deformation on oxygen resulting in a positive density on either side of the Fe–O bond. The hybridization of oxygen appears from the deformation maps to be closer to $sp^2$ than $sp^3$, suggesting a $\pi$-interaction between Fe and O.

## Conclusions

The experimental electron density distribution of a five-coordinate, high-spin iron(III) porphyrin has been obtained from accurate low-temperature X-ray diffraction data. As expected, only small distortions from spherical symmetry are observed for the Fe d-electron distribution, confirming the high-spin nature of the complex. A small quadrupole deformation on the iron atom is observed, producing an electric field gradient at the iron nucleus with positive sign. A contribution of similar magnitude and sign also results from the observed distribution of atomic charges. The total electric field gradient deduced from the X-ray data is in agreement in both sign and magnitude with Mössbauer quadrupole splitting measurements.

With one complete porphyrin molecule in the asymmetric unit, this represents one of the largest charge density studies attempted, in terms of both data collection and computer refinement of results. Although more time and effort was obviously required than for studies of small molecules, the accuracy of the results compares favorably with those from smaller molecules. Also, in this study fewer problems were encountered with the 4s population on the transition-metal atom than in previous studies, probably because the large unit cell results in more low-angle data, which help to define the diffuse density features. It thus appears that the only limitations to studies on large biologically significant molecules will be the requirements that the crystals be of adequate quality and that sufficient instrument and computing time be available.

**Acknowledgment.** The authors thank Dr. F. Baert for assistance in solving the structure. Support of this work by the National Institutes of Health (Grant HL-23884) and the National Science Foundation (Grant CHE-7905897) is gratefully acknowledged. C.L. is grateful to NATO for providing him with a postdoctoral fellowship.

**Registry No.** Fe(TPP)$OCH_3$, 29189-59-1.

**Supplementary Material Available:** Listings of least-squares planes (Table VII), atomic thermal parameters (Table IX), and observed and calculated structure amplitudes (48 pages). Ordering information is given on any current masthead page.

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# Electronic Structure of Tetraphosphabicyclo[1.1.0]butane

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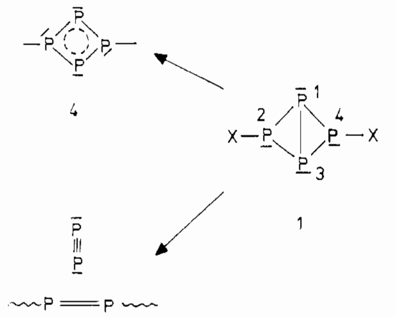
The electronic nature of the title compound tetraphosphabicyclo[1.1.0]butane is analyzed. Accordingly, $\pi'$- ($\pi$-) donors or acceptors exert considerable effect on the bond lengths of the parent compound. The central bond possesses olefinic character, as is known for the case of bicyclo[1.1.0]butane. The structures of the radical cations are explored. The fragmentation of the title compound as well its reaction to its monocyclic isomer, which is isovalent with $N_2S_2$, is evaluated.

Although the phospha analogue **1** of bicyclo[1.1.0]butane has been postulated as an intermediate in the reaction of white phosphorus with alkyl halides,[1] its synthesis and structural elucidation have only been verified recently.[2] **1** is isovalent with the well-known bicyclo[1.1.0]butane[3] (**2**). Because of the similarities noted, it is surprising that its structure differs from **2**. In **1** (X = $N(SiR_3)_2$) the bond between the bridgehead atoms P(1)P(3) is shorter by 0.1 Å compared with the bonds to the peripheral phosphorus atoms (P(1)P(3) = 2.128 Å; P(1)P(2) = 2.228 Å.[2] The folding angle between the planes spanned by the three-membered rings is 95.5°. Hence, the central bond P(1)P(3) in **1** is shorter than a PP single bond (2.230 Å in diphosphane[4]) and, at the same time, longer than a PP double bond (2.034 Å in diphenyldiphosphaethylene[5]). In **2** the bridgehead bond C(1)C(3) and the peripheral CC bonds are equal (C(1)C(3) = 1.497 Å; C(1)C(2) = 1.498 Å).[6]



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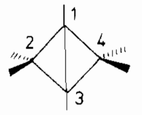
1

3



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In the present publication we deal with the electronic structure of **1**. In more detail we will evaluate the following aspects in our study: (1) The electronic structure of **1** will be analyzed and compared with that of **2**. (2) A theory of substituent effects on the bonding properties in **1** will be presented. It will be shown that electron-releasing or electron-accepting substituents considerably alter the bonding properties in parent

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(1) C. Brown, R. F. Hudson, and G. A. Wartew, *Phosphorus Sulfur*, **5**, 67 (1978); see also H. Quast, *Nachr. Chem., Tech. Lab.*, **27**, 120 (1979).

(2) E. Niecke, R. Rüger, and B. Krebs, *Angew. Chem., Int. Ed. Engl.*, **21**, 544 (1982).

(3) For a discussion of its properties see e.g.: K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965); K. B. Wiberg and J. Lavanish, *J. Am. Chem. Soc.*, **88**, 5272 (1966); K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

(4) (a) For structural investigations on this compound see: S. G. Frankiss, *Inorg. Chem.*, **7**, 1931 (1968); B. Beagley, A. R. Conrad, J. M. Freeman, J. J. Monaghan, and B. G. Norton, *J. Mol. Struct.*, **11**, 371 (1972); J. R. Durig, L. A. Carreira, and J. D. Odom, *J. Am. Chem. Soc.*, **96**, 2688 (1974); M. Baudler and L. Schmidt, *Z. Anorg. Allg. Chem.*, **289**, 219 (1957); *Naturwissenschaften*, **44**, 488 (1953). (b) For theoretical studies see: R. Ahlrichs, R. Heinzmann, and C. Zirc, *Theor. Chim. Acta*, **43**, 29 (1976); A. H. Cowley, W. D. White, and M. C. Damasco, *J. Am. Chem. Soc.*, **91**, 1922 (1969); J.-B. Robert, H. Marsmann, and J. R. Van Wazer, *J. Chem. Soc. D*, 356 (1970); E. L. Wagner, *Theor. Chim. Acta*, **23**, 127 (1971).

