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Heats of Reaction of Chelated Olefin and Other Ligands with Dichlorobis(benzonitrile)palladium(II)

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Received June 7, 1971

The heats of the reaction

$$[PdCl_2(C_6H_5CN)_2] + L\text{-}L \xrightarrow{CH_2Cl_2} [PdCl_2(L\text{-}L)] + 2C_6H_5CN$$

where L-L is a bidentate chelate ligand are reported. The enthalpies range from −5 to −50 kcal/mol and are in the order diphos > diars > TMEDA ~ py > 1,5-cyclooctadiene ~ norbornadiene > 1,5-hexadiene > dipentene > cyclooctatetraene > dicyclopentadiene. Solvation energies of TMEDA and the olefins have been determined or estimated and probable bond energies are in the orders N donor > olefin donor and cyclooctadiene, norbornadiene > 1,5-hexadiene, cyclooctatetraene. *p*-Benzoquinone and duroquinone do not react with $[PdCl_2(C_6H_5CN)_2]$ at room temperature. The infrared spectra of these compounds are briefly discussed.

Introduction

There has been an impressive growth in the number and variety of metal–olefin compounds prepared in the last 20 years.[1–4] Interest in these compounds stems largely from attempts to elucidate the nature of the metal–olefin bond, their use as model compounds in homogeneous catalysis, and their use as catalysts in a variety of olefin isomerizations and polymerizations.[3] Information pertaining to the strength of the metal–olefin bond is of fundamental importance in all these areas.

There is little known regarding the stability of chelated metal–olefin compounds. A qualitative ordering of some olefins with platinum has been given[5] and the relative stabilities of some rhodium–olefin compounds have been reported.[6] Muhs and Wiess reported formation constants of a variety of olefinsilver compounds in ethylene glycol.[7] The relative stabilities of nitrogen donors, monoolefins, halide ions, and water with platinum have been determined in water.[8]

Experimental Section

Apparatus and Procedure.—Calorimetric measurements were made using a Guild solution calorimeter[9] equipped with a baseline compensator. Checks with previously reported enthalpies were occasionally made (heat of neutralization of hydrochloric acid and sodium hydroxide; heat of solution of potassium chloride) and agreement, within 2%, was observed. The heats of reaction were obtained by addition of the solid $[PdCl_2(C_6H_5CN)_2]$ to 200 ml of dichloromethane solution containing the dissolved base. All of the reactions were very rapid, being complete within 30 sec. A large excess of base was treated with $[PdCl_2(C_6H_5CN)_2]$ except for diphos and dias (see Table I). All reported heats are corrected for the heat of solution of $[PdCl_2(C_6H_5CN)_2]$ (8.43 ± 0.19 kcal/mol). The error reported in Table I is the standard deviation from four or five independent determinations. In no cases were there any detectable trends of observed heat of reaction with concentration of base or palladium compound.

TABLE I

HEAT OF REACTION OF $[PdCl_2(C_6H_5CN)_2]$ WITH VARIOUS LIGANDS

Ligand	$-\Delta H$, kcal/mol	$10^4[PdCl_2(C_6H_5CN)_2]$,[a] M	10^3[Ligand],[a] M
Dicyclopentadiene	4.9 ± 0.1	1.53–1.99	4.55–5.51
Cyclooctatetraene	5.6 ± 0.1	1.37–2.12	4.15–5.05
Cyclododecatriene	5.9 ± 0.1	1.77–2.64	3.78–4.63
Dipentene[b]	6.8 ± 0.3	1.32–3.53	2.79–3.77
Hexadiene	8.0 ± 0.4	1.28–1.72	3.44–4.95
Cyclooctadiene	13.0 ± 0.4	0.801–1.33	4.67–5.15
Norbornadiene	13.3 ± 0.8	0.766–0.974	0.75–3.51
Pyridine	26.0 ± 0.7	0.698–0.905	7.86–8.34
TMEDA	27.3 ± 1.7	0.144–0.194	0.178–0.362
diars	35.2 ± 0.7	1.38–1.91	0.0575–0.0983
diphos	50.5 ± 1.7	0.99–2.77	0.0412–0.0573

[a] Range of concentrations used in evaluation of heat of reaction. [b] Olefin was gas chromatographically impure.

