{23}$	109.0 (3)
$\text{Se}_b\text{Fe}_1\text{C}_{11}$	149.3 (2)	$\text{Se}_b\text{Fe}_2\text{C}_{21}$	164.5 (3)
$\text{Se}_b\text{Fe}_1\text{C}_{12}$	89.7 (3)	$\text{Se}_b\text{Fe}_2\text{C}_{22}$	92.0 (3)
$\text{Se}_b\text{Fe}_1\text{C}_{13}$	106.2 (3)	$\text{Se}_b\text{Fe}_2\text{C}_{23}$	95.1 (3)
$\text{C}_{11}\text{Fe}_1\text{C}_{12}$	95.0 (4)	$\text{C}_{21}\text{Fe}_2\text{C}_{22}$	94.3 (4)
$\text{C}_{11}\text{Fe}_1\text{C}_{13}$	103.5 (4)	$\text{C}_{21}\text{Fe}_2\text{C}_{23}$	97.5 (4)
$\text{C}_{12}\text{Fe}_1\text{C}_{13}$	95.7 (4)	$\text{C}_{22}\text{Fe}_2\text{C}_{23}$	101.8 (4)
PtSe_aFe_1	90.74 (3)	PtSe_bFe_1	90.68 (3)
PtSe_aFe_2	95.73 (3)	PtSe_bFe_2	95.19 (3)
$\text{Fe}_1\text{Se}_a\text{Fe}_2$	63.63 (4)	$\text{Fe}_1\text{Se}_b\text{Fe}_2$	63.67 (4)
$\text{PtP}_a\text{C}_{a11}$	110.1 (2)	$\text{PtP}_b\text{C}_{b11}$	113.6 (2)
$\text{PtP}_a\text{C}_{a21}$	119.6 (2)	$\text{PtP}_b\text{C}_{b21}$	121.2 (2)
$\text{PtP}_a\text{C}_{a31}$	112.8 (2)	$\text{PtP}_b\text{C}_{b31}$	107.4 (2)
$\text{C}_{a11}\text{P}_a\text{C}_{a21}$	107.0 (3)	$\text{C}_{b11}\text{P}_b\text{C}_{b21}$	102.7 (3)
$\text{C}_{a11}\text{P}_a\text{C}_{a31}$	103.8 (3)	$\text{C}_{b11}\text{P}_b\text{C}_{b31}$	106.7 (3)
$\text{C}_{a21}\text{P}_a\text{C}_{a31}$	102.2 (3)	$\text{C}_{b21}\text{P}_b\text{C}_{b31}$	104.1 (3)
$\text{F}_{c1}\text{C}_{11}\text{O}_{11}$	178.8 (7)	$\text{Fe}_2\text{C}_{21}\text{O}_{21}$	179.3 (7)
$\text{F}_{c1}\text{C}_{12}\text{O}_{12}$	177.8 (9)	$\text{Fe}_2\text{C}_{22}\text{O}_{22}$	177.2 (8)
$\text{F}_{c1}\text{C}_{13}\text{O}_{13}$	178.5 (9)	$\text{Fe}_2\text{C}_{23}\text{O}_{23}$	176.9 (8)
$\text{P}_a\text{C}_{a11}\text{C}_{a12}$	117.8 (5)	$\text{P}_b\text{C}_{b11}\text{C}_{b12}$	120.6 (5)
$\text{P}_a\text{C}_{a11}\text{C}_{a16}$	124.2 (5)	$\text{P}_b\text{C}_{b11}\text{C}_{b16}$	121.2 (5)
$\text{C}_{a12}\text{C}_{a11}\text{C}_{a16}$	118.0 (6)	$\text{C}_{b12}\text{C}_{b11}\text{C}_{b16}$	118.2 (6)
$\text{C}_{a11}\text{C}_{a12}\text{C}_{a13}$	121.3 (7)	$\text{C}_{b11}\text{C}_{b12}\text{C}_{b13}$	120.3 (8)
