Hard Ligands as Donors to Soft Metals. Part 3.[1] Cationic Bis(solvent) Complexes of Palladium(II); Cations for Catalysis

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Treatment of [Pd(dppe)Cl_2], dppe = $Ph_2PCH_2CH_2PPh_2$, with 2 equivalents of a silver(I) salt in the presence of a solvent ligand (solvent) leads to the formation of [Pd(dppe)(solvent)$_2$]Y_2 where Y = ClO_4 or BF_4. In this way stable complexes with solvent = pyridine, *O*-bonded dimethyl sulphoxide, dimethylformamide, benzonitrile, *o*-toluonitrile, acetone, or water as well as (solvent)$_2$ = 1,6-dicyanohexane or *o*-phthalonitrile have been isolated and characterised. Complexes with solvent = methanol, ethanol, acetonitrile, or tetrahydrofuran are stable in solution; on attempted isolation the ethanol complex deposits palladium metal, the methanol and tetrahydrofuran perchlorate complexes yield the bis(perchlorato)-complexes [Pd(dppe)($OClO_3$)$_2$], and the acetonitrile complex yields mainly [Pd(dppe)(NCMe)$_2$][ClO_4]$_2$ with a small amount of perchlorate-co-ordinated complex. The co-ordinated perchlorate ligands are readily displaced in solution by any of the solvent ligands; the bis(acetone) complex is very sensitive to moisture yielding [Pd(dppe)(OH_2)$_2$][ClO_4]$_2$ on exposure to air. Attempts to displace acetone from [Pd(dppe)($OCMe_2$)$_2$]$^{2+}$ and perchlorate from [Pd(dppe)($OClO_3$)$_2$] by carbon monoxide failed. The solvent molecules dichloromethane and benzene do not form palladium(II) complexes of the present type; treatment of [Pd(dppe)Cl_2] with 2 equivalents of silver(I) perchlorate in dichloromethane–benzene yields [Pd(dppe)($OClO_3$)$_2$]. Preliminary investigation of the catalytic abilities of these palladium(II) complexes has shown that [Pd(dppe)($OCMe_2$)$_2$][ClO_4]$_2$ catalyses the hydrogenation of styrene to ethylbenzene at atmospheric pressure and 30 °C, which is remarkably high activity for palladium(II).

TRANSITION-METAL complexes containing weakly bonded ligands have been widely implicated in catalytic cycles. However, relatively few such complexes have been isolated and characterised and thus relatively little is known about the factors that influence their stability. Furthermore, their very existence is often more a result of speculation than direct experimental observation. Accordingly, in the present paper we report the isolation, characterisation, and properties of a series of palladium(II) complexes [Pd(dppe)(solvent)$_2$]$^{2+}$ (dppe = $Ph_2PCH_2CH_2PPh_2$) in which solvent is a weak donor ligand such as water, alcohol, acetone, and nitrile. This work is an extension of our previous work with weak donor ligands (solvent) which led to the isolation and characterisation of [Pd(dien)(solvent)]$^{2+}$ and [M(L–L)(solvent)Cl]$^+$ where dien = diethylenetriamine, M = palladium(II) or platinum(II), and L–L = a bidentate ligand with two methylene groups between the donor atoms.[1-3] The range of solvent ligands for which a complex of the type [M(L–L)(solvent)Cl]$^+$ could be isolated was fairly limited since very weak donor ligands were eliminated and the chloride-bridged dimeric complexes [M_2(L–L)$_2$$Cl_2$]$^{2+}$ formed.

