lute configuration of Δ-(−)-$[Co((S)\text{-}pn)_3]^{3+}$ has been determined by X-ray methods.[22]

The most striking feature of the ^{59}Co nmr spectra is the appearance of two resonances of relative area 1.6:1.0 for Λ-$[Co((S)\text{-}pn)_3]Cl_3$. Although four diastereomers exist in principle for $[Co((S)\text{-}pn)_3]^{3+}$, usually only two isomers, differing in helicity, are isolated. These "isomers" may each contain cis and trans species, and indeed MacDermott[23] succeeded in separating the cis and trans forms of Δ-$[Co((R)\text{-}pn)_3]Br_3$. Thus, we tentatively assign the two signals observed for Λ-$[Co((S)\text{-}pn)_3]Cl_3$ to cis and trans forms of this complex. Line widths of the two signals are not sufficiently different to justify detailed assignments; however, it would seem reasonable on statistical grounds to assign the predominant signal to the trans isomer. The Δ isomer exhibits an unusually broad signal, and the existence of two resonances for this isomer is not firmly established. Λ-$[Co((S)\text{-}pn)_3]Cl_3$ is stable at elevated temperatures. However, when solvent is removed from the Δ isomer by gentle heating[24] and the sample is later redissolved, ^{59}Co nmr of the new solution reveals three signals. One of these has a chemical shift very close to that of the Δ isomer before heating, and chemical shifts of the other two are within error of the values found for the Λ isomer. Apparently Δ-$[Co((S)\text{-}pn)_3]Cl_3$ partially isomerizes to the more stable Λ isomers during the above process.

The absorption maxima of $[Co(en)_3]^{3+}$ and $[Co((S)\text{-}pn)_3]^{3+}$ are within the limits of error of each other, and only small chemical shift differences are expected using eq 1. Since the observed chemical shift differences are appreciable, it is clear that eq 1 is not followed here. Only one CD band is observed for the Δ isomer;[25] this has a maximum near the weighted average of the two maxima for Λ-$[Co((S)\text{-}pn_3]^{3+}$. Thus the relative chemical shifts of these Δ and Λ diastereomers are not simply related to their relative CD maxima.

Attempts were made to examine ^{59}Co nmr spectra of several other diastereomeric cobalt(III) complexes having mixed O and N donor atoms. However, the spectra of these complexes could not be obtained on our instrument, presumably as a result of efficient quadrupole relaxation. Mixed-donor complexes of cobalt(III) have quadrupole coupling constants at least an order of magnitude larger than those having identical donor elements,[26] and this is expected to lead to larger line widths by a factor of at least 100 for the mixed-donor complexes.

Registry No. $Co(acac)_3$, 21679-46-9; $Co(tfthbd)_3$, 41875-84-7; *trans*-$Co(tfac)_3$, 41768-43-8; *cis*-$Co(tfac)_3$, 41768-44-9; *trans*-$Co(bzac)_3$, 33990-23-7; *cis*-$Co(bzac)_3$, 33990-24-8; *trans*-$Co(ppd)_3$, 41768-47-2; *cis*-$Co(ppd)_3$, 41765-60-0; Δ-*cis*-$Co[(+)\text{-}atc]_3$, 32490-75-8; Λ-*cis*-$Co[(+)\text{-}atc]_3$, 32592-77-1; Δ-*trans*-$Co[(+)\text{-}atc]_3$, 32490-74-7; Λ-*trans*-$Co[(+)\text{-}atc]_3$, 32490-73-6; Δ-*trans*-$Co[(-)\text{-}hmcar]_3$, 25797-15-3; Λ-*trans*-$Co[(-)\text{-}hmcar]_3$, 25797-14-2; Δ-*trans*-$Co[(+)\text{-}hmcar]_3$, 41875-82-5; Λ-*trans*-$Co[(+)\text{-}hmcar]_3$, 41765-61-1; Δ-*cis*-$Co[(-)\text{-}hmcar]_3$, 26582-20-7; Λ-*cis*-$Co[(-)\text{-}hmcar]_3$, 25797-16-4; Δ-*cis*-$Co[(+)\text{-}hmcar]_3$, 41765-62-2; Λ-*cis*-$Co[(+)\text{-}hmcar]_3$, 41875-83-6; $[Co(en)_3]I_3$, 15375-81-2; Δ-$[Co((S)\text{-}pn)_3]Cl_3$, 14516-62-2; Λ-*cis*-$[Co((S)\text{-}pn)_3]Cl_3$, 20470-19-3; Λ-*trans*-$[Co((S)\text{-}pn)_3]Cl_3$, 41765-65-5;, Co, 7440-48-4.

---

[22] Y. Saito, *Pure Appl. Chem.*, 17, 21 (1968).

[23] T. E. MacDermott, *Inorg. Chim. Acta*, 2, 81 (1968).

[24] At this point a greenish color is noticeable; however, the original orange color of the complex returns upon dissolving the greenish product in water.

