which successively varies the input parameters until the best values are found as judged by an evaluation of the fit in terms of root-mean-square deviations. Initial input parameters were obtained from nonexchange spectra. For final fits, a Calcomp routine was used to provide a visual comparison of calculated and experimental spectra. In cases where computer fits of the observed spectra were not possible, the exchange parameters were estimated using the relationship $2\pi\tau_e(\nu_A - \nu_B) = \sqrt{2}$, where $(\nu_A - \nu_B)$ is the frequency difference (hertz) between the two exchanging resonances in the stopped exchange region.[20]

Registry No. $CH_3Co(dh)_2P(OCH_3)_3$, 25586-92-9; $CH_2FCo(dh)_2$-$P(OCH_3)_3$, 43103-52-2; $CHF_2Co(dh)_2P(OCH_3)_3$, 42934-24-7; CF_3Co-$(dh)_2P(OCH_3)_3$, 43103-53-3; $CH_2ClCo(dh)_2P(OCH_3)_3$, 42934-25-8; $CHCl_2Co(dh)_2P(OCH_3)_3$, 42934-26-9; $CH_2BrCo(dh)_2P(OCH_3)_3$, 42934-27-0; $CHBr_2Co(dh)_2P(OCH_3)_3$, 42934-28-1; $CH_2Si(CH_3)_3Co$-$(dh)_2P(OCH_3)_3$, 42934-29-2; $CF_3Co(dh)_2NC_5H_5$, 28136-58-5; $(CH_3)_3SiCH_2Co(dh)_2NC_5H_5$, 42934-31-6.

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Cobalt-59 Nuclear Quadrupole Resonance Spectra of Phosphine- and Phosphite-Substituted Cobalt Carbonyl Compounds[1]

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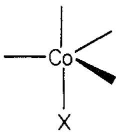
The ^{59}Co nuclear quadrupole resonance (nqr) spectra have been obtained for compounds of the form $XCo(CO)_3L$ and $XCo(CO)_2L_2$, where X is $(C_6H_5)_3Sn$ or other similar group IV metal derivative, and where L is $P(n\text{-}C_4H_9)_3$, $P(OCH_3)_3$, $P(OC_2H_5)_3$, or $P(OC_6H_5)_3$. The infrared spectra in the region of the CO stretching modes are also reported. The effect of axially substituted L on the quadrupole coupling constant *eQq* at cobalt in $XCo(CO)_3L$ depends on the σ-donor and π-acceptor characteristics of X. The results, which can be rationalized in a qualitative manner, indicate that an additive ligand partial field gradient model cannot be applied to compounds of this type without inclusion of interactive terms to account for the competitive π-acceptor effects of the ligands.

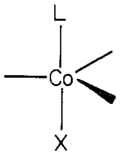
Introduction

The nuclear quadrupole coupling constant, *eQq*, and asymmetry parameter η describe the independent components of the electric field gradient (efg) tensor at a quadrupolar nucleus. The efg tensor is of interest as one of a relatively few observables which can be directly related to the ground state charge distribution in a molecule or ion. During the past few years there has been increased interest in the application of data derived from Mossbauer and pure nuclear quadrupole resonance spectra of solids to evaluating the charge distribution about transition metal atoms. Models in which the field gradient *q* is expressed in terms of additive contributions from the ligands which surround the metal have been employed with considerable success in certain types of compounds.[2]

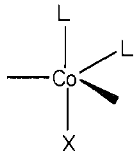
In our laboratory we have measured the ^{59}Co nqr spectra of several organometallic compounds containing five-coordinate cobalt (I), particularly those with the general formula, $XCo(CO)_4$, I.[3-5] In the present paper we report data on phosphine and phosphite substituted compounds $XCo(CO)_3$-L, II, and $XCo(CO)_2L_2$, III. The purpose of the investigation has been to determine the degree to which substitution alters the efg tensor at cobalt and to evaluate, if possible, the applicability of an additive ligand partial field gradient model to the results.



