Heats of Reaction of Triphenyl Phosphite with Some Rhodium–Olefin Compounds

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Abstract: The heats of the following reactions (in CH_2Cl_2) are reported: $[RhCl(olefin)_n]_2 + 2P \rightarrow [Rh_2Cl_2P_2(olefin)_n] + n(olefin)$, $[Rh_2Cl_2P_2(olefin)_n] + 2P \rightarrow [RhClP_2]_2 + n(olefin)$, and $[RhClP_2]_2 + 2P \rightarrow 2[RhClP_3]$, where olefin is norbornadiene, 1,5-cyclooctadiene, 1,3,5,7-cyclooctatetraene, dicyclopentadiene, benzoquinone ($n = 1$), and *cis*-cyclooctene ($n = 2$), and P is triphenyl phosphite, and $[Rh(acac)(olefin)] + 2P \rightarrow [Rh(acac)P_2] +$ olefin (in CH_2Cl_2 or CCl_4) where olefin is 1,5-cyclooctadiene or 1,3,5,7-cyclooctatetraene. Relative displacement energies have been calculated, evidence given that the solvation terms largely cancel to zero, and an identical ordering is found for rhodium(I) and palladium(II) compounds: norbornadiene > 1,5-cyclooctadiene > 1,3,5,7-cyclooctatetraene > dicyclopentadiene. Replacement of two monoolefins by a chelating diolefin in rhodium(I) compounds is strongly exothermic. The similarity of the displacement energies to the heats of adsorption on metallic surfaces and the far-ir spectra of these compounds are briefly discussed.

There has been an impressive growth in the number and variety of metal–olefin compounds in the last 20 years.[1-3] Interest in metal–olefin compounds stems largely from attempts to elucidate the nature of the metal–olefin bond, their use as model compounds in homogeneous catalysis, and as catalysts in a variety of olefin isomerizations and polymerizations.[3] Thermodynamic information relating to the metal–olefin bond is therefore of great interest.

Thermodynamic data for palladium–, platinum–, and silver–olefin compounds have been reviewed.[2,4] The primary reason for obtaining thermodynamic data has been to elucidate the nature of the metal–olefin bond. This has been achieved by varying the electronic, steric, and strain characteristics of the olefin and observing how this affects the metal–olefin interaction. These effects are most directly manifested by enthalpic changes. It is therefore noteworthy to mention that the authors are unaware of any systematic studies in which accurate enthalpic changes have been measured in relatively nonpolar solvents until our first report dealing with palladium(II) compounds.[5] Many studies report only equilibrium constants usually measured in polar solvents such as water and alcohols.[6-9] Interpretation of the equilibrium constants are difficult due to solvation effects and the unknown entropy term. Indeed, different orderings of the stability of olefins toward the argentous ion have been found in water and in ethylene glycol,[10] and vinyl fluoride is less stable toward rhodium(I) than ethylene, but probably has a stronger bond than ethylene.[11] The enthalpic changes which are available are either inaccurate,[11] measured in polar solvents,[12-14] or measured in different phases.[15,16]

This paper is a second in a series in which relative olefin–metal, and in general base–metal, displacement energies will be determined and examined for the presence of specific solvent effects. The first paper was concerned with a number of chelating bases with palladium(II),[5] and this paper extends the work to rhodium(I) compounds. The chelating metal–olefin compounds have been initially chosen because they are unusually "stable," have been well characterized, and are available for most of the transition metals and consequently represent a good series of model compounds for the initial calorimetric studies.

Experimental Section

Organic microanalyses were performed by Instranal Laboratories. Nmr spectra were recorded on a Varian A-60 spectrometer. Ir spectra were recorded on a Beckman IR-12 instrument using cesium iodide plates.

Materials. Baker AR grade dichloromethane was dried with Linde 4A molecular sieves at least 24 hr prior to 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.). The following complexes were prepared using previously reported procedures and recrystallized before use: [RhCl(1,5-cyclooctadiene)]$_2$[17] (*Anal.* Calcd for $C_8H_{12}RhCl$: C, 39.02; H, 4.88. Found: C, 39.10; H, 4.79.), [RhCl(norbornadiene)]$_2$,[18] [RhCl(cyclooctene)$_2$]$_2$[19] (not recrystallized before use) (*Anal.* Calcd for $C_{16}H_{28}RhCl$: C, 53.56; H, 7.88. Found: C, 53.75; H, 8.02.). [RhCl(1,3,5,7-cyclooctatetraene)]$_2$ was prepared by a previously reported procedure,[20] washed with ether, and dried under reduced pressure before use.