[25] A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.*, 49 (1965).

[26] W. van Bronswyk, *Struct. Bonding*, 7, 87 (1970).

Contribution from the Department of Chemistry, Clarkson
College of Technology, Potsdam, New York 13676

Heats of Reaction of Pyridine, Triphenylphosphine, and Triphenyl Phosphite with the Chloro-, Bromo-, and Iodo-1,5-cyclooctadienerhodium(I) Dimers and Dichlorobis(benzonitrile)palladium(II)

WALTER PARTENHEIMER* and EDGAR F. HOY

Received March 1, 1973

The heats for the following reactions in dichloromethane are reported: $[RhX(COD)]_2 + 2B \rightarrow 2[RhX(COD)(B)]$; $[RhX(P(OC_6H_5)_3)_2]_2 + 2P(OC_6H_5)_3 \rightarrow 2[RhX(P(OC_6H_5)_3)_3]$; $[RhX(COD)_2] + 2P(OC_6H_5)_3 \rightarrow [Rh_2X_2(COD)(P(OC_6H_5)_3)_2] + COD$; $[Rh_2X_2(COD)(P(OC_6H_5)_3)_2] + 2P(OC_6H_5)_3 \rightarrow [RhX(P(OC_6H_5)_3)_2]_2 + COD$; $[PdCl_2(C_6H_5CN)_2] + 2B \rightarrow [PdCl_2B_2] + 2C_6H_5CN$; and $[PdCl_2(COD)] + 2P(OC_6H_5)_3 \rightarrow [PdCl_2(P(OC_6H_5)_3)_2] + COD$ (B = pyridine, triphenylphosphine; X = Cl, Br, I; COD = 1,5-cyclooctadiene). Relative displacement energies are for the rhodium compounds, triphenyl phosphite >> 1,5-cyclooctadiene and triphenylphosphine > pyridine, and for the palladium compounds, triphenylphosphine > triphenyl phosphite > pyridine >> cyclooctadiene. Arguments are given that solvent–solute enthalpic contributions are not predominant in the displacement energies. For a given reaction, the effect of varying the halogens upon the observed enthalpies is very small or nonexistent. Equilibrium constants for the first reaction are too high to measure when B = triphenylphosphine and are approximately 5×10^4 when B = pyridine.

Introduction

We have been obtaining enthalpic and kinetic data for metal-olefin compounds[1-3] in order to gain insight into the nature of the metal–olefin bond and its relation to the rates at which these compounds react. We have obtained a large amount of auxiliary enthalpic data on a number of well-known reactions, some of which we wish to report here.

There is an enormous amount of stability constant and enthalpic data[4,5] pertaining to metal–ligand displacement re-

---

[1] W. Partenheimer, *Inorg. Chem.*, 11, 743 (1972).

[2] W. Partenheimer and E. F. Hoy, *J. Amer. Chem. Soc.*, 95, 2840 (1973).

[3] W. Partenheimer and E. H. Johnson, *Inorg. Chem.*, 12, 1274 (1973).

[4] L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Burlington House, London, 1964.

actions. The solvents usually employed for these thermodynamic measurements are water or alcohols where specific solvation effects are expected to be important[6] and the exact structure of the reactants and products are often unknown due to their coordination with the solvent. For example, it has been shown that the relative enthalpic changes corresponding to the reaction of the halide ions with the mercuric ion are $I^- > Br^- > Cl^-$ in water and $Cl^- > Br^- > I^-$ in the gas phase. It is clearly quite dangerous to interpret thermodynamic data obtained in such solvents in terms of such fundamental concepts as "bond strength" and steric hindrance. Our work has been performed in the relatively nonpolar solvent dichloromethane. Although it is well established that dichloromethane hydrogen bonds to bases, the magnitude of this interaction can be estimated and the solvation effects estimated from the extensive data available.

Experimental Section

Organic microanalyses were performed by Instranal Labs. Nmr spectra were recorded on a Varian A-60 spectrometer.

Materials. Baker AR grade dichloromethane and pyridine were dried with Linde 4-A molecular sieves at least 24 hr before use. J. T. Baker, Baker grade, triphenyl phosphite was used as received (*Anal.* Calcd for $C_{18}H_{15}PO_3$: C, 69.67; H, 4.88. Found: C, 69.65; H, 4.96). Eastman Kodak white label triphenylphosphine was recrystallized from benzene-hexane solution before use. Di-μ-chloro-dichloro-(1,5-cyclooctadiene)dirhodium(I) (*Anal.* Calcd for $C_8H_{12}RhCl$: C, 39.02; H, 4.88. Found: C, 39.10; H, 4.79) and its bromo and iodo derivatives were prepared by a previously reported procedure.[7] Di-μ-chloro-(1,5-cyclooctadiene)bis(triphenyl phosphite)dirhodium(I),[8] dichlorobis(benzonitrile)palladium(II), and dichloro(1,5-cyclooctadiene)palladium(II)[9] were prepared as previously described.

