A Facile, High-yield Synthesis of $[Pt_2(PR_3)_2(\mu\text{-}Cl)_2Cl_2]$

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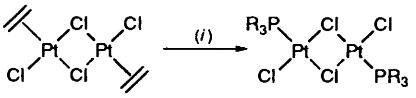
Contrary to previous reports, Zeise's dimer, $[Pt_2(\eta^2\text{-}C_2H_4)_2(\mu\text{-}Cl)_2Cl_2]$, reacts with tertiary phosphines in refluxing toluene or tetrachloroethane to give high yields of the phosphine-substituted analogues $[Pt_2(PR_3)_2(\mu\text{-}Cl)_2Cl_2]$ [PR_3 = PMe_3, PMe_2Ph, PEt_2Ph, $P(C_6H_{11})_2Ph$, $PMePh_2$, $P(C_6H_{11})Ph_2$ or PPh_3]. A wide range of examples has been synthesised and fully characterised by $^{31}P\text{-}\{^1H\}$ and $^{195}Pt\text{-}\{^1H\}$ spectroscopy.

The dinuclear complexes $[Pt_2(PR_3)_2(\mu\text{-}Cl)_2Cl_2]$ (R = alkyl or aryl)[1] are synthetically important as they are susceptible to cleavage of the chloro bridge by nucleophiles such as CO,[2] imines,[3] amines,[3] olefins,[4] sulfoxides[5] and thioethers[6] allowing the formation of a wide range of mononuclear platinum(II) derivatives. The primary method of synthesis of $[Pt_2(PR_3)_2(\mu\text{-}Cl)_2Cl_2]$ has been to reflux a slurry of $[Pt(PR_3)_2Cl_2]$ and $PtCl_2$ in a mixture of xylene and naphthalene the ratio of which is varied in order to obtain the optimum reaction temperature.[7] Alternative solvents which have been recommended include tetrachloroethane[8] and, more recently, *p*-chlorotoluene.[9] The disadvantage of these methods is the necessity to use $PtCl_2$ which can be expensive as a source of platinum compared to $[PtCl_4]^{2-}$, solutions of which are readily obtainable from platinum metal or platinum residues.[10] Thus, we sought an alternative method for the synthesis of $[Pt_2(PR_3)_2(\mu\text{-}Cl)_2Cl_2]$ that would employ $[PtCl_4]^{2-}$

Results and Discussion

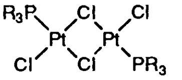
An intuitive starting point for the synthesis of $[Pt_2(PR_3)_2(\mu\text{-}Cl)_2Cl_2]$ from $[PtCl_4]^{2-}$ is Zeise's dimer, $[Pt_2(\eta^2\text{-}C_2H_4)_2(\mu\text{-}Cl)_2Cl_2]$ (Scheme 1). Furthermore, both we and others[11] have developed essentially quantitative syntheses of this material from $[PtCl_4]^{2-}$. The use of Zeise's dimer to prepare $[Pt_2(PPr_3)_2(\mu\text{-}Cl)_2Cl_2]$ was one of the methods explored by Chatt[12] who reported it to give both a poor yield and an impure product. As a consequence, subsequent workers appear to have dismissed this synthetic strategy. We find that refluxing Zeise's dimer with the appropriate phosphine in toluene or tetrachloroethane affords $[Pt_2(PR_3)_2(\mu\text{-}Cl)_2Cl_2]$ in good to high yield (Experimental section). Choice of solvent and length of reflux are critical to ensure purity of the product and optimum yield. An attempt at preparing $[Pt_2\{P(C_6H_{11})_3\}_2(\mu\text{-}Cl)_2Cl_2]$ resulted in isolation of an impure product in low yield with no improvement to the existing literature method of preparation.[13] The complexes isolated were characterised using $^{195}Pt\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR spectroscopies (Table 1) primarily at a magnetic field of 2.1 T. At higher fields the fine structure necessary to analyse the AXX′ and AA′XX′ subspectra characteristic of these dinuclear species is lost due to chemical shift anisotropy broadening.[14]



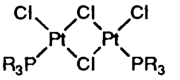
Scheme 1 (*i*) Reflux, PR_3, $Cl_2CHCHCl_2$ or toluene

