Kinetics of Azide Attack on Organonitriles Coordinated to Pentaamminecobalt(III)

J. H. HALL, R. LOPEZ DE LA VEGA and W. L. PURCELL*

Department of Chemistry, University of Miami, Coral Gables, Fla. 33124, U.S.A.

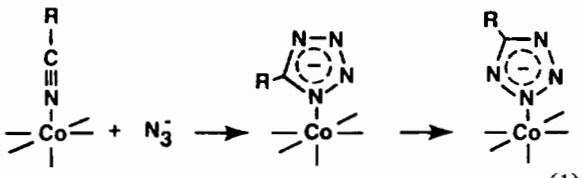
Received November 7, 1984

Abstract

Four new 5-substituted tetrazole complexes of pentaamminecobalt(III) have been synthesized. The N-1 bonded complexes of 5-(*p*-methylphenyl)tetrazole, 5-(*p*-chlorophenyl)tetrazole, 5-(*p*-nitrophenyl)-tetrazole and the N-2 bonded complex of 5-(*m*-formylphenyl)tetrazole. Kinetic studies of the complex formation reaction, wherein azide ion attacks coordinated organonitrile ligands, have been shown to follow a second order rate law, first order in nitrile complex and azide. Rate constants and activation parameters have been determined for five organonitrile complexes and a Hammett type correlation has been established for the formation reaction described by the equation $\log k = 2.42\sigma - 2.44$ at 25 °C and ionic strength 1.0 M. Two mechanisms are proposed for complex formation which are consistent with our observations.

Introduction

Metal coordination of organonitriles is known to be a very effective method of enhancing their susceptibility toward nucleophilic attack at the nitrile carbon [1, 2]. Various transition metals and nucleophiles have been utilized but the system which has been subjected to the most detailed analysis has been hydroxide attack on organonitriles coordinated to pentaamminecobalt(III) [3–6]. The mechanism of that reaction has been examined for a variety of organonitrile complexes, and a linear free energy relation has been established for aromatic nitrile complexes [6]. More recently, azide attack on coordinated organonitriles has been found to occur under surprisingly mild conditions (25 °C, 15 min, aqueous media) yielding the N-1 bonded tetrazole complexes [7]. These complexes convert over to the N-2 bonded form in a very interesting linkage isomerization reaction as shown in eqn. (1) below [8].



(1)

The majority of studies on linkage isomerization reactions have concentrated on the nitrito-to-nitro interconversion [9, 10]. Extensive investigations with various metals and solvents and their kinetic effects are reported in the literature [11–13]. The tetrazole linkage isomerization reaction now affords us the opportunity to explore how changes in the properties of the isomerizing ligand (*e.g.*, electronic and steric factors) affect the mechanism of interconversion. For this reason, as well as the general utility tetrazoles have enjoyed [14], it would be quite beneficial to synthesize a varied assortment of N-1 bonded tetrazolato complexes and, at the same time, study the mechanism of their formation.

In the present paper the mechanism of azide attack on nitrile complexes will be examined. Identification of the attacking nucleophile(s) will be made from variable pH kinetic studies. The rate of azide attack on various substituted benzonitrile complexes will be measured to establish the operation (or lack thereof) of a linear free energy relationship (LFER). Comparisons and contrasts to the hydroxide attack reaction will be made. Beside the mechanistic information which can be gained from a LFER, rates of azide attack on other organonitrile complexes of pentaamminecobalt(III) can be predicted and, thus, lead to more efficient syntheses of N-1 bonded tetrazolato complexes while minimizing formation of the N-2 bonded isomer.

Experimental

All chemicals were reagent grade unless otherwise specified. Solutions were prepared using house supplied distilled water which was passed through a

*Author to whom correspondence should be addressed.

0020-1693/85/$3.30

mixed bed ion exchange resin prior to use. Standard sodium hydroxide was prepared by dilution of stock solutions made from Baker analytical concentrates (J. T. Baker Chemical Co.). Sodium azide solutions were standardized using the method of Arnold [15]. Sodium perchlorate solutions were prepared and standardized as described previously [16].

