Cyclopalladated Derivatives of 2,4'-Bipyridine

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2,4'-Bipyridine ($C_{10}H_8N_2$) reacts with palladium(II) acetate in acetic acid to form the cyclopalladated dimer [{Pd($C_{10}H_7N_2$)(μ-O_2CMe)}$_2$]. Metathesis with aqueous lithium chloride results in the formation of the chloro-bridged analogue [{Pd($C_{10}H_7N_2$)(μ-Cl)}$_2$], which reacts with monodentate or bidentate ligands to form mononuclear complexes [PdCl($C_{10}H_7N_2$)L], [Pd($C_{10}H_7N_2$)L_2]Cl (L = PBu^n_3) or [Pd($C_{10}H_7N_2$)L] (L = pentane-2,4-dionate or S_2CNEt_2) respectively.

Cyclometallated complexes possess a chelation stabilised metal–carbon σ bond[1–6] and those systems which incorporate a heterocyclic donor atom are of particular interest,[6] in that they may be compared with 'classical' co-ordination compounds of chelating heterocyclic ligands. It has recently become apparent that 2,2'-bipyridine may adopt a *C,N*-cyclometallated bonding mode, in addition to the more familiar *N,N'* mode,[6–10] and it is possible that such species may be implicated as intermediates in some of the reactions of 2,2'-bipyridine complexes.[9–11] As part of a more extensive investigation into the reactions of co-ordinated ligands,[12] the palladium(II) complexes of 2,4'-bipyridine (**1**) have been studied.

Results and Discussion

The reaction of $Li_2[PdCl_4]$ or $Na_2[PdCl_4]$ with 2,4'-bipyridine in aqueous or aqueous ethanolic solution resulted in the formation of insoluble yellow complexes of the type [Pd($C_{10}H_8N_2$)$_2Cl_2$], which did not react with PBu^n_3 under the mild conditions required for the cleavage of the chloro-bridged dimers [{Pd($C_{10}H_7N_2$)(μ-Cl)}$_2$]. These complexes were not further investigated, but were thought to be the 'expected' *N*-bonded species.

In contrast, the reaction of 2,4'-bipyridine (**1**) with palladium(II) acetate in acetic acid at 100 °C afforded a clear yellow solution, from which yellow-brown crystals of the acetato-bridged complex [{Pd($C_{10}H_7N_2$)(μ-O_2CMe)}$_2$] (**2**) were obtained upon concentration. The acetato-bridged complex (**2**) was converted to the chloro-bridged analogue by reaction with an excess of aqueous lithium chloride solution, to give [{Pd($C_{10}H_7N_2$)(μ-Cl)}$_2$] (**3**) as a pale yellow microcrystalline solid. Although no satisfactory mass spectra could be obtained for these complexes, they are assigned a dimeric structure by analogy with other cyclopalladated compounds prepared by similar routes, *e.g.* [{Pd(L)Cl}$_2$] (HL = 2-phenylpyridine[6,13] or benzo[*h*]quinoline[14]).

The dimeric complexes (**2**) and (**3**) are stable to air and water. The acetato-bridged complex (**2**) exhibits bands in its i.r. spectrum at 1 708 and 1 830 cm^{-1}, which are absent in the chloro-bridged species (**3**).

Treatment of a suspension of (**3**) in chloroform with two equivalents of PBu^n_3 led to the formation of a pale yellow solution, from which the complex [PdCl($C_{10}H_7N_2$)(PBu^n_3)] (**4**) could be isolated as a white solid. The mass spectrum of (**4**) showed a parent ion centred at *m/z* 498 (^{106}Pd, ^{35}Cl) showing the expected isotope pattern, which is compatible with the formulation as a cyclometallated product. Small amounts of the yellow compound, [Pd($C_{10}H_7N_2$)(PBu^n_3)$_2$]Cl (**5**), were also formed. The ^{1}H n.m.r. spectrum of (**5**) clearly demonstrates the formation of a Pd–C bond, and only shows seven resonances in the aromatic region (Figure). The site of palladation is clearly C$^{3'}$, with H$^{2'}$ appearing as a singlet (δ 8.57) and H$^{5'}$,H$^{6'}$ as an AB quartet (δ 8.39 and δ 8.05). The broadening of the lowest field resonance, centred at δ 8.85, is quite noticeable, although it is observed as a doublet (J = 5.8 Hz) at lower fields (80 MHz). This resonance may be assigned to H^6, which is shown by decoupling experiments to be coupled to the doublet of doublets centred at *ca.* 7.45, which is thus assigned to H^5. Similarly, the apparent triplet of doublets at δ 7.87 is assigned to H^4, and the doublet at δ 8.51 to H^3.The assignment of the doublet at δ 8.85 to H^6 rather than H^3 is on the basis of the broadening, expected from a proton adjacent to the nitrogen atom, and the coupling constant, which is typical for J(H^{5}H^6) in pyridine and 2,2'-bipyridine ligands and complexes. Consistent

