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Thermodynamic Analysis of Metal–Ligand Bond Formation in the Organo(*N*,*N*′-bis(acetylacetonato)ethylenediimine)cobalt(III) System

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Thermodynamic parameters for addition of a number of ligands to five-coordinate organo(*N*,*N*′-bis(acetylacetonato)-ethylenediimine)cobalt(III), RCo(bae), complexes have been determined. The enthalpies of formation of the 1:1 adducts offer a quantitative assessment of the magnitude of the thermodynamic trans influence for these systems. The strength of the ligand–cobalt bond formed is determined primarily by the inductive properties of the trans alkyl or aryl ligand. By comparing the data found for the systems studied here with previous data available for the methylcobaloxime system, it is apparent that the nature of the cis ligands may be even more important than that of the trans ligands in determining the acceptor strength of the cobalt center.

Introduction

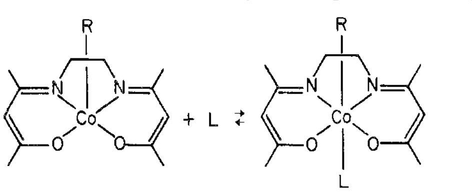
In the literature available on the general class of cobalt complexes collectively referred to as vitamin B_{12} model compounds, one can find an enormous amount of information pertinent to the cis and trans effects in these systems. These phenomena have been studied by x-ray crystallography and infrared, nuclear magnetic resonance, and electronic spectroscopy, as well as by thermodynamic and kinetic measurements of ligand substitution. This body of information has been reviewed thoroughly.[1-3] Virtually all of the thermodynamic measurements on the cis and trans effects in both vitamin B_{12} and the so-called B_{12} model compounds have been measurements of equilibrium constants for displacement of one ligand by another. Much of this work has been carried out in aqueous or polar organic solvents in which solvation effects can contribute significantly to the measured parameters. Pratt and Thorp have correctly pointed out that the formation constants reflect changes in both enthalpy and entropy but that only the enthalpy term reflects changes in bond energies caused by the cis and trans effects.[1] In very few cases have enthalpies of formation of metal–ligand bonds been obtained which bear on the cis and/or trans effect in these cobalt systems. It is the purpose of this article to report our measurements of the enthalpies of formation of a number of cobalt–ligand bonds in the alkyl(or aryl)(*N*,*N*′-bis(acetylacetonato)ethylenediimine)cobalt(III), RCo(bae), system.

In addition to the fact that this general class of complexes is considered B_{12} model compounds, the chemistry which these compounds display is inherently interesting. The ability to form stable carbon–cobalt bonds and the variety of organic ligands which can be attached to cobalt offer a versatile system with which to study the internal factors influencing the strength of a metal–ligand bond in the position trans to the carbon ligand. Furthermore, the availability of complexes with a variety of cis ligand systems offers the possiblity of quantitatively assessing factors governing the cis effect. Previous enthalpic measurements for the formation of a metal–ligand bond in methylcobaloxime have been reported by Courtright et al.[4] These workers have also reviewed the importance of obtaining such data in as inert a solvent as possible. Guschl and Brown have also reported a few enthalpies of formation of methylatocobalt(III) chelates with trimethyl phosphite and 1-(2-trifluoromethylphenyl)imidazole.[5] The results reported below substantially increase the amount of enthalpy data available on metal–ligand bond formation for these cobalt systems and demonstrate the substantial effect on metal–ligand *bond energy* caused by other ligands in the complex.

Results

The five-coordinate complexes RCo(bae), R = CH_3, CH_2Cl, *p*-$MeOC_6H_4$, *p*-FC_6H_4, C_6H_5, and CF_3, were prepared by modifications of previously reported procedures. The chloromethyl derivative appears to have not been prepared previously. The preparation employed for the trifluoromethyl derivative has not been used before for this compound.

The thermodynamic data reported here are for the addition of a sixth ligand to the RCo(bae) system, eq 1. The complexes



(1)

RCo(bae) are known to be monomeric five-coordinate species in solution[6] unlike the alkylcobaloximes which are dimers in solution.[7]

The thermodynamic data were obtained by a spectral method as outlined in the Experimental Section. The data used to calculate the thermodynamic parameters are available as supplementary material. Table I summarizes the thermodynamic parameters for ligand association for each of the systems studied.

