Contribution from the Department of Chemistry,
The University of Texas at Arlington, Arlington, Texas 76019

Substituent Effect of Chelated Cobalt. 4. A ^{19}F NMR Study of *p*- and *m*-Fluorophenyl(ligand)cobaloximes[1,2]

KENNETH L. BROWN* and LI-YOUNG LU

Received April 17, 1981

^{19}F NMR chemical shifts for *m*- and *p*-fluorophenyl(ligand)cobaloximes with 21 different axial ligands are reported along with these for the cationic, monoprotonated cobaloximes in three acids. These chemical shifts have been correlated with those of other monosubstituted fluorobenzenes via the Taft dual substituent parameter equation to provide values of the inductive and resonance substituent parameters for these cobaloxime-chelated cobalt centers. The results show pronounced π-electron donation from cobalt to the covalently bound organic ligand which varies substantially with the nature of the cobalt center. A linear $\sigma_R^\circ-\sigma_I$ relationship has been found which includes all 24 data points in an excellent correlation. These results are compared to those for the ^{19}F NMR chemical shifts of *m*- and *p*-fluorobenzyl(ligand)cobaloximes from the literature to show that substantial hyperconjugation must occur in the latter compounds.

Introduction

In recent studies,[1,3,4] we have attempted to assess the substituent effect of chelated cobalt centers on covalently bound organic ligands using the bis(dimethylglyoximato) or cobaloxime system which has been widely used as a model system for the biochemically relevant cobalamin chelates. A quantitative understanding of such effects should provide an experimental, rather than theoretical, basis for understanding the carbon–cobalt bond as well as provide substantial predictive ability regarding reactivities of functional groups on organic ligands covalently bound to cobalt. Both of these goals will undoubtedly be important in an eventual understanding of the enzymatic reactions catalyzed by coenzyme-B_{12}-requiring enzymes.

In some of our earlier work,[3,4] we used the formalism of the Taft dual substituent parameter equation[5] (eq 1) in which P^i

$$P^i = \sigma_I\rho_I^i + \sigma_R\rho_R^i \quad (1)$$

is some correlatable property of a substituted-benzene derivative (ratio of rate or equilibrium constants for substituted and unsubstituted compounds or NMR shifts of substituted relative to unsubstituted compounds), σ_I and σ_R are the inductive and delocalization substituent parameters, respectively, ρ_I and ρ_R are the susceptibilities of the correlatable parameter in question to inductive and resonance effects, respectively, and the superscript i refers to the substitution position (i.e. meta or para). Application of this formalism to the rate constants for saponification of the methyl esters of (*m*-carboxyphenyl)- and (*p*-carboxyphenyl)cobaloximes[3] showed that very little, if any, resonance donation of the benzoic acid type[5] from cobalt to the bound aryl ligand occurs when the trans axial ligand is water or hydroxide ion. Subsequent studies[4] of the effect of various axial ligands on these saponifications seemed to show that substantial resonance donation of this type could occur with certain π bonding trans axial ligands (such as CN^- and NO_2^-). However, further studies of the inductive effect of cobaloxime-chelated cobalt centers[1] revealed certain inconsistencies in the earlier work and have raised the possibility that the mechanism of saponification of the cobaloxime-substituted methyl benzoates may not be the same as that of the basis set compounds used to determine the ρ values used in the correlation with eq 1. Consequently, it is of interest to determine the extent of resonance interaction of such chelated cobalt centers with bound organic groups and particularly the effect of axial ligands thereon in a system in which such mechanistic complications cannot occur.

Hill and co-workers[6] previously reported the ^{19}F NMR shifts of *m*- and *p*-$FC_6H_4Co[(DO)(DOH)pn]X$ (various X) and concluded that substantial resonance interaction of the cobalt center with the covalently bound aryl group occurs when the substituent is in the para position. Our preliminary analysis of this data via eq 1[3] agreed with this conclusion and further showed a substantial effect of the nature of the trans axial ligand on the resonance substituent constant, σ_R. Because of the extreme sensitivity of ^{19}F NMR chemical shifts of substituted fluorobenzenes to resonance effects[3,5] and the availability of large amounts of data on which to base eq 1,[7,8] this is an ideal system for studying the resonance effects of chelated cobalt centers. We consequently undertook an ^{19}F NMR study of fluorophenylcobaloximes which is the subject of this report.

Experimental Section

Materials. Monofluorobenzene, triphenylphosphine, EDTA, potassium nitrate, potassium chloride, potassium cyanide, sodium perchlorate, sodium thiocyanate, sodium and potassium hydroxide, methanol, chloroform, Me_2SO, deuterated solvents, and inorganic acids were obtained in the highest purity commercially available and used without further purification.

m- and *p*-bromofluorobenzene were redistilled and stored over type 4A molecular sieve. Substituted pyridines were recrystallized or redistilled under argon. Primary amines and alkyl sulfides were redistilled and stored under argon. Thiols were redistilled under argon daily. Tetrahydrofuran was dried over KOH, refluxed overnight over $LiAlH_4$, and distilled from excess $LiAlH_4$ immediately before use. Stock solutions of fluorophenylcobaloximes were stored cold in the dark and used for several successive days. Stock solutions of thiols and potassium cyanide were made fresh daily.

***m*-$FC_6H_4Co(D_2H_2)OH_2$** was prepared essentially by the procedure of Schrauzer.[9] *m*-Fluorophenylmagnesium bromide (0.06 mol) was prepared in freshly distilled tetrahydrofuran under a continuous argon purge from *m*-fluorobromobenzene and a slight excess of magnesium. After the spontaneous reaction had subsided, the reaction mixture was refluxed for 30 min. The Grignard reagent was then added

(1) Part 3, see: Brown, K. L.; Zahonyi-Budo, E. *Inorg. Chem.* **1981**, *20*, 1264–1269.
(2) Abbreviations: $RCo(D_2H_2)L$ = organo(ligand)bis(dimethylglyoximato)cobalt(III) = organo(ligand)cobaloxime; RCo[(DO)(DOH)pn]X = organo(ligand)[(biacetyl oxime imino)(biacetyl oximato)iminopropane-1,3]cobalt.
(3) Brown, K. L.; Awtrey, A. W.; LeGates, R. *J. Am. Chem. Soc.* **1978**, *100*, 823–828.
(4) Brown, K. L.; Awtrey, A. W. *J. Organomet. Chem.* **1980**, *195*, 113–122.
(5) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys.-Org. Chem.* **1973**, *10*, 1–80.
(6) Hill, H. A. O.; Morallee, K. G.; Cernivez, F.; Pellizer, G. *J. Am. Chem. Soc.* **1972**, *94*, 277–279.
(7) Taft, R. W.; Price, E.; Fox, I. R.; Lewis, I. C.; Anderson, K. K.; Davis, G. T. *J. Am. Chem. Soc.* **1963**, *85*, 709–724.
(8) Taft, R. W.; Price, E.; Fox, I. R.; Lewis, I. C.; Anderson, K. K.; Davis, G. T. *J. Am. Chem. Soc.* **1963**, *85*, 3146–3156.
(9) Schrauzer, G. N. *Inorg. Synth.* **1968**, *11*, 61–70.

