

Table I. Pmr Spectral Data^a for [LCo(DH)₂(CH₃OH)]⁺ Complexes^b

RR' ₂ P	CH ₃ OH shift, τ (J _{PH} , ^b Hz)	Oxime methyl shift, τ (J _{PH} , Hz)	ECA ^c	TCA ^d	pK _a ^e	Σ ³ χ _i ^f
(<i>c</i> -C ₆ H ₁₁) ₃ P	7.460 (1.2)	7.51 (0.5)	173	179	9.70	0.3
(<i>i</i> -C ₃ H ₇) ₃ P	7.420 (0.9)	7.52 (0.5)	164	160	7.97	3.0
(C ₆ H ₅) ₃ P	7.395 (1.5)	7.83 (0.8)	159	145	2.73	12.9
(<i>m</i> -C ₄ H ₉)(C ₆ H ₅) ₂ P ^g	7.310 (1.3)	7.89 (0.7)	140	140		10.0
(CH ₃) ₂ (C ₆ H ₅) ₂ P	7.265 (1.3)	7.95 (0.7)	132	136	4.6	11.2
(CH ₃ O)(C ₆ H ₅) ₂ P	7.250 (1.5)	7.90 (0.7)	129	132		16.3
(2-(CN)C ₂ H ₄) ₃ P	7.245 (1.5)	7.47 (0.8)	129	130	1.36	21.9
(<i>o</i> -CH ₃ C ₆ H ₄ O) ₃ P ⁱ	7.240 (2.7)	7.90 (0.6)	128	141		28.2
(<i>n</i> -C ₄ H ₉) ₃ P ^h	7.230 (1.2)	7.56 (0.8)	127	130	8.43	4.2
(CH ₃) ₂ (C ₆ H ₅) ₂ P	7.200 (1.3)	7.81 (0.7)	125	127	6.50	9.5
(CH ₃ O) ₂ (C ₆ H ₅) ₂ P	7.200 (1.9)	7.79 (0.5)	125	120		19.7
(<i>i</i> -C ₃ H ₇ O) ₃ P	7.180 (2.3)	7.59 (0.5)	124	122	3.4	18.9
(C ₆ H ₅ O) ₃ P	7.170 (2.9)	7.78 (0.5)	123	121		29.1
(CH ₃) ₃ P ^j	7.145 (1.0)	7.59 (0.6)	<117	118	8.65	7.8
C ₂ H ₅ C(CH ₃ O) ₃ P ^j	7.155 (2.7)	7.59 (0.5)	<117	101		30.6

^a Varian HA100 (8% TMS reference and lock signal, frequency sweep mode) instrument for complexes dissolved in reagent grade methanol (at 24°). The shifts were insensitive to both concentration and traces of water and acid (but not base) and were easily reproduced (τ ± 0.01) with a JEOL MH100 or Varian A60 instrument (the latter was used to ensure that no complex signal was obscured by the ¹³C satellite of solvent CH₃OH). We estimate that for the slightly broader CH₃OH signal the coupling constants (which were determined at expanded scales) are accurate only to within ± 0.2 Hz. ^b Complexes were introduced as nitrates, which readily solvate, or prepared in CH₃OH by adding AgNO₃ to the chloride complex. The complexes were pure (pmr and elemental analyses) except for the (CH₃)₂(C₆H₅)₂P and (CH₃)₂(C₆H₅)₂P compounds which were contaminated with [L₂Co(DH)₂]X (the triplet signal from these did not interfere with the nmr measurements). ^c Experimental cone angle. ^d Tolman cone angle ref 1 and 2. ^e C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960); W. A. Henderson and C. A. Streuli, *J. Amer. Chem. Soc.*, **82**, 5791 (1960). (*i*-C₃H₇)₃P assumed to be same as (*i*-C₄H₉)₃P, and (*i*-C₃H₇O)₃P estimated from E. M. Thorsteinson, Ph.D. Thesis, Northwestern University, Evanston, Ill., 1966. ^f Reference 8. ^g (C₂H₅)(C₆H₅)₂P, essentially identical. ^h (C₆H₅CH₂)₃P, ECA = 130°, TCA not determined. ⁱ (*o*-(*i*-C₃H₇)C₆H₄O)₃P, essentially identical. ^j (2-(Cl)C₂H₄O)₃P, (C₂H₅O)₃P, and (CH₃O)₃P have identical CH₃OH shifts at τ 7.15 and TCA ~ 110°.

the methyl resonance no longer shifts, whereas the electronic properties of L do change.