In addition to the systems summarized in Table I, qualitative information concerning the ligand–metal bond has been obtained for other bases as follows. None of the oxygen or sulfur bases investigated showed complexation to CH_3Co(bae). For C_6H_5Co(bae) in *o*-$C_6H_4Cl_2$ solvent, addition of the bases—THT, Et_3N, DMA, DMTA, THF, or Me_2SO[8]—also gives no spectral change associated with formation of a six-coordinate species. For the stronger ligand acceptor CF_3Co(bae) weak complex formation occurred with DMA DMTA, Et_3N, and THF but the equilibrium constants were small, i.e., <5, and accurate thermodynamic parameters could not be obtained.

The thermodynamic parameters for the CH_3Co(bae)–py system given in Table I are included with no indication of error limits. While reproducible data was obtained which gave suitable error limits, there was evidence that the complex decomposed slightly in the spectrometer cell, probably due to photolysis. All attempts were made to minimize this but the thermodynamic parameters reported for this system should be viewed with the possibility that they may contain a systematic error due to this complication.

Discussion

Solvation Considerations. Although it was possible to study a few of the systems in the very inert solvent cyclohexane, it was necessary to employ the less inert solvent *o*-dichlorobenzene to compare data for all the systems in a common solvent system. Drago et al. have discussed the solvation properties of *o*-dichlorobenzene compared to those of the inert solvents CCl_4 and C_6H_{12}.[9] In the present case, we certainly recognize that the solvent interacts to some extent with the

Table I. Thermodynamic Parameters for RCo(bae)-Ligand System[a]

No.	Acceptor complex	Ligand	Solvent	ΔH, kcal mol^{-1}	ΔS, cal mol^{-1} K^{-1}	K_a, L. mol^{-1} [c]
1	$CF_3Co(bae)$	Dimethyl sulfoxide	*o*-Dichlorobenzene	-3.7 ± 0.2	-4.7 ± 0.8	54
2		Tetrahydrothiophene	*o*-Dichlorobenzene	-4.3 ± 0.3	-8.8 ± 1.0	17
3		Pyridine	*o*-Dichlorobenzene	-14.2 ± 0.9	-28.6 ± 2.9	14 700
4	*p*-$MeOC_6H_4Co(bae)$	Pipyridine	Cyclohexane	-9.8 ± 1.3	-22.3 ± 4.1	230
5		Pyridine	Cyclohexane	-9.8 ± 0.4	-23.9 ± 1.2	95
6		Pyridine	*o*-Dichlorobenzene	-6.4 ± 0.5	-14.6 ± 1.4	31
7	$C_6H_5Co(bae)$	Pyridine	*o*-Dichlorobenzene	-5.5 ± 0.3	-12.2 ± 1.0	22
8	*p*-$FC_6H_4Co(bae)$	Pyridine	*o*-Dichlorobenzene	-5.7 ± 0.3	-11.2 ± 1.0	58
9	$CH_2ClCo(bae)$	Pyridine	*o*-Dichlorobenzene	-9.0 ± 0.4	-18.4 ± 1.4	400
10	$CH_3Co(bae)$	Pyridine	*o*-Dichlorobenzene	-5.5[b]	-10.5[b]	56

[a] Temperature 298 K. [b] Although rather small error limits (less than 10%) were calculated for this system, there is evidence of introduction of a systematic error due to decomposition of the complex in the spectrometer cell (see text). Therefore, these should be treated as approximate values. [c] Values for K_a at 298 K were calculated from the best least-squares line for ln K vs. $1/T$ plots.

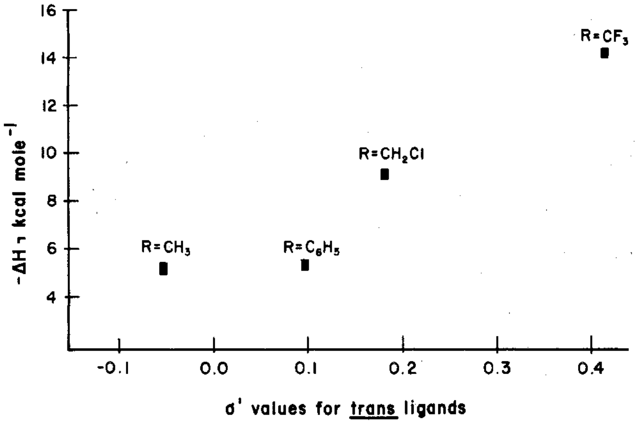


Figure 1. Plot of the Taft inductive parameter, σ', for the R group vs. $-\Delta H$ for association of RCo(bae) with pyridine in *o*-dichlorobenzene.

uncomplexed acid. However, the comparisons between systems can only be made in this solvent. Furthermore, for a given acid with various bases (e.g., $CF_3Co(bae)$) the enthalpies reported here are very likely different from those expected for a completely inert solvent by a constant amount because the association between solvent and free acid is surely the dominant solvation interaction.

