$(NO)^{2+}$. Trigonal-bipyramidal nitrosyl complexes usually contain a linear Co-NO moiety[22] (*cf.* $Co(NO)(das)_2{}^{2+}$ with ν_{NO} 1852 cm^{-1}); however, the expected increase in ν_{NO} from 1635 cm^{-1} (mull) is not seen in methanol. Therefore, the reactive nitrosyl complex in methanol is thought to be *cis*-$Co(en)_2(NO)(CH_3OH)^{2+}$, not the trans isomer as earlier[2] formulated based on electronic spectra.

The infrared spectrum (Figure 1) of $Co(en)_2(NO_2)Cl_2$, isolated from the NO oxidation of $Co(en)_2(NO)Cl_2$ in methanol, shows it to be the cis isomer; however it is solvated by methanol as shown by pmr data (Figure 3A) and elemental analysis. The CH_3OH:Co ratio of 0.3-0.5 suggests that methanol is not coordinated but instead is trapped in the solid lattice. This form of $Co(en)_2(NO_2)Cl_2$ is far more soluble in DMSO than an authentic sample of *cis*-$Co(en)_2(NO_2)Cl_2$. Recrystallization from HCl-H_2O removes the lattice methanol but leaves the methylene resonances unchanged (Figure 3B); the pmr spectrum of the methylene protons both before and after recrystallization is identical with that of the authentic cis isomer.

Production of *cis*-$Co(en)_2(NO_2)Cl_2$ from a methanolic solution of $Co(en)_2NO(CH_3OH)^{2+}$ is most simply explained by ligand oxidation with retention of the Co-N bond. On the other hand, formation of labile Co(II) would be expected to produce a mixture of cis and trans products; the free NO_2 produced concurrently could attack ethylenediamine[23] or, more probably, the solvent.[24] Neither is observed. Although we find no evidence for production of *trans*-$Co(en)_2(NO_2)Cl_2$ in the reaction under study, its formation and subsequent isomerization to the less soluble[5] cis isomer cannot be rigorously excluded. However, when the ligand oxidation was carried out at 0° for only 1 hr, in order to minimize isomerization, the isolated product was still entirely cis.

Conclusions

By varying the ratio of en to Co(II), three different reactions of NO have been characterized: 3:1, formation of $Co(en)_3Cl_3$ *via* oxidation; 2:1, oxidation of the intermediate nitrosyl complex to the nitro complex; 1:1, reductive nitrosylation in the presence of base. The reactivity of NO parallels that of O_2 (ligand and/or metal oxidation); however, the ability of NO and NO_2 to function as ligands limits its versatility. Although the exact role of pyridine in the oxidation of $Co(NO)(DMG)_2$ is not known, the possibility of ligand oxidation by excess NO in the preparation of nitrosyl complexes, especially when the nitrosyl may be characterized as NO^-, must be considered.

Acknowledgement. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. NO, 10102-43-9; *trans*-$Co(en)_2(NO)Cl_2$, 42741-15-1; $Co(en)_3Cl_3$, 13408-73-6; *cis*-$Co(en)_2(NO_2)Cl_2$, 14221-34-2; $Co(NO_2)(DMG)_2 \cdot py$, 42741-17-3; $Co(NO)(DMG)_2$, 36509-25-8.

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Solvent and Alkyl Substituent Effects on the Kinetics of Base Exchange in Alkylbis(dimethylglyoximato)cobalt(III)-Trimethyl Phosphite Complexes[1]

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The rate of dissociation of $P(OCH_3)_3$ from the methylatobis(dimethylglyoximato)cobalt(III)-$P(OCH_3)_3$ complex, $CH_3Co(dh)_2$-$P(OCH_3)_3$, was observed using nmr techniques in solvents of varying dielectric constant, and the rate at 100° was found to decrease by a factor of about 2 over the range of solvents from toluene to nitrobenzene. Replacement of protons in the OHO bridges of the planar ligand system by deuterium results in no observable change in the $P(OCH_3)_3$ dissociation rate. Substitution of axial CH_3 by haloalkyl groups results in a decrease in rate, which, however, does not follow the expected inductive order. Replacement of CH_3 by $(CH_3)_3SiCH_2$ results in an increase in rate. The relative ordering of dissociation rates in bromobenzene at 110° is $CH_2Si(CH_3)_3 > CH_3 > CH_2F > CHF_2 > CH_2Cl > CF_3 \approx CHCl_2 \approx CH_2Br > CHBr_2$. The ratio of fastest to slowest rate in the series is about 200. The base dissociation is thus shown to be subject to a strong trans effect due to alkyl group substitution.

