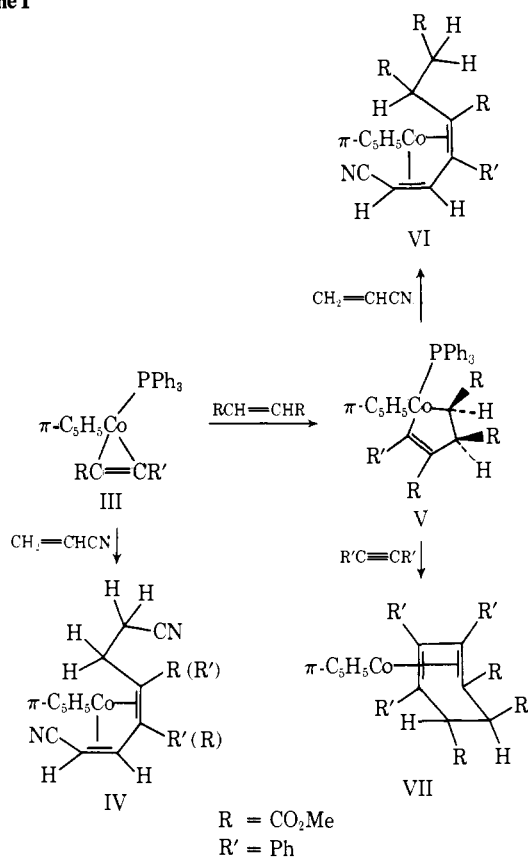
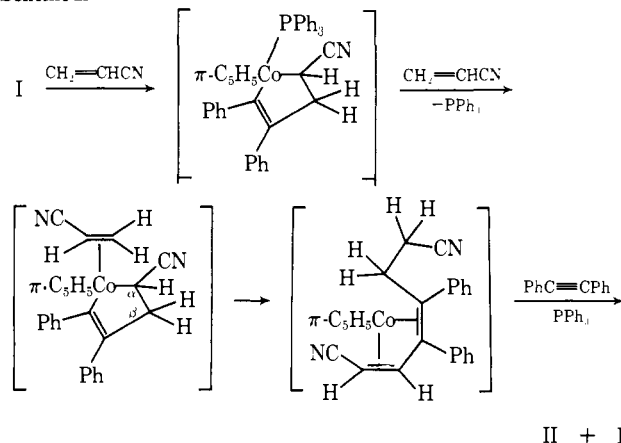


Scheme I



Scheme II



of hydrogen⁶ affording the diene complex intermediate analogous to IV or VI.

In contrast, the reaction of diphenylacetylene with methacrylonitrile produces a compound formulated as $(\text{PhC}_2\text{Ph})_2(\text{CH}_2\text{C}(\text{Me})\text{CN})$ (VIII), mp 190–191°, in 320% yield based on I.⁷ The ir and pmr spectral data of VIII are best accommodated by the structure shown in the figure, in which one of the methyl protons of the methacrylonitrile molecule has transferred to the diphenylacetylene carbon.

Compound VIII is presumably formed also *via* the

(6) Hydrogen may transfer either from the attacking acrylonitrile to the cobaltacyclopentene α -carbon or from the β -carbon of the cobaltacyclopentene ring to the attacking acrylonitrile. Taking into account the model reaction $\text{V} \rightarrow \text{VI}$, the authors prefer the former case.

(7) In these cooligomerization reactions, a considerable amount of cyclobutadiene complex, $\pi\text{-C}_5\text{H}_5\text{Co}(\text{PhCCPh})_2$, is obtained, which may be formed readily on heating X.⁴ Therefore, the formation of X from I and diphenylacetylene is supposed to be a main reason for rather poor catalytic activity of I.