Materials.—Baker AR grade dichloromethane was dried with Linde 4A Molecular Sieves at least 24 hr prior to use. All liquid bases were distilled, at either atmospheric or reduced pressure, under nitrogen, into a receiver containing Linde 4A Molecular Sieves. All the olefins were gas chromatographically pure except for 1,5-cyclooctadiene, which contained approximately 2% 1,3-cyclooctadiene, and dipentene, which contained ~5% impurities. Strem diphos and dias were recrystallized, and benzoquinone and duroquinone were sublimed before use. $[PdCl_2(C_6H_5CN)_2]$ was prepared as previously described.[10] Only the first crop of crystals, which precipitated from the benzonitrile solution upon cooling, was used in the calorimetry experiments. *Anal.* Calcd for $PdCl_2N_2C_{14}H_{10}$: C, 43.83; H, 2.63. Found: C, 44.19; H, 2.48. All of the compounds used in this work have been previously described.[11]

Infrared Spectra.—The ir mull spectra were recorded on a Beckman IR-12 instrument using polyethylene and cesium iodide plates. CH_2Cl_2 solutions (0.02 M) of $[PdCl_2(C_6H_5CN)_2]$ before and after the addition of olefins were examined in the 2000–2400-cm^{-1} region (see Results).

Results

Characterization of the Reaction.—Before interpretation of the heats of reaction can be given, one

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[1] F. R. Hartley, *Chem. Rev.*, **69**, 799 (1969); see also other review articles quoted therein.

[2] C. P. M. Beverwijk, G. J. M. Van der Kerk, A. J. Leusink, and J. G. Noltes, *Organometal. Chem. Rev., Sect. A*, 215 (1970).

[3] U. Belluco, B. Crociani, R. Pictropaulo, and P. Uguagliati, *Inorg. Chim. Acta Rev.*, **3**, 19 (1970).

[4] E. O. Fischer and H. Werner, "Metal Pi-Complexes," Elsevier, New York, N. Y., 1966; this is a comprehensive review of polyolefinmetal compounds.

[5] J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 2496 (1957).

[6] H. C. Volger, M. M. P. Gaasbeck, H. Hogeveen, and K. Vrieze, *Inorg. Chim. Acta*, **3**, 145 (1969).

[7] M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, **84**, 4697 (1962).

[8] R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc. A*, 324 (1967).

[9] Design of the instrument is essentially the same as that described by E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. Duggleby, *J. Amer. Chem. Soc.*, **87**, 1541 (1965).

[10] M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *ibid.*, **60**, 882 (1938).

[11] (a) (**1**)$PdCl_2$, (**6**)$PdCl_2$ (boldface number refers to ligand in Figure 1): J. Chatt, L. M. Vallarino, and L. M Venanzi, *J. Chem. Soc.*, 3413 (1957); (b) (**2**)$PdCl_2$: H. P. Fritz and H. Keller, *Chem. Ber.*, **95**, 158 (1962); (c) (**3**)$PdCl_2$: E. Kuljian and H. Frye, *Z. Naturforsch. B*, **19**, 651 (1964); (d) (**5**)$PdCl_2$: K. A. Jensen, *Acta Chem. Scand.*, **7**, 866 (1953); (e) (**7**)$PdCl_2$: M. Avram, E. Sliam, and C. D. Nenitzescu, *Ann.*, **636**, 184 (1960); (f) (**10**)$PdCl_2$, (**11**)$PdCl_2$: A. D. Westland, *J. Chem. Soc.*, 3060 (1965).

