Allylammonium Complexes of Palladium(II)

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Three new allylammonium complexes of palladium(II) are reported: $(CH_2{:}CH\cdot CH_2\cdot NH_3^+)_2[PdCl_4]^{2-}$, a salt in which there is no covalent bonding between the allylammonium and tetrachloropalladate(II) ions, $[Pd(CH_2{:}CH\cdot CH_2\cdot NH_3)Cl_3]$ and $Na[Cl_2PdCl_2PdCl(CH_2{:}CH\cdot CH_2\cdot NH_3Cl)]$ in which the allylammonium groups are co-ordinated by palladium–olefin bonds. The i.r. and Raman spectra of $[Pd(CH_2{:}CH\cdot CH_2\cdot NH_3)Cl_3]$ indicate considerable mixing of the C=C stretching and CH_2 deformation modes, although the C=C stretching mode appears to make a slightly greater contribution to the band at 1536 cm^{-1} and the CH_2 deformation to that at 1270 cm^{-1}. The electronic spectrum of $[Pd(CH_2{:}CH\cdot CH_2\cdot NH_3)Cl_3]$ has four bands in the region 20,000—38,500 cm^{-1}, all with molar extinction coefficients of 210 or less, which are assigned to *d–d* transitions.

ALTHOUGH a number of olefin complexes of palladium(II) with multidentate ligands containing at least one olefinic functional group have been reported, relatively few stable palladium(II) complexes of mono-olefins have been reported.[1] The object of the present work was to prepare some such complexes in order to study their vibrational and electronic spectra. Previous work with platinum(II) had shown that the zwitterionic complexes of the allylammonium ion, such as $[Pt(CH_2{:}CH\cdot CH_2\cdot NH_3)Cl_3]$, were readily isolated in a pure form and were stable in the crystalline state, whereas the ionic complexes of neutral olefins such as ethylene or allyl alcohol were more difficult to isolate pure † and were less stable, decomposing slowly to platinum metal.[2,3] Accordingly, the preparation of allylammonium–palladium(II) complexes were investigated.

Treatment of a solution of Na_2PdCl_4 in acetic acid containing 0·1M perchloric acid with allylamine resulted in the formation of three complexes. The first, $(CH_2{:}CH\cdot CH_2\cdot NH_3^+)_2[PdCl_4]^{2-}$, was formed when the acetic acid was saturated with sodium chloride. The second, $[Pd(CH_2{:}CH\cdot CH_2\cdot NH_3)Cl_3]$, was formed when no extra sodium chloride was added. The third, $Na^+[Cl_2PdCl_2PdCl(CH_2{:}CH\cdot CH_2\cdot NH_3Cl)]^-$, was formed in the absence of added sodium chloride but using equimolar quantities of allylamine and Na_2PdCl_4 as opposed to the 10-fold excess of allylamine used in preparing the first two complexes.

$(CH_2{:}CH\cdot CH_2\cdot NH_3^+)_2[PdCl_4]^{2-}$ is a red crystalline compound formed under identical conditions to $(CH_3\cdot CH_2\cdot CH_2\cdot NH_3^+)_2[PdCl_4]^{2-}$. It is stable in acetic acid containing 0·1M-perchloric acid and in dry air, but decomposes slowly in moist air and rapidly in water or magnesium-dried methanol to give palladium metal. This hydrolysis probably involves the formation of a palladium(II)–olefin intermediate since warming a suspension of $(CH_2{:}CH\cdot CH_2\cdot NH_3^+)_2[PdCl_4]^{2-}$ in acetic acid at *ca.* 50 °C converts it to the palladium(II)–olefin complex $[Pd(CH_2{:}CH\cdot CH_2\cdot NH_3)Cl_3]$, which can be isolated and which reacts instantaneously with water to deposit palladium metal.

The vibrational spectra of $(CH_2{:}CH\cdot CH_2\cdot NH_3^+)_2[PdCl_4]^{2-}$ exhibited bands at **1646** (i.r.) and **1650** cm^{-1}

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† Isolation can be facilitated by using salts of bulky cations, but these cations interfere in the subsequent spectral investigations.

[1] F. R. Hartley, *Chem. Rev.*, 1969, **69**, 799.

[2] R. G. Denning and L. M. Venanzi, *J. Chem. Soc.*, 1963, **3241**.

