where I_0t is the amount of light absorbed by the sample (einstein L^{-1}); ϵ_A, ϵ_L, and ϵ_B are the molar extinction coefficients of $M(CO)_6$, ligand, and $M(CO)_5L$, respectively, at the irradiation wavelength; and $[A]_0$ and $[L]_0$ are the initial concentrations of $M(CO)_6$ and ligand and [B] is the concentration of $M(CO)_5L$ at time *t*.

A conventional flash apparatus was used, with solutions degassed by freezing–pumping–thawing cycles. Because the final optical density was not zero, only one flash was made per solution. Filters were used to absorb light below 330 nm.

Irradiation. The same equipment was used to make irradiations of 313, 334, and 366 nm.[1] Filters used together with the monochromator are described in the literature.[20] For the irradiation at 254 nm, a 4-W Sylvania mercury low-pressure lamp was used with a chemical filter only.[20] Actinometry procedures have been previously described.[1]

Acknowledgment. We thank Professor E. Vander Donckt and Dr. L. Wilputte for interesting discussions. We also thank Dr. M. Benedek of the microanalytical department for accurate weighings. A.C. acknowledges a fellowship from the "Institut pour l'encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture" (IRSIA).

Registry No. $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; $Cr(CO)_5$(pyridine), 14740-77-3; $Cr(CO)_5CH_3CN$, 15228-38-3; $W(CO)_5$(pyridine), 14586-49-3; pyridine, 110-86-1; CH_3CN, 75-05-8; cyclohexane, 110-82-7; benzene, 71-43-2; benzophenone, 119-61-9.

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(21) We thank a reviewer who pointed out that the viscosity effect measured in the photoaquation[5] of $Co(CN)_6^{3-}$ can be ascribed to an incorrect experimental procedure.[6]

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Electronic Structure of Alkylidynetricobalt Nonacarbonyl Clusters, $RCCo_3(CO)_9$, Based on ^{59}Co Nuclear Quadrupole Resonance Spectroscopy

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The ground-state electronic structure of $RCCo_3(CO)_9$ clusters, where R is H, CH_3, C_6H_5, $C_6H_5C(O)$, CF_3, $C_2H_5C(O)O$, Cl, $CH_3C(O)O$, CH_3O, and $(C_2H_5)_3Si$ has been examined by ^{59}Co NQR spectroscopy. This series represents a range of electron-donating and electron-withdrawing substituents. The ^{59}Co nuclear quadrupole coupling constants are found to correlate with the Hammett σ function and the σ_R^- resonance parameter for the R groups. The correlation provides evidence that the apical carbon atom in the cluster transmits electronic character between the R group and the cobalt atoms by a π-resonance mechanism and not by a through-bond inductive mechanism. The ^{35}Cl resonance in $ClCCo_3(CO)_9$ when combined with other data indicates a significant amount of Cl–C multiple-bond character. Thus, NQR data at both ends of the molecule reveal electron delocalization and resonance transmission through the apical carbon atom. The benzoyl derivative has an irregular behavior in the solid state compared to the other complexes. However, its ^{13}C NMR spectrum gives evidence of a normal structure in solution.

Introduction

The class of metal cluster compounds known as alkylidynetricobalt nonacarbonyls, $RCCo_3(CO)_9$, has attracted considerable attention in recent years. Much of this interest stems from the variety of R groups which can be bonded to the methylidyne carbon atom and their encumbant chemistry. The syntheses, reactions, and physical properties of these complexes have been compiled in several reviews.[1-3]

Our interest in these complexes is directed toward understanding the ground-state electronic structure in the cluster.[4] The approach to this problem has been to investigate the ^{59}Co nuclear quadrupole resonance spectra as a function of variation in the R group through a range of strongly electron-withdrawing to strongly electron-donating groups. The substituents studied are second-row-element-based with the exception of the chloro- and triethylsilylmethylidynetricobalt nonacarbonyl. By examining how the cobalt atoms respond to "push–pull" electronic effects, additional information on the bonding characteristics of the Co_3–C–R framework has been experimentally obtained. The only picture of bonding in these complexes which is consistent with the results is one which allows significant π-electronic transmission through the apical carbon atom in the cluster.

