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# Preparation and characterization of aryltellurolato-bridged dinuclear complexes of platinum(II)

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## Abstract

Complexes of the type $[Pt_2Cl_2(\mu\text{-}X)(\mu\text{-}TeAr)(PR_3)_2]$ (X = Cl or TeAr; Ar = Ph, 4-$MeC_6H_4$, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$; $PR_3 = PEt_3$, $P^nBu_3$ or $PMe_2Ph$) and $[Pt_2(\mu\text{-}TeAr)_2(P\text{–}C)_2]$ (Ar = 4-$MeC_6H_4$, 4-$MeOC_6H_4$; P–C = ${}^tBu_2PCMe_2CH_2$) have been prepared. These complexes were characterized by elemental analyses, and multinuclear NMR ($^1H$, $^{13}C$, $^{31}P$, $^{125}Te$ and $^{195}Pt$) spectroscopy. The stereochemistry of the complexes in solution has been discussed on the basis of NMR data.

## Introduction

The dinuclear complexes of platinum and palladium of the type $[M_2X_2(\mu\text{-}SR)(\mu\text{-}Y)(PR_3)_2]$ (M = Pt or Pd) have been widely investigated [1–12] and the catalytic properties of some of these complexes in homogeneous hydrogenation and hydroformylation reactions have been assessed [2,3]. The analogous SeR-bridged compounds, recently reported by us [13], have properties similar to those of thiolato-bridged derivatives. The $RTe^-$ bridged compounds may, however, exhibit unusual bonding properties and reactivity due to the markedly different electronegativities and ionic radii of the bridging atom. The ligand chemistry of organotellurium derivatives has been of much interest in the past several years [14]. In transition metal complexes the ligands $RTe^-$ and $R_2Te$ behave in a monodentate or bridging fashion. Dimeric complexes of palladium(II), $[Pd_2(TeR)_2(\mu\text{-}TeR)_2(PPh_3)_2]$, have been reported by Chia and McWhinne [15]. Recently Khandelwal et al. [16,17] have reported the synthesis of dinuclear platinum and palladium complexes with bridging $RTe^-$ ligands employing the following reaction route:

$$2[MCl(TeR)]_n + 2nPPh_3 \longrightarrow n[M_2Cl_2(\mu\text{-}TeR)_2(PPh_3)_2]$$
$$(M = Pt \text{ or } Pd)$$

Table 1

$^1H$ and $^{31}P$ NMR data for aryltellurolato-bridged dinuclear platinum(II) complexes

| Complex | $^{31}P\{^1H\}$ NMR data | | | | $^1H$ NMR data |
|---|---|---|---|---|---|
| | Solvent | $\delta$ (ppm) | $^1J$(Pt–P) (Hz) | Other $^nJ$ values (Hz) | $\delta$ (ppm) |
| Ia | $CH_2Cl_2$ | 9.3 | 3838 | $^2J$(Pt–Pt) 861 | 0.85–2.10 (m, 30H, $PEt_3$); 3.85 (s, 3H, OMe); 6.80 (d, 8 Hz, 2H, 2- and 6-$C_6H_4$); 8.00 (d, 8 Hz, 2H, 3-and 5-$C_6H_4$) |
| Ib | $C_6D_6$ | 0.2 | 3802 | $^2J$(Pt–Pt) 835 | 0.85–1.15 (m, 54H, $PBu_3$); 7.30 (m, 3H, Ph); 8.00 (m, 2H, Ph) |
| Ic | $CH_2Cl_2$ | 0.8 | 3815 | $^2J$(Pt–Pt) 880 | 1.00–1.80 (br, m, 54H, $PBu_3$); 3.90 (s, 3H, OMe); 6.87 (d, 8Hz, 2H, 2- and 6-$C_6H_4$); 8.05 (d, 8 Hz, 2H, 3- and 5-$C_6H_4$) |
| Id | $CH_2Cl_2$ | 0.8 | 3815 | $^2J$(Pt–Pt) 880 | 1.00–1.90 (m, 57H, $PBu_3$ + O–C–Me); 4.15 (q, 7 Hz, 2H, $OCH_2$– ) 6.87 (d, 8 Hz, 2H, 2- and 6-$C_6H_4$); 8.05 (d, 8 Hz, 2H, 3- and 5-$C_6H_4$). |
| Ie | $CH_2Cl_2$ | −18.2 | 3949 | – | 1.64 (d, 12 Hz, 6H, $PMe_2$); 1.82 (d, 12 Hz, 6H, $PMe_2$); 6.80–7.40 (m, 15H, PPh + Ph) |
| If | $CH_2Cl_2$ | −17.2 | 3952 | – | 1.66 (d, 12 Hz, 6H, $PMe_2$); 1.83 (d, 12 Hz, 6H, $PMe_2$); 3.79 (s, 3H, OMe); 6.45 (d, 8 Hz, 2H, 2- and 6-$C_6H_4$); 7.14–7.30 (m, 12H, PPh + $C_6H_4$) |
| Ig | $CH_2Cl_2$ | −18.7 | 3956 | – | 1.46 (t, 7 Hz, 3H, O–C–Me); 1.64 (d, 12 Hz, 6H, $PMe_2$); 1.82 (d, 12 Hz, 6H, $PMe_2$); 4.00 (q, 7 Hz, 2H, O–$CH_2$–O); 6.47 (d, 8 Hz, 2H, 2- and 6-$C_6H_4$); 7.17–7.78 (m, 12 Hz, PPh + $C_6H_4$) |
| Ih | $CH_2Cl_2$ | −17.4 | 3937 | – | 1.61 (d, 12 Hz, 6H, $PMe_2$); 1.80 (d, 12 Hz, 6H, $PMe_2$); 2.33 (s, 3H, Me); 6.77 (d, 8 Hz, 2H, 2- and 6-$C_6H_4$); 7.19–7.40 (m, 12H, PPh + $C_6H_4$) |

