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Hard Ligands as Donors to Soft Metals. 2. Cationic Monomeric and Dimeric Complexes of Palladium(II) and Platinum(II): Toward the Isolation of Weakly Bonded Species

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The replacement of chloride ligands in $[M(\widehat{L\,L})Cl_2]$ (M = Pd, Pt; $\widehat{L\,L}$ = bidentate ligand with two methylene groups between the donor atoms) by the neutral ligands (S) pyridine, dimethyl sulfoxide (Me_2SO), dimethylformamide (DMF), PPh_3, and $P\text{-}n\text{-}Pr_3$ to yield cationic $[M(\widehat{L\,L})(S)Cl]^+$ complexes has been achieved by treating the dichloro complexes with a silver(I) salt in the presence of the neutral ligand. When the bidentate ligand is $Ph_2AsCH_2CH_2PPh_2$, $^{31}P\{^1H\}$ NMR shows that tertiary phosphines preferentially enter trans to arsenic and that this preference is greater for platinum(II) than palladium(II). When chloride abstraction from $[M(\widehat{L\,L})Cl_2]$ is carried out in the presence of weaker donor ligands such as acetonitrile, alcohols, acetone, ethers, benzene, and dichloromethane, the cationic chloride-bridged dimeric complexes $[M_2(\widehat{L\,L})_2Cl_2]^{2+}$ are isolated as their perchlorate salts; the same product is obtained when the reaction is carried out in the presence of carbon monoxide. Conductance studies show that the position of the equilibrium $[M(\widehat{L\,L})Cl_2] + S \rightleftharpoons [M(\widehat{L\,L})(S)Cl]^+ + Cl^-$ is highly dependent on the nature of S. Thus dissociation to yield the cationic species is enhanced by the use of strong donor solvents ($Me_2SO \gtrsim DMF \gg$ acetonitrile). It is concluded that the ability of ligands (S) to form cationic $[M(\widehat{L\,L})(S)Cl]^+$ complexes is tertiary phosphine $\approx$ pyridine $>$ oxygen-coordinated $Me_2SO > DMF \gg MeCN \approx CO$. $[Pd(Ph_2PCH_2CH_2PPh_2)(DMF)Cl](ClO_4)$ promotes the slow hydrogenation of styrene in dmf solution at room temperature under 1 atm of hydrogen. Since $[Pd(Ph_2PCH_2CH_2PPh_2)Cl_2]$ is unable to catalyze olefin hydrogenation at all under these conditions, the presence of a weak donor ligand has enhanced the ability of palladium(II) complexes to activate olefins.

Introduction

Transition-metal complexes are being increasingly studied as catalysts for the reactions of unsaturated organic molecules such as olefins, acetylenes, and aromatic compounds. A survey of the known thermodynamic data for olefin and acetylene complexes of transition metals shows that the stability constants for the formation of these complexes are low.[1] Since complex formation between a transition metal and an unsaturated organic molecule is an essential feature of the catalytic activity of the metal, there are two routes open for the systematic design of potential catalysts. In the first, a coordinatively unsaturated complex that can bond to the organic substrate through its vacant site is used; such a complex would mimic the action of titanium(III) in the Ziegler–Natta polymerization catalysts.[2,3] In the second, a complex with one or more weak donor ligands that can readily be displaced by the organic substrate is used. In general, such compounds are prepared in solution. For platinum-group metals, weak donor ligands are often solvent molecules, for example $[Pd(C_2H_4)(H_2O)Cl_2]$ in the Wacker process[4] and $[Rh(PPh_3)_2(solvent)Cl]$ and $[Rh(PPh_3)_2(solvent)H_2Cl]$ in olefin hydrogenations.[5] Relatively little work has been undertaken to isolate and characterize such complexes, for the very good reason that they are highly labile. However, in order to systematically advance the understanding of the factors that are important for the formation and stability or instability of palladium(II) and platinum(II) complexes of weak donor ligands, we have attempted to prepare and characterize a number of these complexes.

In the present paper we report a series of cationic complexes prepared by removing one chloride ligand from dichloro complexes of palladium(II) and platinum(II) in the presence of various donors, and in a subsequent paper we shall report a series of dicationic complexes in which no halide ligands are present. A preliminary investigation of these complexes containing weak donor ligands demonstrates that they do have a much higher ability to activate substrates such as olefins than the corresponding complexes with stronger donor ligands such as halides. This supports our original postulate that the presence of weak donor ligands should enhance catalytic activity.

