Thus, the total energy input is fairly efficiently converted to a useful chemical energy source in the form of H_2. These considerations merely show that electrode photoassistance agents do provide viable mechanisms for storage of optical energy. It is wholly inappropriate at the present time to make detailed, rigorous comparisons of TiO_2, SnO_2, and $SrTiO_3$, since the ultimate efficiencies are likely to be a sensitive function of electrode preparation and cell design. Nonetheless, the $SrTiO_3$ does have the best demonstrated efficiency.

The high energy conversion efficiencies claimed here are, in part, a consequence of the very small bias required from an external power supply. We are currently undertaking detailed studies of the photoelectrodes in order to probe the properties which influence the current-voltage characteristics. While the usefulness with regard to solar energy will remain minimal unless wavelength response is substantially red-shifted, the optical to chemical energy conversion efficiency can be improved for $SrTiO_3$ by simply attempting to photoassist a more endothermic reaction than the electrolysis of H_2O.

Note Added in Proof: Findings similar to those reported here have just appeared in a preliminary communication: J. G. Mavroides, J. A. Kafalas, and D. F. Kolesar, *Appl. Phys. Lett.*, **28**, 241 (1976).

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References and Notes

(1) Fellow of the Alfred P. Sloan Foundation, 1974–1976.
(2) Fannie and John Hertz Foundation Fellow.
(3) M. S. Wrighton, D. L. Morse, A. B. Ellis, D. S. Ginley, and H. B. Abrahamson, *J. Am. Chem. Soc.*, **98**, 44 (1976).
(4) M. S. Wrighton, D. S. Ginley, P. T. Wolczanski, A. B. Ellis, D. L. Morse, and A. Linz, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 1518 (1975).
(5) R. W. G. Wycoff, "Crystal Structures", 2nd ed, Vol. 1, Wiley, New York, N.Y., 1963.
(6) For a discussion of semiconductor photoelectrode decomposition cf. H. Gerischer and W. Mindt, *Electrochim. Acta*, **13**, 1239 (1968).
(7) For reviews cf. (a) T. Freund and W. P. Gomes, *Catal. Rev.*, **3**, 1 (1969); (b) V. A. Myamlin and Yu. V. Pleskov, "Electrochemistry of Semiconductors", Plenum Press, New York, N.Y., 1967; (c) H. Gerischer in "Physical Chemistry", Vol. IXA, H. Eyring, D. Henderson, and W. Jost, Ed., Academic Press, New York, N.Y., 1970, Chapter 5.
(8) A. Fujishima and K. Honda, *Nature (London)*, **238**, 37 (1972), and *Bull. Chem. Soc. Jpn.*, **44**, 1148 (1971).
(9) J. Keeney, D. H. Weinstein, and G. M. Haas, *Nature (London)*, **253**, 719 (1975).
(10) W. Gissler, P. L. Lensi, and S. Pizzini, *J. Appl. Electrochem.*, **6**, 9 (1976).
(11) (a) K. L. Hardee and A. J. Bard, *J. Electrochem. Soc.*, **122**, 739 (1975); (b) F. Mollers, J. J. Tolle, and R. Memming, *ibid.*, **121**, 1160 (1974); (c) H. Yoneyama, H. Sakamoto, and H. Tamura, *Electrochim. Acta*, **20**, 341 (1975); (d) A. J. Nozik, *Nature (London)*, **257**, 383 (1975); (e) T. Ohnishi, Y. Nakato, and H. Tsubomura, *Ber. Bunsenges. Phys. Chem.*, **79**, 523 (1975); (f) A. Fujishima, K. Kohayakawa, and K. Honda, *Bull. Chem. Soc. Jpn.*, **48**, 1041 (1975).
(12) A. H. Kahn and A. J. Leyendeker, *Phys. Rev.* [*Sect.*] *A*, **135**, 1312 (1964).
(13) D. C. Cronemeyer, *Phys. Rev.*, **87**, 876 (1972).
(14) M. Nagasawa and S. Shionoya, *J. Phys. Soc. Jpn.*, **30**, 1118 (1971).
(15) (a) T. A. Noland, *Phys. Rev.*, **94**, 724 (1954); (b) M. Cardona, *ibid.*, **140**, A 651 (1965); (c) M. I. Cohen and R. F. Blunt, *ibid.*, **168**, 929 (1968).
(16) C. H. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
(17) "Powder Diffraction File", Inorganic Vol., No. PD1S-5IRB, Set 5-0634, Joint Committee on Powder Diffraction Standards, Philadelphia, Pa., 1960.
(18) W. H. Melhiush, *J. Opt. Soc. Am.*, **52**, 1256 (1962).
(19) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analyses", 3rd ed, Macmillan, New York, N.Y., 1952, p 600.
(20) We have determined the current-voltage properties of SnO_2 and TiO_2 in 9.5 M NaOH and have never obtained properties as good as those reported here for $SrTiO_3$. It is clear, however, that such properties will be a significant function of electrode material and its treatment in preparation.
(21) M. D. Archer, *J. Appl. Electrochem.*, **5**, 17 (1975).
(22) W. J. Moore, "Physical Chemistry", 3rd ed, Prentice-Hall, Englewood Cliffs, N.J., 1962, p 172.