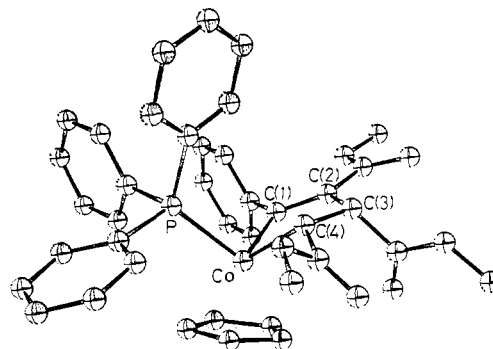
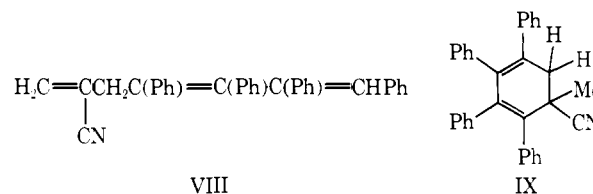


Figure 1. The molecular geometry of $\pi\text{-C}_5\text{H}_5\text{Co}(\text{PPh}_3)[(\text{PhC}_2\text{CO}_2\text{Me})(\text{MeO}_2\text{CH})_2]$ (V).

cobaltacyclopentene intermediate which is successively attacked by diphenylacetylene. If no transfer of hydrogen occurred, this reaction is expected to produce a cyclohexadiene derivative (IX) according to the model



reaction $\text{V} \rightarrow \text{VII}$, but actually one of the methyl hydrogens transfers to the attacking diphenylacetylene molecule thus forming the straight-chain product. The alternative mechanism, *i.e.*, attack by methacrylonitrile upon the cobaltacyclopentadiene intermediate followed by hydrogen transfer has been excluded since the treatment of cobaltatetraphenylcyclopentadiene complex, $\pi\text{-C}_5\text{H}_5\text{Co}\cdot\text{C}(\text{Ph})=\text{C}(\text{Ph})\cdot\text{C}(\text{Ph})=\text{C}(\text{Ph})(\text{PPh}_3)$ (X), with methacrylonitrile, gave only IX (10%) and 1,2,3,4-tetraphenyl-5- α -methylvinylpyridine (19%) as organic products, and hence no hydrogen transfer was observed.

Thus it is obvious that the relative coordination abilities between the acetylene and the olefins govern the reaction paths and consequently determine the products.

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 Received March 18, 1974

Variations in Molecular Geometry along the Isoelectronic Series $\text{Co}_2(\text{CO})_8$, $[\text{FeCo}(\text{CO})_8]^-$, and $[\text{Fe}_2(\text{CO})_8]^{2-}$

Sir:

$\text{Co}_2(\text{CO})_8$ is an example of a compound whose solid state and solution structures are different. While X-ray studies¹ have indicated a C_{2v} , double CO-bridged structure (I) in the crystal, infrared studies² have shown that in solution the molecule exists as an equilibrium mixture of (I) and the nonbridged D_{3d} isomer (II). We wish to report that interesting changes occur in the geometry of this species as its charge is systematically varied (*i.e.*, as each Co atom is replaced by Fe^-).

(1) G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Crystallogr.*, 17, 732 (1964).

(2) (a) K. Noack, *Spectrochim. Acta*, 19, 1925 (1963); (b) G. Bor, *ibid.*, 19, 2065 (1963).

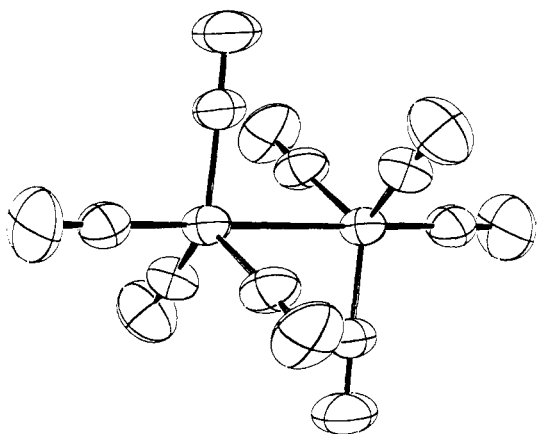
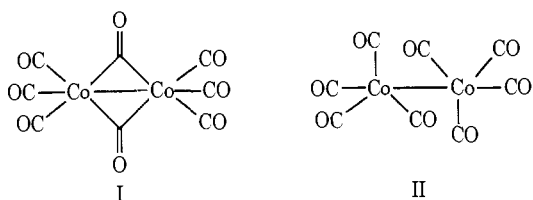


Figure 1. The molecular geometry of the $[\text{Fe}_2(\text{CO})_8]^{2-}$ anion. A crystallographic center of symmetry, which lies at the center of the Fe-Fe bond, relates the two halves of the molecule to each other. The Fe-Fe bond distance is 2.787 (2) Å.