0020-1669/81/1320-4178$01.25/0

dropwise to a slurry of 0.01 mol of chloroaquocobaloxime[10] in 75 mL of freshly distilled tetrahydrofuran under a continuous argon purge at 0 °C. After the addition was complete, the reaction mixture was warmed to room temperature and then refluxed for 15 min. The reaction mixture was hydrolyzed by pouring into 100 mL of ice-cold 10% HCl and then neutralized with 0.1 M dibasic potassium phosphate. The resulting mixture was extracted several times with petroleum ether to remove bis(3-fluorobiphenyl) and then cooled and filtered. The solid was washed with water, ethanol, and ether, and dried and recrystallized from methanol–water; yield 64%. Anal. Calcd for $CoC_{14}H_{20}N_4O_5F \cdot {}^1/_2CH_3OH$ (detected by ^1H NMR): C, 41.63; H, 5.30; N, 13.40; F, 4.54. Found: C, 41.52; H, 5.53; N, 13.24; F, 4.49. NMR ($CDCl_3$–methanol-d_4): δ_{Me_4Si} 2.15 (S, 12 H), 6.05–7.33 (m, 3.88 H).

***p*-$FC_6H_4Co(D_2H_2)OH_2$** was prepared similarly from chloroaquocobaloxime and a six-fold excess of *p*-fluorophenylmagnesium bromide in tetrahydrofuran; yield 78%. Anal.: C, H, N, F. NMR ($CDCl_3$–methanol-d_4): δ_{Me_4Si} 2.16 (S, 12 H), 6.15–7.11 (m, 4.05 H).

Mercaptoacetic acid was methylated by the procedure of Schmelka and Spoerri[11] using dimethyl sulfate in 51% yield.[1] Methyl *S*-methylmercaptoacetate was obtained by esterification with methanol[12] in 41% yield.[1]

Methods. All work with arylcobaloximes was performed in dim light, and solutions were protected with aluminum foil. Glass-distilled, deionized water was used when needed. EDTA (10^{-4} M) was used to retard air oxidation of thiolate anions. For work with anionic ligands, ionic strength was maintained at 1.0 M with KCl, KNO_3, or $NaClO_4$.

Apparent equilibrium constants, K_f^{app}, for formation of fluorophenylcobaloxime adducts (eq 2 and 3) from various axial ligands

$$FC_6H_4Co(D_2H_2)OH_2 + L \rightleftarrows FC_6H_4Co(D_2H_2)L \quad (2)$$

$$K_f = [FC_6H_4Co(D_2H_2)L]/[FC_6H_4Co(D_2H_2)OH_2][L] \quad (3)$$

and protonation constants, K_p, for formation of cationic organocobaloximes by equatorial protonation of the oxime oxygens (eq 4 and 5) were determined spectrophotometrically at room temperature

$$FC_6H_4Co(D_2H_2)OH_2 + AH \rightleftarrows FC_6H_4Co(D_2H_3)OH_2^+ + A^- \quad (4)$$

$$K_p = [FC_6H_4Co(D_2H_3)OH_2^+][A^-]/[FC_6H_4Co(D_2H_2)OH_2][AH] \quad (5)$$

(25 ± 1 °C) on a Cary 14 or Cary 219 spectrophotometer by the method previously described.[13] For anionic ligands, ionic strength was maintained at 1.0 M with KCl, KNO_3, or $NaClO_4$.

Proton NMR measurements were made on a Varian T-60 NMR spectrometer. ^{19}F NMR measurements were made either on a Bruker WH-90 Fourier transform NMR spectrometer operating at 84.660 MHz at a sweep width of 1000 Hz or on a Bruker WP-200 Fourier transform NMR spectrometer operating at 188.28 MHz at a sweep width of 2500–8000 Hz at 27 ± 2 °C. Samples (generally 0.01 M or less in fluorophenylcobaloxime) were prepared in $CHCl_3$, Me_2SO, or methanol, and the solvents were made 10% (v/v) in Me_2SO-d_6 or methanol-d_4 or 50% (v/v) in $CDCl_3$ to provide an internal lock signal. All samples contained monofluorobenzene (in threefold molar excess over cobaloxime) as an internal reference and sufficient ligand (as calculated from the measured binding constants) to form the liganded complexes to >97%. The only exceptions were the samples of hydroxo derivatives of the cobaloximes where formation of a dianion via equatorial oxime-bridged proton dissociation[14,15] (i.e., $FC_6H_4Co(D_2H)OH^{2-}$) was detected spectrophotometrically. In this case, the sample was made 0.50 M in KOH which gave a solution of about 95% $FC_6H_4Co(D_2H_2)OH^-$ but only about 5% $FC_6H_4Co(D_2H)OH^{2-}$ by calculation from the measured equilibrium constants.

Table I. ρ values for the Correlation of ^{19}F NMR Chemical Shifts of Meta- and Para-Substituted Fluorobenzenes via Equation 1[a]

solvent	substituent position	ρ_I	ρ_R	n^b	f^c
methanol	meta	−5.69	0.12	9	0.12
	para	−8.91	−31.48	15	0.06
Me_2SO	meta	−5.13	0.59	9	0.14
	para	−8.37	−30.34	12	0.08
$CHCl_3$	meta	−5.16	−0.10	9	0.14
	para	−7.28	−30.22	15	0.07

[a] All data from Taft et al.;[7,8] 27 ± 2 °C. [b] Number of substituents included in the correlation. [c] f is the ratio of the root mean square of the deviations from the fit to the root mean square of the data values.[5] $0.1 < f < 0.2$ indicates an acceptable fit while $f < 0.1$ indicates an excellent fit.[16]

In keeping with the definition of Taft and co-workers,[7,8] whose data form the basis sets for correlations via eq 1, all chemical shifts are reported in parts per million from monofluorobenzene with positive values denoting resonances upfield from the reference and negative values denoting shifts downfield from the reference.