Apparatus and Procedure. Calorimetric measurements were made using a Guild solution calorimeter equipped with a base line compensator. Heats of reaction of the rhodium compounds and of dichloro-(1,5-cyclooctadiene)palladium(II) were measured by incremental addition of triphenyl phosphite to a 200-ml solution of the metal complex in dichloromethane with a 0.2- or 2.0-ml Gilmont micrometer buret. The enthalpies of the remaining palladium compounds were measured as previously described.[1,10] All measurements were obtained at ambient room temperature (21-24°). All heats have been corrected for the heat of solution of the acid or base added.

Results

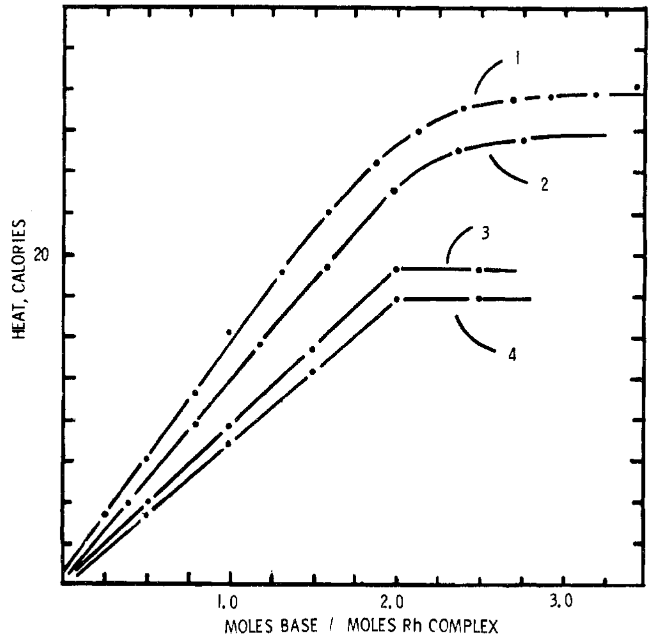

Figure 1. Calorimetric titration curves for the reaction of $[RhCl(COD)]_2$ with B: curve 1, X = I, B = pyridine; curve 2, X = Cl, B = pyridine; curve 3, X = Br, B = $P(C_6H_5)_3$; curve 4, X = Cl, B = $P(C_6H_5)_3$.

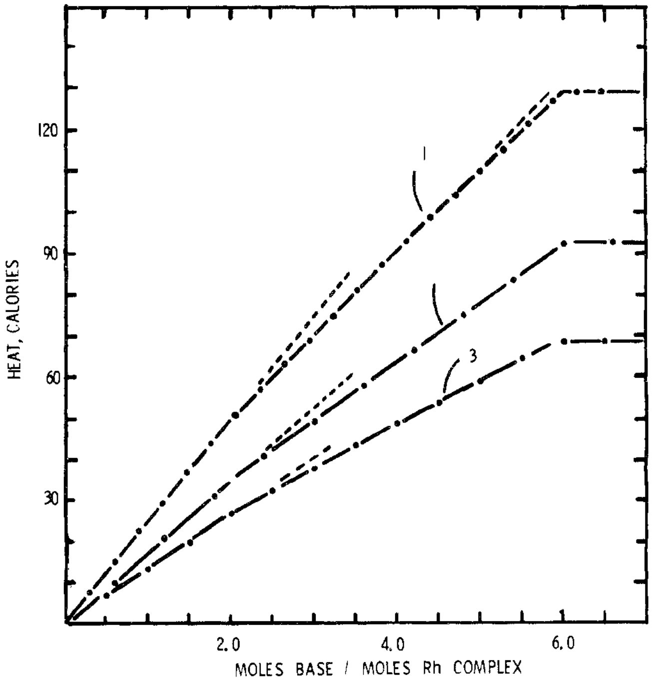

Figure 2. Calorimetric titration curves for the reaction of $[RhX(COD)]_2$ with triphenyl phosphite: curve 1, X = Br; curve 2, X = Cl; curve 3, X = I.

Calorimetric titration curves, see Figures 1 and 2, can be constructed from the incremental addition of the bases to the rhodium compounds. Addition of triphenylphosphine to $[RhX(COD)]_2$ (X = Cl, Br, I) results in calorimetric titration curves that are straight lines with a sharp breaking point when the mole ratio (moles of base/moles of metal complex) is 2.0. The calorimetric titration curves corresponding to the addition of pyridine to $[RhX(COD)]_2$ (X = Cl, Br, I) are curved and have a slope of zero at an approximate mole ratio of 2.5. The addition of triphenyl phosphite to the compounds of the type $[RhX(COD)]_2$ results in titration curves composed of four lines of differing slopes (sometimes barely perceptible) which have breaking points at mole ratios of 2.0, 4.0, and 6.0.

