whereas the Pt–Cl (bridging) stretching force constant is much smaller than those of Zeise's salt. This result suggests that the bridging Pt–Cl bond is much weaker than the terminal Pt–Cl bond. A similar result has been obtained from the normal coordinate analysis of the Al_2Cl_6 molecule[15] which yielded the values of 2.35

and 1.05 mdyn/Å for the terminal and bridging Al–Cl stretching force constants, respectively.

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Kinetics of Ligand Exchange in Tetrahedral Complexes. Ligand Exchange with Some Tertiary Phosphine Complexes of Nickel(II) and Cobalt(II) by Proton Magnetic Resonance[1]

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Abstract: The kinetics of exchange of ligand, L, in pseudo-tetrahedral complexes of the type ML_2X_2 (where M = Co, Ni; X = Cl, Br, I; and L = triphenylphosphine, tri-*p*-tolylphosphine, or *n*-butyldiphenylphosphine) with excess phosphine has been studied in deuteriochloroform solution. Kinetic parameters for the exchange between −60 and 60° have been obtained by proton magnetic resonance by using shift and line-width techniques. The ligand exchange follows second-order kinetics with the nickel(II) complexes being more labile than their cobalt(II) analogs. The lability of a particular series increases slightly in the order I < Br < Cl. The new dihalobis(*n*-butyldiphenylphosphine)cobalt(II), $Co(BPP)_2X_2$, complexes have kinetic parameters for ligand exchange similar to those of the triarylphosphines.

A kinetic study of triphenylphosphine (TPP) exchange with some pseudo-tetrahedral complexes was recently reported by us in a preliminary communication.[2] This was the first reported investigation of ligand exchange in "tetrahedral" divalent first-row transition metal complexes. Results of this sort are important in establishing the mechanism of ligand exchange and assessing the importance of ligand-field effects in this class of compound. We present here a more comprehensive account of this work and have extended the study to chloro as well as bromo and iodo complexes. The study of tri-*p*-tolylphosphine (TTP) complexes enabled us to use an alternative nmr shift technique in addition to the line-width method employed earlier.[2] The pmr spectra of these complexes are well known[3–5] as is their pseudo-tetrahedral structure in solution.[6–10]

The new dihalobis(*n*-butyldiphenylphosphine)cobalt(II) complexes were synthesized in order to determine the effect on the ligand-exchange kinetics of substitution of an aryl group by an alkyl group.

Procedure

Nuclear magnetic resonance techniques for studying exchange kinetics are well known and have frequently been applied to systems reported in the current literature.[11–15] Two of these methods were used in this study.

Method I. Kinetic parameters can be obtained from the measured line width at half-height, $\Delta\nu_{1/2}$ (cps), of an isotropically shifted[3] resonance of a proton on a coordinated ligand. In such a system the effective transverse relaxation time of a ligand proton, T_2, is given by $(1/T_2) = \pi\Delta\nu_{1/2}$. This is related to T_{2m}, the transverse relaxation time in the absence of exchange, and τ_m, the average residence time of a ligand in the complex, by[12,16]

$$1/T_2 = 1/T_{2m} + 1/\tau_m \tag{1}$$

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Equation 1 is valid under conditions of slow exchange where $\tau_m \Delta \omega_m \gg 1$ ($\Delta \omega_m$ is the difference in resonance frequency for coordinated and uncoordinated ligand). A practical limitation to the application of method I is that the complex concentration must be great enough to permit accurate measurement of the line widths.

Method II. Swift and Connick[11] extended McConnell's solution[17] of the modified Bloch equations to conditions of dilute solutions of paramagnetic ions. This gave eq 2 for the shift of the excess ligand resonance from its diamagnetic position, $\Delta \omega_f$, in the presence of a small concentration of complex. P_m is the mole

$$\Delta \omega_f = \frac{P_m \Delta \omega_m}{[(\tau_m/T_{2m}) + 1]^2 + (\tau_m \Delta \omega_m)^2} \quad (2)$$

ratio of coordinated to total ligand and the remaining symbols have been defined previously. Equation 2 can be solved for τ_m as a function of temperature provided $1/T_{2m}$ and $\Delta \omega_m$ are known as a function of temperature. These quantities are best obtained from measurements at low temperatures where exchange is slow and separate resonances are observed for coordinated and uncoordinated ligand. The low-temperature data can be extrapolated to higher temperature regions since $\Delta \omega_m$ and $\log(1/T_{2m})$ are proportional to $1/T$.

