Journal of Organometallic Chemistry, 238 (1982) 231—234
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

BINUCLEAR ALKYNYLPLATINUM(II) COMPLEXES

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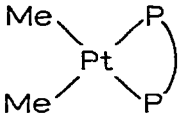
(Received April 6th, 1982)

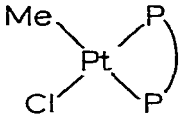
Summary

New face-to-face dimers of formula $[Pt_2(C{\equiv}CR)_4(\mu\text{-dppm})_2]$, R = CF_3 or CH_3 and dppm = $Ph_2PCH_2PPh_2$, have been prepared but attempts to prepare binuclear diarylplatinum(II) complexes have been unsuccessful.

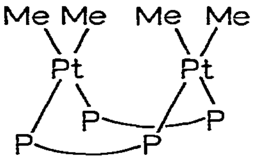
In earlier papers it has been shown that both $PtMe_2(dppm)$ and $PtClMe(dppm)$ can exist in both a monomeric form with chelating dppm ligands (dppm = $Ph_2PCH_2PPh_2$) or in binuclear form with bridging dppm ligands, structures (I—IV) [1,2].



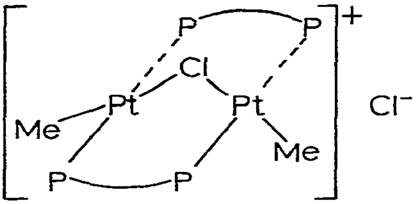
(I)



(II)



(III)



(IV)

It has also been shown that in $[Pt_2Me_3(\mu\text{-dppm})_2]^+$ there is no bridging methyl group whereas in $[Pt_2H_3(\mu\text{-dppm})_2]^+$ there is a bridging hydride [3,4]. Since alkynyl and aryl groups are better bridging groups than are methyl groups in many organometallic compounds [5], we have investigated the chemistry of alkynyl and aryl complexes of platinum with dppm ligands in the hope of isolating complexes with μ-alkynyl or μ-aryl groups. This aim has not been successful but evidence is presented that the alkynyl derivatives have face-to-face structures (V), rather than monomeric structures (VI).

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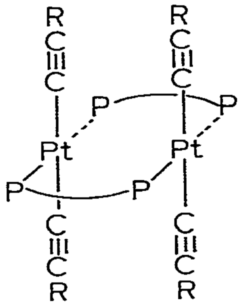
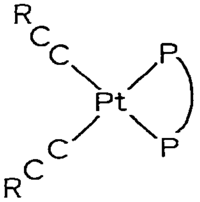


(Va), R = Me
(Vb), R = CF_3



(VI)

These face-to-face dimers have not previously been characterised in $Pt_2(\mu\text{-dppm})_2$ complexes although they are well-known in rhodium(I) and palladium(II) complexes [6—9] *.

Experimental

NMR spectra were recorded using a Varian XL 100 NMR spectrometer, and general techniques have been described elsewhere [1,3,4].

trans-Pt(4-MeC$_6$H$_4$)$_2$(SMe$_2$)$_2$

This was prepared from a suspension of $[PtCl_2(SMe_2)_2]$ (0.5 g) in dry ether with excess $(4\text{-MeC}_6H_4)_2Mg$ (5 ml, 1.1 *M*, prepared from 4-MeC_6H_4MgBr in ether with 1,4-dioxane and centrifuged to remove the $MgBr_2$-dioxane complex) under an atmosphere of N_2. The solution was stirred for 3 h at room temperature, then hydrolysed with aqueous ammonium chloride. The organic layer was separated and the residue extracted with dichloromethane. The combined organic layers were dried and evaporated under vacuum to give the product, which was recrystallised from CH_2Cl_2 ether. Yield 45%. Anal.: Found: C, 42.9; H, 5.3. $C_{18}H_{26}S_2Pt$ calcd.: C, 43.1; H, 5.2%. NMR in C_6D_6: δ(MeS) 1.70 ppm, ^3J(PtH) 61 Hz; δ(MeC) 2.70 ppm. The product was air stable.