$[\text{Fe}_2(\text{CO})_8]^{2-}$ was prepared in the manner of Hieber and Brendal³ and precipitated as its $[(\text{Ph}_3\text{P})_2\text{N}]^+$ salt by addition of a methanolic solution of $[(\text{Ph}_3\text{P})_2\text{N}]^+\text{Cl}^-$. Recrystallization from a 2:1:1 mixture of acetonitrile, acetone, and ethyl acetate afforded red-brown crystals of $[(\text{Ph}_3\text{P})_2\text{N}]_2^+ [\text{Fe}_2(\text{CO})_8]^{2-} \cdot 2\text{CH}_3\text{CN}$: space group $P\bar{1}$ (triclinic); $a = 17.942(4)$, $b = 12.944(3)$, $c = 10.532(3)$ Å, $\alpha = 93.21(2)$, $\beta = 115.35(1)$, $\gamma = 106.72(2)^\circ$; $V = 2071.1$ Å³; $Z = 1$; 3765 reflections (Mo $K\alpha$ radiation; 2θ limit 45°) were collected on a Nonius CAD-3 diffractometer. The structure was solved by heavy atom methods and refined to a present R factor of 8.8%.⁴

The $[\text{Fe}_2(\text{CO})_8]^{2-}$ anion has a D_{3d} geometry⁵ (Figure 1) with an unbridged Fe-Fe bond of length 2.787 (2) Å. Table I lists average molecular parameters in the molecule. A crystallographic center of symmetry is situated at the center of the anion, and the two sets of staggered equatorial carbonyl groups are slightly bent toward each other, as expected.⁶ The configuration of $[\text{Fe}_2(\text{CO})_8]^{2-}$ therefore resembles the structure of $\text{Co}_2(\text{CO})_8$ in solution; this finding confirms earlier infrared and Mössbauer studies⁷ on this anion.

The contrast between the solid state structures of C_{2v} for $\text{Co}_2(\text{CO})_8$ and D_{3d} for $[\text{Fe}_2(\text{CO})_8]^{2-}$ now prompted

(3) W. Hieber and G. Brendal, *Z. Anorg. Allg. Chem.*, **289**, 324 (1957).

(4) Most computations in this work were performed using CRYM, an amalgamated set of crystallographic programs developed by R. E. Marsh at the California Institute of Technology. Also used was UCIGLS, a group refinement program by R. J. Doedens and J. A. Ibers.

(5) An earlier X-ray structure determination of the $[\text{Fe}(\text{en})_2]^{2+}$ salt of the $[\text{Fe}_2(\text{CO})_8]^{2-}$ anion was reported as part of an abstract to the Seventh International Symposium of the International Union of Crystallography (F. S. Stephens, *Acta Crystallogr.*, **21**, A154 (1966)) but no details of the molecular structure were given other than that the anion had D_{3d} geometry. An Fe-Fe distance of 2.75 Å for this compound was later quoted by Dahl: Footnote 56 in L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7312 (1970).

(6) R. Bau, S. W. Kirtley, T. N. Sorrell, and S. Winarko, *J. Amer. Chem. Soc.*, **96**, 988 (1974).

(7) K. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc. A*, 2339 (1969).