[3] R. G. Denning, F. R. Hartley, and L M. Venanzi, *J. Chem. Soc. (A)*, 1967, **324**.

(Raman) due to the unco-ordinated double bond. Although the Raman spectrum was weak and difficult to observe due to a very strong fluorescence band centred *ca.* 1450 cm^{-1}, a weak band at 1316 cm^{-1} was assigned to the C–H deformation mode of an unco-ordinated olefin observed at 1295 cm^{-1} in allylammonium chloride, 1297 cm^{-1} in propene,[4] and 1342 cm^{-1} in ethylene.[4] $(CH_2{:}CH\cdot CH_2\cdot NH_3^+)_2[PdCl_4]^{2-}$ showed a complex band structure in the region 3300—2400 cm^{-1} with a particularly broad central band *ca.* 3120 cm^{-1} identical to that in $(CH_3\cdot CH_2\cdot CH_2\cdot NH_3^+)_2[PdCl_4]^{2-}$ and characteristic of a quaternary ammonium salt.[5]

$[Pd(CH_2{:}CH\cdot CH_2\cdot NH_3)Cl_3]$ is a yellow crystalline compound that is indefinitely stable in dry air but decomposes rapidly in moist air and instantaneously in water to deposit palladium metal. The i.r. spectrum shows the same complex band structure around 3120 cm^{-1} as found in $(CH_2{:}CH\cdot CH_2\cdot NH_3^+)_2[PdCl_4]^{2-}$ indicating the presence of a quaternary ammonium group; the lack of any sharp bands in the N–H stretching region is further confirmation of the absence of direct nitrogen to palladium co-ordination.[6] The i.r. and Raman spectra between 1200 and 1550 cm^{-1} indicate the presence of a palladium–olefin π-bond (see below).

Since the rate of hydrolysis of olefins co-ordinated to palladium(II) is inversely proportional to the proton concentration,[7] an attempt was made to prepare $[Pd(CH_2{:}CH\cdot CH_2\cdot NH_3)Cl_3]$ in acidic aqueous solution. With hydrochloric acid palladium metal was deposited at acid concentrations below 2M; and at concentrations above 2M, although no palladium metal was deposited, electronic spectroscopy indicated that no olefin complex was formed due to the high chloride concentration driving the equilibrium

$$[PdCl_4]^{2-} + CH_2{:}CH\cdot CH_2\cdot NH_3^+ \rightleftharpoons [Pd(CH_2{:}CH\cdot CH_2\cdot NH_3)Cl_3] + Cl^-$$

to the left. With perchloric acid decomposition occurred at acid concentrations below 9M although in 8M-perchloric acid about a week was required for complete decomposition. Above 9M the olefin complex was formed and appeared to be stable. The three isobestic points found in the electronic spectra of a series of solutions containing varying concentrations of allylamine (Figure 1) indicate that only one palladium(II)–olefin complex is formed in 9M-perchloric acid.

The vibrational spectra of metal–olefin complexes are currently the subject of some controversy largely because the C=C stretching vibration, ν(C=C), and the in-phase, CH$_2$ deformation, δ(CH$_2$), have the same symmetry and so interact extensively.[1] The band *ca.* 1500 cm^{-1} (hereafter called band 1) has generally been considered to arise largely from ν(C=C), although recently it has been suggested[8] that in $K^+[Pt(C_2H_4)Cl_3]^-$, band 1 is due largely to δ(CH$_2$). However, subsequent work on complexes such as $[Pt(Me_2C{:}CMe_2)Cl_2]_2$ has suggested that ethylene is a special case resulting from the close similarity of the ν(C=C) and δ(CH$_2$) frequencies in the free olefin.[9] This is further indicated by the present results (Table 1) since the large difference in the intensities of bands 1 and 2 in $K^+[Pt(C_2H_4)Cl_3]^-$, which was a significant part of the evidence used in assigning band 1 predominantly to δ(CH$_2$), is not found in the allylammonium complexes. This suggests that the relative contributions of the ν(C=C) and δ(CH$_2$) modes to both bands 1 and 2 are more similar in the allylammonium than in the ethylene complex. One way of considering the contributions of the ν(C=C) and δ(CH$_2$) modes to bands 1 and 2 involves the two-stage scheme illustrated in Figure 2. In the first stage ν(C=C) is decreased due to the weakening of the multiple bond that accompanies co-ordination, whilst to a first approximation δ(CH$_2$) is hardly altered. Two possibilities arise at this stage: either (a) ν(C=C) lies above δ(CH$_2$) or (b) ν(C=C) lies below δ(CH$_2$). In the second stage ν(C=C) and δ(CH$_2$) interact, as a result of their having the same symmetry, to yield the two bands actually observed in the spectra (Table 1). This interaction should result in