Table I summarizes the calorimetric results. When the titration curves were linear, the enthalpic changes were calculated by calculating the slopes of the lines using the least-squares method. The standard deviations reported in Table I were obtained by computing the enthalpy for each incremental addition and then computing the precision of the mean from these values. The fractional standard deviation of the reported enthalpic changes was nearly always less than 2%. The

---

(5) J. J. Christensen and R. M. Izatt, "Handbook of Metal-Ligand Heats," Marcel Dekker, New York, N. Y., 1970.

(6) J. J. Christensen and R. M. Izatt, "Physical Methods in Inorganic Chemistry," Interscience, New York, N. Y., 1968, Chapter 11.

(7) J. Chalk and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

(8) L. M. Haines, *Inorg. Chem.*, 9, 1517 (1970).

(9) M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Amer. Chem. Soc.*, **60**, 882 (1938).

(10) Solid dichlorobis(benzonitrile)palladium(II) is added to a dichloromethane solution containing the base, resulting in a rapid liberation of heat. Equilibrium and ir studies of the palladium compound indicate that benzonitrile is liberated and polynuclear species form, probably $[PdCl_2(C_6H_5CN)]_2$, when it is placed in solution [see ref 1; M. Kubota, B. A. Denechaud, P. M. McKinney, T. E. Needham, and G. O. Spessard, *J. Catal.*, 18, 119 (1970); W. Kitching and C. J. Moore, *Inorg. Nucl. Chem. Lett.*, 4, 691 (1968); H. Dietl, H. Reinheimer, J. Moffat, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 92, 2276 (1970)]. The reactive species in solution may therefore not be $[PdCl_2(C_6H_5CH)_2]$. As a consequence, relative displacement energies of benzonitrile from palladium cannot be established.

Table I. Experimentally Determined Enthalpic Data

	$-\Delta H$, kcal/mol	No. of data points	Designation
$[RhX(COD)]_2 + 2py \rightarrow 2[RhX(COD)py]$			**1**
X = Cl	19.2 ∓ 0.6	7	**1a**
X = Br	19.7 ∓ 0.6	6	**1b**
X = I	18.4 ∓ 0.6	13	**1c**
$[RhX(COD)]_2 + 2P(C_6H_5)_3 \rightarrow 2[RhX(COD)(P(C_6H_5)_3)]$			**2**
X = Cl	27.3 ∓ 0.3	4	**2a**
X = Br	29.1 ∓ 0.1	4	**2b**
X = I	30.4 ∓ 0.4	3	**2c**
$[RhX(P(OC_6H_5)_3)_2]_2 + 2P(OC_6H_5)_3 \rightarrow 2[RhX(P(OC_6H_5)_3)_3]$			**3**
X = Cl	22.8 ∓ 0.2[a]	3	
	24.2 ∓ 0.9[a]	3	
	23.8 ∓ 0.4	2	
Av.	23.6[c]		**3a**
X = Br	23.4 ∓ 0.4	7	**3b**
X = I	23.0 ∓ 0.3	4	**3c**
$[RhX(COD)]_2 + 2P(OC_6H_5)_3 \rightarrow [Rh_2X_2(COD)(P(OC_6H_5)_3)_2] + COD$			**4**
X = Cl	28.5 ∓ 1.3	3	
	27.8 ∓ 0.6	3	
Av.	28.2		**4a**
X = Br	30.1 ∓ 0.5	6	**4b**
X = I	30.2 ∓ 0.9	3	**4c**
$[Rh_2X_2(COD)(P(OC_6H_5)_3)_2] + 2P(OC_6H_5)_3 \rightarrow [RhX(P(OC_6H_5)_3)_2]_2 + COD$			**5**
X = Cl	23.0 ∓ 0.2[a]	3	
	23.5 ∓ 0.4[a]	3	
	23.9 ∓ 0.3[b]	2	
Av.	23.5[c]		**5a**
X = Br	25.0 ∓ 0.4	7	**5b**
X = I	24.6 ∓ 0.2	4	**5c**
$[PdCl_2(C_6H_5CN)_2] + 2B \rightarrow [PdCl_2B_2] + 2C_6H_5CN$			**6**[d]
B = py	26.0 ∓ 0.8	5	**6a**
$B = P(C_6H_5)_3$	39.0 ∓ 1.1	4	**6b**
B = COD	13.0 ∓ 0.4[c]	5	**6c**
$[PdCl_2(COD)] + 2P(OC_6H_5)_3 \rightarrow [PdCl_2(P(OC_6H_5)_3)_2] + COD$			**7**
	21.2 ∓ 0.5	5	**7**

[a] Starting material was $[RhCl(COD)]_2$. [b] Starting material was $[Rh_2Cl_2(COD)(P(OC_6H_5)_3)_2]$. [c] Previously reported, see ref 1. [d] See footnote 10.

enthalpic changes for the reactions of $[RhX(COD)]_2$ with pyridine, whose titration curves were curved, were determined by dividing the total heat evolved in the reaction by the moles of metal complex present. The fractional standard deviations of these reactions were assumed to be 3.0%.

