spectrum shows no parent peak but shows a peak at m/e213 corresponding to the molecular ion minus a fluorine $C_4F_7O_2$. Other strong peaks are m/e 119 (C_2F_5), m/e 100 (C_2F_4) , m/e 69 CF₃, m/e 50 (CF₂), and m/e 47 (CFO).

In the preparation of perfluoro(ethyl acetate) a 1.74-g sample of ethyl acetate was admitted into a four-zone gradient reactor² with zones cooled to -100° . After the fluorination procedure, the product was collected, fractionated, and purified by glc (fluorosilicone QFI-0065 13% on Chromasorb p) yielding the following products: CF₃CO₂C₂F₅, g (5%); CF₃CO₂CHFCF₃, 0.85 g (20%); 0.23 CF₃CO₂CF₂CF₂H, 0.05 g (1.2%); FCO₂CHFCF₃, 0.5 g (1.4%); also the -196° trap contained 2 g of a mixture of about equal parts CF₃CFO and CHF₂CFO.

Anal. Calcd. for C₄F₈O₂: C, 20.706; F, 65.503. Found: C, 20.65; F, 65.48.

Perfluoro(ethyl acetate) is a moisture sensitive gas (bp 21.4°) which easily rearranged to 2 mol of trifluoroacetyl fluoride. The infrared spectrum and ¹⁹F nmr are in agreement with that published by Shreeve and coworkers.⁶ The major product isolated from the reaction of ethyl acetate and elemental fluorine is the trifluoroacetic acid ester of the unstable alcohol α -hydrotetrafluoroethyl alcohol. This fluoro alcohol ester is a moisture sensitive liquid (bp 31.7°) which can be converted by a Lewis base into a equimolar mixture of trifluoroacetyl fluoride and trifluoroacetaldehyde. The product was identified by a molecular weight determination (214.2, vs. 214 for C₄F₇HO₂), infrared, and ¹⁹F and ¹H nuclear magnetic resonance. The infrared spectrum exhibits bands at 2995 (w), 1830 (s), (vC==O), 1420 (w), 1370 (w), 1331 (w), 1300 (s), 1248 (s), 1218 (vs), 1198 (vs), 1140 (s), 1105 (vs), 1062 (m), 920 (m), 733 (m), 698 (m), 628 (w), 580 (w), 550 (w) cm⁻¹. The ¹⁹F and ¹H nuclear magnetic resonance spectrum is summarized in Chart II. A major factor affecting yields in this reaction is presumed to be the rearrangement of perfluoro(ethyl acetate) to two moles of trifluoroacetyl fluoride catalyzed by hydrogen fluoride which is produced in the reaction. If this problem were overcome the quantity of ester recovered could increase markedly. The β -hydrotetrafluoroethyl trifluoroacetate was also fully characterized.

Chart II

$$\begin{array}{c} O \\ C_{a}F_{3} - C \\ + 78.98 \\ F_{c} \\ - 6.03 \\ + 154.25 \\ J_{ab} = & -0 \\ Hz \\ J_{ac} = & 0.5 \\ Hz \\ J_{bc} = & 50.53 \\ Hz \\ J_{bd} = & 3.05 \\ Hz \\ J_{c4} = & 5.87 \\ Hz \end{array}$$

The yields of the most important by-products CF₃CFO and CHF₂CFO are often obtained in yields as high as 40%; CF₄, OCF₂, and possibly FCO₂C₂F₅ are also produced in the reaction.

For the preparation of *perfluoropivaloyl fluoride*, a 2-ml sample (1.961 g, 0.0188 mol) was injected into the evaporator of the fluorination reactor (a six-zone modification).² The reactor was cooled to -78° during the fluorination procedure.