Results and Discussion

ρ values for use with eq 1 in the three solvents used in this study were calculated from the extensive data of Taft et al.[7,8] for the ^{19}F NMR chemical shifts of monosubstituted fluorobenzenes and the σ_I and σ_R° values listed by Ehrenson et al.[5] by least-squares fit to eq 1 and are listed in Table I. As seen in the table, all the correlations meet Topsom's criteria for good or excellent fits.[16] Furthermore, the susceptibility to resonance effects in the meta position (i.e., ρ_R^m) can be seen to be vanishingly small in all solvents as is to be expected from considerations of simple resonance theory. Finally, it can be seen that the agreement between the ρ values in all three solvents is excellent, indicating that the substituents chosen for use in the correlations show little, if any, effects of differential solvation in these three solvents.

Table II shows the ^{19}F NMR chemical shifts and formation constants of the hydroxocobaloximes and the equatorially protonated cobaloximes formed by reaction with three different inorganic acids. Compared with the species formed in methanol from the aquo complexes (probably the methanol adduct), the hydroxocobaloxime substituent can be seen to be substantially more inductively electron donating in agreement with our earlier measurements[3] and simple chemical intuition. The hydroxo species are only slightly less resonance donating than the neutral methanol adduct, however. Of more interest are the cationic cobaloximes formed in $HClO_4$, H_2SO_4, and HCl solutions. Crumbliss and co-workers[17,18] have shown that solid organocobaloximes obtained from HCl solutions are, in fact, inner-sphere complexes of chloride ion with equatorially protonated alkylcobaloximes, although the solution structure of these species is unknown. The data in Table II show that the monoprotonated solution species formed in perchloric and sulfuric acid solutions have essentially identical meta and para ^{19}F NMR shifts and produce cobalt centers which are slightly inductively electron withdrawing (i.e., $\sigma_I > 0$), as might be expected for cationic species, although they remain resonance donating. The species formed in HCl solution is clearly different from either of those having substantially different ^{19}F NMR shifts and producing a cobalt center which is ever so slightly inductively electron donating. It seems reasonable to conclude that the solution species formed in HCl is, in fact, an inner-sphere chloride complex, while the species formed in sulfuric and perchloric acids, whose conjugate bases are

(10) Ablov, A. V.; Samus, B. A.; Samus, N. M. *Russ. J. Inorg. Chem.* **1960**, *5*, 410–414.
(11) Schmelka, I. R.; Spoerri, P. E. *J. Org. Chem.* **1957**, *22*, 1721–1722.
(12) Mooradian, A.; Cavallito, C. J.; Bergman, A. J.; Lawson, E. J.; Sater, C. M. *J. Am. Chem. Soc.* **1949**, *71*, 3372–3374.
(13) Brown, K. L. *Inorg. Chim. Acta* **1979**, *37*, 1513–1519.
(14) Brown, K. L.; Chernoff, D.; Keljo, D. J.; Kallen, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 6697–6704.
(15) Brown, K. L.; Lyles, D.; Pencovici, M.; Kallen, R. G. *J. Am. Chem. Soc.* **1975**, *97*, 7338–7346.
(16) Topsom, R. T. *Prog. Phys.-Org. Chem.* **1976**, *12*, 1–20.
(17) Crumbliss, A. L.; Bowman, J. T.; Gaus, P. L.; McPhail, A. T. *J. Chem. Soc., Chem. Commun.* **1973**, 415–416.
(18) Crumbliss, A. L.; Gaus, P. L. *Inorg. Chem.* **1975**, *14*, 486–490.

Table II. ^{19}F NMR Chemical Shifts and Formation Constants of Hydroxofluorophenylcobaloximes and Protonated Fluorophenylcobaloximes[a]

substituent	acid	meta K_f or K_p, M^{-1}	meta δ[b]	para K_f or K_p, M^{-1}	para δ[b]	σ_I[c]	$\sigma_R°$[c]
$Co(D_2H_2)OH_2(CH_3OH)$			+0.980		+9.750	−0.178	−0.260
$Co(D_2H_2)OH^-$		42.5 ± 1.6[d]	+2.620	39.7 ± 0.8[e]	10.840	−0.465	−0.213
$Co(D_2H_3)OH_2^+$	$HClO_4$	21.7 ± 1.7	−0.535	30.8 ± 4.0	+8.088	+0.088	−0.282
$Co(D_2H_3)OH_2^+$	H_2SO_4	21.0 ± 0.6	−0.600	19.2 ± 1.0	+8.084	+0.099	−0.284
$Co(D_2H_3)Cl$	HCl	50.0 ± 1.5	0.000	33.7 ± 1.2	+8.622	−0.006	−0.272

[a] Formation constants and ^{19}F chemical shifts measured in methanol. [b] ^{19}F NMR chemical shifts in ppm from internal monofluorobenzene. Positive values indicate shifts upfield of the reference. [c] Calculated from the ^{19}F NMR shifts and eq 1 with use of the ρ values in Table I for methanol. [d] Shows evidence of further reaction with hydroxide ion to form the dianion m-$FC_6H_4Co(D_2H)OH^{2-}$, with $K_f = 0.46\ M^{-1}$ (ionic strength 3.8 M with $NaClO_4$). [e] Shows evidence of further reaction with hydroxide ion to form the dianion p-$FC_6H_4Co(D_2H)OH^{2-}$, with $K_f = 0.28\ M^{-1}$ (ionic strength 3.8 M with $NaClO_4$).

