Activation of Dichloromethane by Palladium(0) and Platinum(0) Phosphine Complexes: Synthesis and Structure of [{N($CH_2CH_2PPh_2$)$_3$}M(CH_2Cl)](BPh_4), M = Pd, Pt

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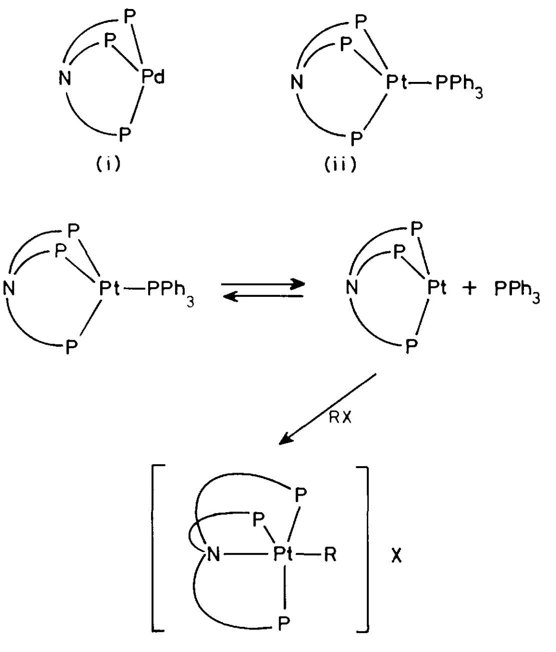
The Pd(0) trico-ordinate out-of-plane (np_3)Pd, [np_3 = N($CH_2CH_2PPh_3$)$_3$], and the Pt(0) pseudotetrahedral (np_3)Pt(PPh_3) complexes react, under mild conditions, with CH_2Cl_2 yielding (M–CH_2–Cl) complexes; [(np_3)Pt(CH_2Cl)]BPh_4·CH_2Cl_2 has been structurally characterised by *X*-ray analysis: variable temperature $^{31}P\{^1H\}$ n.m.r. spectroscopy measurements have shown that the eighteen electron complex (np_3)Pt(PPh_3) can dissociate in solution, giving the strong nucleophilic species (np_3)Pt.

The remarkable recent interest in halogenomethyl complexes of transition metals stems from their potential use as carbene precursors. Thus the oxidative addition of dihalogenomethanes to low valent metal complexes appears to be a useful way to generate (M–CH_2X) units. While many products have been isolated from oxidative addition of iodo and di-iodoalkanes,[1] the activation of dichloromethane requires strong nucleophiles and relatively few cases have been reported.[2]

The synthesis of a (chloromethyl)platinum(II) complex from a dichloromethane reaction has been accomplished only by the photoinduced addition of CH_2Cl_2 to (C_2H_4)Pt(PPh_3)$_2$.[2f] We report here that the complexes (np)$_3$)Pd and (np_3)Pt(PPh_3), [np_3 = tris(2-diphenylphosphinoethyl)amine], react under mild conditions with CH_2Cl_2 to afford five-co-ordinated chloromethyl derivatives with the formula [(np_3)M(CH_2Cl)]$^+$, in practically quantitative yields. The complex (np_3)Pd, (**1**), for which an out-of-plane trico-ordinate geometry (i) was ascertained by *X*-ray analysis, has recently been found to undergo facile oxidative addition with alkyl halides, to give five co-ordinated [(np_3)PdR]X derivatives.[3a,b]

The complex (np_3)Pt(PPh_3), (**2**), has been prepared, as yellow crystals, in almost quantitative yield, by the reaction shown in equation (1).

$$(C_2H_4)Pt(PPh_3)_2 + np_3 \xrightarrow[\text{THF/room temp.}]{\text{under } N_2} (np_3)Pt(PPh_3) + PPh_3 + C_2H_4 \quad (1)$$



Scheme 1.