Trans Influence. In analogy with the terminology used in platinum chemistry, the ground-state manifestations of the effect of a trans ligand on a particular metal–ligand bond should be referred to as the *trans influence*.[10] Inspection of the data reported in Table I reveals, as expected, a substantial effect of the alkyl or aryl ligand on the strength of the bond formed. The trends in enthalpies toward pyridine appear to depend on the inductive properties of the trans ligand. Figure 1 shows the relationship between the measured enthalpies for RCo(bae) with pyridine and the inductive parameter, σ', of Taft[11] for the R group. It appears as if acceptor properties of the cobalt (for a given cis ligand system) depend predominantly upon the ability of the trans ligand to withdraw or donate electron density in an inductive fashion. However, the variation in enthalpies of the three *p*-ZPhCo(bae) species does not follow the inductive properties of the group in the para position. One would expect the *p*-OMe derivative to give an enthalpy between those for the *p*-H and *p*-F derivatives. Unless there is a small amount of Co→L back-donation into axial ligand π^* orbitals, the anomalously large enthalpy of the *p*-OMe derivative toward pyridine cannot be explained. Brown et al. have argued that cobalt→ligand π bonding is necessary to explain the marked stability of phosphine and phosphite complexes of methylcobaloxime.[7,12] The rather small but definite trends in the magnitude of enthalpies for the phenylato derivatives toward pyridine (*p*-OMe > *p*-F ≳ *p*-H) parallels the σ_{para} parameters for the para substituents which combine inductive and resonance effects. Despite these observations, the enthalpy values for the three phenyl derivatives are rather close to each other compared to the total range of enthalpies. Thus, the conclusion that inductive effects dominate the strength of the cobalt–pyridine bond is still sound.

For the complexes studied here, the trans ligand clearly stabilizes a metal–ligand bond according to the order $CF_3 > CH_2Cl > C_6H_5 \gtrsim CH_3$. This ordering is qualitatively similar to the abilities of these groups to kinetically stabilize a particular ligand ($P(OMe)_3$) trans to the alkyl group in alkylcobaloximes.[13] The enthalpies reported in Table I also parallel observed chemical reactivities of the complexes. The complexes when originally prepared are red and contain a coordinated water in the position trans to the organo ligand. The removal of water results in a dramatic red to green change as the complex becomes five-coordinate. The ease of removal of water parallels the observed enthalpies. For instance, the methyl derivative loses water spontaneously in benzene solution at room temperature while the trifluoromethyl derivative does so only slowly in boiling benzene.

Cis Influence. The enthalpy data provided in this article together with that reported earlier by Courtright et al.[4] for methylcobaloxime furnish at least a qualitative idea about the magnitude of the cis influence in the two systems. In terms of the energetics of metal–ligand bond formation, the cis influence appears to be even more substantial than the trans influence. Consider the methylcobaloxime–pyridine system reported by Courtright. For this system ΔH is −20.8 kcal mol^{-1}. In our work, we have determined an enthalpy of −5.5 kcal mol^{-1} for the $CH_3Co(bae)$–py system. Thus the change in cis ligands from $(dmg)_2$ to bae has resulted in a larger change in ΔH toward pyridine than the difference between changing the trans ligand from CH_3 to CF_3. Clearly the $(dmg)_2$ ligand system renders the cobalt considerably more electron deficient than the bae system. This striking difference in the properties of the $CH_3Co(dmg)_2$ and $CH_3Co(bae)$ systems has been observed kinetically by Guschl and Brown.[5] In studying the ligand exchange of 1-(2-trifluoromethylphenyl)imidazole with these two complexes these workers have found an Arrhenius activation energy of 28 kcal mol^{-1} with $CH_3Co(dmg)_2$ while a value of 9 kcal mol^{-1} was obtained with $CH_3Co(bae)$. This is also reflected in the strong tendency of the alkylcobaloximes to dimerize while the alkyl–Co(bae) systems are monomeric.