Experimental Section

Syntheses. The alkylidynetricobalt nonacarbonyls used in this work have been reported before. Synthetic procedures reported in the literature were followed for $RCCo_3(CO)_9$, R = H,[5] Cl,[5] Br,[5] CH_3,[5] $C(O)CH_3$,[5] $C(O)OC_2H_5$,[5] OCH_3,[5] $C(O)C_6H_5$,[5] CF_3,[6] C_6H_5,[7] CH_3CHOH,[8] CO^+,[9] $C_5H_5FeC_5H_4C(O)$,[9] $CH_3C(O)O$,[10] and $C(O)N(CH_3)_2$.[11] The $(C_2H_5)_3Si$ derivative was obtained from Professor D. Seyferth. All solvents used were dried and degassed, and all reactions were carried out under an atmosphere of nitrogen in Schlenk ware. The only exception was the CF_3 derivative, for which autoclaving was necessary. In most cases, the purification of the products was different from that reported, however.

Dry column chromatography[12] was found to be a simple and useful method for purifying these complexes. This technique has the advantage of retaining the resolution of thin layer chromatography but allowing a preparative-scale separation. In general, the support (silica gel or alumina) was packed into a nylon column having dimensions of approximately 1.5 × 25 in. with a glass wool plug and vent holes at the bottom. The sample to be separated (1–3 g) was dissolved in a minimum amount of solvent, and a small amount of support was added (about 5–7 g). The solvent was removed under vacuum. The resulting powder was layered on top of the support in the nylon column and then covered with a layer of sand. The column was developed in the normal manner, except that separation was complete when the solvent front reached the bottom of the column. The amount of solvent

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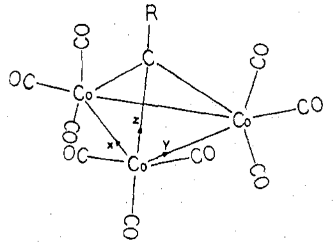


Figure 1. The structure of RCCo$_3$(CO)$_9$ clusters. The axis system is the principal axes of the Co electric field gradient tensor.

required was considerably less than that needed for wet column methods. For a normal column only 100–250 mL of solvent was required, whereas a wet column required several liters for separation. After the column developed, the components of interest were removed by simply cutting the column apart with scissors. In most cases several washings with hexane or benzene removed the sample from the support, but in some cases methanol was required to deactivate the support and free the sample. The technique normally required the activity of the support to be the same as TLC plates. Thus, water must be added and the activity checked. For alumina (Fisher) and silica gel (Baker Analyzed, 60–200 mesh) supports, deactivation was not necessary in most cases, but this was probably due to the age of the supports used. When deactivation was necessary it was accomplished by adding the appropriate amount of water and equilibrating by stirring for several hours. A "Rotovap" open to the atmosphere worked well for this.

Identification of the products was made by accurate correlation of the melting points and IR spectra with those in the literature.[5-11]

Spectra. The NQR data were obtained on a spectrometer system which has been described before.[13] Uncertainty in the measurement of the center line of the resonance multiplet produces a possible error of about 0.01 MHz in the resonance frequency data. Spectra were obtained on 0.5–2 g of sample. The method of purification proved to be quite important in determining whether or not the NQR spectrum could be seen. This was most vividly illustrated in the case of BrCCo$_3$(CO)$_9$, which showed a weak set of resonances on one occasion. Rather than measure the frequencies of weak resonances, it was hoped that the intensities could be increased by an additional recrystallization. From that point onward the signals could never be found again in spite of repeated syntheses and exhaustive manipulations of the sample. It can be said that the bromo compound does give coupling constants very similar to those in the chloro compound, as expected, but the precise values were never measured. Several other samples behaved in a similar way in that one method of purification yielded resonances while another did not. We attribute these difficulties to crystal strains, disorder, and perhaps impurities which lead to rapid quadrupole relaxation. No NQR spectra were seen for complexes where R = C(O)CH$_3$, C$_5$H$_5$FeC$_5$H$_4$C(O), CH$_3$C(OH)H, C(O)N(CH$_3$)$_2$, and OCCCo$_3$(CO)$_9$$^+PF_6$$^-$.

IR spectra were recorded on a Perkin-Elmer 180 double-grating spectrometer for purposes of comparison with literature values. Solvents and conditions were matched to the literature reports.

NMR spectra were recorded on a Bruker HFX-90 spectrometer at 305 K by Dr. Walter J. Freeman. A sweep width of about 9 kHz with about 1000 scans was employed. In order to ensure observation of the carbonyl spectra, a 5–7-sec delay time between pulses was used. The spectra were broad band and proton decoupled.