[Pt(4-MeC$_6$H$_4$)$_2$(dppm)]

To a solution of *trans*-$[Pt(4\text{-MeC}_6H_4)_2(SMe_2)_2]$ (0.05 g) in ether was added dppm (0.05 g) in ether. The product formed as a white precipitate, which was filtered off and washed with ether. Yield 80%. Anal.: Found: C, 61.2; H, 4.8. $C_{39}H_{36}P_2Pt$ calcd.: C, 61.5; H. 4.7%. NMR in $CDCl_3$: $\delta(CH_2P_2)$ 4.30 ppm, ^2J(PH) 9.4, ^3J(PtH) 21.6 Hz; $\delta(CH_3C)$ 2.14 ppm; $\delta(^{31}P)$ —42.1 ppm, ^1J(PtP) 1400 Hz.

[PtCl(4-MeC$_6$H$_4$)(dppm)]

This was prepared by reaction of $[Pt(4\text{-MeC}_6H_4)_2(dppm)]$ (0.18 g) in CH_2Cl_2 with ethereal HCl (0.23 mmol). The white powder which precipitated was filtered off and washed with ether. Yield 84%. Anal.: Found: C, 54.0; H, 4.2. $C_{32}H_{29}ClP_2Pt$ calcd.: C, 54.5; H, 4.1%. NMR in $CDCl_3$: $\delta(CH_2P_2)$ 4.32 ppm, ^2J(PH) 11, 9, ^3J(PtH) 46 Hz; $\delta(CH_3)$ 2.18 ppm; $\delta(^{31}P)$ —44.9, $^1J(PtP^A)$ 1225; $\delta(P^B)$ —45.8, $^1J(PtP^B)$ 3850 Hz, ^2J(PP) 41 Hz.

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* Compounds V, R = Ph, 4-MeC_6H_4, have recently been reported. P.G. Pringle and B.L. Shaw, J. Chem. Soc. Chem. Comm., (1982) 581.

[{Pt(C≡CMe)$_2$(dppm)}$_2$]

This was prepared by reaction of [PtCl$_2$(dppm)] (0.4 g) in benzene with excess MeC≡CLi in ether (prepared from propyne and methyllithium) at room temperature for 3 h. After hydrolysis and work-up in the usual way, the product was recrystallised from CH$_2$Cl$_2$/ethanol. Yield 54%. Anal.: Found: C, 56.9; H, 4.3. $C_{31}H_{28}P_2Pt$ calcd.: C, 56.6, H, 4.3%. IR (Nujol) ν(C≡C) 2130 cm^{-1}; ν(PtCl) absent. NMR in CDCl$_3$: δ(CH$_2$P$_2$) 3.80 ppm, ^3J(PtH) 24 Hz; δ(CH$_3$) 1.32 ppm, ^4J(PtH) 13 Hz; δ(^{31}P) 7.4 ppm, ^1J(PtP) 2600 Hz.

[{Pt(C≡CCF$_3$)$_2$(dppm)}$_2$]

This was prepared in a similar way but using CF$_3$CCLi in ether, and was recrystallised from CH$_2$Cl$_2$/petroleum ether. Yield 48%. Anal.: Found: C, 49.0; H. 3.1; F, 13.9. $C_{31}H_{22}F_6P_2Pt$ calcd.: C, 48.6; H, 2.9; F, 14.9%. IR (Nujol), ν(C≡C) 2120, 2137, 2162 cm^{-1}, ν(PtCl) absent. NMR in CDCl$_3$; δ(CH$_2$P$_2$) 4.32 ppm, ^2J(PH) 5 Hz, ^3J(PtH) 36 Hz; δ(^{31}P) 6.52 ppm, ^1J(PtP) 3080 Hz; ^3J(PtP) 40 Hz; δ(CF$_3$) 46.7 ppm from CFCl$_3$, ^4J(PtF) 28 Hz.