A possible reaction mechanism would appear to be simple ethylene substitution, however $^{31}P\text{-}\{^1H\}$ NMR spectra of reaction mixtures show that this is not the case. Thus, treatment of dichloromethane solutions of Zeise's dimer with 2 molar equivalents of PMe_2Ph at −60 °C reveal that at this temperature the dominant reaction is the formation of $[Pt(PMe_2Ph)_3Cl]^+$ arising from both bridge cleavage and ethylene substitution.[15] Over several days at room temperature this species slowly reacts with unconverted $[Pt_2(\eta^2\text{-}C_2H_4)_2(\mu\text{-}Cl)_2Cl_2]$ to form *cis*-$[Pt(PMe_2Ph)_2Cl_2]$. At elevated temperatures, reaction mixtures which have not reached completion contain $[Pt(PR_3)_2Cl_2]$ as the only phosphorus-containing species other than $[Pt_2(PR_3)_2(\mu\text{-}Cl)_2Cl_2]$ for all phosphines studied. What else is in solution at these higher temperatures is as yet unknown. It is probably primarily $[Pt_2(\eta^2\text{-}C_2H_4)_2(\mu\text{-}Cl)_2Cl_2]$ although this material starts to decompose at elevated temperatures.[16] Alternatively, it may be solvated $PtCl_2$. Whatever the nature of these platinum species, they react cleanly with $[Pt(PR_3)_2Cl_2]$ to generate $[Pt_2(PR_3)_2(\mu\text{-}Cl)_2Cl_2]$.

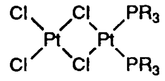
Complexes of stoichiometry $[Pt_2(PR_3)_2(\mu\text{-}Cl)_2Cl_2]$ may exist in three isomeric forms, however, except for the triphenylphosphine derivative, only the *trans* isomers have been characterised.[17] Two isomers of $[Pt_2(PPh_3)_2(\mu\text{-}Cl)_2Cl_2]$ have been isolated, the orange *sym-trans* and the yellow *sym-cis*. Heating the *trans* isomer in tetrachloroethane converts it into the *cis* isomer which can be reconverted back into the *trans* by heating in chloroform.[18] We can confirm this observation, but both $^{195}Pt\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR spectroscopies indicate that in tetrachloroethane *solution* the *trans* isomer predominates. Interestingly, the $^{31}P\text{-}\{^1H\}$ spectra of several of the dimers in $CDCl_3$ indicated the possible presence of small amounts (< 1%) of the *cis* isomer in solution. However, we were only able to obtain confirmatory $^{195}Pt\text{-}\{^1H\}$ NMR evidence in one case, $[Pt_2(PMePh_2)_2(\mu\text{-}Cl)_2Cl_2]$.



sym-trans



sym-cis



asym

Experimental

Toluene was distilled from sodium and hexane from sodium–potassium alloy. 1,1,2,2-Tetrachloroethane and chloroform were used as supplied. The NMR spectra were recorded using a Bruker AC-300 (^1H at 300.15 MHz, ^{195}Pt at 64.2 MHz) or a JEOL EX-90 spectrometer (^{31}P at 36.2 MHz, ^{195}Pt at 19.1 MHz). Phosphorus-31 spectra were referenced using an external sample of $P(OPh)_3$, δ 126.5. The ^{195}Pt shifts were measured to high frequency of Ξ 21.4 MHz. All spectra were measured at room temperature unless otherwise stated.

Table 1 The $^{31}P-\{^1H\}$ and $^{195}Pt-\{^1H\}$ NMR data for the $[Pt_2(PR_3)_2(\mu-Cl)_2Cl_2]$ complexes in $CDCl_3$

PR_3	δ(P)	^1J(PPt)/Hz	^3J(PPt)/Hz	^4J(PP)/Hz	δ(Pt)	^2J(PtPt)/Hz
$P(C_6H_{11})_3$	19.6	3873	−22	< 1	1167	147
PMe_3	−23.9	3858	−25	5	1123	*a*
PMe_2Ph	−18.7	3934	−25	5	1151	209
PEt_2Ph	3.5	3926	−24	3	1154	227
$P(C_6H_{11})_2Ph$	17.9	3977	−22	3	1150	210
$PMePh_2$ (*trans*)	−3.4	4004	−25	5	1171	274
$PMePh_2$ (*cis*)	−4.2	3911	*a*	*a*	1155	*a*
$P(C_6H_{11})Ph_2$	7.9	3940	−24	4	1253	299
PPh_3 (*trans*)	4.5	4100	−25	5	1185	*a*
	3.5[b]	4097	*a*	*a*	1201[b]	≈305
PPh_3 (*cis*)	1.8[b]	4020	*a*	*a*	1190[b]	*a*

[a] Unobserved. [b] In $C_2H_2Cl_4$–$CDCl_3$ at 55 °C.