Results and Discussion

Structural Implications. The crystal structures of several RCCo$_3$(CO)$_9$ complexes have been reported.[10,14-18] All of these show the basic structural unit reproduced in Figure 1. Each cobalt atom possesses three carbonyl groups, two cobalt atoms, and one C–R group in its coordination sphere. The 18-electron rule is satisfied.

A quantitative model for the electric field gradient which incorporates the detailed bond angles is not easily derived for these compounds. Such a model would have little experimental utility in these complexes because of the number of variable parameters which would be involved. However, one can quite readily understand the broad features of the cobalt electric field gradient from conclusions of the additive electric field gradient model[19] for an octahedral metal atom in a facial isomer of stoichiometry MA$_3$B$_2$C. In this case M = Co, A = CO, B = Co, and C = C–R. The electric field gradient model is based on true octahedral geometry, while the coordination sphere in these complexes is actually somewhat distorted. Nevertheless, the trends expected in the electric field gradient as a function of ligand variation should be obtainable from the electrostatic model. The contribution of the three CO ligands to the cobalt electric field gradient will cancel if the CO–Co–CO angles are 90°. The largest component of the electric field gradient, q_{zz}, in electrostatic units then arises from the partial electric field gradient contributions of the two Co–Co bonds and the Co–CR bond. These are indicated as [Co] and [C–R], respectively (eq 1). The approximate

$$\begin{aligned} q_{zz} &= \{2[\text{C-R}] - 2[\text{Co}]\}e \\ q_{yy} &= \{[\text{Co}] - [\text{C-R}]\}e \qquad (1) \\ q_{xx} &= \{[\text{Co}] - [\text{C-R}]\}e \end{aligned}$$

configuration of the principal axes of the electric field gradient tensor is shown in Figure 1. If it is assumed that the Co–Co bonds are essentially constant in nature as R is varied, then the ^{59}Co coupling constant, e^2Qq_{zz}/h, is sensitive only to variations in the C–R ligand according to eq 1. Even if the contributions of the carbonyl groups to the cobalt electric field gradient do not cancel entirely, it is reasonable to assume that the variation in carbonyl ligands and the metal–metal bond as R changes is likely to be small. An indication of the validity of this assumption comes from the rather small observed change in η as R is varied. According to q_{zz} in eq 1, one should be able to view, at least in a qualitative way, a direct correlation between the ^{59}Co electric field gradient and the electronic donor and acceptor properties of the variable group R.

Table I summarizes the ^{59}Co NQR data obtained for these systems. Since ^{59}Co is an $I = {}^7/_2$ nucleus, up to three resonances per crystallographically inequivalent cobalt atom could be present in each stoichiometric unit. In most cases, however, the $m_I = \pm{}^3/_2 \leftrightarrow \pm{}^1/_2$ transition was not observed because its intensity tends to be much lower than the $\pm{}^3/_2 \leftrightarrow \pm{}^5/_2$ or $\pm{}^5/_2 \leftrightarrow \pm{}^7/_2$ transition in cobalt. A broad-band scan was employed in all cases to ensure that no resonances above 20 MHz were present. From the two or three resonances observed, the nuclear quadrupole coupling constant, e^2Qq_{zz}/h, and the electric field gradient asymmetry parameter, η, can be calculated.[20] Some minor ambiguities in the assignment for several compounds obviously exist, but these neither produce important differences from the values reported nor would they change any of the conclusions developed in this paper.

In all except one case (the chloro derivative) the asymmetric unit of the cell appears to contain a formula unit having three crystallographically inequivalent cobalt atoms. In the case of the ethyl ester derivative, the asymmetric unit of the cell appears to be even more complicated in that two crystallographically inequivalent formula units are probably present. Two of the complexes (R = CH$_3$[14] and CH$_3$C(O)O[10]) for which data appear in Table I have been subjected to x-ray crystal structure determinations. Both are found to contain three crystallographically inequivalent cobalt atoms in accordance with their NQR spectra. The asymmetry parameters for all complexes are in a range of 0.068 to 0.287 with 0.1–0.2 range being dense with values. No obvious trend in these values exists, and even if there were a trend the small range of values would make any conclusions rather tenuous. On the other hand, a broad range of values for the coupling constants is found. The average values for the coupling constants are tabulated along with the range of values giving rise to these averages. The range from the average is about 4 MHz or less in all cases except the benzoyl derivative. Hence it appears