Characterisation of [Pd(dppe)(solvent)$_2$]Y_2 complexes

Solvent	Y	Microanalysis (%) [a] C	H	N	Conductance,[b] B/ohm^{-1} l$^{\frac{1}{2}}$ equivalent$^{-\frac{1}{2}}$	Electronic spectrum [c] $\lambda_{max.}$/nm
py	BF_4	50.9 (51.7)	4.2 (4.1)	3.2 (3.3)	338	307 (sh)
dmf	ClO_4	45.1 (45.2)	4.7 (4.5)	3.2 (3.3)	346	344
NCPh	ClO_4	53.4 (52.8)	4.0 (3.8)	3.1 (3.1)	338	307 (sh)
NCC_6H_4Me-*o*	ClO_4	53.8 (53.8)	4.2 (4.1)	2.9 (3.0)	355	310 (sh)
$\frac{1}{2}NCC_6H_4CN$-*o*	ClO_4	49.1 (49.1)	3.2 (3.4)	3.3 (3.4)	334	351
$\frac{1}{2}NC(CH_2)_6CN$	ClO_4	47.9 (48.6)	4.2 (4.3)	3.1 (3.3)	463	343
OH_2 [d]	ClO_4	41.5 (42.2)	3.6 (3.8)	0.0 (0.0)	185 [e]	351

[a] Calculated values are given in parentheses. [b] $B = (\Lambda_0 - \Lambda_e)/c^{\frac{1}{2}}$ (Λ_0 = extrapolated equivalent conductivity at zero concentration, Λ_e = observed equivalent conductivity at concentration *c*), obtained in nitromethane over the concentration range 10^{-5}—10^{-2} equivalent l^{-1}. [c] In dichloroethane solution. [d] Cl 9.2 (9.6); P 8.6 (8.4%). [e] Molar conductance in 10^{-3} mol dm^{-3} nitromethane solution. The molar conductances of 2 : 1 electrolytes typically lie between 115 and 250 with an average value of 160 ohm^{-1} cm^2 mol^{-1} in these solutions.[15]

EXPERIMENTAL

Methanol was dried by refluxing over magnesium turnings (5 g l^{-1}) for 30 min and then distilled under nitrogen and stored over molecular sieves. Ethanol was dried by an azeotropic distillation with benzene (150 g 95% EtOH and 74 g benzene) under nitrogen and stored over molecular sieves. Other solvents and silver salts were dried as described previously.[1] Spectra, conductances, and analyses were determined as before.[1] The complex [Pd(dppe)Cl_2] was prepared by the literature method.[1] Microanalyses, conductances, and electronic spectra of [Pd(dppe)(solvent)$_2$]Y_2 complexes where Y = ClO_4 or BF_4 are given in the Table.

[Pd(dppe)(py)$_2$][BF_4]$_2$.—The complex [Pd(dppe)Cl_2] (0.575 g, 0.001 mol) was dissolved in dichloromethane–pyridine (py) (2 : 1 v/v; 30 cm^3) and Ag[BF_4] (0.233 g, 0.002 mol) dissolved in nitromethane (20 cm^3) added with stirring. After stirring for 3 h the solution was taken to dryness *in vacuo* and extracted with nitromethane (5 × 10-cm^3 aliquots). The extracts were reduced to small volume and a white solid precipitated by dropwise addition of diethyl ether. The product was recrystallised from nitromethane by precipitation with diethyl ether and dried *in vacuo* at room temperature. Yield 0.32 g (35%).

$[Pd(dppe)(dmf)_2][ClO_4]_2$.—The complex $[Pd(dppe)Cl_2]$ (0.575 g, 0.001 mol) was dissolved in dichloromethane (25 cm^3) and $Ag[ClO_4]$ (0.414 g, 0.002 mol) dissolved in dimethylformamide (dmf) (25 cm^3) added with stirring. After stirring for 2 h the precipitate was filtered off and the solution was reduced to small volume *in vacuo*. A cream solid precipitated by dropwise addition of diethyl ether. The solid was filtered off, washed with diethyl ether (10 cm^3), and dried *in vacuo* at room temperature. Yield 0.55 g (65%).

$[Pd(dppe)(NCR)_2][ClO_4]_2$ ($R = C_6H_5$ *or* C_6H_4Me-*o*).—The complex $[Pd(dppe)Cl_2]$ (0.575 g, 0.001 mol) was dissolved in dichloromethane–RCN (7 : 1 v/v, 40 cm^3) and $Ag[ClO_4]$ (0.414 g, 0.002 mol) dissolved in nitromethane (25 cm^3) added with stirring. After stirring for 3 h the solution was filtered and reduced to small volume *in vacuo*. A yellow solid was precipitated by dropwise addition of diethyl ether. The product was filtered off, washed with diethyl ether (10 cm^3), and dried *in vacuo* at room temperature. Yield 45—55%.