(5) M. Yoshifuji, I. Shima, and N. Inamoto, *J. Am. Chem. Soc.*, **103**, 4587 (1981).

(6) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50**, 1976 (1969).

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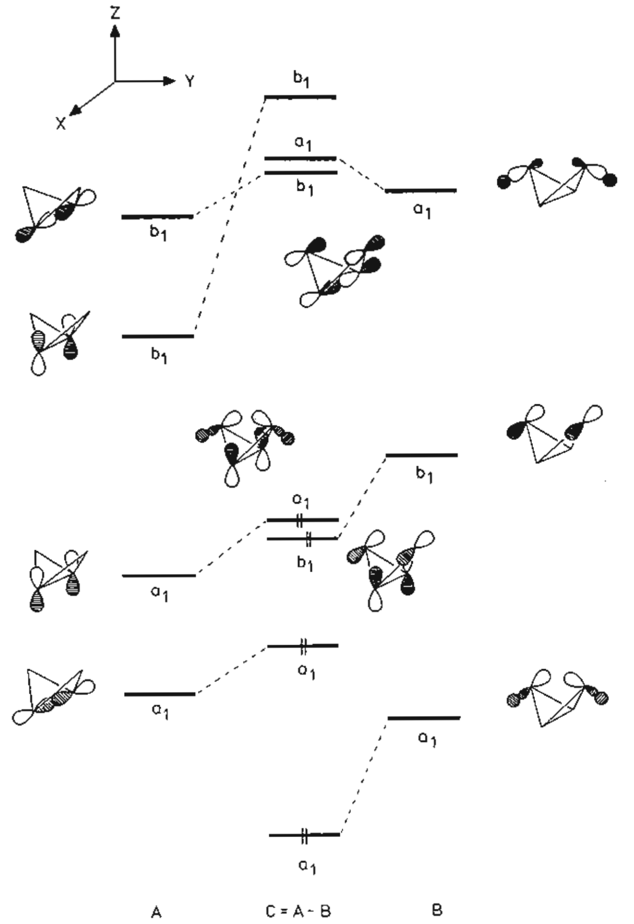

**Figure 1.** Interaction diagram for the composition of the molecular orbital system of tetraphosphabicyclo[1.1.0]butane (C) from the fragment orbitals of an inner set (A) and outer set (B). Symmetry designations are with respect to $C_{2v}$.

**1** (X = H). (3) Finally, we will draw conclusion regarding the reactivity of **1**. The electronic features for (a) the fragmentation to **3** and (b) the formation of the monocyclic analogue **4** will be explored.

## Computational Methods

Quantum-mechanical calculations were performed at various levels of sophistication. Semiempirical SCF calculations were carried out with the MNDO approximation,[7a] optimizing all structures with the Davidon–Fletcher–Powell algorithm[7b] within the method of finite differences. The EH approximation[8] was employed for the construction of orbital correlation diagrams and for qualitative investigation of the role of 3d orbitals at P in bonding.[9] Finally, the conclusion reached from the semiempirical calculations were tested against the result of ab initio calculations. The following three basis sets were used: basis I, ab initio STO-3G level[10a] (mainly used for geometry optimization); basis II, P[10s,6p] in the contraction (5, 5 × 1/4, 2 × 1) using Gaussian functions, taken from Huzinaga's tables,[10b] and H[3s] in the contraction (2, 1); basis III, basis II with additional polarization functions at P, with the orbital exponent $\zeta(d) = 0.50$. We note that basis II and basis III are of "double-$\zeta$ quality".

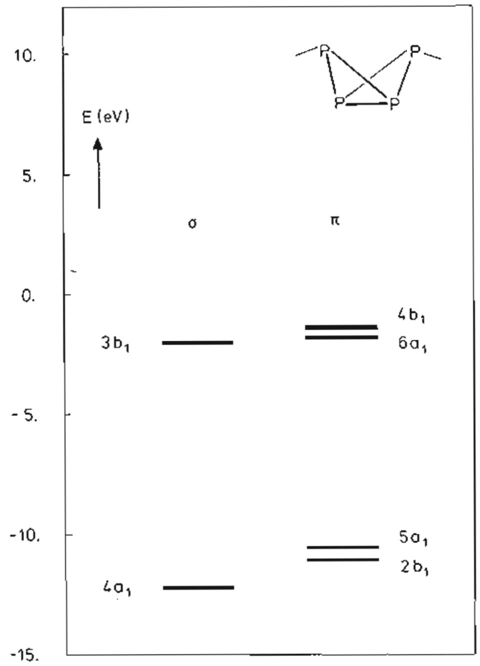

**Figure 2.** Frontier orbital energies (in eV) for **1** (X = H) and computed by the MNDO method. Symmetry designations are according to $C_{2v}$.

## Results and Discussion

**a. Electronic Structure of Parent 1.** First we propose a general and simple picture of bonding in **1** (X = H). It is given by the interaction diagram in Figure 1. Part A (inner set of fragment orbitals) corresponds to the bonding and antibonding combination of $\sigma$ ($\sigma^*$) and $\pi$ ($\pi^*$) orbitals at the central bond P(1)P(3) in **1**. Part B (outer set of fragment orbitals) is viewed as two atoms P(2) and P(4), which interact with three fragment A orbitals: a bonding or antibonding combination of $sp^3$ hybrid orbitals of $a_1$ symmetry and of a fragment orbital of two nonoverlapping $p_x$ orbitals of $b_1$ symmetry. Of course any real B orbitals will include other symmetry orbitals in addition, e.g. negative combinations of the hybrid orbitals and the $p_x$ orbitals. In $C_{2v}$ these orbitals belong to $b_2$ and $a_2$, respectively; therefore, in our analysis they do not interact with the inner set A of fragment orbitals and will not contribute to them. Eight electrons are placed in this scheme to form the bonds. Four can be thought of as coming from the $\sigma$ and $\pi$ levels in set A and four from the B fragment.

The bonding picture we describe here is similar to the inorganic chemist's description of metal–olefin complexes such as Zeise's salt, first presented by Dewar[11] and Chatt and Duncanson.[12] We have electron donation from the fragment orbitals at A to the fragment orbitals at B and vice versa. These processes weaken or strengthen the central bond P(1)P(3) from its original double-bond strength.