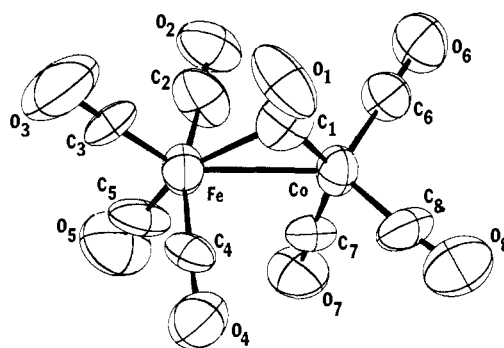


Figure 2. The molecular geometry of the $[\text{FeCo}(\text{CO})_8]^-$ anion. A noncrystallographic mirror plane passes through the two metal atoms and all odd-numbered carbonyls. Note the asymmetric nature of the C_1O_1 bridge. The coordination of atoms C_1 - C_5 about the iron atom is roughly square pyramidal, with C_3 as apex. The coordination of atoms C_1 , C_6 , C_7 , and C_8 about Co is roughly tetrahedral, with one angle (C_1 - Co - C_7) badly distorted. It should be pointed out here that the X-ray data are unable to distinguish between Fe and Co; the particular designation shown here is an assignment based on chemical intuition (see text).

Table I. Selected Molecular Parameters in $[(\text{Ph}_3\text{P})_2\text{N}]_2^+ [\text{Fe}_2(\text{CO})_8]^{2-} \cdot 2\text{CH}_3\text{CN}$

Bond lengths (Å)		Bond angles (deg)	
(A) $[\text{Fe}_2(\text{CO})_8]^{2-}$ Anion			
Fe-Fe	2.787 (2)	Fe-Fe-C(ax)	177.9 (4)
Fe-C(ax)	1.743 (16)	Fe-Fe-C(eq)	83.3 (5) ^a
Fe-C(eq)	1.769 (17) ^a	C(ax)-Fe-C(eq)	96.7 (6) ^a
C-O	1.143 (14) ^a	C(eq)-Fe-C(eq)	118.7 (5) ^a
		Fe-C-O	117.8 (8) ^a
(B) $[(\text{Ph}_3\text{P})_2\text{N}]^+$ Cation			
P-N	1.572 (7) ^a	P-N-P	141.8 (6)
P-C	1.785 (4) ^a	N-P-C	110.8 (13) ^a

^a Averaged values.

the question of which of these two geometries the intermediate $[\text{FeCo}(\text{CO})_8]^-$ would adopt.⁸ Surprisingly, it turned out to be neither.

$[(\text{Ph}_3\text{P})_2\text{N}]^+ [\text{FeCo}(\text{CO})_8]^-$ was prepared using Ruff's method and recrystallized from ether-hexane: space group $P\bar{1}$ (triclinic); $a = 10.58(2)$, $b = 15.35(3)$, $c = 12.66(3)$ Å, $\alpha = 96.3(1)$, $\beta = 97.4(1)$, $\gamma = 92.3(1)^\circ$; $V = 2023$ Å³; $Z = 2$. Sensitivity of the crystals to X-rays necessitated a rapid data collection and the application of scaling methods to account for crystal deterioration; 2193 reflections representing data up to a 2θ maximum of 40° , were collected using Mo $K\alpha$ radiation. This structure was also solved by heavy atom methods and refined to a current R factor of 9.8%.

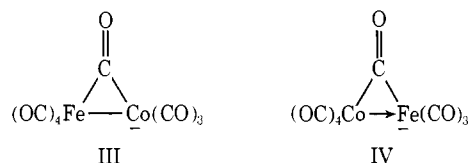
The geometry of $[\text{FeCo}(\text{CO})_8]^-$ (Figure 2) consists of $\text{M}(\text{CO})_4$ and $\text{M}(\text{CO})_3$ fragments asymmetrically bridged⁹ by the eighth carbonyl group. The molecule is approximately bisected by the plane which contains the two metal atoms and the odd-numbered carbonyl groups.

The distinction between the iron and cobalt atoms is

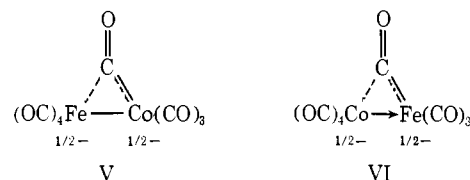
(8) J. K. Ruff, *Inorg. Chem.*, **7**, 1818 (1968). In this paper, the presence of bridging carbonyl infrared stretch at 1776 cm^{-1} led to the postulation of a C_{2v} structure (I) for $[\text{FeCo}(\text{CO})_8]^-$.