Table III. ^{19}F NMR Chemical Shifts and Formation Constants for Fluorophenyl(pyridine)cobaloximes[a]

axial ligand	pK_a^L[b]	meta K_f, M^{-1}	meta δ[c]	para K_f, M^{-1}	para δ[c]	σ_I[d]	$\sigma_R°$[d]
Me_2SO			1.860		10.270	−0.389	−0.231
4-cyanopyridine	2.24[e]	(5.44 ± 1.8) × 10	1.430	(5.52 ± 1.2) × 10	9.483	−0.305	−0.228
4-(carboxamido)pyridine	3.77[e]	(3.47 ± 0.6) × 10^2	1.550	(3.59 ± 0.4) × 10^2	9.560	−0.328	−0.225
4-(carboxamido)pyridine[f]	3.77[e]		1.115[f]		9.702[f]	−0.201	−0.252
pyridine	5.56[g]	(7.24 ± 0.58) × 10^2	1.660	(5.90 ± 0.28) × 10^2	8.750	−0.346	−0.193
4-methylpyridine	6.36[e]	(1.69 ± 0.09) × 10^3	1.745	(1.24 ± 0.06) × 10^3	[h]		
4-aminopyridine	9.40[e]	(3.89 ± 0.47) × 10^4	2.051	(1.01 ± 0.13) × 10^4	9.976	−0.424	−0.212

[a] Formation constants and ^{19}F chemical shifts measured in Me_2SO except as noted. [b] pK_a of the conjugate acid of the ligand in water; ionic strength 1.0 M; 25 °C. [c] ^{19}F NMR chemical shifts in ppm from internal monofluorobenzene. Positive values indicate shifts upfield of the reference. [d] Calculated from the ^{19}F NMR shifts and eq 1 with use of the ρ values in Table I for Me_2SO. [e] Reference 14. [f] ^{19}F NMR shifts measured in methanol. [g] Reference 3. [h] Insufficiently soluble.

Table IV. ^{19}F NMR Chemical Shifts and Formation Constants for Fluorophenyl(ligand)cobaloximes with Neutral Ligands[a]

axial ligand	pK_a^L[b]	meta K_f, M^{-1}	meta δ[c]	para K_f, M^{-1}	para δ[c]	σ_I[d]	$\sigma_R°$[d]
MeOH			0.980		9.750	−0.178	−0.260
glycine ethyl ester	7.86[e]	(2.02 ± 0.24) × 10^3	1.583	(2.05 ± 0.16) × 10^3	9.660	−0.283	−0.227
2,2-dimethoxyethylamine	8.86[f]	(2.35 ± 0.18) × 10^3	1.626	(1.99 ± 0.19) × 10^3	9.638	−0.291	−0.224
2-methoxyethylamine	9.68[f]	(3.64 ± 0.30) × 10^3	1.690	(2.35 ± 0.35) × 10^3	9.738	−0.302	−0.224
n-propylamine	10.80[f]	(4.03 ± 0.41) × 10^3	1.754	(2.76 ± 0.23) × 10^3	9.793	−0.313	−0.222
S-methyl-2-mercaptoethanol		6.78 ± 0.46	0.813	8.37 ± 0.17	9.044	−0.148	−0.245
methyl *S*-methylmercaptoacetate		0.92 ± 0.08	0.731	0.74 ± 0.17	9.154	−0.134	−0.253
triphenylphosphine[g]		(3.21 ± 0.41) × 10^2	0.608	(5.10 ± 0.08) × 10^2	9.653	−0.125	−0.289

[a] Formation constants and ^{19}F NMR chemical shifts measured in methanol except as noted. [b] pK_a of the conjugate acid of the ligand in water; ionic strength 1.0 M; 25 °C. [c] ^{19}F NMR chemical shifts in ppm from internal monofluorobenzene. Positive values indicate shifts upfield of the reference. [d] Calculated from the ^{19}F NMR chemical shifts and eq 1 with use of the ρ values in Table I for methanol. [e] Reference 1. [f] Reference 14. [g] All measurements in $CHCl_3$.

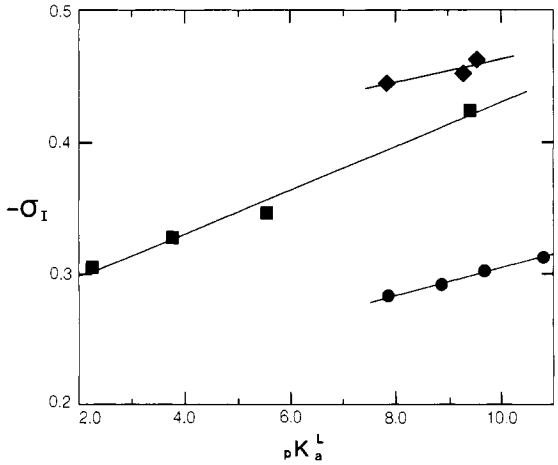


Figure 1. Plots of $-\sigma_I$ for $Co(D_2H_2)L$ vs. pK_a^L, the pK_a of the conjugate acid of the axial ligand: (●) L = RNH_2, slope = 0.0104 ± 0.0007, intercept = 0.200 ± 0.006; (■) L = 4-X-py, slope = 0.0166 ± 0.0016, intercept = 0.264 ± 0.009; (♦) L = RS^-, slope = 0.00853 ± 0.00386, intercept = 0.378 ± 0.034. The solid lines are least-squares fits.

much weaker nucleophiles, are cationic aquo complexes and, hence, may be recoverable as outer-sphere salts of the acid anions from such solutions.

Table III shows the ^{19}F NMR chemical shifts and calculated σ_I and $\sigma_R°$ values for the aquo complexes in Me_2SO (i.e., Me_2SO adducts) and for a series of 4-substituted pyridine adducts also in Me_2SO. Table IV shows these data for a series of primary amine and *S*-methyl sulfide adducts in methanol. As seen in these tables, the σ_I values show a regular increase in electron-donating ability of the cobalt center with increasing basicity of the amine or pyridine axial ligand. These excellent correlations of $-\sigma_I$ with axial ligand basicity for nitrogenous ligands are shown graphically in Figure 1. Such correlations have been obtained previously with σ_I values derived by correlation of the acidities of (carboxyethyl)(ligand)cobaloximes with those of other 2-substituted propionic acids[1] in water. Although the slopes of the present correlations (see legend to Figure 1) are in reasonably good agreement with those previously determined,[1] the intercepts are significantly different, those of the current correlations being about 0.18 higher than those of the earlier correlations. This reflects the fact that