I



II



III

Results and Discussion

Nearly all the phosphine- and phosphite-substituted compounds synthesized in the course of this work are new compounds. Acquisition of nqr data has proved difficult. Several compounds failed to yield observable resonances despite repeated syntheses and spectrometer scans. Attempts to synthesize more highly substituted compounds, $XCo(CO)L_3$, failed to yield sufficient material for successful nqr work. Despite these difficulties, however, a substantial body of new nqr data, listed in Table I, has been acquired. The infrared spectra in the region of the CO stretching modes, taken in cyclohexane solution, are listed in Table II.

It is evident from the data in Table I that substitution can produce substantial changes in *eQq* at cobalt. The $XCo(CO)_3L$ compounds are all judged to be axially substituted, even though in a few cases the asymmetry parameter departs significantly from zero, the value it should have for strict threefold axial symmetry. Clark, *et al.*, have pointed out[6] that relatively small symmetry-breaking effects can produce large changes in η, while at the same time not greatly affecting *eQq*. It seems likely that the rather large values for η seen in all three $Ph_3MCo(CO)_3P(OPh)_3$ (Ph = phenyl) compounds are due to the particular conformations about the P-O and O-C bonds adopted in the coordinated ligand. Even in solution the axial symmetry at cobalt is less than

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(1) This research was supported by the National Science Foundation in part through Contract NSF GH-33634 with the Materials Research Laboratory, University of Illinois, and in part through research Grants GP 6396X and GP 30256X.

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Table I. ^{59}Co Nuclear Quadrupole Resonance Spectra at 27° of Substituted Cobalt Carbonyl Compounds

Compd	ν_3	ν_2	ν_1	eQq	η
$Ph_3GeCo(CO)_4$	22.486	15.641		109.63	0.05
$Ph_3SnCo(CO)_4$[a]	22.304	14.852		104.11	0.05
$Ph_3SnCo(CO)_3P(OCH_3)_3$	22.322	14.871		104.19	0.04
$Ph_3SnCo(CO)_2[P(OCH_3)_3]_2$	22.017	14.088	10.496	104.20	0.37
$Ph_3SnCo(CO)_3P(OPh)_3$	23.491	15.264		110.44	0.27
$Ph_3SnCo(CO)_2[P(OPh)_3]_2$	19.798	12.499		95.40	0.55
$Ph_3SnCo(CO)_3P(n\text{-}C_4H_9)_3$[b]	22.107	14.727		103.18	0.04
$Ph_3GeCo(CO)_3P(OPh)_3$	24.065	15.664	9.67	113.02	0.25
$Ph_3PbCo(CO)_3P(OPh)_3$	25.599	16.656		120.28	0.26
$(CH_3)_3SnCo(CO)_3P(OPh)_3$	22.259	14.830		103.88	0.03
$Cl_3SnCo(CO)_3P(OPh)_3$	34.167	22.768		159.46	0.03
$Hg[Co(CO)_4]_2$[c]	24.00	15.99		112.0	0.05
	23.75	15.81		110.8	0.0
$Hg[Co(CO)_3P(OPh)_3]_2$	24.387	15.844		114.65	0.27
	22.901	15.243		106.91	0.06

[a] From ref 3. [b] Resonances were observed at 65°; no lines were observed at room temperature. [c] From ref 4.