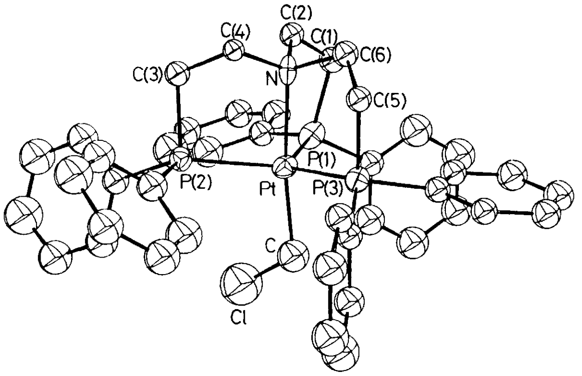


Figure 1. Perspective view of the complex cation $[(np_3)Pt(CH_2Cl)]^+$. ORTEP drawing with 30% probability ellipsoids. Important bond distances and angles: (Pt-P) 2.343(9)—2.399(10), (Pt-N) 2.18(2), (Pt-C) 2.06(4), (C-Cl) 1.76(5) Å, (P-Pt-P) (117.1—121.9), (N-Pt-P) (83.4—86.0), (N-Pt-C) 173.8(14), (Pt-C-Cl) 118.3(21)°.

The i.r. spectrum of (**2**) shows a band at 2800 cm^{-1}, characteristic of the (C–H) stretching vibration of (CH_2–N), in np_3 metal complexes where the tripodal phosphine acts as a tridentate ligand, with the apical nitrogen atom unco-ordinated.[3b,4] These data, together with the ${}^{31}P\{^1H\}$ n.m.r. spectrum,† which shows a sharp doublet (3P) at δ −11.9 and a sharp quartet (1P) at δ 12.4 [^2J(PP) 80 Hz], with ^{195}Pt satellites [^1J(PPt) 3657 Hz, np_3; ^1J(PPt) 4438 Hz, PPh_3], are consistent with a pseudotetrahedral geometry (ii).‡

The reactions of (**1**) and (**2**) with CH_2Cl_2 occur at room temperature. Complexes of formulae $[(np_3)Pd(CH_2Cl)]BPh_4 \cdot 0.5thf \cdot 2CH_2Cl_2$, (**3**), (thf = tetrahydrofuran) (yield 95%) and $[(np_3)Pt(CH_2Cl)]BPh_4 \cdot CH_2Cl_2$, (**4**) (yield 93%) can be isolated by addition of $NaBPh_4$ in thf/hexane or ethanol respectively, followed by solvent evaporation.§ ^{1}H N.m.r. spectra¶ of (**3**) and (**4**) show respectively, a quartet at δ 4.44 [^3J(HP) 7.5 Hz] and a quartet at δ 4.4 [^3J (HP) 7.7 Hz] with ^{195}Pt satellites [^2J(HPt) 57 Hz], attributable to the (M–CH_2–Cl) groups, the three phosphorus atoms of np_3 being equivalent. The ${}^{31}P\{^1H\}$ n.m.r. spectra in CD_2Cl_2 solution show a singlet at δ 10.31 and a singlet at δ 12.11 with ^{195}Pt satellites [^1J(PPt) 3059 Hz] for (**3**) and (**4**) respectively.

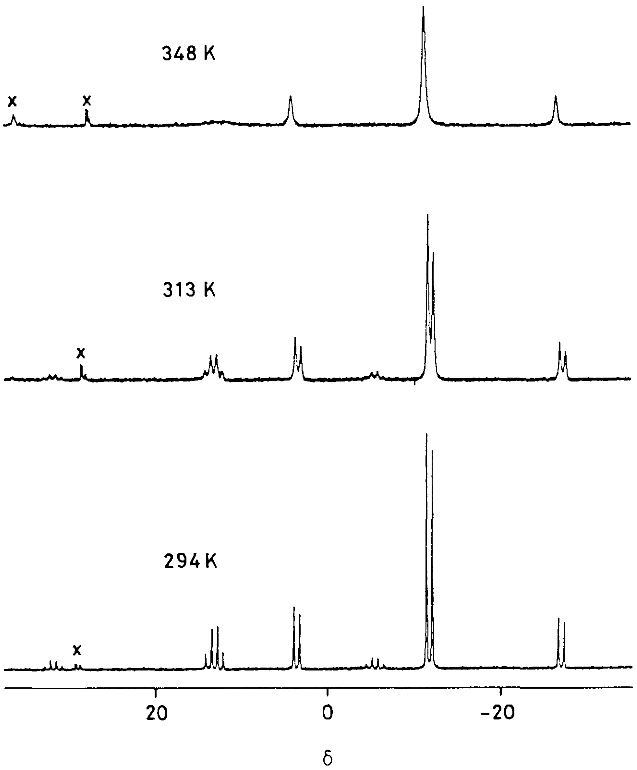


Figure 2. The variable-temperature ${}^{31}P\{^1H\}$ n.m.r. spectrum of $(np_3)Pt(PPh_3)$ (the signals marked by x are due to impurities).

