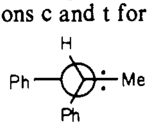
Table I. Photolysis of 5 at Various Temperatures[a]

R in 5	[(*E*)-6] [(*Z*)-6][b]	
	0 °C	−196 °C
Ph	1.4	1.9
Me	2.1	4.9
Et	1.7	2.2
i-Pr	4.0	0.9
t-Bu	8.0	2.1

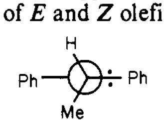
[a] Methylcyclohexane solutions ca. 25 mM in diazo were used. All products were identified by gas chromatography comparisons with authentic samples and gas chromatography-mass spectroscopy techniques. Total product yields are 70–85%. Other minor products detected in each experimental condition were the ketone and its azine. No prominent formation of other products, e.g., C–H insertion product, was noted even at −196 °C. [b] Average of duplicate runs are tabulated; reproducibility was <±5%.

Support is lent to the above argument by the finding[9] that an H atom generated in a rigid neopentane crystal at −196 °C can travel a long distance and even intermolecularly. Furthermore, it has been generally accepted[10] that reactions in the solid state occur with minimum atomic or molecular movement even at ambient temperature since a large change of external shape of the reaction cavity, occupied by the molecules which will participate in the reaction, with the atomic movements constituting this reaction will be resisted by the close-packed environment. If one accepts[4,11] that H migration occurs from the singlet state of carbene, that, by analogy with the radical, a phenyl group can migrate in the triplet manifolds, and that these two arylcarbene electronic states can at least interconvert, if not come to equilibrium, the observed inversion of temperature dependency of migratory aptitude can be interpreted to indicate that cool solution favors the triplet-side reaction as a result of energetic advantage whereas the restricted mobility enforced by the solid matrix may place a premium on the triplet reaction and favor reaction from the singlet side.

One more interesting feature of the results in Figure 1 is that the stereochemistry of the 1,2-H shift ([3]/[2] ratio) is also significantly sensitive to the reaction phase. Although the plot of [3]/[2] vs. T^{-1} shows some scatter, the obvious trend is that the *Z* isomer significantly increases once a rigid matrix is formed. Moreover, similar matrix effects on the stereochemistry of the 1,2-H shift were also observed in other arylcarbene systems (Table I). The mechanism of 1,2-H shift indicated[12] to be favorable involves an electrophilic pull of gauche hydride through the vacant p orbital of the singlet carbene, starting from approximate carbene conformations c and t for formation of *E* and *Z* olefins, respectively.

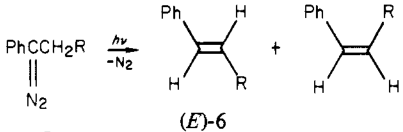


c



t

The ratio of *E*/*Z* olefins produced will be then determined[12a] by the relative populations of the conformers, which are affected by steric as well as electrostatic factors. If one assumes that the steric interaciton between Ph–Ph is greater than Ph–Me, one would expect that the *E* isomer (**2**) would be favored in the rigid-matrix reaction since the more stable conformer predominates at low temperature and since the matrix imposes[2a] severe steric demands on the reaction within it. One notes from Table I, however, that more *E* isomer is formed from **5** (R = Me) than from **5** (R = Ph) at ambient temperature and that increase in the *E*/*Z* ratio caused by the matrix was more significant in **5** (R = Me) than in **5** (R = Ph), indicating that steric interaction between Ph–Me is greater than for Ph–Ph. This implies that the Ph ring on the carbenic carbon may be relatively perpendicular[12f,13] to the vacant carbene orbital and hence the steric interaction with the methyl group becomes important whereas the Ph ring on the β carbon may twist from the vacant orbital so as to reduce the steric repulsion with the adjacent Ph group. In order to obtain deeper insight into the nature of this interesting matrix effect on stereochemistry, we further examined the temperature dependence of stereoselectivity in the 1,2-H shift in the photolysis of a series of diazo compounds[3,5] (Table I). Contrary to the above results, indicating that the reaction is more stereoselective toward the more stable isomer in a rigid matrix, apparently the less stable olefin comes to predominate in a rigid matrix as the R group is successively displaced with a more bulky group. The origin of the anomalous matrix effect is quite interesting. It has been suggested[14] in the photochemical 1,2 shift of alkyl azide that the *tert*-butyl group is sufficiently large to experience significant nonbonded repulsion with the lone-pair electrons on adjacent nitrogen. It may be suggested, then, that such nonbonded repulsion between a bulky R group and the carbene unshared electrons, which is not important at ambient temperature, becomes significant in a rigid matrix due to the close packing. Alternatively, it is very tempting to assume that, in a matrix environment, the nascent carbene is forcibly paired with the leaving N_2 due to the limited diffusibility and hence rapid H migration occurs before leaving N_2 has completely left the neighborhood of the carbene center. Apparently, this would reduce the population of conformer leading to *E* olefin as a result of steric repulsion between the more bulky R group and N_2. We have recently demonstrated[2c] that such effect of leaving group on the intermolecular reaction courses of carbene is dominant in a rigid matrix.



