Binuclear Platinum(II)–dppm Acetylides and the Formation of Fluxional Complexes of the Type [Pt(η^1-dppm)$_2$ (C≡CR)$_2$] (dppm = $Ph_2PCH_2PPh_2$)

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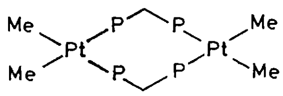
High-yield syntheses of two new types of dppm ($Ph_2PCH_2PPh_2$) complexes are described: (i) the fluxional complexes *trans*-[Pt(C≡CR)$_2$(η^1-dppm)$_2$], and (ii) the 'face-to-face' binuclear complexes [Pt_2(C≡CR)$_4$(η^2-dppm)$_2$] (R = Ph or *p*-tolyl).

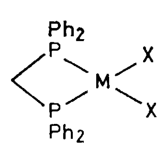
There is much interest in co-ordination compounds containing the ligand $Ph_2PCH_2PPh_2$ (dppm), *e.g.* in complexes with metal–metal bonds,[1] in 'A-frames,'[2] and in binuclear species containing 8-membered rings, such as (1).[3] The ligand dppm can also form 4-membered chelate rings of type (2).

It is well established that complexes of the type [$PtMe_2(PR_3)_2$] have the methyl ligands mutually *cis*.[4–6] A *cis*-$PtMe_2$ arrangement is also found in the binuclear species (1), which shows interesting fluxional behaviour but is unstable in solution and slowly reverts to the mononuclear species (2; M = Pt, X = Me).[3] However, it has also been established that complexes of the type *trans*-[Pt(C≡CR′)$_2$L$_2$] (L = tertiary phosphine) are much more stable than the corresponding *cis*-complexes.[5–9] One might thus expect that a binuclear complex of type (3) (see Scheme 1), with mutually *trans* P-nuclei, would be stable with respect to decomposition to (2; M = Pt, X = C≡CR).

We have now treated (2; M = Pt, X = Cl) with 2 mol. equiv. of LiC≡CR (R = Ph or *p*-tolyl) in tetrahydrofuran (THF)–toluene and obtained the binuclear complexes (3) as yellow, crystalline, air-stable complexes in *ca.* 90% yields. The 'face-to-face' structure, with *trans*-phosphines, follows from (i) microanalytical and molecular weight data, (ii) a single band in the i.r. spectrum due to ν(C≡C) (at 2105 cm^{-1}, R = *p*-tolyl), (iii) the value of ^1J(Pt–P) = 2836 Hz (R = *p*-tolyl) typical of *trans*-phosphines co-ordinated to platinum(II), (iv) a

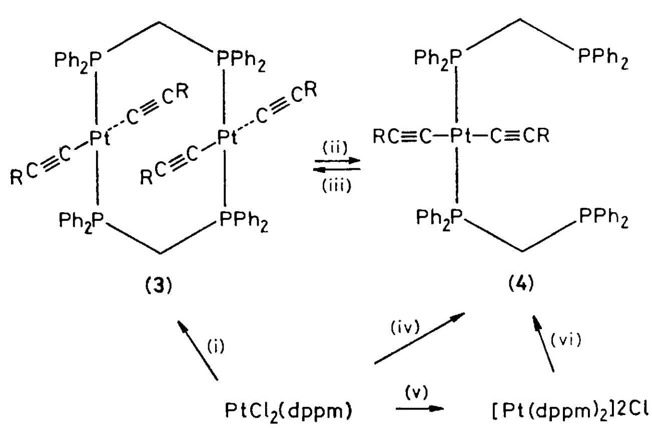


(1)



(2)