There is absolutely no correlation between σ_{MMR} and the electronic properties of L.^{7,8} Ligands of similar bulkiness but different basicities, Bu₃P and (CNCH₂CH₂)₃P, have similar shifts. Changes in the chemical shifts of protons of nonvarying ligands in a related series of cobalt complexes depend on cobalt anisotropy differences, induced mainly by the donor atom of the ligand which is varied.⁹

Bulky ligands are known to distort the geometry of cobalt complexes with "planar" tetradentate macrocyclic ligands.¹⁰ Cotton and Norman have reported the structure of (C₆H₅)₃PRh(DH)₂Cl.¹¹ The normals to the dioxime planes form an angle of 17.1°. Most probably, as the bulkiness of L increases in the [LCo(DH)₂(CH₃OH)]⁺ series, the dioximes are increasingly bent.

A plot of σ_{MMR} vs. oxime methyl resonances (σ_{OMR}) for complexes where R and R' are not anisotropic has a slope of ca. -4. This slope agrees well with calculations based on McConnell's equation¹³ with cobalt as the anisotropic center. Additionally, the complexes deepen in color and change from yellow to dark brown as the size of L increases. The electronic properties and, hence, anisotropy of the complexes probably change as the dioxime ligands bend.

A completely empirical expression¹⁵ was used to fit σ_{MMR} to TCA and thereby obtain new empirical cone angles, ECA (Table I). The σ_{MMR} may in fact serve as a useful steric parameter. Scaling against Tolman's values has the advantage of relating our values to ligands with TCA < 120°, however.

Tolman, Seidel, and Gosser reported stability constants (K) for NiL₄ complexes.² They found that, although (*o*-CH₃C₆H₄O)₃P formed complexes of similar but greater stability than did CH₃(C₆H₅)₂P, these complexes were in turn much more stable than that with (C₆H₅)₃P. Our cone angles give the correct order and predict a much lower value of K for (C₆H₅)₃P. If the cone angles for Et₃P and Bu₃P are equal, then our angles predict that the Ni(Et₃P)₄ complex should be slightly more stable than Ni[(*o*-CH₃C₆H₄O)₃P]₄ as was found.

The σ_{OMR} show a slight but fairly regular decrease as ECA increases in ligands which do not contain CN groups or aromatic rings. Higher field shifts of dioxime methyl protons in complexes containing aromatic rings are attributed to anisotropic shielding, which depends on both distances and orientation of the rings. It might be expected that P(C₆H₅)₃ (σ_{OMR} = 7.83) should show greater shielding than P(C₆H₅)₂CH₃ (7.95) or P(C₆H₅)₂(OCH₃) (7.90). That it does not suggests that the phenyl group orientations are not the same. We conclude that the arithmetic average Tolman² suggested for calculating TCA for unsymmetrical PR'₂ tends to give cone angles which are too large when R is bulky. The good agreement between ECA and TCA for unsymmetrical ligands results from using what we consider to be a low TCA = 145° for P(C₆H₅)₃ in the average.

Steric bulk is not an absolute quantity and different cone angles may be required for octahedral and tetrahedral complexes or for light and heavy metal systems. Additionally, these angles are not a good measure of free ligand size.¹⁶ However, our angles work well for NiL₄ complexes.

Although the results presented here provide strong support for Tolman's concepts, we believe our results have two additional important features. First, the technique appears most promising for determining the cone angle of ligands of low symmetry or of ligands for which "strain"²² introduces uncertainty. Second, it is clear that in suitable cases, changes in chemical shifts can be interpreted. In most cases, shifts or changes in shifts are too complex for useful analysis. Proton chemical shifts of ligands coordinated to cobalt(III) seem to be an exception to the rule. Although differences in proton shifts are small, the accuracy of pmr measurements overcomes this deficiency. The dependence of such shifts on the electronic properties of the coordinated ligands have been noted previously.^{9,17} Our work represents the first evidence that steric factors are also important.