Table II. Infrared Spectra in the 1900–2100-cm^{-1} Range of Substituted Cobalt Carbonyl Compounds in Cyclohexane

Compd	ν_{CO}, cm^{-1}[a]		
$Ph_3SnCo(CO)_3P(OCH_3)_3$	2034 w	1971 s	1960 s
$Ph_3SnCo(CO)_2[P(OCH_3)_3]_2$	1974 s	1929 s	
$Ph_3SnCo(CO)_3P(OC_2H_5)_3$	2033 w	1971 s	1958 s
$Ph_3SnCo(CO)_3P(OPh)_3$	2038 w	1975 s	1966 s
$Ph_3SnCo(CO)_2[P(OPh)_3]_2$	1994 m	1943 s	
$Ph_3SnCo(CO)_3P(n\text{-}C_4H_9)_3$	1991 w	1948 br, s	
$Ph_3SnCo(CO)_3P(Ph)_3$	1989 w	1956 s	
$Ph_3GeCo(CO)_3P(OPh)_3$	2045 w	1980 s	1973 s
$Ph_3PbCo(CO)_3P(OPh)_3$	2035 w	1975 s	1967 s
$(CH_3)_3SnCo(CO)_3P(OPh)_3$	2030 w	1961 br, s	
$Cl_3SnCo(CO)_3P(OPh)_3$	2074 w	2017 br, s	
$Hg[Co(CO)_3P(OPh)_3]_2$	2050 w	2023 w	2013 w
	1990 w	1973 s	

[a] Key: s = strong, br = broad, m = medium, w = weak.

Table III. Changes in eQq Resulting from Axial Substitution of $XCo(CO)_4$ Compounds

X	$-\Delta eQq$, MHz	$\Delta eQq/(eQq)_0$	Ref
$eQq[XCo(CO)_4 - XCo(CO)_3P(n\text{-}C_4H_9)_3]$			
$(C_6H_5)_3Sn$	−1	−0.01	3, *a*
Cl_3Si	−17	−0.13	3, 5
Cl_3Ge	6	0.04	3, 5
Cl_3Sn	10	0.06	3, 5
$eQq[XCo(CO)_4 - XCo(CO)_3P(C_6H_5)_3]$			
$(C_6H_5)_3Ge$	3	0.03	*b*
$(C_6H_5)_3Sn$	9	0.09	*b*
Cl_3Ge	−3	−0.02	3, 5
Cl_3Sn	−2	−0.01	3,[c] *b*
$eQq[XCo(CO)_4 - XCo(CO)_3P(OC_6H_5)_3]$			
$(C_6H_5)_3Ge$	3	0.03	*a*
$(C_6H_5)_3Sn$	6	0.06	3, *a*
$(C_6H_5)_3Pb$	10	0.09	3, *a*
$(CH_3)_3Sn$	7	0.07	4, *a*
Cl_3Sn	−4	−0.025	3, *a*

[a] Present work. [b] A. N. Nesmeyanov, G. K. Semin, E. V. Bryuchova, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1936 (1969). [c] A 77°K value for $Cl_3SnCo(CO)_4$ was estimated from room-temperature data for comparison with the 77°K data for $Cl_3SnCo(CO)_3P(C_6H_5)_3$ (footnote *b*) by adding 2 MHz, since this is the change in eQq observed in the same temperature interval for $Cl_3GeCo(CO)_4$.

threefold, as evidenced by the relatively large splitting of the E species CO stretching mode in these compounds (Table II). The overall distribution of intensity in the ir CO stretching modes is, however, consistent with near-axial symmetry and quite inconsistent with cis substitution. A similar splitting occurs also in the ir spectrum of $Ph_3SnCo(CO)_3P(OCH_3)_3$, although η in this instance is only about 0.04. In $Cl_3SnCo(CO)_3P(OPh)_3$, η is nearly zero and the small ir splitting is incompletely resolved.

If a given ligand L possesses approximately the same σ- and π-bonding characteristics with respect to Co as CO, replacement of CO by that L would not result in significant alteration of the efg at cobalt. This seems to be the case for $P(OCH_3)_3$ substitution on $Ph_3SnCo(CO)_4$, since in the series $Ph_3SnCo(CO)_4$, $Ph_3SnCo(CO)_3P(OCH_3)_3$, $Ph_3SnCo(CO)_2[P(OCH_3)_3]_2$, involving both axial and equatorial replacement of CO, eQq does not vary significantly. The fact that the equivalence is not exact is shown by the substantial departure of η from zero in the disubstituted compound.