(9) These have now been observed in a dozen or so compounds. See the following papers and the references quoted in them: (a) H. B. Chin and R. Bau, *J. Amer. Chem. Soc.*, **95**, 5068 (1973); (b) R. Bau, J. C. Burt, S. A. R. Knox, R. M. Laine, R. P. Phillips, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 726 (1973); (c) F. A. Cotton, B. A. Frenz, and L. Kruczyński, *J. Amer. Chem. Soc.*, **95**, 951 (1973).

difficult to make. While electron-counting considerations would tend to favor III, the alternate assignment, IV, cannot be entirely ruled out.



This ambiguity persists even when a formalism involving a fractional electron count (one-half/three-halves) is assigned to the asymmetric carbonyl bridge.



The improbability of having electron donation to a negatively charged or partially negative atom would lead one to favor III over IV, and on this basis our preference is to assign the atom with our terminal CO's as Fe.¹⁰ It should be emphasized, however, that this is an assignment and not an experimental finding.¹¹ The Fe-Co distance of 2.585 (3) Å, together with other selected molecular parameters, are listed in Table II.

Table II. Selected Molecular Parameters in [(Ph₃P)₂N]⁺[FeCo(CO)₈]⁻

(A) [FeCo(CO) ₈] ⁻ Anion			
Bond lengths (Å)			
Fe-Co	2.585 (3)	Fe-C ^a	1.687 (9) ^b
Co-C ₁	1.774 (20)	Co-C ^a	1.744 (20) ^b
Fe-C ₁	2.210 (19)	C-O ^a	1.175 (10) ^b
C ₁ -O ₁	1.178 (24)		
Bond angles (deg)			
Co-C ₁ -O ₁	151.2 (16)	C ₁ -Fe-C ₂	89.3 (8)
Fe-C ₁ -O ₁	128.7 (14)	C ₁ -Fe-C ₃	91.8 (8)
Co-Fe-C ₁	42.5 (5)	C ₁ -Fe-C ₄	82.6 (7)
Fe-Co-C ₁	57.4 (6)	C ₁ -Fe-C ₅	158.9 (9)
C ₁ -Co-C ₆	97.4 (9)	C ₂ -Fe-C ₃	100.2 (10)
C ₁ -Co-C ₇	136.4 (9)	C ₂ -Fe-C ₄	164.1 (9)
C ₁ -Co-C ₈	105.1 (9)	C ₂ -Fe-C ₅	88.0 (10)
C ₆ -Co-C ₇	102.8 (9)	C ₃ -Fe-C ₄	93.8 (9)
C ₆ -Co-C ₈	110.3 (9)	C ₃ -Fe-C ₅	109.2 (10)
C ₇ -Co-C ₈	103.5 (9)	C ₄ -Fe-C ₅	94.6 (9)
(B) [(Ph ₃ P) ₂ N] ⁺ Cation			
Bond lengths (Å)		Bond angles (deg)	
P-N	1.568 (9) ^b	P-N-P	138.5 (8)
P-C	1.793 (6) ^b	N-P-C	111.7 (7) ^b

^a Refers to terminal carbonyl groups. ^b Averaged values.

Thus, what we have here is a remarkable variation in geometry along an isoelectronic series, involving two, one, and zero carbonyl bridges as the series Co₂(CO)₈, [CoFe(CO)₈]⁻, and [Fe₂(CO)₈]²⁻ is traversed. One could rationalize this in terms of the observed elongation of M-M distance along this series (arising from in-

(10) On the other hand, it could be argued that the presence of a neutral, six-coordinate cobalt in Co₂(CO)₈ and a negatively charged, five-coordinate iron in [Fe₂(CO)₈]²⁻ would be consistent with formulation IV.

(11) The very slight difference in electron density between iron (26 electrons) and cobalt (27 electrons) would make their differentiation prohibitively difficult with X-ray techniques.

creasing electron-electron repulsion), making carbonyl bridging less feasible.