Ultraviolet–visible spectra were obtained using a Cary Model 17 spectrophotometer. pH measurements were made with a Radiometer-Copenhagen Model 26 pH meter equipped with a glass-calomel combination electrode utilizing saturated NaCl in place of the usual KCl to avoid $KClO_4$ precipitation. Infrared spectral data were obtained from a Perkin-Elmer Model 599 spectrometer using KI pellets*.

The kinetics of azide attack were followed at the wavelength where isosbestic behavior was observed for the tetrazole linkage isomerization reaction. This ensured that the observed spectral changes were entirely due to the nucleophilic attack reaction (step one in eqn. (1)). The wavelengths (in nm) used for the various organonitrile ligands were as follows: *p*-tolunitrile, 481; benzonitrile 479; *p*-chlorobenzonitrile, 484; *m*-formylbenzonitrile, 483; *p*-nitrobenzonitrile, 483. Absorbance *versus* time traces were made on the Cary 17 spectrophotometer in the majority of cases although some of the faster reactions were followed on a stopped-flow temperature-jump (SFTJ) apparatus operating in the stopped-flow mode. The SFTJ was constructed by Dr. Jon Simplicio based upon the design of Erman and Hammes [17]. The Cary 17 and the SFTJ were each equipped with a Forma Scientific Model 2095 refrigerated-heating water bath and circulator which controlled the temperature to better than ±0.5 °C. Ionic strength of solutions was adjusted to 1.00 M using standard sodium perchlorate solutions. The pH of the solutions was controlled using acetic acid/acetate buffers. Kinetic studies were done under pseudo-first-order conditions using at least a ten-fold molar ratio of azide to complex. Complex concentrations were normally 1×10^{-3} M while azide concentrations were varied from 2×10^{-2} M to 0.50 M. Rate constants were extracted from absorbance *vs.* time traces as described previously [16].

All ionic azide concentrations were calculated from the experimentally measured pH values for the solutions and the total azide ($HN_3 + N_3^-$) concentration. The pK_a's appropriate for the 1.0 M ionic strength solutions employed in these studies were as follows: 15 °C, 4.51; 25 °C, 4.44; 35 °C, 4.39; 45 °C, 4.33 [18].

*Elemental analyses were performed by Atlantic Microlabs Inc., Atlanta, Ga., U.S.A.

Synthesis

Perchlorate salts of organonitrile complexes were prepared by either of two methods: from trifluoromethanesulfonatopentaamminecobalt(III) trifluoromethanesulfonate ('triflate') using the procedure in reference 19, or from azidopentaamminecobalt(III) perchlorate using the procedure in reference 20. Purity of the organonitrile complexes was established by comparison of visible spectral properties with reported literature values when available (the complex of *p*-chlorobenzonitrile represents the only new nitrile complex in this study) [3, 6, 16, 20, 21].

p-Chlorobenzonitrilepentaamminecobalt(III) Perchlorate, $[(NH_3)_5Co(p\text{-}ClC_6H_4CN)](ClO_4)_3 \cdot 1.3H_2O$

This complex was prepared from triflate with acetone as the solvent [19]. The *p*-chlorobenzonitrile ligand was used as received (Aldrich Chemical Co.) without further purification. *Anal.*, calcd. for $CoC_7H_{19}N_6Cl_4O_{12} \cdot 1.3H_2O$: C, 13.93; H, 3.61; N, 13.93. Found: C, 13.97; H, 3.61; N, 13.96. Infrared: 2290 cm^{-1} (nitrile stretch). Visible: $\lambda_{max(\epsilon)}$, 468 nm (79.5 M^{-1} cm^{-1}).