$\text{C}_{a12}\text{C}_{a13}\text{C}_{a14}$	119.8 (8)	$\text{C}_{b12}\text{C}_{b13}\text{C}_{b14}$	120.4 (9)
$\text{C}_{a13}\text{C}_{a14}\text{C}_{a15}$	120.7 (8)	$\text{C}_{b13}\text{C}_{b14}\text{C}_{b15}$	120.5 (9)
$\text{C}_{a14}\text{C}_{a15}\text{C}_{a16}$	119.6 (7)	$\text{C}_{b14}\text{C}_{b15}\text{C}_{b16}$	119.4 (8)
$\text{C}_{a15}\text{C}_{a16}\text{C}_{a11}$	120.6 (7)	$\text{C}_{b15}\text{C}_{b16}\text{C}_{b11}$	121.1 (7)
$\text{P}_a\text{C}_{a21}\text{C}_{a22}$	120.4 (5)	$\text{P}_b\text{C}_{b21}\text{C}_{b22}$	119.4 (6)
$\text{P}_a\text{C}_{a21}\text{C}_{a26}$	120.5 (5)	$\text{P}_b\text{C}_{b21}\text{C}_{b26}$	120.0 (6)
$\text{C}_{a22}\text{C}_{a21}\text{C}_{a26}$	119.2 (6)	$\text{C}_{b22}\text{C}_{b21}\text{C}_{b26}$	120.6 (7)
$\text{C}_{a21}\text{C}_{a22}\text{C}_{a23}$	119.9 (7)	$\text{C}_{b21}\text{C}_{b22}\text{C}_{b23}$	118.5 (9)
$\text{C}_{a22}\text{C}_{a23}\text{C}_{a24}$	120.0 (7)	$\text{C}_{b22}\text{C}_{b23}\text{C}_{b24}$	120.9 (11)
$\text{C}_{a23}\text{C}_{a24}\text{C}_{a25}$	120.6 (8)	$\text{C}_{b23}\text{C}_{b24}\text{C}_{b25}$	119.9 (11)
$\text{C}_{a24}\text{C}_{a25}\text{C}_{a26}$	119.7 (7)	$\text{C}_{b24}\text{C}_{b25}\text{C}_{b26}$	121.2 (10)
$\text{C}_{a25}\text{C}_{a26}\text{C}_{a21}$	120.6 (7)	$\text{C}_{b25}\text{C}_{b26}\text{C}_{b21}$	118.8 (8)
$\text{P}_a\text{C}_{a31}\text{C}_{a32}$	119.7 (5)	$\text{P}_b\text{C}_{b31}\text{C}_{b32}$	118.9 (6)
$\text{P}_a\text{C}_{a31}\text{C}_{a36}$	121.5 (6)	$\text{P}_b\text{C}_{b31}\text{C}_{b36}$	123.3 (6)
$\text{C}_{a32}\text{C}_{a31}\text{C}_{a36}$	118.6 (7)	$\text{C}_{b32}\text{C}_{b31}\text{C}_{b36}$	117.8 (7)
$\text{C}_{a31}\text{C}_{a32}\text{C}_{a33}$	120.2 (8)	b ₃₁ b ₃₂ b ₃₃	121.1 (8)
$\text{C}_{a32}\text{C}_{a33}\text{C}_{a34}$	120.7 (9)	b ₃₂ b ₃₃ b ₃₄	119.5 (9)
$\text{C}_{a33}\text{C}_{a34}\text{C}_{a35}$	120.6 (11)	b ₃₃ b ₃₄ b ₃₅	120.5 (9)
$\text{C}_{a34}\text{C}_{a35}\text{C}_{a36}$	119.8 (10)	b ₃₄ b ₃₅ b ₃₆	119.8 (8)
$\text{C}_{a35}\text{C}_{a36}\text{C}_{a31}$	120.0 (9)	b ₃₅ b ₃₆ b ₃₁	121.4 (8)