Preparation of Di-μ-chloro-bis(p-benzoquinone)dirhodium(I). Sublimed *p*-benzoquinone (0.1533 g, 1.42 mmol) was added to a

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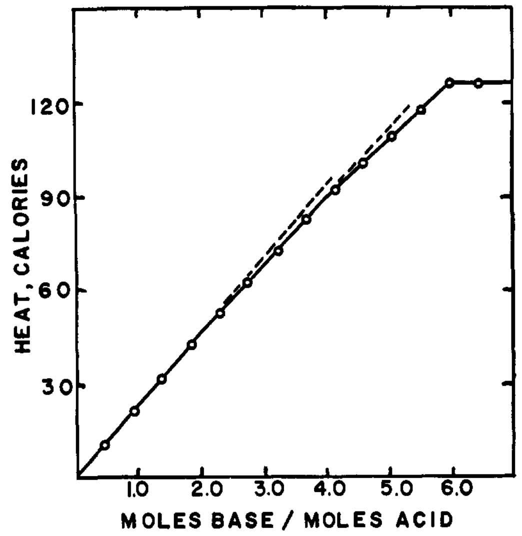

Figure 1. Calorimetric titration curve of di-μ-chloro-bis(dicyclopentadiene)dirhodium(I) with triphenyl phosphite. Initial concentration of the rhodium complex is 0.001625 mol.

solution of 0.5014 g (0.699 mmol) of [RhCl(cyclooctene)$_2$]$_2$ in 100 ml of dichloromethane. The resultant bright red precipitate was filtered, washed with anhydrous ether, and dried under reduced pressure yielding 0.2655 g (0.539 mmol) of product. *Anal.* Calcd for $C_6H_4O_2RhCl$: C, 29.19; H, 1.64. Found: C, 29.24; H, 2.24.

Preparation of Di-μ-chloro-(dicyclopentadiene)dirhodium. [RhCl(cyclooctene)$_2$]$_2$ (0.7267 g, 1.01 mmol) was added to a solution of 2 ml of dicyclopentadiene in 20 ml of dichloromethane. The solution was stirred for 1 hr, filtered, washed with petroleum ether, and recrystallized from dichloromethane–hexane yielding 0.4350 g (0.804 mmol) of product. *Anal.* Calcd for $C_{10}H_{12}RhCl$: C, 44.39; H, 4.43. Found: C, 44.12; H, 4.48.

Preparation of Acetylacetonato(1,3,5,7-cyclooctatetraene)rhodium(I). Di-μ-chloro-bis(cyclooctene)dirhodium(I) (1.204 g, 1.679 mmol) was added slowly to a 300-ml dichloromethane solution containing 1.021 g (3.364 mmol) of thallium(I) acetylacetonate. Cyclooctatetraene (3 ml) was added to the resultant slurry; the mixture was stirred for 1 hr, and filtered using Elite filter aid. The filtrate was evaporated under reduced pressure, and the resultant solid was recrystallized from carbon tetrachloride–hexane yielding 0.8602 g (2.81 mmol) of the desired product. Nmr and ir data of the product were similar to that previously reported.[20]

Preparation of Acetylacetonato(1,5-cyclooctadiene)rhodium(I). The preparation was identical with that of acetylacetonato(1,3,5,7-cyclooctatetraene)rhodium (I).

Apparatus and Procedure. Calorimetric measurements were made using a Guild solution calorimeter equipped with a base line compensator. Heats of reaction were measured by incremental addition of triphenyl phosphite to a 200-ml solution of the rhodium compound in dichloromethane with an 0.2- or 2-ml Gilmont micrometer buret.

[RhCl(benzoquinone)]$_2$ was not sufficiently soluble for the calorimetric measurements; however, [Rh$_2$Cl$_2$(benzoquinone)$_2$(P(OC$_6$H$_5$)$_3$)$_2$] was. The latter compound was prepared *in situ* by addition of the exact requisite amounts of *p*-benzoquinone and triphenyl phosphite to [RhCl(cyclooctene)$_2$]$_2$ in 200 ml of dichloromethane. [Rh(acac)(P(OC$_6$H$_5$)$_3$)$_2$] is only partially soluble in carbon tetrachloride and precipitation occurred upon addition of triphenyl phosphite to [Rh(acac)(olefin)]. Calorimetrically, the addition of triphenyl phosphite to [Rh(acac)(olefin)] results in an initial rapid liberation of heat due to the reaction, followed by a very slow liberation of heat due to precipitation of the product, [Rh(acac)(P(OC$_6$H$_5$)$_3$)$_2$]. We have found that the heat of reaction determined before a precipitation process is the same as when no precipitation occurs if the precipitation is not too rapid.[21]