Experimental Section

Acetonitrile was dried over molecular sieve for 24 h and then distilled over P_2O_5 (5 g L^{-1}) under dry nitrogen and stored over molecular sieve. Acetone was dried by refluxing over anhydrous $CaSO_4$ (10 g L^{-1}) under dry nitrogen and fractionally distilled immediately prior to use. Storage of such dry acetone is not recommended. Dichloromethane was dried over anhydrous $CaSO_4$ (5 g L^{-1}) for 24 h and then distilled onto molecular sieve. Dimethylformamide was distilled in vacuo onto molecular sieve. Pyridine was stored over KOH (5 g L^{-1}) for 24 h and then fractionally distilled prior to use. Silver salts were dried at 56 °C in vacuo (10^{-3} torr). Infrared spectra were recorded as Nujol and hexachlorobutadiene mulls between CsI plates on a Perkin-Elmer 577 spectrometer. ^1H NMR spectra were obtained in CD_2Cl_2 solutions ($\sim$10%) with Me_4Si as internal standard on a Perkin-Elmer R32 spectrometer. ^{31}P NMR spectra (Table III) were obtained in $CDCl_3/CD_2Cl_2$ solution on a JEOL 100-MHz instrument by Dr. M. Murray and in $MeNO_2$ solution on a JEOL 60-MHz instrument by Dr. W. McFarlane. Conductivity studies were performed by using a Universal Wayne-Kerr bridge with a glass cell containing platinum electrodes. Solution electronic spectra were recorded in 10-mm quartz cells by using a Pye-Unicam SP 1700 spectrophotometer. A Pye Series 104 chromatograph (Type 6 analyzer) equipped with a flame-ionization detector was used for gas–liquid chromatographic analyses. Microanalyses were performed at the microanalytical laboratories of the University of Kent and University College, London.

$[M(\widehat{L\,L})Cl_2]$ [M = Pd(II), Pt(II); $\widehat{L\,L}$ = $Ph_2PCH_2CH_2PPh_2$ (dpe), $Ph_2AsCH_2CH_2PPh_2$ (ape), $Ph_2AsCH_2CH_2AsPh_2$ (dae), $PhSCH_2CH_2SPh$ (dte), $MeSCH_2CH_2SMe$ (dse), or 2 $P\text{-}n\text{-}Bu_3$]. The complexes $[M(dpe)Cl_2]$ were prepared as previously described;[6] the others were prepared and characterized similarly. *trans*-$[M(P\text{-}n\text{-}Bu_3)_2Cl_2]$ compounds were prepared by literature methods.[7,8]

$[M_2(\widehat{L\,L})_2Cl_2](ClO_4)_2$. $[M(\widehat{L\,L})Cl_2]$ (1 mmol) was dissolved in dichloromethane–acetonitrile (30 cm^3, 2:1 v/v), and $AgClO_4$ (0.207 g, 1 mmol) dissolved in nitromethane (20 cm^3) was added with stirring. After the mixture had been stirred for 6 h, the white silver chloride

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

[2] P. Cossee in "The Stereochemistry of Macromolecules", Vol. 1, A. D. Ketley, Ed., Marcel Dekker, New York, 1967, Chapter 3.

[3] T. Keii, "Kinetics of Ziegler-Natta Polymerization", Chapman and Hall, London, 1972.

[4] F. R. Hartley, *Chem. Rev.*, **69**, 799 (1969).

[5] M. H. J. M. de Croon, P. F. M. T. van Nisselrooij, H. J. A. M. Kuipers, and J. W. E. Coenen, *J. Mol. Catal.*, **4**, 325 (1978).

[6] J. A. Davies, F. R. Hartley, and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1705 (1979).

[7] F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1549 (1935).

[8] S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, **6**, 1133 (1967).

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Table I. Analtyical and Physical Data on the Complexes $[M_2(\overset{\frown}{L\,L})_2Cl_2](ClO_4)_2$[a]

M	$\overset{\frown}{L\,L}$	color	% C[a]	% H[a]	% N[a]	ν(M–Cl), cm^{-1}
Pd	dpe	yellow	49.8 (48.8)	3.9 (3.8)	0.0 (0.0)	273[b]
Pd	ape	yellow	45.0 (45.7)	3.1 (3.5)	0.0 (0.0)	276[b]
Pd	dae	yellow	42.0 (42.0)	3.5 (3.4)	0.9 (0.9)[c]	278[b]
Pd	dte	orange	34.6 (34.5)	3.1 (2.9)	0.0 (0.0)	295[b]
Pt	dpe	white	40.5 (41.0)	3.6 (3.6)	1.7 (1.8)[d]	276[b]
Pt	ape	white	39.6 (40.4)	3.0 (3.1)	0.0 (0.0)	272[b]
Pt	dae	white	39.9 (38.3)	2.9 (2.7)	0.0 (0.0)	273[b]
Pt	dte	white	30.2 (29.2)	2.7 (2.5)	0.0 (0.0)	286[b]
Pd	2 *n*-Bu_3P	yellow	44.6 (44.6)	8.1 (8.4)	0.0 (0.0)	*e*
Pt	2 *n*-Bu_3P	white	39.0 (39.2)	7.3 (7.4)	0.0 (0.0)	310, 273

[a] Anal. found (calculated). [b] In addition to the band quoted, a shoulder is observed to higher wavenumber (see text). [c] Nitromethane adduct (1:1). [d] Nitromethane adduct (2:1). [e] Could not be unambiguously assigned.

