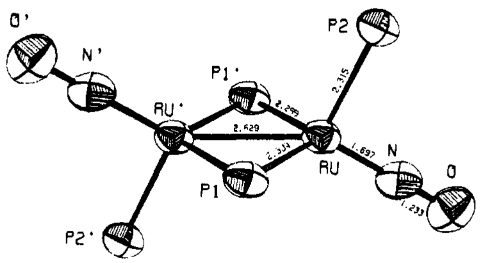

Figure 1. A perspective drawing of the inner coordination geometry of $[Ru(NO)(\mu\text{-}P(C_6H_5)_2)(P(CH_3)(C_6H_5)_2)]_2$ with the phosphorus substituents omitted for clarity. The estimated standard deviations for the bond lengths (Å) are: Ru–Ru; 0.002; Ru–P, 0.004; Ru–N, 0.012; N–O, 0.012. Important bond angles (deg) are: Ru–P(1)–Ru′, 69.7 (1); P(1)–Ru–P(1)′, 110.3 (1); P(1)–Ru–P(2), 102.0 (1); P(1)′–Ru–P(2), 106.1 (1); N–Ru–P(1), 123.5 (4); N–Ru–P(1)′, 113.4 (4); N–Ru–P(2), 98.4 (4); Ru–N–O, 174.1 (9).

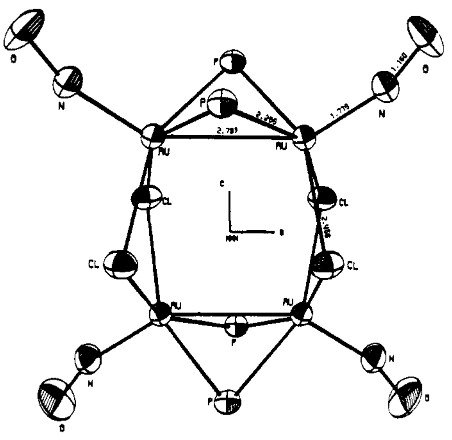

Figure 2. A perspective drawing of the inner coordination geometry of $[RuCl(NO)(\mu\text{-}P(C_6H_5)_2)]_4$. The phenyl rings are omitted for clarity. The estimated standard deviations for the bond lengths (Å) are: Ru–Ru, 0.002; Ru–Cl, 0.002; Ru–P, 0.002; Ru–N, 0.007; N–O, 0.010. Important bond angles (deg) are: Ru–P–Ru, 75.14 (7); Ru–Cl–Ru, 96.11 (8); P–Ru–P, 79.71 (10); Cl–Ru–Cl, 80.61 (8); Ru–N–O, 160.3 (8); P–Ru–N, 104.1 (2); Cl–Ru–N, 106.1 (2).

geometry about each ruthenium atom (neglecting metal–metal bonding) is square pyramidal with two chlorines and two phosphido groups in the basal plane and the nitrosyl ligand at the apex. The Ru atom is displaced 0.62 Å out of the basal plane toward the apical nitrosyl. One intriguing and noteworthy aspect of this structure is the slightly bent mode of nitrosyl coordination which has a Ru–N–O bond angle of 160.3 (8)° and a Ru–N distance of 1.779 (7) Å. While this distance is longer than that found in **1**, it does not differ significantly from corresponding values in $RuH(NO)(P(C_6H_5)_3)_3$, $[Ru(NO)(diphos)_2]^+$, and other Ru complexes containing linearly coordinated nitrosyl.[1] The ruthenium–nitrosyl bond in **2** thus exhibits considerable metal–ligand π interaction despite the 160.3° Ru–N–O bond angle. This type of slightly bent coordination, which is intermediate between the linear and 120° bent modes of NO bonding, has been suggested by us[1] for discrete tetragonal-pyramidal complexes with a 21-electron count. (This count is based on 10 electrons from the ligand σ^b functions, 4 electrons in the π^b NO set, and 7 electrons from the metal ion which, in this case, is formally Ru(I).) The occurrence of metal–metal bonding in **2** apparently does not affect this conclusion regarding NO bonding although it does alter slightly the bonding scheme presented previously.[1]