Individual heat data from which the enthalpic changes were calculated are available in the Masters Report of E. F. Hoy and can be obtained from the author (W. P.).

Discussion

Characterization of the Reactions. Correct interpretation of the calorimetric data is ultimately dependent upon the knowledge of the species present in solution. The molecularity of $[RhCl(COD)]_2$,[7] $[Rh_2X_2(COD)(P(OC_6H_5)_3)_2]$[8] (X = Cl, Br), $[RhX(P(OC_6H_5)_3)_2]_2$ (X = Cl, Br),[8] and $[RhX(P(OC_6H_5)_3)_3]$ (X = Cl, Br)[8] in solution has been established by molecular weight measurements. Conductivity measurements of many of these compounds indicate that they are nonionic.[7,8]

All of the reactions involving the rhodium compounds given in Table I have been previously reported,[7,8] and those involving the palladium compounds have been previously established.[1] We have further substantiated these reactions in solution by incremental addition of a base to a deuteriochloroform solution containing the metal complex and observing the changes *via* pmr. For example, the olefinic absorption at 5.72 ppm (τ scale) in $[RhCl(COD)]_2$ disappears when 1 mol of pyridine is added and a new absorption at 5.79 ppm appears. The reactions which occur when triphenyl phosphite is added to the rhodium compounds were similarly characterized. The pmr data and calorimetric titration curves are fully consistent with the given reactions and leave little doubt that they are as written. The enthalpic change corresponding to the reaction of triphenyl phosphite with the isolated intermediate $[Rh_2Cl_2(COD)(P(OC_6H_5)_3)_2]$ is the same as that observed when triphenyl phosphite is added to $[Rh(COD)Cl]_2$ concomitantly (see Table I, reactions 3 and 5) providing further evidence for this sequence of reactions.

Equilibrium Constants. Equilibrium constants for the reaction of pyridine with $[RhX(COD)]_2$ (eq 1, Table I) may be calculated since the equilibrium concentration of the product, [X], can be calculated by the expression

$$[X] = H/(\Delta H V)$$

where H is the heat evolved upon addition of a given amount of pyridine, ΔH is the known molar enthalpy for the reaction (the calorimetric titrations were continued until the reaction was complete), and V is the volume of solution in liters. The values of the equilibrium constants are $(3.2 \pm 1.1) \times 10^4$, $(5.5 \pm 1.6) \times 10^4$, and $(2.9 \pm 0.2) \times 10^4$ $l.\ mol^{-1}$ for the chloro, bromo, and iodo derivatives, respectively. The large errors in the chloro and bromo derivatives are attributable to the "flatness" of the titration curves (see Figure 1) causing at least one of the terms in the equilibrium expression to be a difference of two similar numbers. As a result, on a statistical basis we cannot distinguish the relative thermodynamic stabilities of the chloro, bromo, and iodo derivatives. The linearity of the titration curves in the bridge-splitting reaction with triphenylphosphine (eq 2, Table I, Figure 1) indicates a very large equilibrium constant ($>5 \times 10^5$ $l.\ mol^{-1}$); *i.e.*, for each incremental addition of base, the reaction has gone essentially to completion. The bridge-splitting reactions for triphenylphosphine have therefore larger equilibrium constants than those for pyridine. This result may have been anticipated in terms of "hard-soft" acid-base theory since the soft acid, rhodium(I), would prefer the soft base triphenylphosphine over the hard base pyridine, but the intrinsic strength of acid-base interactions must also be considered (see following discussion).

Solvent-Solute Enthalpic Contributions. Before the displacement energies in Tables I and II can be interpreted in terms of metal-ligand interactions, one must consider the enthalpic contribution due to the solvent-solute interactions. Equations 4, 5, 7, and 8-12 are of the type

$$AB + B' \rightarrow AB' + B$$

where AB and AB′ are acid-base adducts and B and B′ are two different bases. It has been shown in a limited number of cases that enthalpic changes of reactions of this type are the same in polar, weakly basic solvents (benzene, *o*-dichlorobenzene) as they are in inert (noncomplexing) solvents such as cyclohexane or carbon tetrachloride.[11] The reactions include transition metals as well as bases with widely differing polarity.[12] This result probably means that (1) the bases are not specifically interacting with the solvents, and (2) the solvation energies of the reactants and products are cancelling

---

(11) R. S. Drago, M. S. Nozari, and G. L. Vogel, *J. Amer. Chem. Soc.*, 94, 90 (1972).

(12) M. S. Nozari and R. S. Drago, *Inorg. Chem.*, 11, 280 (1972).

