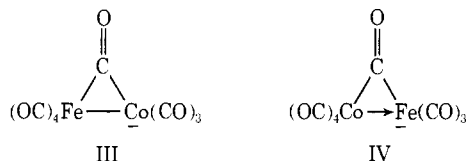
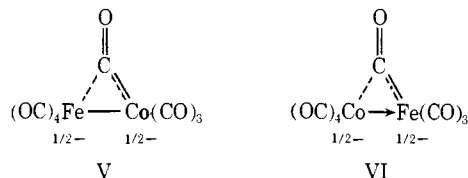


difficult to make. While electron-counting considerations would tend to favor III, the alternate assignment, IV, cannot be entirely ruled out.



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.<sup>10</sup> It should be emphasized, however, that this is an assignment and not an experimental finding.<sup>11</sup> 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  $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{FeCo}(\text{CO})_8]^-$

(A) $[\text{FeCo}(\text{CO})_8]^-$ Anion			
Bond lengths (Å)			
Fe-Co	2.585 (3)	Fe-C <sup>a</sup>	1.687 (9) <sup>b</sup>
Co-C <sub>1</sub>	1.774 (20)	Co-C <sup>a</sup>	1.744 (20) <sup>b</sup>
Fe-C <sub>1</sub>	2.210 (19)	C-O <sup>a</sup>	1.175 (10) <sup>b</sup>
C <sub>1</sub> -O <sub>1</sub>	1.178 (24)		
Bond angles (deg)			
Co-C <sub>1</sub> -O <sub>1</sub>	151.2 (16)	C <sub>1</sub> -Fe-C <sub>2</sub>	89.3 (8)
Fe-C <sub>1</sub> -O <sub>1</sub>	128.7 (14)	C <sub>1</sub> -Fe-C <sub>3</sub>	91.8 (8)
Co-Fe-C <sub>1</sub>	42.5 (5)	C <sub>1</sub> -Fe-C <sub>4</sub>	82.6 (7)
Fe-Co-C <sub>1</sub>	57.4 (6)	C <sub>1</sub> -Fe-C <sub>5</sub>	158.9 (9)
C <sub>1</sub> -Co-C <sub>6</sub>	97.4 (9)	C <sub>2</sub> -Fe-C <sub>3</sub>	100.2 (10)
C <sub>1</sub> -Co-C <sub>7</sub>	136.4 (9)	C <sub>2</sub> -Fe-C <sub>4</sub>	164.1 (9)
C <sub>1</sub> -Co-C <sub>8</sub>	105.1 (9)	C <sub>2</sub> -Fe-C <sub>5</sub>	88.0 (10)
C <sub>6</sub> -Co-C <sub>7</sub>	102.8 (9)	C <sub>3</sub> -Fe-C <sub>4</sub>	93.8 (9)
C <sub>6</sub> -Co-C <sub>8</sub>	110.3 (9)	C <sub>3</sub> -Fe-C <sub>5</sub>	109.2 (10)
C <sub>7</sub> -Co-C <sub>8</sub>	103.5 (9)	C <sub>4</sub> -Fe-C <sub>5</sub>	94.6 (9)
(B) $[(\text{Ph}_3\text{P})_2\text{N}]^+$ Cation			
Bond lengths (Å)		Bond angles (deg)	
P-N	1.568 (9) <sup>b</sup>	P-N-P	138.5 (8)
P-C	1.793 (6) <sup>b</sup>	N-P-C	111.7 (7) <sup>b</sup>

<sup>a</sup> Refers to terminal carbonyl groups. <sup>b</sup> 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  $\text{Co}_2(\text{CO})_8$ ,  $[\text{CoFe}(\text{CO})_8]^-$ , and  $[\text{Fe}_2(\text{CO})_8]^{2-}$  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  $\text{Co}_2(\text{CO})_8$  and a negatively charged, five-coordinate iron in  $[\text{Fe}_2(\text{CO})_8]^{2-}$  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  $C_{2v} \rightleftharpoons C_s \rightleftharpoons D_{3d}$  actually mirrors the rearrangement of  $\text{Co}_2(\text{CO})_8$  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  $[\text{FeCo}(\text{CO})_8]^-$  type may have to be seriously considered, at least in certain cases, when carbonyl rearrangement processes are studied.<sup>12</sup>

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(12) The intermediacy of species of the type  $(\text{OC})_5\text{M}\cdot\text{CO}\cdot\text{M}(\text{CO})_4$  has been postulated in certain substitution reactions of  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Re}_2(\text{CO})_{10}$ : 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.

