dipole moments but exaggerates intermolecular effects because it represents the inner shell orbitals so poorly. One clearly needs to carry out calculations including polarization functions on the monomers[15] to hope for more quantitatively correct dimerization energies. However, one expects the relative energies predicted by the 431G basis to be more reliable than those predicted by STO-3G[23] and thus amide–H_2O H bonding (the average of $C=O\cdots H$—O and N—$H\cdots OH_2$) to be ca. equo-energetic to amide–amide H bonding.

Recent ab initio calculations by Alagona, et al.,[24] who used a basis set somewhat lower in total energy than STO-3G, but higher than 431G, find qualitatively similar results for the formamide–H_2O surface, with $C=O\cdots H$ hydrogen bonding stronger than N–$H\cdots O$.

Relation to Experimental Studies

The results presented here are of most direct relevance to gas phase and inert matrix studies and a number of important experimental studies suggest themselves. Precise structural studies of 1:1 amide–water complexes might be carried out by the supersonic nozzle beam method for studying weakly bound complexes.[25] Low-temperature matrix ir studies or amide–H_2O ir studies in an inert solvent should provide definitive evidence whether in the most stable formamide–H_2O complex the amide is a proton donor or acceptor. Similar studies would give some insight into the relative H-

bonding ability of different amides, such as N-methylacetamide and N-methylformamide. As noted above, one is not certain about the difference between formamide H bonding (studied in this paper) and N-methylacetamide H bonding (ref 1), so one would like to have more precise theoretical estimates for the effects of added methyl groups on the amide–amide and amide–H_2O H-bond strengths. One would also like to determine experimental ΔH dimerization for formamide, N-methylformamide, N-methylacetamide, and
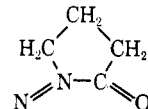
by a number of different spectroscopic techniques.

Finally, one should note that the studies of Kuntz[26] are consistent with an average hydration of only one water per peptide linkage in polypeptides, most of the hydration being due to cationic or anionic side chains. From the above, it appears that it is the $C=O$ rather than the N–H that is being hydrated. These are clearly a number of avenues for further experimental and theoretical studies of amide–amide and amide–H_2O hydrogen bonding.

(23) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 94, 2371 (1972).
(24) G. Alagona, A. Pullman, E. Scrocco, and J. Tomasi, *Int. J. Peptide Res.*, 5, 251 (1973).
(25) T. R. Dyke, B. J. Howard, and W. Klemperer, *J. Chem. Phys.*, 56, 2442 (1972).

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Calorimetric Investigation of the Reaction of Pyridine with Compounds of the Type Di-μ-chloro-dichlorobis(olefin)dipalladium(II)

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Abstract: The following reactions have been characterized via nmr, uv, and microcalorimetry: $[PdCl_2(olefin)]_2$ + 2py → 2$[PdCl_2(olefin)(py)]$ and $[PdCl_2(olefin)(py)]$ + py → $[PdCl_2(py)_2]$ + olefin, where olefin = ethylene, cis-butene, cyclopentene, cyclohexene, cycloheptene, cis-cyclooctene, and styrene. The enthalpy changes for these reactions are reported and the relative displacement energies of the ligands from the metal are 14.3 (py), 2.7 (C_8H_{14}), 1.6 (C_7H_{12}), 0.5 (C_2H_4), 0.4 (C_6H_{10}), 0.3 (styrene), and 0.0 (C_5H_8) kcal/mol. The equilibrium constants were too high to measure under the experimental conditions used. This and previously published data suggest that the σ contribution to the metal–olefin bond is more important than the π contribution for Ag(I) and Pd(II) and that the metal has increasing π character Ag(I) < Pd(II) < Rh(I) $\sim$ Pt(II). The enthalpic data are related to catalytic phenomena, ionization potentials of the olefins, qualitative stability of metal–olefin compounds, and the decrease in the double bond stretching frequency upon coordination to the metal.

W e have recently reported a series of studies involving the characterization of reactions involving metal–olefin compounds in weakly polar solvents via nmr and calorimetric techniques.[1-3] A recent review has summarized the available thermodynamic data pertaining to metal–olefin compounds.[4] We have previously pointed out the problems in interpreting the available thermodynamic data due to the

(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) F. R. Hartley, *Chem. Rev.*, 73, 163 (1973).

methods and solvents used.[2] In this paper, we continue a systematic approach to this class of complexes by extending our work to palladium(II) monoolefin compounds.

