We obtained the unsubstituted benzyl triethylcarbinyl diester **1b** from benzyl bromide and potassium monotriethylcarbinyl pimelate. Transesterification of the 1-triethylcarbinyl-7-methyl 3-ethylpimelate at 25° (25 mm) yielded 7-benzyl 1-triethylcarbinyl 3-ethylpimelate (**1d**). Cyclization by the procedure already described yielded mixtures of triethylcarbinyl and benzyl $\beta$-keto esters, which could not be separated by chromatography. The mixed keto esters were hydrogenolyzed using 10% Pd–C as catalyst in ether, washed with aqueous bicarbonate, and concentrated to yield triethylcarbinyl keto esters; nmr established the presence of less than 1% of benzyl esters in both cases.

The distribution of label in the keto esters was determined by decarboxylation in refluxing 25% aqueous ethanolic 3 *N* hydrochloric acid; the evolved $CO_2$ was counted as barium carbonate.[15] The cyclohexanone and 3-ethylcyclohexanone were extracted into benzene and total activity was determined; the solutions then were analyzed by glpc to obtain ketone specific activities. Cyclization yields and distribution of label in the $\beta$-keto esters are shown in Table I.

The unidirectional closure of 1-triethylcarbinyl-7-aralkyl pimelates described here provides a route to unambiguously labeled or substituted triethylcarbinyl cyclohexanone-2-carboxylates which is superior to the existing multistep method.[16-18] Our method requires fewer steps, can be used with compounds containing acid-sensitive substituents, and is capable of extension to the synthesis of other than six-carbon rings.

The use of esters in which one carboxyl provides attachment to a resin support affords a clear benefit over the benzyl case in specificity and greatly simplified isolation and purification of the mixed diester and $\beta$-keto ester. We are presently investigating the generalization of this method, including the utilization of any hyperentropic effects available from solid phase mixed esters.

[15] F. H. Woeller, *Anal. Biochem.*, **2**, 508 (1961).

[16] D. Vorlander, *Ann. Chem.*, **294**, 300 (1877).

[17] R. von Schilling and D. Vorlander, *ibid.*, **308**, 195 (1899).

[18] S. Mukherjee, *J. Indian Chem. Soc.*, **39**, 347 (1962).

[19] Supported in part by the U. S. Army Research Office, Durham, N. C.

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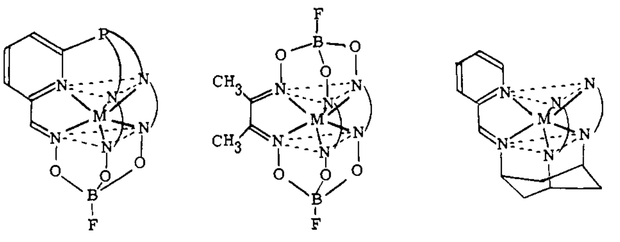
## Trigonal-Prismatic Coordination. Complexes of Intermediate Geometry

*Sir:*

Trigonal-prismatic coordination has recently been reported for $[M(PccBF)]^+$,[1] $[Co(dmg)_3(BF)_2]$,[2] and $[M(py_3tach)]^{2+}$.[3] Each of these complexes contains three five-membered diimine chelate rings as shown in I.



$M(PccBF)^+$ $Co(dmg)_3(BF)_2$ $M(py_3tach)^{2+}$

I

Both $[Co(dmg)_3(BF)_2]$ and $[M(PccBF)]^+$ have each set of imine functions, those that make up a triangular face of the coordination polyhedron (one from each diimine chelate ring), bound through nitrogen to "capping groups" forming "clathro chelates" that encapsulate the metal ions. However, $[M(py_3tach)]^{2+}$ is of an open-trifurcated type,[4] and only the imine functions of one triangular face are bound to a capping group. We wish to report on complexes of 1,1,1-tris(pyridine-2-aldiminomethyl)ethane, $[M(py_3TPN)]^{2+}$, which are of the second, or open-trifurcated type.

In the absence of metal ions, condensation of 1,1,1-tris(aminomethyl)ethane (TPN) with pyridine-2-carboxaldehyde results in 1-methyl-4,6,10-tri($\alpha$-pyridyl)-3,5,2-triazatricyclo[3.3.1.1.$^{3,7}$]decane.[5] When the condensation takes place in the presence of ferrous ions, the uncaged diimine form of the ligand ($py_3TPN$) is obtained as the Fe(II) complex.[5] The Fe(II) complex of tris(pyridine-2-aldiminomethyl)methane has also been prepared.[6]

Condensation of TPN with pyridine-2-carboxaldehyde in refluxing methanol in the presence of metal perchlorates [Zn(II), Ni(II), Fe(II), Co(II), and Mn(II)] and recrystallization from acetonitrile or acetonitrile–ethanol results in the pure[7] complexes $[M(py_3TPN)](ClO_4)_2$: Zn(II), colorless and diamagnetic; Ni(II), dark red orange, 3.04 BM; Fe(II), dark violet, 0.93 BM; Co(II), dark red orange, 4.66 BM; Mn(II), light orange, 5.85 BM.