Table II. Analytical and Physical Data of $[M(\overset{\frown}{L\,L})(PR_3)Cl](ClO_4)$ Complexes

complex	% C[a]	% H[a]	*B*[b]	*B'*[c]	ν(M–Cl), cm^{-1}	λ_{max} (ϵ_{mol})[d]
$[Pd(dpe)(PPh_3)Cl](ClO_4)$	58.8 (58.6)	4.4 (4.4)	363	186	313	334 (15 400)
$[Pd(dpe)(PPr_3)Cl](ClO_4)$	52.0 (52.5)	5.8 (5.7)			312	322 (13 500)
$[Pt(dpe)(PPh_3)Cl](ClO_4)$	53.4 (53.3)	4.2 (4.0)	357	138	308	277 sh (16 600)
$[Pt(dpe)(PPr_3)Cl](ClO_4)$	46.7 (47.3)	5.2 (5.1)			322	268 sh (14 700)
$[Pd(ape)(PPh_3)Cl](ClO_4)$	55.9 (56.0)	4.3 (4.3)	360	176	304	340 (13 800)
$[Pd(ape)(PPr_3)Cl](ClO_4)$	49.0 (49.9)	5.3 (5.4)			313	325 (12 800)
$[Pt(ape)(PPh_3)Cl](ClO_4)$	51.1 (51.2)	3.8 (3.8)	376	191	312	282 sh (15 800)
$[Pt(ape)(PPr_3)Cl](ClO_4)$	45.0 (45.1)	4.8 (4.9)			320	272 sh (16 600)

[a] Anal. found (calculated). [b] From $\Lambda_E = \Lambda_o - Bc^{1/2}$ with linear regression correlation >0.99; *B* in units of Ω^{-1} $L^{1/2}$ $equiv^{-1/2}$ was determined in acetonitrile solution by using concentrations in the range 10^{-2}–10^{-5} equiv L^{-1}; *B* values for a typical 1:1 electrolyte in acetonitrile lie between 300 and 450 Ω^{-1} $L^{1/2}$ $equiv^{-1/2}$.[10] [c] As in footnote *b*; *B'* was determined in nitromethane solution by using concentrations in the range 10^{-2}–10^{-5} equiv L^{-1}; *B* values for three typical 1:1 electrolytes in nitromethane have been reported between 151 and 216 Ω^{-1} $L^{1/2}$ $equiv^{-1/2}$.[11] [d] λ_{max} in nm, ϵ_{mol} in L mol^{-1} cm^{-1}; determined in dichloromethane solution.

precipitate was removed by filtration and the solution reduced to a small volume in vacuo. An oil was precipitated by the addition of diethyl ether. After separation, the oil was dissolved in dichloromethane and filtered, and a solid was precipitated by dropwise addition of diethyl ether. The complex was filtered, washed with ethanol (5 cm^3) and diethyl ether (10 cm^3), and dried in a stream of nitrogen (yields 45–65%). The same experimental method commencing with $[M(\overset{\frown}{L\,L})Cl_2]$ dissolved in dichloromethane–acetone (30 cm^3, 2:1 v/v) also allowed isolation of these products. Analytical and physical data are in Table I.

$[Pd(dpe)(S)Cl](ClO_4)$ (S = pyr, DMF). $[Pd(dpe)Cl_2]$ (0.575 g, 1 mmol) was dissolved in dichloromethane–S (30 cm^3, 2:1 v/v), and $AgClO_4$ (0.207 g; 1 mmol) dissolved in nitromethane (20 cm^3) was added with stirring. After being stirred for 6 h, the solution was taken to dryness in vacuo and then extracted with dichloromethane (three 10-cm^3 aliquots, each containing 1 drop of S). This solution was filtered and reduced to small volume in vacuo, and a solid was precipitated by dropwise addition of diethyl ether. The product was washed with ethanol (5 cm^3) and diethyl ether (10 cm^3) and dried in a stream of nitrogen. Yields: S = pyr, 0.46 g (70%); S = DMF, 0.39 g (55%). Anal. Calcd for $[Pd(dpe)(pyr)Cl](ClO_4)$: C, 51.8; H, 4.1; N, 1.9. Found: C, 51.6; H, 4.5; N, 1.9. Calcd for $[Pd(dpe)(DMF)Cl](ClO_4)$: C, 48.9; H, 4.4; N, 2.0. Found: C, 49.0; H, 4.1; N, 1.9. Molar conductances in acetone (10^{-3} M solution) are 137.5 and 82.8 Ω^{-1} cm^2 mol^{-1}, respectively, for S = pyr and DMF which are within the range expected for a 1:1 electrolyte (80–150 Ω^{-1} cm^2 mol^{-1}).[9] The pyr and DMF products each exhibited a single band at 327 nm (ε 8800) and at 346 nm (ε 7800), respectively, in their near-UV and visible spectra. No reaction occurred when a sample of the pyridine product was heated at 78 °C under a vacuum of 10^{-3} torr for 7 days, the sample being recovered unchanged (IR: 1605, 1215 cm^{-1}, due to coordinated pyridine). When $[Pd(dpe)(DMF)Cl]ClO_4$ was allowed to stand in air at room temperature for about 6 weeks, $[Pd_2(dpe)_2Cl_2](ClO_4)_2$ was formed. Anal. Calcd for $[Pd_2(dpe)_2Cl_2](ClO_4)_2$: C, 48.8; H, 3.8. Found: C, 48.8; H, 4.0. IR: palladium–chlorine stretching vibration at 273 cm^{-1} (see text).