Thermodynamic studies in water of the formation of palladium olefin compounds have been reported for ethylene, 1-propene, and 1-butene.[5-9] The equilibrium constants become smaller with methyl substitution on the olefin. The reported enthalpic values are very imprecise. A large number of studies pertaining to the formation of silver(I) olefin compounds have been reported. There is very little variation in the enthalpic changes as the olefin is varied;[10] almost always the changes are within experimental error.

Experimental Section

Materials and Apparatus. Baker AR grade dichloromethane was dried with Linde 4A molecular sieves at least 24 hr prior to use. Sargent, reagent grade, pyridine was distilled over barium oxide and stored over Linde 4A molecular sieves. Eastman cyclohexene was washed with an aqueous ferrous sulfate solution and distilled before use. Englehard Industries palladium chloride, Aldrich cyclopentene, cycloheptene, and cis-cyclooctene, Eastman styrene, Matheson ethylene, and Phillip's 99% pure cis-butene were used as received. The calorimetric apparatus and technique has been previously described.[1-3] Nmr, ir, and uv spectra were recorded on a Varian A-60 spectrometer, a Beckman IR-12 instrument using CsI plates, and a Perkin-Elmer 202 spectrometer, respectively.

Preparation of the Palladium Compounds. Compounds of the type di-μ-chloro-dichloro(olefin)dipalladium(II) (olefin = ethylene, cis-butene, cyclopentene, cycloheptene, cyclohexene, cis-cyclooctene, and styrene) were prepared by the method of Kharasch,[11] washed with petroleum ether or pentane, and air dried before use. Recrystallization of the compounds was not attempted due to their low thermal stability. The compounds were characterized via their H nmr and ir spectra. All of the calorimetric studies were performed within 6 hr of the preparation of these compounds.

Results

Characterization of the Palladium Complexes. Table I gives the low frequency ir absorbances of the solid palladium complexes. The absorbances of [PdCl₂-

Table I. Ir Absorbances[a] for Compounds of the Type [PdCl₂(olefin)]₂ in the Region 200–500 cm⁻¹

Olefin	ν(Pd–Cl)[b]	ν(Pd–Cl)[c]	ν(Pd–Cl)[c]	Others
Ethylene	356 s	306 m	273 m	428 m
Butene	340 s	310 m	283 s	461 m, 377 s
Cyclopentene	341 m	310 s	287 m	471 s, 446 s, 427 m, 391 s, 374 s, 330 m, 254 s
Cyclohexene	332 s	295 s	276 m	465 w, 420 w
Cycloheptene	359 s		285 m	
Cyclooctene	355 s	302 w	277 m	459 w, 411 w
Styrene	353 s	302 m	283 s	459 s, 253 w

[a] s = strong, m = medium, w = weak. [b] Terminal palladium–chlorine stretching frequency. [c] Bridging palladium–chlorine stretching frequencies. See ref 6 for a more exact description of these vibrations.

(5) P. M. Henry, *J. Amer. Chem. Soc.*, **86**, 3246 (1964).
(6) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, **152**, 147 (1963); *Chem. Abstr.*, **60**, 184d (1964).
(7) S. V. Pestrikov, I. I. Moiseev, and T. N. Romanova, *Russ. J. Inorg. Chem.*, **11**, 1199 (1966).
(8) S. V. Pestrikov, I. I. Moiseev, and B. A. Tsivilikhovskaya, *Russ. J. Inorg. Chem.*, **11**, 931 (1966).
(9) S. V. Pestrikov, I. I. Moiseev, and L. M. Sverzh, *Russ. J. Inorg. Chem.*, **11**, 1113 (1966).
(10) See the tables reported in ref 4.
(11) M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Amer. Chem. Soc.*, **60**, 882 (1938).
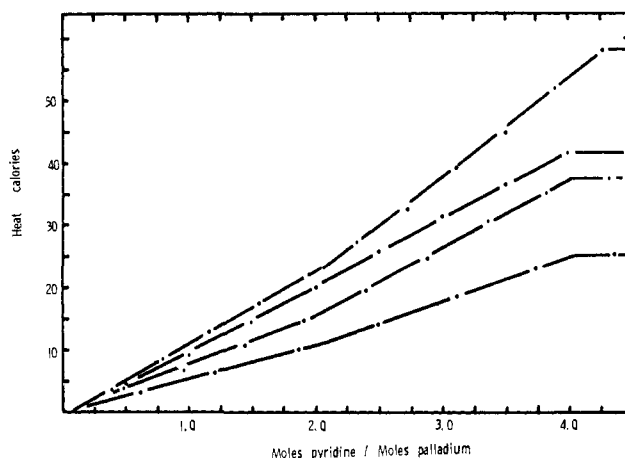
Figure 1. Calorimetric titration curves for the reaction of [PdCl₂-(olefin)]₂ with pyridine. In descending order, olefin = cis-butene, cyclohexene, ethylene, cis-cyclooctene.