Precession photographs indicate that the Zn(II), Ni(II), Co(II), and Mn(II) complexes crystallize in the monoclinic space group $P2_1/c$ and are isomorphous and, therefore, probably isostructural. The Fe(II) complex separates as asymmetric crystals of the orthorhombic space group $P2_12_12_1$ and is probably not isostructural with the other complexes. We are currently engaged in single-crystal X-ray studies of the Zn(II) and Fe(II) complexes. Preliminary results for the Zn(II) complex (present refinement, $R = 11.7$) indicate a large distortion from trigonal-prismatic coordination with an average twist of the two triangular faces of 28°; the geometry is approximately midway between trigonal prismatic and octahedral. Two triangular faces of an octahedron are twisted by an angle of 60°, while the two triangular faces of a trigonal prism are twisted by 0°. Distortion from trigonal prismatic coordination is considerably less for $[Zn(py_3tach)]^{2+}$ (average twist

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[1] J. E. Parks, B. E. Wagner, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 3500 (1970).

[2] E. C. Lingafelter, *et al.*, submitted for publication; N. J. Rose, private communication as cited in ref 1; (b) D. R. Boston and N. J. Rose, *J. Amer. Chem. Soc.*, **90**, 6859 (1968).

[3] (a) R. A. D. Wentworth, W. O. Gillum, and R. F. Childers, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. INOR 194; (b) W. O. Gillum, J. C. Huffman, W. E. Streib, and R. A. D. Wentworth, *Chem. Commun.*, 843 (1969).

[4] F. Lions, *Rec. Chem. Progr.*, **22**, 69 (1961).

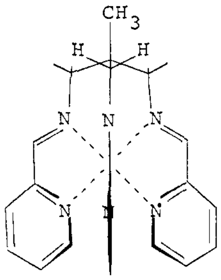
[5] D. A. Durham, F. A. Hart, and D. Shaw, *J. Inorg. Nucl. Chem.*, **29**, 509 (1967).

[6] F. P. Dwyer, N. S. Gill, E. C. Gyarfas, and F. Lions, *J. Amer. Chem. Soc.*, **79**, 1269 (1957).

[7] Typical analytical results: Calcd for $C_{23}H_{24}Cl_2N_6O_8Ni$: C, 43.02; H, 3.77; N, 13.09. Found: C, 43.18; H, 3.88; N, 13.29.

of 4°)[3b] and reflects the greater rigidity of the capping group (a cyclohexane ring) present in py$_3$tach.

If the donors of py$_3$TPN were arranged in a trigonal-prismatic manner, the methylene protons of the capping group would be expected to be equivalent (see II).



II, M(py$_3$TPN)

A distortion from this configuration would lead to a "twist" in the capping group and a resulting nonequivalence of the methylene protons. In the $^1$H nmr spectrum of [Zn(py$_3$TPN)]$^{2+}$, the methylene protons appear as two signals ($\tau$ 5.93 and 5.92, CD$_3$CN solution). For [Fe(py$_3$TPN)]$^{2+}$, the difference in chemical shifts of the methylene signals is larger ($\tau$ 6.12 and 6.08) and suggests a greater octahedral twist for this complex. The nmr spectra of the two complexes are different in other respects; the pyridyl protons of the zinc complex give rise to a resonance pattern similar to that observed for many 2-substituted pyridines,[8] whereas the iron complex gives rise to an entirely different pattern, and the position of the resonance arising from the imine proton differs for the complexes ($\tau$ 1.42, Fe(II) and 1.06, Zn(II)). These differences may also arise in part from an increased octahedral twist in the iron complex. Such distortion for a low-spin d$^6$ system has been proposed for [Fe(PccBF)]$^{+}$ [1] and [Fe(py$_3$tach)]$^{2+}$,[3a] and has been found for [Co(dmg)$_3$(BF)$_2$]$^{+}$.[9]

The absorption envelope for [Ni(py$_3$TPN)]$^{2+}$ (11,230 cm$^{-1}$ (sh), $\epsilon$ 21; 12,440 cm$^{-1}$, $\epsilon$ 28) in the 11,000–13,000-cm$^{-1}$ region is similar in position and shape to that found for octahedral tris($\alpha$-diimine) complexes.[10,11] However, the extinction coefficients are considerably higher than those generally observed for these octahedral complexes and more closely parallel those found for [Ni(py$_3$tach)]$^{2+}$ (11,100 cm$^{-1}$, $\epsilon$ 27.0; 12,100 cm$^{-1}$, $\epsilon$ 26.6)[12] and [Ni(PccBF)]$^{+}$ (9430 cm$^{-1}$, $\epsilon$ 28; 11,000 cm$^{-1}$, $\epsilon$ 27).[1] Although the abnormal extinction coefficients reflect the considerable distortion from octahedral geometry for [Ni(py$_3$TPN)]$^{2+}$, the trigonal component of the ligand field is not dominant and trigonal splitting, found for [Ni(py$_3$tach)]$^{2+}$ and [Ni(PccBF)]$^{+}$, is not observed.