The kinetics of ligand substitution and exchange in bis(dimethylglyoximato) complexes of cobalt(III) have been extensively studied.[2-5] It is evident that alkyl substituents on the axis normal to the planar ligand system strongly labilize the trans position. We have studied the kinetics of base ex-

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(1) This research was supported in part by The National Science Foundation through Grants GP6396X and GP30256X and Contract NSF GH-33634.

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change in methylatobis(dimethylglyoximato)cobalt(III)-base complexes ($CH_3Co(dh)_2$-L) using nmr techniques.[2] Base exchange was found to proceed by a first-order dissociative process, with no evidence of an interchange component. The order of stability of the complexes with respect to base exchange, *e.g.*, $P(n\text{-}Bu)_3 > CNCH_3 > P(C_6H_5)_3 > N(CH_3)_3 \sim SR_2 > O$ donors, suggests that the cobalt center may be viewed as a rather highly polarizable acid site and that for strongly π-acceptor ligands, π bonding from Co may contribute to the stability of the cobalt-ligand bond toward exchange. The latter conclusion is supported by thermochemical studies.[6]

In this article we report results of an attempt to characterize more fully the alkyl-trans base interactions by observation of the effect of changing the alkyl group on the rate of exchange of trimethyl phosphite. In addition, we report the effect of changing solvent on the rate of base exchange in $CH_3Co(dh)_2$-$P(OCH_3)_3$ and the results of an attempt to measure a secondary deuterium isotope effect on the exchange.

Results and Discussion

Solvent Effects. The kinetics of $P(OCH_3)_3$ exchange with $CH_3Co(dh)_2P(OCH_3)_3$ were observed in several solvents of varying dielectric constant. The results are summarized in Table I. The effect of an increase in solvent polarity on the reaction rate is shown in Figure 1, which depicts the calculated line shape for the CH_3 doublet in various solvents at 100° using the values of k_{100} given in Table I. The decrease in exchange rate with increasing solvent polarity, while very evident from the line shapes, is, however, not large. Arrhenius energies for the exchange process were determined from careful fitting of line shapes to spectra over a wide range of temperatures in several of the solvents; these values are also listed in Table I. In all cases listed the uncertainties in the E_a values are within 3 kcal/mol at the 99% confidence level, based on least-squares fitting of the data.

The effect of changing solvent polarity on the rate of trimethyl phosphite exchange, as evidenced by the data in Table I and Figure 1, suggests that the more polar solvents preferentially solvate the ground state as opposed to the transition state. This in turn suggests that the ground state of the molecules is more polar than the transition state in the dissociative process. The relatively small effect of changing solvent polarity on the rate, however, indicates that the change in polarity in the course of the reaction is not large. The fact that the rate and activation parameters are not different for $P(OCH_3)_3$ *as solvent* as compared with the others demonstrates clearly the purely dissociative character of the rate-determining step in the exchange process. This observation is consistent with results from earlier studies in which changes in the concentration of excess base did not alter the observed rates of base exchange.[2]

In view of the small range of values observed for k_{100} in the solvents, it seems extremely unlikely that the true value for E_a should vary significantly as a function of solvent. The two-site exchange system involved in this work is nearly ideal in terms of the degree to which the parameters necessary for the line shape analysis can be specified. It is of some interest, therefore, to explore the origin of the scatter in E_a values. One interesting possibility is that variation in dielectric constant of the solvent over the temperature range of interest could result in an apparent contribution to E_a. Using the isothermal dependence of rate on dielectric constant as a guide, it is possible to predict the direction in which k will vary as a result of the variation in solvent dielectric constant with temperature. The general problem has been discussed at length by Moelwyn-Hughes.[7] Application of these considerations to the present case suggests that the effect is likely to result in an increase in observed E_a of at most 1 kcal/mol in the most polar solvent as compared with the least polar.