(C₂H₄)]₂ agree well with those previously published.[12] All of the compounds exhibited the three absorbances characteristic of the Pd₂Cl₂ ring,[13] except for cyclohexene where one of these is missing. The frequencies are in the previously reported ranges for these vibrational modes.[13] The ratio of the average frequencies for terminal and bridging vibrations is 0.84 ± 0.02 compared to the reported value of 0.80 for other similar compounds.[13] The H nmr data for these compounds (Table II) in d-HCCl₃ were difficult to measure

Table II. Proton Nmr Data[a] for Selected Olefins and Compounds of the Type [PdCl₂(olefin)]₂

Compd	==CH	–CH₂–	CH₃
[PdCl₂(C₄H₈)]₂	3.65 (2)		8.30 (6)
Cyclopentene	4.19 (2)	7.65 (4) 8.14 (2)	
[PdCl₂(C₅H₈)]₂	3.42 (2)	7.78 (6)[b]	
Cyclohexene	4.31 (2)	8.02 (4) 8.37 (4)	
[PdCl₂(C₆H₁₀)]₂	4.08 (2)	7.93 (4) 8.32 (4)	
Cycloheptene	4.15 (2)	7.81 (4) 8.36 (6)	
[PdCl₂(C₇H₁₂)]₂	3.40 (2)	7.56 (4) 8.37 (6)	
cis-Cyclooctene	4.35 (2)	7.86 (4) 8.49 (8)	
[PdCl₂(C₈H₁₄)]₂	3.68 (2)	7.66 (4) 8.50 (8)	

[a] Chemical shifts reported in deuteriochloroform using the τ scale with TMS as the standard. Integrated intensities given in parentheses. [b] Maximum of broad band.

due to their low solubility, but the expected number and intensity of absorbances were observed. The olefinic protons in the complexes were shifted downfield ~0.5 ppm relative to the uncoordinated olefin.

Characterization of the Reactions. Calorimetric titration curves, Figure 1, indicate that two consecutive reactions occur when pyridine is added to the palladium complexes in dichloromethane. The "curves" were

(12) M. J. Grogan and K. Nakamoto, *J. Amer. Chem. Soc.*, **90**, 918 (1968).
(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970, p 213.
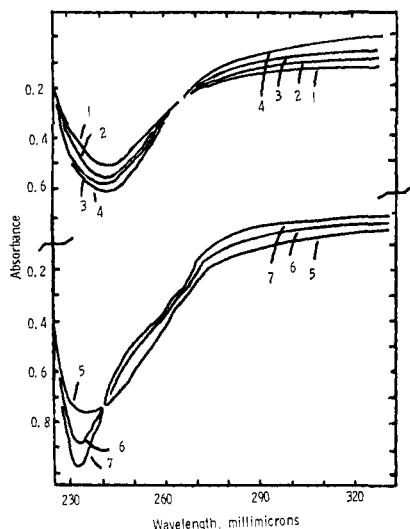
Figure 2. Ultraviolet spectra resulting from the addition of pyridine to [PdCl₂(cyclooctene)]₂ in CH₂Cl₂. Initial concentration of complex was 2.30×10^{-5} M. Mole ratio py/[PdCl₂(C₈H₁₄)]₂: (1) 0.0, (2) 0.43, (3) 0.85, (4) 1.30, (5) 2.10, (6) 3.00, (7) 5.10.