The qualitative picture thus derived is in accordance with the quantum-mechanical calculations. MNDO calculations on parent **1** (X = H) yield the following sequence for the three highest energy occupied and three lowest energy unoccupied MO's (Figure 2). For these orbitals, a similar order is also obtained at an ab initio STO-3G level and EH level of approximation (we will not record these calculations here). The two highest energy occupied MO's are of $a_1$ and $b_1$ symmetries.

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(7) (a) M. J. S. Dewar, M. L. McKee, and H. S. Rzepa, *J. Am. Chem. Soc.*, **100**, 3607 (1978). (b) For a summary of minimization methods in quantum chemistry see D. Garton and B. T. Sutcliffe in "Theoretical Chemistry", Vol. 1, Chemical Society, London, 1974, p 34.

(8) (a) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963). (b) The chosen parameters are as follows: for hydrogen, $I_s = -13.6$ eV and $\zeta$ (Slater exponent) = 1.0; for phosphorus, $I_s = -20.2$ eV, $I_p = -12.49$ eV, $I_d = -6.0$ eV, and $\zeta = 1.6$ for s to d orbitals.

(9) For a lucid discussion of d-orbital participation in phosphorus chemistry see K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969).

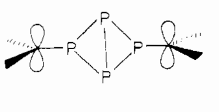
(10) (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *ibid.*, **64**, 5142 (1976); (b) S. Huzinaga, *ibid.*, **42**, 1293 (1965); "Approximate Atomic Functions II", Technical Report, The University of Alberta, 1971.

(11) M. J. S. Dewar, *Bull. Soc. Chim. Belg.*, **18**, C79 (1951); *Nature (London)*, **156**, 784 (1945); *J. Chem. Soc.*, 406 (1946); *Discuss. Faraday Soc.*, No. **10**, 50 (1948).

(12) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

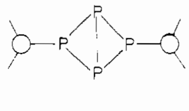
They are constituted from the $\pi$ orbitals at A, although they mix considerably with the $\sigma$ orbitals of like symmetry. The energy difference between $5a_1$ and $2b_1$ is rather small (0.6 eV). A similar situation is achieved for the $3b_1$ and $6a_1$ orbitals. Their energy difference is found to be 0.2 eV. Here however, the $3b_1$ MO is predominantly of the $\sigma$ type while the $6a_1$ MO mixes strongly in the corresponding $\pi$ MO of A. The MO picture of **1**, derived from the interaction of fragment orbitals and confirmed by quantum-mechanical calculations, can easily be related to the Walsh orbitals in bicyclo[1.1.0]butane.[13]

**b. Substituent Effects.** Next we discuss the effect of electron-releasing or electron-accepting substituents on the bonding properties of **1**. In principle, one can differentiate between two extreme geometries for the substituents replacing the hydrogens at P(2) and P(4). A donor (acceptor) orbital at the electron-releasing (-accepting) substituents can interact with the $b_1$ or the $a_1$ orbitals of the skeleton. In the following discussion the different substituents are classified as $\pi$-donors (-acceptors) or $\pi'$-donors (-acceptors), according to the *bisected* or *axial* geometrical arrangement of their p orbitals with respect to the framework of **1**. For symmetry reasons, in the $\pi$-interaction a (bisected) donor or acceptor orbital at a substituent affects only the $b_1$ orbitals. On the contrary, in the $\pi'$-interaction the (axial) substituent orbitals mingle with the $a_1$ orbitals.



π -interaction

(bisected)



π′-interaction

(axial)

On the basis of the fragment orbital picture for **1** (Figure 1), one can predict the following substituent effects on the bonding properties (bond lengths) in parent **1**.

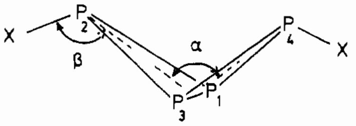
**(1) $\pi$ Effects. (a) Donors.** The $b_1$ level of the outer set B will be raised in energy. The orbital comes into closer proximity to the antibonding $b_1$ levels of the inner set A. As a consequence, the bridgehead bond P(1)P(3) gains more antibonding character. It will be loosened (in reference to unsubstituted **1**).

**(b) Acceptors.** These will have the opposite effect. The $b_1$ level of B is lowered in energy. On this basis its interaction with the $b_1$ levels of A decreases. The bond P(1)P(3) is strengthened. It must be noted that the expectation derived from our model is analogous to the effects of $\pi$-donors and $\pi$-acceptors on the bond lengths in cyclopropane.[14]

**(2) $\pi'$ Effects. (a) Donors.** In this case the $a_1$ levels will be affected. The $a_1$ level of B will be raised in energy, which corresponds to an increase in the electropositive character of this orbital. Electron density will tend to concentrate on the more electronegative atoms.[15,16] Therefore, the bond P(1)P(3) will be strengthened, and consequently, the peripheral bonds will be loosened.

**(b) Acceptors.** These have the opposite effect; the P(1)P(3) bond is loosened, and the peripheral bonds are strengthened.

**Table I.** Bonding Properties of Various Substituted Structures of **1**[a]



| X | P(1)P(3), Å | Δ(P(1)P(3)–P(1)P(2)), Å | α, deg | β, deg |
|---|---|---|---|---|
| H | 2.046 | 0.001 | 102.6 | 103.7 |
| | (2.150) | (−0.026) | (100.8) | (96.5) |
| $H_2N$ (ax) | 1.999 | −0.069 | 103.7 | 112.3 |
| | (2.138) | (−0.053 | (99.2) | (100.9) |
| $H_2N$ (bi) | 2.046 | −0.014 | 105.3 | 109.9 |
| | (2.180) | (0.004) | (100.8) | (103.2) |
| $H_2B$ (ax) | 2.074 | 0.043 | 101.4 | 115.1 |
| $H_2B$ (bi) | 2.029 | −0.023 | 100.2 | 109.6 |
| $H_2C^+$ (ax) | 2.194 | 0.197 | 108.3 | 176.6 |
| $H_2C^+$ (bi) | 2.002 | −0.107 | 93.4 | 117.3 |
| $H_2C^-$ (ax) | 1.958 | −0.127 | 104.1 | 118.3 |
| $H_2C^-$ (bi) | 2.030 | −0.047 | 105.4 | 113.9 |
| F | 2.026 | −0.049 | 102.6 | 112.0 |
| NC | 2.041 | −0.021 | 100.7 | 107.7 |

[a] p orbitals at the substituents are in a bisected (bi) or axial (ax) arrangement with respect to the bicyclic moiety in 1. All structures are completely optimized with respect to $C_s$ symmetry, by either the MNDO or the ab initio STO-3G method (values in parentheses for X = H, $NH_2$).