Table V. ^{19}F NMR Chemical Shifts and Formation Constants for Fluorophenyl(ligand)cobaloximes with Anionic Ligands[a]

axial ligand	pK_a^{L} [b]	meta K_f, M^{-1}	meta δ[c]	para K_f, M^{-1}	para δ[c]	σ_I[d]	σ_R°[d]
methyl mercaptoacetate[e]	7.83[f]	$(1.72 \pm 0.3) \times 10^3$	2.510	$(1.49 \pm 0.40) \times 10^3$	10.333	−0.445	−0.202
methyl mercaptopropionate[e]	9.27[g]	$(1.86 \pm 0.26) \times 10^3$	2.553	$(2.11 \pm 0.54) \times 10^3$	10.457	−0.453	−0.204
2-mercaptoethanol[e]	9.51[f]	$(2.02 \pm 0.32) \times 10^3$	2.603	$(2.24 \pm 0.30) \times 10^3$	10.496	−0.462	−0.203
CN^- [h]	9.00[i]	$>7.5 \times 10^4$	2.549	$>6.7 \times 10^4$	9.949	−0.452	−0.188
Co-SCN^- [j]	0.85[j]	$(1.41 \pm 0.07) \times 10^2$ [k]	1.590	$(1.28 \pm 0.03) \times 10^2$ [k]	9.714	−0.284	−0.228
Co-NCS^- [j]	0.85[j]		1.928		9.894	−0.343	−0.217

[a] Formation constants and ^{19}F NMR chemical shifts measured in methanol. [b] pK_a of the conjugate acid of the ligand, in water; ionic strength 1.0 M; 25 °C. [c] ^{19}F NMR chemical shifts in ppm from internal monofluorobenzene. Positive values indicate shifts upfield of the reference. [d] Calculated from the ^{19}F NMR chemical shifts and eq 1 with use of the ρ values in Table I for methanol. [e] All solutions in sufficient KOH to generate the thiolate anions and 10^{-4} M in EDTA to retard thiol oxidation. [f] Reference 22. [g] Reference 1. [h] In 0.01 M KOH. [i] Reference 23. [j] Reference 24. [k] Ionic strength maintained at 1.0 M with $NaClO_4$.

the σ_I values obtained in the present study are consistently more negative than those obtained in the previous study (average difference for pyridine axial ligands in Me_2SO is −0.148 ± 0.029; for primary amine axial ligands, −0.171 ± 0.010). That these differences are due to solvent effects is adequately demonstrated by the differences in measured ^{19}F NMR chemical shifts and hence in calculated σ_I for fluorophenyl-(4-(carboxamido)pyridine)cobaloximes in methanol and Me_2SO (Table III). The difference in σ_I in the two solvents is fully 0.127, reflecting a major influence of solvation on the electron inductive effect of cobaloxime chelated cobalt centers which is perhaps not unexpected considering the numerous possibilities for hydrogen bonding, electrostatic, and even hydrophobic interactions presented by the bis(dimethylglyoximato) chelating system.

The resonance substituent constants, σ_R°, for the cobaloxime centers with nitrogenous axial ligands, on the other hand, show a remarkable insensitivity both to the basicity of the axial ligand and to the nature of the solvent. Thus, the σ_R° values for the pyridine ligated cobaloximes in Me_2SO vary by at most only 0.022 from the mean (−0.215 ± 0.016) while those for the primary amine ligated cobalt centers in methanol vary at most by only 0.003 from the mean (−0.224 ± 0.002). The relatively minor solvent effect on σ_R° is evidenced by the small difference in σ_R° for 4-(carboxamido)pyridine-ligated cobaloximes in Me_2SO (−0.225) and in methanol (−0.252). With consideration of all the nitrogenous axial ligands in both solvents, the maximum deviation from the mean (−0.223 ± 0.015) is only 0.030 or 2 standard deviations. Such insensitivity to solvent effects is quite common for resonance-donating substituents as demonstrated by Taft et al.[8]

The two methyl sulfide axial ligands provide an interesting contrast to the nitrogen ligands. These exceedingly weakly bound axial ligands (Table IV), which are extremely weak proton bases[19] and presumably interact with the cobalt center mostly via cobalt-to-sulfur π donation, form cobalt centers which are significanly less inductively electron donating than any of the nitrogen ligands. A similar effect was observed in our earlier work[1] although again the σ_I values do not agree presumably because of solvent effects. This effect presumably reflects a decrease in electron density on the cobalt atom due to the reverse donation inherent in the interaction of these ligands with the cobalt center. Perhaps surprisingly the *S*-methyl sulfide ligated cobalt centers are somewhat more resonance donating than those with nitrogenous axial ligands, but the effect is rather small.

Similar effects are seen with triphenylphosphine as the axial ligand (Table IV), also presumably a good π-accepting ligand.[20,21] Unfortunately, since these measurements were made in chloroform, the decrease in inductive donation and increase in resonance donation may not be similarly interpreted in light of the unknown solvent effect on σ_I.

Table V shows the ^{19}F NMR chemical shifts and calculated substituent parameters for cobaloximes with anionic ligands. As expected, these provide the strongest inductively donating cobalt centers. As was the case with the primary amine and pyridine ligands, the values of $-\sigma_I$ for thiolate anion ligated cobalt centers show a regular increase with increasing basicity of the axial ligand (Figure 1). Although the slope of this correlation is, again, in reasonable agreement with that obtained previously,[1] the intercept is substantially increased, again apparently indicating large solvent effects as discussed above. Cyanide ion also produces a cobalt center with extremely strong inductive donation and, in fact, showing a σ_I value in excellent agreement with that previously determined from our study of ((carbomethoxy)phenyl)(ligand)cobaloxime saponification.[4] Interestingly, the three thiolate ligands and cyanide ion produce cobalt centers with the least resonance-donating potential. Since these are among the best π-accepting ligands studied, these observations seem to support the conventional wisdom that metal-to-ligand π donation at one coordination site decreases such donation to other ligands in the coordination sphere.

The ^{19}F NMR spectra of both *p*- and *m*-fluorophenylcobaloximes in saturating thiocyanate showed two distinct resonances of nearly equal intensity for the para isomer and in a ratio of about 1.15:1.0 for the meta isomer, the upfield resonance being the more intense. This is indicative of formation of both *N*- and *S*-liganded isomers with isomerization being slow on the NMR time scale, a phenomenon well established for thiocyanate liganded cobaloximes.[25-28] So that the ^{19}F NMR resonances could be assigned, the ^{1}H NMR spectra of *p*- and *m*-$FC_6H_4Co(D_2H_2)OH_2$ were studied in 1.0 M KSCN (methanol-d_4). Both samples showed two resonances for the equatorial methyl protons, at 2.13 and 2.16 ppm (internal Me_4Si) in a ratio of about 1.08:1.0 for the meta compound and at 2.13 and 2.15 ppm in a ratio of about 1:1 for the para compound. Following Marzilli[27] and Burmeister et al.,[28] the higher field resonance is assigned to the *N*-liganded isomers and the lower field resonance to the *S*-liganded isomers of each compound. From the relative intensities of the meta