Figure 3. Chemical shift of the olefinic protons in [PdCl₂(C₈H₁₄)]₂ as a function of added pyridine.

linear in all cases. The enthalpy change of the reactions was determined by calculating the slope of these lines using the least-squares method. The results are summarized in Table III.[14]

Table III. Calorimetric Data for Palladium Olefin Compounds

[PdCl₂(olefin)]₂ + 2py ⟶ 2[PdCl₂(py)(olefin)]

[PdCl₂(py)(olefin)] + py ⟶ [PdCl₂(py)₂] + olefin

Olefin	$-\Delta H$, kcal/mol Reaction 1	$-\Delta H$, kcal/mol Reaction 2	No. independent determinations[a]	Concn range Pd compd, $M \times 10^3$
Ethylene	21.1 ± 0.4	13.8 ± 0.4	2	3.56–8.00
cis-Butene	16.2 ± 0.3	12.4 ± 0.3	2	4.83–6.18
Cyclopentene	21.5 ± 0.4	14.3 ± 0.3	2	3.94–5.22
Cyclohexene	27.8 ± 0.4	13.9 ± 0.4	2	3.46–3.55
Cycloheptene	16.2 ± 0.3	12.7 ± 0.3	4	4.25–4.88
cis-Cyclooctene	16.6 ± 0.7	11.6 ± 0.2	4	2.74–5.94
Styrene	22.7 ± 0.4	14.0 ± 0.3	2	3.58–4.27

[a] This refers to the number of solutions prepared independently. For each solution 7–18 increments of base were added each resulting in a value of the molar enthalpy.

Figure 2 illustrates the ultraviolet spectrum of di-μ-chloro-dichlorobis(cyclooctene)dipalladium(II) in dichloromethane and the effect on the spectrum when increments of pyridine are added. An isosbestic point at 265 μm is observed when the mole ratio of pyridine/palladium complex ranges from 0 to 2. In the 2–4 mol ratio region, a new isosbestic point occurs at 241 μm and a new absorbance at 233 μm appears.

The effect of incremental addition of pyridine upon the chemical shifts of the olefinic protons of di-μ-chloro-dichlorobis(cyclooctene)palladium(II) is illustrated on Figure 3. Only *one* absorbance is observed for the olefinic protons and this peak shifts upfield as increasing amounts of pyridine are added. When an

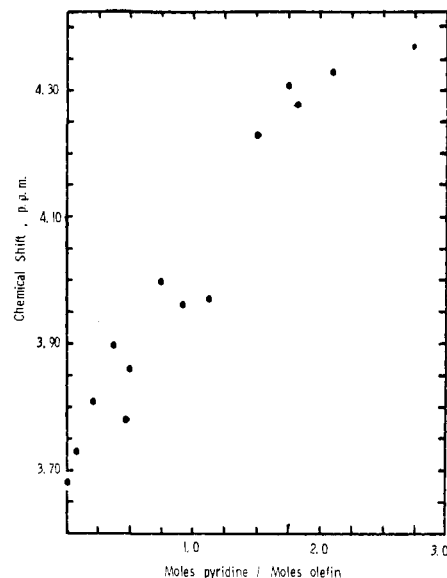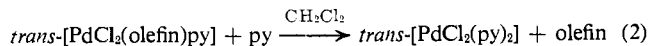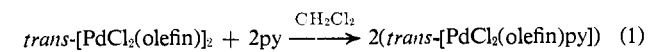(14) See paragraph at end of paper regarding supplementary material.

excess of 2 mol of pyridine is added to 1 mol of olefin, the shift of this peak stops and the absorbance corresponds to that of the uncoordinated olefin. The considerable scatter of the points on Figure 3 is caused by (1) the broadness of the absorbance making the exact value of the chemical shift difficult to ascertain, (2) the low solubility causing considerable noise in the spectrum and making the integrations rather inaccurate, and (3) the relatively small chemical shift range (0.67 ppm) between the coordinated and uncoordinated protons. It was also observed that only one absorption in the olefinic region occurs when uncoordinated cyclooctene is added to [PdCl₂(C₈H₁₄)]₂ and that this peak moves upfield as increasing amounts of free olefin are added.