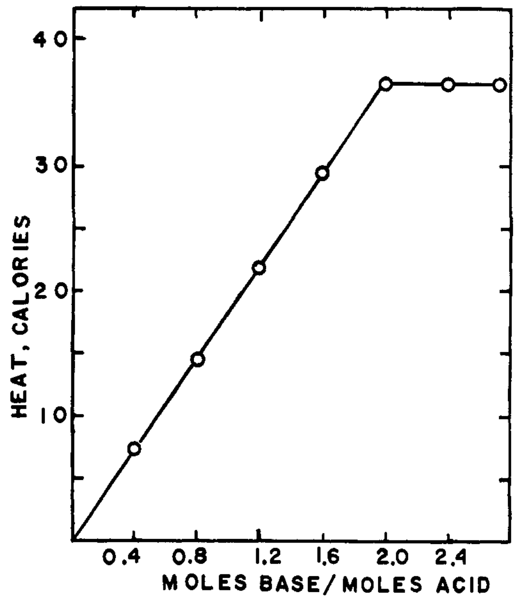

Figure 2. Calorimetric titration curve of acetylacetonato(cyclooctadiene)rhodium(I) with triphenyl phosphite. Initial concention of the rhodium complex is 0.00172 mol.

Results

Calorimetric titration curves (see Figures 1 and 2) can be constructed from the data obtained from the incremental addition of triphenyl phosphite to the rhodium compounds. Figure 1 gives a typical result when the starting compound is of the type [RhCl(olefin)]$_2$. Three different slopes are discernible indicating that three concomitant reactions are occurring. The linearity of the curves indicate that the reactions have very large equilibrium constants. Figure 2 illustrates a typical result when the starting material is of the type [Rh(acac)(olefin)]. Only one reaction is observed.

Table I summarizes the calorimetric results. The enthalpies were found by calculating the slopes of the titration curves using the linear least-squares method. The standard deviation of these slopes (see Table I) was nearly always less than 1% indicating that the incremental addition was very precise. The point of intersection of the lines was calculated from the slopes and intercepts determined by the least-squares method. The breaking points occur when 2, 4, and 6 equiv of triphenyl phosphite is added to [RhCl(olefin)]$_2$ and at 2 equiv of triphenyl phosphite when it is added to compounds of the type [Rh(acac)(olefin)].[22] For example, the calculated breaking points in Figure 1 are 2.01, 4.14, and 5.99 (mole ratio), and the breaking point in Figure 2 is 1.99.[22]

Discussion

Characterization of the Reactions. Correct interpretations of the calorimetric data are ultimately dependent upon the knowledge of the species present in solution. The molecularity of [RhCl(olefin)$_2$][17,18] (olefin = 1,5-cyclooctadiene, norbornadiene, 1,3,5,7-cyclooctatetraene), of [Rh$_2$X$_2$(P(OC$_6$H$_5$)$_3$)$_2$] (X = Cl, Br; olefin = norbornadiene, 1,5-cyclooctadiene),[23]

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[21] The reaction of dichlorobis(benzonitrile)platinum(II) with triphenylphosphine to give dichlorobis(triphenylphosphine)platinum(II) in dichloromethane has an enthalpy of 39.2 ± 0.8 kcal/mol determined before precipitation commenced and 38.4 ± 0.8 kcal/mol after precipitation occurred.

[22] Occasionally two concomitant slopes had nearly the same values which gave very inaccurate breaking points whose values were quite divergent from 2, 4, or 6.

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Table I. Calorimetric Data for Rhodium–Olefin Compounds