**c. Numerical Calculations.** In order to put these qualitative considerations on firmer ground, we have evaluated the structural features of various substituted structures **1** in the two extreme conformations with bisected and axial arrangements of the donor (acceptor) orbitals at the substituents. All geometries, thus computed, were totally optimized with respect to $C_s$ symmetry. The results of our investigations are collected in Table I. It must be noted that the MNDO method (and to a less extent the ab initio STO-3G wave function) yields, in general, too short PP distances, compared with high-quality ab initio calculations on model systems.[4b,10a] This, however, does not invaliditate the trends in the bond alterations revealed from the numerical calculations.

A negative value for Δ indicates a loosening, and a positive value for Δ, a strengthening of the peripheral bonds (P(1)P(2) = P(1)P(4) = P(2)P(3) = P(3)P(4)), at times in reference to the bridgehead bond P(1)P(3).

In the case of $\pi'$-donors (X = $NH_2$, $CH_2^-$; axial conformations), the expected shrinking of the bond P(1)P(3) is observed. At the same time the peripheral bonds (e.g. P(1)P(2)) elongate. Similar considerations hold true for the case of the $\pi$-acceptors (bisected conformations with X = $BH_2$, $CH_2^+$). On the contrary, $\pi'$-acceptors ($BH_2$, $CH_2^+$; axial conformations) elongate the bond P(1)P(3) and simultaneously shorten P(1)P(2) and P(1)P(4) (P(2)P(3) and P(3)P(4), respectively), in agreement with the qualitative predictions.

The numerical test for the substituent $NH_2$ was also performed by means of geometry optimization at an ab initio STO-3G level. The results agree with the MNDO calculations. A difference however is obtained for the case of X = $NH_2$ in a bisected conformation. According to MNDO, the P(1)P(3) bond is not altered while it is slightly at an ab initio STO-3G level.[17] In general the bond alterations exerted from the $\pi'$-type substituent effects are larger with MNDO than

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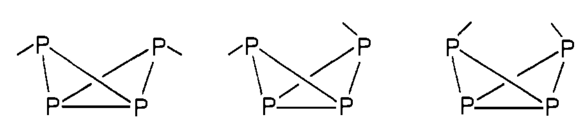
(13) M. Pomerantz and E. W. Abrahamson, *J. Am. Chem. Soc.*, **88**, 3970 (1966).

(14) (a) R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970); (b) H. Günther, *ibid.*, 5173 (1970); (c) see also S. Durmaz and H. Kollmar, *J. Am. Chem. Soc.*, **102**, 6942 (1980).

(15) For a lucid discussion of polarization see L. Libit and R. Hoffmann, *J. Am. Chem. Soc.*, **96**, 1370 (1974).

(16) See also: H. A. Bent, *Chem. Rev.*, **61**, 275 (1961); A. D. Walsh, *Discuss. Faraday Soc.*, **No. 2**, 18 (1947); A. D. Walsh, *Trans. Faraday Soc.*, **42**, 56 (1946); **43**, 60, 158 (1947).

(17) (a) It is known that ab initio calculations without polarization functions in the basis set overestimate the amount of ring strain in cyclic systems (see e.g. W. J. Hehre, *Acc. Chem. Res.*, **9**, 399 (1976)). For the case at hand, the bridgehead bond will be more strained than the peripheral ones. Therefore minimal basis set calculations preferentially underestimate the stability of the central bond. In contrast, semiempirical SCF methods tend to overestimate the stability of strained bonds. On the basis of these apparent deficiencies of quantum-mechanical methods, a definite reason for the response of the central P(1)P(3) bond to $\pi$-donors cannot be provided by our calculations. (b) For an ab initio study of bonding in **3** see M. D. Newton and J. M. Schulman, *J. Am. Chem. Soc.*, **94**, 767 (1972).



| | exo/exo | exo/endo | endo/endo |
|---|---|---|---|
| | $C_{2v}$ | $C_s$ | $C_{2v}$ |
| LUMO[a] | -1.90 ($b_1$) | -1.87 (a'') | -2.14 ($b_1$) |
| HOMO[a] | -10.54 ($a_1$) | -10.95 (a'') | -10.93 ($b_1$) |
| (HOMO-1)[a] | -11.13 ($b_1$) | -11.14 (a'') | -11.03 ($b_2$) |
| ΔE[b] | 0. | 1.2 | 8.7 |

[a] energies in eV

[b] relative energies in kcal per mole

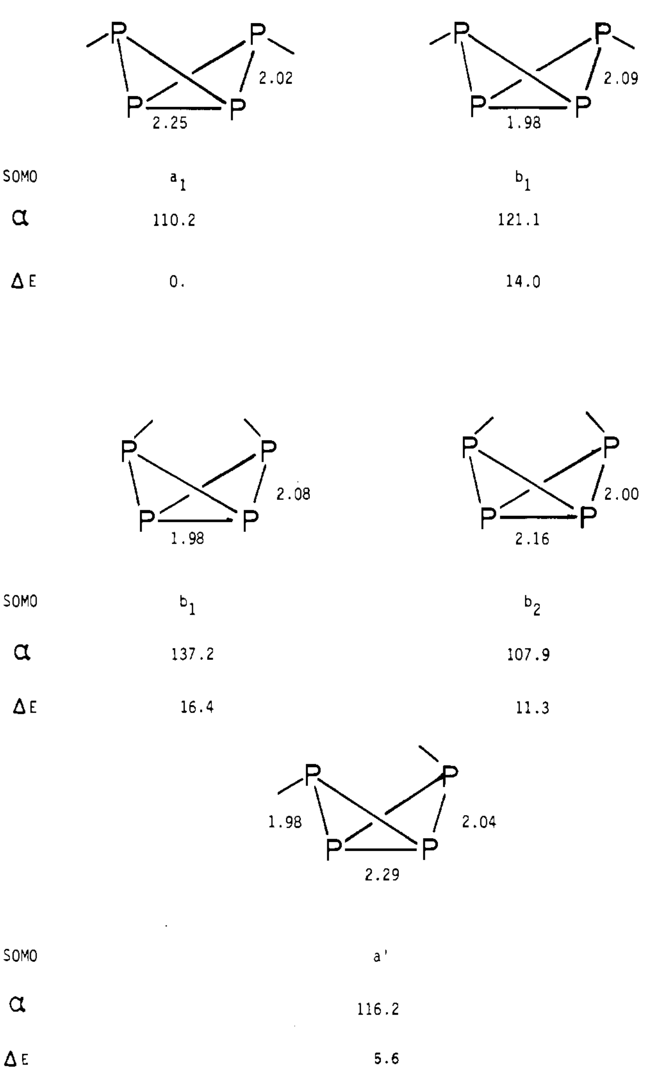
**Figure 3.** Different structural isomers of **1** (R = H) and their frontier orbital energies (in eV), computed with the MNDO approximation.