Discussion

Characterization of the Reactions. All available evidence indicates that the following two reactions occur consecutively when compounds of the type [PdCl₂-(olefin)]₂ are reacted with pyridine.

$$trans\text{-}[PdCl_2(olefin)]_2 + 2py \xrightarrow{CH_2Cl_2} 2(trans\text{-}[PdCl_2(olefin)py]) \quad (1)$$

$$trans\text{-}[PdCl_2(olefin)py] + py \xrightarrow{CH_2Cl_2} trans\text{-}[PdCl_2(py)_2] + olefin \quad (2)$$

Compounds of the type [PdCl₂(olefin)]₂ have been characterized in the solid state by X-ray diffraction[15] (olefin = C₂H₄ and C₆H₅CH=CH₂) and ir studies[12] and in solution by molecular weight measurements[11,16] (in benzene) and ir studies[12,17] (in dichloromethane and chloroform). Our attempts to isolate compounds of the type [PdCl₂(olefin)(py)] failed, although an unstable related compound [PdCl₂(C₂H₄)-(pyridine N-oxide)] has been reported.[18] The calorimetric solutions were evaporated and in all cases the

(15) J. R. Holden and N. C. Baenziger, *J. Amer. Chem. Soc.*, **77**, 4984, 4987 (1955).

(16) M. S. Kharasch and T. A. Ashford, *J. Amer. Chem. Soc.*, **58**, 1733 (1936).

(17) G. F. Pregaglia, F. Conti, B. Minasso, and R. Ugo, *J. Organometal. Chem.*, **47**, 165 (1973).
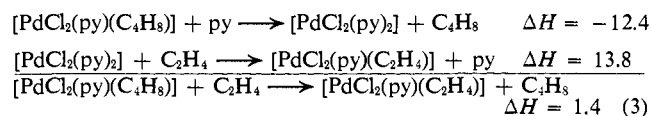
(18) W. H. Clement, *J. Organometal. Chem.*, **10**, P19 (1967).

solids isolated had ir spectra identical with an authentic sample of *trans*-[PdCl₂(py)₂].

The product of reaction 1 could be either the cis or trans geometrical isomer or a mixture of these two. Ethylene is a much stronger trans director than the chloride ion[19] so one would expect the *initial* product formed to be predominantly the trans isomer. It has been established that cis isomers of the type [PdCl₂(am)₂] (am = amine) are unstable[20] and that they completely revert to the trans isomer in the presence of excess amine in dimethoxymethane.[21] Therefore the initially formed trans isomer would not revert to the cis isomer.[22] The analogous bridge splitting reaction with platinum has been very well characterized[23] and in all but one case the trans isomer forms in solution and in the solid state. If significant quantities of the cis isomer were present in solution, one might expect that slow evaporation of the calorimetric solutions would yield the less soluble cis isomer. However the ir spectra of all the products suggests that the trans isomer was isolated. Thus all of the evidence points toward the trans isomer being formed in solution.

The calorimetric titration curves and the uv study firmly establish that two consecutive reactions occur, each consuming the requisite number of moles of pyridine. The nmr study establishes that the olefin is being displaced in the second reaction, not in the first. One cannot individually observe the coordinated and uncoordinated olefinic protons in the nmr spectrum indicating that a fast exchange of the two olefinic species is occurring. Additional evidence for this interpretation is provided from the observation that addition of free olefin to a solution of [PdCl₂(olefin)]₂ results also in one olefinic absorption.

Relative Displacement Energies. As discussed previously,[2,3] reaction 2 can be rearranged to give relative displacement energies. For example

[PdCl₂(py)(C₄H₈)] + py ⟶ [PdCl₂(py)₂] + C₄H₈ $\Delta H = -12.4$

[PdCl₂(py)₂] + C₂H₄ ⟶ [PdCl₂(py)(C₂H₄)] + py $\Delta H = 13.8$

[PdCl₂(py)(C₄H₈)] + C₂H₄ ⟶ [PdCl₂(py)(C₂H₄)] + C₄H₈ $\Delta H = 1.4$ (3)

Thus the displacement of *cis*-butene from the palladium compound by ethylene is endothermic by 1.4 kcal/mol. The relative displacement energies so calculated and previously reported values for rhodium(I) and silver(I) are given on Table IV. The ligands are arranged so that their dissociation energy from the metal increases as one proceeds *up* the table.