Nature of the Cobalt Center. The nature of the cobalt center in the methylcobaloxime system has received considerable attention. Methylcobaloxime has been referred to as a class B or soft Lewis acid.[12,14,15] Courtright et al. have taken exception to this assignment and concluded that this acid is more correctly formulated as a borderline acid in the HSAB description and that it is, in fact, capable of undergoing relatively strong covalent *and* electrostatic interactions.[4] Unfortunately the methylatocobalt(III) complex of bae does not complex to many of the ligands of interest and only the complex with pyridine has been studied by us. However, the enthalpy parameters for the $CF_3Co(bae)$ system are revealing. The enthalpy for interaction with tetrahydrothiophene (THT) is strikingly low. Note that the pyridine–cobalt bond is fully 10 kcal mol^{-1} more stable than the THT–Co bond. This acid discriminates in favor of pyridine over THT significantly more than methylcobaloxime does. Thus, one would conclude that $CF_3Co(bae)$ is a harder acid or has more class A character (more E character in the E and C description[16]) than methylcobaloxime. Therefore, this acid should be more likely to demonstrate binding to oxygen bases and the complexation observed with Me_2SO is probably an example of this.[17] However, the oxygen bases DMA and THF qualitatively demonstrate very weak binding (if any) with $CF_3Co(bae)$. Courtright et al. have attributed the weak complex formation of methylcobaloxime to oxygen bases to an anomalously large entropy effect.[4] This was based on an estimated enthalpy of adduct formation with THF of −15.8 kcal mol^{-1} but a low equilibrium constant of approximately 2 in THF solvent. Thus the low K would have to be due to an anomalously large negative value for ΔS. These authors have considered two sources for this entropy effect. One is electrostatic association of the oxygen bases with the hydrogen in the O–H–O bridges of the $(dmg)_2$ ligand system. The other is possible orientation problems of the oxygen bases upon coordination if the cobalt lies toward the CH_3 side of the plane of the equatorial ligands. We observe qualitatively similar behavior (i.e., low equilibrium constants toward oxygen bases) for $CF_3Co(bae)$. The association to the O–H–O hydrogen cannot explain this problem since no such hydrogen is present in the bae ligand system. Orientation problems could, of course, still be present in our system although the bae ligand is considerably more flexible than the $(dmg)_2$ ligand system and might be expected to more easily accommodate entering ligands.[18] With respect to this entire question it has been implied that for these systems, the free energy and enthalpy probably do not change in a parallel fashion.[4] Figure 2 shows a plot of $-\Delta H$ vs. $-\Delta S$ for all the systems reported in Table I for the solvent *o*-dichlorobenzene. While this is not a strictly linear plot, it does, however, reveal no anomalous entropy values and, in fact, it appears as if there are at least qualitatively parallel changes for the free energy and enthalpy in the systems reported here. The troublesome problem of the nature of the cobalt interaction with oxygen bases as well as the reported strong interaction with phosphorus bases[4,12] requires additional thermodynamic studies before a thorough understanding of these systems is possible.

Experimental Section

Chemicals and Preparation of Complexes. Cyclohexane and *o*-dichlorobenzene were obtained from Aldrich Chemical Co. Before being used for spectral work these solvents were distilled and stored over Linde 4A molecular sieves. THF used in the preparation of complexes was dried over sodium metal and distilled from lithium aluminum hydride. All of the bases used as ligands were distilled just prior to use.

In most cases ligands and complexes were prepared using modifications of known procedures. *N,N'*-bis(acetylacetone)ethylenediimine, $baeH_2$, was prepared by the method of Martell et al.[19] (*N,N'*-bis(acetylacetonato)ethylenediimine)cobalt(II) was prepared by the method of Everett and Holm[20] modified as follows: anhydrous cobalt(II) bromide was used as the Co(II) source and the time of reaction was increased to 24 h. The phenylatocobalt(III) derivatives were prepared by the method of Costa et al.[21]

Methyl(*N,N'*-bis(acetylacetonato)ethylenediimine)cobalt(III), $CH_3Co(bae)$, was prepared using a modification of the procedure of Costa et al. as follows.[22] A solution of Co(bae), 4.60 g (16.4 mmol), in 100 mL of THF under argon was added to 1% sodium amalgam, 38.38 g (16.4 mmol). The mixture was stirred for 2 h under argon at room temperature. Upon cooling of the system to 0 °C, CH_3I, 2.33 g (16.4 mmol), was added and the mixture stirred an additional 15 min in the dark. The THF solution was then poured into 100 mL of water and placed in a refrigerator overnight after which time red crystals of $CH_3Co(bae){\cdot}H_2O$ were collected. This material was extracted with warm benzene, and after removal of benzene and drying under vacuum at 79 °C for 12 h, green $CH_3Co(bae)$, 2.90 g, was obtained; yield 60%.

