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THE SYNTHESIS OF CATIONIC "A-FRAME" ORGANOPLATINUM(II) DIMERS

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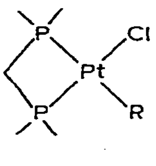
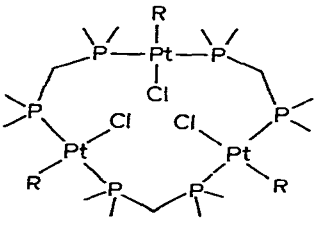
Summary

The complex [Pt(COPh)Cl(cod)] (cod = 1,5-cyclooctadiene) reacts with $Ph_2PCH_2PPh_2$ (dppm) to yield the cationic "A-frame" organoplatinum(II) dimer, $[Pt_2(\mu\text{-Cl})(\mu\text{-dppm})_2(COPh)_2]Cl$. The phenyl and methyl analogues yield both mononuclear [PtRCl(dppm)] and the corresponding dimeric products. Previous work on the methylplatinum complex is not substantiated by these results.

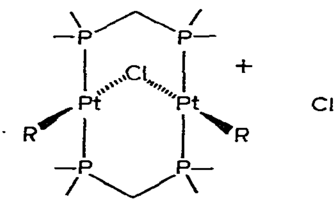
During investigations of the chelate effect of bidentate diphosphines, Bennett and co-workers described [1] the effects of varying the chelate-bite of the ligands $Ph_2P\{CH_2\}_nPPh_2$ on the molecularity of the corresponding $[PtXY(Ph_2P\{CH_2\}_nPPh_2)]_x$ (X = Y = Cl, Me; X = Cl, Y = Me; n = 1, 2, 3) complexes. Of particular interest is the reaction of [PtMeCl(cod)] with $Ph_2PCH_2PPh_2$(dppm) which was reported to yield both the monomer [PtMeCl(dppm)], I, and an oligomer, $[\{PtMeCl(dppm)\}_n]$ which was believed to be a trimeric species, II, on the basis of ^{31}P NMR data, obtained by INDOR techniques and molecular weight data.



I (R = Me, Ph)



II



III (R = Me, Ph, COPh)

Here we report the reactions of the ligand dppm with the related complexes [PtRCl(cod)] (R = Ph, COPh) and show that the oligomeric products are not neutral trimeric species, but rather cationic "A-frame" organoplatinum(II) dimers, III. Comparison of our results with those of other workers for the methyl analogue shows that the latter may also be reformulated similarly.

Initially we observed that the reaction of [Pt(COPh)Cl(cod)] with dppm in chloroform solution yielded a yellow crystalline product and that its $^{31}P\{^1H\}$ NMR spectrum was in accord with the formation of a single phosphorus-containing species. The spectrum appeared entirely typical of the AA'A"A'''XX' spin-system [2] and the magnitudes of the parameters obtained (Table 1) suggested that the dppm ligand was bridging rather than chelating. Thus, the value of ^1J(Pt, P) is typical of the P *trans* to P arrangement as found in a dppm-bridged structure, but not consistent with the P *trans* to Cl arrangement found in a halide-bridged complex where the bidentate ligand is chelating [2].

The first indication that the complex was ionic came when reaction with silver triflate, $AgOSO_2CF_3$, produced a white precipitate of silver chloride, but did not significantly alter the $^{31}P\{^1H\}$ NMR spectrum. Such observations are indicative of a simple anion exchange. In order to confirm the ionic nature of the product, conductivity measurements were obtained at a series of concentrations in acetonitrile solution [3]. The slope of a plot of $\Lambda_0 - \Lambda_E$ vs. $C^{1/2}$ was 544 ohm^{-1} l$^{1/2}$ equiv$^{-1/2}$, clearly indicative of an ionic complex (where Λ_E = conductance at equivalent concentration, C, and Λ_0 = extrapolated conductance at infinite dilution, $C = 0$.) Interestingly, the plot showed some deviation from linearity at higher concentrations (vide infra). To confirm that the same species was present in chloroform and acetonitrile solutions, the $^{31}P\{^1H\}$ NMR spectrum was obtained in MeCN-d_3 (Table 1) and was found to be consistent with that observed for $CDCl_3$ solutions. The spectra typical of this spin-system are extremely complex, consisting of sub-spectra from components with either no active platinum centres ($I = \frac{1}{2}$, abundance = 33.8%), one active centre or two active centres. The latter isotopomer is only ca. 11% total abundance and thus the INDOR method previously used to examine the analogous methyl system is not to be recommended.