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Robert D. Wilson, Robert Bau\*<sup>13</sup>

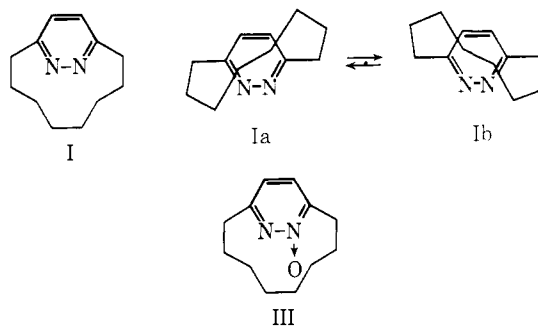
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### [8](3,6)Pyridazinophane. Synthetic and Structural Studies

Sir:

The title compound I is a diaza analog of [8]paracyclophane<sup>1</sup> and belongs to a new class of heterophanes.<sup>2</sup> 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.<sup>3</sup>



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

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(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).

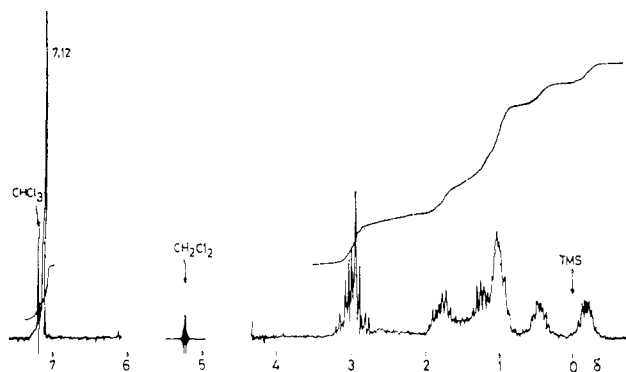


Figure 1. Nmr (100 MHz,  $\text{CDCl}_3$ , room temperature) of I.

with hydrazine hydrate (11.6 mmol) in ethanol (100 ml) for 6 hr. The resulting oil was air sensitive and easily dehydrogenated upon the usual work-up. Distillation at 145–155° (3 mm), followed by column chromatography on silica gel, afforded I (50% yield) as colorless prisms of mp 59–60° (*n*-hexane):<sup>5</sup> ir (Nujol) 3055, 1575, 1538, 1070, 887, 841, 810, 769, 710  $\text{cm}^{-1}$ ; *m/e* 190 ( $\text{M}^+$ ).

The nmr spectrum of I is shown in Figure 1. The multiplet (4 H) at  $\delta$  3 due to benzylic protons clearly shows that the octamethylene chain resides at the one side of the aromatic ring at room temperature. The situation remained unchanged up to 200°. The 2 H signal at  $\delta$  -0.3 is due to each one of methylene protons on  $\text{C}_1$  and  $\text{C}_5$  being shielded by both the diamagnetic ring current of pyridazine and the magnetic anisotropy of nitrogen atoms. The 2 H signal at  $\delta$  0.5 is ascribed to the counterpart of  $\text{C}_4$  and  $\text{C}_5$  methylene protons which are less susceptible to these effects. The signal at  $\delta$  -0.3 disappeared at -72° and at lower temperature a new 1 H peak at  $\delta$  -1.75 appeared (Figure 2). The dynamic change is understood in terms of the conformational equilibrium of  $\text{Ia} \rightleftharpoons \text{Ib}$ . At room temperature there exists a rapid equilibrium between the two enantiomeric conformers due to the pseudorotation of the saturated chain, which is gradually frozen at lower temperature. The energy barrier of the conformational change at the coalescence temperature was estimated to be 9.2 kcal/mol, a remarkably larger value than that of cyclooctane (7.7 kcal/mol).<sup>7</sup>

The aromatic proton of I absorbed at  $\delta$  7.12 (Figure 1) or at relatively higher field compared with that of 3,6-dimethylpyridazine (II) ( $\delta$  7.20).<sup>8</sup> The strain of the pyridazine ring of I is evidenced by its uv spectra:  $\lambda_{\text{max}}^{\text{EtOH}}$  ( $\epsilon$ ) 267 (1260), 314 nm (413);  $\lambda_{\text{max}}^{\text{n-hexane}}$  ( $\epsilon$ ) 270 (1260), 337 nm (442). The benzenoid absorption ( $^1\text{L}_b$ ) of I as compared with that of II<sup>9</sup> experienced a

(5) The new compound gave satisfactory elemental analysis and/or correct molecular peak in its exact mass spectrum.

(6) This indicates that the space surrounded by the octamethylene chain is not wide enough for the pyridazine ring to rotate, although the -CH=CH- moiety of [8]paracyclophane is replaced by -N=N-.