A complete single crystal structure determination of (**4**) was carried out.** The molecular structure of (**4**) consists of $[Pt(np_3)(CH_2Cl)]^+$ cations, BPh_4^- anions and interspersed molecules of CH_2Cl_2. Figure 1 shows a perspective view of the cation with selected bond distances and angles. The metal atom displays a slightly distorted trigonal bipyramidal

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† Recorded at 121.421 MHz by a Varian VXR 300 spectrometer, in C_6D_6 solution referenced to external H_3PO_4.

‡ A similar spectrum has been reported for the complex (triphos)$Pt(PPh_3)$, (triphos = 1,1,1-tris(diphenylphosphinomethyl)-ethane).[5]

§ The reaction of (**2**) has been monitored by ${}^{31}P\{^1H\}$ n.m.r. spectroscopy measurements in CD_2Cl_2. Thus, after *ca.* 1 h 60% of (**2**) had reacted, but 8 h were necessary for the reaction to be completed. The reaction of (**1**) is practically immediate. Complex (**4**) appears less stable than (**3**), as it is decomposed by ethanol.

¶ Recorded at 299.944 MHz, in CD_2Cl_2 solutions referenced to Me_4Si.

** *Crystal data* for (**4**): $[(np_3)Pt(CH_2Cl)]BPh_4 \cdot CH_2Cl_2$, monoclinic, space group $P2_1/n$, a = 34.601(9), b = 17.136(5), c = 10.718(3) Å, β = 94.56(8)°, Z = 4. Data collection was carried out on an Enraf-Nonius CAD4 diffractometer using the ω scan technique with graphite monochromatised (Mo-K_α) radiation within $2\theta \leqslant 40°$. The structure was solved by the heavy atom method, and refined by full-matrix least-squares to give R and R_w factor values both of 0.069 for 2260 absorption corrected (μ = 23.4 cm^{-1}) reflections having [$I \geqslant 3\sigma(I)$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

geometry with the CH_2Cl group in the axial position *trans* to the central nitrogen ligand. The bonding mode of the CH_2Cl fragment is fully comparable to that found in $[Rh(Me_2PCH_2CH_2\text{-}PMe_2)_2Cl(CH_2Cl)]^+$,[2a] [(C–Cl) = 1.76(1) Å, (Rh–C–Cl) = 118.3(2)°], as well as to that reported for *cis*-$[Pt(PPh_3)_2(CH_2I)I]$[1f], in this latter case, however, a larger pyramidalisation of the CH_2–X carbon is observed, probably due to the different ligand crowding around the metal centres.

Bond distances and angles within the co-ordination polyhedron are comparable to those of the closely related $[Pd(np_3)CH_3]^+$ complex, where the (Pd–P), (Pd–N) and (Pd–C) are 2.357(4), 2.23(2) and 2.10(3) Å respectively.[3b] Obviously a similar structure must be attributed to (**3**).

The close reactivities of (**1**) and (**2**)†† suggests, in spite of the room temperature ^{31}P n.m.r. spectrum, that the actual strong nucleophile promoting oxidative addition is an unsaturated trico-ordinate $(np_3)Pt$ species, with geometry (i). Indeed, variable temperature ^{31}P n.m.r. spectra of (**2**) in C_6D_6 solution (Figure 2) have shown that the PPh_3 ligand (and only this!) is dissociating at an appreciable rate up to 313 K. This finding is corroborated by the related ^{31}P spectra in the presence of PPh_3. Thus, we can propose Scheme 1 for the oxidative addition reactions of (**2**).‡‡

This tendency for the out-of-plane trico-ordinate platinum metal complexes (ii) to give oxidative additions, which appears to be stronger than that of the phosphine planar trico-ordinate species, seems in agreement with recent MO studies. In fact, it has been shown when a d^{10} ML_3 system is forced to be pyramidal it possesses a high-lying occupied *xz*, *yz* pair, favourable for oxidative addition in both its energy and hybridisation.[7]

Received, 19th July 1988; Com. 8/02902D

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†† Complex (**2**) has also been found to react with alkyl halides to give five co-ordinated derivatives of formula $[(np_3)PtR]X$; additionally (**2**) is capable of reacting with ethanol, in the presence of $NaBPh_4$, to afford the five-co-ordinated hydride $[(np_3)PtH]BPh_4$.[6]

‡‡ The dissociation reaction probably slows down the overall process with respect to the palladium complex.

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