A Calorimetric and ^1H Nuclear Magnetic Resonance Investigation of the Reaction of Triphenyl Phosphite with Compounds of the Type *trans*-Dichloro(pyridine)(olefin)platinum(II)

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Abstract: The characterization and calorimetric results are reported for the following reactions: $[PtCl_2(olefin)]_2 + 2py \rightarrow 2[PtCl_2py(olefin)]$ (1); $[PtCl_2py(olefin)] + P(OC_6H_5)_3 \rightarrow [PtCl_2py(P(OC_6H_5)_3)] + olefin$ (2); $[PtCl_2py(P(OC_6H_5)_3)] + P(OC_6H_5)_3 \rightarrow [PtCl_2(P(OC_6H_5)_3)_2] + py$ (3). The enthalpies of the reactions are, within 6%, the same in benzene and dichloromethane and the relative displacement energies are triphenyl phosphite ≫ ethylene > cyclooctene > *cis*-butene > styrene > cyclopentene > nitrostyrene > cyclohexene. The displacement energies of Ag(I), Pd(II), Rh(I), Pt(II), and Ni(0) are compared and discussed. The coordination chemical shift of the olefin increases and the platinum-coupling decreases as the metal-olefin interaction increases. All three reactions proceed to completion when equimolar amounts of reactants are added, and reaction 3 has a rate constant of 8.9 ± 0.6 and reactions 1 and 2 have rate constants >80 l. s^{-1} mol^{-1}. A thermodynamic description of the trans effect is given.

We have been interested in obtaining enthalpic and kinetic data on the formation and displacement of olefins with metals which may provide insight into the variety of catalytic processes which involve metal-olefin compounds. Initial studies involved common chelating polyolefins coordinated to palladium(II)[1] and rhodium(I),[2] with subsequent studies on silver(I)[3] and palladium(II)[4] monoolefin compounds. Platinum(II) olefin compounds have a long history, are exceptionally stable, and have been studied extensively by a variety of physical techniques. We were therefore very

Table I. Analytical Data

$[PtCl_2(olefin)]_2$	% calcd C	% calcd H	% found C	% found H
olefin = ethylene	8.17	1.37	8.22	1.35
cis-butene	14.92	2.50	14.90	2.49
cyclopentene	17.95	2.40	17.99	2.45
cyclohexene	20.71	2.90	20.81	2.88
cycloheptene	23.21	3.32	23.80	3.51
cyclooctene	25.53	3.72	26.37	3.78
styrene	25.97	2.18	25.18	2.13
$[PtCl_2(P(OC_6H_5)_3)_2]$	48.77	3.41	48.49	3.42
$PtCl_2(C_5H_5N)(P(OC_6H_5)_3)$[a]	42.15	3.08	41.91	2.97

[a] Calcd for N, 2.14. Found 2.14.

interested in obtaining enthalpic data on platinum olefin compounds.

The enthalpies of formation of compounds of the type $[PtX_3L]^-$ (X = Cl, Br; L = olefinic salts) from $[PtX_4]^{2-}$ have been previously reported[5-9] using water as a solvent. It would be of particular interest to compare our enthalpic data, measured on nonionic compounds in dichloromethane and benzene, with those previously reported on ionic compounds in water where solvation effects can have a dominating influence as has been shown for a series of silver(I) olefin compounds.[10]

Experimental Section

Materials and Apparatus. AR grade dichloromethane and reagent grade benzene were dried with Linde 4A molecular sieves at least 25 h prior to use. Reagent grade pyridine was distilled over barium oxide and stored over Linde 4A molecular sieves. The calorimetric apparatus and technique have been previously described.[1,2] NMR and ir spectra were recorded on Varian A-60 and Perkin-Elmer 202 spectrometers, respectively.

The platinum compounds were prepared in the usual manner, i.e., $[Pt_2Cl_4(C_2H_4)_2]$ by passing ethylene through an aqueous K_2PtCl_4 solution, and compounds of the type $Pt_2Cl_4(olefin)_2$ by displacement of ethylene in $Pt_2Cl_4(C_2H_4)_2$ using benzene as the solvent.[11] All of these compounds were recrystallized and gave satisfactory elemental analyses (see Table I).

Calorimetry. Two different procedures were used.

Procedure A. A known amount of compound of the type $Pt_2Cl_4(olefin)_2$, ~1 × 10^{-3} mol, was dissolved in 200 ml of dichloromethane and incrementally titrated with pyridine until heat was no longer evolved. The solution was then evaporated to dryness and the yellow residue washed with hexane and air-dried. Ir and NMR spectra were recorded on these solids. The solid was then redissolved in either benzene or dichloromethane and incrementally titrated with triphenyl phosphite.

Procedure B. A known amount of complex of the type $Pt_2Cl_4(olefin)_2$ was dissolved in either benzene or dichloromethane, incrementally titrated with pyridine until heat was no longer evolved, and then the same solution titrated with triphenyl phosphite. In each titration at least four increments of base were added, usually from five to ten.

Results

The elemental analyses of the initial compounds used in the calorimetric studies are given in Table I. Also given on Table I is the analyses of the products of the reactions when equal molar quantities of triphenyl phosphite and $[PtCl_2py(C_2H_4)]$ and 2:1 molar quantities of these reagents were added together.