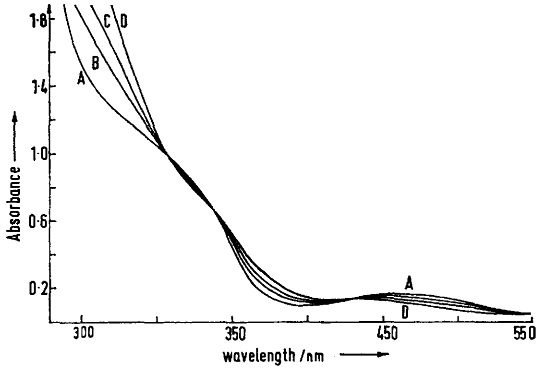

FIGURE 1 Isobestic points for the system allylamine–sodium tetrachloropalladate(II) in 9M aqueous perchloric acid solution, all solutions contain 10^{-3}M-Na$_2$PdCl$_4$; allyl concentrations: A, 0; B, 10^{-3}; C, 10^{-2}; D, 10^{-1} M

TABLE 1

Infrared and Raman spectral results

	Infrared (cm^{-1})		Raman (cm^{-1})		
Compound	Band 1	Band 2	Band 1 (ν_1) *	Band 2 (ν_2) *	$\nu_1 - \nu_2$
$K[Pt(C_2H_4)Cl_3]$	1515vw	1240vw	1520 (1)	1241 (17)	279
$[Pt(CH_2{:}CH\cdot CH_2\cdot NH_3)Cl_3]$	1505vw	1250w	1501 (1)	1249 (2·8)	252
$[Pd(CH_2{:}CH\cdot CH_2\cdot NH_3)Cl_3]$	1535vw	1270vw	1536 (1)	1270 (2)	266

* The number in parentheses is the intensity; the results have been normalised relative to band 1 which has been given an arbitrary intensity of one.

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[4] G. Herzberg, 'Infrared and Raman Spectra of Polyatomic Molecules,' Van Nostrand, 1965.

[5] R. A. Heacock and L. Marion, *Canad. J. Chem.*, 1956, **34**, 1782.

[6] D. V. Claridge and L. M. Venanzi, *J. Chem. Soc.*, 1964, 3419.

[7] M. N. Vargaftik, I. I. Moiseev, and Ya. K. Syrkin, *Doklady Akad. Nauk S.S.S.R.*, 1962, **147**, 399 (*Chem. Abs.*, 1963, **58**, 13740c).

[8] J. Hiraishi, *Spectrochim. Acta*, 1969, **25A**, 749.

[9] D. B. Powell, J. G. V. Scott, and N. Sheppard, *Spectrochim. Acta*, 1972, **28A**, 327.

approximately equal modifications in the frequencies of the two bands arising from stage 1. It is apparent from Figure 2 that similar changes in the frequencies of both bands are only possible in case (a) and thus it is concluded that although both the observed bands are the result of considerable interaction between the two fundamental modes, the band *ca.* 1500 cm^{-1} has a greater contribution from ν(C=C) and that *ca.* 1250 cm^{-1} a greater contribution from δ(CH$_2$).

TABLE 2

Electronic spectra in the region 38,500—20,000 cm^{-1}

Complex	Bands (cm^{-1}) (molar extinction coefficients in parentheses)					
[Pd(CH$_2$:CH·CH$_2$·NH$_3$)Cl$_3$] [a]	23,250 (18·5)	29,500 (70)	32,200 (190)		36,500 (210)	
K[Pt(CH$_2$:CH·CH$_2$OH)Cl$_3$] [b]	23,000 (25)	29,700 (205)		33,800 (840)		37,400 (1970)
K[Pt(C$_2$H$_4$)Cl$_3$] [c]	23,200 (20) [d]	29,800 (250) [d]		34,400 (750)		37,700 (1360)

[a] Solution in glacial acetic acid containing 0·1M perchloric acid. [b] Solution in ethanol, results from ref. 12. [c] Solution in dilute aqueous HCl containing KCl, results from ref. 12. [d] From P. Natarajan and A. W. Adamson, *J. Amer. Chem. Soc.*, 1971, **93**, 5599. In addition the possible existence of a band at 26,300 cm^{-1} (ε = 30) was postulated as it improved the fit of the Gaussian analysis.