with the ab initio STO-3G wave function, and for the case of the $NH_2$ substituent are in better agreement with experimental values.[2]

The role of 3d orbitals in P bonding is a perpetual problem.[9] In our present discussion, the degree of d orbital participation at P(III) cannot be estimated because neither MNDO nor the ab initio STO-3G wave function includes them in the basis set. However, we have analyzed their importance by performing EH calculations with and without inclusions of d orbitals at P in **1** and its derivatives. For the various structures the Mulliken populations were then compared. The calculations, which we will not report here, show that the inclusion of 3d orbitals at P does not alter the qualitative considerations reached by the SCF calculations. These findings that 3d orbitals at P play little role in bonding finds support by ab initio calculations on a variety of structures containing P(III).[18] Therefore, their role will not be further discussed here.

**d. Different Structural Isomers and Radical Cations.** Next, the different structural isomers of **1** (R = H) are investigated. According to optimized MNDO calculations, the energy differences between the various isomers are small (Figure 3). In the least stable conformation the hydrogens at P(2) and P(4) are standing cis to each other. However, noticeable is the change in the symmetry designation of the corresponding frontier orbitals. In the exo/exo conformation the HOMO is of $a_1$ symmetry while the LUMO is $b_1$. In contrast, in the endo/endo conformation the HOMO and LUMO possess like symmetry, $b_1$. In close proximity is a HOMO-1 orbital of $b_2$ symmetry.

Suppose one would now remove an electron from the closed-shell system. Since the energy differences of the highest energy MO's are rather small, an electron can be removed with the same expense from HOMO or from HOMO-1. An exploration of this concept with the MNDO approximation[19] yields the following picture (Figure 4). The most stable isomer is derived from the exo/exo conformation by removing one electron from the HOMO $a_1$. The isomer with the $(b_1)^1$ configuration is considerably higher in energy. The removal of one electron from a bonding ($a_1$) or antibonding ($b_1$) MO with respect to the bridgehead bonds causes a loosening or strengthening of this bond. Since, in the endo/endo conformation, the HOMO and HOMO-1 are in close proximity, their corresponding radical cation isomers are only slightly different in their energy content. It is also interesting to note that, in the open-shell species with $(b_1)^1$ configuration, the folding angle $\alpha$ is enlarged (for a rationalization of this fact, see the orbitals in the interaction diagram in Figure 1).[20]



| | | |
|---|---|---|
| SOMO | $a_1$ | $b_1$ |
| α | 110.2 | 121.1 |
| ΔE | 0. | 14.0 |

| | | |
|---|---|---|
| SOMO | $b_1$ | $b_2$ |
| α | 137.2 | 107.9 |
| ΔE | 16.4 | 11.3 |

| | |
|---|---|
| SOMO | a' |
| α | 116.2 |
| ΔE | 5.6 |

**Figure 4.** Different radical cations computed by the MNDO approximation[19] (SOMO = single occupied molecular orbital; $\alpha$ = folding angle between the planes spanned by the three-membered rings; $\Delta E$ = relative energies of the isomers in kcal $mol^{-1}$.

**e. Fragmentation of 1 to 3.** The title compound, **1**, decomposes above 150 °C to phosphorus and cyclotetraphosphane.[2] This can be thought of by primary formation of $P_2$ plus diphosphaethylene (route to **3**). In order to investigate the mechanism of the fragmentation process, we will analyze it on the basis of an orbital correlation diagram.[21] The matter is illustrated in Figure 5 for the case of assumed $C_s$ symmetry throughout the reaction. The participating orbitals are provided from EH calculations for the individual species. For the ground state, the number of symmetry orbitals in the educt and product side differ. In **1**, the orbital ($3b_2$) correlates with the virtual orbital $a_2$ of $P_2H_2$. Hence, on the basis of these considerations, the concerted fragmentation is symmetry forbidden. Similar results are obtained for the case of $C_2$

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(18) See e.g.: F. Keil and W. Kutzelnigg, *J. Am. Chem. Soc.*, **97**, 3623 (1975); H. Wallmeier and W. Kutzelnigg, *ibid.*, **101**, 2804 (1979); W. Kutzelnigg and J. Wasilewski, *ibid.*, **104**, 953 (1982).

(19) The radical cations were computed by means of the half-electron approximation: (a) M. J. S. Dewar and N. Trinajstic, *J. Chem. Soc. A*, 1220 (1971). (b) F. O. Ellison and F. M. Matheu, *Chem. Phys. Lett.*, **10**, 322 (1971). (c) See also W. W. Schoeller, *Mol. Phys.*, **37**, 1037 (1979).

(20) The reader might refer to the discussion on the radical cation of cyclopropane: J. R. Collins and G. A. Gallup, *J. Am. Chem. Soc.*, **104**, 1530 (1982), and references cited therein.

(21) R. Hoffman and R. B. Woodward, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., West Germany, 1970.