The proton NMR data of the compounds of the type $[PtCl_2(olefin)]_2$ and $[PtCl_2py(olefin)]$ are given on Table II. The compounds $[PtCl_2(olefin)]_2$ are fairly insoluble in chloroform so that the noise level was rather high. This, coupled with the fact that many of the absorbances are broad make the reported chemical shifts somewhat imprecise, ±0.04 ppm. ^{195}Pt-H spin-spin coupling with the olefinic protons is observed in the $[PtCl_2py(olefin)]$ compounds at ambient probe temperature, but not in the $[PtCl_2(olefin)]_2$ compounds. The coordination shift, the difference in the chemical shifts of the coordinated and uncoordinated olefin, of the olefinic protons is either positive or negative depending upon the specific olefin. There is excellent agreement of our NMR data with that previously reported for $[PtCl_2py(olefin)]$ (olefin = ethylene, *cis*-butene).[12]

Three observations were made in the calorimetric titrations of pyridine with the $[PtCl_2(olefin)]_2$ compounds. (1) There is a rapid evolution of heat which ceases within 30 s, the time of complete stirring of the solution. (2) Equal increments of heat are evolved for equal increments of base added. The reaction therefore goes to completion as each increment of pyridine is added. (3) The evolution of heat

Table II. ^1H NMR Data of Selected Olefins and Platinum Metal Olefin Compounds[a]

Compd	δ (=CH)	*J* (Pt –H)	Δ[b]	δ(>CH$_2$)	Δ (Pd)[f]
Ethylene	4.63	—	—	—	—
$[PtClpyC_2H_4]$[e]	5.07 (4)[c]	62	0.44	—	—
$[PtCl_2(C_2H_4)]_2$	5.05	—	0.42	—	−0.12
cis-Cyclooctene	4.33 (2)	—	—	7.82 (4), 8.47 (8)	—
$[PtCl_2py(C_8H_{14})]$	4.36 (2)	67	0.03	7.57 (4), 8.48 (8)	—
$[PtCl_2(C_8H_{14})]_2$	4.28 (2)	—	−0.05	7.78 (4), 8.47 (8)	−0.65
Cycloheptene	4.17 (2)	—	—	7.86 (4), 8.36 (6)	—
$[PtCl_2py(C_7H_{12})]$	4.09	70	−0.08	7.54 (4),[d] 8.33 (6)[d]	—
$[PtCl_2(C_7H_{12})]_2$	4.22 (2)	—	+0.05	7.24 (4), 8.42 (6)	−0.77
cis-Butene	4.53 (2)	—	—	8.38 (6) (-CH$_3$)	—
$[PtCl_2py(C_4H_8)]$	4.27 (2)	70	−0.26	8.20 (6) (-CH$_3$)	—
$[PtCl_2(C_4H_8)]_2$	4.25 (2)	—	−0.28	8.46 (6) (-CH$_3$)	−0.88
Cyclopentene	4.18 (2)	—	—	7.65 (4),[d] 8.05 (2)[d]	—
$[PtCl_2py(C_5H_8)]$	3.77 (2)	74	−0.41	~7.7 (6)[d]	—
$[PtCl_2(C_5H_8)]_2$	3.95[d] (2)	—	−0.23	~7.9 (6)[d]	−0.76
Cyclohexene	4.30 (2)	—	—	7.98 (4), 8.37 (4)	—
$[PtCl_2py(C_6H_{10})]$	3.78 (2)	73	−0.52	~7.5,[d] ~8.0[d] (8)	—
$[PtCl_2(C_6H_{10})]_2$	3.94 (2)	—	−0.36	7.82 (4), 8.40 (4)	—

[a] All data in deuteriochloroform using the τ scale and relative to Me_4Si. [b] Difference between coordinated and uncoordinated olefinic chemical shifts. [c] Relative intensities in parentheses. [d] Center of broad band. [e] Protons of pyridine observed in the range 1.0–2.7 ppm. [f] Coordination chemical shift for $[PdCl_2(olefin)]_2$. See ref 4.

Table III. Summary of Enthalpy Data (kJ mol^{-1})

$$[PtCl_2(olefin)]_2 + 2py \rightarrow 2[PtCl_2(olefin)(py)] \quad (1)$$

$$[PtCl_2(olefin)(py)] + P(OC_6H_5)_3 \rightarrow [PtCl_2(P(OC_6H_5)_3)py] + olefin \quad (2)$$

$$[PtCl_2(P(OC_6H_5)_3)(py)] + P(OC_6H_5)_3 \rightarrow [PtCl_2(P(OC_6H_5)_3)_2] + py \quad (3)$$

	Solvent (reaction no.)				
Olefin	C_6H_6 (1)	CH_2Cl_2 (1)	C_6H_6 (2)	CH_2Cl_2 (2)	C_6H_6 (3)
Ethylene	150 ± 2	151 ± 2	58 ± 1	58 ± 1	—
cis-Butene	—	133 ± 2	68 ± 1	66 ± 1	44.8
Cyclopentene	130 ± 2	130 ± 2	77 ± 1	74 ± 1	44.4
Cyclohexene	—	131 ± 2	82 ± 2	—	43.5
Cycloheptene	—	130 ± 2	65 ± 1	63 ± 1	43.6
cis-Cyclooctene	—	132 ± 3	61 ± 1	—	43.4
Styrene	134 ± 2	135 ± 2	77 ± 1	75 ± 1	44.9, 44.8
p-Nitrostyrene	—	131 ± 2	82 ± 1	77 ± 1	44.5, 43.9
				Mean	44.2 ± 0.6

ceases when more than 2 mol of pyridine are added to 1 mol of $[PtCl_2(olefin)]_2$. Since the reactions go to completion the enthalpy changes were calculated by dividing the heat evolved by the number of moles of base of pyridine added. These enthalpy changes are summarized on Table III.

