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Preparation of Mononuclear and Polynuclear Cyano-Complexes of Palladium(II)

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The abstraction of one cyanide ion from $[Pd(dpe)CN)_2]$ *(dpe =* $Ph_2PCH_2CH_2PPh_2$*) with silver perchlorate in acetonitrile solution yields a complex that has the empirical formula* $[Pd(dpe)CN]ClO_4$ *and is believed to be a mixture of two planar tetramers 4 and 5 both of which involve linear Pd–C≡N–Pd bridges. One of the tetramers has an idealised* C_{4h} *structure each palladium having a* P_2CN *environment, and the other has an idealised* D_{2h} *structure two of the palladiums having* P_2C_2 *environments and two having* P_2N_2 *environments.*

Introduction

We have previously reported [1, 2] that attempts to prepare complexes of the type $[Pd(L\ L)X(S)]^+$ where $L^\frown L$ is a chelating ligand such as $Ph_2PCH_2CH_2PPh_2$ (dpe) and X is a halide ligand are only successful when S is a moderately good donor ligand such as a tertiary phosphine, pyridine, dimethylsulphoxide and dimethylformamide. With poorer donor ligands S such as alkyl- and aryl-nitriles, alcohols, water, acetone or tetrahydrofuran the product isolated is always the halide bridged dimer $[Pd(L^\frown L)X]_2^{2+}$. Since cyano-bridged phosphine complexes of palladium(II) and platinum(II) are uncommon [3, 4] it was of interest to see if it were possible to extend the range of ligands S capable of forming mono-solvento complexes of the type $[Pd(L^\frown L)X(S)]^+$ by replacing the halide ligand X with cyanide. The objective accordingly was to extract one cyano-ligand from the bis-cyano complex $[Pd(L^\frown L)(CN)_2]$ using a silver(I) salt.

Results and Discussion

Previous syntheses of the starting complexes $[Pd(L^\frown L)(CN)_2]$ have always relied upon oxidative-addition of cyanogen to the corresponding palladium(0) complexes [5], although metathetical exchange of halide for cyanide has been used to prepare $[PdL_2(CN)_2]$ where L is a monodentate tertiary phosphine [6, 7]. We found that metathetical exchange of chloride for cyanide using 8 equivalents of cyanide to one of palladium(II) is a very effective and simple route for the preparation of $[Pd(L^\frown L)(CN)_2]$ (Reaction *1*).

$$[Pd(L^\frown L)Cl_2] + 2KCN \rightarrow [Pd(L^\frown L)(CN)_2] + 2KCl \qquad (1)$$

When identical conditions were used in an attempt to prepare the corresponding platinum(II) complex displacement of the dpe occurred as well, yielding $K_2[Pt(CN)_4]$. This suggests that the stability constants for the formation of platinum(II)–cyano complexes are considerably greater than for the formation of the palladium(II) complexes as previously suggested by one of us [8a], although the available data in the literature did not support this view [9, 10]. However more recently [11] $\log_{10}\beta_4$ for the formation of $[Pd(CN)_4]^{2-}$ from $[Pd(H_2O)_4]^{2+}$ has been put at about 63 whilst the corresponding value for platinum(II) has been put at between 65 and 75 in accordance with the present qualitative observations. The platinum(II) complex can be prepared according to reaction (*1*) using two equivalents of cyanide per equivalent of $[Pt(L^\frown L)Cl_2]$, a route analogous to that used previously to prepare $[PtL_2(CN)_2]$ complexes in which L is a monodentate tertiary phosphine [12–14].