5-(p-Nitrophenyl)Tetrazolatopentaamminecobalt-(III) Iodide, N-1 Bonded, $[(NH_3)_5Co(p\text{-}NO_2C_6H_4CN_4)]I_2 \cdot 1.5H_2O$

0.5 g of *p*-nitrobenzonitrilepentaamminecobalt-(III) perchlorate was dissolved in a minimum of pH 5.5 acetate buffer (50 ml in this case). The solution was filtered and 10 ml of 6 M sodium azide (adjusted to pH 6 with acetate buffer) was added with stirring. Caution: operation near or below the pK_a of hydrazoic acid (4.7) should be avoided due to the formatin of toxic HN_3. The reaction was allowed to proceed for 30 s. The mixture was placed in an ice bath and precipitation was induced by dropwise addition of cold, saturated sodium iodide solution. After filtration the solid product was recrystallized by dissolving in a minimum amount of water and precipitating once more with cold sodium iodide solution. It is imperative that the precipitation and recrystallization be done as rapidly as possible in order to minimize the formation of the N-2 bonded isomer. *Anal.*, calcd. for $CoC_7H_{19}N_{10}O_2I_2 \cdot 1.5H_2O$: C, 13.70; H, 3.61; N, 22.77. Found: C, 13.74; H, 3.62; N, 22.74. Infrared: 1260 cm^{-1} (N–N=N, ring). Visible: 472 nm (74 M^{-1} cm^{-1}).

5-(p-Chlorophenyl)Tetrazolatopentaammine-cobalt(III) Iodide, N-1 Bonded, $[(NH_3)_5Co(p\text{-}ClC_6H_4CN_4)]I_2$

The same procedure as above was employed with the *p*-chlorobenzonitrilepentaamminecobalt(III) perchlorate complex except the reaction with azide was allowed to proceed for 6 min. *Anal.*, calcd. for

$CoC_7H_{19}N_9ClI_2$: C, 14.56; H, 3.32; N, 21.83. Found: C, 14.48; H, 3.37; N, 21.74. Infrared: 1250 cm^{-1} (N–N=N, ring). Visible: 473 nm (64.6 M^{-1} cm^{-1}).

5-(p-Methylphenyl)Tetrazolatopentaammine-cobalt(III) Iodide, N-1 Bonded, $[(NH_3)_5Co(p\text{-}CH_3C_6H_4CN_4)]I_2 \cdot 0.5H_2O$

The same procedure as above was again followed, starting with *p*-tolunitrilepentaamminecobalt(III) perchlorate and allowing the reaction with azide to proceed for 60 min. *Anal.*, calcd. for $CoC_8H_{22}N_9I_2 \cdot 0.5H_2O$: C, 16.97; H, 4.09; N, 22.27. Found: C, 16.46; H, 4.11; N, 21.93. Infrared: 1250 cm^{-1} (N–N=N, ring). Visible: 474 nm (63 M^{-1} cm^{-1}).

5-(m-Formylphenyl)Tetrazolatopentaammine-cobalt(III) Perchlorate, N-2 Bonded, $[(NH_3)_5Co(m\text{-}CHOC_6H_4CN_4)](ClO_4)_2 \cdot H_2O$

Starting with *m*-formylbenzonitrilepentaammine-cobalt(III) perchlorate, the above procedure was used with a reaction time with azide of 5 min. The N-1 bonded isomer could not be rapidly isolated due to its high solubility. The mixture was passed through a Dowex 1X-8 50-100 mesh anion exchange column in the chloride form. The resulting solution was then freeze-dried and the resulting yellow powder was recrystallized as the perchlorate salt by dissolving the chloride in a minimum of water and adding sodium perchlorate. *Anal.*, calcd. for $CoC_8H_{20}N_9O_9Cl_2 \cdot H_2O$: C, 17.99; H, 4.15; N, 23.60. Found: C, 17.98; H, 4.15; N, 23.52. Visible: 464 nm (70 M^{-1} cm^{-1}).