Accordingly, we must assume that subtle variations in certain features of the nuclear spin system, which are determined by properties of the solvent, intrude upon the analysis in terms of the simple Bloch equations, to produce the scatter in E_a shown in Table I. A possible source of error in our line shape analysis is the assumption that values of T_{2A} and T_{2B}, given by $1/\pi\Delta_{1/2}{}^{\circ}$ (obtained from spectra in the stopped exchange temperature region) are temperature invariant.

Table I. Solvent Effect on Kinetics of $P(OCH_3)_3$ Exchange from $CH_3Co(dh)_2P(OCH_3)_3$

Solvent	$\epsilon_{100}{}^{c}$	k_{100}, sec^{-1}	$E_a{}^{a}$	A, sec^{-1}	$\Delta H^{\ddagger a}$	$\Delta S^{\ddagger b}$
$C_6D_5CD_3$	2.2	24.7	21.8	1.4×10^{14}	21.0	3.8
C_6H_5Br	4.4	20.3	22.9	5.0×10^{14}	22.1	6.3
$P(OCH_3)_3$	?	20.1	23.6	1.4×10^{15}	22.9	8.3
$CL_2CHCHCl_2$	6.5	18.4	25.6	1.9×10^{16}	24.9	13.5
$Cl(CH_2)_4Cl^{d}$	6.6	18.0	d			
$O\text{-}C_6H_4Cl_2$	7.1	16.6	24.0^{d}	1.9×10^{15d}	23.2^{d}	8.9^{d}
$O\text{-}C_6H_4ClBr$	5.4	15.6	25.4	1.3×10^{16}	24.7	12.7
$O\text{-}C_6H_4NO_2(CH_3)$	15.4	16.6	23.4	8.8×10^{14}	22.7	7.4
$C_6H_5NO_2$	23.6	11.9	24.0	1.4×10^{15}	23.3	8.4

[a] kcal mol^{-1}. [b] cal deg^{-1} mol^{-1}. [c] Estimate based on values of ϵ extrapolated to 100° from lower temperature values: A. A. Maryoff and E. R. Smith, *Nat. Bur. Stand.* (*U. S.*) *Cir.*, **No. 514** (1951). [d] Arrhenius plot shows large scatter.

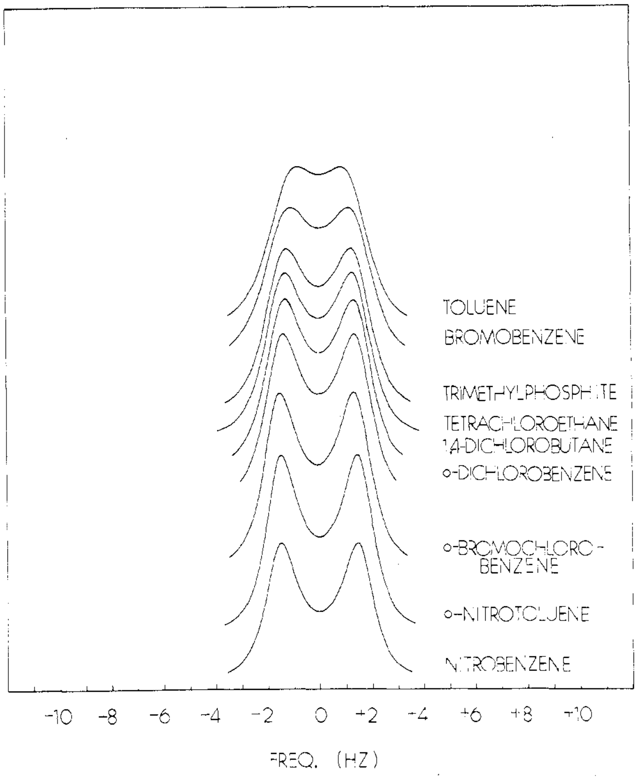

Figure 1. Calculated line shapes using k_{100} values (Table I) for trimethyl phosphite dissociation from $CH_3Co(dh)_2P(OCH_3)_3$ in various solvents at 100°.