Since our earlier work with solvento complexes [2] had shown that, of the solvento ligands that are unable to form $[Pd(L^\frown L)X(S)]^+$ complexes with X = halide, acetonitrile is one of the best donor ligands, we attempted to prepare $[Pd(dpe)CN(MeCN)]^+$ by cyanide abstraction from $[Pd(dpe)(CN)_2]$ using silver perchlorate in the presence of acetonitrile (Reaction *2*).

$$[Pd(dpe)(CN)_2] + AgClO_4 \xrightarrow[\text{stir 3 hours}]{\substack{\text{MeCN}\\ \text{reflux 15 mins}}} [Pd(dpe)CN(MeCN)]ClO_4 \qquad (2)$$

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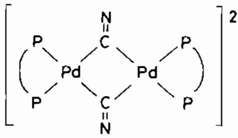
The product showed a single band in the $C\equiv N$ stretching region of the infrared at 2185 cm^{-1} (nujol mull) and at 2180 cm^{-1} (nitromethane solution), which is a region typical of bridging cyanides [15]. No bands attributable to coordinated acetonitrile were observed in the region 2250–2380 cm^{-1}. A broad band at 1080 cm^{-1} together with a band at 620 cm^{-1} indicated the presence of ionic perchlorate. The u.v.–visible spectrum was typical of that found for square-planar palladium(II) with a single shoulder at 274 nm in the near u.v. in dichloroethane solution. Analytical data supported an empirical formula of '$Pd(dpe)(CN)ClO_4$'. Two approaches were used to study the molecularity of this complex. Field desorption mass spectrometry was tried in the hope that a parent ion might be observed; however no mass spectrum could be obtained at all [16]. Molar conductivity plots of $\Lambda_o - \Lambda_e$ against $C^{1/2}$ where Λ_o and Λ_e are the conductances at infinite dilution and at the concentration C equiv.l^{-1} respectively were prepared in acetonitrile and nitromethane. The slopes and Λ_o values were 721 ohm$^{-1}\cdot$l$^{1/2}\cdot$equiv.$^{-1/2}$ and 171 ohm$^{-1}\cdot$l$^{1/2}$ in acetonitrile and 388 ohm$^{-1}\cdot$l$^{1/2}\cdot$equiv$^{-1/2}$ and 108 ohm$^{-1}\cdot$l$^{1/2}$ in nitromethane respectively. Both sets of values are a little below those typical of a 2:1 electrolyte for which typical slopes are in the range 870–1100 ohm$^{-1}\cdot$l$^{1/2}\cdot$equiv$^{-1/2}$ [17] in acetonitrile and 390–510 ohm$^{-1}\cdot$l$^{1/2}\cdot$equiv$^{-1/2}$ [18] in nitromethane solution. Low values are sometimes observed with large ions, so that the present results are not inconsistent with a 2:1 electrolyte. Possible structures for 2:1 electrolytes would be 1, 2, and 3. 1 is most unlikely because, although cyanide is isoelectronic with carbon monoxide it does not act as a bridging ligand in this way [19]. 2 and 3 similarly are not known bridging modes for cyanide and in addition involve 14-electron palladium(II) ions assuming sp^2 hybridisation on both carbon and nitrogen. It is quite possible to describe structures for a 4:1 electrolyte type (4, 5 and 6) that are consistent with the linear $M{-}C\equiv N{-}M$ bridges observed in many cyanide complexes including $Pd(CN)_2$ [20]. Structures 4 and 5 involve a degree of symmetry; structure 6 is analogous to that given by Wells for $Pd(CN)_2$ [20]. In an attempt to distinguish between these structures the $^{31}P\{^1H\}$ nmr spectrum was recorded in CD_3NO_2. The spectrum, which was temperature independent, consisted of two singlets at −71.7 and −63.7 ppm relative to phosphoric acid each of relative intensity 13 and two doublets at −69.3 (J_{P-P} = 3.7 Hz) and −65.15 ppm (J_{P-P} = 2.4 Hz) of relative intensities 9 and 8 respectively. This spectrum is inconsistent with structure 6 which would be expected to show four bands all of equal intensity. It is consistent with neither 4 nor 5 on their own, but is consistent with a mixture of 4 and 5 with two of the J_{P-P} coupling constants being less than the resolution of the instrument, 1.2 Hz. Low phosphorus–phosphorus coupling constants such as observed here are typical of *cis* geometries [8b]. Attempts to observe the resonance from the cyanocarbon atoms in the $^{13}C\{^1H\}$ nmr spectrum [21] were unsuccessful probably due to this resonance being broadened by the close proximity of quadrupolar ^{14}N atoms.