From Table IV one can make the following observations. (1) Triphenylphosphine and pyridine have far higher dissociation energies from their respective metals than do the olefins by ~10 kcal/mol. (2) Methyl substitution, and in general alkyl substitution, increases the strength of the metal–olefin interaction for Ag(I) and Pd(II) and decreases the strength of the metal–olefin interaction for rhodium. This can be seen by comparing the values of toluene and hexamethyl-

(19) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, p 24.

(20) L. Cattalini and M. Martelli, *Gazz. Chim. Ital.*, 98, 831 (1968).

(21) L. Cattalini and M. Martelli, *J. Amer. Chem. Soc.*, 91, 312 (1969).

(22) One is assuming the same behavior in dichloromethane as in 1,2-dimethoxyethane. It has been established that the trans isomers are favored in less polar solvents so this comparison is valid. See D. A. Redfield and J. H. Nelson, *Inorg. Chem.*, 12, 15 (1973), and reference quoted therein.

(23) M. Orchin and P. J. Schmidt, *Inorg. Chim. Acta*, 2, 624 (1969).

Table IV. Relative Displacement Energies

Base	D(Ag(hfacac))^a	D(PdCl₂(py))	D(Rh(acac)(C₂H₄))^b
Triphenyl-phosphine	19.1 ± 0.5		
Pyridine		13.8 ± 0.4	
Cyclooctene	9.3 ± 0.4	2.2 ± 0.2	
Cyclohexane	5.8 ± 0.3		
cis-Butene		1.4 ± 0.3	
Cycloheptene	4.8 ± 0.3	1.1 ± 0.3	
Hexamethyl-benzene	3.1 ± 0.3^d		
Cyclopentene	0.7 ± 0.5		
Toluene	0.0^d		
Ethylene		0.0^c	0.0^c
Cyclohexene		-0.1 ± 0.4	
cis-Butene			-1.8 ± 0.8
Styrene		-0.2 ± 0.3	
Cyclopentene		-0.5 ± 0.3	

^a From ref 3. ^b From ref 28. ^c Arbitrary standard to which bases are compared. This does not imply that ethylene interacts equally strongly with Pd(II) and Rh(I). ^d Data will be reported on in detail elsewhere.

benzene for silver and ethylene and *cis*-butene for the rest of the metals. For palladium, alkyl substitution of any kind results in values equal, within experimental error, or larger than ethylene. (3) For palladium the ordering of the cyclic olefins is cyclooctene > cycloheptene > cyclohexene > cyclopentene. A similar ordering is observed for Ag(I) except for cyclohexene. (4) The displacement energies of palladium(II) are much less sensitive toward alkyl substitution than is silver. For the cyclic olefins, the maximum observed difference for palladium is 2.7 kcal/mol compared with that of 8.6 kcal/mol for silver.

There are a large number of possible contributions to the displacement energies given on Table IV. We will limit the discussion to solvation effects, conformational changes of the olefin, inductive effects, and steric effects, in that order.

The calorimetric data for silver and palladium have been performed in dichloromethane, a weak hydrogen-bonding acid. Therefore, one would expect specific solvent–solute interactions in eq 3, the most obvious ones being the interactions of the two uncoordinated bases. We have measured many of the enthalpies of formation of these base–dichloromethane adducts or the solvent transfer energies into cyclohexane. All of the corrections for the olefins are within experimental error and do not change the ordering of the displacement energies.[24] We are presently investigating some analogous reactions of platinum in both dichloromethane and benzene, as a further check for solvation effects. These will be reported on subsequently.

It is conceivable that among the cyclic olefins a conformational change could occur upon complexation. This may account for the fact that the displacement energy of 1,5-hexadiene, which has a gauche conformation in solution, is lower than 1,5-cyclooctadiene since the former must rearrange to the tub form upon complexation to palladium.[1] To ascertain whether significant conformation changes contribute to the enthalpic changes would require exceptionally precise X-ray crystal determinations of the palladium olefin complexes and knowledge of the conformations of the

(24) W. Partenheimer, *Inorg. Chem.*, submitted for publication.

olefins in solution. There are no X-ray data available. There is experimental evidence that liquid cycloheptene exists in the tub and chair forms.[25,26] The energy difference between the two forms, however, has been estimated to be only 0.67 kcal/mol. This one example suggests that this effect would contribute only a fraction of 0.67 kcal/mol to the displacement energies for cycloheptene.