Both methods give τ_m as a function of temperature. For first-order kinetics, $1/\tau_m = k_1$, while for second-order kinetics $1/\tau_m = k_2[\text{ligand}]$. The second-order rate constant for ligand exchange is given by

$$k_2 = \frac{kT}{h} \exp\left[\frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}\right] \quad (3)$$

where $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are the entropy and enthalpy of activation, respectively. Kinetic parameters may be obtained by plotting $\log(k_2/T)$ vs. $1/T$.

Experimental Section

Preparation of the Complexes. The TPP and TTP complexes were prepared as outlined by Venanzi, et al.,[6,7] and Chatt.[18] They were characterized by their melting point, color, and pmr spectra. n-Butyldiphenylphosphine (BPP) was prepared by the method of Venanzi.[19]

Dibromobis(n-butyldiphenylphosphine)cobalt(II). Boiling ethanol solutions of cobalt(II) bromide hexahydrate (3.4 g) and BPP (5.0 g) were mixed and caused the rapid precipitation of light blue crystals which were collected and vacuum dried, mp 179–181°.

Diiodobis(n-butyldiphenylphosphine)cobalt(II). Sodium iodide (3.0 g) and cobalt(II) nitrate hexahydrate were mixed in ethanol and the solution was filtered. The filtrate was heated and added to 5.0 g of BPP in boiling ethanol. The resulting brown crystals were separated by filtration and vacuum dried, mp 180° dec.

Anal. Calcd for $C_{32}H_{38}P_2I_2Co$: C, 48.20; H, 4.80. Found: C, 48.09; H, 5.00.

Pmr Spectra. The pmr spectra were obtained by using a Varian A-60-A instrument equipped with a variable-temperature probe. The spectra were calibrated by using a wide-range oscillator and frequency counter to impress side bands of the internal standard, 1% tetramethylsilane (TMS), onto the spectra. Line-width and shift data were recorded to within ±1 cps. Samples were prepared by weighing out vacuum-dried complex in dried 2-ml volumetric flasks. The excess ligand was added quickly and diluted to volume with freshly dried (over sodium carbonate) deuteriochloroform, 1%

in TMS. The nmr tubes were dried by heating *in vacuo*. The dried tubes were filled with dry nitrogen and the sample was introduced, all under nitrogen. The sample tubes were frozen in liquid nitrogen and degassed by pumping followed by thawing, refreezing, and further pumping. These precautions must be taken in order to achieve reproducible results.

Magnetic Susceptibilities and Optical Spectra. Solution susceptibility measurements on deuteriochloroform solutions, 2% in TMS, 0.8 M in the $Co(BPP)_2X_2$ complexes, were taken by Evans' method.[20] At 40°, $10^6\chi_m^{cor}$ (μ_{eff}) = 8221 cgs units (4.55 BM) and 7629 cgs units (4.38 BM) for X = Br and I, respectively. Optical spectra were recorded on a Cary Model 14 recording spectrophotometer with complex concentrations $\sim 10^{-3}$ M in methylene chloride as solvent.

Results

TPP Complexes. Since the chemical shifts for the *ortho*, *meta*, and *para* protons of diamagnetic TPP all occur in a narrow range,[21] only method I is suitable for a kinetic study. The line-width variation of the downfield shifted *meta*-proton resonance was used to obtain the kinetic parameters. Figures 1 and 2 show plots of $\log(1/T_2)$ vs. $1/T$ for the *meta*-proton resonance of the cobalt and nickel complexes, respectively, in the presence of various concentrations of excess TPP. $Co(TPP)_2I_2$ is the least labile of the complexes and at low temperature shows the expected[5,12] decrease in $1/T_{2m}$ as the temperature increases. At higher temperatures, as the rate of exchange increases, $1/\tau_m$ becomes important, and $1/T_2$ increases as shown. Kinetic parameters were obtained by extrapolating the $1/T_{2m}$ values to higher temperatures and applying eq 1 and 3. These results are presented in Table I. For

Table I. Kinetic Parameters for Ligand Exchange with MX_2L_2

Complex	k_2 (25°) ± 0.5	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
	L = TPP		
NiCl	3.2×10^5	8.1 ± 0.8	-07 ± 4
NiBr	6.9×10^3	4.7 ± 0.4	-25 ± 2
NiI	6.4×10^2	6.9 ± 0.6	-23 ± 3
CoCl	1.2×10^4	8.8 ± 0.8	-10 ± 4
CoBr	8.7×10^2	7.7 ± 0.5	-19 ± 3
CoI	2.6×10^2	9.1 ± 0.7	-17 ± 4
	L = TTP		
NiCl	1.9×10^4	5.2 ± 0.8	-21 ± 4
NiBr	6.1×10^3	5.2 ± 0.8	-24 ± 4
NiI	5.9×10^3	5.2 ± 0.8	-24 ± 4
CoCl	2.2×10^3	4.4 ± 0.9	-29 ± 5
CoBr	1.8×10^3	5.5 ± 0.9	-25 ± 5
CoI	8.3×10^2	5.9 ± 0.9	-25 ± 5
	L = BPP		
CoBr	8.3×10^3	7.1 ± 0.5	-17 ± 3
CoI	1.1×10^2	7.7 ± 0.6	-23 ± 4