$[Pd(dppe)(NCZCN)][ClO_4]_2$ [$Z = C_6H_4$ *or* $(CH_2)_6$].—The complex $[Pd(dppe)(HOMe)_2][ClO_4]_2$ (0.001 mol) was generated *in situ* as described below and a solution of NCZCN (0.001 mol) in methanol (20 cm^3) added dropwise with vigorous stirring. After 3 h the solution was concentrated *in vacuo* until precipitation occurred. Addition of diethyl ether completed the precipitation and the product was filtered off, washed with diethyl ether, and dried *in vacuo*. Yields 55—60%.

$[Pd(dppe)(OCMe_2)_2][ClO_4]_2$.—**CAUTION:** This complex is explosive (see text). The complex $[Pd(dppe)Cl_2]$ (0.575 g, 0.001 mol) was dissolved in dichloromethane–acetone (1 : 1 v/v, 50 cm^3) and $Ag[ClO_4]$ (0.414 g, 0.002 mol) dissolved in benzene (40 cm^3) added with stirring. After stirring for 3 h the solution was reduced in volume *in vacuo* until precipitation of a yellow solid started and then precipitation was completed by dropwise addition of diethyl ether. The product was filtered off and dried briefly *in vacuo* at room temperature. Yield 0.42 g (51%). It reacted rapidly with moist air to yield $[Pd(dppe)(OH_2)_2][ClO_4]_2$, see below.

$[Pd(dppe)(OClO_3)_2]$.—**CAUTION:** This complex is explosive (see text). The complex $[Pd(dppe)Cl_2]$ (0.575 g, 0.001 mol) was dissolved in dichloromethane (50 cm^3) and $Ag[ClO_4]$ (0.414 g, 0.002 mol) dissolved in benzene (50 cm^3) added with stirring. After stirring for 3 h the solution was filtered and reduced in volume *in vacuo* until precipitation occurred. The solid was filtered off, washed with diethyl ether (10 cm^3), and dried *in vacuo*. Yield 0.46 g (65%).

$[Pd(dppe)(OH_2)_2][ClO_4]_2$.—This complex was formed (*i*) on exposure of $[Pd(dppe)(OCMe_2)][ClO_4]_2$ to moist air, yield 100% (Found: C, 41.5; H, 3.6; Cl, 9.2; N, 0.0; P, 8.6. $C_{26}H_{28}Cl_2O_{10}P_2Pd$ requires C, 42.2; H, 3.8; Cl, 9.6; N, 0.0; P, 8.4%), or (*ii*) on treating $[Pd(dppe)(OClO_3)_2]$ with moist acetone, yield 100% (Found: C, 43.8; H, 3.8; N, 0.0%).

Attempted Preparations.—$[Pd(dppe)(solvent)_2][ClO_4]_2$ (*solvent = methanol or tetrahydrofuran*). The complex $[Pd(dppe)Cl_2]$ (0.575 g, 0.001 mol) was dissolved in a mixture of dichloromethane and the solvent (1 : 1 v/v, 50 cm^3) and $Ag[ClO_4]$ (0.414 g, 0.002 mol) dissolved in benzene (50 cm^3) added with stirring. After stirring for 3 h the solution was filtered and reduced in volume *in vacuo* until precipitation of an oil occurred. Addition of diethyl ether or light petroleum (b.p. 60—80 °C) caused further precipitation of the oil. All attempts to cause solidification by recrystallisation of the oil were unsuccessful. Treating the oil extensively *in vacuo* caused solidification. The product was shown to be identical to $[Pd(dppe)(OClO_3)_2]$ described above.

$[Pd(dppe)(HOEt)_2][ClO_4]_2$. The complex $[Pd(dppe)Cl_2]$ (0.575 g, 0.001 mol) was dissolved in dichloromethane–ethanol (1 : 1 v/v, 50 cm^3) and $Ag[ClO_4]$ (0.414 g, 0.002 mol) dissolved in benzene (50 cm^3) added with stirring. After stirring for 3 h the solution was filtered and reduced in volume *in vacuo*. At this stage, or during attempted precipitation with diethyl ether or light petroleum, decomposition occurred with precipitation of palladium metal.