Table I. ^{59}Co NQR Data for $RCCo_3(CO)_9$ Compounds at 298 K[a]

R	$\nu(^3/_2 \leftrightarrow {^1/_2})$	$\nu(^5/_2 \leftrightarrow {^3/_2})$	$\nu(^7/_2 \leftrightarrow {^5/_2})$	e^2Qq_{zz}/h, MHz	Av e^2Qq_{zz}/h, MHz	η
OCH_3		11.39 (2)	17.12 (2)	79.95	83.00 ± 3	0.068
		11.79 (2)	17.92 (2.5)	83.90		0.180
		12.11 (2)	18.23 (2.5)	85.15		0.088
$OC(O)CH_3$		10.79 (4)	16.25 (3)	75.92	78.46 ± 3	0.102
		11.30 (3.5)	17.03 (2)	79.58		0.108
		11.14 (3.5)	17.03 (2)	79.89		0.222
CH_3[b]				76.66	77.47 ± 1	0.16
				77.64		0.16
				78.12		0.14
H		10.45 (2)	15.97 (3)	74.84	77.34 ± 3	0.216
		10.99 (3)	16.74 (3)	78.41		0.196
		11.13 (3)	16.85 (3)	78.78		0.142
Cl[c]		10.87 (5)	16.33 (4)	76.26	76.26	0.068
C_6H_5		10.21 (1.5)	15.51 (2)	72.75	74.40 ± 2	0.177
		10.46 (2)	15.87 (2)	74.25		0.164
		10.77 (2)	16.30 (2)	76.20		0.139
$C(O)OC_2H_5$			14.01 (3)		68.9 ± 4	
		9.26 (2)	14.15 (3.5)	66.34		0.129
		9.34 (2)	14.22 (3.5)	66.63		0.194
		9.72 (2)	14.74 (2.5)	68.96		0.163
		10.16 (2.5)	15.40 (4)	72.01		0.151
		10.29 (2)	15.64 (3.5)	73.23		0.177
CF_3		9.47 (2)	14.39 (2)	67.39	68.09 ± 1	0.181
		9.60 (2)	14.57 (2)	68.20		0.166
		9.77 (2)	14.71 (2)	68.69		0.085
$Si(C_2H_5)_3$		8.889 (4)	13.762 (4)	64.75	66.69 ± 2	0.278
		9.475 (4)	14.570 (4)	68.54		0.283
$C(O)C_6H_5$		7.05 (3)	10.88 (14)	51.21	66.66 ± 15	0.287
		9.63 (11)	14.70 (13)	68.93		0.214
	6.25 (2)	11.23 (20)	17.06 (13)	79.85		0.172

[a] Values in parentheses are signal-to-noise ratios. All frequencies are in MHz. [b] T. L. Brown, *Acc. Chem. Res.*, 7, 408 (1974). [c] $\nu(^3/_2 \leftrightarrow {^1/_2})$ for ^{35}Cl observed at 31.36 MHz.

that all of these complexes have, with the possible exception of the benzoylmethylidynetricobalt nonacarbonyl, the structure shown in Figure 1.

The benzoyl derivative is very interesting in that it produces a range of coupling constant values greater in magnitude than the range of all the other complexes combined. The assignment of the resonance frequencies in $C_6H_5C(O)CCo_3(CO)_9$ fortunately proved to be inequivocal because no combinations of resonances other than that shown produces an allowed solution to the $I = {^7/_2}$ eigenvalue equation. The resonances shown are the most intense of all alkylidynetricobalt nonacarbonyl clusters studied, and other frequency ranges, where resonances must exist if different assignments are possible, are completely free of signals. Hence the assignments given can be confidently made. This compound appears to contain some rather different cobalt electric field gradient tensors in the solid state. Unfortunately the NQR spectrum does not allow further structural analysis. In order to determine whether any inequivalence in the cobalt atoms also exists in solution, the ^{13}C NMR spectrum of this complex was recorded in $CDCl_3$ solvent. Table II lists the ^{13}C chemical shifts for two clusters and also for acetophenone. At room temperature the spectrum shows no evidence of anomalies in its structure compared to a "normal" cluster, $C_6H_5CCo_3(CO)_9$, where no unusual bonding appears to be present. The methylidyne carbon signal does not appear in either complex probably because of the lack of an Overhauser enhancement at that position, but it has been observed in other complexes.[21,22] The ^{13}CO chemical shift values and line widths in $C_6H_5C(O)CCo_3(CO)_9$ and $C_6H_5CCO_3(CO)_9$ are quite similar to one another. Hence in $CDCl_3$ solution the benzoyl derivative behaves on the NMR time scale as though it is bonded according to the structure shown in Figure 1. Cooling the sample met with complications arising from decreased solubility and lengthened signal-averaging periods. No suitable spectra were obtained. We have undertaken an x-ray crystal structure determination of $C_6H_5C(O)CCo_3(CO)_9$ in the hope of finding out what is taking place.