Results and Discussion

Synthesis and Characterization of New Complexes

The *p*-chlorobenzonitrilepentaamminecobalt(III) perchlorate was assigned the nitrile bonded configuration due to the shift in the nitrile stretching frequency from 2250 cm^{-1} for the free ligand to 2290 cm^{-1} for the complex. Such shifts are characteristic of nitriles upon coordination to pentaammine-cobalt(III) [20]. The other nitrile complexes used in the tetrazole complex syntheses were known to be nitrile bonded from previous studies [3, 6, 16, 20, 21].

In general, to prepare N-1 bonded tetrazolato complexes, azide attack is allowed to proceed for 6 to 10 half-lives. This ensures greater than 99% conversion of the nitrile complex to N-1 bonded tetrazolato complex while minimizing the amount of N-2 bonded isomer formed by subsequent linkage isomerization. Repeated recrystallizations are often necessary in order to eliminate ionic azide which is precipitated along with the iodide salt of the product complex. The number of recrystallizations required vary between 2 and 4 in most cases, but should be minimized due to linkage isomerization. Elimination of azide impurity can be verified by infrared analysis.

Tetrazole ring formation from the coordinated nitrile via azide attack was evidenced by the disappearance of the nitrile stretching absorption and appearance of tetrazole ring deformation bands between 900 and 1100 cm^{-1} in the infrared [22]. N-1 bonding was indicated by a band around 1250 cm^{-1} which has been assigned to the ring unsubstituted N–N=N bend [22, 23]. The λ_{max} at 470–474 nm in the visible region is also consistent with N-1 bonding, N-2 bonded complexes exhibiting a λ_{max} at 462–464 nm [24]. Finally, the observation of a slow second reaction step following azide attack (linkage isomerization) indicates initial N-1 bonding.

The visible peak maxima discussed above indicate that N-1 bonded tetrazolate ligands are weaker than their N-2 bonded analogs, *i.e.*, they have smaller Dq values. Since the MINDO-3 calculations of Nelson et al. [25] indicate that the N-1 nitrogen of a tetrazolate anion is more nucleophilic than nitrogen N-2, this result might seem rather surprising. However, numerous examples have appeared in the literature of steric hindrance affecting ligand crystal field parameters [26]. We believe that the tetrazolate complex linkage isomers represent still another example of such steric effects. While the second spin allowed d–d band of the 5-phenyltetrazolato complexes of cobalt(III) is obscured by the onset of aromatic ring absorptions in the ultraviolet, the band is seen in the N-1 and N-2 bonded 5-methyltetrazolato complexes [7, 24] permitting a calculation of both Dq and B. Such a calculation yields (assuming pure octahedral symmetry for both isomers since both spin allowed transitions are unsplit) values of 2203 and 619 cm^{-1} for Dq and B in the N-1 bonded isomer and 2257 and 611 cm^{-1} for Dq and B in the N-2 bonded complex. While the differences in the Racah parameter for the two isomers is too small to consider as significant, the Dq values clearly show the stronger ligand field for the ligand when N-2 bonded, contrary to the expectation based upon nucleophilicity but consistent with steric congestion between the ring 5-substituent and the ammines on cobalt(III). Note that in the above calculation for N-1 bonded 5-methyltetrazolatopentaamminecobalt-(III), peak maxima for the perchlorate salt of the complex were used (475 and 339 nm) rather than those reported for the iodide in ref. 7.

The N-1 bonded 5-(*m*-formylphenyl)tetrazolato-pentaamminecobalt(III) complex could not be isolated due to its exceedingly high solubility in water as compared to the precursor nitrile complex. However, spectral evidence for its initial formation from the nitrile was seen in the visible region of the spectrum. Repeated spectral scans during the azide attack

reaction showed a rapid shift in the λ_{max} from 468 to 474 nm (consistent with N-1 bonded tetrazolato complex formation from the nitrile) followed by a slower shift in the λ_{max} to 464 nm (formation of the N-2 isomer). The N-2 isomer was isolated as described in the experimental and the bonding assigned both on the basis of the λ_{max} and the absence of the N–N=N bend at 1250 cm^{-1} in the infrared.