$[Pd(dppe)(NCMe)_2][ClO_4]_2$. Using the same method as described for $[Pd(dppe)(NCR)_2][ClO_4]_2$ above, precipitation with diethyl ether or light petroleum always resulted in the formation of a yellow oil which required extensive stirring *in vacuo* for solidification. The product was shown to be a mixture of $[Pd(dppe)(OClO_3)_2]$ and $[Pd(dppe)(NCMe)_2][ClO_4]_2$ (see text).

$[Pd(dppe)(CO)_2][ClO_4]_2$. Solutions of $[Pd(dppe)Cl_2]$ were prepared in (1) dichloromethane (50 cm^3), (2) dichloromethane–acetone (1 : 1 v/v, 50 cm^3), and (3) dichloromethane–methanol (1 : 1 v/v, 50 cm^3) and each was saturated with carbon monoxide for 30 min. A solution of $Ag[ClO_4]$ (0.414 g, 0.001 mol) in benzene (50 cm^3) saturated with carbon monoxide was added to each and the solution purged with carbon monoxide for 30 min. The solutions were then filtered and the solid products obtained were identical to those in the absence of carbon monoxide, described above.

RESULTS AND DISCUSSION

When a solution of $[Pd(dppe)Cl_2]$ is treated with 2 equivalents of a silver(I) salt in the presence of a weak solvent ligand the two chloride ligands are abstracted and the cationic bis(solvent) complex $[Pd(dppe)(solvent)_2]Y_2$, where $Y = ClO_4$ or BF_4, is formed [reaction (1)]. In this way complexes with solvent = pyridine, dimethyl sulphoxide (dmso), dmf, benzonitrile, *o*-toluonitrile,

$$[Pd(dppe)Cl_2] + 2AgY \xrightarrow[\text{excess of solvent}]{\text{room temperature}} [Pd(dppe)(solvent)_2]Y_2 + 2AgCl\downarrow \quad (1)$$

acetone, or water as well as $(solvent)_2$ = 1,6-dicyanohexane or *o*-phthalonitrile have been isolated and characterised (Table). Complexes with solvent = acetonitrile, methanol, ethanol, or tetrahydrofuran have been identified in solution. No complexes with solvent = benzene or dichloromethane could be detected, attempts to prepare them leading to the isolation of $[Pd(dppe)(OClO_3)_2]$ with two co-ordinated perchlorate ligands. We could not displace either acetone from $[Pd(dppe)(OCMe_2)]^{2+}$ or perchlorate from $[Pd(dppe)(OClO_3)_2]$ by use of carbon monoxide.

The complex $[Pd(dppe)(py)_2][BF_4]_2$ prepared by reaction (1) showed i.r. absorption bands at 1 605 and 1 220 cm^{-1} consistent with the presence of co-ordinated pyridine.[4] Although two bands around 1 605 cm^{-1} might be expected for *cis* co-ordination of two pyridine ligands only one sharp band was observed. This is consistent with earlier reports that the high-frequency spectrum of pyridine is little changed on co-ordination.[4] Analytical and molar conductance data confirmed the proposed formulation as $[Pd(dppe)(py)_2][BF_4]_2$. Throughout this work we have used Feltham and Hayter's method [5] of determining the slope of a plot of $(\Lambda_0 - \Lambda_e)$ against $c^{\frac{1}{2}}$ in order to determine electrolyte type. For nitromethane, Feltham and Hayter studied two 1 : 1 electrolytes that had slopes of 183 and 216 and three 2 : 1 electrolytes that had slopes of 420, 465, and 510 ohm^{-1} $l^{\frac{1}{2}}$ $equivalent^{-\frac{1}{2}}$. The results reported here, and others we have obtained,[6] would suggest that 2 : 1 electrolytes in nitromethane may give slopes down to about 323 ohm^{-1} $l^{\frac{1}{2}}$ $equivalent^{-\frac{1}{2}}$. We therefore take the range of slopes for 2 : 1 electrolytes in nitromethane to be between 320 and 510 ohm^{-1} $l^{\frac{1}{2}}$ $equivalent^{-\frac{1}{2}}$.