A crude yield of 4.4 g of material containing perfluoroisobutane, perfluoro-3,3-dimethyl-1-oxacyclobutane, perfluoropivaloyl fluoride, and monohydrooctafluoropivaloyl fluoride was obtained. From this mixture, 2.6 g (52% yield) of perfluoropivaloyl fluoride was isolated. The monohydroacyl fluoride still makes up approximately 20% of the molar yield, the other two products making up most of the remaining material. Perfluoropivaloyl fluoride is a very volatile solid (mp 38-38.5° sealed tube) which sublimes readily at room temperature. The product has been characterized by 19 F nmr (a 95% solution in CCl₄) and consists of a dectet (J = 11.5 Hz) centered at -42.34 ppm and a doublet (J = 11.4 Hz) centered at +67.08 ppm relative to external CFCl₃-CCl₄. The relative integrals were 1:9.5. The mass spectrum exhibits a molecular ion at m/e 266, a P - F at m/e 247, a P – COF₂ at m/e 200, and other strong peaks at m/e 181 (C₄F₇⁺), 178 (C₄F₆O⁺), 159 (C₄F₅O⁺), 131 $(C_3F_5^+)$, 69 (CF₃⁺) (strongest peak), and 47 (COF₂⁺).

The infrared spectrum exhibits bands at 1880 (m) $(\nu(C-O))$, 1855 (sh), 1312 (sh), 1290 (vs), 1215 (m), 990 (s), 739 (w), 710 (w), 660 (w), and 540 (w) wave numbers.

Anal. Calcd for C₅F₁₀O: C, 22.574; F, 71.412. Found: C, 22.38; F, 71.26.

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J. L. Adcock, R. J. Lagow*10

Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139 Received March 20, 1974

The Size of Phosphorus Ligands. An Experimental **Proton Magnetic Resonance Technique for Determining Cone Angles**

Sir:

There is a clear nonlinear relationship between the shift of the methyl resonance of coordinated methanol (σ_{MMR}) and the "bulkiness" or "steric size" of the L ligand in trans- $[LCo(DH)_2(CH_3OH)]^+$, where $L = RR'_2P$ ($R = or \neq R'$ = alkyl, aryl, alkoxy, or phenoxy) and DH = monoanion of dimethylglyoxime, HONC(CH₃)C(CH₃)NO⁻ (Table I). Steric effects of trivalent phosphorus ligands can dominate the chemistry of NiL₄ complexes.^{1,2} A steric parameter, the cone angle (CA, hereafter referred to as TCA), was defined by Tolman.¹ These angles have been correlated with a wide variety of phenomena including stabilities,3 fluxional behavior,⁴ rate constants,⁵ catalytic activities,⁶ and specificities⁶ in product formation. Electronic effects of L are also inherent in such phenomena. From the data in Table I it is clear that a good correlation exists between σ_{MMR} in LCo- $(DH)_2(CH_3OH)^+$ and the TCA of L. At low TCA, <120°,

RR′2P	CH₃OH shift, τ (J _{PH} , ^b Hz)	Oxime methyl shift, $ au$ ($J_{\rm PH}$, Hz)	ECA⁰	TCA ^d	p <i>K</i> a ^e	$\Sigma^3 \chi_{ m i}{}^f$
(c-C ₆ H ₁₁) ₃ P	7.460 (1.2)	7.51 (0.5)	173	179	9.70	0.3
$(i-C_3H_7)_3P$	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
$(n-C_4H_9)(C_6H_5)_2P^{g}$	7.310(1.3)	7.89(0.7)	140	140		10.0
$(CH_3)(C_6H_5)_2P$	7.265 (1.3)	7.95 (0.7)	132	136	4.6	11.2
$(CH_3O)(C_6H_5)_2P$	7.250 (1.5)	7.90 (0.7)	129	132		16.3
$(2-(CN)C_2H_4)_3P$	7.245 (1.5)	7.47 (0.8)	129	130	1.36	21.9
$(o-CH_3C_6H_4O)_3P^i$	7.240 (2.7)	7.90 (0.6)	128	141		28.2
$(n-C_4H_9)_3P^h$	7.230 (1.2)	7.56(0.8)	127	130	8.43	4.2
$(CH_3)_2(C_6H_5)P$	7.200 (1.3)	7.81 (0.7)	125	127	6.50	9.5
$(CH_3O)_2(C_6H_5)P$	7.200 (1.9)	7.79(0.5)	125	120		19.7
$(i-C_3H_7O)_3P$	7.180 (2.3)	7.59(0.5)	124	122	3.4	18.9
$(C_6H_5O)_3P$	7.170 (2.9)	7.78 (0.5)	123	121		29.1
$(CH_3)_3P^i$	7.145 (1.0)	7.59 (0.6)	<117	118	8.65	7.8
$C_2H_3C(CH_2O)_3P^j$	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 ($\tau \pm 0.01$) 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)₃P and (CH₃)₂(C₆H₃)P 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*-C₄H₃)₃P, and (*i*-C₃H₇O)₃P estimated from E. M. Thorsteinson, Ph.D. Thesis, Northwestern University, Evanston, Ill., 1966. ^f Reference 8. ^e (C₂H₃O)₃P, and (CH₃O)₃P have identical *CH*₃OH 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 $(C_6H_5)_3PRh(DH)_2Cl.^{11}$ The normals to the dioxime planes form an angle of 17.1°. Most probably, as the bulkiness of L increases in the $[LCo(DH)_2(CH_3OH)]^+$ series, the dioximes are increasingly bent.