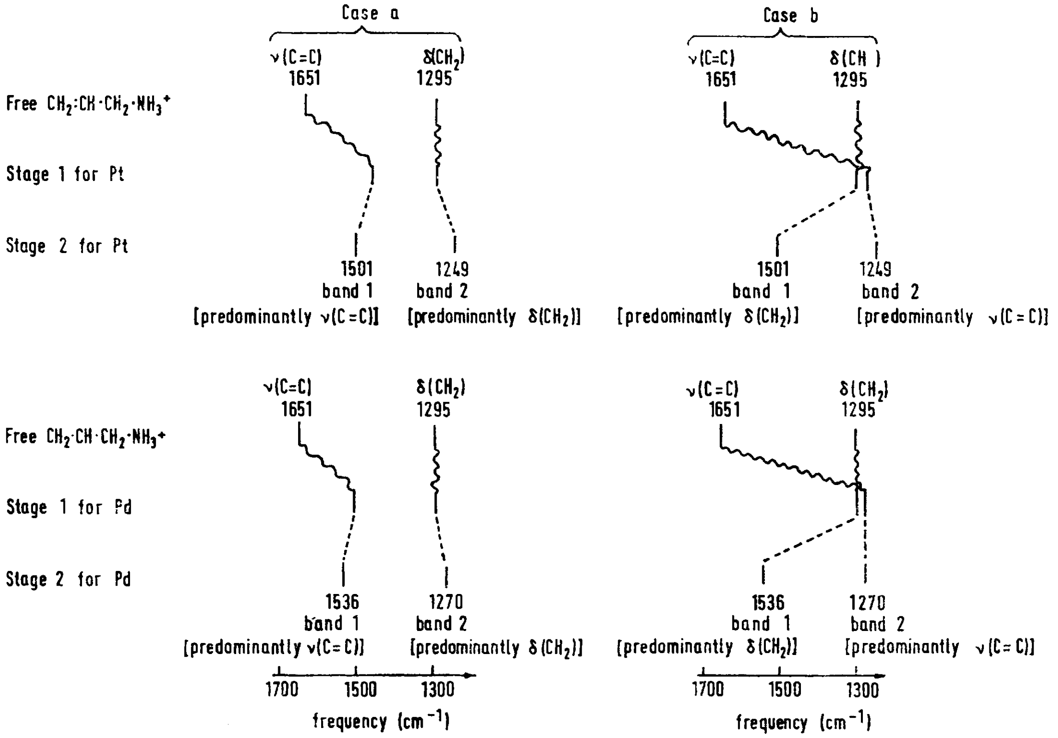

FIGURE 2 Schematic approach to the assignment of the vibrational spectra of [M(CH$_2$:CH·CH$_2$·NH$_3$)Cl$_3$], where M = Pt or Pd. Stage 1, influence of co-ordination on the C=C stretching and the CH$_2$ deformation frequencies of the free olefin; stage 2, interaction of the C=C stretching and CH$_2$ deformation modes in the complex as a result of their having the same symmetry. Case a, as a result of stage 1 ν(C=C) lies at higher frequencies than δ(CH$_2$); case b, as a result of stage 1 ν(C=C) lies at lower frequencies than δ(CH$_2$)

It has been suggested that a measure of the perturbation of the olefin on co-ordination can be obtained by summing the percentage lowering of bands 1 and 2 on co-ordination.[9] This is 12·40% in [Pt(CH$_2$:CH·CH$_2$·NH$_3$)Cl$_3$] and 8·84% in the palladium(II) analogue, which is consistent with the known relative strengths of these two metal–olefin bonds.[1]

Although [Pd(CH$_2$:CH·CH$_2$·NH$_3$)Cl$_3$] is insoluble in most non-aqueous solvents, it is sufficiently soluble in 0·1M-perchloric acid in glacial acetic acid to record its electronic spectrum below 38,500 cm^{-1}. In this range the complex exhibits four bands (Table 2) all of which have sufficiently low extinction coefficients to be assigned to either *d–d* or singlet–triplet transitions. The *d–d* transitions in K$_2$PdCl$_4$ have been observed[10] at 22,100 cm^{-1} (ε 200, assigned to the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition[11]), 25,000 cm^{-1} (ε 250, assigned to the $d_{xz},d_{yz} \longrightarrow d_{x^2-y^2}$ transition[11]), and 30,200 cm^{-1} (ε 1200, assigned to the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition[11]). It is not

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[10] C. M. Harris, S. E. Livingstone, and I. H. Reece, *J. Chem. Soc.*, 1959, 1505.