The complex $[Pd(dppe)(dmf)_2][ClO_4]_2$ shows a very strong relatively broad absorption at 1 630 cm^{-1}, which is sufficiently broad to be made up of two closely spaced absorptions, consistent with direct co-ordination of two dmf ligands to palladium through their carbonyl oxygen atoms.[7] Single absorptions at 1 110br [ν_3-(ClO_4)] and 620 cm^{-1} [$\nu_4(ClO_4)$] indicate that there is no interaction between the perchlorate anion and palladium.[8-12] Microanalysis and conductivity data (Table) confirm the proposed formulation. During thermal analysis the complex exploded after a 10% weight loss corresponding to the loss of 58% of the dmf ligand. It is believed that on heating loss of dmf resulted in the co-ordination of a perchlorate ion with consequent sensitisation (see below).

The complex $[Pd(dppe)(NCPh)_2][ClO_4]_2$ shows two absorptions in the $\nu(C{\equiv}N)$ region at 2 295 and 2 286 cm^{-1} consistent with its formulation as a *cis*-bis(benzonitrile) complex. These bands correspond to increases in $\nu(C{\equiv}N)$ consequent upon co-ordination of 63 and 54 cm^{-1} respectively, indicative of the presence of N–Pd σ bonds.[13] Single perchlorate absorptions at 1 110br and 620 cm^{-1} indicate that there is no perchlorate co-ordination.[8-12] Microanalysis and conductivity data (Table) confirm the proposed formulation. Previous work with dmso had shown that the ' Pd(dppe) ' moiety presents considerable steric crowding at the remaining two sites.[3] It was of interest therefore to determine whether the sterically demanding *o*-toluonitrile could form a similar complex to that formed by benzonitrile. Repetition of reaction (1) led to the isolation of $[Pd(dppe)(NCC_6H_4Me\text{-}o)_2][ClO_4]_2$ which showed bands due to $\nu(C{\equiv}N)$ at 2 278 and 2 273 cm^{-1} indicative of Pd–N σ-bonded *o*-toluonitrile.[13] The marginally lower frequencies of these bands compared with the benzonitrile complex may indicate slightly weaker Pd–N bonds as a consequence of the steric overcrowding. If this is so then these steric constraints might result in a preferred orientation of the nitrile ligands which would result in the methyl groups being inequivalent in the ^1H n.m.r. spectrum. However, the two methyl groups were equivalent in CD_3NO_2 ($\delta = 2.31$ p.p.m.) both at ambient temperature and down to −10 °C. Thus although the diphosphine ligand provides sufficient steric constraints to force dmso to bond *via* oxygen to the ' Pd(dppe) ' moiety, the bonding of aromatic nitriles appears to be normal. The bidentate nitriles *o*-phthalonitrile and 1,6-dicyanohexane both displaced methanol from $[Pd(dppe)(HOMe)_2][ClO_4]_2$ (see below) to yield $[Pd(dppe)(NCZCN)][ClO_4]_2$. Both complexes showed single bands in the C≡N stretching region of their i.r. spectra at higher wavenumbers than in the free ligands [*o*-phthalonitrile, $\nu(C{\equiv}N)$ 2 282 cm^{-1}, $\Delta\nu$ 50 cm^{-1}; 1,6-dicyanohexane, $\nu(C{\equiv}N)$ 2 230 cm^{-1}; $\Delta\nu$ 68 cm^{-1}] indicative of the presence of Pd–N σ bonding.[13] It should be emphasised that the assignment of a monomeric structure to $[Pd(dppe)\{NC(CH_2)_6CN\}][ClO_4]_2$ is tentative, although there is no evidence, such as unusual solubility properties, to suggest a polymeric structure.