Kinetics of Azide Attack

Table I shows the experimental rates of azide attack on benzonitrilepentaamminecobalt(III) as a function of ionic azide concentration, $[N_3^-]$, keeping the total azide concentration, $[HN_3 + N_3^-]$, constant. The observed rate constants are seen to vary linearly with $[N_3^-]$ and clearly are not dependent upon the concentration of HN_3. Hence, the attacking nucleophile in the 5-phenyltetrazolato complex formation reaction is ionic azide rather than hydrazoic acid. We have assumed that HN_3 is a noncompetitive nucleophile in the azide attack reactions of the other aromatic nitrile complexes reported in this study.

TABLE I. Rates of Azide Attack on Benzonitrilepentaamminecobalt(III) at Varying pH While Keeping Total Azide Concentration Constant.[a]

$[HN_3 + N_3^-]$	pH	$[HN_3]$	$[N_3^-]$	k_{obs} (sec^{-1})
0.101	4.00	0.074	0.0269	0.000153
0.101	4.20	0.064	0.0369	0.000232
0.101	4.45	0.050	0.0511	0.000291
0.101	5.10	0.018	0.0829	0.000428
0.101	5.50	0.008	0.0929	0.000450

[a]All concentrations are in mol/liter. Least squares analysis of k_{obs} *versus* $[N_3^-]$ resulted in a slope of 0.0044 and a y-intercept of 6×10^{-5}. The correlation coefficient was 0.993.

For all the complexes studied, the $\log(A_t - A_\infty)$ *vs.* time plots were linear for at least five half-lives. The k_{obs} *vs.* $[N_3^-]$ plots were linear through a ten fold increase in the azide concentration and the intercepts of the plots were zero within experimental error. These results are consistent with a mixed second order rate equation, first order in the concentrations of azide and nitrile complex, eqn. (2). The analogous two term rate law is observed for hydroxide as the attacking nucleophile with nitrile complexes [3, 6, 16].

$$\text{Rate} = k[N_3^-][\text{nitrile complex}] \quad (2)$$

A summary of the experimental rate data for all five complexes is shown in Table II and the activation parameters are given in Table III. Applying the Hammett Equation to the rate data, the line shown in Fig. 1 having an 'excellent' fit is obtained. The linear free energy relationship is described by eqn. (3) below.

$$\log(k) = 2.42\sigma - 2.44 \quad (3)$$

The ρ value of 2.42 is more positive than that obtained for the base hydrolysis reaction of aromatic nitrile complexes [6] where $\rho = 1.93$, indicating that the azide attack reaction is more sensitive to electronic effects than the corresponding hydroxide attack. The positive enthalpy of activation is of the same order of magnitude as the hydroxide attack process. These similarities to the much studied base hydrolysis reaction of coordinated nitriles implicates the nitrile carbon as the site of nucleophilic attack for azide as well as hydroxide. The entropy of activation is negative, consistent with a bimolecular reaction forming only one product.

Two mechanisms have been proposed for tetrazole formation from nitriles and azide ion [27, 28].

TABLE II. Summary of Rate Data of Azide Attack on Coordinated Organonitriles.

Nitrile	Temp. (°C)	k (l/mol sec)[a]
p-tolunitrile	25	0.0015
	35	0.0036
	45	0.0084
benzonitrile	15	0.0012
	25	0.0044
	35	0.0107
p-chlorobenzonitrile	15	0.0040
	25	0.0099
	35	0.0211
m-formylbenzonitrile	15	0.0107
	25	0.025
	35	0.065
p-nitrobenzonitrile	15	0.170
	25	0.324
	35	0.770

[a]Ionic strength, 1.0 ($NaClO_4$).