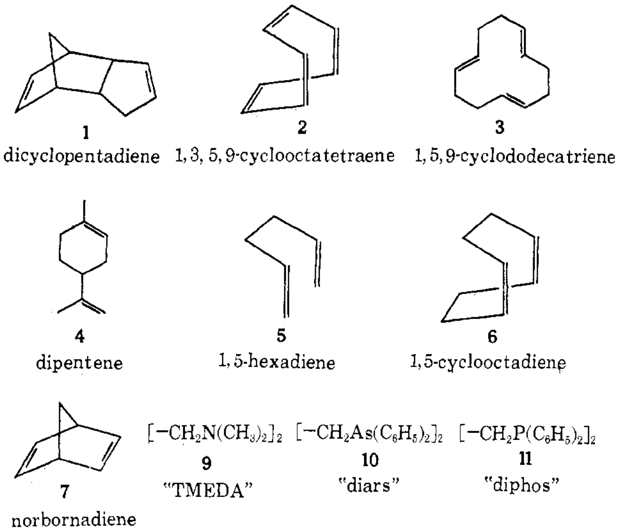

Figure 1.

must establish with a high degree of certainty what the reaction is in solution. The following discussion will show that the reaction of the palladium complex with all the bases is given by

$$[PdCl_2(C_6H_5CN)_2] + L\text{-}L \xrightarrow{CH_2Cl_2} [PdCl_2(L\text{-}L)] + 2C_6H_5CN \quad (1)$$

Since equilibrium constants were not measured, one must establish whether or not the reaction has gone to completion. Such information can be gained from ir spectroscopy. A dichloromethane solution containing benzonitrile has an intense absorption at 2230 cm^{-1}, attributable to the NC stretching frequency. Fresh solutions of $[PdCl_2(C_6H_5CN)_2]$ have a strong absorption at 2291 cm^{-1}, due to the coordinated benzonitrile, and a minor absorption at 2230 cm^{-1}.[12] When, approximately, a 2 molar excess of an olefin or pyridine is added to the $[PdCl_2(C_6H_5CN)_2]$ solution, only one absorption at 2230 cm^{-1} is observed. Exceptions to this are benzoquinone and duroquinone where no changes in the ir spectra were observed. It is therefore established that all of the benzonitrile was displaced from the palladium complex; *i.e.*, the reaction was complete, in all cases except for benzoquinone and duroquinone.

X-Ray crystal studies have established that $[PdCl_2(\text{cyclooctatetraene})]$,[13] $[PdCl_2(\text{norbornadiene})]$,[14] $[PdCl_2(\text{hexadiene})]$,[15] the isoelectronic $[RhCl_2(\text{cyclooctadiene})]_2$,[16] $[PtCl_2(\text{dicyclopentadiene})]$,[17] and $[PtCl_2(\text{dipentene})]$[18] are square-planar compounds, with two double bonds coordinated to the metal atom. Proton nmr studies of $[PdCl_2(\text{cyclooctatetraene})]$, $[PdCl_2(\text{cyclooctadiene})]$ in dichloromethane,[19] and $[PdCl_2(1,5\text{-hexadiene})]$ in $DCCl_3$[15] indicate that the 1,5 olefin bonds are both coordinated to the palladium atom in solution. $[PdI_2(\text{diphos})]$[20] and a number of chelated poly(olefin)platinum compounds[21] have been shown to be monomers in solution.

The ir study eliminates the possibility of a compound such as $[PdCl_2(C_6H_5CN)(\text{olefin})]$ where the olefin is monodentate. A compound of the type $[PdCl_2(\text{olefin})(\text{solvent})]$ is highly unlikely considering the weak basicity of the solvent and the chelating tendency of the olefins.

There is no evidence for formation of a Magnus type salt $[Pd(\text{olefin})_2][PdCl_4]$. $[PdCl_2(1,5\text{-hexadiene})]$[15] and similar platinum-olefin compounds are reported to be nonelectrolytes in nitrobenzene.[5] The ir spectra of all the isolated olefin compounds have two intense absorptions between 280 and 350 cm^{-1}, attributable to metal–halogen stretching modes and consistent with compounds of the type *cis*-$Pd(\text{olefin})Cl_2$.[22] Of course the isolated solid may not be the predominant species in solution but merely the more insoluble one. A salt of the Magnus variety should be less soluble than a compound of the type $[Pd(\text{olefin})Cl_2]$. The compounds $[Pd(\text{diphos})Cl_2]$ and $[Pd(\text{diars})Cl_2]$,[11e,23] prepared by addition of stoichiometric amounts of $[PdCl_2(C_6H_5CN_2)]$ and the ligand, are nonelectrolytes in nitromethane. The related compound $[Pd(\text{diphos})I_2]$ is a monomer in dichloromethane solution.[20]