Table II. ^{13}C NMR Chemical Shifts in ppm[a]

	$C_6H_5C(O)$ $Co_3(CO)_9$	$C_6H_5CCo_3$ $(CO)_9$	$C_6H_5C(O)$ CH_3[b]
=C=O	207.3		196.0
−C≡O	199.1	200.2	
Ipso C	140.4	158.6	136.6
Para C	131.7	128.1	131.6
Meta C	128.7	128.7	128.4
Ortho C	127.8	128.7	128.4

[a] In $CDCl_3$ solution with Me_4Si as an internal standard. [b] J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.

Bonding Implications. To better clarify the ground-state electronic structure of this class of complexes, we chose the tactic of comparing the e^2Qq_{zz}/h values for cobalt in Table I to the electronic transmission parameters for the substituent, R.[25,26] In this way the mechanism of transmission of electron density from R to the cobalt atoms is obtained, and a picture of the electron distribution in the cluster can be developed. From eq 1, stronger electron-donor substituents would be expected to increase the average ^{59}Co coupling constant. Perusal of the data in Table I reveals this to be the case. From the structure shown in Figure 1, the apical carbon atom might be thought of as a classical, saturated, tetrahedral, organic-type carbon atom. In this situation, transmission of electron density from R through that carbon atom to cobalt should follow a through-bond inductive-type mechanism. The σ_I parameter derived by Taft[27] is based on this mechanism of electronic transmission. When a plot of σ_I[28a] vs. e^2Qq_{zz}/h is made for the R groups in Table II, the correlation is found to be random (coefficient of correlation is 0.42). σ_R parameters reflect

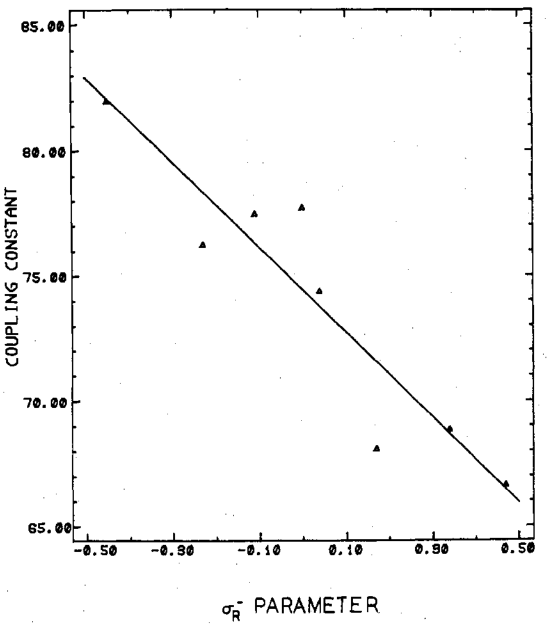


Figure 2. The relationship between the resonance transmission parameter, σ_R^-, of the R groups and the average ^{59}Co coupling constant.