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References and Notes

- (1) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).
- (2) C. A. Tolman, W. C. Seidel, and L. W. Gosser, *J. Amer. Chem. Soc.*, **96**, 53 (1974).
- (3) K. W. Barnett, T. G. Pollman, and T. W. Solomon, *J. Organometal. Chem.*, **36**, C23 (1972); M. Pańkowski and M. Bigorgne, *J. Organometal. Chem.*, **30**, 227 (1971); S. J. Lippard and J. J. Mayerle, *Inorg. Chem.*, **11**, 85 (1972); C. K. Brown and G. Wilkinson, *J. Chem. Soc. A*, 2753 (1970); P. Rigo and A. Turco, *Coord. Chem. Rev.*, **8**, 175 (1972).
- (4) D. H. Gerlach, W. G. Peet, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **94**, 4545 (1972); P. Meakin, E. L. Muetterties, and J. P. Jesson, *ibid.*, **95**, 75 (1973).
- (5) L. G. Marzilli, P. A. Marzilli, and J. Halpern, *J. Amer. Chem. Soc.*, **93**, 1374 (1971); J. Halpern and P. Phelan, *ibid.*, **94**, 1881 (1972); P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *ibid.*, **93**, 4701 (1971); M. Y. Darensbourg, H. L. Conder, D. J. Darensbourg, and C. Hasday, *ibid.*, **95**, 5919 (1973); G. R. Dobson and J. K. Payson, *ibid.*, **95**, 5925 (1973).
- (6) D. Evans, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 3133 (1968); R. L. Pruett and J. A. Smith, *J. Org. Chem.*, **34**, 327 (1969); J. Falbe, "Synthesen mit Kohlenmonoxid," Springer-Verlag, Berlin, 1967, p 4 ff; C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 6785 (1970).
- (7) For a review of the importance of electronic effects of phosphorus donors see J. G. Verkade, *Coord. Chem. Rev.*, **9**, 1 (1972); T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).
- (8) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2953 (1970).
- (9) W. C. Trogler, R. C. Stewart, L. A. Epps, and L. G. Marzilli, *Inorg. Chem.*, **13**, 1563 (1974).
- (10) D. Dodd and M. O. Johnson, *Organometal. Chem. Rev.*, **52**, 1 (1973).
- (11) F. A. Cotton and J. G. Norman, Jr., *J. Amer. Chem. Soc.*, **93**, 80 (1971). Bond lengths are quite similar for cobaloximes.¹² A. Chakrovortz, *Coord. Chem. Rev.*, **13**, 1 (1974).
- (12) W. W. Adams and P. G. Lenhart, *Acta Crystallogr., Sect. B*, **29**, 2412 (1973).
- (13) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).
- (14) The anisotropy of the dioxime ligands can also explain σ_{MMR} but an explanation for σ_{OMR} is not evident.
- (15) The expression was

$$\text{TCA} = \sum_{i=1}^4 C_i \left(1.0 - \frac{0.15}{(\tau - 7.0)} \right)^{i-1}$$

and the method of least squares gave (C_1 – C_4 = 116.7, 81.6, –310.9, and 465.4, respectively). Only symmetric ligands with TCA ≥ 118 were employed. TCA's given by Tolman were used except (1) for $(\text{C}_6\text{H}_5)_3\text{P}$, a value of TCA = 155° was used and (2) for $(\text{-C}_3\text{H}_7\text{O})_3\text{P}$ a TCA = 122°.

- (16) W. C. Trogler, R. C. Stewart, and L. G. Marzilli, *J. Amer. Chem. Soc.*, **96**, 3697 (1974).
- (17) H. A. O. Hill and K. G. Morallee, *J. Chem. Soc. A*, 554 (1969); E. S. Gore, J. C. Dabrowiak, and D. H. Busch, *J. Chem. Soc., Chem. Commun.*, 923 (1972); W. L. Jolly, A. D. Harris, and T. S. Briggs, *Inorg. Chem.*, **4**, 1064 (1965); D. N. Hendrickson and W. L. Jolly, *ibid.*, **9**, 1197 (1970).