[11] P. Day, M. J. Smith, and R. J. P. Williams, *J. Chem. Soc.* (*A*), 1968, 668.

clear why these bands have lower extinction coefficients in $[Pd(CH_2{:}CH{\cdot}CH_2{\cdot}NH_3)Cl_3]$ where the symmetry around the palladium atom is lower than in $[PdCl_4]^{2-}$. The splitting of the energies of the *d*-orbitals in a D_{4h} and a C_{2v} environment is shown in Figure 3. The currently accepted assignment[11] of the spectrum of $[PdCl_4]^{2-}$ indicates that the order of the *d*-orbitals in this complex is that shown in Figure 3(d) as arising from a strong D_{4h} ligand field. Since olefins give rise to higher ligand fields than chloride ions[12] the relative energies of the *d*-orbitals in $[Pd(CH_2{:}CH{\cdot}CH_2{\cdot}NH_3)Cl_3]$ should be that shown in Figure 3(e) in which the energy of the d_{xz} orbital lies below that of the d_{yz} orbital due to the greater involvement of the former in π-back-donation to the olefin. Thus the bands in $[Pd(CH_2{:}CH{\cdot}CH_2{\cdot}NH_3)Cl_3]$ can be tentatively assigned as follows: 23,250 cm^{-1}, $d_{xy} \longrightarrow d_{xz-y^2}$; 29,500 cm^{-1}, $d_{yz} \longrightarrow d_{x^2-y^2}$; 32,200 cm^{-1}, $d_{xz} \longrightarrow d_{x^2-y^2}$; 36,500 cm^{-1}, $d_{z^2} \longrightarrow d_{x^2-y^2}$. It is noteworthy that $[Pd(CH_2{:}CH{\cdot}CH_2{\cdot}NH_3)Cl_3]$ shows no intense bands between 30,000 and 38,500 cm^{-1} whereas its platinum analogue exhibits two intense bands (at 34,700 cm^{-1}, ε 800 and 37,900 cm^{-1}, ε 1800) which have been assigned to platinum *d*→olefin π* transitions.[12] We can offer no explanation for the absence of these bands from the same or a lower energy region of the spectrum in palladium(II)–olefin complexes. We are also currently unable to account for the almost identical energies of the low energy bands in platinum(II)- and palladium(II)-olefin complexes which implies very similar ligand field splittings in the two series of complexes. Normally the ligand field splitting decreases on replacing platinum(II) by palladium(II).

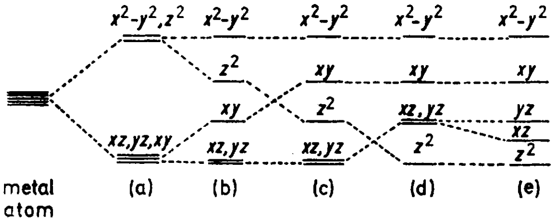

FIGURE 3 The splitting of the energies of the *d*-orbitals in D_{4h} and C_{3v} environments (the *z*-axis is perpendicular to the square-plane and in the C_{2v} environment the *x*-axis is coincident with the C_2 axis); (a), O_h; (b), weak D_{4h}; (c), medium D_{4h}; (d), strong D_{4h}; (e) strong C_{2v} fields.