Table II. Derived Enthalpic Changes

Reaction	How derived	ΔH, kcal/mol
8. $[RhCl(COD)(py)] + P(C_6H_5)_3 \rightarrow [RhCl(COD)P(C_6H_5)_3] + py$	$^1/_2$(**2a**)-$^1/_2$(**1a**)	−4.1
9. $[RhBr(COD)(py)] + P(C_6H_5)_3 \rightarrow [RhBr(COD)P(C_6H_5)_3] + py$	$^1/_2$(**2b**)-$^1/_2$(**1b**)	−4.7
10. $[RhI(COD)(py)] + P(C_6H_5)_3 \rightarrow [RhI(COD)P(C_6H_5)_3] + py$	$^1/_2$(**2c**)-$^1/_2$(**1c**)	−6.0
11. $[PdCl_2(py)_2] + 2P(C_6H_5)_3 \rightarrow [PdCl_2(P(C_6H_5)_3)_2] + 2py$	**6b-6a**	−13.0
12. $[PdCl_2(py)_2] + 2P(OC_6H_5)_3 \rightarrow [PdCl_2(P(OC_6H_5)_3)_2] + 2py$	**14-6a**	−8.2
13. $2[RhCl(COD)P(C_6H_5)_3] + [PdCl_2(py)_2] \rightarrow 2[RhCl(COD)(py)] + [PdCl_2(P(C_6H_5)_3)_2]$	**11-2(8)**	−4.8
14. $[PdCl_2(C_6H_5CN)_2] + 2P(OC_6H_5)_3 \rightarrow [PdCl_2(P(OC_6H_5)_3)_2] + 2C_6H_5CN$	**7-6c**	−34.2

to zero so that there is no net solvation contribution to the observed enthalpic change.[13]

It has been well documented that dichloromethane forms complexes with a variety of bases. In the above reaction, one would have B and B′ interacting specifically with the solvent. One can estimate the solvation contribution to the enthalpic changes in Tables I and II as follows. We have excellent evidence that all of the solvent-solute enthalpic contributions, except for the specific interaction of B and B′ with the solvent, will cancel very nearly to zero. One needs only to be concerned with the enthalpic contribution due to the formation of CH_2Cl_2-B and CH_2Cl_2-B′. Since very few enthalpies of formation (ΔH_f) of dichloromethane adducts are available, we will use those of chloroform instead. A large number of chloroform-base enthalpies of formation are available through use of an empirical equation.[14] Chloroform is a stronger acid than dichloromethane toward dimethylacetamide (DMA) [ΔH_f (CH_2Cl_2-DMA) = −2.2 kcal/mol;[15] ΔH_f ($CHCl_3$-DMA) = −4.8 kcal/mol[14]] and probably toward all the bases discussed here.

Consider reaction 8

$$[RhCl(COD)(py)] + P(C_6H_5)_3 \rightarrow [RhCl(COD)(P(C_6H_5)_3] + py$$

Since ΔH_f [$(CH_3)_3P$-$CHCl_3$] = −3.8 kcal/mol and ΔH_f (py-$CHCl_3$) = −4.8 kcal/mol,[16] the enthalpic solvent-solute contribution is ~3.8-4.8 ~ −1.0 kcal/mol. This is much smaller than the observed enthalpic change of −4.1 kcal/mol. A similar argument holds for reactions 9-11.

Consider reaction 12 involving triphenyl phosphite and pyridine. ΔH_f [$C_2H_5(CH_2O)_3P$-$CHCl_3$] = −2.7 kcal/mol and ΔH_f ($CHCl_3$-py) = −4.8 kcal/mol; hence, the solvent-solute contribution is ~2(2.7-4.8) ~ −4.1 kcal/mol, compared to the observed experimental enthalpic change of −8.2 kcal/mol.

Finally, consider reactions 4, 5, and 7 involving triphenyl phosphite and cyclooctadiene. π bases are weaker than phosphine bases. For example, ΔH_f ($CHCl_3$-C_6H_6) = −1.7 kcal/mol and ΔH_f [$CHCl_3$-$C_2H_5(CH_2O)_3P$] = −2.7 kcal/mol. Consequently, the solvent-solute enthalpic contribution to the observed enthalpic change is endothermic; *i.e.*, the enthalpic difference between the products and reactants is probably greater than measured. In conclusion, we find the estimated solute-solvent enthalpic contributions to be far smaller than the observed enthalpic changes by a factor of 2 or more.

Relative Displacement Energies. We obtain the following displacement energies: for rhodium, COD $\ll$ $P(OC_6H_5)_3$ (eq 4 and 5), py $<$ $P(C_6H_5)_3$ (eq 8-10); for palladium, COD $\ll$ py $<$ $P(OC_6H_5)_3$ $<$ $P(C_6H_5)_3$ (eq 7 and 12). It should be emphasized that the relative displacement energies for the palladium compounds involve the displacement of two ligands, while those of rhodium involve only one ligand. The palladium displacement energies contain a mutual inductive effect of one ligand upon the other.

Recently the importance of intrinsic strength as well as hard or softness of acids and bases has been reemphasized.[17,18] The relative displacement energies serve as an illustration of this point. Triphenylphosphine, triphenyl phosphite, and cyclooctadiene would be considered soft ligands while pyridine is harder than the former three. However, we find that the "intrinsic strength" of triphenylphosphine and triphenyl phosphite is greater than pyridine for palladium(II), but cyclooctadiene is far less than pyridine.