Addition of triphenyl phosphite to a solution of $[PtCl_2py(olefin)]$ results in (1) a rapid evolution of heat that ceases within 30 s until equal molar quantities of the acid and base have been added. Further addition of triphenyl phosphite results in a slower evolution of heat that is complete within 20 min (see Figure 1). This slower reaction ceases when more than 2 mol of triphenyl phosphite is added to 1 mol of $[PtCl_2py(olefin)]$. (2) Equal increments of base added result in equal amounts of heat liberated. This was true throughout the entire titration. The calculation of the enthalpy from the rate controlled reaction will be described later. Enthalpy changes determined using either procedures A and B (Experimental Section) and by using the same procedures but independently prepared and purified compounds were the same within experimental error.

Discussion

Characterization of the Reactions. There is strong experimental evidence that the first reaction proceeds as:

$$[PtCl_2(olefin)]_2 + 2py \rightarrow 2\textit{trans}\text{-}[PtCl_2py(olefin)] \quad (1)$$

Compounds of the type $[PtCl_2(olefin)]_2$ have been previously characterized via x-ray crystal determinations (olefin = cyclopentene and cycloheptene),[13] via ir measurements in dichloromethane (olefin = ethylene),[14] and molecular weight determinations in benzene.[15] We have further characterized these compounds via elemental analysis (Table I), NMR (Table II), and far-ir measurements.[16] All compounds exhibit three metal chlorine stretching frequencies indicative of a symmetrical trans structure for the dimer.[17] Compounds of the type *trans*-$[PtCl_2py(olefin)]$ (olefin = ethylene, *cis*-butene, styrene) have been thoroughly investigated.[12] Their spectra exhibited one strong metal-chlorine stretching frequency at ~340 cm^{-1} indicative of the trans isomer and have no absorbances in the 1610-1700-cm^{-1} region typical for an uncoordinated olefin. Bridge splitting reactions involving compounds of the type $[PtCl_2L]_2$ (L = olefin or phosphine) with amines have been previously characterized and are known to give the trans isomer in solution.[18,19]

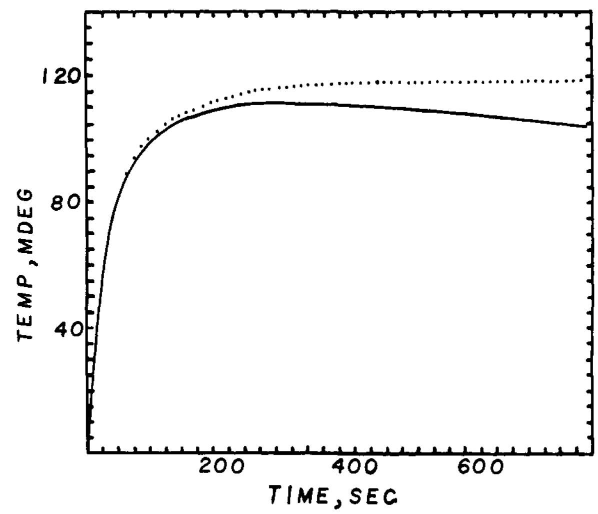

Figure 1. The calorimetric curve resulting from the reaction of 8.03 × 10^{-4} mol of $[PtCl_2(P(OC_6H_5)_3py]$ with 9.39 × 10^{-4} mol of $P(OC_6H_5)_3$ in 200 ml of benzene.

One observes via calorimetric titrimetry that 2 mol of pyridine is consumed per mole of platinum compound consistent with reaction 1.

Addition of triphenyl phosphite to compounds of the type $[PtCl_2py(olefin)]$ results in two consecutive reactions:

$$[PtCl_2py(olefin)] + P(OC_6H_5)_3 \rightarrow [PtCl_2py(P(OC_6H_5)_3)] + olefin \quad (2)$$

$$[PtCl_2pyP(OC_6H_5)_3] + P(OC_6H_5)_3 \rightarrow [PtCl_2(P(OC_6H_5)_3)_2] + py \quad (3)$$

These have been confirmed via calorimetric titrimetry, NMR spectroscopy, and by the isolation and characterization of the products. In one calorimetric run, exactly 1 mol of triphenyl phosphite was added incrementally to a solution initially containing $[PtCl_2py(C_2H_4)]$. Evaporation of this solution resulted in a white solid, which analyzed for $PtCl_2py(P(OC_6H_5)_3)$, exhibited the expected NMR absorbances for triphenyl phosphite and pyridine, and whose ir spectrum had two intense metal chlorine stretching frequencies at 310 and 348 cm^{-1} suggesting the cis isomer. Addition of 2 mol of triphenyl phosphite to 1 mol of $[PtCl_2py(C_2H_4)]$ results in a white solid whose elemental analysis is consistent with a compound of the stoichiometry $[PtCl_2(P(OC_6H_5)_3)_2]$, and whose ir spectrum exhibited two intense metal-chlorine stretching frequencies at 310 and 338 cm^{-1}. Calorimetric titrimetry reveals that addition of triphenyl phosphite to compounds of the type $[PtCl_2py(olefin)]$ results in a initial rapid reaction which consumes exactly 1 mol of base and is followed by a second slow reaction which consumes exactly 1 mol of base before heat is no longer evolved. Consistent with the third reaction, the enthalpy change is independent of the initial olefin complex used (Table III). We have also followed reaction 2 via ^1H NMR spectroscopy. A solution of $[PtCl_2py(cyclooctene)]$ has absorbances at 4.18, 7.55, and 9.45 ppm due to the coordinated olefin present. Addition of an equimolar quantity of triphenyl phosphite results in a NMR spectrum whose chemical shift values and fine structure are identical with free *cis*-cyclooctene. Similar studies were performed on the ethylene and *cis*-butene platinum derivatives.