It is interesting to speculate whether the geometric sequence C_{2v} ⇌ C_s ⇌ D_{3d} actually mirrors the rearrangement of Co₂(CO)₈ in solution. While there is perhaps no direct evidence that this is occurring in this particular system, our result suggests that the intermediacy of singly bridged species of the [FeCo(CO)₈]⁻ type may have to be seriously considered, at least in certain cases, when carbonyl rearrangement processes are studied.¹²

Acknowledgment. We would like to thank the National Science Foundation and the National Institutes of Health for partial support of this research.

(12) The intermediacy of species of the type (OC)₅M·CO·M(CO)₄ has been postulated in certain substitution reactions of Mn₂(CO)₁₀ and Re₂(CO)₁₀: L. I. B. Haines, D. Hopgood, and A. J. Poë, *J. Chem. Soc. A*, 421 (1968); 2826 (1969).

(13) Research Fellow of the Alfred P. Sloan Foundation, 1974-1976.

Henry B. Chin, Michael B. Smith
Robert D. Wilson, Robert Bau*¹³

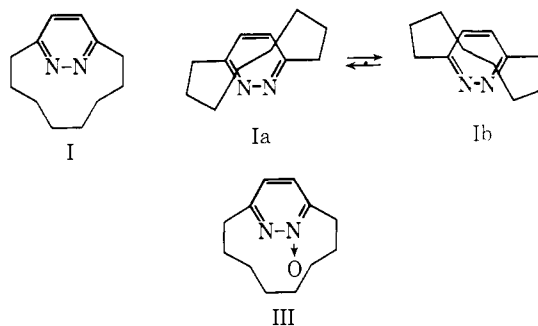
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Received April 15, 1974

[8](3,6)Pyridazinophane. Synthetic and Structural Studies

Sir:

The title compound I is a diaza analog of [8]paracyclophane¹ and belongs to a new class of heterophanes.² The unprecedented observation of the dynamic behavior of the saturated bridge has now been attained by the aid of the heteroaromatic ring discriminating between methylene hydrogens in the vicinity.³



The synthesis has been accomplished by incorporating the pyridazine system into a large alicyclic ring.^{2,4} Thus, cyclododecan-1,4-dione (10 mmol) was heated

(1) (a) D. J. Cram and G. R. Knox *J. Amer. Chem. Soc.*, **83**, 2204 (1961); (b) D. J. Cram, C. S. Montgomery, and G. R. Knox, *ibid.*, **88**, 515 (1966); (c) T. Tsuji and S. Nishida, *ibid.*, **95**, 7519 (1973); (d) G. M. Whitesides, B. A. Pawson, and A. C. Cope, *ibid.*, **90**, 639 (1968).

(2) (a) S. Fujita and H. Nozaki, *Yuki Gosei Kagaku Kyokaiishi*, **30**, 679 (1972); (b) S. Hirano, T. Hiyama, S. Fujita, and H. Nozaki, *Tetrahedron*, in press; (c) H. Nozaki, T. Koyama and T. Mori, *ibid.*, **25**, 5357 (1969); (d) W. E. Parham and J. F. Dooley *J. Amer. Chem. Soc.*, **89**, 985 (1967); (e) W. E. Parham, R. W. Davenport, and J. B. Biasotti, *Tetrahedron Lett.*, 557 (1969); (f) C. F. H. Allen and J. A. VanAllen, *J. Org. Chem.*, **18**, 882 (1953); (g) S. Fujita and H. Nozaki, *Bull. Chem. Soc. Jap.*, **44**, 2827 (1971).

(3) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965. Recent development on the conformational analysis of cyclic compounds is seen in F. A. L. Anet and J. J. Wagner, *J. Amer. Chem. Soc.*, **93**, 5267 (1971).

(4) The synthetic approach has been also successful in the preparation of [6]metacyclophanes, whose hexamethylene bridge is the shortest one in metacyclophane derivatives. See S. Hirano, T. Hiyama, S. Fujita, and H. Nozaki, *Chem. Lett.*, 707 (1972).