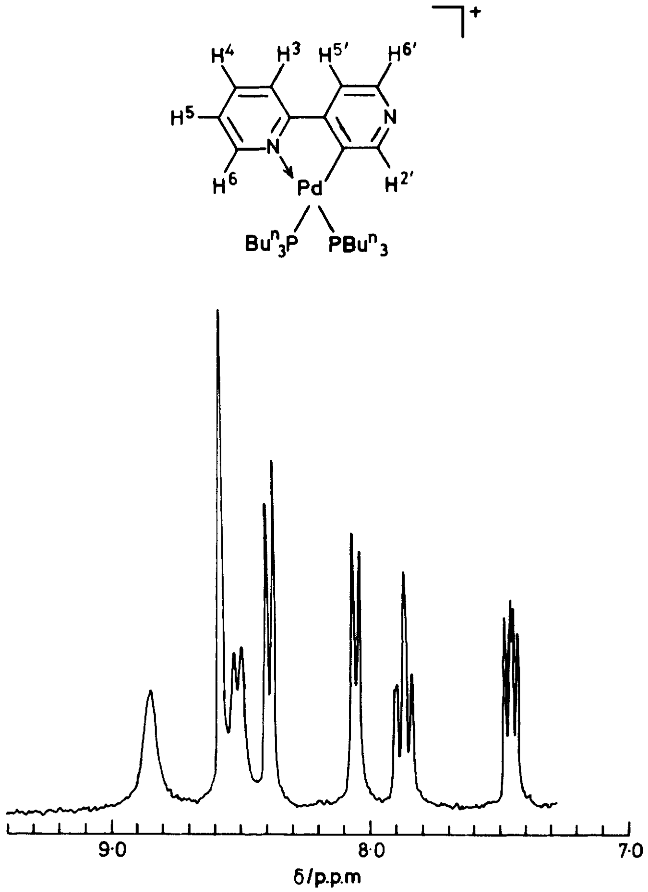

Figure. Hydrogen-1 n.m.r. spectrum (250 MHz) showing the aromatic region of the complex [Pd($C_{10}H_7N_2$)(PBu^n_3)$_2$]Cl (**5**) in $(CD_3)_2CO$ solution with this assignment is a coupling constant of 6.9 Hz associated with the doublet at δ 8.51, typical of $J(H^3H^4)$ in 2,2′-bipyridines.

The ^1H n.m.r. spectrum of complex (**4**) is not so readily interpreted. However, the ^{13}C n.m.r. spectrum of this complex (in $CDCl_3$) exhibits the expected ten resonances in the aromatic region, seven of which are directly coupled to a proton. One of the resonances, at δ 154.8, exhibits a $^2J(C-P)$ coupling of 9.6 Hz. This very low value is compatible with the phosphine occupying the *cis* position with respect to the metal–carbon bond, as is found in other cyclometallated complexes of this type.[15,16]

Treatment of (**3**) with an equivalent amount of methanolic sodium pentane-2,4-dionate (pd) results in the formation of the neutral complex, $[Pd(C_{10}H_7N_2)(pd)]$, as a yellow crystalline solid. The ^1H n.m.r. spectrum of this compound differs from that of the phosphine-substituted compound (**5**) in a number of respects, although it closely resembles that of (**4**). Firstly, the methyl resonances of the pentane-2,4-dionate group are non-equivalent, appearing as singlets at δ 2.05, separated by 2 Hz. This is expected for a pentane-2,4-dionate complex of this type, in which one of the methyl groups is on the same side of the square plane as the cyclometallated pyridine ring, and the other is on the same side as the co-ordinated pyridine ring. The unique methine proton is observed as a singlet at δ 5.5. The differences in the aromatic region of the spectrum may be interpreted in terms of a change in symmetry of the complex, associated with the strain introduced by the chelating pentane-2,4-dionate. This argument is supported by the similarity of the spectra of $[Pd(C_{10}H_7N_2)L]$ (L = pd or S_2CNEt_2). The most noticeable differences are in the chemical shifts of H^3 and $H^{5'}$, which are expected from studies of octahedral 2,2′-bipyridine complexes.[4] These shifts are most probably due to twisting about the interannular C–C bond, to relieve unfavourable non-bonded interactions between the ligands. It is noticeable that neither $H^{2'}$ (δ 8.61) nor H^6 (δ 8.71) experiences any marked shifts with respect to the phosphine complex (**5**).

The reaction of (**3**) with $Na(S_2CNEt_2)$ proceeds smoothly, to give a yellow solution from which the complex $[Pd(C_{10}H_7N_2)(S_2CNEt_2)]$ may be isolated. The ^1H n.m.r. spectrum of this complex exhibits the same features observed in the pentane-2,4-dionate complex, and it is clear that the two ethyl groups of the *N,N′*-diethyldithiocarbamate are non-equivalent, as expected from the different environments of the ethyl groups resulting from hindrance to rotation about the N–C bond.