$Na^+[Cl_2PdCl_2PdCl(CH_2{:}CH{\cdot}CH_2{\cdot}NH_3Cl)]^-$ is a red crystalline complex similar in structure to $[Cl_2PdCl_2PdCl(CH_3{\cdot}CH{:}CHX)]^-$, where $CH_3{\cdot}CH{:}CHX$ is an enol ester, which has been postulated as an intermediate in the palladium(II) catalysed *cis–trans*-isomerisation of enol esters in acetic acid.[13] Its formulation is based on: (i) the excellent elemental analysis; (ii) its instantaneous reaction with water or moist air to deposit palladium metal, which is consistent with the presence of a palladium(II)–olefin bond, (iii) the i.r. spectrum above 650 cm^{-1} is virtually identical to that of $[Pd(CH_2{:}CH{\cdot}CH_2{\cdot}NH_3)Cl_3]$ indicating a co-ordinated double bond and a free quaternary ammonium group. It is not strictly possible to distinguish on the evidence available between a 1 : 1 mixture of sodium chloride and the zwitterionic $[Cl_2PdCl_2PdCl(CH_2{:}CH{\cdot}CH_2{\cdot}NH_3)]$ and the sodium salt $Na^+[Cl_2PdCl_2PdCl(CH_2{:}CH{\cdot}CH_2{\cdot}NH_3Cl)]^-$ although we favour the latter because the product had a consistent analysis over several preparations.

EXPERIMENTAL

Preparation of the Complexes.—All precipitates were filtered off in a dry-box under 'white spot' nitrogen, washed with glacial acetic acid containing 0·1M-perchloric acid followed by sodium-dried light petroleum (b.p. 30—40 °C) and dried *in vacuo* before being analysed.

$(CH_2{:}CH{\cdot}CH_2{\cdot}NH_3^+)_2[PdCl_4]^{2-}$.—Allylamine (0·30 g; 5·0 mmol) was added dropwise at room temperature to a well-stirred solution of Na_2PdCl_4 (0·183 g; 0·5 mmol) in glacial acetic acid (100 ml) saturated with sodium chloride and containing 0·1M-perchloric acid. An immediate red precipitate formed (Found: C, 19·7; H, 4·1; N, 7·8. $C_6H_{16}Cl_4N_2Pd$ requires C, 19·75; H, 4·4; N, 7·7%).

$[Pd(CH_2{:}CH{\cdot}CH_2{\cdot}NH_3)Cl_3]$.—*Method* 1. Allylamine (0·30 g; 5·0 mmol) was added to a solution of Na_2PdCl_4 (0·183 g; 0·5 mmol) in glacial acetic acid (100 ml) containing 0·1M-perchloric acid and the solution heated to 65° for 5 min before being frozen rapidly by immersing the flask in liquid nitrogen. On thawing, fine yellow crystals, which were analysed as soon as they were dry, were obtained (Found: C, 13·2; H, 2·9; N, 5·1. $C_3H_8Cl_3NPd$ requires C, 13·3; H, 3·0; N, 5·2%).

Method 2. A suspension of $(CH_2{:}CH{\cdot}CH_2{\cdot}NH_3^+)_2[PdCl_4]^{2-}$ (0·10 g; 0·273 mmol) in glacial acetic acid (20 ml) containing 0·1M-perchloric acid was heated to 50 °C. The red crystalline material gradually became yellow, and after 5 min, the mixture was cooled and the yellow crystals filtered off (Found: C, 12·8; H, 2·7; N, 4·8. $C_3H_8Cl_3NPd$ requires C, 13·3; H, 3·0; N, 5·2%).

$Na[Cl_2PdCl_2PdCl(CH_2{:}CH{\cdot}CH_2{\cdot}NH_3Cl)]$.—Solutions of Na_2PdCl_4 (0·110 g; 0·3 mmol) in glacial acetic acid (200 ml) containing 0·1M-perchloric acid and allylamine (0·0174 g; 0·3 mmol) in the same solvent (200 ml) were mixed and kept at room temperature for a week during which time a red crystalline precipitate was slowly formed (Found: C, 7·2; H, 1·5; N, 2·7; Na, 5·0. $C_3H_8Cl_6NNaPd_2$ requires C, 7·1; H, 1·6; N, 2·8; Na, 4·5%).

Analyses.—Microanalyses were carried out at University College, London. Sodium was determined using a flame photometer after decomposing the sample in aqueous solution.

Spectra.—Electronic spectra were recorded on a Unicam SP 800 spectrophotometer and resolved into their component Gaussian bands using a DuPont 301 Curve Resolver. I.r. spectra were recorded on Beckman IR 11 and Perkin-Elmer 337 spectrophotometers and Raman spectra on Spex 1401 (krypton laser 5680 Å excitation) and Cary 81 (helium–neon 6328 Å excitation) spectrometers.

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[12] R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1967, 1322.

[13] P. M. Henry, *J. Amer. Chem. Soc.*, 1971, **93**, 3547.