Table II. Geometries and Energies of **1** and Corresponding Energy Minima on the Electronic Hypersurface, Obtained from Energy-Optimized MNDO and ab Initio Calculations

(A) Geometries

| molecule | symm group | opt geom | MNDO | basis I | basis III |
|---|---|---|---|---|---|
| $P_2$ | $D_{\infty h}$ | $r$(PP) | 1.693 | 1.808 | |
| $P_2H_2$ | $C_{2h}$ | $r$(PP) | 1.833 | 1.965 | 2.004 (2.034)[c] |
| | | ∢(HPP) | 100.5 | 95.0 | |
| 4 | $D_{2h}$ | $r$(P(1)P(3)) | 2.972 | 3.201 | |
| | | $r$(P(1)P(2)) | 1.936 | 2.072 | |
| | | $\alpha$ | 180.0 | 180.0 | |
| | | $\beta$ | 180.0 | 180.0 | |
| | $C_{2v}$ | $r$(P(1)P(3)) | 2.902 | 3.122 | |
| | | $r$(P(1)P(2)) | 1.948 | 2.111 | |
| | | $\alpha$ | 146.0 | 141.9 | |
| | | $\beta$ | 145.4 | 126.8 | |
| | $C_s$ | $r$(P(1)P(3)) | 2.959 | 3.191 | |
| | | $r$(P(1)P(2)) ($r$(P(1)P(4))) | 1.972 (1.927) | 2.104 (2.092) | |
| | | $\beta_1$ ($\beta_2$) | 132.5[a] (161.9)[b] | 128.8[a] (133.2)[b] | |

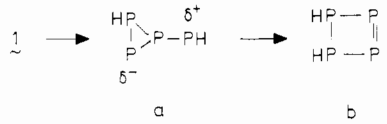
(B) Energies

| | MNDO | | basis I | | basis II[f] | | basis III[f] | |
|---|---|---|---|---|---|---|---|---|
| molecule | $H_f$,[d] kcal | $E_{rel}$,[e] kcal | $E$, au | $E$, kcal | $E$, au | $E$, kcal | $E$, au | $E$, kcal |
| 1 ($C_{2v}$) | 14.5 | 0 | 1348.932 06 | 0 | −1363.389 37 | 0 | −1363.591 31 | |
| $P_2$ ($D_{\infty h}$) | 40.7 | 53.6 | −673.763 96 | 154.0 | −681.116 46 | 20.3 | −681.203 77 | 34.6 |
| $P_2H_2$ ($C_{2h}$) | 27.4 | | −674.922 63 | | −682.240 58 | | −682.332 40 | |
| 4 ($D_{2h}$) | 41.8 | 27.3 | −1348.671 58 | 163.4 | −1363.297 70 | 57.5 | | |
| 4 ($C_{2v}$) | 40.7 | 26.2 | −1348.697 72 | 147.0 | −1363.306 96 | 51.7 | | |
| 4 ($C_s$) | 39.0 | 24.5 | −1348.709 72 | 139.5 | −1363.319 50 | 43.8 | | |

[a] Hydrogens are endo with respect to the ring moiety. [b] Hydrogens are exo with respect to the ring moiety. [c] Experimental value;[5] ∢(HPP) assumed from basis I. [d] Heats of formation. [e] Relative energies. [f] Geometrical parameters were taken from basis I (for 4) or from experiment (for **1**, see ref 2; for $P_2$ $r$(PP) = 1.839 Å[10a]); for $P_2H_2$ the parameters were obtained from optimization at basis III.

symmetry during the course of the reaction.

An alternative route to **3** requires the breakage of one of the peripheral bonds in the primary step, e.g. P(3)P(4) to a 1,3-dipole (a), which in a second step undergoes the common



ring-expansion reaction[22] to b. In a subsequent step the latter fragments to **3**, similar to the case of cyclobutane.[23]]

From the viewpoint of energy, the fragmentation of **1** (X = H) is endothermic. This is substantiated by the semiempirical and ab initio SCF calculations for the various local minima of the electronic hypersurface of $P_4H_2$ (Table II). The inclusion of d functions in the (ab initio) basis set (basis III) does not essentially alter this picture. However, the d functions at P are of greater advantage to the more strained structure. In other words, **1** becomes more stable with respect to its fragmentation products $P_2H_2$ and $P_2$.

We also note that the calculations with the least quality (MNDO and basis I) grossly underestimate the equilibrium distance of the PP bond (see Table IIA). This deficiency of ab initio minimal basis set calculations is well documented.[10a]

**f. Bond-Stretch Isomerism in 1 and Formation of Monocyclic 4.** In this, the last section of our report, we analyze the relation of bicyclic **1** to its monocyclic analogue **4**. We first discuss the bond stretching of the central bond P(1)P(3) in **1** (X = H). Figure 6 shows an orbital correlation diagram for the rearrangement of **1** to planar **4**. The picture is derived from EH calculations (without d orbitals in the basis set). In the ground state, the breakage of the bond P(1)P(3) is symmetry forbidden since it requires the crossing of the orbitals HOMO and LUMO.[24] However, the crossing of orbitals

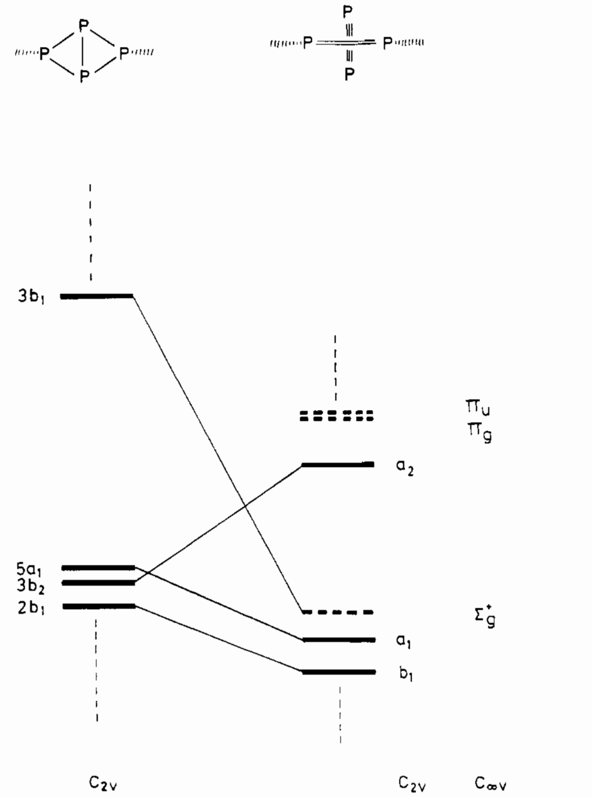


**Figure 5.** Orbital correlation diagram for the concerted fragmentation of **1** to **3**, extruded from EH calculations (without d orbitals). Symmetry designations refer to local symmetry assignments; dotted lines refer to the orbitals of $P_2$.