The nqr data for the series $Ph_3SnCo(CO)_4$, $Ph_3SnCo(CO)_3P(OPh)_3$, $Ph_3SnCo(CO)_2[P(OPh)_3]_2$ shows evidence that $P(OPh)_3$ is a significantly weaker σ donor than CO. The approximation that the populations of the cobalt 3d orbitals are the major factor in determining q_{zz} leads to the expression[3]

$$q_{zz} = q_{320}\,[N_{d_{z^2}} + {}^1\!/_2(N_{d_{xz}} + N_{d_{yz}}) - (N_{d_{xy}} + N_{d_{x^2-y^2}})]$$

where the N_d represent cobalt 3d orbital populations. The evidence accumulated to date strongly indicates that in $XCo(CO)_4$ compounds the last term, with the negative sign, is greater than the sum of the first two terms. If replacement of the axial CO by L leads to a net loss in the populations of the d_{z^2} and d_{xz},d_{yz} orbitals relative to the d orbitals in the equatorial plane, q_{zz} increases. This is what occurs on replacement of axial CO by $P(OPh)_3$ in $Ph_3SnCo(CO)_4$. When a second $P(OPh)_3$ is introduced, in an equatorial position, eQq is *lowered* considerably relative to the monosubstituted compound. The site symmetry at cobalt is reduced to C_s, which means that the orientation of q_{zz} is no longer confined to the Co–Sn bond axis. Nevertheless, if we assume that the replacement of CO by $P(OPh)_3$ is not a large perturbation, the lower value of eQq suggests that the populations of the equatorial d_{xy} and $d_{x^2-y^2}$ orbitals are decreased by the radial substitution. These observations are consistent with the hypothesis that $P(OPh_3)_3$ is a weaker σ donor than CO, and that its π-acceptor capability is not materially greater than that of CO and possibly less. The higher CO stretching frequencies for the $P(OPh)_3$ substituted compounds as compared with the analogous $P(OCH_3)_3$ derivatives (Table II) are consistent with the view that $P(OPh)_3$ is a relatively weaker σ donor and/or stronger π acceptor than $P(OCH_3)_3$.

Table III shows the change in eQq at cobalt resulting from axial substitution of CO by L in $XCo(CO)_4$ compounds. The results shown are taken from all the available literature as well as from Table I. The ΔeQq values represent comparatively small differences in large numbers. Variations in lattice effects might contribute as much as perhaps 1–2 MHz to ΔeQq. In a few instances one or both of the compounds in a given pair exhibits more than one eQq due to nonequivalence in the lattice. In these cases the average of the values, which differ by 2 MHz or less, has been employed. In one instance, it was necessary to estimate a value for eQq at 77°K from room-temperature data. Fortunately, the nqr data at both room temperature and 77°K are known for a few other compounds, so the estimate can be made with some confidence. All of the above factors taken together suggest that the ΔeQq values are not significant for our purposes at a level below about 2 MHz.

The results show first of all that the effect of a given axial substituent depends on the nature of the group trans to it. The fact that similar X groups lead to closely similar ΔeQq

for a given L supports the contention that the variations seen in ΔeQq are not merely random but are in fact related to the nature of both X and L. In $XCo(CO)_4$ compounds, the angles between the axial and radial Co–C bond axes are generally a few degrees greater than 90°. Substitution of phosphine or phosphite for axial CO should have the effect of making that angle nearer 90°. The very low infrared intensity of the highest frequency (A_1) carbonyl stretching mode is evidence that the equatorial CO groups are nearly coplanar in the $XCo(CO)_3L$ compounds. We assume, therefore, that the angular changes accompanying substitution are not important in determining ΔeQq.