5 (*E*)-6 (2)

Expanded studies in this area are now in progress in order to probe the viability of our mechanistic hypothesis.

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[13] Recently, it has been demonstrated[12f] that stereochemistry is very sensitive to the conformation of the phenyl group in rearrangement of 1-phenyl-1-propylidenes. It has been suggested that electron-donor para substituents favor a planar conformation for singlet phenylcarbenes, whereas electron-withdrawing para substituents are presumed to enhance twisting of the phenyl group to a perpendicular conformation. MINDO/3 calculations indicate that an unsubstituted phenyl group favors a planar conformation: Miller, R. J.; Yang, L. S.; Shechter, H. *J. Am. Chem. Soc.* **1977**, *99*, 938.

[14] (a) Abramovitch, R. A.; Kyba, E. P. *J. Am. Chem. Soc.* **1971**, *93*, 1537. (b) Kyba, E. P.; Abramovitch, R. A. *Ibid.* **1980**, *102*, 735.

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Received May 19, 1980

Accurate and Sensitive Determination, by a New Cobalt-59 Nuclear Magnetic Resonance Method, of Electron Acceptance and Hydrogen Bond Donation by Protic Solvents

Sir:

The vast potential of ^{59}Co NMR, with a chemical shift range of over 14 000 ppm,[1] has remained almost untapped:[2-5] a large

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[1] Kidd, R. G.; Goodfellow, R. J. In "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978; pp 195–278.

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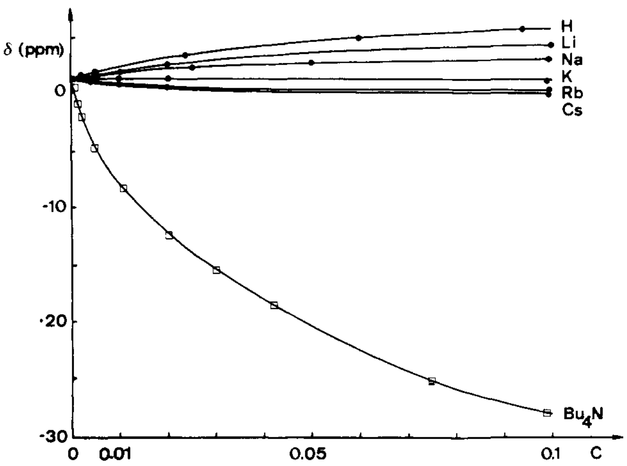
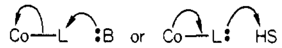


Figure 1. Concentration dependence of the ^{59}Co chemical shift (ppm) for $Co(CN)_6^{3-}$, in the presence of various counterions.

quadrupole moment $Q = 0.404$ b^6 couples with the electrostatic field gradient (q) at the nucleus to render line widths prohibitively large for high-resolution work. In addition, all Co^{II} (d_7) compounds are paramagnetic. To bypass these impediments, we use low-spin and symmetrical (O_h) Co^{III} complexes. By an appropriate choice of the ligand L, these CoL_6 entities can be tailored at will for a great variety of efficacious measurements: the net charge can be greater than or less than zero. Ligands can be chosen to have hard/soft acid/base behavior toward the surrounding medium (solvent). While the ligands shelter the metal from direct contact with and reduction by the environment, they relay to it even minute alterations in the electron density at peripheral atoms:



Furthermore, when using ionic complexes, one can easily observe counterion- and concentration-dependent chemical shifts and line widths which are characteristic of a given solvent. Choice of an appropriate counterion can also help to solubilize the cobalt salt in low-polarity solvents. These combined factors make ^{59}Co NMR a somewhat less sensitive (smaller chemical shift range) but more versatile probe of ionic solvation than ^{205}Tl NMR.[7,8] A major (although easily overcome) practical drawback of the cobalt-59 method is the requirement of good temperature stability (±0.02 °C) inside the spectrometer probe: cobalt-59 chemical shifts indeed exhibit a temperature dependance of up to several ppm per degree,[9] like other heavy nuclei.[10,11] On the other hand, magnetic susceptibility corrections are sufficiently small to be negligible in most cases.[12]

The method will be illustrated here by some applications centered on the $Co(CN)_6^{3-}$ anion.[13] Since a good part of the negative charge is partitioned between the terminal nitrogens,[14] this complex serves as a sensitive probe toward electrophilic centers.[15] The influence of the counterions has been studied in aqueous solution, with the univalent alkali metal cations H^+ and $(n\text{-Bu})_4N^+$. As shown in Figure 1, increasing the concentration of the salt leads to small downfield chemical shifts for H^+, Li^+, and Na^+ and to small upfield shifts for Rb^+ and Cs^+. The $(n\text{-Bu})_4N^+$ salt, on the contrary, exhibits a fairly large upfield shift.