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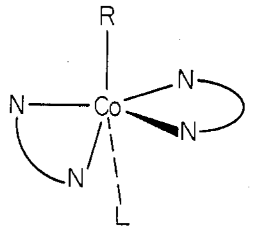
The possibility exists that at higher temperature the proton relaxation times are changed as a result of the changed solvent properties. For example, the spin-lattice relaxation time for ^{59}Co, which should be very temperature dependent since it is dominated by quadrupolar relaxation, could produce an effect on T_2 at the protons *via* the scalar interaction between these protons and cobalt. It is not easy to test this point in the present case, because the changes, if they occur, are not large. Indeed, if it were not for the small separation of the lines, small variations in T_2 would have no observable effect.

Secondary Deuterium Isotope Effect. In an attempt to define further the transition state in the dissociative process we have observed the magnitude of the secondary isotope effect resulting from deuteration of the protons in the OHO bridges in the planar ligand system. These bridges represent examples of especially strong hydrogen bonding; the OHO stretching frequency is in the vicinity of 1750 cm^{-1}.[8,9] If the frequencies of the OHO bridge vibrational modes are materially changed in the transition state relative to the ground state, the difference in zero-point energies makes a significant contribution to $\Delta G^{\ddagger}$.[10] Replacement of protium by deuterium in this case should then lead to a significant alteration in rate. For example, we assume that the OHO asymmetric stretching mode, ν_s, is at 1750 cm^{-1} and calculate the ratio k_H/k_D at 100°, assuming that the only effect of deuterium substitution in the bridge is a decrease in ν_s by the factor of $1/\sqrt{2}$. The ratio k_H/k_D for an increase in ν_s (which would correspond to an increase in $d(O\cdots O)$) of about 300 cm^{-1} in going to the transition state is 0.85. For a decrease of 300 cm^{-1} (corresponding to a decrease in $d(O\cdots O)$), k_H/k_D is 1.17.

In addition to ν_s there are two other modes, the O-H in-plane bend, ν_b, and the out-of-plane N-OH torsion, ν_t, whose frequencies are liable to alter in formation of the transition state.[11] These modes are known to increase in many instances upon hydrogen-bond formation, but the indications are that their relative changes with increasing strength of the hydrogen bond are considerably smaller than for ν_s. Unfortunately, ν_b and ν_t have not been assigned with any degree of rigor in the cobaloxime case, but the tentative assignments to the 980-880-cm^{-1} region[10] suggest that they are not likely to undergo a large shift in forming the transition state. Furthermore, the zero-point vibrational energies associated with the lower frequency modes are smaller than for ν_s.

A detailed comparison was made of the nmr line shapes for $P(OCH_3)_3$ exchange from $CH_3Co(dh)_2P(OCH_3)_3$ in C_6H_5Br for the protium-bearing compound and that with >95% deuterium in the bridge positions. No difference in line shapes was discernible at temperatures around the coalescence temperature, where line shape is very sensitive to small changes in rate. We therefore conclude that $k_H/k_D = 1.00 \pm 0.15$, where the uncertainty involves an estimate of possible short term temperature fluctuations, as well as line shape uncertainties. It thus appears very likely that the OHO stretching mode changes frequency by no more than about 400 cm^{-1} in the transition state configuration during $P(OCH_3)_3$ dissociation. (A factor of 100 cm^{-1} was added to the estimated limit to allow for a small countering effect from ν_b and ν_t changes of opposite sign.) The empirical relationships between OHO stretching frequency and $O\cdots O$ distance are fairly linear in the region around $d(O\cdots O)$ ∿0.245 nm, with a slope ∿50 cm^{-1}/0.001 nm.[12] Thus, a 400-cm^{-1} change in frequency would correspond to an alteration in $d(O\cdots O)$ of about 0.008 nm.

The results of the deuteration study rule out the possibility that changes in the energy of the OHO bond bridges contribute significantly to $\Delta G^{\ddagger}$ for phosphite dissociation. They also limit to some degree the possible geometrical arrangement in the transition state. It seems very unlikely, for example, that the transition state could involve extensive distortion toward a trigonal bipyramidal intermediate, as in I. On the other hand, the results do not preclude a substantial movement of the cobalt out of the plane as in II.