Table IV. Relative Displacement Energies, kJ mol^{-1}

Base	Ag(hfacac)[a]	$PdCl_2$(py)[b]	Rh(acac)-(C_2H_4)[c]	$PtCl_2$(py)	Ni(P(O-*o*-tolyl)$_3$)$_2$[c]
Triphenylphosphine	80 ± 2	—	—	—	—
Triphenyl phosphite	—	—	—	58 ± 1	—
Pyridine	—	58 ± 2	—	—	—
cis-Cyclooctene	39 ± 2	9.2 ± 0.8	—	—	—
Cyclohexene	24 ± 1	—	—	—	—
cis-Butene	—	5.9 ± 1.3	—	—	—
Cycloheptene	20 ± 1	4.6 ± 1.3	—	—	—
Hexamethylbenzene	13 ± 1	—	—	—	—
Cyclopentene	3 ± 2	—	—	—	—
Toluene	0.0[d]	—	—	—	—
Ethylene	—	0.0[d]	0.0[d]	0.0[d]	0.0[d]
cis-Cyclooctene	—	—	—	−2 ± 1	—
Cycloheptene	—	—	—	−5 ± 1	—
Cyclohexene	—	−0.4 ± 2	—	—	—
cis-Butene	—	—	−8 ± 3	−10 ± 1	—
Styrene	—	−0.8 ± 1	—	−19 ± 1	−8.3
Cyclopentene	—	−2 ± 1	—	−19 ± 1	—
Nitrostyrene	—	—	—	−24 ± 1	—
Cyclohexene	—	—	—	−24 ± 1	—
Tri-*o*-tolyl phosphite	—	—	—	—	−14 ± 2
cis-Cyclooctene	—	—	—	—	−21 ± 3
Cyclopentene	—	—	—	—	−23.0 ± 3
Cycloheptene	—	—	—	—	−23.3 ± 3
Cyclohexene	—	—	—	—	−32 ± 5

[a] Reference 3. [b] Reference 4. [c] Reference 20. [d] Arbitrary standard to which other bases are compared. [e] Reference 21.

Relative Displacement Energies. Table IV gives the relative displacement energies for some silver(I), palladium(II), and platinum(II) compounds (all measured calorimetrically; the silver and palladium compounds in dichloromethane and the platinum compounds in benzene) and rhodium(I) and nickel(0) compounds (measured spectrophotometrically in toluene and benzene, respectively).[20,21] For the nickel(0) compounds the enthalpy change has been calculated from equilibrium constants assuming that the entropy change is negligible; an assumption that has been shown to be valid for three olefins. The bases are arranged with increasing displacement energies proceeding up the table. The standard chosen for each metal is arbitrary. The values of 0.0 given to ethylene for palladium, platinum, rhodium, and nickel does not imply that ethylene is bonded equally strongly to all three metals. We place the most confidence in the relative displacement energies of the silver, palladium, and platinum compounds since these enthalpies were measured directly via microcalorimetry.

The data on Table III lend support that enthalpic contributions due to solvent-solute interactions are not significant. Benzene is a weakly π basic, nonpolar solvent whose dielectric constant is 2.28 and dichloromethane is a weakly acid, polar solvent with a dielectric constant of of 9.08. The enthalpy difference observed for the same reaction in these two solvents is slight, the differences ranging from 0 to 6%. Enthalpies for reaction 2 are generally slightly lower in dichloromethane. Most important the trends as the olefin is varied are exactly the same in both solvents. These data indicate that the overall solvation energies are very nearly cancelling in these reactions. The enthalpy values are nearly the same in two solvents of differing acid character and whose van der Waals interactions should be significantly different. Certainly dichloromethane is specifically interacting with the free triphenyl phosphite and olefins in these reactions but their effect on the overall enthalpy is slight because (1) dichloromethane is a much weaker acid than the platinum(II) atom toward these bases and (2) the triphenyl phosphite and olefin solvent interactions will partially or wholly cancel since these bases appear on opposite sides of the chemical equation.

We previously used dichloromethane as a solvent in the silver compounds Ag(hfacac)(olefin),[3] since they react with benzene[22] and many of them are insufficiently soluble in cyclohexane, and for the palladium compounds, [$PdCl_2$(olefin)]$_2$ which are too insoluble in benzene and cyclohexane. The fact that platinum(II) discriminates between the olefins in exactly the same way in dichloromethane and benzene gives us confidence that this is also true in the silver and palladium systems. Another supportive fact is that we have recently determined the heat of the following reaction and obtained values of −45.6 kJ mol^{-1} in cyclohexane and −41.5 kJ mol^{-1} in dichloromethane:

$$\mathrm{Ag(hfacac)(C_8H_{14}) + P(C_6H_5)_3 \rightarrow Ag(hfacac)(P(C_6H_5)_3) + C_8H_{14}}$$

This result is very similar to what we have observed in the platinum system.