Olefin	$-\Delta H$, kcal/mol	Standard deviation of slope	No. of data points
(1) $[RhCl(olefin)]_2 + 2P^f \longrightarrow [Rh_2Cl_2(olefin)P_2]$ + olefin			
Norbornadiene	28.1 ± 0.7	0.08	4
1,5-Cyclooctadiene	28.2 ± 0.7	0.04	3
	29.4 ± 0.7	0.14	3
1,3,5,7-Cyclooctatetraene	27.6 ± 0.7	0.60	4
Dicyclopentadiene	28.5 ± 0.7	0.12	4
cis-Cyclooctene[a]	31.8 ± 0.8	*d*	2
	32.2 ± 0.8	*d*	2
(2) $[Rh_2Cl_2(olefin)P_2] + 2P \longrightarrow [RhClP_2]_2$ + olefin			
Norbornadiene[b]	22.6 ± 0.6	0.04	5
1,5-Cyclooctadiene	23.0 ± 0.6	0.06	3
	23.4 ± 0.6	0.28	3
	23.9 ± 0.6[c]	*d*	2
1,3,5,7-Cyclooctatetraene	25.2 ± 0.6	0.14	4
Dicyclopentadiene	26.3 ± 0.7	0.18	4
cis-Cyclooctene	30.3 ± 0.8	*d*	2
	30.2 ± 0.8	*d*	2
Benzoquinone	33.5 ± 0.8	0.08	3
(3) $[RhClP_2]_2 + 2P \longrightarrow 2[RhClP_3]$			
	24.2 ± 0.6	0.22	3
Norbornadiene[e]	21.5 ± 0.5	0.12	4
1,5-Cyclooctadiene	22.8 ± 0.6	0.04	3
	23.8 ± 0.6[c]	*d*	2
1,3,5,7-Cyclooctatetraene	23.6 ± 0.6	0.22	4
Dicyclopentadiene	22.6 ± 0.6	0.08	5
cis-Cyclooctene	23.4 ± 0.6	*d*	2
	23.4 ± 0.6	*d*	2
Benzoquinone	24.2 ± 0.6	0.20	3
(4) $[Rh(acac)(olefin)] + 2P \xrightarrow{CCl_4} [Rh(acac)P_2]$ + olefin			
1,5-Cyclooctadiene	23.8 ± 0.6	0.07	5
1,3,5,7-Cyclooctatetraene	28.3 ± 0.7	0.20	3
(5) $[Rh(acac)(olefin)] + 2P \xrightarrow{CH_2Cl_2} [Rh(acac)(P)_2]$ + olefin			
1,5-Cyclooctadiene	21.4 ± 0.5	0.10	5
	21.9 ± 0.5	0.06	3
1,3,5,7-Cyclooctatetraene	25.8 ± 0.6	0.01	5

[a] Starting material has stoichiometry $[RhCl(cyclooctene)_2]_2$. [b] Values obtained using $[RhCl(olefin)_2]_2$ as starting material, except where footnoted. [c] Starting material was $[Rh_2Cl_2(olefin)(P(OC_6H_5)_3)_2]$. [d] Standard deviation was not defined since only two points were available. [e] Starting material in all but the first enthalpy was $[RhCl(olefin)]_2$. The olefin given refers to the initial rhodium olefin compound used. [f] P = triphenyl phosphite.

of $[RhX(P(OC_6H_5)_3)_2]_2$ (X = Cl, Br),[23] of $[RhX((P(OC_6H_5)_3)_3]$[23] (X = Cl, Br), and of $[Rh(acac)(C_8H_8)]$[20] in solution has been established by molecular weight measurements. Conductivity measurements on many of these compounds indicate that they are nonionic.[17,23] X-Ray crystal structures have been reported for $[RhCl(C_8H_{12})]_2$[24] and $[Rh_2Cl_2(C_8H_{12})(P(OC_6H_5)_3)_2]$.[25]

The following reactions have been reported for the cyclooctadiene and norbornadiene derivatives[23]

$$[RhCl(olefin)]_2 + 2P \longrightarrow [Rh_2Cl_2(olefin)P_2] + \text{olefin} \quad (1)$$

$$[Rh_2Cl_2(olefin)P_2] + 2P \longrightarrow [RhClP_2]_2 + \text{olefin} \quad (2)$$

$$[RhClP_2]_2 + 2P \longrightarrow 2[RhClP_3] \quad (3)$$

where P is triphenyl phosphite and olefin is the chelating diolefin. Since every olefin and its rhodium derivatives reported have unique chemical shifts associated with the olefinic protons, one can observe the first two consecutive reactions *via* nmr by starting with $[RhCl(olefin)]_2$ and incrementally adding triphenyl phosphite. Using this method, we have established that these reactions also occur with cyclooctatetraene, dicyclopentadiene, cyclooctene, and the benzoquinone derivatives. The following reactions were also monitored by nmr

$$[Rh(acac)(olefin)] + 2P \longrightarrow [Rh(acac)P_2] + \text{olefin} \quad (4)$$

where olefin is cyclooctadiene or cyclooctatetraene.

The calorimetric titration curves (see Results) are consistent with the above observations and confirm that three consecutive reactions occur. Confirmation of the reaction given by eq 3 is given by the fact that the same enthalpy is observed for addition of base in the 4–6 mol of base/mol of acid region (see Table I) regardless of the starting olefin–rhodium compound. The only exception to this is norbornadiene which seems significantly low. The weighted mean value of the nine determinations (eq 3, Table I) is 23.2 ± 0.8 with a fractional standard deviation of 3.4%. If one discards the value obtained from the norbornadiene compound, then one obtains a weighted mean value of 23.4 ± 0.6 or a fractional standard deviation of 2.5%. The latter value corresponds close to what we normally observe with our instrument. All of the standard deviations reported on Table I were calculated assuming a fractional standard deviation of 2.5%.