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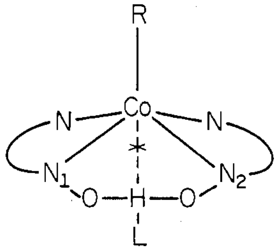

II

If the cobalt were raised 0.035 nm above the plane defined by the four nitrogens, and if the Co-N bond distances and the geometry of each dimethylglyoxime molecule remained unchanged, the N_1-N_2 distance would decrease by about 0.0086 nm. The resultant change in $O\cdots O$ distance could be less than this, because if the $O\cdots O$ repulsive forces change steeply with O-O distance in this range, much of the compression would be relieved *via* N-O bending. In the five-coordinate alkyl cobalt complex methylato-*N,N'*-ethylenebis(acetylacetoniminato)cobalt(III),[13] the cobalt is in a roughly square-pyramidal configuration, about 0.012 nm above the mean plane of the four basal coordinating atoms. It thus appears that II is a reasonable model for the transition state in the dissociation of $P(OCH_3)_3$ from $CH_3Co(dh)_2P(OCH_3)_3$.

Effect of Alkyl Substitution. The kinetics of ligand exchange from $CH_3Co(dh)_2P(OCH_3)_3$ are readily followed by observation of the doublet in the proton magnetic resonance spectrum due to the scalar interaction of the axial methyl group or planar ligand methyl protons with ^{31}P of the trans base. Exchange of base results in collapse of these doublets. Table II lists several alkyl groups trans to the exchanging base which were studied, the solvent in which the exchange was evaluated, the coalescence temperature T_c, the value for the ^1H-^{31}P coupling (J_{obsd}), giving rise to the doublet used in the kinetics evaluation, and additional data derived from analysis of the nmr line shapes over a range of temperatures.

Because of poor signal-to-noise characteristics for the protons of the haloalkyl groups, it was necessary to employ the methyl resonance of the planar ligands in the line shape studies. The scalar interaction with ^{31}P is considerably smaller than ^{31}P coupling to the trans methyl. Nevertheless, the rate constant for base exchange can be estimated with fairly good accuracy at the coalescence temperature. This procedure, however, does not facilitate comparisons among

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Table II. Nmr and Ligand Exchange Parameters for $RCo(dh)_2P(OCH_3)_3$ Compounds

R group	J_{obsd}, Hz	T_c	k_{110}
		C_6H_5Br	
CH_3	6.8	104	48 ± 5
CH_2F	3.5	100	35 ± 5
CHF_2	3.4	101	24 ± 4
CF_3	3.0	$\sim$130	3.0 ± 0.7
CH_2Cl	3.5	118	8.4 ± 1
$CHCl_2$	3.0	128	3.4 (+0.9, −0.5)
CH_2Br	3.5	$\sim$130	3.5 ± 1
$CHBr_2$	3.1	$\sim$138	1.8 ± 0.7
$CH_2Si(CH_3)_3$	5.0	75	380–280[a]
		Other Solvents	
CH_2F[b]	3.5	95	53 ± 10
CH_2Br[c]	3.5	128	4 ± 0.8
$CHCl_2$[c]	3.0	$\sim$130	3 ± 0.7
$CHBr_2$[c]	3.1	$\sim$138	$\sim$2
CF_3[d]	3.0	$\sim$130	3.0

[a] The upper and lower estimates are based on assumed E_a values of 23 and 20 kcal/mol, respectively. [b] $C_6D_5CD_3$. [c] $O\text{-}C_6H_4BrCl$. [d] $Cl_2CHCHCl_2$.

alkyl groups. For this purpose it is most desirable to have relative rate constants at a given temperature. Accordingly, we obtained line shapes whenever possible for each compound over a range of temperature in the exchange region. From these observed line shapes we obtained, through line shape fitting procedures, estimates for the reciprocal exchange time, τ_e, and, from these, estimates of the rate constants for exchange. The Arrhenius plot for $P(OCH_3)_3$ exchange in the CH_3 compound has been reported previously.[2] The experiment has been redone in connection with the present work, using a modified line shape fitting procedure, with precisely the same result. Because the coupling constant J_{obsd} is so small for the other systems, accurate fittings of the line shapes are possible only over a rather narrow range of temperatures. We cannot hope, therefore, to obtain particularly accurate values for the Arrhenius energies. Values of E_a on the order of 28 kcal/mol were obtained for several of the haloalkyl compounds which could be studied in bromobenzene over the temperature interval of interest. The uncertainties in these Arrhenius energies are fairly large, on the order of 5 kcal/mol at the 90% confidence level. Accordingly, we have assumed an E_a value of 23 kcal/mol in arriving at estimates of the rate constant for base exchange at 110° on the basis of data obtained at higher temperatures. In the case of the $(CH_3)_3SiCH_2$ substituent, E_a was also assumed to be at most 23 kcal/mol in extrapolating upward to 110° from the observed coalescence at 75°. The resultant values for the rate constants for base exchange at 110°, k_{110}, are listed in Table II, along with estimates of the uncertainties based on the uncertainty in the rate constant and/or coalescence temperature and assuming a ±3 kcal/mol uncertainty in E_a. Because the interval of extrapolation is rather small, the likely errors incurred in even the worst case are not too serious. The coalescence temperature for the $CHBr_2$ and CF_3 compounds could not be reached before the compound had undergone some decomposition. It was possible, however, to make a rough estimate of the rate at the highest temperature observed from the line shape, since extensive line broadening was evidenced at this point. While the resultant estimated values τ_c are probably not far from correct, the associated uncertainties are larger than for the other compounds.