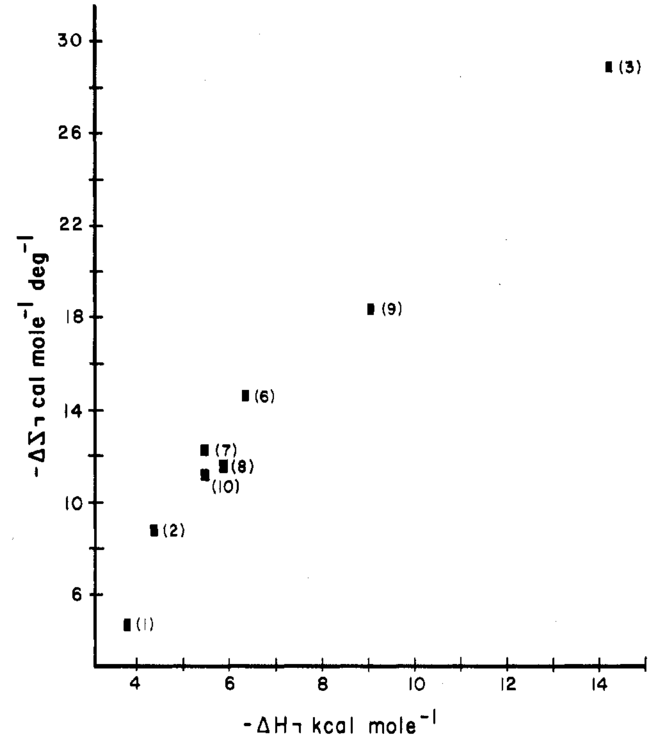


Figure 2. Plot of $-\Delta S$ vs. $-\Delta H$ of ligand bond formation for all the systems listed in Table I for the solvent *o*-dichlorobenzene. The numbers on this diagram refer to the numbering system for the acid–base pairs in Table I.

Chloromethyl(*N,N'*-bis(acetylacetonato)ethylenediimine)cobalt(III), $CH_2ClCo(bae)$, was prepared as follows. A solution of Co(bae), 0.55 g (1.95 mmol), in 100 mL of THF under argon was added to 1% sodium amalgam, 4.55 g (1.95 mmol), and the reduction was allowed to proceed for only 3–4 min. After this time the amalgam was removed, 1.5 mL of CH_2Cl_2 added, and the solution stirred for 3 h in the dark. The solution was poured into 100 mL of water and allowed to stand in the refrigerator for 2.5 days after which time red crystals of $CH_2ClCo(bae){\cdot}H_2O$ were collected. Upon drying of the product at 79 °C under vacuum, green $CH_2ClCo(bae)$, 0.13 g, was obtained; yield 23%.

Trifluoromethyl(*N,N'*-bis(acetylacetonato)ethylenediimine)cobalt(III), $CF_3Co(bae)$, was prepared from an aqueous methanol solution as follows. The ligand, $baeH_2$, 2.24 g (10.0 mmol), and $CoCl_2{\cdot}6H_2O$, 2.38 g (10.0 mmol), were dissolved in 320 mL of methanol. After purging of the solution with N_2, 1.6 g of 50% aqueous NaOH dissolved in 10 mL of methanol was added. This was followed by addition of sodium borohydride, 1.0 g (26.4 mmol), in 10 mL of water, and solid $PdCl_2$, 0.08 g. After 10 min CF_3Br, 3.1 g (20.8 mmol), contained in a rubber balloon was attached to the top of the reaction flask. The mixture was stirred for 1.5 h at room temperature in the dark after which time 10 mL of acetone was added. The reaction mixture was then filtered and 500 mL of water added to the filtrate. Upon remaining in the refrigerator for 1 day this solution gave red crystals of $CF_3Co(bae){\cdot}H_2O$ which were collected by filtration. The bound water was removed by heating at 79 °C for at least 24 h under vacuum affording the emerald green $CF_3Co(bae)$; 1.07 g, yield 30%. This compound was identical with that prepared previously by an alternate method.[23]

Spectral Measurements. Absorbance measurements were carried out on a Cary Model 14 or Beckman DU UV–visible spectrometer. Both instruments were equipped with thermostated cell compartments. The absorbance data were obtained as difference spectra at 650 nm using free cobalt complex in the sample compartment and solutions of complex plus ligand in the reference compartment.

