

A $^{31}\text{P}\{^1\text{H}\}$ NMR Study of the Reactions of $[\text{PtCl}_2\text{-L}_2]$ ($\text{L} = \text{RCN}$; $\text{L}_2 = 1,5\text{-cyclooctadiene}$) Complexes with Bidentate Ligands. The Effects of Solubility on Product Distribution

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Platinum complexes of weak donor ligands are useful starting materials for the syntheses of other complexes [1–3], where it is generally assumed that the weakly bound ligands are simply replaced by incoming nucleophiles. In fact, such reactions are often taken for granted and little effort is devoted to product characterization. We have recently described [4] reactions of bidentate phosphorus ligands with platinum diolefin complexes, $[\text{PtXY}(\text{cod})]$ ($\text{X}, \text{Y} = \text{halide, alkyl or aryl}$; $\text{cod} = 1,5\text{-cyclooctadiene}$), where, in most but not all cases, simple displacement of the diolefin was found to occur. In particular, the reactions of $[\text{PtClR}(\text{cod})]$ ($\text{R} = \text{Me, Ph or COPh}$) with bis(diphenylphosphino)methane (dppm) are extraordinary since they yield the unexpected, 'A-frame' products $[\text{Pt}_2(\mu\text{-Cl})\text{R}_2(\mu\text{-dppm})_2]\text{Cl}$ [5, 6]. We now report reactions of the complexes $[\text{PtCl}_2\text{L}_2]$ ($\text{L} = \text{MeCN or PhCN}$; $\text{L}_2 = \text{cod}$) with a series of bidentate phosphorus ligands $[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]$; $n = 1(\text{dppm})$, $n = 2(\text{dppe})$, $n = 3(\text{dppp})$, where the expected substitution product, $[\text{PtCl}_2(\text{PP})]$, is not always obtained.

Treatment of $[\text{PtCl}_2(\text{cod})]$ in chloroform solution with 1 mol. equiv. dppe caused considerable precipitation, and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the remaining solution indicated that $[\text{PtCl}_2(\text{dppe})]$ was the only soluble, phosphorus-containing species present (see Table I). When *cis*- $[\text{PtCl}_2(\text{NCR})_2]$ ($\text{R} = \text{Me or Ph}$) was similarly treated a mixture of products resulted, as evidenced by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, although a significant amount of white solid was precipitated. The two complexes present in solution were identified as $[\text{PtCl}_2(\text{dppe})]$ and $[\text{Pt}(\text{dppe})_2]\text{Cl}_2$. The latter could also be produced quantitatively by a separate reaction of $[\text{PtCl}_2(\text{cod})]$ with 2 mol. equiv. dppe (although the ionic product was only sparingly soluble in chloroform also). The relative amounts of the two complexes produced appear to be critically dependent on the reaction conditions (*vide infra*).

Reactions of $[\text{PtCl}_2(\text{cod})]$ with 1 mol. equiv. dppm, dppp or appe, and of *cis*- $[\text{PtCl}_2(\text{NCMe})_2]$

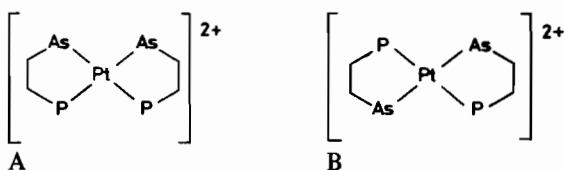
TABLE I. $^{31}\text{P}\{^1\text{H}\}$ NMR Data^a obtained for CDCl_3 Solution at 25 °C.

Complex	$\delta\text{P}(\text{ppm})^b$	$^1\text{J}(\text{Pt,P})$ (Hz)
$[\text{PtCl}_2(\text{dppm})]$	-64.6	3074
$[\text{PtCl}_2(\text{dppe})]$	40.9	3618
$[\text{PtCl}_2(\text{dppp})]$	-6.2	3408
$[\text{PtCl}_2(\text{appe})]$	42.5	3562
$[\text{Pt}(\text{dppm})_2]\text{Cl}_2$	-37.8	2036
$[\text{Pt}(\text{dppe})_2]\text{Cl}_2$	47.0	2360
$[\text{Pt}(\text{dppp})_2]\text{Cl}_2$	-13.5	2246
$[\text{Pt}(\text{appe})_2]\text{Cl}_2$	51.9	2793
	49.2	2312

^aSpectra were obtained on JEOL FX-90Q and FX-100 spectrometers operating in the FT mode at 36.20 and 40.26 MHz, respectively. ^bChemical shifts are relative to external H_3PO_4 , positive shifts representing deshielding.

with dppp, quantitatively produced the complexes $[\text{PtCl}_2(\text{L}_2)]$ (see Table I), and no ionic products could be detected.