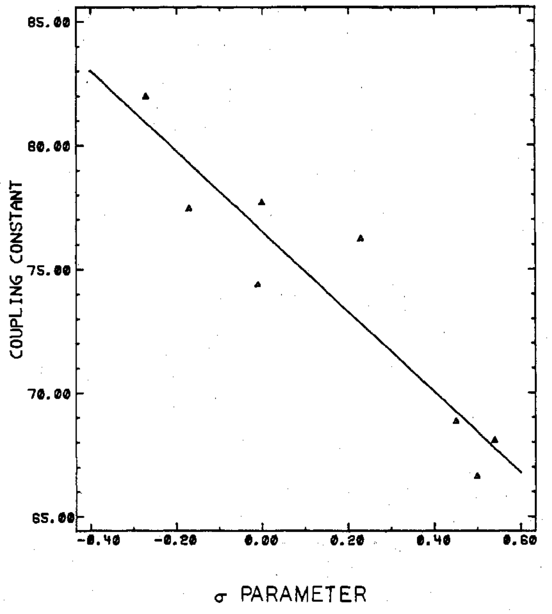
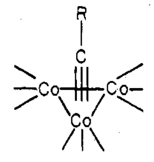


Figure 3. The relationship between the Hammett σ function for R and the average ^{59}Co coupling constant.

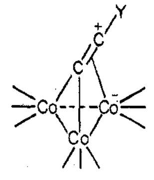
resonance transmission of electronic effects through a π system. When the generalized resonance parameter, σ_R^-,[28b] is plotted against e^2Qq_{zz}/h (the result is shown in Figure 2), the coefficient of correlation is −0.93. The Hammett function, σ,[29] which is a combination of resonance and inductive transmission, gives the result shown in Figure 3 with a coefficient of correlation of −0.94. It is not surprising that some inherent scattering occurs in the data points in these plots considering the fact that an average coupling constant must be used. Yet it is interesting that σ_R^- and σ correlate with e^2Qq_{zz}/h for ^{59}Co in a significant manner but that σ_I does not. The conclusion to which this leads is that R is able to transmit electronic character to the cobalt atoms through the apical carbon atom but that it does so via a resonance-type mechanism much more strongly than an inductive-type mechanism. Evidence from electrochemical studies of $RCCo_3(CO)_9$ compounds also suggests that a π-transmission component is important at the methylidyne carbon atom.[30] Bond et al.[30] found that electrode potentials for a series of $RCCo_3(CO)_9$ compounds were sensitive to R but not in a way compatible with a simple inductive electron-transfer mechanism.

The tendency to transmit π-electron density from R to the cobalt atoms provides some information about the probable ground-state electronic structure in these clusters. Viewing the methylidyne carbon atom as a saturated four-coordinate carbon atom seems to be inappropriate in these systems.[2] It may be more appropriate to view these complexes using a delocalized electron model. For example, if the apical carbon atom is considered to be sitting in a delocalized "bed" of electron density produced by the $Co_3(CO)_9$ portion of the molecule, much as a metal interacts with an aromatic ring in metallocene complexes, then the need to draw localized two-electron bonds does not necessarily exist. Something like delocalized carbyne bonding between the carbon atom and the three cobalt atoms can be envisioned (structure I). The carbon atom no longer needs to be thought of as a four-coordinate entity engaging in four localized two-center–two-electron bonds. It happens that, in this complex, classical two-electron bonds can be drawn between each atom because the CCo_3 tetrahedron is a 4-atom, 6-bond pair nido cluster.[33] The NQR data presented here indicate that localized bonding is not a suitable description, however. The valence strokes drawn between the cobalt atoms and the carbon atom better represent distances of closest contact and not covalent bonds. Of course a molecular orbital description obviates the need of valence strokes altogether.

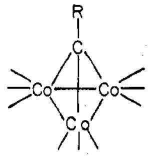


I

Alternatively, a model which permits, at least in a localized bond sense, transmission of the π character of R to cobalt involves a contribution of an "ethylidyne"-type structure (II) to the methylidyne structure (III). Structure II might exist for those R groups which have considerable delocalizable π-electron density. Such a structural possibility was pointed out in the acylium ion derivative, $OCCCo_3(CO)_9^+$, and other carbocations by Seyferth et al.[21,31,32] A requirement for such a structure is flexibility at the apical carbon atom, and the extent to which this exists and varies as a function of R is not yet known. It is certainly possible that the required flexibility exists in the carbocation complexes but might not exist in the neutral systems. Nevertheless, insofar as localized electron structures are valid for metal clusters, a combination of II and III is consistent with the results found here.



II



III

The chloro derivative, $ClCCo_3(CO)_9$, deserves a further comment because it has a second NQR probe site in the molecule situated at the end opposite the cobalt atoms. The ^{35}Cl resonance frequency appears at a rather low value for a C–Cl bond. An axially symmetric ^{35}Cl–C bond is subject to an electric field gradient variation which is directly related to the population of the chlorine p orbitals, $N_{p_z} - (N_{p_x} + N_{p_y})/2$.