$Ni(TPP)_2Br_2$ and $Ni(TPP)_2Cl_2$, values of $1/T_{2m}$ were obtained by assuming the slope of the low-temperature $1/T_2$ curve for the corresponding iodo complex and apparent second-order kinetic behavior in the low-temperature region.

A comparison of Figures 1 and 2 indicates that the lability of the nickel complexes is greater than their co-

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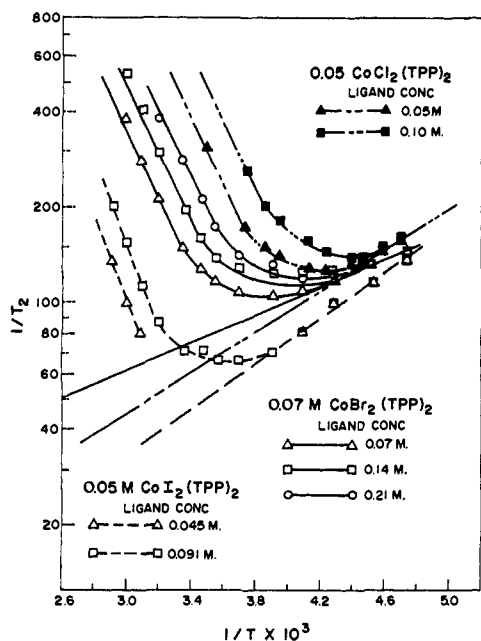
Figure 1. Plot of log ($1/T_2$) vs. $1/T$ for deuteriochloroform solutions of dihalobis(triphenylphosphine)cobalt(II) complexes with various concentrations of excess triphenylphosphine (TPP) as indicated. The points for $CoI_2(TPP)_2$ at a TPP concentration of 0.045 M between $1/T$ = 3.2 and 4.0 were omitted because of precipitate formation in this range.
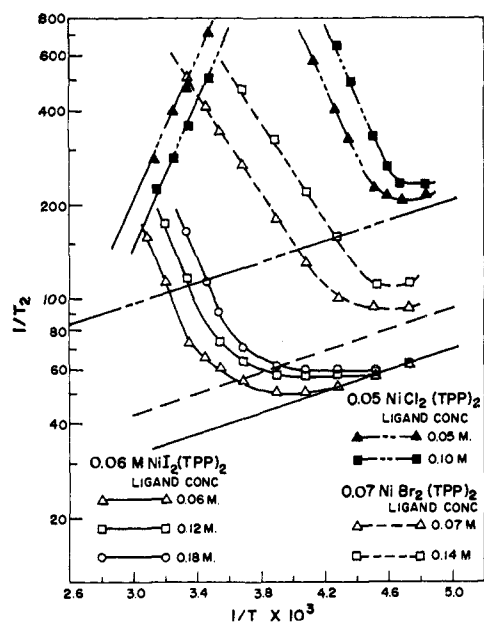

Figure 2. Plot of log ($1/T_2$) vs. $1/T$ for deuteriochloroform solutions of dihalobis(triphenylphosphine)nickel(II) complexes with various concentrations of excess triphenylphosphine (TPP) as indicated.

balt counterparts. The order of increasing TPP lability, I < Br < Cl, is evident. Second-order kinetic behavior is indicated by the data in these figures and in Table I. The error estimates in Table I were made by drawing limits on the log (k_2/T) vs. $1/T$ plots. The k_2 values have relatively small errors since very short interpolations were performed, whereas extremely large extrapolations were required for $\Delta S^{\ddagger}$ values.
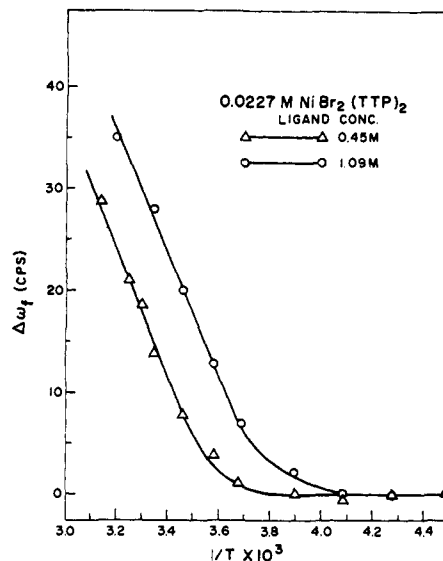

Figure 3. Plot of $\Delta \omega_f$ vs. $1/T$ for deuteriochloroform solutions of $NiBr_2(TTP)_2$ with various concentrations of excess tri-p-tolylphosphine (TTP) as indicated.