Calculation of Thermodynamic Results. The changes in absorbance of the system with addition of various amounts of ligand can be analyzed to simultaneously deduce the equilibrium constant and ($\epsilon_C - \epsilon_A$). ϵ_C and ϵ_A are the values for the molar absorptivities of the 1:1 complex and free acid, respectively. The method of calculation involves simultaneous solution of K^{-1} and ($\epsilon_C - \epsilon_A$) using a computer solution of the Rose–Drago equation.[24-28] For each acid–base pair a series of simultaneous equations are solved and displayed graphically as plots of K^{-1} vs. ($\epsilon_C - \epsilon_A$) to allow a visual assessment of the quality of the data in addition to the statistical parameters obtained from the calculation. The reader is referred to ref 26 for a useful discussion of the technique. The enthalpies and entropies for complex formation were determined from the temperature dependence of the equilibrium constant using a least-squares routine.

Because of the very large amount of data collected in this type of work it is necessary to condense it to a manageable form which still allows the reader to assess its quality. Table II (supplementary material) summarizes the data as follows: for each equilibrium constant determination (i.e., one acid–base pair at a given temperature) the equilibrium constant is reported along with the conditional standard deviation for K and the ratio of the marginal standard deviation to the conditional standard deviation. This information will allow the reader to appreciate the nature of the K^{-1} vs. ($\epsilon_C - \epsilon_A$) plots without the necessity of reproducing all of the plots.

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

Registry No. $CF_3Co(bae)(Me_2SO)$, 61522-63-2; $CF_3Co(bae)(THT)$, 61522-64-3; $CF_3Co(bae)(py)$, 61522-65-4; *p*-$MeOC_6H_4Co(bae)(pip)$, 61522-66-5; *p*-$MeOC_6H_4Co(bae)(py)$, 25793-78-6; $C_6H_5Co(bae)(py)$, 41659-59-0; *p*-$FC_6H_4Co(bae)(py)$, 61522-67-6; $CH_2ClCo(bae)(py)$, 61543-15-5; $CH_3Co(bae)(py)$, 18115-79-2; $CF_3Co(bae)$, 61527-77-3; *p*-$MeOC_6H_4Co(bae)$, 41659-50-1; $C_6H_5Co(bae)$, 41686-71-9; *p*-$FC_6H_4Co(bae)$, 61522-68-7; $CH_2ClCo(bae)$, 61522-69-8; $CH_3Co(bae)$, 41744-14-3; Co(bae), 15744-72-6.

Supplementary Material Available: Table II, giving all measured equilibrium constants, conditional standard deviations, and ratios of marginal to conditional standard deviations (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) J. M. Pratt and R. G. Thorp, *Adv. Inorg. Chem. Radiochem.*, **12**, 375 (1969).

(2) J. M. Pratt, "Inorganic Chemistry of Vitamin B_{12}", Academic Press, New York, N.Y., 1972, Chapter 8.

(3) D. G. Brown, *Prog. Inorg. Chem.*, **18**, 177 (1973).

(4) R. L. Courtright, R. S. Drago, J. A. Nusz, and M. S. Nozari, *Inorg. Chem.*, **12**, 2809 (1973).

(5) R. J. Guschl and T. L. Brown, *Inorg. Chem.*, **12**, 2815 (1973).

(6) G. Costa, G. Mestroni, G. Tauzher, and L. Stefani, *J. Organomet. Chem.*, **6**, 181 (1966).

(7) L. M. Ludwick, and T. L. Brown, *J. Am. Chem. Soc.*, **91**, 5188 (1969).

(8) Abbreviations for ligands used in this article are as follows: THT, tetrahydrothiophene; Et_3N, triethylamine; DMA, *N,N*-dimethylacetamide; DMTA, *N,N*-dimethylthioacetamide; THF, tetrahydrofuran; Me_2SO, dimethyl sulfoxide; py, pyridine; pip, piperidine; bae, *N,N'*-bis(acetylacetonato)ethylenediimine; $(dmg)_2$, bis(dimethylglyoximato).