The results in Table III can be accounted for by recognizing that bonding to the equatorial CO groups is affected by changes in bonding along the axis. When axial CO is replaced by a strong σ donor, weak π-acceptor group such as $P(n\text{-}C_4H_9)_3$, the net effect is an increased electron density at the metal, with concomitant raising of the metal d orbital energies. There is thus increased π bonding from d_{xz},d_{yz} to the radial CO groups (note the relatively low CO stretching frequencies in $Ph_3SnCo(CO)_3P(n\text{-}C_4H_9)_3$), as well as to the trans X group, if that group is a π acceptor. In purely empirical terms, it appears that when the trans group is a strong π acceptor ($SnCl_3$, $GeCl_3$) the lowering in $(N_{d_{xz}} + N_{d_{yz}})$ more than compensates for the increase in $N_{d_{z^2}}$ and decrease in $(N_{d_{xy}} + N_{d_{x^2-y^2}})$, with a resultant slight increase in eQq. As the trans group becomes a weaker π acceptor the loss of charge from d_{xz},d_{yz} *via* π bonding to X decreases, with the result that ΔeQq decreases and in fact becomes negative. We predict on the basis of these considerations that eQq for $(CH_3)_3SnCo(CO)_3P(n\text{-}C_4H_9)_3$ or $CH_3Co(CO)_3P(n\text{-}C_4H_9)_3$, as examples, will be considerably smaller than for the corresponding tetracarbonyl compounds.

When the substituting ligand is a moderately strong π acceptor, the situation is approximately reversed, apparently because of the ability of the ligand to withdraw charge from d_{xz},d_{yz} *via* π bonding. Thus, we find that when π-acceptor ligands such as $GeCl_3$ or $SnCl_3$ are trans to PPh_3 or $P(OPh)_3$, ΔeQq is slightly negative. On the other hand, the presence of a more weakly π-accepting trans ligand such as Ph_3M or $(CH_3)_3M$ leads to positive ΔeQq values. Under these circumstances the π-acceptor character of L is enhanced, and its σ-donor capabilities are relatively less important.

Whether or not these *ad hoc* explanations are found satisfying, the nqr results do show that the effect on the electron distribution at cobalt of a ligand which is potentially a π acceptor as well as a σ donor is significantly dependent on its position (axial *vs.* equatorial) and, in the case of axial substitution, on the ligand trans to it. A simple ligand additivity model requires that ΔeQq be a characteristic constant for each of the three ligands L in Table III. This is quite obviously not the case. It has already been recognized that a simple ligand additivity model might not apply in cases where ligands are capable of π-bonding interaction with the metal.[2,6] Unfortunately, the data base for five-coordinate species is as yet too limited to permit an evaluation of additional ligand parameters which might account for the discrepancies. Hopefully it will be possible to considerably enlarge the nqr data base by the application of more powerful pulse techniques for nqr spectroscopy.

In our view, a successful semiempirical field gradient model for organometallic compounds of the type studied here will require a term (or terms) expressive of the *interactions between* ligands. The interactive terms must represent the essentially competitive nature of the π-acceptor actions of the ligands and the coupling between σ-donor and π-acceptor aspects of a given ligand.

Experimental Section

Nuclear quadrupole resonance spectra were obtained as described previously.[3,4] Frequencies were determined to within about 0.005 MHZ. Infrared spectra were obtained on a Beckman IR-7 instrument, frequency calibrated using water vapor and gaseous CO spectra.

Most of the compounds reported here were prepared in a glove box with a dry nitrogen atmosphere. Tetrahydrofuran (THF) was distilled under nitrogen from sodium and/or $LiAlH_4$ and stored over sodium wire.

$(C_6H_5)_3GeCo(CO)_4$ and $Cl_3GeCo(CO)_4$ were prepared by previously published procedures.[7]

In a typical preparation of a monosubstituted compound $R_3M\text{-}Co(CO)_3L$, a THF solution of the appropriate group IV metal chloride, R_3MCl, was stirred for 15 min with a THF solution of a molar equivalent of $NaCo(CO)_3L$.