1:8:18:8:1 quintet pattern, in the ^{1}H–{^{31}P} n.m.r. spectrum, due to CH_2 (coupled to platinum-195),[10] and (v) the complex ^{31}P–{^{1}H} n.m.r. pattern due to an AA′A″A‴X_n spin system. 'Face-to-face' complexes of rhodium of the type [$Rh_2Cl_2(CO)_2$-(dppm)$_2$] are known[12,13] and face-to-face complexes have been postulated as intermediates in platinum(II) chemistry,[14,15] but not hitherto prepared. These binuclear complexes of type (3) are stable in $CDCl_3$ solution for several days but react readily with dppm (in CH_2Cl_2 solution or C_6H_6 suspension at 20 °C) to give the unusual complexes, *trans*-[Pt(C≡CR)$_2$(dppm)$_2$] (4), containing monodentate dppm, in essentially quantitative yields. On heating a toluene solution of *trans*-[Pt(C≡CPh)$_2$-(dppm)$_2$] under reflux the binuclear species (3; R = Ph) is



Scheme 1. *Reagents and conditions:* (i) RC≡CLi in THF–toluene, reflux 14 h (R = Ph or *p*-tolyl), (ii) 1.3 mol. equiv. of dppm in C_6H_6 or CH_2Cl_2 (R = Ph or *p*-tolyl), (iii) reflux in toluene (R = Ph), (iv) RC≡CLi and dppm in THF–benzene, reflux 1 h, (v) dppm in CH_2Cl_2, (vi) RC≡CLi in THF (R = Ph).