TABLE III. Activation Parameters for the Reaction of Azide with Organonitrile Complexes of Pentaamminecobalt(III).

nitrile	$\Delta H^\ddagger$	$\Delta S^\ddagger$
p-tolunitrile	15.7 ± 0.1	−18.7 ± 1
benzonitrile	18.8 ± 2	−6.4 ± 6
p-chlorobenzonitrile	14.1 ± 0.5	−20.4 ± 2
m-formylbenzonitrile	15.3 ± 0.8	−14 ± 3
p-nitrobenzonitrile	12.6 ± 1.4	−18 ± 5

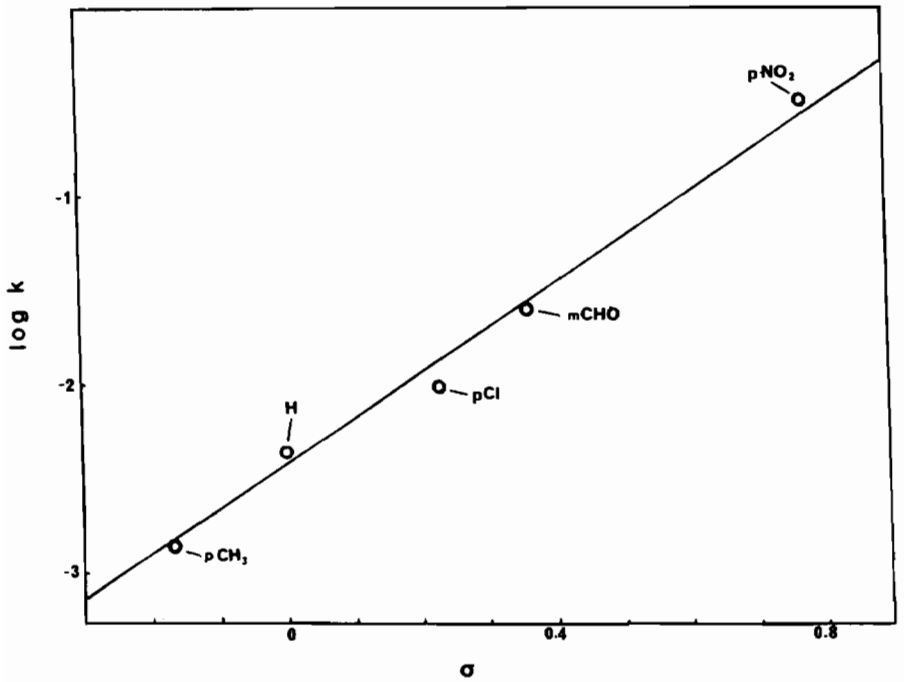
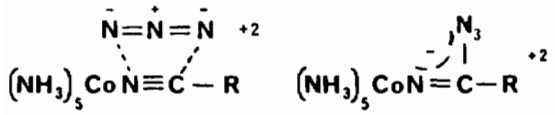


Fig. 1. Hammett plot of azide attack rate constants for aromatic nitriles coordinated to the pentaamminecobalt(III) moiety at 25 °C and ionic strength 1.0 M. Correlation coefficient, R = 0.996.

Either would be consistent with our observations. One mechanism involves a concerted 1,3 dipolar cycloaddition across the nitrile bond resulting in tetrazole formation as depicted in structure **I** below. However, it should be noted that the concerted attack mechanism does not require simultaneous attack at nitrile carbon and nitrogen. The second mechanism would involve initial azide attack on the nitrile carbon forming an imidoyl azide intermediate (structure **II**) which then rapidly cyclizes to form our product.



I II

While our study has not precisely defined the transition state structure for this nucleophilic attack reaction, the discovery of a second nucleophile which obeys a Hammett type correlation and the predictive qualities of that correlation (eqn. (3)) suggests that still more nucleophiles may be found that are capable of attacking coordinated nitrile functions under mild conditions. Equation (3) also permits the determination of ideal reaction times for the preparation and isolation of a variety of N-1 bonded 5-substituted-tetrazolato complexes of pentaamminecobalt(III) with a minimum of contamination from the N-2 bonded linkage isomer.