Attempted Preparation of $[Pd(dpe)(CO)Cl](ClO_4)$. $[Pd_2(dpe)_2Cl_2](ClO_4)_2$ (0.548 g, 0.5 mmol) was dissolved in nitromethane–acetonitrile (30 cm^3, 2:1 v/v) and the solution saturated with carbon monoxide. After being stirred under an atmosphere of carbon monoxide (ca. 30 psi) for 4 h at 45 °C, the solution was reduced to small volume in vacuo and an oil precipitated by addition of diethyl ether. After separation, the oil was dissolved in dichloromethane, the solution was filtered, and a solid was precipitated by dropwise addition of diethyl ether. The complex was filtered, washed with ethanol (5 cm^3) and diethyl ether (10 cm^3), and dried in a stream of nitrogen [yield 0.53 g (97%)]. Anal. Calcd for $[Pd_2(dpe)_2Cl_2](ClO_4)_2$: C, 48.8; H, 3.8. Found: C, 48.0; H, 3.8. IR: palladium–chlorine stretching vibration at 273 cm^{-1} (see text). Other dimeric species, $[M(\overset{\frown}{L\,L})Cl]_2(ClO_4)_2$ [M = Pd(II), Pt(II); $\overset{\frown}{L\,L}$ = dpe, ape, dae, dte], were also unaffected by stirring under a carbon monoxide atmosphere.

$[Pd(dpe)(PPh_3)Cl](ClO_4)$. $[Pd_2(dpe)_2Cl_2](ClO_4)_2$ (0.548 g, 0.5 mmol) was dissolved in nitromethane–acetonitrile (30 cm^3, 2:1 v/v), and PPh_3 (0.26 g, 1 mmol) dissolved in dichloromethane (20 cm^3) was added with stirring. After being stirred for 3 h, the solution was reduced to small volume in vacuo and a white solid precipitated by dropwise addition of diethyl ether. The solid was isolated, recrystallized from nitromethane by precipitation with diethyl ether, washed with ethanol (5 cm^3) and diethyl ether (10 cm^3), and dried in vacuo [yield 0.33 g (72%)]. Analytical and physical data are given in Table II and $^{31}P\{^1H\}$ NMR spectra in Table III.

$[M(\overset{\frown}{L\,L})(PR_3)Cl](ClO_4)$ ($\overset{\frown}{L\,L}$ = dpe, ape; M = Pt, R = Ph, *n*-Pr; M = Pd, R = *n*-Pr). $[M(\overset{\frown}{L\,L})Cl_2]$ (0.001 mol) was dissolved in dichloromethane–acetonitrile (30 mL, 2:1 v/v), and PR_3 (0.001 mol) dissolved in dichloromethane (20 cm^3) was added. $AgClO_4$ (0.207 g, 0.001 mol) dissolved in nitromethane (20 cm^3) was added with stirring. After being stirred for 6 h, the solution was filtered and reduced to a small volume in vacuo, and a solid was precipitated with diethyl ether. The product was filtered, washed with ethanol (5 cm^3) and diethyl ether (10 cm^3), and dried in vacuo at 78 °C (yields 65–80%). Analytical and physical data are given in Table II and $^{31}P\{^1H\}$ NMR spectra are recorded in Table III.

Hydrogenation Reactions. The ability of $[Pd(dpe)(DMF)Cl](ClO_4)$ (**1**), $[Pd(dpe)(pyr)Cl](ClO_4)$ (**2**), and $[Pd(dpe)Cl_2]$ (**3**) to expedite the hydrogenation of olefins was examined as follows. Solutions of **1** (2 mmol in 50 cm^3 of DMF), **2** (2 mmol in 50 cm^3 of dichloromethane–pyridine, 1:1 v/v), and **3** (2 mmol in 50 cm^3 of dichloromethane) were saturated with hydrogen, and freshly distilled styrene (1.04 g, 10 mmol) was added. The solutions were vigorously stirred at room temperature under an atmosphere of hydrogen. The hydrogen

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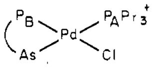
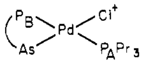
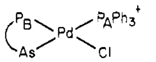
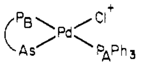
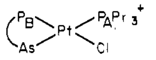
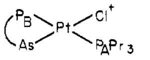
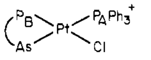
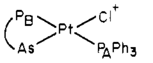
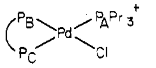
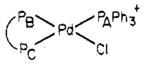
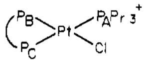
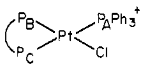
(9) W. J. Geary, *Coord. Chem. Rev.*, 7, 81 (1971).