Assessing the degree of metal–metal bonding in systems such as **1** and **2** is fraught with difficulties, but it is clear from the structural parameters that a significant difference in the metal–metal bonding does exist between these systems. If the noble gas rule is followed in assigning metal–metal bond orders, then the 2.787-Å Ru–Ru bond in **2** has a bond order of 1 and the much shorter 2.629-Å Ru–Ru bond in **1** has formal bond order of 2. These distances may be compared with Ru–Ru bond lengths ranging from 2.650 Å in elemental ruthenium[14] to 2.848 Å in $Ru_3(CO)_{12}$[15] and the range 2.70–2.95 Å observed in a number of ruthenium carbonyl cluster compounds.[16] This comparison of distances underscores the problem in assigning metal–metal bond orders.[17] An alternative formulation of **1** which eliminates the necessity of the Ru–Ru double bond is $[RuH(NO)(\mu\text{-}P(C_6H_5)_2)L]_2$ but infrared, nmr, and chemical evidence do not support the presence of a hydride. Further studies of these systems designed to examine the relationship of metal–metal bonding with mode of nitrosyl coordination and the reactivity of these systems toward small molecules are in progress.[18]

Acknowledgments. We wish to thank Mr. Donald G. VanDerveer for measuring the nmr spectra of the compounds and to acknowledge the National Science Foundation (NSF Grant GP-23139) and the Advanced Research Projects Agency for support of this work.

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(17) A referee has also suggested that the Ru–Ru bond in **2** is constrained to its larger value by virtue of nonbonded repulsions between Cl atoms across the tetranuclear cluster (the Cl···Cl vector which parallels the Ru–Ru bond). However, we believe a shorter Ru–Ru bond in **2** could be accommodated by a decrease in the Ru–Cl–Ru bond angle from the observed value of 96.11° with no increase in Cl···Cl contacts. This suggestion, though, does point out one more possible factor in determining the most stable geometry of a system and, hence, the observed metal–metal bond length.

(18) Listings of coordinates and anisotropic temperature factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-6240. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Richard Eisenberg,* Arthur P. Gaughan, Jr.
Cortlandt G. Pierpont, Joseph Reed, Arthur J. Schultz
Department of Chemistry, Brown University
Providence, Rhode Island 02912

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Electron Paramagnetic Resonance of Free Radicals in an Adamantane Matrix. IV. The Structure of the *tert*-Butyl Radical

Sir:

It is well known that the methyl radical is planar[1] and that sequential replacement of hydrogen by fluorine

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(1) G. Herzberg, "The Spectra and Structures of Simple Free Radicals," Cornell University Press, Ithaca, N. Y., 1971.

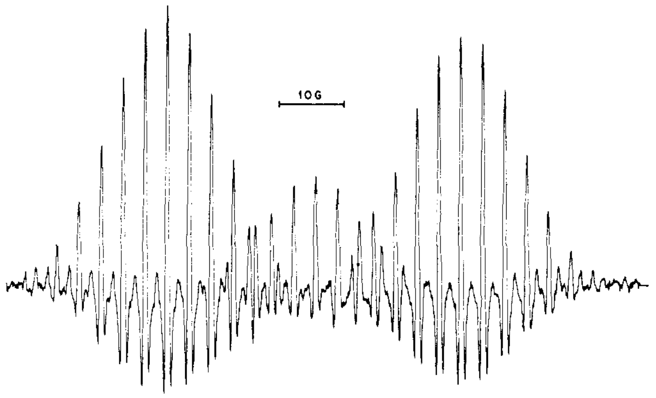

Figure 1. Second derivative epr spectrum of $(CD_3)_3{}^{13}C\cdot$ in adamantane-d_{16} at 10°. The small group of lines in the center of the spectrum is due to $(CD_3)_3{}^{12}C\cdot$.

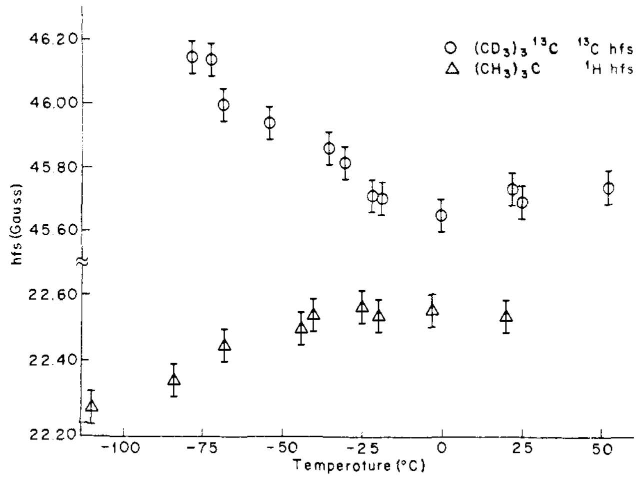

Figure 2. ^{13}C and ^1H hyperfine splittings *vs.* temperature.