When $[\text{PtCl}_2(\text{cod})]$ was treated with 2 mol. equiv. dppm, dppe or dppp, and when $[\text{PtCl}_2(\text{appe})]$ ($\text{appe} = \text{Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2$) was treated with 1 mol. equiv. appe, in chloroform solution the bis(bidentate ligand) platinum(II) dications were formed quantitatively. The dppe complex was the least soluble, considerable white solid being precipitated rapidly, whereas $[\text{Pt}(\text{dppm})_2]\text{Cl}_2$ produced a yellow solution, and $[\text{Pt}(\text{dppp})_2]\text{Cl}_2$ and $[\text{Pt}(\text{appe})_2]\text{Cl}_2$ only slowly precipitated as large, colorless crystals. Two isomers were formed for $[\text{Pt}(\text{appe})_2]\text{Cl}_2$ in approximately 2:1 ratio, the major isomer being that in which the two phosphorus atoms occupy mutually *cis*-positions [7] (structure A), as expected in terms of the relative *trans*-influences of tertiary phosphines and arsines [8, 9].



Addition of 2 mol. equiv. dppe to a suspension of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ in CDCl_3 also produced $[\text{Pt}(\text{dppe})_2]\text{Cl}_2$, free triphenylphosphine ($\delta\text{P} - 5.7$) being the only other phosphorus-containing species in solution.

Chloride ion abstraction from $[\text{PtCl}_2(\text{dppe})]$ by 2 mol. equiv. AgSO_3CF_3 , followed by addition of 1 mol. equiv. dppe produced $[\text{Pt}(\text{dppe})_2][\text{SO}_3\text{-CF}_3]_2$ ($\delta\text{P} 46.9$, $^1\text{J}(\text{Pt,P}) 2350$ Hz), among other, unidentified products. The NMR parameters for this complex are almost identical to those obtained with

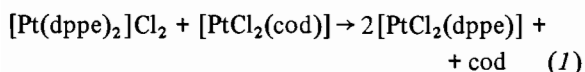
the chloride counterion, indicating that there is no significant interaction between the dication and Cl^- in CDCl_3 solution. Addition of excess $\text{Bu}_4\text{N}^+\text{I}^-$ to a solution of $[\text{Pt}(\text{dppe})_2]\text{Cl}_2$ caused no change in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, even after 7 days.

When a chloroform solution of $[\text{Pt}(\text{dppm})_2]\text{Cl}_2$ was treated with excess $\text{Bu}_4\text{N}^+\text{I}^-$, complete conversion to a new species ($\delta\text{P} -58.6$, $^1\text{J}(\text{Pt},\text{P})$ 2188 Hz) occurred. This change in chemical shift and coupling constant is likely to be due to ion-pairing between the $[\text{Pt}(\text{dppm})_2]^{2+}$ and I^- ions. The complex is totally insoluble in benzene or acetone, but slight changes in solvent polarity, by addition of benzene or methanol to the chloroform solution, caused systematic variations in δP and $^1\text{J}(\text{Pt},\text{P})$, as expected for ion-paired species [10]. The magnitudes of these changes were small, however, and may simply reflect changes in solvating ability.