The p_z orbital on chlorine is considered to form the Cl–C σ bond. The low value of the ^{35}Cl resonance frequency means that either the Cl–C bond is relatively ionic in the complex, which causes a large N_{p_z} value for chlorine, or that Cl → C π bonding is occurring, which causes N_{p_x} and N_{p_y} to be less than two electrons apiece, or both. If σ-bond ionicity were responsible, then the $CCo_3(CO)_9$ group would have to be a rather strong σ donor. The ^{35}Cl resonance frequency is in the range of that found for $(CH_3)_2CHCl$ and $(CH_3)_3CCl$.[34] Evidence is available which indicates that the $CCo_3(CO)_9$ group is electron withdrawing, however. Therefore, a considerable amount of Cl→C π bonding must be occurring. This π bonding tendency between the R group and the apical carbon is consistent with the fact that the C–R bond is often found to be shorter than a single bond[2] and the fact that ν(C–Cl) in $ClCCo_3(CO)_9$ occurs at a rather high frequency in the infrared spectra (906 cm^{-1}).[35] The NQR data when coupled with the other data available are consistent with a significant amount of π character in the C–Cl bond. A highly ionic σ bond is less consistent with the data available.

The triethylsilyl derivative behaves as more of an electron-withdrawing agent than might be anticipated from its substituent parameter.[28] It was not included as a data point in Figures 2 and 3. More work is needed with substituents having low-lying unfilled energy states before detailed comments can be made about their electronic participation with the cobalt atoms.

In summary, NQR data at both ends of the $RCCo_3(CO)_9$ complex (^{59}Co and ^{35}Cl) indicate a significant amount of delocalization of electron density in the region of the apical carbon atom. This delocalization is responsible for extensive π transmission of electron density between the Co atoms and the substituent group, R.

Registry No. $CH_3OCCo_3(CO)_9$, 41751-68-2; $CH_3C(O)OCCo_3(CO)_9$, 13682-05-8; $CH_3CCo_3(CO)_9$, 13682-04-7; $HCCo_3(CO)_9$, 15664-75-2; $ClCCo_3(CO)_9$, 13682-02-5; $C_6H_5CCo_3(CO)_9$, 13682-03-6; $C_2H_5OC(O)CCo_3(CO)_9$, 19425-32-2; $CF_3CCo_3(CO)_9$, 18433-88-0; $(C_2H_5)_3SiCCo_3(CO)_9$, 64115-67-9; $C_6H_5C(O)CCo_3(CO)_9$, 40730-01-6.

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Proton Chemical Shifts and Diamagnetic Anisotropy in Cobalt(III) Pentaammine Complexes

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Measurements of the diamagnetic susceptibility anisotropy of a single crystal of $[Co(NH_3)_5Cl]Cl_2$ are reported. From these, the susceptibility anisotropy of the $[Co(NH_3)_5Cl]^{2+}$ ions is calculated and correlated with the chemical shift difference between cis and trans protons in aqueous solution. If the point-dipole approximated anisotropic magnetization of the cobalt d electrons is regarded as the origin of the chemical shift difference, then the chemical shift difference calculated from the measured anisotropy is larger than the observed difference by 1.0 ppm. The predicted sign is correct. Even though the calculated and observed shift differences differ, the angular part $(1-3\cos^2\theta)$ of the point-dipole approximation holds well, as shown by proton chemical shift measurements on 12 pentaammines and the hexaammine. This extended series also shows the inadequacy of the correlation of chemical shifts with wavelength of the lowest energy absorption in the optical spectra. It is suggested that the effects which may be responsible for the discrepancy of 1.0 ppm are electric field effects, moments higher than dipoles, significant amplitudes of low-frequency bending vibrations, and uncertainty about the point at which the point dipole should be placed.

In the course of studies of the reactions of cobalt pentaammines, $[Co(NH_3)_5X]^{n+}$ where X is a monodentate ligand, we have accumulated a large number of nuclear magnetic resonance (NMR) data for ^{59}Co, ^{14}N, and ^{1}H nuclei in these complexes. We had noticed that the proton shifts bore no obvious relationship to the rate coefficients for proton exchange (see Table I) and that the shift data strongly implicated the magnetic anisotropy of the metal d electrons as the most

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