(10) This range was determined by us, using a series of known 1:1 electrolytes.

(11) R. G. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

Table III. $^{31}P\{^1H\}$ NMR Spectral Data of $[M(\widehat{LL})(PR_3)Cl]^+$ Complexes

no.	complex	$\delta(P_A)^a$	$\delta(P_B)^a$	$\delta(P_C)^a$	$J(P_AP_C)^b$	$J(P_AP_B)^b$	$J(P_BP_C)$	$J(^{195}PtP_A)^b$	$J(^{195}PtP_B)^b$	$J(^{195}PtP_C)^b$
1		−13.4	−64.7			15				
2		−12.5	−62.2			422				
3		−24.6	−67.2			11				
4		−21.0	−71.6			367				
5		−7.2	−44.2			15		2651	3544	
6		−7.5	−55.5			377		c	c	
7		−21.3	−47.7			14		2845	4225	
8		−20.8	−55.9			397		2313	2386	
9		−12.1	−44.0	−41.9	408	21	11			
10		−8.8	−33.9	−33.0	415	21	7			
11		−7.8	−42.6	−52.2	370	17	6	2249	3546	2212
12		−21.9	−44.6	−52.1	387	14	7	2393	3533	2421

[a] Chemical shifts in parts per million downfield of H_3PO_4. [b] Coupling constants in hertz. [c] Not determined due to there being an insufficient amount of this, the less abundant, isomer in solution

pressure was maintained at 1 atm by using a constant-pressure device. After 72 h the solutions were analyzed by gas–liquid chromatography using a 10% SE-30 on siliconized Celite (85–100 mesh) column at 112 °C with a carrier gas (nitrogen) pressure of 6.95 psi. Comparison with quantitative amounts of standards demonstrated that **1** allowed ca. 10% conversion of styrene to ethylbenzene while **2** and **3** allowed quantitative recovery of styrene. During the course of these reactions no decomposition of the complexes **1**, **2**, or **3** to palladium metal was observed.

Results and Discussion

A systematic study of the value of reaction 1 for the preparation of monosolvent-substituted complexes was made by dissolving $[Pd(dpe)Cl_2]$ (dpe = $Ph_2PCH_2CH_2PPh_2$) in a 1:1 mixture of dichloromethane and the solvent under study and treating this solution with 1 equiv of a silver(I) salt (Y = perchlorate or tetrafluoroborate) at room temperature. When the solvent (S) was pyridine (pyr) reaction 1 led to the isolation

$$[Pd(dpe)Cl_2] + AgY \xrightarrow[\text{room temp}]{1:1\ CH_2Cl_2/S} [Pd(dpe)(S)Cl](Y) + AgCl\downarrow \quad (1)$$

of an air-stable complex, $[Pd(dpe)(pyr)Cl](ClO_4)$ (see Experimental Section). When the solvent was dimethylformamide (DMF), a yellow solid was isolated which exhibited a band at 1630 cm^{-1} in its infrared spectrum, consistent with DMF coordination through oxygen.[12] Microanalyses and molar conductivity in acetone were consistent with the formulation $[Pd(dpe)(DMF)Cl](ClO_4)$. This complex was significantly less stable than both the pyridine complex and the corresponding oxygen-coordinated Me_2SO complex $[Pd(dpe)(Me_2SO)Cl](ClO_4)$ described previously[6] in that on being allowed to stand at room temperature and atmospheric pressure in air, it liberated DMF and yielded the chloride-bridged dimer (reaction 2). In contrast, the pyridine complex

$$2[Pd(dpe)(DMF)Cl](ClO_4) \rightarrow [Pd_2(dpe)_2Cl_2](ClO_4)_2 + 2DMF \quad (2)$$

was unaltered after heating in vacuo (10^{-3} torr) at 78 °C for 7 days, while these same conditions were necessary to remove Me_2SO from $[Pd(dpe)(Me_2SO)Cl](ClO_4)$.[6] Thus we conclude that the ability of these three ligands to bond to palladium(II) is pyridine > oxygen-coordinated Me_2SO > DMF.

Attempts to repeat reaction 1 with a range of other solvents, including acetone, methanol, acetonitrile, tetrahydrofuran, and benzene, led exclusively to the formation of dimeric complexes (reaction 3). Thus we conclude that the chloride of a "Pd-

$$2[Pd(dpe)Cl_2] + 2AgY \xrightarrow[\text{room temp}]{1:1\ CH_2Cl_2/\text{solvent}} [Pd_2(dpe)_2Cl_2](Y)_2 + 2AgCl\downarrow \quad (3)$$

$(dpe)Cl^+$" moiety is a better donor than any of these weak donor solvents. In order to determine the extent to which the dimerization was a function of the presence of the dpe ligand, we replaced this ligand by a range of other bidentate ligands (ape, dae, and dte). In the case of both palladium(II) and platinum(II), dimer formation analogous to reaction 3 occurred in every case. Since the cis geometry resulting from the use of these ligands may have been responsible for the failure to isolate a monosolvent-substituted product, trans complexes of