In regard to solvation effects, it is significant to compare our results to those published for $PtCl_3$(olefin)$^-$ compounds in water.[5-9] Previously it was found that any electron donating group on the olefin results in a lowering of the relative displacement energy of the olefin. Table IV shows that the same is true for [$PtCl_2$py(olefin)] compounds in benzene since any alkyl or aryl substitution on ethylene results in a lower relative displacement energy. Furthermore the enthalpy difference between $CH_2{=}CHCH_2NH_3^+$ and *cis*-$CH_3CH{=}CHCH_2NH_3^+$ toward $PtCl_3^-$ is 4.6 kJ mol^{-1} and the difference between ethylene and *cis*-butene toward $PtCl_2$py is 10 kJ mol^{-1}. There is about a 5 kJ mol^{-1} lowering per methyl group in both chemical systems.

We shall now discuss and compare the relative displacement energies of the metals on Table IV. Triphenylphosphine, pyridine, and triphenyl phosphite interact far stronger than do the olefins for silver(I), palladium(II), and platinum(II) compounds, respectively, in contrast to the Ni(0) compounds where *o*-tolyl phosphite has an intermediate alue. The position of *o*-tolyl phosphite is apparently not due to its steric characteristics since one can compare the different behavior of the three-coordinate nickel(0) and four-coordinate Pt(II) compounds. Steric constraints ought to be greater in the Pt(II) compounds. This observation may suggest that amines and phosphines in general interact much more strongly than olefins for "class T" compounds (Ag(I), Pd(II), Pt(II), Rh(I)) but not in "class S" compounds (Ni(0)).[23] The distinction between class T and class S is that in class S the olefin is much more perturbed than in class T perhaps resulting from a much greater olefin-metal interaction; so much greater that the olefins are now of comparable strength to nitrogen and phosphine donors.

For silver and palladium methyl substitution results in a stabilization of the metal-olefin interaction (compare hexamethylbenzene and toluene for silver; *cis*-butene and ethylene for palladium) and a destabilization for rhodium, platinum, and nickel compounds. If one assumes the Chatt-Dewar-Duncanson model of metal-olefin bond,[24,25] the σ contribution is more important than the π contribution for silver(I) and palladium(II) and vice versa for rhodium(I), platinum(II), and nickel(0) since an alkyl group is an electron donating group. A recent x-ray study of $[PtCl_2(olefin)]_2$ complexes reports a shorter metal-olefin, bond for cycloheptene than cyclopentene,[13] suggesting a stronger interaction with the former in agreement with our thermodynamic data. Steric interactions between cycloheptene and the olefins and the ligands were also proposed[13] but these are apparently not as important as the electronic interactions in determining the relative displacement energies for these two cycloolefins.

It is particularly interesting to note that nitrostyrene is not interacting as strongly as styrene toward platinum(II). From this experimental fact alone one might think that the σ contribution is more important than the π contribution as has been previously proposed for a series of palladium compounds.[26] We suspect that this is not so for the following reasons. (1) ESCA measurements on platinum olefin compounds indicate a net donation of charge from the metal to the olefin.[27] (2) The π contribution may be more important than the σ contribution for the styrenes but the *differences* in the π orbitals may be greater than those of the π^* orbitals accounting for the observed relative displacement energies of the styrenes. It should also be mentioned that the bonding model assumed may be erroneous as a recent theoretical treatment indicates.[28]

One can also make the following observations from Table IV. (1) the cyclic olefins interact differently with each metal: for Ag(L), $C_8 > C_6 > C_7 > C_5$; for Pd(II), $C_8 > C_7 > C_6 > C_5$; for Pt, $C_8 > C_7 > C_5 > C_6$; and for Ni(0), $C_8 > C_5 > C_7 > C_6$. Only in the nickel compounds does the ordering agree with the strain energies of the olefins.[29] This result may have been anticipated since only in Ni(0) is there a significant amount of bond lengthening of the olefinic bond.[23] (2) The selectivity of the metal toward the olefins appears to go through a minimum in the series Ag(I), Pd(II), Pt(II), and Ni(0) with the minimum at palladium. This may be anticipated if the relative amount of π contribution to the metal-olefin bond increases in the same order. Silver would have a relatively high selectivity since its bonding is predominantly of σ character which would then respond readily to changes in π orbital of the olefin. Palladium would have less selectivity since there would be more π character in the bond. The synergism of the bond would tend to keep the metal-olefin interaction about the same. For platinum and nickel the π character of the bond predominates and hence the selectivity of these metals increases since they now respond more readily to changes in the π^* orbitals. The selectivity of Ni(0) is greater than for platinum(II) probably because of the greater degree of π metal-olefin bonding; i.e., platinum(II) shows class T behavior and Ni(0) class S behavior.[23] The ordering of selectivity observed here is different from those previously given[21] but the later ordering was based on equilibrium constants, not enthalpy changes.