The infrared spectra of the Zn(II), Ni(II), Co(II), and Mn(II) complexes are quite similar and different from that of the Fe(II) complex. An imine stretch, occurring in the 1650–1660-cm$^{-1}$ region for the other complexes, is either absent or has shifted under the pyridine bands for the iron complex; similar behavior has been reported for [M(py$_3$tach)]$^{2+}$ [3a] and has been attributed to rotation about the imine bond to yield octahedral coordination for Fe(II). Differences in the pyridine bands and in the 1200–1400-cm$^{-1}$ region may also be the result of octahedral coordination for [Fe(py$_3$TPN)]$^{2+}$.

In the case of metal complexes of py$_3$TPN, two distinct types of complexes are found. Since the sexadentate ligand py$_3$TPN is less rigid than py$_3$tach and the clathro chelate ligands, it is probable that octahedral coordination is attained for the iron complex, [Fe(py$_3$TPN)] (ClO$_4$)$_2$.

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(8) W. Bruegel, *Z. Elektrochem.*, **66**, 159 (1962).

(9) D. R. Boston and N. J. Rose, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. INOR 96.

(10) M. A. Robinson, J. D. Curry, and D. H. Busch, *Inorg. Chem.*, **2**, 1178 (1963).

(11) L. J. Wilson and N. J. Rose, *J. Amer. Chem. Soc.*, **90**, 6041 (1968).

(12) J. E. Sarneski and F. L. Urbach, *Chem. Commun.*, 1025 (1968).

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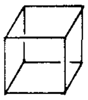
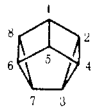
## Silver(I)- and Palladium(II)-Catalyzed Isomerizations of Cubane. Synthesis and Characterization of Cuneane

*Sir:*

We have found that silver(I) and palladium(II) effect quantitative, catalytic isomerization of cubane (**1**) to cuneane (**2**), the parent of an important carbon ring system.[1] Cuneane is the second of the three possible saturated (CH)$_8$ isomers to be synthesized; the first being cubane itself.[2] The rearrangement of cubane to cuneane parallels closely the Ag(I)-catalyzed isomerizations of the homocubyl and 1,1′-bishomocubyl systems reported recently by Dauben[3] and by Paquette.[4]



**1**



**2**

Cuneane is a volatile, mobile liquid: fp −1–0°; ir (gas, 10 cm) $\nu$ 3056 (s), 1252 (m), 1158 (w), 1044 (w), 927 (m), 883 (w), 845 (w), 804 (m), and 750 (m) cm$^{-1}$; nmr (CDCl$_3$, 100 MHz) $\delta$ 2.7 (2 H, m, H-1,5), 2.3 (2 H, m, H-3,7), 2.1 ppm (4 H, m, H-2,4,6,8).[5] Confirmation of the structure assigned cuneane from its origins comes principally from the $^{13}$C nmr spectrum: $\delta$ (in parts per million upfield from $^{13}$CS$_2$) 152.3 (2 C, d, $J$ = 153 Hz, C-1,5), 161.0 (4 C, d, $J$ = 175 Hz, C-2,4,6,8), 163.2 (2 C, d, $J$ = 162 Hz, C-3,7).[6] Thus, cu-

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(1) Pentacyclo[3.3.0.0$^{2,4}$.0$^{3,7}$.0$^{6,8}$]octane. The name "cuneane" has been adopted for simplicity and is derived from the Latin *cuneus*, a wedge; *cf.*, for example, cuneate, wedge-shaped. Only the octamethyl compound, prepared by way of a diene photoisomerization, has been reported previously [R. Criegee and R. Askani, *Angew. Chem., Int. Ed. Engl.*, **7**, 537 (1968)].

(2) P. E. Eaton and T. W. Cole, Jr., *J. Amer. Chem. Soc.*, **86**, 962, 3157 (1964). Cuneane should be ~30–40 kcal/mol less strained than cubane. The as yet unknown third isomer in the set, 2,2′:4,4′-bis(bicyclobutyl), should be intermediate in strain energy.

(3) W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, and D. L. Whalen, *Tetrahedron Lett.*, 787 (1970).

(4) L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 2584 (1970).

(5) Appropriate analytical and mass spectroscopic data have been obtained.