Since the calorimetric experiments were performed with an excess of base present, formation of compounds such as $[Pd(L\text{-}L)_2]Cl_2$ is possible. There are, however, no known olefin compounds of this type. Very pure $[PdCl_2(py)_2]$, $[PdCl_2(\text{TMEDA})]$, and $[PdCl_2(\text{dicyclopentadiene})]$ were isolated from solutions containing large excesses of base. The compounds $[Pd(\text{diphos})Cl_2]$, $[Pd(\text{diphos})_2]Cl_2$, $[Pd(\text{diars})Cl_2]$, and $[Pd(\text{diars})_2]Cl_2$ have been previously characterized.[11f] Calorimetric titrations with diphos and diars were performed. The titration curve for the diphos system is shown on Figure 2. Good evidence for formation of both compounds in dichloromethane is shown. The enthalpies obtained when excess of $[PdCl_2(C_6H_5CN)_2]$ was present corresponds to the formation of the 1:1 complex.[24]

The formation of five-coordinate species is possible in the presence of excess base. However, there was no heat evolved when a 21 molar excess of cyclooctadiene was added to $[PdCl_2(\text{cyclooctadiene})]$. $[Pd(\text{TMEDA})Cl_2]$ probably does not interact with excess TMEDA since it does not interact with the iodide ion.[11f]

Experimental Data.—The heats of reaction with various bases are summarized in Table I. The ir

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[12] Small amounts of $PdCl_2$ and other species are probably forming in solution: M. Kubota, B. A. Denechaud, P. M. McKinney, T. E. Needham, and G. O. Spessard, *J. Catal.*, **18**, 119 (1970). This would not affect the interpretation of the results.

[13] C. V. Goebel, *Diss. Abstr. B*, **28**, 625 (1967).

[14] N. C. Baenziger, C. F. Richards, and J. R. Doyle, *Acta Crystallogr.*, **18**, 924 (1965).

[15] I. A. Zakharova, G. A. KuKina, T. S. Kuli-Zade, I. I. Moiseev, G. YuiPek, and M. A. Porai-Koshits, *Russ. J. Inorg. Chem.*, **11**, 1364 (1966).

[16] J. A. Ibers and R. G. Snyder, *Acta Crystallogr.*, **15**, 923 (1962).

[17] N. C. Baenziger, J. R. Doyle, G. F. Richards, and C. L. Carpenter, "Advances in the Chemistry of Coordination Compounds," Macmillan, New York, N. Y., 1961, p 136.

[18] N. C. Baenziger, R. C. Nedrud, and J. R. Doyle, *Acta Crystallogr.*, **18**, 237 (1965).

[19] W. Partenheimer, W. Bennett, and J. R. Doyle, *Inorg. Chem.*, in press.

[20] M. J. Hudson, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 40 (1968).

[21] (**1**)$PtCl_2$(bromoform): J. R. Doyle and H. B. Jonassen, *J. Amer. Chem. Soc.*, **78**, 3965 (1956); (**2**)PtI_2(bromoform): K. A. Jensen, *Acta Chem. Scand.*, **7**, 868 (1953); (**7**)$PtCl_2(1,2\text{-}C_2H_4Cl_2)$: R. J. Alexander, N. C. Baenziger, C. Carpenter, and J. R. Doyle, *J. Amer. Chem. Soc.*, **82**, 535 (1960); (**4**)$PtCl_2$(benzene): J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 2622 (1952); (**5**)$PdCl_2$(nitrobenzene): see ref 15.

[22] D. M. Adams, "Metal Ligand and Related Vibrations," E. Arnold Ltd., London, 1967, p 75.

[23] diars is *o*-phenylenebis(dimethylarsine).

[24] The enthalpies obtained when large excesses of diphos were added do not represent *just* the formation of the 2:1 complex since some $[Pd(\text{diphos})_2Cl]Cl$ is also present.[11f] The titration curve with diars was somewhat more complicated, but the same interpretation can be made in the region where excess $[PdCl_2(C_6H_5CN)_2]$ was present.