(19) Arnett, E. M. *Prog. Phys.-Org. Chem.* **1963**, *1*, 223–403.
(20) Venanzi, L. M. *Pure Appl. Chem.* **1980**, *52*, 1117–1129.
(21) Caldwell, A. N.; Monojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1977**, 2265–2269.
(22) Lienhard, G. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1966**, *88*, 3982–3995.
(23) Reenstra, W. W.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 5780–5791.
(24) Jencks, W. P.; Regenstein, J. In "Handbook of Biochemistry"; Chemical Rubber Co.: Cleveland, 1970; pp J187–J226.
(25) Marzilli, L. G.; Stewart, R. C.; Epps, L. A.; Allen, J. B. *J. Am. Chem. Soc.* **1973**, *95*, 5796–5798.
(26) Norbury, A. H.; Shaw, P. E.; Sinha, A. I. P. *J. Chem. Soc., Dalton Trans.* **1975**, 742–748.
(27) Marzilli, L. G. *Inorg. Chem.* **1972**, *11*, 2504–2506.
(28) Kargol, J. A.; Lavin, K. D.; Crecely, R. W.; Burmeister, J. L. *Inorg. Chem.* **1980**, *19*, 1515–1522.

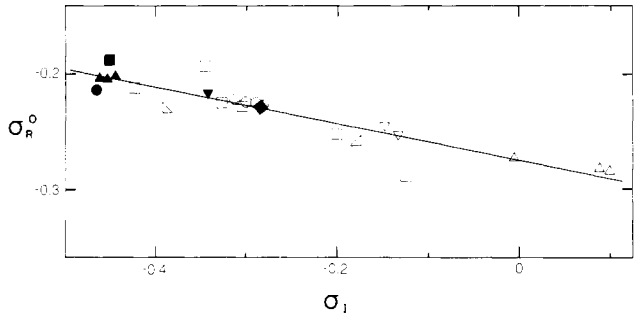
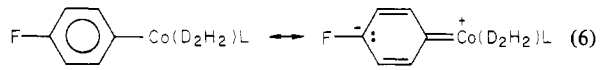


Figure 2. Plot of σ_R° vs. σ_I for $Co(D_2H_2)L$: (●) L = OH^-; (■) L = CN^-; (♦) L = SCN^-; (▼) L = NCS^-; (▲) L = RS^-; (◿) L = X-py; (○) L = RNH_2; (▽) L = $RSCH_3$; (△) $Co(D_2H_3)OH_2^+$; (△) L = CH_3OH; (◺) L = Me_2SO; (⏢) L = $P(Ph)_3$. The solid line is a least-squares fit, slope = −0.160 ± 0.015, intercept = 0.276 ± 0.005, N = 24, f = 0.048.

compound's resonances, the higher field ^{19}F NMR resonance is then assigned to the *N*-liganded species and the lower field one to the *S*-liganded species. Similar assignments were made for the para compounds by analogy, thus contradicting Burmeister's contention[28] that organocobaloximes show "a great preference for the nitrogen end of thiocyanate". The substituent constants for the NCS^-- and SCN^--liganded cobaloxime centers are, however, rather unremarkable except for the fact that the values of $-\sigma_I$ are rather small compared to those of the other anionic cobaloximes studied (Tables II and V), particularly the *S*-liganded species. This may indicate substantial back-donation from the metal to the axial ligand, thus lowering the net electron density on the cobalt atom, but the expected decrease in resonance donation to the aryl ligand is not observed.

Figure 2 shows a plot of σ_R° vs. σ_I for all of the cobaloxime substituents investigated. As the figure shows, an excellent σ_R–σ_I correlation is obtained for these substituents (N = 24, f = 0.048). Omission of the single data point in chloroform (for L = $P(Ph)_3$, the most deviant point) changes the slope, intercept, and f value only slightly (slope = −0.151 ± 0.012, intercept = −0.272 ± 0.004, f = 0.039, N = 23). Taft[8] has noted that although such relationships are by no means general for all substituents, they do occur among certain series of structurally closely related substituents. In particular, such relationships have been found only for relatively simple structures in which the first atom of the substituent is from the first row of the periodic table and bears at least one unshared electron pair. Taft[8] has called such substituents united atom-like first row pair donors (UAFPD's) and characterized them as substituents for which both the inductive and resonance parameters are directly controlled by the effective nuclear charge of the first atom. The σ_R°–σ_I relationship for such substituents has a slope of +0.40 and an intercept of −0.54, i.e., σ_R° and σ_I vary in the same direction. The present case is obviously completely different since the first atom of the substituent is a transition metal and the slope of the correlation is negative. If one assumes that axial ligands which increase the inductive donating ability of the cobalt atom do so by placing additional electron density on the cobalt atom one would expect this to result in an increase in π donation if the usual resonance structure for π donation into σ_R°-type detecting groups holds (eq 6). One must then conclude either



(6)

that this is not the correct type of resonance structure for π donation from cobalt substituents or that increased electron density on the cobalt atom causes sufficient distortion of the metal atom orbitals involved in π donation to decrease their overlap with the π system of the aryl ligand.

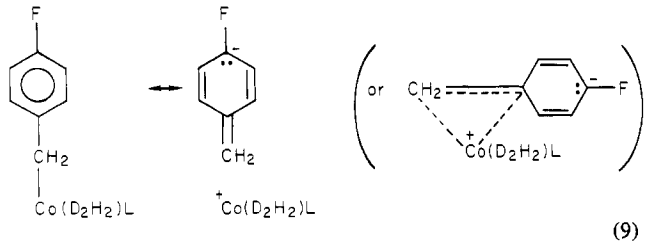
Nonetheless, the existence of a σ_R°–σ_I correlation for such cobaloxime substituents allows the elimination of the σ_R° variable from eq 1 so that both meta and para ^{19}F NMR chemical shifts may be correlated with σ_I alone, as in eq 7 and 8. These equations have been derived with the use of σ_R°–σ_I

$$\delta_{^{19}F}{}^p = -3.973\sigma_I + 8.408 \quad (7)$$

$$\delta_{^{19}F}{}^m = -5.464\sigma_I - 0.098 \quad (8)$$

correlation without the single data point in chloroform (i.e., L = $P(Ph)_3$) and the average ρ values in methanol and Me_2SO (Table I), although very similar results are obtained if the chloroform data are included. Statistical tests of these equations using all 23 data points show that they are excellent correlations (f = 0.035 for para ^{19}F NMR chemical shifts and f = 0.080 for the meta shifts).