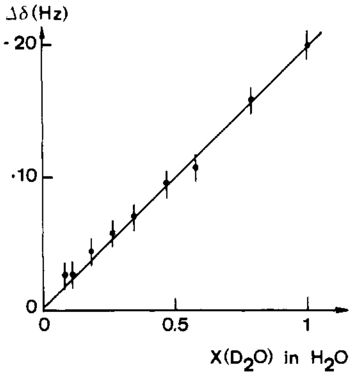


Figure 2. Plot of the ^{59}Co chemical shift (Hz) for $K_3Co(CN)_6$ (0.1 M) in H_2O–D_2O mixtures; the linearity indicates a lack of preferential solvation in the binary mixture.

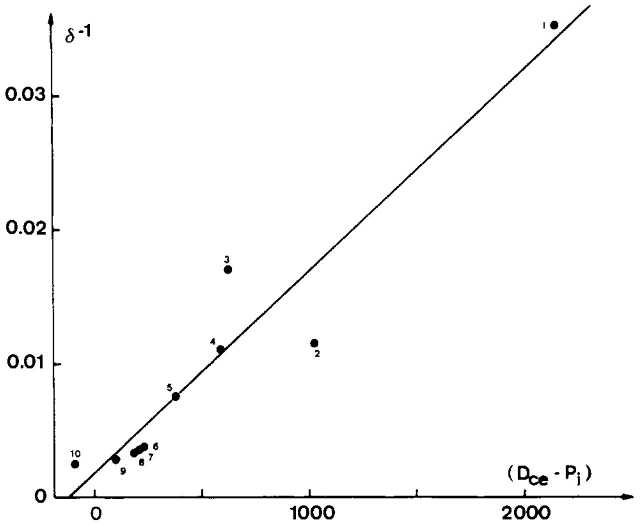


Figure 3. Plot of the reciprocal chemical shift ($10^6\delta^{-1}$) for $[(n\text{-Bu})_4N]_3Co(CN)_6$ against the difference between the density of cohesive energy D_{ce} and the internal pressure P_i (J·cm^{-3}). The more strongly self-associated solvents have the greatest $D_{ce} - P_i$ values (ρ = 0.96 for 10 points). Solvents: H_2O (1), formamide (2), ethanediol (3), methanol (4), ethanol (5), propylene carbonate (6), acetonitrile (7), Me_2SO (8), DMF (9), and HMPT (10).

Table I

salt	solvent	ε(25 °C)	δ^a	$\Delta\nu_{1/2}$,^{b} Hz
$K_3Co(CN)_6$ (0.1 M)	H_2O	78.36	+1.05 ± 0.04	3.2
	D_2O	77.936	0.0 (ref)	4.4
$(n\text{-Bu}_4N)_3Co(CN)_6$ (0.1 M)	H_2O	78.36	−28.5 ± 0.1	19.5
	D_2O	77.936	−32.2 ± 0.1	26.3
	CH_3OH	32.7	−91.0 ± 0.1	25.0
	CH_3OD	c	−94.1 ± 0.1	
	CD_3OD	c	−96.1 ± 0.1	

^{a} Reference 13. ^{b} Reference 26. ^{c} Not available.

We are thus in the presence of two competing effects: (a) With small metallic cations having a high charge density, the small

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(11) In $CpV(CO)_4$, for instance, ^{51}V $d\delta/dt$ = 0.6 ppm/°C: Rehder, D., private communication.

(12) All chemical shifts reported in this study are uncorrected.

(13) 18.97-MHz spectra are referenced to an external solution (coaxial tube) of 0.1 M $K_3Co(CN)_6$ in D_2O. This reference solution also serves as an internal thermometer,[9] after calibration with a thermistor probe. All experiments were run at 33.05 ± 0.02 °C. The choice of $K_3Co(CN)_6$ in D_2O as a reference is particularly appropriate since its chemical shift is independent of concentration in the 0.1–10^{-4} M domain and does not require extrapolations to infinite dilution.