The acetone complex $[Pd(dppe)(OCMe_2)_2][ClO_4]_2$ could be isolated when reaction (1) was carried out in the presence of rigorously dried acetone. The i.r. spectrum showed a sharp band at 1 666 cm^{-1} with several weak shoulders on its lower wavenumber side. This band is assigned to $\nu(C{=}O)$ and represents a decrease of 48 cm^{-1} on co-ordination indicative of a σ-Pd–O bond.[14] The C–C–O deformation band at 1 223 cm^{-1} in free acetone drops to 1 142 cm^{-1} on co-ordination. No absorptions attributable to water or hydroxo-ligands were present either around 3 200 or 1 630 cm^{-1}. The perchlorate bands at 1 110br and 620 cm^{-1} demonstrate the absence of any anion co-ordination.[8-12] The molar conductance in 10^{-3} mol dm^{-3} nitromethane solution of 186 ohm^{-1} cm^2 mol^{-1} indicated a 2 : 1 electrolyte.[15] The extreme moisture sensitivity made a conductivity dilution study unwise. On brief exposure to the atmosphere the i.r. absorptions at 1 666 and 1 142 cm^{-1} disappeared and a broad band at 3 250 cm^{-1} and a barely resolved double peak at 1 630 cm^{-1} appeared. The product so obtained analysed as the bis(aquo) complex $[Pd(dppe)(OH_2)_2][ClO_4]_2$ and had a molar conductance consistent with this. The complex $[Pd(dppe)(OCMe_2)_2][ClO_4]_2$ was heat and shock sensitive making simple operations such as drying or sealing in ampoules extremely hazardous; accordingly no microanalytical data were obtained. In its electronic spectrum in dichloroethane it showed a band at 351 nm.

Total halide abstraction from $[Pd(dppe)Cl_2]$ in the presence of methanol, tetrahydrofuran, or benzene gave clear yellow solutions [$\lambda_{max.} = 332$ (methanol) or 338 nm (tetrahydrofuran)]. On working-up these solutions all three gave identical products with i.r. spectra having bands at 1 145vs, 1 020s(sh), 895s(sh), 620m, and 610m that are clearly indicative of co-ordinated perchlorate ligands.[8-12] No absorptions attributable to co-ordinated water or hydroxo-ligands were observed. The absence of a strong broad band at 1 110 cm^{-1} indicated the absence of any unco-ordinated perchlorate and suggested that the product was $[Pd(dppe)(OClO_3)_2]$, a complex with two unidentate perchlorate ligands attached to the same palladium atom. The molar conductivity in 10^{-3} mol dm^{-3} dichloroethane solution was 6.7 ohm^{-1} cm^2 mol^{-1}

supporting its formulation as a non-electrolyte, since this value is well below that expected for a cationic complex.[15] On adding a small amount of tetrahydrofuran to this solution the molar conductance rises sharply to 26.1 ohm^{-1} cm^2 mol^{-1} and the absorbance in the electronic spectrum shifts from 319 to 338 nm, both of which suggest the rapid formation of $[\mathrm{Pd(dppe)(thf)_2}][\mathrm{ClO_4}]_2$. When $[\mathrm{Pd(dppe)(OClO_3)_2}]$ is dissolved in acetonitrile or methanol solution the molar conductances of 10^{-3} mol dm^{-3} solutions are 239 and 191 ohm^{-1} cm^2 mol^{-1} respectively which implies the formation of the 2 : 1 electrolytes $[\mathrm{Pd(dppe)(NCMe)_2}][\mathrm{ClO_4}]_2$ and $[\mathrm{Pd(dppe)(HOMe)_2}][\mathrm{ClO_4}]_2$.[15] Consistent with this, these solutions have maxima in their electronic spectra at 349 and 332 nm respectively. Attempts to isolate the bis(methanol) and bis(tetrahydrofuran) complexes always yielded the bis(perchlorato)-complex, whilst attempts to isolate the bis(acetonitrile) complex appeared to yield a mixture of products. Thus the i.r. spectrum of the isolated solid showed two bands in the $\nu(\mathrm{C{\equiv}N})$ region at 2 292 and 2 316 cm^{-1}, consistent with the presence of σ-bonded acetonitrile,[13] but analytical data for $[\mathrm{Pd(dppe)(NCMe)_2}][\mathrm{ClO_4}]_2$ were repeatedly low in nitrogen, in variable amounts, indicating that some loss of acetonitrile and its replacement by perchlorate may be occurring during isolation.