TTP Complexes. The separation of the p-methyl resonance in diamagnetic TTP from the other ligand resonances (ortho and meta) allowed the application of method II to these systems. A typical result is illustrated by the data in Figure 3 where $\Delta \omega_f$ is plotted vs. $1/T$ for Ni(TTP)$_2$Br$_2$. Here $\Delta \omega_f$ is the isotropic shift of the excess TTP methyl resonance from its diamagnetic position (-143 cps from TMS). The temperature variation of the methyl chemical shift of TTP alone was less than 1 cps over the temperature range studied and therefore was ignored. Representative isotropic shift data for the TTP complexes studied are presented in Table II. Similar $1/T_{2m}$ values were found for all the TTP complexes. The slope and intercept values, obtained from a plot of log [$\Delta \nu_{1/2}$ (cps)] vs. $1/T$, are 1.76 × 10^2 and 0.845, respectively. Values of $\Delta \omega_m \times T$ [10^{-5}(cps °K)] for the M(TTP)$_2$X$_2$ complexes NiCl$_2$, NiBr$_2$, NiI$_2$, CoCl$_2$, CoBr$_2$, and CoI$_2$ are 2.65, 2.68, 2.63, 2.16, 2.31, and 2.31, respectively.

Application of eq 2 and 3 to these data produced the kinetic parameters presented in Table I. Again the kinetic behavior is such that $1/\tau_m = k_2$[ligand], where k_2 is constant. A fairly sizable experimental error must be assigned to these results since the complexes were of limited solubility and TTP tends to oxidize or react with the solvent at higher temperatures as evidenced by the appearance of an extra peak in the diamagnetic position. Above 60° the complexes were found to decompose irreversibly and rather rapidly. Owing to solubility problems the variation of the concentration of excess TTP was less than desired. Although they are less pronounced, the lability trends found for TPP are also found for TTP. The cobalt complexes are less labile than the nickel contrary to an earlier report.[5]

BPP Complexes. Kinetic parameters for exchange of BPP with Co(BPP)$_2$Br$_2$ and Co(BPP)$_2$I$_2$ were obtained by method I by using the measured line widths of the downfield-shifted phenyl meta-proton resonance. The experimental results are shown in Figure 4, and the derived kinetic parameters are listed in Table I.

Table II. Isotropic Shift Parameters ($\Delta\omega_f$, in cps) for Tri-p-tolylphosphine (TTP) with the Complexes M(TTP)₂X₂

	NiCl₂	NiBr₂	NiI₂	CoCl₂	CoBr₂	CoI₂
			MX₂			
1/T	0.50	0.45	0.50	0.50	0.80	0.60
			TTP, M			
$\times$ 10³	0.0838	0.0912	0.0880	0.0705	0.0735	0.0905
			P_m			
4.60	0.0	...	...	...	...	...
4.40	1.0	...	...	...	...	...
4.25	2.0	...	...	...	...	...
4.08	3.0	...	...	...	...	...
4.03	4.0	...	0.0	...	...	...
4.00	6.0	0.0	0.0	...	...	...
3.95	7.0	...	...	...	...	...
3.88	9.0	0.0	1.0	...	...	...
3.77	18.0	...	...	...	0.0	...
3.74	24.0	...	...	...	0.0	...
3.68	...	1.0	3.0	...	1.0	...
3.58	...	4.0	6.0	...	2.0	0.0
3.46	...	8.0	12.0	0.0	4.0	0.0
3.35	...	16.0	19.0	2.0	5.0	0.5
3.25	...	21.0	23.0	4.0	6.0	1.5
3.14	...	29.0	28.0	10.0	9.0	3.0
3.03	...	dᵃ	dᵃ	13.0	11.0	5.0
2.94	...	...	...	16.0	dᵃ	7.0
2.88	...	...	...	dᵃ	...	dᵃ

ᵃ Decomposition.