$[Rh(C_8H_8)Cl]_2$[20] has been reported to be unstable in solution. The calorimetric titration curves and nmr studies involving this compound were, however, similar to the other rhodium compounds so that the calorimetric data can be used with confidence. [Rh(norbornadiene)Cl]$_2$ is known to react with norbornadiene, C_7H_8, to produce $[Rh(C_7H_8)_2Cl]$.[26] In our calorimetry experiments, the norbornadiene released when triphenyl phosphite is allowed to react with $[Rh(C_7H_8)Cl]_2$ will in turn react with the remaining rhodium–norbornadiene compound present, producing an additional heat. Using the reported equilibrium constant and enthalpy value,[26] we have calculated that the amount of heat released due to this reaction is negligible in our experiments. The linearity of the calorimetric titration curve in the region 0–2 base/rhodium mole ratio further substantiates this calculation.

Relative Base–Metal Displacement Energies. A displacement reaction of the type

$$[M(olefin)L_n] + C_8H_8 \longrightarrow [M(C_8H_8)L_n] + \text{olefin} \quad (5)$$

where C_8H_8 is 1,3,5,7-cyclooctatetraene and L is some ligand, can be written as the difference of two dissociation energies

$$[M(olefin)L_n] \longrightarrow ML_n + \text{olefin} \quad (D_1)$$

$$[ML_n] + C_8H_8 \longrightarrow [M(C_8H_8)L_n] \quad (-D_2)$$

One can arbitrarily choose as a standard the dissociation energy of cyclooctatetraene (D_2) and allow it to have a value of zero. Using eq 5 one can then determine the *relative* dissociation energies for a series of olefins. For example, using the enthalpy data on Table I

$$[Rh_2Cl_2(C_7H_8)P_2] + 2P \longrightarrow [RhClP_2]_2 + C_7H_8$$
$$\Delta H = -22.6 \text{ kcal/mol}$$

$$[RhClP_2]_2 + C_8H_8 \longrightarrow [Rh_2Cl_2(C_8H_8)P_2] + 2P$$
$$\Delta H = 25.2 \text{ kcal/mol}$$

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(25) J. Coetzer and F. Gafner, *Acta Crystallogr., Sect. B*, **26**, 985 (1970).

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where C_7H_8 is norbornadiene. Adding the last two equations

$$[Rh_2Cl_2(C_7H_8)P_2] + C_8H_8 \longrightarrow [Rh_2Cl_2(C_8H_8)P_2] + C_7H_8$$
$$\Delta H = 2.6 \text{ kcal/mol}$$

The last equation is of type given by eq 5. Since the dissociation energy of cyclooctatetraene is defined as zero, one concludes that the dissociation energy of norbornadiene is 2.6 kcal/mol higher than cyclooctatetraene. We will be evaluating relative dissociation energies for different metals in the same manner. Since the absolute dissociation energy of cyclooctatetraene varies from metal to metal, we will use the term relative *displacement* energy rather than dissociation energy to emphasize this point. Displacement energies derived in this manner are tabulated in Table II. In Table II, we have also included our previously reported enthalpic data for the reactions

$$[PdCl_2(C_6H_5CN)_2] + B \longrightarrow [PdCl_2B] + 2C_6H_5CN$$

where B is a chelating olefin or base. We again use cyclooctatetraene as our standard and evaluate relative displacement energies of the type

$$[PdCl_2B] \longrightarrow PdCl_2 + B$$

Table II. Relative Base–Metal Displacement Energies[a] (kcal/mol)

Base	D(Pd-(base)Cl_2)	D($Rh_2Cl_2P_2$-(base))	D(Rh(acac)-(olefin))
diphos[b]	45.1		
dias[b]	29.8		
Triphenyl phosphite		25.2	
TMEDA[b]	21.7		
Norbornadiene	7.7	2.6	
Cyclooctadiene	7.4	1.8	4.4
1,5-Hexadiene	2.4		
Dipentene	1.2		
Cyclooctatetraene	0.0	0.0	0.0
Dicyclopentadiene	−0.7	−1.1	
Benzoquinone		−8.3	

[a] Relative to cyclooctatetraene. Positive values are displacement energies higher than cyclooctatetraene. [b] diphos = bis(1,2-diphenylphosphino)ethane, dias = bis(1,2-diphenylarseno)ethane, and TMEDA = tetramethylethylenediamine.