References

1 B. N. Storhoff and H. C. Lewis, *Coord. Chem. Rev., 23,* 1 (1977).
2 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry, 4th edn.', Wiley-Interscience, New York, 1980, p. 142.
3 D. Pinnell, G. B. Wright and R. B. Jordan, *J. Am. Chem. Soc., 94,* 6104 (1972).
4 D. A. Buckingham, F. R. Keene and A. M. Sargeson, *J. Am. Chem. Soc., 95,* 5649 (1973).
5 R. J. Balahura and W. L. Purcell, *Inorg. Chem., 18,* 937 (1979).
6 R. Lopez de la Vega, W. R. Ellis and W. L. Purcell, *Inorg. Chim. Acta, 68,* 97 (1983).
7 W. R. Ellis and W. L. Purcell, *Inorg. Chem., 21,* 834 (1982).
8 W. L. Purcell, *Inorg. Chem., 22,* 1205 (1983).
9 R. G. Pearson, P. N. Henry, T. G. Bergmann and F. Basolo, *J. Am. Chem. Soc., 76,* 5920 (1954).
10 R. K. Murmann and H. Taube, *J. Am. Chem. Soc., 78,* 4886 (1956).
11 F. Basolo and G. S. Hammaker, *Inorg. Chem., 1,* 1 (1962).
12 W. G. Jackson, G. A. Lawrence, P. A. Lay and A. M. Sargeson, *Inorg. Chem., 19,* 904 (1980).
13 W. G. Jackson, G. A. Lawrence, P. A. Lay and A. M. Sargeson, *Aust. J. Chem., 35,* 1561 (1982).
14 H. Singh, A. S. Chawla, V. K. Kapoor, D. Paul and R. K. Malhotra, *Prog. Med. Chem., 17,* 215 (1980).
15 J. W. Arnold, *Ind. Eng. Chem., Anal. Ed., 17,* 215 (1945).
16 R. J. Balahura, P. Cock and W. L. Purcell, *J. Am. Chem. Soc., 96,* 2739 (1974).
17 J. E. Erman and G. G. Hammes, *Rev. Sci. Instr., 37,* 746 (1966).
18 S. Castillo-Blum and A. G. Sykes, *Inorg. Chem., 23,* 1049 (1984).

19 N. E. Dixon, W. G. Jackson, M. J. Lancaster, G. A. Lawrence and A. M. Sargeson, *Inorg. Chem., 20,* 470 (1981).
20 R. J. Balahura, *Can. J. Chem., 52,* 1767 (1974).
21 A. Zanella, private communication.
22 E. Lieber and T. Enkoji, *J. Org. Chem., 26,* 1049 (1961).
23 E. Lieber, C. N. Rao, C. N. Pillai, J. Ramachandran and R. D. Hites, *Can. J. Chem., 36,* 801 (1958).
24 R. J. Balahura, W. L. Purcell, M. E. Victoriano, M. L. Lieberman, V. M. Loyola, W. Fleming and J. W. Fronabarger, *Inorg. Chem., 22,* 3602 (1983).
25 N. E. Takach, E. M. Holt, N. W. Alcock, R. A. Henry and J. H. Nelson, *J. Am. Chem. Soc., 102,* 2968 (1980).
26 (a) R. S. Drago, D. W. Meek, M. D. Joesten and L. LaRoche, *Inorg. Chem., 2,* 124 (1963);
(b) A. B. P. Lever, J. Lewis and R. S. Nyholm, *J. Chem. Soc.,* 4761 (1964);
(c) A. B. P. Lever, S. M. Nelson and T. M. Shepherd, *Inorg. Chem., 4,* 810 (1965);
(d) A. B. P. Lever and S. M. Nelson, *J. Chem. Soc. A:,* 859 (1966);
(e) M. Parris and N. F. Feiner, *Inorg. Nucl. Chem. Lett., 3,* 337 (1967).
27 P. K. Kadaba, *J. Org. Chem., 41,* 1073 (1976).
28 R. Husigen, in E. A. Padwa (ed.), '1,3 Dipolar Cycloaddition Chemistry', Wiley-Interscience, New York, 1984, Chap. 1.