Many of the displacement energies can be rationalized in terms of electronic effects if one assumes (a) the Chatt-Duncanson-Dewar model of the metal-olefin bond[27] and (b) that the enthalpic contributions due to simultaneous changes in the bonding of the non-olefinic ligands when the olefin is varied are negligible, i.e., the displacement energies can be interpreted solely in terms of the variations in the metal–olefin bond. The methyl group is an electron donating group and should therefore augment the σ metal–olefin bond and diminish the strength of the π bond. Thus from the second observation (see above) one may conclude that palladium(II) and silver(I) have a greater σ contribution than π contribution to the metal–olefin bond and for rhodium(I) the opposite is true. The interpretation had been previously given for rhodium(I).[28] From the third observation, one finds that generally as the alkyl chain attached to the olefin increases so does the metal–olefin interaction. This is expected since the electron donating power of the chain increases as the chain length increases.[29] Since palladium(II) is less sensitive toward alkyl substitution than silver, observation 4 suggests that the π and σ contributions of the metal–olefin bond are more nearly equal in palladium (assuming that the different steric characteristics of the silver and palladium compounds are not causing this effect). One can therefore conclude that the π character in the metal–olefin bond increases in the order Ag(I) < Pd(II) < Rh(I). Thermodynamic studies on platinum(II)[30] compounds suggest that the π contribution is greater than the σ contribution in the platinum–olefin bond. One therefore also has the ordering Ag(I) < Pd(II) < Pt(II). We feel that these enthalpic data provide strong experimental evidence for the Chatt-Duncanson-Dewar model of the metal-olefin bond since the reversal of displacement energies would be difficult to explain any other way.

For palladium, the relative dissociation energies decrease as the ionization potentials increase for ethylene and cis-butene[31] and in the series cyclopentene, cyclohexene, cycloheptene, and cyclooctene.[32] Ionization potentials correspond at least approximately to the energy of the highest occupied molecular orbital of the system (Koopman's theorem),[33] which would be the π orbital in the olefins. Since the σ bond is formed via overlap of the π orbital of the olefin with the appropriate higher energy metal orbitals, one can relate the increasing strength of the σ bond with the decrease in the energy difference of the orbitals forming the σ bond. This result is of course expected from simple molecular orbital theory.

Steric or nonbonding interactions between the olefin and the palladium moiety are suggested by the relative displacement energies. Any alkyl or aryl substituent on ethylene should result in a higher displacement energy than ethylene. We observe, however, that the displacement energies of ethylene, cyclopentene, cyclohexene, and styrene are nearly the same. Nonbonding interactions of the olefin with the palladium metal or cis chlorine ligands can cause twisting of the olefin relative to the square plane containing the metal and the nonolefinic ligands and/or prevent close contact of the olefin and the metal. This decreases the overlap of the orbitals causing a decrease in the relative displacement energies. An X-ray crystal structure of [PdCl$_2$-(styrene)]$_2$ indicates that the metal lies closer to the =CH$_2$ group than the =CH(C$_6$H$_5$) group conceivably as a result of the steric bulk of the phenyl group. We do find that styrene has a lower displacement energy than does ethylene.[34] X-Ray crystal structures on platinum complexes suggest that steric interactions between the metal and the carbon atom adjacent to the double bond occurs.[35–37]

One of the physical properties that originally led to the suggestion that the metal–olefin bond may have π character was the observation that olefins form very stable complexes with platinum(II) but not with acids such as boron alkyl compounds.[38] The suggested ordering of increasing π character in the metal–olefin bond, Ag(I) < Pd(II) < Pt(II) and Ag(I) < Pd(II) < Rh(I), is exactly the same as the increasing qualitative stability of these compounds. Thus, silver olefin compounds are often detected only in solution and if the solid complex is isolated it usually rapidly decomposes when exposed to the atmosphere. Palladium(II) olefin compounds decompose easily, often within hours, compared with those of platinum which are indefinitely stable. The same statements can be made for Ag(I), Pd(II), and Rh(I) olefin compounds where rhodium is the most stable of the series. The reported decrease in the double stretching frequency of ethylene upon coordination is 40 cm^{-1} for Ag(C$_2$H$_4$)$^+$, 96 cm^{-1} for [PdCl$_2$(C$_2$H$_4$)]$_2$, 103 cm^{-1} for [Rh(C$_2$H$_4$)$_2$Cl]$_2$, and 107 cm^{-1} for [PtCl$_2$(C$_2$H$_4$)]$_2$.[39] We thus find that the decrease in the double bond stretching frequency corresponds with the suggested increase in the π character of the double bond.