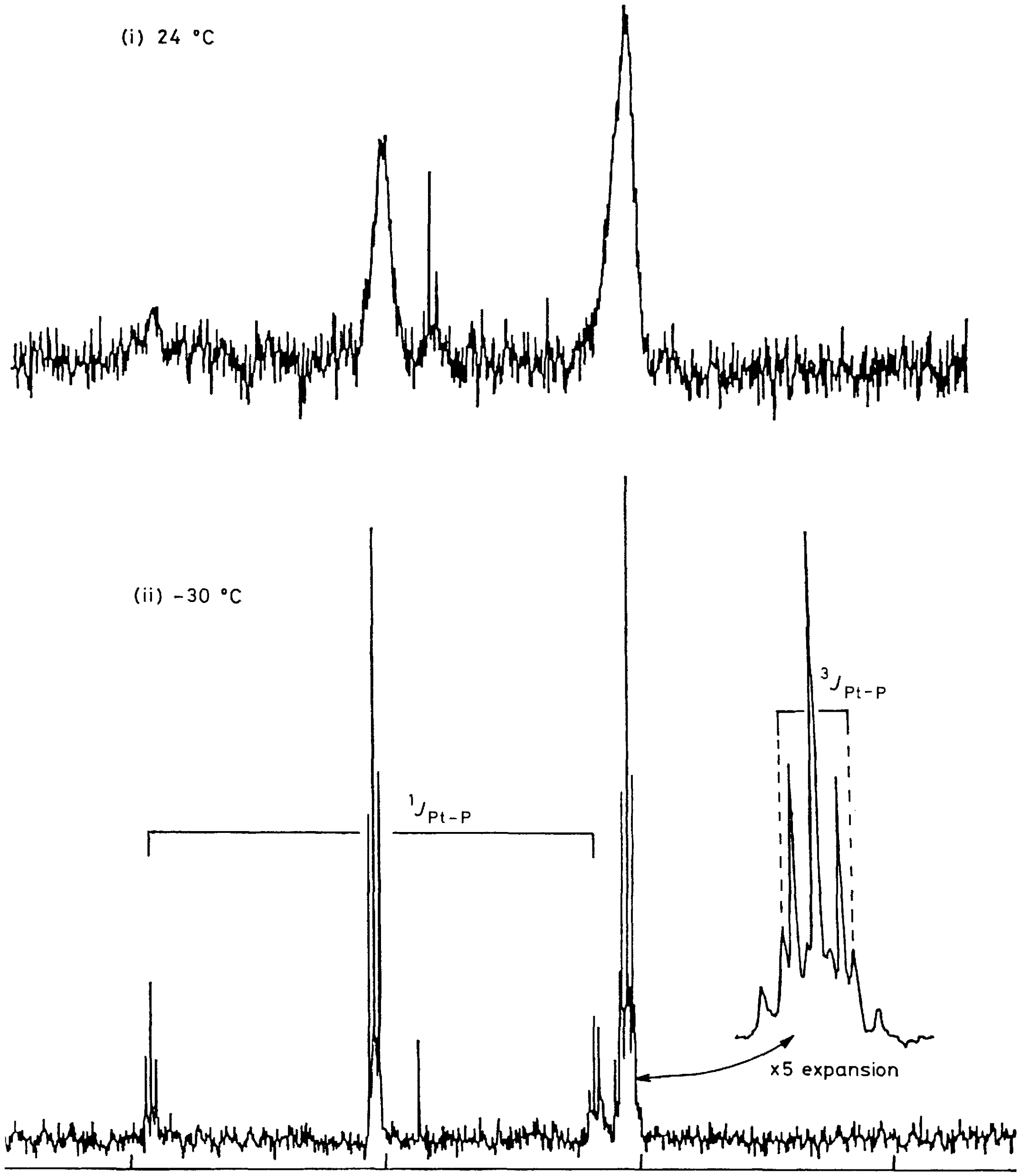


Figure 1. $^{31}P-\{^1H\}$ N.m.r. spectrum of *trans*-[Pt(C≡CPh)$_2$(η^1-dppm)$_2$] in $CDCl_3$: (i) at 24 °C, (ii) at −30 °C. The 'virtual triplets' at −30 °C are a consequence of the large value of ^2J(P–Pt–P) (*trans*) in the AA′XX′ pattern. The spectrum at 24 °C is independent of concentration. When heated above 24 °C (in [$^2H_8$]toluene) the spectrum of *trans*-[Pt(C≡CPh)$_2$(η^1-dppm)$_2$] broadens but before the fast exchange limit can be reached decomposition to give the 'dimer' (**3**) and free dppm occurs. The complexes *trans*-[Pt(C≡CR)$_2$(η^1-dppm)$_2$], with R = *p*-tolyl or methyl, are also fluxional at room temperature and give similar spectra to the phenylacetylide complex at −30 °C.

precipitated in 60% yield. Complexes of type (**4**) can easily be prepared from *cis*-[PtCl$_2$(dppm)] in one step by treatment with LiC≡CR (R = Ph or *p*-tolyl) (2 mol. equiv.) in the presence of 1 mol. equiv. of dppm. They can also be prepared by treating the salts [Pt(dppm)$_2$]2Cl[16] with LiC≡CR (2 mol. equiv.) in THF. These and other conversions are shown in Scheme 1. The complexes of type (**4**) are fluxional, as shown by $^{31}P-\{^1H\}$ n.m.r. spectroscopy at variable temperatures (see Figure 1). At or below −30 °C the $^{31}P-\{^1H\}$ n.m.r. spectrum (Figure 1, ii) corresponds to the static structure (**4**; R = Ph). The line-widths and appearance of the spectrum at 24 °C (Figure 1, i) are independent of the concentration of (**4**), showing that the process is intramolecular and we interpret the process in terms of a rapid P–P exchange, *viz.* PtPh$_2$PCH$_2\overset{*}{P}$Ph$_2$ ⇌ PtPh$_2\overset{*}{P}$CH$_2$-PPh$_2$. There is no tendency for complexes of type (**4**) to revert to chelates of type (**2**; M = Pt, X = C≡CR). This contrasts with the unstable nickel complex [NiCl$_2$(η^1-dppm)$_2$] which readily reverts to the chelate [NiCl$_2$(η^2-dppm)] in solution.[17,18]

Preliminary work suggests that complexes of types (**3**) and (**4**) have much potential in synthesis. Thus the complexes of type (**4**) act as diphosphines without fission of the P–Pt–P linkages. They may be oxidised (H_2O_2) to *trans*-[Pt(C≡CR)$_2$ {PPh$_2$CH$_2$P(=O)Ph$_2$}$_2$], quaternized with methyl iodide to give *trans*-[Pt(C≡CR)$_2$ {Ph$_2$PCH$_2$PPh$_2$Me}$_2$]$^{2+}$2I$^-$, and react with metal salts to give heterobimetallic systems, which we are investigating. We are also studying the selective fission of the acetylide groups in complexes of type (3).

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