These complexes are of pseudo-tetrahedral coordination in solution as evidenced by their magnetic moments and optical spectra. The optical spectra are very similar to those of the corresponding TPP[8] complexes and related ditertiary phosphine complexes.[22]

Discussion

A bimolecular mechanism for ligand exchange proceeding through a pentacoordinate transition state is quite reasonable for tetracoordinate complexes. Indeed, stable pentacoordinate secondary phosphine complexes of the type M(R₂HP)₃X₂ are known,[23,24] and the crystal structure of Co[(C₆H₅)PH]₃Br₂ indicates that the configuration around the cobalt is intermediate between trigonal bipyramidal and square pyramidal.[25] Bimolecular kinetics are also generally observed for reactions of tetracoordinate square-planar complexes.[26] Thus the present findings of second-order kinetics are to be expected, especially since a dissociative mechanism would require a tricoordinate transition state which in a noncoordinating solvent medium, such as chloroform, seems unreasonable.

Perhaps the most striking finding in the present study is that the nickel complexes are more labile than the corresponding cobalt ones. This trend shows up primarily in rate constants, k_2 (25°), and in enthalpies of activation, $\Delta H^{\ddagger}$ (see Table I), except for the chloride cases where the entropies seem to be anomalous. The rate of a ligand-exchange reaction like the present one

Figure 4. Plot of log ($1/T_2$) vs. $1/T$ for deuteriochloroform solutions of dihalobis(n-butyldiphenylphosphine)cobalt(II) complexes with various concentrations of excess n-butyldiphenylphosphine (BPP) as indicated.

will depend on the difference between the ground-state energy of the reactants (in this case equal to that of the products) and the transition-state energy. While a great number of factors affect the relative energies of these two states, one factor in particular, the ligand-field stabilization energy (lfse), is expected to be different for cobalt and nickel. The lfse for tetrahedral cobalt (d⁷) and nickel (d⁸) are $^6/_5\Delta_t$ and $^4/_5\Delta_t$, respectively, where Δ_t is the splitting between the lower e and upper t₂ levels. By taking Δ_t for the MCl₄²⁻ species,[27,28] a rough estimate for the difference in the lfse contribution to the ground-state energies between the cobalt and nickel complexes is 3.0 kcal/mole. This rough estimate is probably somewhat low since phosphorus causes larger ligand-field splittings than halides. An estimate of the lfse of the pentacoordinate transition state must be even more tenuous since the geometry is unknown. However, both trigonal-bipyramidal and square-pyramidal geometries cause approximately equal lfse's for the cobalt and nickel cases.[29,30] Thus it is not unreasonable that the increased lability of the present tetrahedral nickel complexes over the cobalt ones is at least in part due to ligand-field effects. The opposite trend, cobalt more labile than nickel, is generally observed in octahedral complexes of these ions and can be explained by similar arguments.

Other trends to be noted in our data are less obvious. While it seems that the general order of lability increases in the order I < Br < Cl as has been observed earlier, this effect is not very marked for the TTP systems. Further it does not seem to be reflected very much in the $\Delta H^{\ddagger}$ values, but is apparently due to a composite of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ effects, and militates against arguments such as were put forth earlier[4] based on

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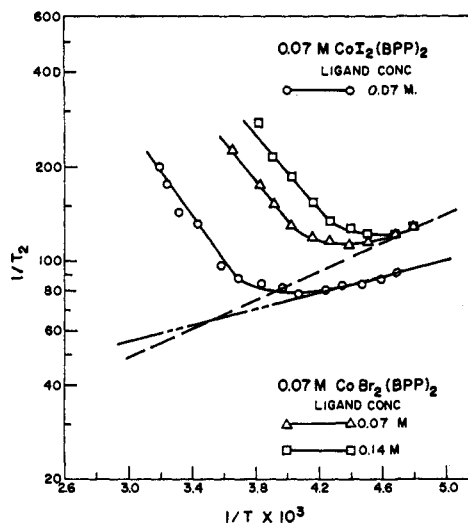
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differences in π-bonding ability between the halide ligands since such differences would be expected to show up in $\Delta H^{\pm}$.

Nor can any definite conclusions be reached regarding the relative labilities of the three phosphine ligands studied, TPP, TTP, and BPP. If the less precise chloride data are ignored, TPP appears to exchange somewhat more slowly than TTP in analogous systems, but the effect is not marked. The rate of exchange of BPP in the tetrahedral cobalt complexes appears to be more affected by the nature of the halogen than are the TPP and TTP analogs; however, no general conclusions can be reached on the basis of the present limited data, save that the lability of tetrahedral phosphine complexes is not very dependent on the nature of the phosphine for the cases studied.