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One of the common justifications for obtaining information on homogeneous solutions of organometallic compounds is that this information perhaps can be extrapolated to catalysis in heterogeneous systems such as metal surfaces. One qualitative similarity between this work and surface phenomena involves the known ability of palladium metal to catalyze reactions involving olefins and the ability of nitrogen and phosphorus containing bases to poison catalytic surfaces. As previously suggested one possible reason for the above behavior is that the nitrogen and phosphorus donors are too strongly chemisorbed by the surface, eventually covering all the catalytic sites.[40,41] Our relative displacement energies are consistent with this since pyridine and triphenylphosphine have much higher values than do the olefins. We had observed a similar result with polyolefins previously.[1] The

relative displacement energies for palladium generally increase when electron donating substituents are present on the olefin. It has previously been observed[42] that increasing π electron density in the olefin results in higher adsorption equilibrium constants on metallic palladium. The similarity of our data to surface phenomena is encouraging.

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Microwave Spectrum, Structure, Dipole Moment, and Coriolis Coupling of 1,1-Difluoroallene

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Abstract: The microwave spectra of five isotopic species of 1,1-difluoroallene, H_2CCCF_2, $H_2{}^{13}CCCF_2$, $H_2C^{13}CCF_2$, $HDCCCF_2$, and D_2CCCF_2, have been recorded from 12.4 to 40.0 GHz. A-type transitions were observed and R-branch assignments have been made for the ground and two vibrationally excited states. The following structural parameters have been determined: $r(C_1{=}C_2) = 1.302 \pm 0.012$ Å; $r(C_2{=}C_3) = 1.306 \pm 0.002$ Å; $r(C_1–F) = 1.323 \pm 0.011$ Å; $r(C_3–H) = 1.086 \pm 0.003$ Å; $\angle HC_3H = 117.8 \pm 0.2°$; $\angle C_2C_3H = 121.1 \pm 0.1°$; $\angle FC_1F = 110.2 \pm 1.0°$; $\angle C_2C_1F = 124.9 \pm 0.5°$. The value of the dipole moment was obtained from Stark splittings to be 2.07 $\pm$ 0.03 D. Coriolis coupling was observed between the two low-frequency $C{=}C{=}C$ bending modes. The dipole moment and structural values are compared with those of similar molecules.

An important objective of a theory of chemical shifts of diamagnetic molecules is the quantitative estimation of ^{13}C and ^1H nmr chemical shifts in organic molecules. This goal has often seemed remote due to problems associated with the gauge of the vector potential describing the magnetic field.[1] However, preliminary applications[2] of a recent gauge-invariant *ab initio* theory of magnetic shielding[3] have given results for ^{13}C and ^1H chemical shifts which are in good agreement with experiment. To further document the performance of this method it is important to test it against experimental information for a variety of molecules. If sufficiently consistent success is obtained, this will allow some confidence to be acquired in its predictive power.

It is also important that the experimental systems chosen for the initial studies be inherently simple with

respect to their structure and number of atoms and yet exhibit the major types of substituent effect on shielding at carbon nuclei (*e.g.*, inductive and mesomeric effects). A class of compounds which is particularly attractive from this point of view is the fluorocarbons. To this end we have recently determined the ^{13}C chemical shifts of the fluoroallenes, $C_3F_nH_{4-n}$.[4] The measured ^{13}C shifts were compared to those predicted by SCF perturbation theory calculations employing a slightly extended Gaussian basis set of GIAO in an *ab initio* molecular orbital scheme.[3] For these calculations, the geometry used was estimated from the standard geometrical model developed by Pople and Gordon.[5] Although the level of agreement between the experimental data and the predicted results was good, it is essential to employ the best structural data possible in such calculations. With this goal in mind, we in-

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