Increased electron withdrawal on the part of the alkyl group, as a result of halogen substitution, results in a slowing in the kinetics of trimethyl phosphite exchange. On the other hand, substitution by a more electron-releasing alkyl group such as $(CH_3)_3SiCH_2$ results in increased exchange rate. The general results are thus those to be expected on the basis of simple inductive considerations. The powerful trans effect exerted by the alkyl groups is evident from the wide range in values of k_{110}, which span more than two orders of magnitude. We were unable to synthesize reasonably pure samples of the trichloromethyl or tribromomethyl compounds.

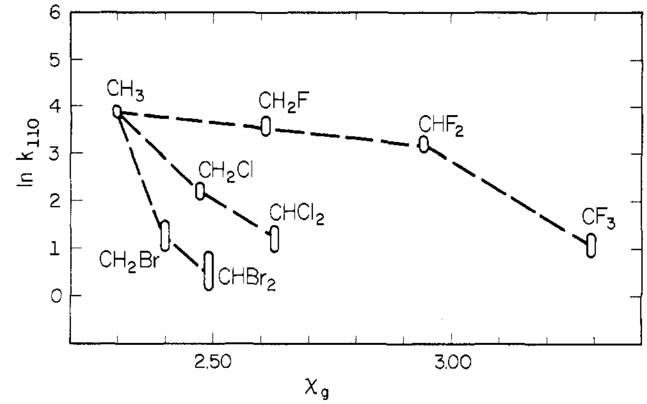

Figure 2. Log rate constants for dissociation of trimethyl phosphite from $RCo(dh)_2P(OCH_3)_3$ at 110° as a function of the group electronegativity of R.

Comparisons of relative rates among the haloalkyl groups raise several interesting questions. Figure 2 shows a graph of log k_{110} *vs.* the effective group electronegativity of the alkyl group.[14,15] This graph reveals that the alterations in rate resulting from halogen substitution are not those expected on the basis of simple inductive considerations. The decrease in exchange rate upon successive replacement of hydrogen by fluorine results in a decrease in k_{110} of only about an order of magnitude in going from CH_3 to CF_3. Replacement of hydrogen by chlorine or bromine, on the other hand, results in a much larger decrease in exchange rate. Bromine substitution results in an even larger decrease in rate than for chlorine, again contrary to expectations based upon their relative electronegativities.

It seems unlikely that the unusual effects observed can be ascribed to a simple steric interaction between the haloalkyl groups and the planar ligand system. The size of the substituted alkyl group increases in the order F < Cl < Br. In order that repulsive interactions with the planar ligand be responsible for a decreased rate of base dissociation, the haloalkyl groups would have to experience a *larger* degree of steric interaction with the planar ligands in the transition state as compared with the ground state. Since the rate process is, however, dissociative, with no evidence of an interchange component, the cobalt is approaching five coordination, as in II. This situation should result in less, not more, steric repulsion between the haloalkyl group and the planar ligands. We should thus observe, if anything, a steric acceleration of rate.