In reactions 8-10 steric effects are not predominant since the bulky triphenylphosphine is replacing pyridine and also because the reactions become increasingly more exothermic as the size of the halogen atoms increases (Cl < Br < I). This may suggest that the electronic interaction of the rhodium(I)-phosphorus atoms is greater than that of the rhodium-nitrogen atoms.

As a consequence of the absolute magnitude of the displacement energies for palladium (eq 11 and 12) being considerably larger than those of rhodium (eq 8-10), the ligand exchange reaction given by eq 13 is exothermic and probably spontaneous.

Other Comments. We were quite surprised to find that in the five reactions reported in Table I where the halide was varied, the observed enthalpic changes were nearly all the same. This means that (1) the differences in the electronic and steric effects of the halides in these complexes are very small or that (2) the effect of varying the halide on the enthalpy of the reactant is nearly the same as that on the product so that they effectively cancel out. These data do not imply that the "strengths" of the halogen bridges are nearly the same since the observed enthalpy change for the reaction reflects a simultaneous variation of inductive and steric effects in both the reactant and product. In other words, we are observing an enthalpic variation in the breaking of the bridges *and* the making of the metal-ligand bond.

It has been reported that the bridge-splitting reactions of some rhodium compounds with amines occur easily when the halogen is chloride or bromide, but the iodo compounds tend to be unstable and revert toward the bridged species.[7] If this observation implies a lower equilibrium constant for the iodo derivative, the lower value must be mostly due to the entropy terms.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and to the National Defense Education Act, Grant No. 70.02605.1 for a fellowship to E. F. H.

---

(13) For examples showing the effect of specific solvent-solute interactions, for the definition of terms used here, and for an excellent leading article discussing the difficulties involved in interpreting enthalpic changes of reactions in solution, see M. S. Nozari and R. S. Drago, *J. Amer. Chem. Soc.*, 94, 6877 (1972).

(14) R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Amer. Chem. Soc.*, 93, 6014 (1971).

(15) R. S. Drago, T. F. Bolles, and R. J. Niedzielski, *J. Amer. Chem. Soc.*, 88, 2718 (1966).

(16) Throughout this discussion we will substitute similar bases. For example, here we assume that the ΔH_f [$(CH_3)_3P$-$CHCl_3$] is the same as ΔH_f [$(C_6H_5)_3P$-$CHCl_3$]. The enthalpic differences will be slight.

(17) R. S. Drago and R. A. Kabler, *Inorg. Chem.*, 11, 3144 (1972).

(18) R. G. Pearson, *Inorg. Chem.*, 11, 3146 (1972).

Registry No. $[RhCl(COD)]_2$, 12092-47-6; $[RhBr(COD)]_2$, 12092-45-4; $[RhI(COD)]_2$, 12092-49-8; $[RhCl(COD)py]$, 41812-78-6; $[RhBr(COD)py]$, 33271-94-2; $[RhI(COD)py]$, 33136-41-3; $[RhCl(COD)(P(C_6H_5)_3)]$, 31781-57-4; $[RhBr(COD)(P(C_6H_5)_3)]$, 33136-93-5; $[RhI(COD)(P(C_6H_5)_3)]$, 33136-94-6; $[RhCl(P(OC_6H_5)_3)_2]_2$, 25966-16-9; $[RhBr(P(OC_6H_5)_3)_2]_2$, 26309-79-5; $[RhI(P(OC_6H_5)_3)_2]_2$, 41777-37-1; $[RhCl(P(OC_6H_5)_3)_3]$, 16592-65-7; $[RhBr(P(OC_6H_5)_3)_3]$, 25966-18-1; $[RhI(P(OC_6H_5)_3)_3]$, 41777-40-6; $[Rh_2Cl_2(COD)(P(OC_6H_5)_3)_2]$, 31781-80-3; $[Rh_2Br_2(COD)(P(OC_6H_5)_3)_2]$, 31781-81-4; $[Rh_2I_2(COD)(P(OC_6H_5)_3)_2]$, 41812-86-6; $[PdCl_2(COD)]$, 12107-56-1; $[PdCl_2(P(OC_6H_5)_3)_2]$, 29891-44-9; C_6H_5CN, 100-47-0; C_5H_5N, 110-86-1; $P(C_6H_5)_3$, 603-35-0; $P(OC_6H_5)_3$, 101-02-0; COD, 111-78-4; $[PdCl_2(C_6H_5CN)_2]$, 14220-64-5; $[PdCl_2(py)_2]$, 14872-20-9; $[PdCl_2(P(C_6H_5)_3)_2]$, 13965-03-2; $[PdCl_2(COD)_2]$, 12257-74-8.