(9) R. S. Drago, M. S. Nozari, and G. C. Vogel, *J. Am. Chem. Soc.*, **94**, 90 (1972).

(10) (a) F. Basolo and R. G. Pearson "Mechanisms of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1967; (b) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).

(11) R. W. Taft in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, Chapter 13.

(12) T. L. Brown, L. M. Ludwick, and R. S. Stewart, *J. Am. Chem. Soc.*, **94**, 384 (1972).

(13) R. J. Guschl, R. S. Stewart, and T. L. Brown, *Inorg. Chem.*, **13**, 417 (1974).

(14) J. M. Pratt and R. G. Thorp, *J. Chem. Soc. A*, 187 (1966).

(15) D. N. Hague and J. Halpern, *Inorg. Chem.*, **6**, 2059 (1967).

(16) (a) R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965); (b) R. S. Drago, G. C. Vogel, and T. E. Needham, *ibid.*, **93**, 6014 (1971).

(17) Me_2SO can bond to the cobalt center through both the S and O atoms. In its binding to methylcobaloxime, DMSO coordinates through both atoms with the ratio of O binding to S binding of about 4.5.[7] $CF_3Co(bae)$ is a harder base (see text) than methylcobaloxime so a considerably greater degree of O bonding is expected for this acid. However, the data on Me_2SO should be considered with this possibility of two donor atoms in mind.

(18) M. Calligaris, G. Nardin, and L. Randaccio, *Coord. Chem. Rev.*, **7**, 385 (1972).

(19) A. E. Martell, R. L. Belford, and M. Calvin, *J. Inorg. Nucl. Chem.*, **5**, 170 (1958).

(20) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **88**, 2442 (1966).

(21) G. Costa, G. Mestroni, G. Tauzher, and L. Stefani, *J. Organomet. Chem.*, **6**, 181 (1966).

(22) G. Costa, G. Mestroni, and G. Pellizer, *J. Organomet. Chem.*, **11**, 333 (1968).

(23) A. van den Bergen, K. S. Murray, and B. O. West, *J. Organomet. Chem.*, **33**, 89 (1971).

(24) (a) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959); (b) N. J. Rose and R. S. Drago, *ibid.*, **81**, 6142 (1959).

(25) G. C. Vogel and L. A. Searby, *Inorg. Chem.*, **12**, 936 (1973).

(26) T. J. Bengelsdijk and R. S. Drago, *J. Am. Chem. Soc.*, **97**, 6466 (1975).

(27) R. S. Drago and T. D. Epley, *J. Am. Chem. Soc.*, **91**, 2883 (1969).

(28) The general minimization routine, SIMPLEX, has been copyrighted by J. P. Chandler of the University of Indiana Physics Department, 1965.

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Kinetics of Oxidative Addition to Iridium(I) Complexes[1]

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The effect of the ligand L on the rate of trans addition of CH_3I to *trans*-$Ir(CO)ClL_2$ has been investigated. The tertiary phosphine ligands L were chosen to determine the effects of electronic modifications, the effect of substituent position of the substituted triphenylphosphine, effects of a series of alkyl-substituted phosphine ligands in which the number and size of the alkyl groups is varied, and the effects of stepwise change in a phenyl-substituted phosphine in which the number of substituted phenyl groups is changed from 0 to 3. The use of various types of σ constants in Hammett linear free energy relationships is discussed. Application of substituent constants derived for substituents attached to phosphorus for cases where reaction does not involve direct attack on phosphorus to the data yields a linear relationship between log k and $\sum \sigma^{ph}$ with a slope of −2.27 and a correlation coefficient of 0.99.

Introduction

The kinetics of oxidative addition reactions of transition metal complexes with d^8 and d^{10} electron configurations has received considerable attention in recent years. The impetus for these investigations has been to gain a greater understanding of the electronic and steric factors influencing this reaction which is a vital step in the functioning of many of these compounds as homogeneous catalysts. Following the report[3] on the effects of the halide on the rates of oxidative addition of H_2, O_2, and CH_3I to $Ir(CO)X(Ph_3P)_2$, several investigators cited evidence,[4] although largely qualitative, that seemingly minor changes in the phosphine ligand caused large