$Na(Co(CO)_3P(OC_6H_5)_3 \cdot 2THF$. The procedure of Hieber and Lindner[8] was employed in preparing this intermediate. The very air-sensitive compound was usually employed in subsequent reactions without isolation but can readily be isolated as the THF disolvate. The compound $[Co(CO)_3P(OC_6H_5)_3]_2$ was prepared as described previously.[9]

$(C_6H_5)_3GeCo(CO)_3P(OC_6H_5)_3$. In the glove box, 11 mmol of $NaCo(CO)_3P(OC_6H_5)_3$ in 100 ml of THF was added to a solution of 11.2 mmol of $(C_6H_5)_3GeCl$ in 20 ml of THF. The mixture was stirred for 15 min and the solvent removed under vacuum. Outside the glove box the residue was stirred with distilled water for 30 min. The dried crude product was recrystallized from di-*n*-butyl ether, yielding an off-white crystalline solid. The same procedure was employed in synthesizing $(C_6H_5)_3SnCo(CO)_3P(OC_6H_5)_3$ and $(C_6H_5)_3PbCo(CO)_3P(OC_6H_5)_3$. The latter compound is yellow.

$(CH_3)_3SnCo(CO)_3P(OC_6H_5)_3$. This compound is prepared as described for the triphenyl derivatives, except that recrystallization, from pentane, was carried out in the glove box because the product is air sensitive.

$Cl_3SnCo(CO)_3P(OC_6H_5)_3$. A solution containing 5.0 g (5.5 mmol) of $[Co(CO)_3P(OC_6H_5)_3]_2$ in 125 ml of CH_2Cl_2 was flushed with nitrogen, and 3.5 ml (30 mmol) of $SnCl_4$ was added. The mixture was stirred overnight and filtered and the filtrate reduced to near dryness under vacuum. The residue was extracted with 100 ml of hexane, from which the yellow product was recovered.

$Hg[Co(CO)_3P(OC_6H_5)_3]_2$. In the glove box, 11.0 mmol of $Na\text{-}Co(CO)_3P(OC_6H_5)_3$ in 100 ml of THF was added to 20 ml of THF containing 1.5 g (5.5 mmol) of $HgCl_2$. After stirring for 30 min, solvent was removed under vacuum. The residue was extracted with benzene and filtered and the yellow product precipitated by addition of pentane. It was recrystallized from cyclohexane.

$(C_6H_5)_3SnCo(CO)_3P(OCH_3)_3$. In the glove box 5.0 g (14.5 mmol) of $Co_2(CO)_8$ was dissolved in 100 ml of THF and the solution filtered to remove traces of insoluble impurities. To the filtrate was slowly added 7.0 ml (59.3 mmol) of $P(OCH_3)_3$. The mixture was stirred and heated to 60° for 30 min. Upon cooling to room temperature, the mixture was treated with 10% sodium amalgam; the solution turns yellow. After 30 min the solution was filtered and added to 20 ml of THF, containing 11 g (28 mmol) of $(C_6H_5)_3SnCl$, and stirred for 15 min. Solvent was removed under vacuum and the residue treated with methanol. The crude product was recovered as an off-white crystalline solid upon recrystallization from cyclohexane.

$(C_6H_5)_3SnCo(CO)_3P(C_6H_5)_3$. In the glove box 5.0 g (6.2 mmol) of $[Co(CO)_3P(C_6H_5)_3]_2$, prepared as previously described,[10] was stirred in 120 ml of THF with 10% sodium amalgam for about 18 hr. After filtering the filtrate was added to 20 ml of THF containing 4.8 g (12.5 mmol) of $(C_6H_5)_3SnCl$. The mixture was stirred for 15 min and solvent removed under vacuum. The residue was treated with distilled water for 30 min. Recrystallization from di-*n*-butyl ether yielded a pale yellow solid.