The data so far discussed are entirely in accord with a product of structure III. To examine whether the complex existed as discrete ions in solution, molecular weight data were obtained osmometrically for chloroform solutions.

TABLE 1

$^{31}P\{^1H\}$ NMR SPECTROSCOPIC DATA OF ORGANOPLATINUM(II) dppm DERIVATIVES

Complex	δP (ppm) [a]	^1J(Pt, P) (Hz)	^3J(Pt, P) (Hz)	^2J(P, P)	^4J(P, P)
[PtPhCl(dppm)] [b]	—43.2	3909			
	—40.3	1213	—	41.5	—
[PtMeCl(dppm)] [b]	—37.1	3921			
	—32.3	1235	—	41.5	—
$[Pt_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2(COPh)_2]Cl$ [b]	5.9	3354	48	28	≤3
$[Pt_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2(COPh)_2]Cl$ [c]	6.4	3355	49	27	≤3
$[Pt_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2Ph_2]Cl$ [b]	8.4	3037	39	29	≤3
$[Pt_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2Me_2]Cl$ [b]	13.3	3030	34	30	≤3

[a] Relative to external H_3PO_4, more positive shifts represent deshielding. [b] $CDCl_3$ solution. [c] MeCN-d_3 solution.

The results thus obtained were irreproducible when a low concentration of the complex was used; however, at high concentrations (ca 0.5×10^{-2} mol l^{-1} based on the formula weight of III) a molecular weight of 1360 was obtained. This molecular weight is consistent with a neutral dimer of formula [{Pt(COPh)-Cl(dppm)}$_2$] (MW = 1440) and would initially appear to be in disagreement with formulation of the product as III. However, Dixon and co-workers have examined the problem of obtaining molecular weight data osmometrically for large, complex ions [4] and have shown that the derived molecular weight will tend to that of the undissociated neutral derivative at high concentration, if ion association occurs in solution. Evidence that ion association does occur with the present system comes from the conductivity studies previously mentioned, where deviations from linearity at high concentration occur, a common problem when ion association is present [3].

Additional evidence that structure III is the correct formulation comes from the solid state infrared spectrum of the product, which shows no absorptions in the region 250—330 cm^{-1}, where ν(M—Cl—M) modes occur in symmetrical cationic platinum(II) dimers of bidentate diphosphines [5], but a weak band at ca. 235 cm^{-1} which may be attributed to the single M—Cl—M bridging mode, *trans* to the high *trans*-influence aroyl group. The latter absorption occurs as a shoulder on the cut-off region of the CsI optics and accordingly any assignment must be tentative.

The analogous reaction of [PtPhCl(cod)] with dppm yielded a product whose $^{31}P\{^1H\}$ NMR spectrum showed the presence of both mononuclear and dinuclear species, I and III, in solution. The ratio of monomer : dimer was estimated from peak heights to be ca. 1 : 4. The spectrum of the mononuclear component showed the presence of inequivalent phosphorus donors with values of ^1J(Pt, P) in accord with structure I. The spectrum of the dinuclear component (Table 1) was very similar to that of the aroyl analogue and the product is accordingly assigned structure III.

The reaction of [PtMeCl(cod)] with dppm yielded both monomeric and dimeric products, I and III, assigned on the basis of their $^{31}P\{^1H\}$ NMR spectroscopic data (Table 1). We understand that Puddephatt and co-workers [6] have recently prepared the complex III (R = Me) by a variety of routes and have investigated its chemistry in depth. Their reformation of the oligomer as a cationic "A-frame" methylplatinum(II) dimer substantiates our results on the phenyl and aroyl analogous. This work is described as part of our ongoing study of the chemistry of [PtXY(cod)] complexes [7].

Acknowledgement

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