causes increasing deviation from planarity.[2] These observations were satisfactorily explained by molecular orbital calculations,[3,4] but it remained for Pauling[5] to produce a concise argument as to why the geometry of those radicals should so strongly depend upon the nature of the substituents. He stated that the electronegativity difference between the atoms M and X in a free radical of the form $\dot{M}X_3$ is the major factor in determining its geometry. For an electronegativity difference $E(M) - E(X) \geq 0.2$, the radical should be planar; for $E(M) - E(X) \leq 0.0$, the radical should be pyramidal with the XMX bond angle $\leq 109°\ 28'$; and for $0.0 \leq E(M) - E(X) \leq 0.2$, the bond angle should be between 109° 28′ and 120°. There is ample experimental evidence that this rule is qualitatively correct for large differences in electronegativity;[6] however, there are no structural data for radicals wherein the electronegativity difference is in the critical region of 0.0–0.2. An extremely interesting case occurs when M is the same element as X, since the predicted bond angle is 109° 28′. Thus Pauling's rule[5] predicts that tertiary alkyl radicals have tetrahedral bond angles whereas they are generally thought to be planar.[7] Because the central atom hyperfine splitting (hfs) affords a rather direct measure of the hybridization, and thus the geometry, of a radical, we sought to determine the $\alpha_{^{13}C}$ hfs in the *tert*-butyl radical. Although that radical is well known, there is little mention of the value of the $\alpha_{^{13}C}$ hfs in the literature. Watson[8] reported the maximum component of the ^{13}C hyperfine tensor for the *tert*-butyl radical **1** in γ-irradiated single-crystal, 2,2,2-trimethylacetamide at 77°K but was unable to obtain the rest of the axial tensor. Hesse and Roncin[9] reported the ^{13}C hfs for the *tert*-butyl radical in X-irradiated *tert*-butyl chloride at 86°K; however, they interpreted anisotropic features in the epr spectrum as isotropic hfs and, therefore, drew incorrect conclusions regarding the geometry of the radical. Our approach to the problem was to prepare the radical by X-irradiation of *tert*-butyl chloride in an adamantane matrix, in which suitable radicals are known to yield isotropic epr spectra over a wide range of temperatures.[10] Unfortunately, the isotropic ^{13}C hfs was an even multiple of the ^1H hfs, thus precluding accurate measurement of the ^{13}C hfs. To remove that degeneracy and to decrease inhomogeneous broadening by the matrix, we prepared the isotopically substituted radical, 1,1-dimethylethyl-*1*-^{13}*C*-d_9 (**2**), by X-irradiation of the chloride in adamantane-d_{16} (Figure 1). The ^{13}C hfs in radical **2** and the ^1H hfs in radical **1** are plotted as a function of temperature in Figure 2. We believe that the apparent temperature displacement between the two curves is due to the difference in zero-point energies resulting from isotopic substitution.

The observed ^{13}C hfs lies between the values expected for a planar radical (27 G) and a tetrahedral radical (>100 G). Furthermore, the negative temperature coefficient cannot be accommodated by a planar radical since increasing the vibrational amplitude of a planar radical would increase the s character of the singly occupied orbital and thus increase in ^{13}C hfs. Additional experimental evidence for nonplanarity is given by the positive temperature coefficient observed for the ^1H hfs, since a negative temperature coefficient would be predicted for a planar radical as a result of reduced hyperconjugation at increased vibrational amplitudes. Therefore, the experimental evidence suggests that the *tert*-butyl radical has a nonplanar equilibrium geometry.

An estimate of the bond angle in the *tert*-butyl radical can be made by Coulson's method.[11] Using our value of 46.2 G for the isotropic ^{13}C hfs and Watson's[8] value of 92 G for the maximum anisotropic ^{13}C hfs, we obtain a bond angle of 117.3°. Another indication of the nonplanarity can be obtained from semiempirical INDO calculations[12] which are summarized in Table I. The bond lengths and the CCC angle were first adjusted to give the minimum energy; then the hyperfine splittings

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Table I. Hyperfine Splittings Calculated by INDO[13]

CCCC dihedral angle, deg	C–C–C angle, deg	Energy, au	$a_{^{13}\mathrm{C}}$, G	$a_{^{1}\mathrm{H}}$, G
41.69	114.0	−34.26398439	74.73	27.25
38.13	115.0	−34.26920943	64.47	27.95
34.18	116.0	−34.27427814	59.96	28.67
29.67	117.0	−34.27919785	52.16	29.42
24.28	118.0	−34.28397676	44.04	30.20
17.20	119.0	−34.28862434	35.50	31.02
0.0	120.0	−34.29315149	26.90	31.89

were calculated for 1° increments in the bond angle. The INDO calculation predicts a planar radical but the deformation energy is predicted to be small. The bond angle corresponding to the observed ^{13}C hfs is 117.8°.