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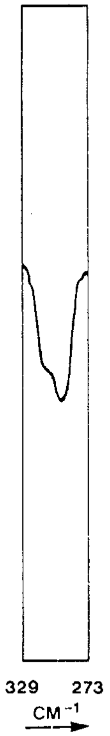

Figure 1. Infrared spectrum of [Pd(dte)Cl_2] in the palladium–chloride stretching region.

both palladium(II) and platinum(II) with *n*-Bu_3P were treated in a similar manner; however, in each case dimerization (as in reaction 4) took place in preference to monosolvent-substituted complex formation.

$$2\textit{trans}\text{-}[\mathrm{M}(n\text{-}\mathrm{Bu_3P})_2\mathrm{Cl_2}] + 2\mathrm{AgClO_4} \xrightarrow[\text{room temp}]{\text{1:1 CH}_2\text{Cl}_2\text{/MeCN}} [\mathrm{M_2}(n\text{-}\mathrm{Bu_3P})_4\mathrm{Cl_2}](\mathrm{ClO_4})_2 + 2\mathrm{AgCl}\downarrow \quad (4)$$

The infrared spectra of the chloride-bridged cationic complexes require comment. While the spectra of the complexes of the monodentate phosphine *n*-Bu_3P show the two bands in the metal–chlorine stretching region described previously,[13] the complexes of the bidentate ligands show the lower wavenumber band as a sharp peak, but the higher wavenumber band is only observed as a shoulder on the side of this (Figure 1). This is in general agreement with the observations of Clark et al., although these authors reported only a single broad band.[14] In view of the errors associated with assigning precise wavenumbers to such shoulders, we have not recorded their positions in Table I.

Palladium(II) phosphine halide complexes are generally ineffective as hydrogenation catalysts,[15] although in the presence of added $SnCl_2$ or $GeCl_2$, [Pd(PPh_3)$_2$$Cl_2$] does catalyze the hydrogenation of polyunsaturated esters to monoolefins at hydrogen pressures above 13.6 atm.[16] Also, it has been reported that [Pd(dpe)Cl_2] catalyzes the reduction of butadiene largely to monoolefin by using an initial pressure of about 6.8 atm.[17] Since [Pd(dpe)Cl_2] is unable to catalyze the hydrogenation of a monoolefin such as styrene at atmospheric pressure and room temperature (see Experimental Section), we examined the effectiveness of [Pd(dpe)(pyr)Cl](ClO_4) and [Pd(dpe)(DMF)Cl](ClO_4) as catalysts. While the pyridine complex was totally inactive, the DMF complex did promote the very slow reduction of styrene to ethylbenzene under these very mild conditions, achieving a turnover of one-half in a period of 72 h (see Experimental Section). This result is consistent with the greater lability of DMF than of pyridine, and while there are many better catalysts for this reduction, the fact that a cationic palladium(II) phosphine complex can promote the hydrogenation of styrene under ambient conditions does support our thesis that the incorporation of weak donor ligands into a metal complex can promote substrate activation. This is particularly well demonstrated in the present case because the replacement of a good donor ligand such as a halide ion by the neutral weak donor ligand DMF results in the formation of cationic palladium(II) complexes, which are known to react more reluctantly with olefins than neutral palladium(II) complexes.[18,19]

It has previously been shown that the cationic palladium(II) complex [Pd_2(dpe)$_2$$Cl_2$]($BF_4$)$_2$ does not undergo bridge cleavage with carbon monoxide even under high pressure (30 atm) at elevated temperature (120 °C).[20] Since cationic carbonyl complexes are of intrinsic interest because of their relation to cationic olefin and acetylene complexes which may be regarded as behaving as metal-induced carbonium ions,[21,22] we attempted to prepare [Pd(dpe)(CO)Cl]Y by removing a chloride ligand from [Pd(dpe)Cl_2] in acetonitrile solution in the presence of carbon monoxide. With pressures of carbon monoxide of up to 2 atm no carbonyl complex could be obtained; instead, the familiar chloride-bridged dimer [Pd_2(dpe)$_2$$Cl_2$]$Y_2$ was obtained. We conclude that it is the cationic nature of [Pd(dpe)(CO)Cl]$^+$, together with the fact that carbon monoxide is trans to a phosphine ligand, which results in insufficient π back-donation from metal to carbon monoxide to form a metal–carbonyl bond that is sufficiently strong to withstand competition from "Pd(dpe)Cl$^+$" moieties that leads to dimer formation. In agreement with this suggestion, we understand that Shaw has recently synthesized cationic *trans*-carbonylphosphine complexes of palladium and platinum and has found that while stable at low temperature they rearrange to the cis isomers on warming to ambient temperature.[23] Such rearrangement is not possible in the present system.