We have thus far ignored solvation effects. We believe that the reported displacement energies are very close to those that would be found in the gas phase for the following reasons.

A dissociation energy is very similar to the formation of a Lewis acid–base adduct

$$A + B \longrightarrow AB$$

where A is the acid, B some base, and AB the adduct. It has been shown that if the acid, base, and the adduct interact nonspecifically with a solvent (van der Waals interactions only) that the resultant enthalpy of formation is very nearly that found in the gas phase.[27] It has also been shown[28] that if one measures the enthalpy of the reaction

$$AB + B' \longrightarrow AB' + B$$

and the following relationship holds

$$\Delta H_{\text{solvent A}} = \Delta H_{\text{solvent B}} + \text{constant}$$

then the bases, B and B′ are interacting nonspecifically with the solvent.

From Table I we have

$$[Rh(acac)(C_8H_{12})] + 2P \xrightarrow{CH_2Cl_2} [Rh(acac)P_2] + C_8H_{12}$$
$$H = -21.6 \text{ kcal/mol}$$

$$[Rh(acac)(C_8H_{12})] + 2P \xrightarrow{CCl_4} [Rh(acac)P_2] + C_8H_{12}$$
$$H = -23.8 \text{ kcal/mol}$$

$$[Rh(acac)(C_8H_8)] + 2P \xrightarrow{CH_2Cl_2} [Rh(acac)P_2] + C_8H_8$$
$$\Delta H = -25.8 \text{ kcal/mol}$$

$$[Rh(acac)(C_8H_8)] + 2P \xrightarrow{CCl_4} [Rh(acac)P_2] + C_8H_8$$
$$\Delta H = -28.3 \text{ kcal/mol}$$

We find that $\Delta H_{CCl_4} = \Delta H_{CH_2Cl_2} - 2.4$. We conclude that either the olefins do not specifically interact with the solvents or that the specific interactions are exactly the same. In either case, the solvation terms for the olefins will be equal and will cancel to zero when the displacement energies are calculated. Evidence has already been given that the solvation terms of two similar metal complexes are very nearly the same and cancel to zero in reactions of the type given in eq 6 when nonspecific interactions are occurring.[28] In conclusion, since dissociation energies are very similar to adduct formation, the solvation terms for the olefins and the metal compounds should cancel very closely to zero when the displacement energies are calculated. They should in turn be very close to what would be expected in the gas phase. It should be mentioned, however, that specific solvent-solute interactions probably do exist for the phosphorus, arsenic, and nitrogen donors given in Table II.[29]

Examination of Table II reveals that the ordering of metal–olefin displacement energies is exactly the same for both palladium and rhodium. This may have been anticipated since palladium(II) and rhodium(I) are isoelectronic and form structurally similar compounds. This result gives us added confidence that the metal–olefin displacement energies are not predominantly determined by solvation effects. *p*-Benzoquinone has the lowest metal–olefin displacement energy for the rhodium(I) series and this is consistent with the observation that the analogous palladium(II) compound has not been reported.[5]

An exact analysis of these displacement energies is not possible at the present time since the conformation of most of the coordinated and uncoordinated olefins is not accurately known. The displacement energies would depend upon the following. (1) The metal–olefin "bond strength," *i.e.*, a proper matching of the molecular orbitals giving maximum overlap. According to the Chatt–Duncanson–Dewar model, maximum overlap would be achieved by having the olefinic carbon atoms perpendicular to the square plane containing the metal and the ligands and having the two double bonds form a 90° angle with the metal. (2) The conformation of strain in and conjugation present in the uncoordinated olefin. Lower displacement energies would be observed if the free olefin is conforma-

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(28) M. S. Nozari and R. S. Drago, *Inorg. Chem.*, 11, 280 (1972), and references cited therein.

(29) The heat of solution of tetramethylethylenediamine in dichloromethane is −1.4 kcal/mol.

tionally much different than the coordinated olefin. Considerable strain present in an olefin may be released somewhat upon coordination; hence, increasing amounts of strain would yield higher displacement energies. Loss of conjugation energy upon coordination of the olefin to the metal would result in lower displacement energies. (3) Significant steric interactions of the coordinated olefin with the other ligands would decrease the displacement energy.