It is clear that 2,4′-bipyridine can act as an *N,C*-bidentate ligand, in which the M–C bond is stabilised by cyclometallation, in a process akin to the chelate effect. This ligand is of particular interest, as it indicates a way in which the reactivity of a co-ordinated pyridine ligand may be modified. The relevance of these results to the 2,2′-bipyridine system is obvious, and it seems likely that cyclometallation of co-ordinated 2,2′-bipyridines is more prevalent than is at present thought. Investigations into cyclometallation reactions of 2,3′-bipyridine and 2,2′-bipyridine are currently underway.

Experimental

N.m.r. spectra were recorded on Bruker WM250 or WM80 spectrometers, in $CDCl_3$ or $(CD_3)_2CO$ solution; i.r. spectra were recorded on a Perkin-Elmer 983 spectrophotometer. 2,4′-Bipyridine (Aldrich) and palladium(II) acetate (Johnson-Matthey) were used without further purification. Solvents were distilled before use, and reactions were conducted under an atmosphere of dry dinitrogen.

Synthesis of Acetato-bridged Dimer (**2**).—2,4′-Bipyridine (0.156 g, 1 mmol) was added to a warm solution of palladium(II) acetate (0.244 g, 1 mmol) in acetic acid (25 cm^3), and the resultant brown solution maintained at 100 °C for 6 h, after which period it had become pale yellow. The solution was concentrated *in vacuo* to about half volume, and then allowed to cool, when pale yellow crystals of the acetato-complex $[\{Pd(C_{10}H_7N_2)(O_2CMe)\}_2]\cdot 2H_2O$ were deposited (0.300 g, 88%) (Found: C, 42.7; H, 3.5; N, 8.1. $C_{24}H_{24}N_4O_6Pd_2$ requires C, 42.6; H, 3.5; N, 8.3%).

Synthesis of Chloro-bridged Dimer (**3**).—$[\{Pd(C_{10}H_7N_2)(O_2CMe)\}_2]\cdot 2H_2O$ (0.250 g, 0.37 mmol) was stirred with a solution of lithium chloride (1 g) in water (10 cm^3) for 3 h at 80 °C, after which period the pale yellow solid was collected by filtration and air-dried to give $[\{Pd(C_{10}H_7N_2)(\mu-Cl)\}_2]\cdot 3H_2O$ (**3**) (0.200 g, 84%) (Found: C, 36.9; H, 2.8; N, 8.6. $C_{20}H_{20}Cl_2N_4O_3Pd_2$ requires C, 37.0; H, 3.1; N, 8.6%).

Synthesis of $[Pd(ClC_{10}H_7N_2)(PBu^n_3)]$ (**4**).—The chloro-bridged dimer (**3**) (0.250 g, 0.42 mmol) was suspended in chloroform (15 cm^3) and stirred with PBu^n_3 (0.170 g, 0.84 mmol) at room temperature for 2 h. After this period, a clear pale yellow solution had been obtained. The solution was concentrated *in vacuo* to give a waxy yellow solid. This was recrystallised from diethyl ether–chloroform to give (**4**) as a white crystalline solid (0.370 g, 88%) (Found: C, 53.0; H, 6.6; N, 5.5. $C_{22}H_{34}ClN_2PPd$ requires C, 52.9; H, 6.8; N, 5.6%). Small amounts of the pale yellow material, $[Pd(C_{10}H_7N_2)(PBu^n_3)_2]Cl$ (**5**), were obtained from the mother-liquors.

Synthesis of $[Pd(C_{10}H_7N_2)(S_2CNEt_2)]$.—The chloro-bridged dimer (**3**) (0.250 g, 0.42 mmol) suspended in methanol (5 cm^3) was treated with a solution of $Na(S_2CNEt_2)$ (0.171 g, 1 mmol) and the mixture heated to reflux for 2 h, after which period a clear yellow solution was obtained. This was evaporated *in vacuo* to give a yellow solid, which was chromatographed over silica (chloroform eluant) to give $[Pd(C_{10}H_7N_2)(S_2CNEt_2)]$ (0.260 g, 76%) (Found: C, 43.9; H, 4.3; N, 10.1. $C_{15}H_{17}N_3PdS_2$ requires C, 44.0; H, 4.2; N, 10.3%).

Synthesis of $[Pd(C_{10}H_7N_2)(pd)]$.—The chloro-bridged dimer (**3**) (0.250 g, 0.42 mmol) was suspended in methanol (15 cm^3) and treated with Na(pd) (0.10 g, 0.84 mmol). After heating to reflux for 1 h, the yellow solution was evaporated to dryness, and the residue recrystallised from methanol to give yellow needles of the complex $[Pd(C_{10}H_7N_2)(pd)]$ (0.240 g, 80%) (Found: C, 49.7; H, 3.7; N, 7.75. $C_{15}H_{14}N_2O_2Pd$ requires C, 49.9; H, 3.9; N, 7.8%).

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