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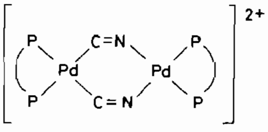

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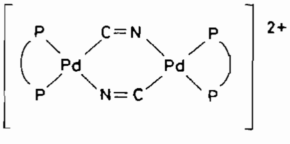

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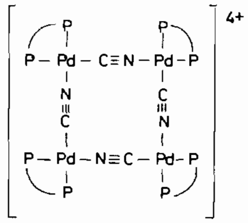

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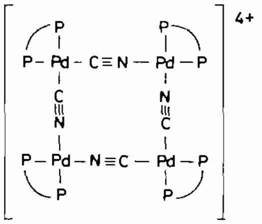

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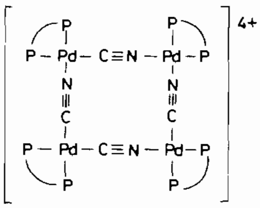

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The complex $[Pd(dae)(CN)_2]$, dae = $Ph_2AsCH_2CH_2AsPh_2$, undergoes a reaction with one equivalent of silver perchlorate to yield a product entirely analogous to that described above for dpe.

In conclusion treatment of $[Pd(L^\frown L)(CN)_2]$ with one equivalent of silver perchlorate in acetonitrile solution does not yield the solvento complex $[Pd(L^\frown L)CN(MeCN)]ClO_4$ but rather a cyano-bridged complex which is believed to be tetrameric $[Pd_4(L^\frown L)_4(CN)_4](ClO_4)_4$, the cation being a mixture of 4 and 5.

Experimental

$[Pd(L^\frown L)(CN)_2]$, L = dpe and dae

$[Pd(L^\frown L)(Cl_2]$ (0.001 mol) dissolved in dichloromethane (20 ml) was added to a solution of KCN (0.008 mol) in warm methanol (50 ml) and refluxed with stirring for 3 hours. After evaporation to dryness, extraction into dichloromethane (5 × 10 ml aliquots) and reduction to small volume white crystals of $[Pd(L^\frown L)(CN)_2]$ were precipitated by dropwise addition of diethylether. Yield 70%. *Anal.* Found: C, 60.2; H, 4.5; N, 4.8%; $[Pd(dpe)(CN)_2]$ Calcd: C, 60.4; H, 4.3; N, 5.0%; ν_{CN} = 2141 and 2136 cm^{-1}. Found C, 51.5; H, 3.8; N, 4.1; $[Pd(ape)(CN)_2]$ Calcd. C, 52.1; H, 3.8; N, 4.3%; ν_{CN} = 2142 cm^{-1} insufficiently resolved to assign separate frequencies to the two absorptions.

$[Pd_4(L^\frown L)_4(CN)_4](ClO_4)_4$, L = dpe and dae

$[Pd(L^\frown L)(CN)_2]$ (0.001 mol) was dissolved in acetonitrile (30 ml). Silver perchlorate (0.001 mol) dissolved in acetonitrile (20 ml) was added with stirring. The solution was refluxed for 15 minutes and then stirred for a further 3 hours whilst cooling during which time a white precipitate formed. The solution was evaporated to dryness, extracted with dichloromethane (5 × 10 aliquots) and after filtration and reduction to small volume a white palladium complex was precipitated by dropwise addition of diethylether. The product was recrystallised twice from nitromethane/diethylether. *Anal.* Found: C, 50.7; H, 3.9; N, 2.3; P, 9.9; Cl, 5.4; $[Pd_4(dpe)_4(CN)_4](ClO_4)_4$ Calcd: C, 51.4; H, 3.8; N, 2.2; P, 9.8; Cl, 5.6%.

$^{31}P\{^1H\}$ nmr spectra were recorded in CD_3NO_2 solution on a Jeol 100 MHz spectrometer.

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