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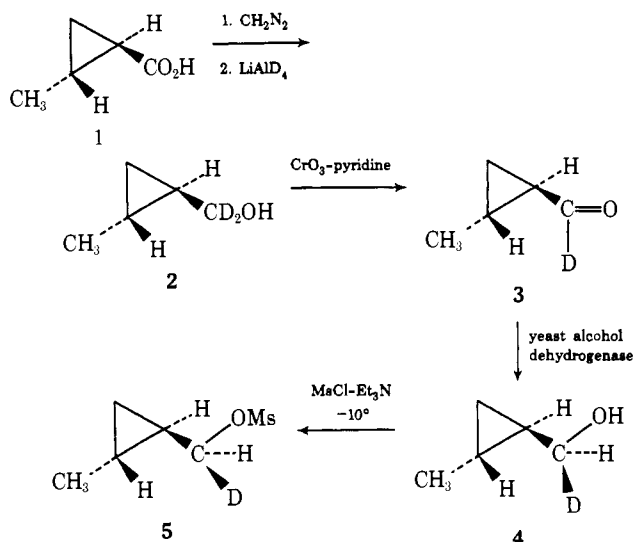
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The (*trans*-2'-Methylcyclopropyl)methyl System. Stereochemistry of Ionization, Rearrangement, and Solvent Capture¹

Sir:

Acceptance of bisected structures for cyclopropylcarbinyl cations is based on a growing body of experimental² and theoretical work.^{2,3} However, except for molecular orbital calculations,³ all of the available evidence which strongly supports bisected cations was obtained with secondary and tertiary systems.² Recently Olah and coworkers⁴ challenged the concept that the parent cation (a primary system) is bisected and have proposed an unsymmetrically bridged structure on the basis of ¹³C chemical shift comparisons. Subsequently the use of ¹³C chemical shifts to decide between bisected and bridged structures was questioned,⁵ but there were still no direct experimental data to support a bi-

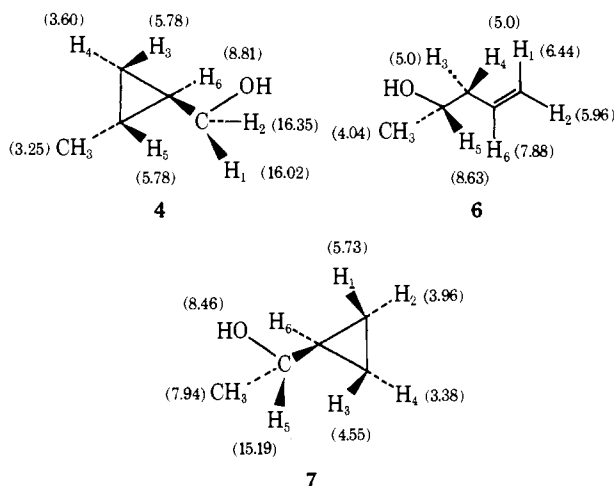
Scheme I



sected cation for primary cyclopropylcarbinyl systems. In this communication we present stereochemical evidence which bears on this important structural question.

Methanesulfonate **5** was prepared from optically active *trans*-2-methylcyclopropanecarboxylic acid by the sequence of reactions shown in Scheme I. Assuming that yeast alcohol dehydrogenase reduction of aldehyde **3** is stereospecific,⁶ the alcohol⁷ used to prepare **5** was a mixture of diastereomers—77% 1*S*, 1'*R*, 2'*R* and 23% 1*S*, 1'*S*, 2'*S*.

Hydrolysis of **5** (77% 1*S*, 1'*R*, 2'*R*) in 60% acetone-water with 2 equiv of γ -collidine, $k^{25^\circ} = (8.2 \pm 0.2) \times 10^{-2} \text{ sec}^{-1}$, gave three major products,⁸ **4** (26%), **6** (56%), and **7** (18%). The ²H distribution in each alcohol was deduced by measuring ¹H nmr intensities for samples where the chemical shifts of protons H₁–H₄ were separated as far as possible using Eu(fod)₃. Chemical shift assignments⁹ for **4** (0.235 mmol of Eu(fod)₃/0.413 mmol),¹⁰ **6** (0.076 mmol of Eu(fod)₃/0.384 mmol),¹¹ and **7** (0.118 mmol of Eu(fod)₃/0.257 mmol)¹² are summarized below. Although alcohols **4**,



6, and **7** are each inseparable mixtures of four ²H isomers, the mole fractions of ²H isomers for each skeletal isomer (²H at positions H₁–H₄) correspond directly to the ²H intensities listed in Table I.

An abbreviated mechanism is presented in Scheme II to account for the observed ²H distribution. Using the data in Table I,¹³ the stereochemistries of five individual steps—ionization of **5**, reaction of **8** with solvent at C₁, rearrangement of **8** to its enantiomer and to **9**, and reaction of **9** with