Results and discussion

Attempts to prepare binuclear diarylplatinum complexes with dppm ligands analogous to complex III were unsuccessful. Thus reaction of either *trans*-[Pt(4-MeC$_6$H$_4$)$_2$(SMe$_2$)$_2$] with dppm or of [PtCl$_2$(dppm)] with ditolylmagnesium gave only the monomeric [Pt(4-MeC$_6$H$_4$)$_2$(dppm)] with chelating dppm. This is readily characterised as a monomer by the ^{31}P chemical shift of δ −42.1 ppm (from trimethylphosphate reference) and by the low value of ^1J(PtP) of 1400 Hz, typical of phosphorus atoms in a strained ring and *trans* to a carbon donor with a high *trans* influence [1,10]. The structure is the same as that for [PtPh$_2$(dppm)] which has been established by X-ray crystallography [10].

More interesting was the reaction of [PtCl$_2$(dppm)] with trifluoropropynyllithium to give the binuclear complex Vb. This is characterised as a dimer by the ^{31}P NMR spectrum which contains a singlet at δ +6.52 ppm, with two sets of complex satellites due to the isotopomers containing ^{195}Pt atoms with the coupling constants ^1J(PtP) 3080 Hz and ^3J(PtP) 40 Hz. The shift is similar to that found in many "A-frame" complexes of dppm, while the magnitude of ^1J(PtP) indicates the presence of mutuallly *trans* phosphines [1—4]. The ^{1}H NMR spectrum contains a single resonance due to the CH$_2$P$_2$ protons with the 1/8/18/8/1 intensity pattern due to coupling with ^{195}Pt expected for a complex with μ-dppm ligands and with a plane of symmetry containing the Pt$_2$P$_2$C skeleton [1—4]. The ^{19}F NMR spectrum contained a singlet with a coupling constant ^4J(PtF) very similar to values found for several complexes *trans*-[Pt(C≡CCF$_3$)$_2$L$_2$] [11]. Together with the analytical data, this provides firm evidence for the binuclear structure (Vb), and is certainly not consistent with the monomeric structure VI. Similarly, the propynylplatinum complex Va is characterised spectroscopically. This complex is less soluble than Vb and decomposed slowly in solution making it more difficult to characterise. In some synthesis of Va a second product was formed having δ(^{31}P) at −28.6 ppm as well as at +7 ppm, ^1J(PtP) 2600 Hz, the high field peak showing no resolved coupling to ^{195}Pt. The appearance is suggestive of a monodentate dppm ligand as seen previously in $[Pt_2H(\mu\text{-dppm})_2(\eta'\text{-dppm})]^+$ [12]. The ^1H NMR spectrum contained CH_3C and CH_2P_2 signals with relative intensities of 3/2 suggesting a possible formulation as *trans*-$[Pt(CCMe)_2(\eta^1\text{-dppm})_2]$ but the complex could not be purified and characterised further.

The methyl, aryl and alkynyl derivatives display quite different behaviour, and it is interesting to speculate on the reasons. In platinum(II) complexes with monodentate phosphine ligands, L, the derivatives $[PtR_2L_2]$ are always *cis* when R = Me, they may be *cis* or *trans* when R = aryl and they are almost always *trans* when R = alkynyl [13]. Thus the different structures adopted in complexes III and V may simply reflect the stereochemical preference of the methyl and alkynyl ligands. Whilst monomeric I is more stable than dimeric III, it is clear that the reverse is true for the alkynyl derivatives and that V is more stable than VI. Again this probably just reflects the preference for the *trans*-bis(alkynyl)platinum structure. The face-to-face structure V should also be favored due to the low steric demands of the alkynyl ligands. It is not clear why binuclear arylplatinum complexes analogous to III or V could not be prepared.

We have not been able to convert either [Pt(4-tolyl)$_2$(dppm)] or complexes V to the cationic dimers $[Pt_2R_3(\mu\text{-dppm})_2]^+$ by reaction with HCl, H[BF$_4$] or H[PF$_6$], so that we cannot comment on the ability of the aryl or alkynyl groups to bridge in these desired compounds.

Acknowledgments

We thank NSERC (Canada) for generous financial support.

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