The geometry of the *tert*-butyl radical was also determined by *ab initio* molecular orbital calculations using the STO-3G basis.[13,14] Because of computer time considerations, the methyl groups were constrained to be tetrahedral, and the radical was constrained to have C_3 symmetry. The optimum values for the CC and CH bond lengths, the CCC bond angles, and the HCCC dihedral angles[15] are 1.526 Å, 1.087 Å, 117.6°, and 14.8°, respectively.

The ~117.5° bond angle indicated by our work is outside the error limits indicated by Pauling for his relationship if we assume $E(\mathrm{M}) - E(\mathrm{X}) = 0$. However, it is probably incorrect to take the electronegativity of the methyl group equal to that of carbon. In fact, one might use the measurement of the bond angle in the *tert*-butyl radical as a measure of the electronegativity of the methyl group. A calculation using Pauling's equations and our bond angle yields an electronegativity of 2.36 for methyl relative to 2.5 for carbon. Substitution of carbon for hydrogen at the β position would be expected to make the radical more nearly tetrahedral; thus *tert*-butyl would be expected to be the most nearly planar of all tertiary alkyl radicals.

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(15) The CCCH dihedral angle refers to the angle with respect to the CCC plane which places the CH bond anti to the CC bond and on the side of the reference plane opposite to the out-of-plane carbon atom.

(16) Petroleum Research Fund Postdoctoral Fellow.

David E. Wood, Lawrence F. Williams[16]
Department of Chemistry, University of Connecticut
Storrs, Connecticut 06268

Richard F. Sprecher,* William A. Lathan
Department of Chemistry, Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

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A Carbon-13 and Hydrogen-1 Nuclear Magnetic Resonance Study of the Conformations of 3′,5′- and 2′,3′-Cyclic Nucleotides. A Demonstration of the Angular Dependence of Three-Bond Spin–Spin Couplings between Carbon and Phosphorus

Sir:

It has been demonstrated recently that the ^{13}C nuclear magnetic resonance spectra of nucleotides[1-3] and polynucleotides[2,3] contain three-bond couplings between ^{13}C and ^{31}P which vary from 1 to 10 Hz in magnitude. It has been suggested that these couplings are sensitive to the dihedral angles between the planes ^{31}P–O–C and O–C–^{13}C in these compounds, and therefore are useful for conformational analyses.[2,3] To test this hypothesis we have studied the ^{13}C and ^{1}H nmr spectra of the 3′,5′- and 2′,3′-cyclic nucleotides of uridine (U), cytidine (C), adenosine (A), and guanosine (G), and also of thymidine 3′,5′-cyclic phosphate and $N^6,O^{2'}$-dibutyryladenosine 3′,5′-cyclic phosphate. Our data confirm the angular dependence of the $^3J_{\mathrm{POCC}}$, and yield values for the trans and gauche couplings in these compounds of 8 and 2 Hz, respectively.

X-Ray studies on single crystals of adenosine 3′,5′-phosphate[4] and adenosine 3′,5′-phosphonate[5] have indicated that the ribose and phosphate rings of these compounds are rigid, and that the ribose ring has the twist conformation 3′-endo,4′-exo ($^3T_4$)[5] or 4′-exo,3′-endo ($_4T^3$).[4] Molecular models indicate that, in contrast to the uncyclized 3′ and 5′ nucleotides,[6-9] the ribose rings of these compounds are incapable of converting between various puckered forms. They thus serve as excellent models for the calibration of the proposed angular dependence. In the $^3T_4$ conformation[5] the phosphate is trans relative to C_2' and gauche relative to C_4'.

^{13}C resonances were assigned by comparison with earlier data on nucleosides and nucleotides.[2,3] The ^{31}P splittings are evident on the resonances of carbons 2′, 3′, 4′, and 5′. In the six 3′,5′-cyclic nucleotides studied, the couplings P–C_2' are 8.0 ± 0.3 Hz, which gives a value for the trans coupling. On the other hand, the P–C_4' couplings are 4.6 ± 0.2 Hz. Since the gauche coupling takes place *via* two routes (PO-$C_5'C_4'$ and PO$C_3'C_4'$) we can only estimate the single path gauche coupling to be approximately 2 Hz. It is also interesting to note that the $^2J_{\mathrm{POC}}$ couplings to carbons 3′ (4.2 ± 0.5 Hz) and 5′ (7.2 ± 0.2 Hz) are different, but essentially constant throughout the series. Although they are not expected to be angular dependent, these couplings do reflect the different environments or

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