It is of interest to compare the present results with ^{19}F NMR chemical shifts reported by Johnson and co-workers[29,30] for *m*- and *p*-fluorobenzyl(ligand)cobaloximes. Some of these data are shown in Table VI along with the σ_I and σ_R° values for the substituents $CH_2Co(D_2H_2)L$ calculated via application of eq 1. As seen in the table, not only is the expected attenuation of the inductive effect of the cobalt center by interposition of a methylene group between the cobalt atom and the aryl group not seen but also the $CH_2Co(D_2H_2)L$ substituents appear substantially *more* electron donating than the $Co(D_2H_2)L$ substituents. This is obviously the result of and, in fact, an excellent example of true hyperconjugation or $\sigma \rightarrow \pi$ conjugation[31] (eq 9). With consideration of the huge increase in



(9)

apparent electron donation of $CH_2Co(D_2H_2)L$ over that of $Co(D_2H_2)L$, the hyperconjugation structure must make a major contribution to the benzylcobaloximes. It is, however, unclear why essentially all of this effect seems to show up in the σ_I substituent constant rather than in σ_R°. With σ_I taken as an indicator of the extent of hyperconjugation, it is clear

Table VI. ^{19}F NMR Chemical Shifts of *m*- and *p*-Fluorobenzyl(ligand)cobaloximes[a]

ligand	$\delta_{^{19}F}{}^p$	$\delta_{^{19}F}{}^m$	σ_I[b]	σ_R°[b]	pK_a[c]
CN^-	8.49	3.89	−0.727	−0.092	9.00[d]
NO^{2-}	7.80	3.68	−0.690	−0.080	3.29[e]
NCO^-	7.50	3.64	−0.680	−0.072	3.92[e]
Cl^-	7.04	3.56	−0.671	−0.060	−7.0[f]
I^-	6.52	3.49	−0.661	−0.046	−10.0[e]
$P(Ph)_3$	4.97	2.97	−0.567	−0.020	

[a] Data from ref 29 and 30 in CH_2Cl_2. [b] Calculated from eq 1 and the ρ values given in Table I for chloroform. [c] pK_a of the conjugate acid of the ligand. [d] Reference 22. [e] Reference 24. [f] Reference 32.

(29) Dodd, D.; Johnson, M. D.; Fong, C. W. *J. Chem. Soc., Dalton Trans.* **1974**, 58–64.
(30) Bied-Charreton, C.; Gaudemer, A.; Chapman, C. A.; Dodd, D.; Gupta, B. D.; Johnson, M. D.; Lockman, B. L.; Septe, B. *J. Chem. Soc., Dalton Trans.* **1978**, 1807–1813.
(31) Traylor, T. G.; Berwin, H. J.; Jerkunica, J.; Hall, M. L. *Pure Appl. Chem.* **1972**, *30*, 599–606.
(32) Bell, R. P. "The Proton in Chemistry"; Cornell University Press: Ithaca, NY, 1973; p 91.

that $-\sigma_I$ increases with the basicity of the axial ligand, L, indicating that an increase in electron density placed on cobalt leads to an increase in the effect, supporting the hyperconjugation structures of eq 9. This is in direct contrast to the fluorophenylcobaloximes where $-\sigma_R^\circ$ (as an indicator of direct conjugation of cobalt with the aryl group) was found to decrease with increasing electron density on cobalt. It is also of interest to note that in Table VI changing L from Cl^- to I^- has very little effect on the measured ^{19}F NMR shifts and hence on the calculated values of σ_I for the $CH_2Co(D_2H_2)L$ substituents. Since I^- is known to interact with some aryl groups via involvement of unoccupied acceptor d orbitals,[5] such d-orbital interactions evidently do not occur with the cobalt atom in such complexes or they do not substantially effect the stability of the hyperconjugation structures of eq 9.

It should, finally, be pointed out that Bromilow et al.[33] have recently firmly demonstrated that the resonance effect of a given substituent, X, in a para-disubstituted benzene depends on the nature of the para detecting group Y and have suggested substitution of eq 10 (dual substituent parameter nonlinear

$$P = \sigma_I\rho_I + \sigma_R^\circ\rho_R/(1 - \epsilon\sigma_R^\circ) \qquad (10)$$

resonance effects or DSP-NLR) for the simpler eq 1 (dual substituent parameter or DSP) for para-disubstituted benzenes. In this equation, ϵ is treated as a fit parameter to be maximized for each data set and to allow for such nonlinear resonance effects. However, these authors have applied this approach to para-substituted fluorobenzene ^{19}F NMR chemical shifts and obtained a maximized value of 0.21 for ϵ. Application of eq 10 to the present data using this value of ϵ shows that the nonlinear resonance effect is extremely minor for para-substituted fluorobenzenes. This treatment caused no change whatsoever (to three significant figures) in any of the values of σ_I reported herein for cobaloxime-chelated cobalt centers and caused only minor changes in the calculated σ_R° values (in the third significant figure). Hence, while such nonlinear resonance effects are undoubtedly extremely important in some cases,[33] they are a very minor effect in the current case.

(33) Bromilow, J.; Brownlee, R. T. C.; Craik, D. J.; Sadek, M.; Taft, R. W. *J. Org. Chem.* **1980**, *45*, 2429-2438.

Acknowledgment. This research was supported by the Robert A. Welch Foundation, Houston, Texas (Grant Y-749), and, in part, by the National Science Foundation (Grant CHE78-18723, South Carolina Magnetic Resonance Laboratory). We are grateful to Dr. Ben Shoulders, The University of Texas at Austin, and to Dr. Paul D. Ellis and Dr. Ruth Inners, South Carolina Magnetic Resonance Laboratory, for their kind assistance in obtaining the ^{19}F NMR spectra.