The enthalpy information can be combined with a number of other studies providing some insight into the nature of trans effect. The trans labilizing influence of ethylene is greater than *cis*-butene and styrene in compounds of the type [PtCl(olefin)(py)].[30] The NQR frequencies of the trans chloride ligand in compounds of the type $[PtCl_3(olefin)]^-$ increase ethylene < *cis*-butene < styrene, the same ordering as their relative displacement energies. It was suggested that as the NQR frequency decreases, the platinum-chlorine bond weakens.[31] If this interpretation is correct, then as the metal-olefin interaction increases a concomitant decrease in the metal-chlorine bond order trans to it occurs. This may be the thermodynamic description of the changes occurring in the trans effect. We can also note that the relative dissociation energies are norbornadiene > 1,5-cyclooctadiene for palladium(II) and rhodium(I) compounds.[1,2] Assuming this is also true for platinum, then increasing metal-olefin interaction of these chelating olefins also results in a decrease of the observed NQR frequencies.[31]

The ^1H NMR data on Table II are arranged in the same order as the relative displacement energies. For compounds of the type $[PtCl_2py(olefin)]$ the coordination chemical shift, Δ, increases as the metal-olefin interaction increases. Furthermore the coordination chemical shift is negative for cyclohexene and gradually becomes positive on ascending the table. The platinum-hydrogen coupling constants between the platinum atom and the olefinic protons in general increase as the metal-olefin interaction decreases. None of these observations has previously been made. It was observed previously that in the compounds $[PtCl_2(olefin)]$, (olefin = norbornadiene, 1,5-cyclooctadience, 1,3,5,7-cyclooctatetraene) that the coordination chemical shifts decrease and platinum-hydrogen coupling constants both increase in this order.[32] For palladium and rhodium the relative dissociation energies are norbornadiene > 1,5-cyclooctadiene > 1,3,5,7-cyclooctatetraene.[1,2] Assuming the same ordering for platinum, we have exactly the same observations for chelating olefins as for monoolefins; i.e., increasing metal-olefin interaction results in an increase in the chemical coordination shift of the olefins and a decrease in the platinum-hydrogen coupling. There is no agreement in the interpretation of the coordination chemical shift and the platinum-hydrogen coupling in metal olefin compounds.[33]

We observed that the coordination chemical shifts are always greater for platinum than for isostructural palladium compounds. (See Table II). The difference ranges from 0.53 to 0.82 ppm for compounds of the type $[PtCl_2(olefin)]_2$ and 0.41-0.92 ppm for $[MX_2(olefin)]$ (M = Pd, Pt; X = Cl, Br; olefin = 1,5-cyclooctadiene, 1,3,5-cyclooctatriene, 1,3,5,7-cyclooctatetraene, norbornadiene).[32] Two explanations for these results are that the amount of π character in the platinum compounds is greater than in palladium, or it may be simply due to the larger size of platinum which therefore has a larger diamagnetic susceptibility.

Rate constants were calculated for reaction 3 using a previously described procedure.[34] The actual rise in temperature is given by the solid line in Figure 1. The dotted line results when the actual temperature is corrected for heat loss. The enthalpy of the reaction was evaluated by dividing the heat evolved by the limiting amount of reagent. The constancy in the enthalpy values (Table III) further confirms the correctness of the procedure. Excellent fits to the curved portions of the graph were obtained by assuming the rate is first order with respect to both of the reagents. The values of the rate constant from six different curves were 9.5, 9.3, 8.4, 10.2, 9.1, and 6.8 l. mol^{-1} s^{-1} or 8.6 ± 0.6. The standard deviation of the calculated and observed temperatures was 0.0005 for the six curves with some trending observed in two cases. One can place a limit on the rates of reactions 1 and 2 of not less than 80 l. mol^{-1} s^{-1} since these reactions are complete in the time of mixing.