The bis(perchlorato)-complex is extremely air sensitive, the multiple bands associated with the co-ordinated perchlorate being rapidly lost and bands at 1 090, 930, and 620 cm^{-1} indicative of free perchlorate appearing together with a broad band at 3 250 cm^{-1} and a band at 1 630 cm^{-1} indicative of co-ordinated water. Analytical data further support the formation of $[\mathrm{Pd(dppe)(OH_2)_2}][\mathrm{ClO_4}]_2$. As expected, $[\mathrm{Pd(dppe)(OClO_3)_2}]$ was extremely sensitive to mechanical and thermal shock and on occasions spontaneously detonated with no apparent external stimulus! We advise against the large-scale preparation of this complex as its shock sensitivity as an isolated solid represents an **EXTREME HAZARD**. After its initial isolation and characterisation $[\mathrm{Pd(dppe)(OClO_3)_2}]$ was always handled in solution and no attempt was made to submit it for microanalysis.

Total halide abstraction from $[\mathrm{Pd(dppe)Cl_2}]$ in the presence of dry ethanol resulted in a pale yellow solution. This solution was quite stable, but as soon as the solvent was removed in order to isolate the bis(ethanol) complex decomposition to palladium metal and acetaldehyde took place.

We previously reported that the cationic carbonyl complexes $[\mathrm{M(L{-}L)(CO)Cl}]^+$, where M = palladium(II) and platinum(II) and L–L is a bidentate ligand, could not be prepared;[1] all attempts led instead to the dimeric chloride-bridged product $[\mathrm{M_2(L{-}L)_2Cl_2}]^{2+}$. Since the $[\mathrm{Pd(dppe)(solvent)_2}][\mathrm{ClO_4}]_2$ complexes described above have no halide ligands present that could lead to competition with carbon monoxide, carbon monoxide was passed through a solution of $[\mathrm{Pd(dppe)(OCMe_2)_2}][\mathrm{ClO_4}]_2$. On work-up the product obtained was $[\mathrm{Pd(dppe)(OCMe_2)_2}][\mathrm{ClO_4}]_2$ with no evidence for carbonyl co-ordination. Since co-ordinated perchlorate is a weaker ligand than acetone and $[\mathrm{Pd(dppe)(OClO_3)_2}]$ reacts with acetone to yield the bis(acetone) complex, carbon monoxide was bubbled into a solution of $[\mathrm{Pd(dppe)(OClO_3)_2}]$ generated in benzene–dichloromethane solution. Again no reaction occurred and only the bis(perchlorato)-complex could be isolated. The electronic spectra of solutions of $[\mathrm{Pd(dppe)(OCMe_2)_2}][\mathrm{ClO_4}]_2$ and $[\mathrm{Pd(dppe)(OClO_3)_2}]$ showed no change upon purging with carbon monoxide. We ascribe the extreme weakness of the palladium–carbonyl bond in these complexes to the large positive charge (2+) on the complex ion, which significantly reduces the capacity of palladium to provide the π-back donation necessary to stabilise the Pd–CO bond.

In summary, the present results show that the order of ability of weak solvent ligands to form cationic palladium(II) complexes $[\mathrm{Pd(dppe)(solvent)_2}]^{2+}$ is: $\mathrm{CH_2Cl_2} \sim \mathrm{CO} \sim \mathrm{C_6H_6} \lll \mathrm{EtOH} < \mathrm{MeOH} \sim \mathrm{thf} < \mathrm{MeCN} < \mathrm{Me_2CO} < \mathrm{RCN} < \mathrm{dmf} < \mathrm{dmso}$ (*O*-bonded) $<$ py. In the solid state the perchlorate ion displaces ligands below acetonitrile whereas in solution it is in turn displaced by ligands above ethanol.

It was of interest to determine whether or not the presence of weak donors enhanced the catalytic ability of the complexes. It does. The ion $[\mathrm{Pd(dppe)(OCMe_2)_2}]^{2+}$ is an active catalyst for the hydrogenation of olefins at 30 °C and 1 atm (101 325 Pa) pressure.[16] This is indeed remarkable activity and we are not aware of any other cationic palladium(II) species that catalyse olefin hydrogenation under ambient conditions.

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