Contribution from the William A. Noyes Laboratory,
University of Illinois, Urbana, Illinois 61801

Nature of the Cobalt Center in Methylcobaloxime

ROBERT L. COURTRIGHT, RUSSELL S. DRAGO,* JAMES A. NUSZ, and M. S. NOZARI

Received January 10, 1973

There is considerable uncertainty in the literature about the nature of the cobalt center in methylcobaloxime and similar compounds. In trying to understand which bases will preferentially bind to the cobalt, various criteria which are not directly related to the strength of bonding have been used by various investigators to label the cobalt as a class B or soft center, while others have concluded that it is class A or hard. It is impossible reliably to infer anything about the strength of intermolecular interactions from data in which entropy and solvation contributions have not been factored out, so the often-raised question about the nature of the cobalt center remains unresolved. By using recently reported procedures for obtaining solvation-minimized enthalpies in CH_2Cl_2 and for factoring out constant contributions to measured enthalpies from dimerization or intramolecular interactions, we have been able to measure thermodynamic data which bear directly on the question of bond strength. The entropy term is seen to be the main cause for the poor coordination ability of oxygen donors to this acid. Accordingly, the poor coordination tendencies of oxygen donors compared to sulfur donors are not due to a weaker bond strength or soft character of the cobalt. The data obtained can be fit to our E and C equation and they indicate that methylcobaloxime is a strong acid in which both the E and C properties are large and important in describing the interaction. The C/E ratio is comparable to that found for the borderline acid boron trifluoride and considerably smaller than that for the soft acid iodine. This system is the first in which extra stabilization of an adduct (in this case with phosphite ligands) over that expected from the E and C parameters is found. A π-back-bonding interaction is considered as a potential cause.

Introduction

Methylatobis(dimethylglyoximato)cobalt(III), or methylcobaloxime,[1a] has aroused interest because of its possibilities as a model for vitamin B_{12}. Schrauzer[1b,c] has extensively investigated the chemistry of the cobaloximes and claimed they can be used as models for vitamin B_{12}. A crystal structure on a substituted alkylcobaloxime shows the in-plane Co–N and the Co–C bond lengths to be identical with those in coenzyme vitamin B_{12}.[2] Regardless of the ability of these compounds to model vitamin B_{12}, the cobaloximes merit study for they are unusual chemical compounds in that they form relatively stable compounds with alkyl groups bonded directly to a first-row transition metal atom.

The nature of the cobalt center in methylcobaloxime and related compounds has been the object of considerable speculation.[3-5] It has been compared to both cobalt(II) and cobalt(III) complexes. The lability of the attached ligand L in $CH_3Co(DMG)_2L$ is very atypical of Co(III) complexes. Some authors claim metal–ligand π back-bonding is important,[5b] in this class of compounds, while others claim it is not.[3]

Several authors[4,5b] have claimed that methylcobaloxime is a class B or soft acid. This assignment of the acid character provided further stimulation for our research because, in our E and C correlation of acids and bases,[6,7] very few class B or soft or large C/E ratio acids have been studied. Furthermore, the conflicting conclusions drawn in earlier work about the nature of the cobalt center in this novel transition metal system require a more definitive set of experimental results which bear more directly on the bond strength.

In this research, enthalpies of interaction of methylcobaloxime with various bases have been calorimetrically determined. In order for these values to be true measures of bond strength, the data must be free of significant solvation contributions; otherwise, they provide no information regarding the nature and strength of the metal–ligand bond. Because of the insolubility of methylcobaloxime in poorly solvating solvents such as cyclohexane and carbon tetrachloride, these studies must be carried out in the relatively polar solvent dichloromethane. However, previous work in this laboratory has led to a procedure for eliminating solvent effects for certain systems studied in polar solvents.[8-10] Utilizing this procedure, it is possible to correct the enthalpies measured in a polar solvent for solvation contributions.

These solvation minimized enthalpies for methylcobal-

---

(1) (a) G. N. Schrauzer, *Accounts Chem. Res.*, 1, 97 (1968), and references therein; (b) G. N. Schrauzer and L. P. Lee, *J. Amer. Chem. Soc.*, 90, 6541 (1968); (c) G. N. Schrauzer, L. P. Lee, and J. W. Sibert, *ibid.*, 92, 2997 (1970).

(2) P. G. Lenhert, *Chem. Commun.*, 980 (1967).

(3) H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Chem. Brit.*, 5, 156 (1969); Firth, *et al.*, *J. Chem. Soc. A*, 381 (1969), and references therein.

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

(5) T. L. Brown, L. M. Ludwick, and R. S. Stewart, *J. Amer. Chem. Soc.*, 94, 384 (1972); (b) L. M. Ludwick and T. L. Brown, *ibid.*, 91, 5188 (1969).

(6) R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Amer. Chem. Soc.*, 93, 6014 (1971).

(7) R. S. Drago and B. B. Wayland, *J. Amer. Chem. Soc.*, 87, 3571 (1965).

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

(9) M. S. Nozari and R. S. Drago, *Inorg. Chem.*, 11, 280 (1972).

(10) M. S. Nozari, C. D. Jensen, and R. S. Drago, *J. Amer. Chem. Soc.*, 94, 3162 (1972).