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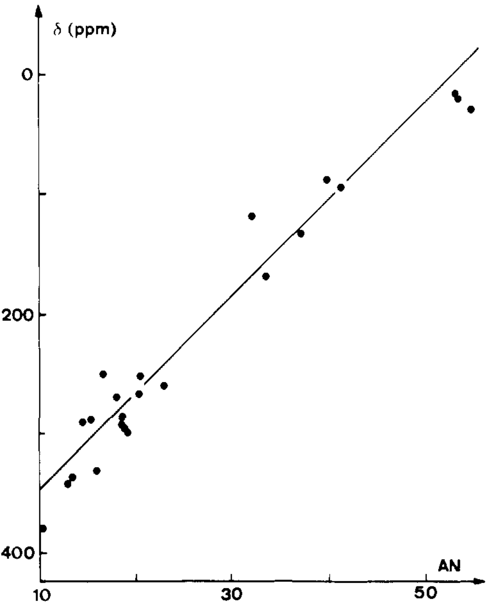
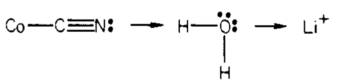


Figure 4. Plot of the ^{59}Co chemical shift δ (ppm) for $[(n\text{-Bu})_4N]_3Co(CN)_6$ against the Gutmann acceptor number (AN)[25] (ρ = 0.98 for 27 points).

depletion of cobalt valence electrons, due to polarization from the cyanide ligands and the solvent molecules, leads to a small downfield shift of the cobalt resonance:



$$Co{-}C{\equiv}N\!: \longrightarrow H{-}\underset{\displaystyle H}{\underset{|}{\ddot{O}}}\!: \longrightarrow Li^+$$

(b) For large metallic cations with low charge density and little electronic overlap, as well as for the tetrabutylammonium cation, which has no possible electronic overlap at all, Coulombic attraction results in a net diamagnetic shielding. In addition, quaternary ammonium ions, being less solvated, are more strongly associated to the $Co(CN)_6^{3-}$ anion and start forming molecular aggregates in water above a concentration of ca. 50 mM.[16]

Despite the cobalt center being separated from the solvent by the cyanide ligands, the solvent isotope effect[17-19] is substantial: a chemical shift difference of 1.05 ± 0.04 ppm is observed between H_2O and D_2O (a weaker hydrogen bond donor than H_2O[17]) with the potassium salt (Figure 2). The $n\text{-Bu}_4N^+$ salt, not being fully dissociated like the potassium salt, is even more sensitive to isotope effects because its dissociation constants respond to subtle decreases in the dielectric constant[20] of the isotopically labeled solvent (Table I). We are even able to measure a secondary solvent isotope effect of ~2 ppm between CH_3OD and CD_3OD.

With protic solvents SH, a downfield shift of the ^{59}Co resonance occurs upon hydrogen bonding to the cyanide ligands and in proportion to the strength of this hydrogen bond. Thus we are able to rank solvents according to their strength as hydrogen bond *donors* by plotting the reciprocal of the ^{59}Co chemical shift δ against the difference between the density of cohesive energy (D_{ce}) and the internal pressure (P_i), which measures the density of hydrogen bonding[21,22] (Figure 3). Since $Co(CN)_6^{3-}$ is an overall electron donor, we have also correlated the ^{59}Co chemical shift measurements with the acceptor number (AN) for the solvent molecules, as determined by Gutmann[25] from ^{31}P chemical shifts for tributylphosphine oxide (Figure 4).

We shall report elsewhere other applications, ranging from accurate determination of the Dimroth–Reichardt E_T parameter,[21] to quantitative investigation into the thermodynamics of the hydrophobic effect.

Acknowledgment. We thank Fonds de la Recherche Fondamentale Collective, Brussels, for award of Grants 2.4504.78 and 21420.D, which made possible purchase of the Bruker WP-80 spectrometer used in this study.

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Received August 4, 1980

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*Book Reviews**

Kirk-Othmer Encyclopedia of Chemical Technology. Third Edition. Volume 9 (Enamels to Ferrites). Volume 10 (Ferroelectronic to Fluorine Compounds). Edited by M. Grayson et al. John Wiley and Sons, New York. 1980. Volume 9: xxiv + 902 pp. $145.00. Volume 10: xxvi + 962 pp. $145.00.

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The title contains a pair of acronyms for the Los Alamos Scientific Laboratory Pulsed High Energy Radiographic Machine Emitting X-rays. The machine is a linear electron accelerator that produces very intense bursts of bremsstrahlung for short durations, suitable for radiography of systems in a state of rapid change. This is particularly applicable to the study of detonations and substances undergoing the effects of explosive or other sources of shock waves.

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