When chloride abstraction from [M($\widehat{L\,L}$)Cl_2], where M = Pt or Pd and $\widehat{L\,L}$ is a range of bidentate ligands, is effected in acetonitrile solution in the presence of a tertiary phosphine ligand, the cationic [M($\widehat{L\,L}$)(PR_3)Cl]$^+$ complexes are formed (see Experimental Section). Analytical and physical data (Table II) confirmed the nature of these products. The $^{31}P\{^1H\}$ NMR spectra (Table III) of the [Pd(dpe)(PR_3)Cl]$^+$ complexes were 12-line spectra typical of AMX-type spin systems. There was retention of phosphorus–phosphorus coupling indicating that no phosphine dissociation was taking place and hence that no dissociation/dimerization analogous to reaction 2 was occurring. The [Pt(dpe)(PR_3)Cl]$^+$ complexes similarly showed the expected 36-line spectra with no loss of either phosphorus–phosphorus or platinum–phosphorus coupling, indicating that the integrity of the complex was maintained in $CDCl_3$/CD_2Cl_2 solution. The availability of complexes of the unsymmetrical bidentate ligand $Ph_2AsCH_2CH_2PPh_2$ gave us the opportunity to examine whether the incoming monodentate phosphine ligand would effect replacement of the chloride

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Table IV. Proportion (%) of the Two Isomers Present in the Product of Reaction 5

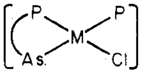
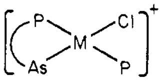
M	R		
Pd	Pr	86	14
Pd	Ph	67	33
Pt	Pr	90	10
Pt	Ph	88	12

Table V. Conductivity Data for $[M(\widehat{L\ L})Cl_2]$ in Some Donor Solvents

	MeCN		DMF		Me_2SO	
complex	Λ_M[a]	p, %[b]	Λ_M[a]	p, %[b]	Λ_M[a]	p, %[b]
$[Pd(dpe)Cl_2]$	7.4	5.1	5.6	7.2	9.6	29.5
$[Pt(dpe)Cl_2]$	5.2	3.6	5.2	6.7	4.6	14.1
$[Pd(ape)Cl_2]$	1.6	1.1	3.9	5.0	4.2	12.9
$[Pt(ape)Cl_2]$	1.0	0.7	0.8	1.0	0.4	1.2
$[Pd(dae)Cl_2]$	0.7	0.5	2.8	3.6	1.3	4.0
$[Pt(dae)Cl_2]$	0.9	0.6	1.2	1.5	0.5	1.5
$[Pd(dse)Cl_2]$	0.8	0.5	0.6	0.8	0.2	0.6
$[Pt(dse)Cl_2]$	1.4	1.0	1.6	2.1	2.5	0.8
$[Pd(dte)Cl_2]$	3.5	2.4	15.0	19.3	6.2	19.1
$[Pd(en)Cl_2]$	0.4	0.3	1.2	1.5	2.6	8.0
$[Pd(cod)Cl_2]$[c]	0.5	0.3	3.8	4.9	0.4	1.2
acceptable range of Λ_M values for a 1:1 electrolyte (mean)	92–199 (145)		65–90 (77.5)		23–42 (32.5)	

[a] Molar conductivities (Ω^{-1} cm^2 mol^{-1}) were measured at 20 °C as 10^{-3} M solutions in the appropriate solvent, after equilibration at 35 °C (water bath) for 6 h. [b] p is the value of Λ_M expressed as a percentage of the mean value for a 1:1 electrolyte in the appropriate solvent [i.e., $p = (\Lambda_M/(\text{mean value for a 1:1 electrolyte}) \times 100]$. [c] cod = 1,5-cyclooctadiene.

moiety trans to phosphorus or trans to arsenic. The $^{31}P\{^1H\}$ NMR spectra (Table III) of the products of reaction 5 showed

$$[M(Ph_2AsCH_2CH_2PPh_2)Cl_2] + AgClO_4 + PR_3 \xrightarrow{CH_2Cl_2/MeCN/MeNO_2\ (4:1:2)} [M(Ph_2AsCH_2CH_2PPh_2)(PR_3)Cl](ClO_4) + AgCl\downarrow \quad (5)$$

that both isomers were present. The spectra were assigned in accordance with previous results for related palladium(II) and platinum(II) complexes.[24] The less abundant isomer formed in eq 5 had a 4-line AX-type spectrum with a large J(P–P) value (ca. 400 Hz), indicating it was the isomer with phosphine substituted trans to the phosphorus of ape. The more abundant isomer had an AX-type spectrum with a small J(P–P) value (ca. 15 Hz), indicating that the phosphine was coordinated trans to arsenic (Table IV). This result is clearly the consequence of a fine balance of opposing factors: (i) entropy will favor a mixture of isomers; (ii) the trans effect of tertiary phosphines is usually greater than that of tertiary arsines,[25] favoring the incoming phosphine being trans to P; (iii) the site cis to $AsPh_2$ will be less sterically hindered than that cis to the more bulky PPh_2,[26] favoring the incoming phosphine being trans to P; (iv) competition for metal π-electron density between two mutually trans phosphines will favor the incoming phosphine being trans to the weaker π-acceptor As group.