^a The numbers in parentheses are the estimated standard deviations in the last significant digit. ^b Atoms are labeled in agreement with Figure 1 and Tables III-V.

sonable that tetrahedral clusters may show a propensity for ring expansion (eq 4) of the type described in this paper and that the



contribution of strain to the reactivity of the $\text{Fe}_2(\mu\text{-E}_2)(\text{CO})_6$ compounds will be maximized for the tellurium derivative. As an apparent manifestation of the strain inherent in small, closed clusters which contain heavy nonmetals, the attempted synthesis of $\text{Co}_2(\mu\text{-Sb}_2)(\text{CO})_6$, in a manner analogous to that for the known $\text{Co}_2(\mu\text{-As}_2)(\text{CO})_6$,¹⁷ affords only the heterocubane, $\text{Co}_4(\mu_3\text{-$

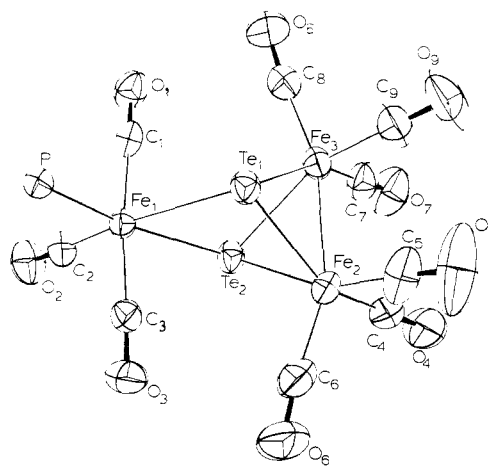


Figure 3. ORTEP plot of the nonhydrogen atoms of the $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9\text{PPh}_3$ molecule with thermal ellipsoids drawn at the 50% probability level.

$\text{Sb})_4(\text{CO})_{12}$.⁵⁴ The formation of this tetracobalt species can be thought to arise from the face-to-face coupling of two homolytically ruptured $\text{Co}_2(\mu\text{-Sb}_2)(\text{CO})_6$ moieties. Consistent with this proposal, we have found that $\text{Fe}_2(\mu\text{-Te}_2)(\text{CO})_6$ thermally decomposes to $\text{Fe}_4(\mu_3\text{-Te})_4(\text{CO})_{12}$.⁵⁵ Pursuant to the concept that these $\text{Fe}_2(\mu\text{-E}_2)$ clusters are strained, we note that Dahl and co-workers have presented elaborate and convincing arguments for the presence of bent bonds in these compounds.⁵⁶ Bent bonds are considered symptomatic of strain in carbocyclic systems.

Consistent with our proposal that the reactivity of the $\text{Fe}_2(\mu\text{-E}_2)(\text{CO})_6$ compounds is also dependent on electronic factors, we note that $\text{Co}_2(\mu\text{-As}_2)(\text{CO})_6$ ¹⁷ does not react with **1**. The chemical dormancy of this cobalt compound is in accord with the suggestion that the bond order between the nonmetals in this cluster is higher than that in the $\text{Fe}_2(\mu\text{-E}_2)(\text{CO})_6$ series.⁴⁴

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Registry No. 1, 12120-15-9; $(\text{CO})_6\text{Fe}_2(\mu_3\text{-S}_2)\text{Pt}(\text{PPh}_3)_2$, 75249-93-3; $(\text{PPh}_3)(\text{CO})_5\text{Fe}_2(\mu_3\text{-S}_2)\text{Pt}(\text{PPh}_3)_2$, 76185-28-9; $(\text{CO})_6\text{Fe}_2(\mu_3\text{-S}_2)\text{Pd}(\text{PPh}_3)_2$, 75249-92-2; $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Se}_2)\text{Pt}(\text{PPh}_3)_2$, 76185-30-3; $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Te}_2)\text{Pt}(\text{PPh}_3)_2$, 76185-29-0; *trans*- $\text{Pt}(\text{SePh})_2(\text{PPh}_3)_2$, 52653-84-6; *cis*- $\text{Pt}(\text{SePh})_2(\text{PPh}_3)_2$, 76188-91-5; $\text{Pt}(\text{SePh})_2(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$, 80462-61-9; $\text{Fe}_2(\mu_2\text{-S}_2)(\text{CO})_5(\text{PPh}_3)$, 71568-25-7; $\text{Fe}_2\text{S}_2(\text{CO})_6$, 14243-23-3; $\text{Fe}_2(\mu_2\text{-Se}_2)(\text{CO})_6$, 71341-69-0; $\text{Fe}_2\text{Te}_2(\text{CO})_6$, 76185-27-8; $\text{Pd}(\text{PPh}_3)_2\text{C}_2\text{H}_4$, 33395-22-1; $\text{PtCl}_2(\text{dppp})$, 59329-00-9; Ph_2Se_2 , 1666-13-3.

Supplementary Material Available: Thermal parameters (Table III), the calculated hydrogen positions (Table IV), a crystal structure analysis report, and structure factor tables for $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Se}_2)\text{Pt}(\text{P}(\text{C}_6\text{H}_5)_3)_2$ (40 pages). Ordering information is given on any current masthead page.

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