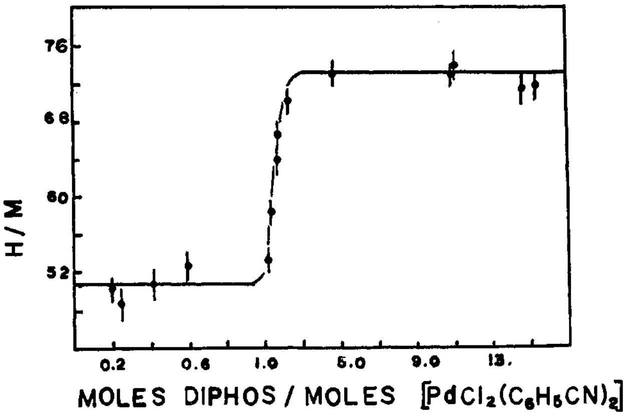


Figure 2.—Calorimetric titration of diphos and $[PdCl_2(C_6H_5CN)_2]$ in dichloromethane. H is the heat evolved in calories, and M is the moles of limiting reagent.

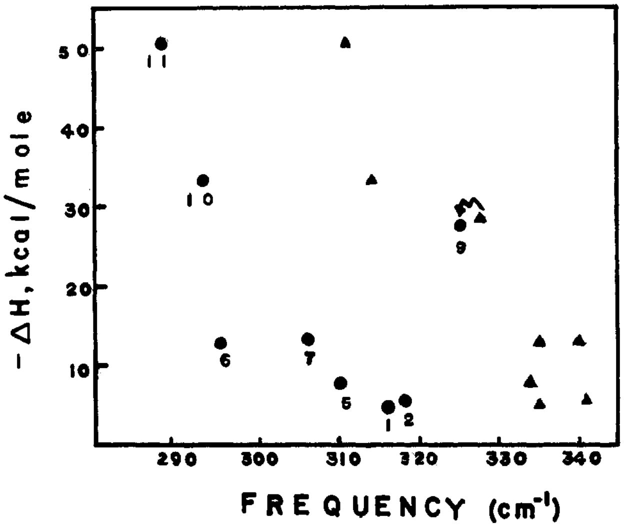


Figure 3.—Metal-chlorine vibrational modes in $[PdCl_2(L)]$ vs. heats of reaction: O, M-Cl(A_1); Δ, M-Cl(B_1); numbers refer to ligands in Figure 1.

stretching frequencies corresponding to the metal–halogen modes are given in Figure 3.

Discussion

Interpretation of the Heats of Reaction.—The observed heat of the reaction given in eq 1, ΔH_{obsd}, can be written in terms of bond energies, ΔH, and solvation energies, ΔH_s

$$\Delta H_{\text{obsd}} = 2\Delta H_{\text{Pd-L}} - 2\Delta H_{\text{Pd-N}} + 2\Delta H_{s,C_6H_5CN} + \Delta H_{s,\text{Pd(L-L)Cl}_2} - \Delta H_{s,\text{Pd}(C_6H_5CN)_2Cl_2} - \Delta H_{s,\text{L-L}} \quad (2)$$

If differences between two reactions are considered

$$\Delta(\Delta H_{\text{obsd}}) = 2\Delta H_{\text{Pd-L}} - 2\Delta H_{\text{Pd-L}'} + \Delta H_{s,\text{Pd(L-L)Cl}_2} - \Delta H_{s,\text{Pd(L}'\text{-L}')\text{Cl}_2} - \Delta H_{s,\text{L-L}} + \Delta H_{s,\text{L}'\text{-L}'} \quad (3)$$

where L and L′ are two different ligands.

The differences between two heats of reaction are seen to be proportional to the difference of their respective palladium–ligand bond energies. The solvation terms however complicate such a straightforward interpretation. We can anticipate that the solvation energies will be relatively small in dichloromethane, and since differences in solvation energies of similar species are involved, the overall contribution from these terms will be small.

Some of these solvation energies can be determined, or reasonable values can be estimated (see Table II).