In all the work described so far in this paper, silver(I) was used to remove a chloride ligand to provide a vacant site at the metal center for solvent coordination. It was of interest to determine whether solvents such as DMF were sufficiently powerful donors to displace some of the chloride without the assistance of silver(I) (reaction 6). We investigated this using

$$[M(\widehat{L\ L})Cl_2] + S \rightleftharpoons [M(\widehat{L\ L})S(Cl)]^+ + Cl^- \quad (6)$$

the molar conductivity to monitor the reaction. The results (Table V) show clearly that the position of equilibrium 6 lies well to the left for acetonitrile but rather less to the left for DMF and Me_2SO, confirming our earlier conclusion that the ability of these three ligands to bond to palladium(II) and platinum(II) is $Me_2SO > DMF \gg MeCN$. Of the bidentate ligands, dte appears to promote chloride substitution the most followed by dpe, whereas ethylenediamine is rather ineffective in this role.

Acknowledgment. Thanks are expressed to Dr. W. P. Griffith for helpful discussion and to Drs. W. McFarlane and M. Murray for the $^{31}P\{^1H\}$ NMR spectra reported in Table III.

Registry No. **1**, 73558-12-0; **2**, 73558-14-2; **3**, 19978-61-1; $[Pd_2(dpe)_2Cl_2](ClO_4)_2$, 72476-84-7; $[Pd_2(ape)_2Cl_2](ClO_4)_2$, 73558-16-4; $[Pd_2(dae)_2Cl_2](ClO_4)_2$, 73558-18-6; $[Pd_2(dte)_2Cl_2](ClO_4)_2$, 73558-20-0; $[Pt_2(dpe)_2Cl_2](ClO_4)_2$, 73558-22-2; $[Pt_2(ape)_2Cl_2](ClO_4)_2$, 73558-24-4; $[Pt_2(dae)_2Cl_2](ClO_4)_2$, 73558-26-6; $[Pt_2(dte)_2Cl_2](ClO_4)_2$, 73558-28-8; $[Pd_2(n\text{-}Bu_3P)_4Cl_2](ClO_4)_2$, 73558-30-2; $[Pt_2(n\text{-}Bu_3P)_4Cl_2](ClO_4)_2$, 73558-31-3; $Pd(ape)Cl_2$, 73558-32-4; $Pd(dae)Cl_2$, 14647-19-9; $Pd(dte)Cl_2$, 21215-89-4; $Pt(dpe)Cl_2$, 14647-25-7; $Pt(ape)Cl_2$, 73558-32-4; $Pt(dae)Cl_2$, 14647-20-2; $Pt(dte)Cl_2$, 22455-18-1; *trans*-$Pd(n\text{-}Bu_3P)_2Cl_2$, 17523-47-6; *trans*-$Pt(n\text{-}Bu_3P)_2Cl_2$, 15391-01-2; $[Pd(dpe)(PPh_3)Cl](ClO_4)$, 73558-34-6; $[Pd(dpe)(PPr_3)Cl](ClO_4)$, 73558-36-8; $[Pt(dpe)(PPh_3)Cl](ClO_4)$, 73558-38-0; $[Pt(dpe)(PPr_3)Cl](ClO_4)$, 73558-40-4; $[Pd(ape)(PPh_3)Cl](ClO_4)$, 73558-42-6; $[Pd(ape)(PPr_3)Cl](ClO_4)$, 73558-44-8; $[Pt(ape)(PPh_3)Cl](ClO_4)$, 73558-46-0; $[Pt(ape)(PPr_3)Cl](ClO_4)$, 73558-48-2; $[Pd(ape)(PPr_3)Cl]^+$ (isomer 1), 73609-80-0; $[Pd(ape)(PPr_3)Cl]^+$ (isomer 2), 73609-81-1; $[Pd(ape)(PPh_3)Cl]^+$ (isomer 3), 73609-82-2; $[Pd(ape)(PPh_3)Cl]^+$ (isomer 4), 73609-83-3; $[Pt(ape)(PPr_3)Cl]^+$ (isomer 5), 73609-84-4; $[Pt(ape)(PPr_3)Cl]^+$ (isomer 6), 73609-85-5; $[Pt(ape)(PPh_3)Cl]^+$ (isomer 7), 73609-86-6; $[Pt(ape)(PPh_3)Cl]^+$ (isomer 8), 73609-87-7; $[Pd(dpe)(PPr_3)Cl]^+$, 73558-35-7; $[Pd(dpe)(PPh_3)Cl]^+$, 73558-33-5; $[Pt(dpe)(PPr_3)Cl]^+$, 73558-39-1; $[Pt(dpe)(PPh_3)Cl]^+$, 73558-37-9; $Pd(dse)Cl_2$, 15282-04-9; $Pt(dse)Cl_2$, 15407-56-4; $Pd(en)Cl_2$, 15020-99-2; $Pd(cod)Cl_2$, 12107-56-1; styrene, 100-42-5.

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