Table 2 Experimental conditions and yields

				Microanalytical data[a]	
PR_3	Solvent	Reflux time (min)	Yield (%)	C	H
PMe_3	Toluene	20	87		
PMe_2Ph	Toluene	50	73		
PEt_2Ph	Toluene	50	66	27.55 (27.80)	3.25 (3.45)
$P(C_6H_{11})_2Ph$	$C_2H_2Cl_4$	60	80	39.40 (40.00)	5.10 (5.05)
$PMePh_2$	$C_2H_2Cl_4$	60	58	33.40 (33.50)	2.65 (2.80)
$P(C_6H_{11})Ph_2$	$C_2H_2Cl_4$	60	86	40.50 (40.45)	4.10 (3.95)
PPh_3	$C_2H_2Cl_4$	45	80		

[a] For complexes not previously fully characterised; calculated values in parentheses.

Elemental analysis were performed by the Microanalytical Laboratories, Department of Chemistry, University of Manchester.

Syntheses.—Zeise's dimer, $[Pt_2(\eta^2-C_2H_4)_2(\mu-Cl)_2Cl_2]$. An aqueous solution of 0.25 mol dm^{-3} $[PtCl_4]^{2-}$ (prepared by reduction of $[PtCl_6]^{2-}$ by hydrazine hydrochloride) was degassed by passing dry nitrogen gas through the solution for 10 min and a sufficient amount of concentrated hydrochloric acid added to make the solution 1 mol dm^{-3} in HCl. The solution was placed in a pressure reactor and pressurised to 100 psi (*ca.* 6.895 × 10^5 Pa) of ethene, then stirred for 48 h during which time the reactor was occasionally repressurised to 100 psi. All volatiles were subsequently removed *in vacuo* leaving a bright yellow residue containing Zeise's salt, $K[Pt(\eta^2-C_2H_4)Cl_3]\cdot H_2O$, and KCl. Extraction into ethanol, filtration and removal of the ethanol *in vacuo* afforded pure Zeise's salt.

Zeise's salt (1.9 g, 5.2 mmol) was dissolved in ethanol (100 cm^3) and concentrated HCl (1.5 cm^3, 18 mmol) added. The solution was shaken for 2 min then filtered to remove the precipitated KCl. Removal of all volatiles *in vacuo* while slowly warming the reaction mixture to 60 °C afforded Zeise's dimer in essentially quantitative yield based on $[PtCl_4]^{2-}$.

$[Pt_2(PR_3)_2(\mu-Cl)_2Cl_2]$. Zeise's dimer was dissolved in toluene or tetrachloroethane (15 cm^3 per 0.1 g) (see Table 2 for appropriate solvent) and the tertiary phosphine added (2 mol per mol of Zeise's dimer). The solution was refluxed with continuous stirring for the appropriate time (see Table 2), then allowed to cool to room temperature. Solvent was removed *in vacuo* in the case of tetrachloroethane, the solvent may be removed on a rotary evaporator and reused without purification. The products were dissolved in chloroform and the solution filtered. Recrystallisation was carried out by concentrating the chloroform solution and adding the minimum volume of hexane before cooling to −30 °C. {The complexes $[Pt_2(PMe_3)_2(\mu-Cl)_2Cl_2]$ and $[Pt_2(PPh_3)_2(\mu-Cl)_2Cl_2]$ were recovered without recrystallisation by removing the chloroform *in vacuo*.} This afforded the maximum yield of yellow to orange solid product. Occasionally, especially in larger-scale reactions when tetrachloroethane was used as a solvent, the samples were contaminated with traces of highly coloured impurities. These may be removed by dissolution in chloroform and addition of a *little* decolourising charcoal.

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