The available information on metal–olefin compounds do generally support the observed orderings on Table II. The conformation of the cyclooctadiene is in the tub form in solution[30] and when coordinated to rhodium.[24,25] Cyclooctadiene possesses a fair amount of strain energy.[31] The coordinated olefin has its double bonds perpendicular to the plane containing the metal and the ligands, and the chelated double bonds make an angle of 90° with the metal.[24,25] All of these factors favor a relatively high displacement energy which is observed. Norbornadiene is coordinated to palladium(II) in a similar fashion as cyclooctadiene[32] but a considerable amount of strain in the free olefin ($\sim$35 kcal/mol)[33] may account for the slightly higher displacement energy of norbornadiene than cyclooctadiene. It has been already suggested that the palladium–1,5-hexadiene displacement energy should be lower than the palladium–cyclooctadiene displacement energy since 1,5-hexadiene has a gauche conformation in solution.[30] Cyclooctatetraene is known to be in the tub form in solution.[34] Cyclooctatetraene may have a lesser displacement energy than cyclooctadiene since it has lesser strain energy than cyclooctadiene[33] and would lose some of its conjugation energy ($\sim$8 kcal/mol)[34] upon complexation.

Other Comments

We had mentioned earlier that many workers have postulated steric, strain, and electronic factors affecting the metal–olefin interaction having a knowledge only of the equilibrium constant. The danger in ignoring the entropy term can be shown by combining our data with some that have been previously reported.[8] Using the data in Table I we can calculate the enthalpy for the reaction

$$[\mathrm{RhCl(C_8H_8)}]_2 + \mathrm{C_{10}H_{12}} \longrightarrow [\mathrm{RhCl(C_{10}H_{12})}]_2 + \mathrm{C_8H_8}$$
$$\Delta H = 2.0 \text{ kcal/mol}$$

where C_8H_8 is cyclooctatetraene and $C_{10}H_{12}$ is dicyclopentadiene. The reported equilibrium constant for this reaction in chloroform is 6000.[8] We thus have a reaction with a very favorable free energy but with a positive enthalpic term. Similarly, the rhodium–cyclooctadiene compound is reported to be much more stable than cyclooctatetraene[8] yet the enthalpy is only weakly exothermic, -1.6 kcal/mol.

The replacement of 2 mol of the monodentate olefin cyclooctene by the chelating olefin 1,5-cyclooctadiene is a strongly exothermic process. This can be shown as

$$[\mathrm{Rh_2Cl_2(C_8H_{14})_2P_2}] + 2\mathrm{P} \longrightarrow [\mathrm{RhClP_2}]_2 + 2\mathrm{C_8H_{14}}$$
$$\Delta H = -30.1 \text{ kcal/mol}$$

$$[\mathrm{RhClP_2}]_2 + \mathrm{C_8H_{12}} \longrightarrow [\mathrm{Rh_2Cl_2(C_8H_{12})P_2}] + 2\mathrm{P}$$
$$\Delta H = 23.2 \text{ kcal/mol}$$

Addition of the previous two equations gives

$$[\mathrm{Rh_2Cl_2(C_8H_{14})_2P_2}] + \mathrm{C_8H_{12}} \longrightarrow [\mathrm{Rh_2Cl_2(C_8H_{12})P_2}] + 2\mathrm{C_8H_{14}}$$
$$\Delta H = -6.9 \text{ kcal/mol}$$

Similarly

$$[\mathrm{RhCl(C_8H_{14})_2}]_2 + 2\mathrm{C_8H_{12}} \longrightarrow [\mathrm{RhCl(C_8H_{12})}]_2 + 4\mathrm{C_8H_{14}}$$
$$\Delta H = -10.3 \text{ kcal/mol}$$

The "chelate effect," illustrated above, has therefore a large exothermic term as well as a presumably large positive enthropic term. A common qualitative observation is that chelating olefin–metal compounds are far more stable than monoolefinic–metal compounds. This observation can thus be at least partially explained by thermodynamic arguments.

Significant long-range inductive effects are present in these molecules as illustrated by the heat of reaction of triphenyl phosphite with $[\mathrm{Rh(C_7H_8)Cl}]_2$ and $[\mathrm{Rh_2(C_7H_8)P_2Cl_2}]$. An enthalpy difference of 2.8 kcal/mol is observed when the norbornadiene ligand is replaced by two triphenyl phosphite ligands three atoms (Rh–Cl–Rh) away from the reaction site. Other examples can be obtained from Table I.

Examination of Table III shows that the rhodium–chlorine stretching frequencies decrease as the displacement metal–olefin dissociation energies increase, but that this correspondence is not found for the similar palladium(II) compounds. It has been proposed that the decrease in the metal–chlorine frequencies reflect an increase in the σ-bond character of the trans ligand,[35] although difficulties with this interpretation have already been pointed out.[5]

Table III. Metal–Chlorine Stretching Frequencies in Compounds of the Type $[\mathrm{Pd(olefin)Cl_2}]$ and $[\mathrm{Rh(olefin)Cl}]_2$[a]

Olefin	ν(Pd–Cl) (A_1)	ν(Pd–Cl) (B_1)	ν(Rh–Cl) (A_1)	ν(Rh–Cl) (B_1)
Norbornadiene	306	340	239 (sh)	247
Cyclooctadiene	295	334	254	279
1,5-Hexadiene	310	333		
Cyclooctatetraene	318	342	260	283
Dicyclopentadiene	316	334	265[b]	287
p-Benzoquinone			318[c]	318

[a] Olefins arranged in order of decreasing metal–olefin displacement energies. [b] There is also an absorption at 245 cm^{-1}. [c] Absorption is broad.