References and Notes

(1) W. Partenheimer, *Inorg. Chem.*, **11**, 743 (1972).
(2) W. Partenheimer and E. Hoy, *J. Am. Chem. Soc.*, **95**, 2840 (1973).
(3) W. Partenheimer and E. H. Johnson, *Inorg. Chem.*, **12**, 1274 (1973).
(4) W. Partenheimer and B. Durham, *J. Am. Chem. Soc.*, **96**, 3800 (1974).
(5) R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc. A*, 324, 238 (1967).
(6) F. R. Hartley and L. M. Venanzi, *J. Chem. Soc. A*, 330 (1967).
(7) R. G. Denning and L. M. Venanzi, *J. Chem. Soc. A*, 336 (1967).
(8) R. Spagna, L. M. Venanzi, and L. Zambonelli, *Inorg. Chim. Acta*, **4**, 475 (1970).
(9) R. M. Milburn and L. M. Venanzi, *Inorg. Chim. Acta*, **2**, 97 (1968).
(10) S. P. Wasik and W. Tsang, *J. Phys. Chem.*, **74**, 2970 (1970).
(11) J. Chatt and M. Z. Searle, *Inorg. Synth.*, **5**, 210 (1957).
(12) M. Orchin and P. J. Schmidt, *Inorg. Chim. Acta Rev.*, **2**, 123 (1968).
(13) J. Bordner and D. W. Wertz, *Inorg. Chem.*, **13**, 1639 (1974).
(14) M. J. Grogan and K. Nakamoto, *J. Am. Chem. Soc.*, **90**, 918 (1968).
(15) J. Chatt, *J. Chem. Soc.*, 3340 (1959).
(16) W. Parenheimer and B. Durham, *J. Inorg. Nucl. Chem. Lett.*, **10**, 1143 (1974).
(17) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2d ed, Wiley-Interscience, New York, N.Y., p 213.
(18) J. Chatt, *J. Chem. Soc.*, 2301 (1950); 653 (1951).
(19) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 2445 (1957); 3858 (1955).
(20) R. Cramer, *J. Am. Chem. Soc.*, **89**, 4621 (1967).
(21) C. A. Tolman, *J. Am. Chem. Soc.*, **98**, 2780 (1974).
(22) We have observed that the NMR spectra of "Ag(hfacac)(cyclooctene)" in dichloromethane and in benzene are significantly different. The chemical shifts are different in the two solvents and neither of their values correspond to the free olefin suggesting that a compound such as [Ag(hfacac)(cyclooctene) (benzene)] forms in benzene.
(23) F. R. Hartley, *Angew. Chem., Int. Ed. Engl.*, **11**, 596 (1974).
(24) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951).
(25) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).
(26) E. M. Ban, R. P. Hughes, and J. Powell, *J. Chem. Soc., Chem. Comm.*, 591 (1973). See also for platinum styrene compounds, D. G. Cooper, G. K. Hamer, J. Powell, and W. F. Reynolds, *ibid.*, 449 (1973).
(27) D. T. Clark, D. Briggs, and D. B. Adams, *J. Chem. Soc., Dalton Trans.*, 169 (1973).
(28) N. Rosch, R. P. Messmer, and K. H. Johnson, *J. Am. Chem. Soc.*, **96**, 3855 (1974).
(29) P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Am. Chem. Soc.*, **92**, 2377 (1970).
(30) P. D. Kaplan, P. Schmidt, and A. Brause, *J. Am. Chem. Soc.*, **91**, 85 (1969).
(31) J. P. Yesinowski and T. L. Brown, *Inorg. Chem.*, **10**, 1097 (1971).
(32) W. Partenhelmer, Ph.D. Thesis, University of Iowa, 1968.
(33) See, for example, D. G. Cooper, R. P. Hughes, and J. Powell, *J. Am. Chem. Soc.*, **94**, 9244 (1972), and references quoted therein.
(34) T. Meites, L. Meites, and J. N. Jaitley, *J. Phys. Chem.*, **73**, 3801 (1969).

Thermodynamic and Spectroscopic Studies of the Reaction of Lewis Bases with Di-μ-chloro-tetracarbonyldirhodium(I)

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Abstract: A detailed calorimetric and spectroscopic study of the acid-base chemistry of $[(CO)_2RhCl]_2$ in poorly solvating media is presented. Enthalpies of adduct formation with ten bases are reported which vary considerably in their basic properties; e.g., nitrogen, sulfur, and oxygen donors are reported. The data can be correlated with the E and C model thus extending this treatment for the first time to low-valent, second-row transition metal systems. An enthalpy of 22.6 kcal mol^{-1} of dimer is required to cleave the chloro bridges. The procedure for factoring this bridge cleavage enthalpy out of the measured enthalpy data is described. We are now in a position to predict enthalpies of adduct formation with all of the bases in the E and C correlation and can understand why many substances do not effect bridge cleavage. The structures of the complexes in solution are deduced from infrared and ^{13}C NMR studies.

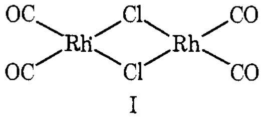
Recent work from this laboratory[3] has concerned itself with the study of quantitative aspects of Lewis acid-base interactions. The relationship first proposed by Drago and Wayland in 1965[4,5] (eq 1)

$$-\Delta H = E_A E_B + C_A C_B \qquad (1)$$

has been tested on numerous systems, but, to date, only two transition metal complexes have been included in the correlation, namely, bis(hexafluoroacetylacetonato)copper(II)[6] and methylatobis(dimethylglyoximato)cobalt(III).[7] We thought it would be enlightening to attempt an extension of the correlation to other transition-metal-containing Lewis acids, particularly to one containing a low-valent second-row transition metal. The acid-base interaction in metal systems is potentially more complex than in the simple systems studied previously[3] because a π back-bonding contribution to the stability of the M-L bond may exist.

Metal complexes of this type are interesting because of their importance in a number of catalytic reactions. For example, the well-known hydrogenation catalyst $[(C_6H_5)_3P]_3RhCl$[8] can be considered as the $(C_6H_5)_3P$ adduct of $\{[(C_6H_5)_3P]_2RhCl\}_2$. Recently, Tolman et al.[9] have investigated the system RhCl-triarylphosphine-H_2-olefin. Kinetic data indicated that the species RhP_2Cl was an important intermediate in the reaction with H_2. In many catalytic processes, coordinatively unsaturated intermediates of this type are very important. A characteristic reaction of this type of compound is the addition of a ligand to the open coordination position. The energetics and kinetics of this type of reaction are usually difficult to study. By determining the bridge cleavage enthalpy of the chloro-bridged dimer, we can derive thermodynamic data for interaction of the species $Rh(CO)_2Cl$ with a series of bases.

The complex di-μ-chloro-tetracarbonyldirhodium(I) (I) is



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