TABLE II

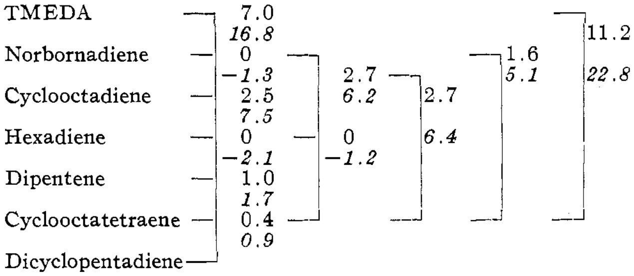
SOLVATION ENERGIES (KCAL/MOL) OF SOME OLEFINS AND TMEDA

Olefin	$-\Delta H_{\text{vap}}$	$+\Delta H_{\text{soln}}$[e]	$-\Delta H_s$
1,5-Hexadiene	7.06[a]	0.50 ± 0.05	6.6
Norbornadiene	7.8[a]	0.3	7.5
Cyclooctadiene	9.4[a]	0.29 ± 0.08	9.1
Dicyclopentadiene	10.2[b]	0.3	9.9
Dipentene	10.2[c]	0.3	9.9
Cyclooctatetraene	10.3 ± 0.1[d]	0.17 ± 0.05	10.1 ± 0.2
TMEDA	8.9[a]	−1.4 ± 0.1	10.3

[a] Estimate, taken from R. A. Dreisbach, "P-V-T Relationships of Organic Compounds," Handbook Publishers, Sandusky, Ohio, 1952. [b] P. E. Burchfield, *J. Amer. Chem. Soc.*, **64**, 2501 (1942). [c] G. A. Rudakov and S. Ya. Korotov, *J. Appl. Chem. USSR*, **10**, 312 (1937); *Chem. Abstr.*, **31**, 4554 (1937). [d] D. W. Scott, M. E. Gross, G. D. Oliver, and H. M. Huffman, *J. Amer. Chem. Soc.*, **71**, 1634 (1949). [e] Those values with error limits were determined calorimetrically. The others were estimated.

The largest solvation term should be $\Delta H_{s,\text{L-L}} - \Delta H_{s,\text{L}'\text{-L}'}$ since these are Lewis acid–base interactions. If one assumes that the term $\Delta H_{s,\text{Pd(L-L)Cl}_2} - \Delta H_{s,\text{Pd(L}'\text{-L}')\text{Cl}_2}$ is as large as the term $\Delta H_{s,\text{L-L}} - \Delta H_{s,\text{L}'\text{-L}'}$, that the errors in the solvation energies are ±0.2 kcal/mol, and that the sign of the unknown solvation term is assigned to give a *minimum* bond energy difference, then the values in Scheme I can be computed. The ligands are given in order of decreasing palladium–ligand bond strength. The italic numbers will be discussed.

SCHEME I



An alternative way of ascertaining if significant bond energy differences exist is to evaluate the magnitude of the term $(\Delta H_{s,\text{Pd(L-L)Cl}_2} - \Delta H_{s,\text{Pd(L}'\text{-L}')\text{Cl}_2})$ which would make the bond energy difference exactly equal to zero. The italic numbers on the above scheme are these values. For comparison, the term $(\Delta H_{s,\text{L}} - \Delta H_{s,\text{L}'})$ ranges from 0 to 3.7 kcal/mol (see Table II) with an average value of 1.5 kcal/mol. Significant bond energy differences are therefore highly probable whenever this number is greater than 4 kcal/mol.

The order is roughly in agreement with the stability constants determined for Ag^+ in ethylene glycol (cyclooctadiene ≫ norbornadiene > hexadiene > dipentene)[7] and with the olefin-exchange reactions with rhodium(I) (norbornadiene ≫ cyclooctadiene ≫ dicyclopentadiene > cyclooctatetraene).[6]

It is presently believed that the optimum geometry of an olefin complex has one plane containing the olefinic carbon atoms perpendicular to the square plane containing the metal and ligands. This would maximize the overlap between the appropriate π orbitals on the metal and olefin.[25] In [$PtCl_2$(dipentene)], one of two double bonds is not perpendicular to the square plane. One would expect a similar geometry in [$PdCl_2$(dipentene)]. Hence, it would be expected that the average olefin–metal bond strength in the dipentene complex would be less than that for [$PdCl_2$(cyclooctadiene)]. One might also expect the metal complexes of cyclododecatriene and dicyclopentadiene to have nonparallel double bonds in the complex. Our data indicate that all three of these olefins form weaker bonds to palladium than do the cyclooctadiene and norbornadiene palladium complexes.