Registry No. *m*-$FC_6H_4Co(D_2H_2)OH_2$, 78965-43-2; *p*-$FC_6H_4Co(D_2H_2)OH_2$, 57104-73-1; *m*-$FC_6H_4Co(D_2H_2)OH^-$, 78965-44-3; *p*-$FC_6H_4Co(D_2H_2)OH^-$, 78965-45-4; *m*-$FC_6H_4Co(D_2H_3)OH_2^+$, 78965-46-5; *p*-$FC_6H_4Co(D_2H_3)OH_2^+$, 78965-47-6; *m*-$FC_6H_4Co(D_2H_3)Cl$, 78965-48-7; *p*-$FC_6H_4Co(D_2H_3)Cl$, 78965-49-8; *m*-$FC_6H_4Co(D_2H_2)Me_2SO$, 78965-50-1; *p*-$FC_6H_4Co(D_2H_2)Me_2SO$, 78965-51-2; *m*-$FC_6H_4Co(D_2H_2)$(4-cyanopyridine), 78965-52-3; *p*-$FC_6H_4Co(D_2H_2)$(4-cyanopyridine), 78965-53-4; *m*-$FC_6H_4Co(D_2H_2)$(4-(carboxamido)pyridine), 78965-54-5; *p*-$FC_6H_4Co(D_2H_2)$(4-(carboxamido)pyridine), 78965-55-6; *m*-$FC_6H_4Co(D_2H_2)$(pyridine), 78965-56-7; *p*-$FC_6H_4Co(D_2H_2)$(pyridine), 42194-70-7; *m*-$FC_6H_4Co(D_2H_2)$(4-methylpyridine), 78965-57-8; *m*-$FC_6H_4Co(D_2H_2)$(4-aminopyridine), 78965-58-9; *p*-$FC_6H_4Co(D_2H_2)$(4-aminopyridine), 78965-59-0; *m*-$FC_6H_4Co(D_2H_2)$(glycine ethyl ester), 78965-60-3; *p*-$FC_6H_4Co(D_2H_2)$(glycine ethyl ester), 78965-61-4; *m*-$FC_6H_4Co(D_2H_2)$(2,2-dimethoxyethylamine), 78965-62-5; *p*-$FC_6H_4Co(D_2H_2)$(2,2-dimethoxyethylamine), 78965-63-6; *m*-$FC_6H_4Co(D_2H_2)$(2-methoxyethylamine), 78965-64-7; *p*-$FC_6H_4Co(D_2H_2)$(2-methoxyethylamine), 78965-65-8; *m*-$FC_6H_4Co(D_2H_2)$(*n*-propylamine), 78965-66-9; *p*-$FC_6H_4Co(D_2H_2)$(*n*-propylamine), 78965-67-0; *m*-$FC_6H_4Co(D_2H_2)$(*S*-methyl-2-mercaptoethanol), 78965-68-1; *p*-$FC_6H_4Co(D_2H_2)$(*S*-methyl-2-mercaptoethanol), 78965-69-2; *m*-$FC_6H_4Co(D_2H_2)$(methyl *S*-methylmercaptoacetate), 78965-70-5; *p*-$FC_6H_4Co(D_2H_2)$(methyl *S*-methylmercaptoacetate), 78965-71-6; *m*-$FC_6H_4Co(D_2H_2)$(triphenylphosphine), 78965-72-7; *p*-$FC_6H_4Co(D_2H_2)$(triphenylphosphine), 78965-73-8; *m*-$FC_6H_4Co(D_2H_2)$(methyl mercaptoacetate), 78965-74-9; *p*-$FC_6H_4Co(D_2H_2)$(methyl mercaptoacetate), 78965-75-0; *m*-$FC_6H_4Co(D_2H_2)$(methyl mercaptopropionate), 78965-76-1; *p*-$FC_6H_4Co(D_2H_2)$(methyl mercaptopropionate), 78965-77-2; *m*-$FC_6H_4Co(D_2H_2)$(2-mercaptoethanol), 78965-78-3; *p*-$FC_6H_4Co(D_2H_2)$(2-mercaptoethanol), 78965-79-4; *m*-$FC_6H_4Co(D_2H_2)CN^-$, 78965-80-7; *p*-$FC_6H_4Co(D_2H_2)CN^-$, 78965-81-8; *m*-$FC_6H_4Co(D_2H_2)SCN^-$, 78965-82-9; *p*-$FC_6H_4Co(D_2H_2)SCN^-$, 78965-83-0; *m*-$FC_6H_4Co(D_2H_2)NCS^-$, 78965-84-1; *p*-$FC_6H_4Co(D_2H_2)NCS^-$, 78965-85-2.

Contribution from the Department of Chemistry, La Trobe University, Bundoora, Victoria, 3083, Australia

Applications of Molybdenum-95 Nuclear Magnetic Resonance Spectroscopy. 3.[1] Arenemolybdenum Tricarbonyl Derivatives

ANTHONY F. MASTERS,* ROBERT T. C. BROWNLEE, MAXWELL J. O'CONNOR,* and ANTHONY G. WEDD

Received December 31, 1980

The direct observation of the naturally abundant ^{95}Mo NMR spectra of $[LMo(CO)_3]$ (L = cycloheptatriene, mesitylene, *o*-, *m*-, and *p*-xylene, toluene, cyclopentadienyl anion) compounds are reported and discussed. Narrow resonances ($W_{h/2} \approx 6$ Hz) are observed, and the signals are the most shielded reported to date. The ^{95}Mo NMR chemical shift is related to the molybdenum-arene bond strength for L = arene. Arene exchange between $[LMo(CO)_3]$ derivatives is not detected at 38 °C in dichloromethane.

Introduction

We have recently demonstrated the potential of ^{95}Mo NMR spectroscopy in the study of molybdenum carbonyls.[2] Several important aspects emerged from our preliminary study. Thus, despite the quadrupole moment associated with this $I = {}^5/_2$ nucleus, line widths were often very narrow, allowing a combination of both sharp signals and rapid data accumulation and hence the possibility of routine detection of signals from dilute solutions. These benefits, coupled with the wide ^{95}Mo NMR chemical shift range observed to date (>4000 ppm)[2,3] have the further consequence that subtle electronic effects at

(1) For Part 2, see: Masters, A. F.; Gheller, S. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Inorg. Chem.* **1980**, *19*, 3866-3868.
(2) Masters, A. F.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G.; Cotton, J. D. *J. Organomet. Chem.* **1980**, *195*, C17-C20.
(3) (a) Lutz, O.; Nolle, A.; Kroneck, P. *Z. Naturforsch.* **1976**, *31A*, 454-456. (b) Lutz, O.; Nolle, A.; Kroneck, P. *Ibid.* **1977**, *32A*, 505-506.

0020-1669/81/1320-4183$01.25/0