(7) (a) The value is naturally smaller than that of 4-[8]paracyclophanes (ca. 12 kcal/mol) (ref 1d) but should be deemed to be large for 12-membered ring compound; (b) F. A. L. Anet and J. S. Hartman, *J. Amer. Chem. Soc.*, **85**, 1204 (1963).

(8) The recorded chemical shift of II is  $\delta$  7.5 (neat) (D. G. Farnum, R. J. Alaimo, and J. M. Dunston, *J. Org. Chem.*, **32**, 1130 (1967)). The paramagnetic shift of the ring protons in I is due to the strain caused by octamethylene chain. The effect by a short bridging is seen in S. Fujita, T. Kawaguchi, and H. Nozaki, *Tetrahedron Lett.*, 1119 (1971).

(9)  $\lambda_{\text{max}}^{\text{EtOH}}$  ( $\epsilon$ ) 258 (1835), 312 nm (325);  $\lambda_{\text{max}}^{\text{n-hexane}}$  ( $\epsilon$ ) 259 (1560), 263 (1568), 341 nm (319).

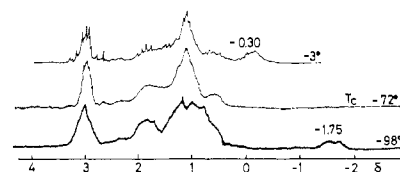


Figure 2. Temperature-dependent nmr (60 MHz, Freon 11) of I.

9–11-nm bathochromic shift and a hypochromic effect due to the bridging. In contrast, no apparent wavelength difference was observed with respect to the  $n-\pi^*$  absorption ( $>300$  nm) of both compounds I and II, although the  $\epsilon$  of I was larger than that of II. Apparently the strain due to bridging releases I from the forbiddenness of the  $n-\pi^*$  transition. The smaller bathochromic shift in I (337 (*n*-hexane)–314 (EtOH) = 23 nm) than II (341 (*n*-hexane)–312 (EtOH) = 29 nm) is ascribed to the octamethylene chain, which is forced to solvate on the one side of the pyridazine ring intramolecularly in I.

Oxidation of I with 1 equiv of perbenzoic acid gave pyridazinophane monoxide (III).<sup>5,10,11</sup> This is a chiral ansa compound.

(10) Bp 140–150° (0.1 mm); ir (neat) 3060, 1584, 1553, 1370, 1330  $\text{cm}^{-1}$ ; mass spectral, *m/e* 206 ( $\text{M}^+$ ), 189 ( $\text{M}^+ - \text{OH}$ ); nmr ( $\text{CCl}_4$ )  $\delta$  -0.3 to +0.1 (m, 2 H) 0.1–2.2 (m, 10 H), 2.3–2.5 (m, 1 H), 2.74 (t, 2 H), 3.48 (double t,  $J = 12.5, 4.5$  Hz, 1 H), 6.86 (d,  $J = 7.7$  Hz, 1 H), 7.37 (d,  $J = 7.7$  Hz, 1 H).

(11) This is in contrast to the chemical behavior of [7](2,6)pyridinophane which is resistant to oxidation (ref 2g). It is suggested that the success or failure of oxidizing heterophanes depends on the dynamic behavior of the bridging chain.

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## Pentamethyl Complexes of Niobium and Tantalum

Sir:

The known examples of mononuclear neutral binary methyl complexes of the transition metals are  $\text{Ti}(\text{CH}_3)_4$ ,<sup>1</sup>  $\text{Zr}(\text{CH}_3)_4$ ,<sup>2</sup>  $\text{Cr}(\text{CH}_3)_4$ ,<sup>3</sup> and  $\text{W}(\text{CH}_3)_6$ .<sup>4</sup> (Dimethylmanganese<sup>5</sup> is probably polymeric.) Pentamethyltantalum has now been prepared and isolated and is reported here along with the remarkably stable dmpe adducts ( $\text{dmpe} = (\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$ ),  $\text{Ta}(\text{CH}_3)_5\text{-}(\text{dmpe})$  and  $\text{Nb}(\text{CH}_3)_5(\text{dmpe})$ .

The addition of 2 mol of methyl lithium (in diethyl ether) to a diethyl ether solution of yellow  $\text{Ta}(\text{CH}_3)_5\text{Cl}_2$ <sup>6</sup> at -78° produced a homogeneous yellow solution. Lithium chloride was precipitated upon warming to 0° and the color of the solution deepened slightly. The solution was filtered after 0.5 hr and the ether removed

(1) (a) K. Clauss and C. Beermann, *Angew. Chem.*, **71**, 627 (1959); (b) H. J. Berthold and G. Groh, *Z. Anorg. Allg. Chem.*, **319**, 230 (1963).

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