$(C_6H_5)_3SnCo(CO)_3P(n\text{-}C_4H_9)_3$. In the glove box 1.31 g (1.9 mmol) of $[Co(CO)_3P(n\text{-}C_4H_9)_3]_2$, prepared as described previously,[11] was treated with about 5% sodium amalgam in 50 ml of THF. After

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Table IV. Analytical Data (%)

	C		H		Co		Other		
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$Ph_3GeCo(CO)_3P(OPh)_3$	61.82	61.72	3.99	3.81	7.78	7.81			
$Ph_3SnCo(CO)_3P(OPh)_3$	58.31	58.38	3.76	3.78	7.34	7.30	14.78	14.56	(Sn)
$Ph_3PbCo(CO)_3P(OPh)_3$	52.53	52.61	3.39	3.52	6.61	6.68	23.23	22.82	(Pb)
$(CH_3)SnCo(CO)_3P(OPh)_3$	46.71	47.09	3.92	3.93	9.55	9.58	19.24	19.46	(Sn)
$Cl_3SnCo(CO)_3P(OPh)_3$	37.19	37.95	2.23	2.36	8.69	8.19	15.67	15.05	(Cl)
$Hg[Co(CO)_3P(OPh)_3]_2$	45.56	45.23	2.73	2.73	10.65	10.51	18.12	18.01	(Hg)
$Ph_3SnCo(CO)_3P(OCH_3)_3$	46.71	46.93	3.92	4.16	9.55	9.51	19.24	19.51	(Sn)
$Ph_3SnCo(CO)_3P(OC_2H_5)_3$	49.20	49.09	4.59	4.49	8.94	8.16	18.01	18.71	(Sn)
$Ph_3SnCo(CO)_3PPh_3$	62.02	61.99	4.00	3.99	7.80	7.80	15.72	15.36	(Sn)
$Ph_3SnCo(CO)_3P(n\text{-}C_4H_9)_3$	57.00	57.05	6.09	6.20	8.48	8.50	17.07	16.54	(Sn)
$Ph_3SnCo(CO)_2[P(OPh)_3]_2$	61.96	62.19	4.18	4.49	5.43	5.46	10.93	10.69	(Sn)
$Ph_3SnCo(CO)_2[P(OCH_3)_3]_2$	43.79	44.32	4.66	4.70	8.26	8.33	16.64	16.78	(Sn)

30 min the yellow solution was filtered and added to 1.5 g (3.9 mmol) of $(C_6H_5)_3SnCl$ in 10 ml of THF. The mixture was stirred for 30 min and solvent removed under vacuum. The residue was washed with water and purified by recrystallization from methanol.

$(C_6H_5)_3SnCo(CO)_2[P(OC_6H_5)_3]_2$. In the glove box $ClCo(CO)_2[P(OC_6H_5)_3]_2$ was prepared according to the procedure of Hieber and Duchatsch.[12] A procedure of the same workers[13] was then employed to obtain a solution of 2.7 mmol of $NaCo(CO)_2[P(OC_6H_5)_3]_2$ in 125 ml of THF. To this was added 10 ml of THF containing 1.05 g (2.7 mmol) of $(C_6H_5)_3SnC)$; the mixture was then stirred for 15 min. Solvent was removed under vacuum. The product was extracted with benzene. After filtration the desired product was precipitated as an off-white solid by addition of pentane.

$(C_6H_5)_3SnCo(CO)_2[P(OCH_3)_3]_2$. $CH_3Co(CO)_2[P(OCH_3)_3]_2$ was prepared using the procedure described by Heck.[14] In the glove box 4.9 g (12.1 mmol) of this material was dissolved in 10 ml of THF. A solution of 0.7 g (13 mmol) of $NaOCH_3$ in 15 ml of methanol was added and the mixture stirred for several hours. The solvent was removed under vacuum and the residue washed with pentane, filtered, and dried. It was stirred with 25 ml of THF and added to a solution of 4.8 g (12.2 mmol) of $(C_6H_5)_3SnCl$ in 20 ml of THF. The mixture was stirred 30 min and solvent removed under vacuum. The residue was stirred with methanol and filtered. The product was obtained as an off-white solid upon recrystallization from pentane.