In the case of $[\text{Pt}(\text{dppp})_2]\text{Cl}_2$, addition of excess $\text{Bu}_4\text{N}^+\text{I}^-$ caused a slow displacement of dppp, which was oxidized to $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ (δP 35.5) [11] in the process. After 24 h $[\text{Pt}(\text{dppp})_2]^{2+}$ was no longer present and the only platinum-phosphorus complex detected in solution was $[\text{PtCl}_2(\text{dppp})]$. After standing for 7 days an approximately 1:1:2 mixture of $[\text{PtCl}_2(\text{dppp})]$, $[\text{PtI}_2(\text{dppp})]$ ($\delta\text{P} -9.7$, $^1\text{J}(\text{Pt},\text{P})$ 3218 Hz) and $[\text{PtCl}(\text{dppp})]$ ($\delta\text{P} -6.9$, $^1\text{J}(\text{Pt},\text{P})$ 3225 Hz, $^2\text{J}(\text{P},\text{P})$ 21 Hz; $\delta\text{P} -8.7$, $^1\text{J}(\text{Pt},\text{P})$ 3385 Hz) was observed. The initial formation of $[\text{PtCl}_2(\text{dppp})]$, despite the presence of excess iodide, suggests that, in this case at least, there is some interaction between the dication and Cl^- , which is enhanced to the extent of dppp displacement by the vastly increased halide ion concentration upon $\text{Bu}_4\text{N}^+\text{I}^-$ addition. If there was no $[\text{Pt}(\text{dppp})_2]^{2+}\cdots\text{Cl}^-$ interaction, it would be expected that the iodide-containing complexes would also be produced initially whereas, in fact, they are only formed subsequently by halide metathesis.

Thus, in the presence of excess halide ions the $[\text{Pt}(\text{dppe})_2]^{2+}$ ion maintains its integrity, whereas the dppm and dppp analogs undergo reactions to form ion-paired and $[\text{PtX}_2(\text{dppp})]$ complexes, respectively.

The reactivity of $[\text{Pt}(\text{dppe})_2]\text{Cl}_2$ was further investigated as follows. The complex was isolated from the reaction of $[\text{PtCl}_2(\text{cod})]$ with 2 mol. equiv. dppe in chloroform, and was treated with an equimolar amount of $[\text{PtCl}_2(\text{cod})]$ in chloroform. After 48 h the solvent was removed, the residue was treated with CDCl_3 and filtered, and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was recorded. This indicated the presence of $[\text{PtCl}_2(\text{dppe})]$ only (see Table I) and, since very little material was filtered off, virtually quantitative reaction must have occurred (equation (1)).



A similar reaction of $[\text{Pt}(\text{dppe})_2]\text{Cl}_2$ with *cis*- $[\text{PtCl}_2(\text{NCMe})_2]$ caused >95% conversion to $[\text{PtCl}_2(\text{dppe})]$, a trace amount of the dication still being observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum after 48 h. (With K_2PtCl_4 no reaction of the dication took place, owing to the insolubility of K_2PtCl_4 in chloroform).

Thus it appears that in the reactions of $[\text{PtCl}_2(\text{cod})]$ or *cis*- $[\text{PtCl}_2(\text{NCR})_2]$ with dppe the thermodynamically favored product is $[\text{PtCl}_2(\text{dppe})]$, and if the reaction time is sufficiently long this complex is produced quantitatively. The nature of the products isolated after short reaction times, however, depends to a large extent on the solubilities of the complexes involved in the chosen solvent. The ionic complex $[\text{Pt}(\text{dppe})_2]\text{Cl}_2$ is only sparingly soluble in halocarbon solvents, so it precipitates in large measure whenever it is formed. Addition of dppe to a solution of the reasonably soluble $[\text{PtCl}_2(\text{cod})]$ thus produces $[\text{PtCl}_2(\text{dppe})]$, whereas with the less soluble *cis*- $[\text{PtCl}_2(\text{NCMe})_2]$ some $[\text{Pt}(\text{dppe})_2]\text{Cl}_2$ is formed with the relatively small amount of *cis*- $[\text{PtCl}_2(\text{NCMe})_2]$ in solution, and the ionic complex is precipitated. With time, equilibration leads to $[\text{PtCl}_2(\text{dppe})]$ as the ultimate product, but when the reaction mixture is worked up prematurely a mixture of *cis*- $[\text{PtCl}_2(\text{NCMe})_2]$, $[\text{Pt}(\text{dppe})_2]\text{Cl}_2$ and $[\text{PtCl}_2(\text{dppe})]$ is obtained.

Thus it is clear that these, apparently straightforward, reactions involve a fine balance between kinetic and thermodynamic factors, which is considerably affected by the solubilities of the reactants and products. The above results suggest that caution must be exercised in utilizing the products of such reactions without thorough characterization.

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