A plot of $\sigma_{\rm MMR}$ vs. oxime methyl resonances ($\sigma_{\rm OMR}$) 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 expression¹³ 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 $(o - CH_3C_6H_4O)_3P$ formed complexes of similar but greater stability than did $CH_3(C_6H_5)_2P$, these complexes were in turn much more stable than that with $(C_6H_5)_3P$. Our cone angles give the correct order and predict a much lower value of K for $(C_6H_5)_3P$. 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[$(o - CH_3C_6H_4O)_3P$]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 $P(C_6H_5)_3$ ($\sigma_{OMR} = 7.83$) should show greater shielding than $P(C_6H_5)_2CH_3$ (7.95) or $P(C_6H_5)_2(OCH_3)$ (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'R₂ 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 $P(C_6H_5)_3$ 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"² 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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- (15) The expression was

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 (C_6H_5)₃P, a value of TCA = 155° was used and (2) for (*i*- C_3H_7O)₃P a TCA = 122°.

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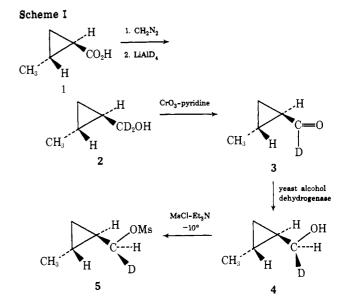
William C. Trogler, Luigi G. Marzilli*

Department of Chemistry, The Johns Hopkins University Baltimore, Maryland 21218 Received July 5, 1974

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

Sir:

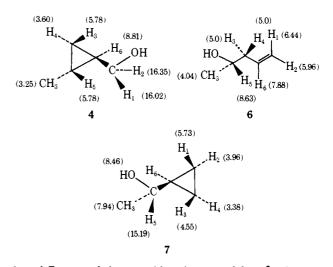
Acceptance of bisected structures for cyclopropylcarbinyl cations is based on a growing body of experimental² and theoretical work.^{2,3} However, except for molecular orbital calculations,³ all of the available evidence which strongly supports bisected cations was obtained with secondary and tertiary 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-



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% 1S, 1'R, 2'R and 23% 1S, 1'S, 2'S.

Hydrolysis of 5 (77% 1S, 1'R, 2'R) in 60% acetone-water with 2 equiv of γ -collidine, $k^{25} = (8.2 \pm 0.2) \times$ 10^{-2} sec⁻¹, gave three major products;⁸ 4 (26%), 6 (56%), and 7 (18%). The 2 H distribution in each alcohol was deduced by measuring ¹H nmr intensities for samples where the chemical shifts of protons H_1-H_4 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 $Eu(fod)_3/0.384 \text{ mmol})$,¹¹ and 7 (0.118 mmol of $Eu(fod)_3/$ $(0.257 \text{ mmol})^{12}$ are summarized below. Although alcohols 4,



6, and 7 are each inseparable mixtures of four 2 H isomers, the mole fractions of ²H isomers for each skeletal isomer $(^{2}H \text{ at positions } H_{1}-H_{4})$ correspond directly to the ^{2}H 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 stepsionization of 5, reaction of 8 with solvent at C_1 , rearrangement of 8 to its enantiomer and to 9, and reaction of 9 with