The palladium complex of cyclooctatetraene has weaker palladium–olefin bonds than that of cyclooctadiene. It has been previously suggested that this may be due to the large distance between the nonconjugated double bonds and the loss of conjugation resulting from coordination of the tetraene.[6]

One interesting application of this calorimetric data is that they show that the isomerization of 3-vinylcyclohexene to cyclooctadiene *via* [$PdCl_2(C_6H_5CN)_2$][26] is a thermodynamically favored process (ignoring entropy effects). The heat of reaction of vinylcyclohexene with [$PdCl_2(C_6H_5CN)_2$] should be very nearly the same as that of dipentene. Making this assumption, one can write

$$[\mathrm{PdCl_2(vinylcyclohexene)}] + \mathrm{cyclooctadiene} \xrightleftharpoons{\mathrm{CH_2Cl_2}} [\mathrm{PdCl_2(cyclooctadiene)}] + \text{3-vinylcyclohexene} + 6.2\ \mathrm{kcal/mol}$$

There has been considerable interest in the infrared spectra of metal–olefin compounds, particularly in attempts to evaluate relative metal–olefin bond strengths. The calorimetric data presented here become of considerable importance in checking the various correlations and interpretations that have been made.

One such correlation is that between the M–Cl stretching frequencies and the various types of ligands in compounds of the type *cis*-PtL_2X_2 (X = Cl, Br, I) and $Pt_2L_4X_2$. In both studies, the Pt–X stretching frequencies were sensitive to changes in the trans ligand.[27,28] Figure 3 shows that the A_1 vibrational mode of the complexes studied here is also very sensitive to the trans ligand and that exactly the same order of L affecting the A_1 vibrational mode is found: N donor > olefin > As donor > P donor.

The *interpretation* of this result given previously, however, leads to an uncomfortable conclusion. Assuming that (1) changes in frequencies parallel changes in force constants, (2) coupling of vibrational modes is negligible, and (3) the M–Cl bonds have only a small amount of double-bond character, previous workers have concluded that the decrease in $\nu_{\mathrm{M-Cl}}$ parallels an increase in the σ-bond character in M–L bond.[29] We then have increasing σ-bond character: Pd–N < Pd–olefin < Pd–As < Pd–P. This result is in accord with the MO calculation which gives σ-bond strength P > N in the Pt–L bond.[30] The observed relative bond strengths are N > olefin. Hence, the Pd–N bond must have considerably more π character than the Pd–olefin bond, a result that is unacceptable to the currently held view of metal–ligand bonding in these compounds.[31] Certainly a reconsideration of the above assumptions should be made.

It is very surprising that duroquinone and *p*-benzoquinone do not react spontaneously with [$PdCl_2(C_6H_5CN)_2$]. The infrared spectra of a dichloromethane solution containing these quinones and [$PdCl_2(C_6H_5CN)_2$] indicate that benzonitrile is still coordinated to the metal. No heat was evolved when the quinones were mixed with palladium complex in dichloromethane, and no change in color occurred. There is a variety of evidence to support the contention that these quinones are chemically very similar to the chelating olefins discussed in this paper.[32]

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

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(25) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(26) H. Frye, E. Kulijan, and J. Viebrock, *Inorg. Nucl. Chem. Lett.*, **2**, 119 (1966).

(27) D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964).

(28) D. M. Adams and P. J. Chandler, *ibid.*, *A*, 588 (1969).

(29) One must also assume that the calorimetric trend found in solution parallels the ir data determined in the solid state.

(30) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., p 27.

(31) A MO calculation gives the π character in the Pt–L bond as olefin > N. See ref 28.

(32) See for example G. G. Aleksandrov, Yu. T. Struchkov, and S. B. Gubin, *J. Organometal. Chem.*, **25**, 243 (1970); M. D. Glick and L. F. Dahl, *ibid.*, **3**, 200 (1965).