There is, however, another source of repulsive steric interaction which would give rise to the observed effects on the rate of base dissociation, namely steric repulsive interaction between the halogen atoms and the filled d_{xz},d_{yz} orbitals on cobalt. This form of repulsive interaction would be increas-

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Table III. Analyses of Compounds

R	Formula	Mol wt	Calcd			Found		
			% C	% H	% N	% C	% H	% N
			$RCo(dh)_2P(OCH_3)_3$					
CH_3	$C_{12}H_{26}O_7N_4PCo$	428.3	33.65	6.12	13.08	33.53	6.14	12.95
CH_2F	$C_{12}H_{25}O_7N_4FPCo$	446.3	32.29	5.66	12.56	31.89	5.35	12.42
CH_2Cl	$C_{12}H_{25}O_7N_4ClPCo$	462.7	31.15	5.45	12.11	31.88	5.69	12.38
CH_2Br	$C_{12}H_{25}O_7N_4BrPCo$	507.2	28.42	4.98	11.05	28.71	5.17	11.17
CHF_2	$C_{12}H_{24}O_7N_4F_2PCo$	464.2	31.04	5.22	12.07	31.25	5.17	12.16
$CHCl_2$	$C_{12}H_{24}O_7N_4Cl_2PCo$	497.1	28.99	4.87	11.27	28.88	4.88	11.57
$CHBr_2$	$C_{12}H_{24}O_7N_4Br_2PCo$	586.1	24.59	4.13	9.56	25.00	4.29	9.44
			$RCo(dh)_2NC_5H_5$					
CF_3	$C_{14}H_{19}O_4N_5Co$	437.3	38.45	4.39	16.02	39.92	4.63	16.38
$(CH_3)_3SiCH_2$	$C_{13}H_{30}O_4N_5SiCo$	455.5	44.82	6.65	15.38	45.27	6.69	15.03

ed by any alteration in molecular geometry which increased the nonbonding electronic charge density on the side of the molecule opposite the departing ligand. But if the transition state has the geometry depicted in II, and if there is some degree of orbital following as the geometry changes in passing to the transition state, an increase in nonbonding charge density on the alkyl side of the molecule is precisely what does occur. An analysis of this situation, in terms of orbital rehybridization, has been given by Bennett and Mason.[16] We propose, therefore, that a steric repulsion between the nonbonding d_{xz},d_{yz} electrons on cobalt and the nonbonding electrons on chlorine and bromine is responsible for a steric inhibition of dissociation.

There is yet another consequence of the proposed repulsive interactions which could have an appreciable effect on the kinetics of trimethyl phosphite exchange. The repulsive interaction between the halogen and the d_{xz},d_{yz} electrons would be reduced by a π-back-bonding interaction between cobalt and phosphorus. There are both kinetic and thermodynamic lines of argument for supposing that such an interaction exists in the methyl compound.[2,6] Now replacement of methyl by haloalkyl groups should reduce the extent of π bonding, since increased electron withdrawal by the alkyl group increases the effective charge on cobalt and lowers the energy of the nonbonding d electrons. Thus, in the series CH_3-CH_2F-CHF_2-CF_3, the increased acid strength of cobalt toward phosphite in the σ bond is partially offset by the concomitant loss of π-back-bonding stabilization. (It might be noted parenthetically that fluoroalkyl groups have essentially the same van der Waals radii as methyl, so there is no steric contribution to the kinetics.) In the fluoroalkyl series, therefore, the rate does not change dramatically. In the chloro and bromo series, on the other hand, π back bonding may be promoted by the steric repulsion described above, further stabilizing the cobalt-phosphorus bond against dissociation.

Experimental Section

Materials. The trimethyl phosphite adduct of methylatobis(dimethylglyoximato)cobalt(III) was prepared from the ligand-free dimer, which in turn was prepared by removal of water from methylaquocobaloxime by heating *in vacuo* at 80° for several hours. The methylaquocobaloxime was prepared by previously described procedures.[17] To prepare the adduct, freshly distilled trimethyl phosphite was added to a benzene solution of dimer, followed by removal of the solvent to give the crystalline yellow solid. Deuteration of this compound was achieved *in situ* by the addition of 50 μl of D_2O to 1 μl of a bromobenzene solution of the trimethyl phosphite adduct. In separate experiments it was determined that the presence of small amounts of water in bromobenzene does not affect the trimethyl phosphite exchange rate.