Analytical data for all the compounds are presented in Table IV.

Registry No. $NaCo(CO)_3P(OC_6H_5)_3$, 32138-74-2; $(C_6H_5)_3GeCl$, 1626-24-0; $[Co(CO)_3P(OC_6H_5)_3]_2$, 21118-36-5; $SnCl_4$, 7646-78-8; $HgCl_2$, 7487-94-7; $NaCo(CO)_3P(C_6H_5)_3$, 33570-17-1; $(C_6H_5)_3SnCl$, 639-58-7; $NaCo(CO)_3P(n\text{-}C_4H_9)_3$, 29477-05-2; $NaCo(CO)_2[P(OC_6H_5)_3]_2$, 14564-38-6; $Ph_3GeCo(CO)_4$, 30406-47-4; $Ph_3SnCo(CO)_3P(OCH_3)_3$, 42989-50-4; $Ph_3SnCo(CO)_2[P(OCH_3)_3]_2$, 42989-51-5; $Ph_3SnCo(CO)_3P(OPh)_3$, 42929-50-0; $Ph_3SnCo(CO)_2[P(OPh)_3]_2$, 42989-52-6; $Ph_3SnCo(CO)_3P(n\text{-}C_4H_9)_3$, 42989-53-7; $Ph_3GeCo(CO)_3P(OPh)_3$, 42989-54-8; $Ph_3PbCo(CO)_3P(OPh)_3$, 42989-55-9; $(CH_3)_3SnCo(CO)_3P(OPh)_3$, 42989-56-0; $Cl_3SnCo(CO)_3P(OPh)_3$, 42989-57-1; $Hg[Co(CO)_3P(OPh)_3]_2$, 42989-58-2; $Ph_3SnCo(CO)_3P(OC_2H_5)_3$, 42989-59-3; $Ph_3SnCo(CO)_3P(Ph)_3$, 36158-66-4.

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Circular Dichroism of Diamine-*uns-cis*-Trimethylenediamine-*N,N'*-diacetatocobalt(III) Complexes

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A series of cobalt(III) complexes containing trimethylenediamine-*N,N'*-diacetate anion (TMDDA) and ammonia, ethylenediamine (en), trimethylenediamine (tn), 2,2'-dipyridyl (dipy), or 1,10-phenanthroline (phen) in the remaining two coordination positions were prepared and their optical isomers resolved. From the absorption and circular dichroism (CD) spectra the complexes are concluded to be the uns-cis isomers. The absorption and CD spectra for newly resolved *uns-cis*-$[Co(EDDA)(NH_3)_2]^+$ and newly prepared and resolved *uns-cis*-$[Co(EDDA)(tn)]^+$ are also reported. It was found that the central chelate ring size of EDDA and TMDDA and the ring size of bidentate ligands affect the shape of CD spectra in the same fashion.

Introduction

Circular dichroism (CD) studies[1-5] of Co(III) complexes with either ethylenediamine-*N,N'*-diacetate (EDDA) or the *N,N'*-dimethyl (DMEDDA) or *N,N'*-diethyl (DEEDDA) derivative coordinated in the s-cis geometry have been carried out extensively during the past several years. These s-cis complexes have been of interest because their CD spectra seem to depend primarily on the EDDA backbone[1,3,5] and the contribution from the asymmetric nitrogens.[4] The uns-cis isomers have been studied less extensively because of the difficulty in their isolation.[6] Legg[7] separated the four isomers of *uns-cis*-[Co(EDDA)(*S*-pn)]$^+$ by ion-exchange chromatography and *uns-cis*-[Co(EDDA)dipy]$^+$ has been resolved.[8] The preparation of *uns-cis*-EDDA

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