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(22) W. W. Schoeller, *J. Org. Chem.*, **45**, 2161 (1980).

(23) (a) See e.g. E. V. E. Doering and A. R. Mastrocola, *Tetrahedron, Suppl.*, No. **9**, *37*, 329 (1981), and references cited therein. (b) On the contrary the related bicyclo[1.1.0]butane (**3**) rearranges thermally to 1,3-dienes: K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1235 (1968); L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, *J. Am. Chem. Soc.*, **92**, 7002 (1970); G. L. Closs and P. E. Pfeffer, *ibid.*, **90**, 2452 (1968); S. Weinstein, J. H. Leftin, J. Krebs, and E. Gil-Av, *J. Chem. Soc. D*, 1616 (1971).

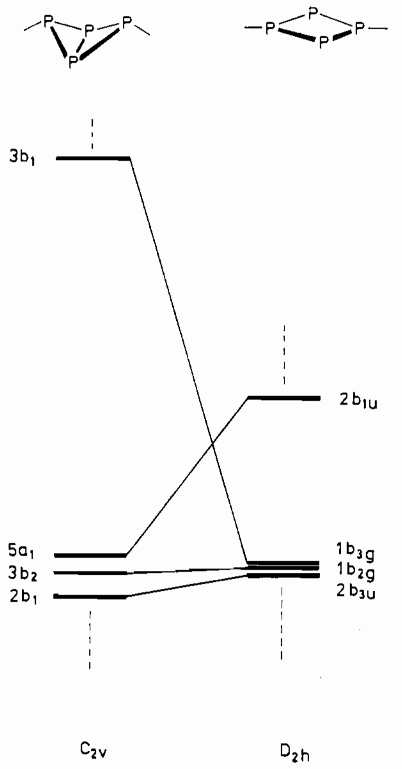

**Figure 6.** Orbital correlation diagram for the reaction of **1** (X = H) to planar **4**, deduced from EH calculations (without d orbitals).

becomes symmetry allowed in the first singly excited states (singlet or triplet) and in the dication. This view is supported by MNDO calculations. For **1**, the triplet as well as the singlet with the configurations $^{1,3}[(a_1)^1(b_1)^1]$ rearranges without activation barriers to the corresponding states of **4**.

We have examined all structural alternatives for the closed-shell singlet of **4**. According to the semiempirical and ab initio calculations, it is in its lowest energy in $C_s$ symmetry. Most noticeable is its unusual structure, which we have summarized in Table II. It prefers a puckered structure[25] in which the hydrogens are slightly tilted out of plane, one exo and one endo with respect to the ring moiety. The unexpected equilibrium structure for **4** might be attributed to the following tendencies: (1) The breakage of the bond P(1)P(3) in **1** causes an electron deficit at the unsubstituted phosphorus atoms. There, to each phosphorus atom seven rather than eight electrons can be formally assigned. (2) On the assumption that **4** would be planar ($D_{2h}$ symmetry), two electrons at each phosphorus atom (P(1) and P(3)) can be placed in either (a) the $\pi$ orbitals or (b) the $\sigma$ orbitals, these orbitals being perpendicular or being in the plane of the four-membered ring system. On this basis the single electron at each phosphorus atom is then in the $\sigma$ (case 2a) or the $\pi$ orbital space (case 2b). Consequently, they span a four-center $\pi$-system containing either eight (case 2a) or six $\pi$ electrons (case 2b). The former arrangement of electrons is destablizing overall. It will be reduced if the hydrogens are tilting out of plane of the four-membered ring system.

As revealed at all levels of quantum-mechanical methods, the various conformations of **4** are always higher in energy than **1** (see Table II). With the aid of the MNDO method, we also have examined the existence of an energetically low-lying triplet state in **4**. Accordingly, it lies 9.6 kcal mol$^{-1}$ below the lowest energy singlet state.

It must be noted that **4** is a novel structure, which has not been detected so far. It is isovalent with the well-known $S_2N_2$.[26] On the basis of the present discussion on $P_4H_2$, we predict the existence of a bicyclic $S_2N_2$ (analogous to **1**) as well. A general discussion of the equilibria of bicyclic vs. monocyclic structures (analogous to the case of **1** and **4**) derived from all possible combinations of the atoms (groups) P, N, S, and O will be presented in a separate study.

Suppose one removes two electrons from the HOMO in **1** (X = H). According to the correlation diagram in Figure 6, the bond stretching becomes symmetry allowed. In fact, MNDO calculations suggest that the dication of **1** is not stable. It rearranges without an energy barrier to the monocyclic (planar) dication of **4**. The case is analogous to the first excited state of **1** (see previous discussion).

## Conclusions

Our findings can be summarized as follows:

(1) Tetraphosphabicyclo[1.1.0]butane (**1**) possesses two energetically high-lying as well as two low-lying orbitals of $a_1$ and $b_1$ symmery. In agreement with the bonding situation in inorganic three-membered ring systems,[27] the presence of these orbitals causes the following changes in geometry by substituents in **1**: (a) $\pi'$-Donors strengthen the bridgehead bond P(1)P(3) and weaken the PP bonds to the peripheral atoms. (b) $\pi'$-Acceptors do the opposite. They loosen P(1)-P(3) and strengthen the other bonds. (c) $\pi$-Donors and $\pi$-acceptors exert the same bonding effects, as has been previously stressed for cyclopropane.[14] However, for the case of $\pi$-donors, the effect is in variance with the MNDO calculations.

(2) The presence of two high-lying, energetically closely spaced frontier orbitals reveals for the cation radicals various isomers, which are comparable in energy.

(3) According to an orbital correlation diagram, the concerted fragmentation of **1** (R = H) to **3** is a symmetry-forbidden process in the ground state. A similar consideration holds true for the bond stretching of P(1)P(3) in **1**. The species **1** and **4** (R = H) possess approximately the same energy content. The latter is predicted to assume a nonplanar structure. The ring opening of **1** to **4** is symmetry allowed in the dication and the first singly excited states (triplet and singlet).