A justification for studying the properties of organometallic compounds has been to relate these to catalytic reactions which take place on the surface of metals.[36] Of fundamental interest, is the strength of chemisorption of molecules on the surface since this is related to the weakening of chemical bonds in the adsorbed moiety and also to the rate of desorption. A pertinent question is whether the relative displacement energies determined in this work can be related to

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heats of adsorption. It has already been shown that heats of adsorption have similar values to heats of reactions in the gas phase.[37,38] Two qualitative similarities can be noted between our work and surface phenomena. If a species has too high a heat of chemisorption, it will be too tenaciously held to the surface and will retard its catalytic activity. Common catalytic poisons are nitrogen and phosphorus donors. Reactions of olefins are commonly catalyzed by metal surfaces. The relative displacement energies of the nitrogen and phosphorus donors are much higher than the polyolefins consistent with these observations. In studies involving competitive adsorption, apparently diolefins are chemisorbed more strongly than simple olefins.[36] We have found that the displacement energy of two monoolefins is less than all the polyolefins studied here.

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Synthesis and Far-Infrared Spectra of Ferric Octaethylporphine Complexes

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Abstract: Ferric octaethylporphine (OEP) complexes of the types Fe(OEP)X ($X^- = CH_3COO^-, F^-, Cl^-, Br^-, I^-, N_3^-$, and NCS^-) and $[Fe(OEP)L_2](ClO_4)$ (L = γ-picoline, imidazole and benzimidazole) have been prepared, and their infrared spectra have been measured in the 4000–100-cm^{-1} region. The Fe–N(OEP), Fe–X, and Fe–L stretching bands have been assigned based on metal isotope substitution ($^{54}Fe/^{56}Fe$).

Heme coenzymes are of great importance in biological systems and as such have been investigated extensively by chemists. In hemoglobin, the iron is in the ferrous state, whereas it is in the ferric state in cytochromes and methemoglobin.

Ferric porphyrins containing axial ligands have been studied by a number of physicochemical methods. X-Ray analyses have been carried out on methoxyiron(III) mesoporphyrin IX dimethyl ester,[1] chloroiron(III) tetraphenylporphine[2] and bis(imidazole)tetraphenylporphinatoiron(III) chloride.[3] Mössbauer spectroscopy has been used extensively to study the structure and bonding of these and related complexes.[4–6] Proton magnetic resonance spectra have been reported,[7,8] and electronic spectra have been measured and assigned.[9,10] According to these investigations, ferric complexes containing axial ligands can be high or low spin depending upon the temperature and the nature of the axial ligand. In general, the central metal–nitrogen skeleton is square pyramidal in high-spin complexes and square planar in low-spin complexes.

Thus far, almost no infrared studies have been reported in ferric porphyrin complexes containing axial ligands. It is anticipated that low-frequency infrared spectra will provide valuable information about the structure of the complex and the strength of the iron–ligand bonds. The main purposes of this paper are to report the facile preparation of ferric octaethylporphine (OEP) complexes containing axial ligands and to correlate their far-infrared spectra with structural and bonding information obtained by other methods.

Experimental Section

Preparation of Compounds. Octaethylporphine (OEP) was prepared according to the method of Inhoffen, *et al.*,[11] and purified by chromatography on alumina (Brockmann Grade III) with chloroform.[12] Deep red crystals were obtained by recrystallization from a chloroform–methanol mixture.

Fe(OEP)(CH_3COO). Finely pulverized iron metal (120 mg) was refluxed in 30 ml of glacial acetic acid under nitrogen until iron powder was dissolved.[11] After 100 mg of OEP was added to this solution, it was maintained under gentle refluxing for 1 hr and allowed to cool to room temperature. Air was introduced into the reaction mixture for several hours. Lustrous blue-black crystals were collected, washed with ether, and dried in air. Recrystallization from acetic acid yielded 100 mg of Fe(OEP)(CH_3OO).

Fe(OEP)X ($X^- = F^-, Cl^-, Br^-, I^-, N_3^-$, and NCS^-). A chloro-

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