Most of the desired halomethyl cobaloximes were synthesized using the general procedure outlined by Schrauzer for the synthesis of methyl(pyridinato)cobaloxime,[18] substituting $P(OCH_3)_3$ for pyridine. In all but one synthetic effort, the halomethyl bromides were used as alkylating agents. CH_2ClBr, $CHCl_2Br$, and CCl_3Br were purchased from the Aldrich Chemical Co. and used without further purification after routine examination by proton nmr. CH_2Br_2 was used after simple distillation. $CHBr_3$, CH_3I, and $(CH_3)_3SiCH_2Cl$ were used without further purification, as were the CHF_2Br and CF_3Br gases obtained from Matheson Chemical Co. The purity of each newly synthesized cobaloxime was deduced by elemental analysis and proton nmr spectra, obtained in methylene chloride or bromobenzene. The elemental analyses are given in Table III.

The monofluoromethylcobaloxime was isolated from a reaction mixture to which CHF_2Br had been added. To isolate the difluoromethylcobaloxime, it was necessary to prepare the aquo adduct, remove the bound water *in vacuo* at 80°, and add trimethyl phosphite to the ligand-free material. The trifluoromethylcobaloxime adduct of pyridine was first synthesized and characterized.[19] The pyridine was then replaced *in situ* by excess trimethyl phosphite. The same procedure which was used to prepare the CF_3 cobaloxime was used to prepare $(CH_3)_3SiCH_2Co(dh)_2P(OCH_3)_3$ *in situ*.

Nmr samples used for line shape analysis were degassed and sealed under vacuum and stored in Dry Ice-acetone slushes until ready for use. Except for the study carried out in neat $P(OCH_3)_3$, free $P(OCH_3)_3$ was present in one to three times the concentration of complex.

All solvents were distilled and stored over freshly activated Linde 4A molecular sieves. The observed boiling ranges of solvents used for nmr studies were: toluene, 111-112°; bromobenzene, 155-156°; 1,1,2,2-tetrachloroethane, 142-143°; 1,4-dichlorobutane, 155-156°; *o*-dichlorobenzene, 176-177°; *o*-bromochlorobenzene, 205-207°; *o*-nitrotoluene, 224°; nitrobenzene, 207-209°; and methylene chloride, 39.5-40.5°. Trimethyl phosphite was freshly distilled (boiling range 111-112°) prior to use.

Nmr Spectra. Varian Model T-60, A60A, A56/60, and HA-100 spectrometers were used to obtain the nmr spectra. All line shape studies were carried out on the A-56/60 and HA-100 instruments, both equipped with Varian temperature controllers. Temperature measurements were made using an iron-constantan thermocouple with frequent calibrations made with methanol and ethylene glycol standards. The accuracy of the measurements is estimated at ±2°.

Line Shape Analyses. The nmr spectra were analyzed on a Xerox Data Systems Sigma 5 computer using a general two-site computer program. Input parameters were (1) 20 to 30 ordered pairs of shift and intensity of absorption, the sum of which defines the observed line shape, (2) the chemical shift difference between the two exchanging sites, (3) the relative population of the downfield A site (P_A), and (4) the transverse relaxation times of sites A and B (T_{2A} and T_{2B}). An iterative fitting routine is included to calculate the best value of τ_e, the exchange parameter, for a given set of input parameters. The first-order rate constant for the dissociation k_1 was obtained from the relationship $k_1 = 1/2\tau_e$ which reduces to $k_1 = 1/\tau_e$ in the special case where the exchange sites are produced by scalar coupling to a single nucleus of spin $^1/_2$.

Input parameters were optimized by a supplementary program

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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; $CH_2FCo(dh)_2P(OCH_3)_3$, 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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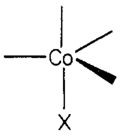
The ^{59}Co nuclear quadrupole resonance (nqr) spectra have been obtained for compounds of the form $XCo(CO)_3L$ and $XCo(CO)_2L_2$, where X is $(C_6H_5)_3Sn$ or other similar group IV metal derivative, and where L is $P(n\text{-}C_4H_9)_3$, $P(OCH_3)_3$, $P(OC_2H_5)_3$, or $P(OC_6H_5)_3$. The infrared 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 $XCo(CO)_3L$, 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.



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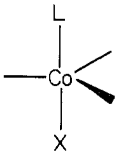
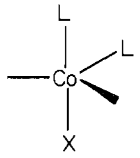


II



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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