The similarity of the electronic structure of **1** to that of bicyclo[1.1.0]butane (**2**) is apparent. Our model ascribes "olefinic character" to the central bond, especially if $\pi$-donors are attached to the peripheral atoms (axial conformation). As has been investigated in detail for **2**, tetraphosphabicyclo[1.1.0]butane (**1**) should be an interesting target for the studies of cycloaddition reactions. This aspect seems the more interesting, since **1** possesses a symmetric ($a_1$) and antisymmetric ($b_1$) HOMO and a low-lying LUMO of like symmetries.

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[24] (a) For the related case of bond-stretch isomerism in hydrocarbons see W.-D. Stohrer and R. Hoffman, *J. Am. Chem. Soc.*, **94**, 779 (1972). (b) As has been stressed by these authors for the case of tricyclo-[2.2.0]octane, in analogy Lewis acids should also reduce the forbiddenness of the reaction of **1** to **4**.

[25] Pertinent examples of puckered four-membered ring systems have been discussed in detail recently: K. Krogh-Jespersen, P. v. R. Schleyer, J. A. Pople, and D. Cremer, *J. Am. Chem. Soc.*, **100**, 4301 (1978); K. Krogh-Jespersen, D. Cremer, J. D. Dill, J. A. Pople, and P. v. R. Schleyer, *ibid.*, **103**, 2589 (1981); W. W. Schoeller, *ibid.*, **101**, 4811 (1979).

[26] M. J. Cohen, A. F. Garito, A. J. Heeger, A. G. MacDiarmid, C. M. Mikulski, M. S. Saran, and J. Kleppinger, *J. Am. Chem. Soc.*, **98**, 3844 (1976); C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garito, and A. J. Heeger, *ibid.*, **97**, 6358 (1975); see also H. W. Roesky, *Angew. Chem., Int. Ed. Engl.*, **18**, 91 (1979).

[27] W. W. Schoeller and Th. Dabisch, *J. Chem. Soc., Dalton Trans.*, in press.

drhein-Westfalen. The computer time was generously provided by the Rechenzentrum der Universität Bielefeld and by the Rechenzentrum der Universität Köln. Some of the calculations were also carried out at the Interdata 8/32 minicomputer (Universität Bochum), sponsored by the Deutsche Forschungsgemeinschaft. We also thank Professor V. Staemmler for interesting discussions and valuable suggestions and the reviewers for useful comments.

**Registry No.** **1** (X = H), 51272-82-3; **1** (X = H), radical cation, 86834-53-9; **1** (X = $NH_2$), 86834-48-2; **1** (X = $CH_2^{-}\cdot$), 86834-49-3; **1** (X = $BH_2$), 86834-50-6; **1** (X = $CH_2^{+}\cdot$), 86834-51-7; **4**, 86834-52-8; diphosphaethylene, 41916-72-7.

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# Electronic Structure of Metal Clusters. 4. Photoelectron Spectra and Molecular Orbital Calculations on Cobalt, Iron, Ruthenium, and Osmium Sulfide Nonacarbonyl Clusters

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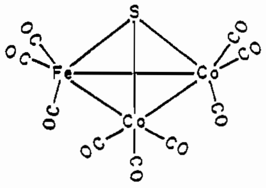
Gas-phase, ultraviolet photoelectron (PE) spectra and molecular orbital (MO) calculations are reported for $SCo_3(CO)_9$, $SH_{n-1}Fe_nCo_{3-n}(CO)_9$ ($n$ = 1–3), $S_2Fe_3(CO)_9$, and $SH_2M_3(CO)_9$ (M = Fe, Ru, Os). The first PE spectra reported for mixed-metal clusters are included in this series. As Co atoms are replaced by the isoelectronic FeH unit, the spectra show the loss of a Co band and the appearance of an Fe band. This phenomenon suggests that the d bands localize upon ionization. In a comparison with the PE spectrum of $M_3(CO)_{12}$ (M = Fe, Ru, Os), the major spectral changes for $SH_2M_3(CO)_9$ (M = Fe, Ru, Os) are the loss of a band corresponding to direct M–M interactions and the appearance of bands due to a mixture of energy-equivalent M–H–M and M–S interactions. The spectra also show a substantial rearrangement of the bands due to the $t_{2g}$-like electrons, which are usually considered M–CO $\pi$ bonding. An antibonding interaction between a S orbital and the $t_{2g}$-like orbitals is responsible for a unique band in the spectra which occurs at high ionization energy between the M–M bonding band and the main $t_{2g}$-like band.

## Introduction

Metal–sulfur clusters are interesting because of their implication in poisoning of catalysts by sulfur and as models for hydrodesulfurization catalysts.[1] The systematic investigation of $Co_2(CO)_8$-catalyzed hydroformylations with olefinic compounds and sulfur impurities resulted in the identification of various cobalt and cobalt carbonyl sulfides including $SCo_3(CO)_9$.[2] While studying the reaction of synthesis gas with thiophene in the presence of $Co_2(CO)_8$ and $Fe(CO)_5$, Khattab et al. isolated $SFeCo_2(CO)_9$. This mixed-metal cluster was among the first carbonyl compounds containing a metal–metal bond between two different transition-metal atoms and the first mixed-metal sulfide carbonyl cluster.[3] The advances in the field of transition-metal cluster chemistry in the past decade are evident by the numerous reviews discussing the preparation of new cluster compounds of increasing nuclearity and complexity.[4] These compounds are of additional interest because of the similarities between chemisorption on transition-metal surfaces and the chemistry of conventional transition-metal clusters.[5] Despite the early synthesis and novelty of these sulfide carbonyl clusters, their chemistry has not been as thoroughly investigated as the isostructural $RCCo_3(CO)_9$ clusters.[6]

The crystal structure of $SCo_3(CO)_9$ confirmed that the molecular geometry consists of a triangle of cobalt tricarbonyl fragments capped by a S atom.[7] The X-ray structure determination of $SFeCo_2(CO)_9$ (**1**) showed it to be isomorphous with $SCo_3(CO)_9$.[8] The sulfur atom in the paramagnetic $SCo_3(CO)_9$ cluster contributes four electrons to the $Co_3(CO)_9$



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