| | | | | | |
|---|---|---|---|---|---|
| IIa$_{trans}$ | $C_6D_6$ | −2.4 | 3056 | $^4J$(P–P)19,<br>$^3J$(Pt–P)41<br>$^2J$(Te–P)$_{trans}$ 345<br>$^2J$(Te–P)$_{cis}$19 | 0.84–1.80 (m, 54H, $PBu_3$) [a]; 3.77 (s, 3H, OMe);<br>6.70 (d, 8 Hz, 2H, 2- and 6-$C_6H_4$); 7.75–7.88<br>(m, 2H, 3 and 5-$C_6H_4$) [a] |
| IIa$_{cis}$ | | −2.94 | 3004 | $^2J$(Te–P)$_{trans}$ 340 | 3.72 (s, 3H, OMe); 3.82 (s, 3H, OMe); 6.59 (d, 8 Hz, 2H, 2- and 6-$C_6H_4$); 6.82 (d, 8 Hz, 2H, 2- and 6-$C_6H_4$) |
| IIb | $CH_2Cl_2$ | −15.4 | 2998 | – | 1.64–1.82 (m, 12H, $PMe_2$); 3.76, 3.78 (s, 6H, OMe); 6.51, 6.58 (d, 8 Hz, 4H, 2- and 6-$C_6H_4$); 7.30–7.60 (m, 14H, PPh + $C_6H_4$) |
| IIc | $CH_2Cl_2$ | −12.6 | 3041 | | 1.44 (t, 7 Hz, 6H, O–C–Me); 1.61–1.89 (m, 12H, $PMe_2$);<br>4.02 (m, 4H, O–$CH_2$–); 6.45–6.59 (m, 4H, 2- and 6-$C_6H_4$)<br>7.36–7.59 (m, 14H, PPh + $C_6H_4$) |
| IIIa | $C_6D_6$ | −5.6 | 2832 | $^3J$(Pt–P)39<br>$^4J$(P–P)5 | 1.34 (d, 14 Hz, 4H, P–$CH_2$–); 1.50 (d, 14 Hz, 12H, $CMe_2$);<br>1.52 (d, 13 Hz, 36H, P$^t$Bu$_2$); 2.30, 2.26 (s, 6H, Me);<br>6.85 (t, 8 Hz, 4H, 2- and 6-$C_6H_4$); 7.58,<br>7.82 (d, 7 Hz, 4H, 3- and 5-$C_6H_5$) |
| IIIb | $C_6D_6$ | −5.4 | 2824 | $^3J$(Pt–P)41<br>$^4J$(P–P)5 | 1.30 (d, 17 Hz, 4H, P–$CH_2$–); 1.42 (d, 14 Hz, 12H, $CMe_2$)<br>1.51 (d, 13 Hz, 36H, P$^t$Bu$_2$); 3.74, 3.76 (s, 6H, OMe);<br>6.62 (t, 8 Hz, 4H, 2- and 6-$C_6H_4$); 7.59 (d, 8 Hz, 2H, 3- and 5-$C_6H_4$); 7.81 (d, 8 Hz, 2H, 3- and 5-$C_6H_4$) |

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[a] Overlapping resonances for the *cis* and *trans* isomers were observed. s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

As part of our program on the dinuclear complexes of platinum and palladium stabilized through different bridging groups, we attempted to synthesize the $RTe^-$ bridged derivatives by the forementioned route. However, this method when M = Pt, R = $C_6H_4OMe$-4 [17] did not yield the expected product as revealed by microanalyses and $^{31}P$ NMR data which indicated the formation of a mixture of products. Subsequently we synthesized the aryltellurolato bridged complexes of platinum(II) by the route described below and characterized the products by multinuclear NMR.

## Results and discussion

The reactions of halogen-bridged dinuclear platinum(II) complexes with NaTeAr gave aryltellurolato-bridged complexes as shown in eqs. 1–3.

$$[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2] + NaTeAr \longrightarrow \underset{(I)}{[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TeAr)(PR_3)_2]} + NaCl \tag{1}$$

| Ar | $PR_3$ | |
|---|---|---|
| 4-$MeOC_6H_4$ | $PEt_3$ | Ia |
| Ph | $P^nBu_3$ | Ib |
| 4-$MeOC_6H_4$ | $P^nBu_3$ | Ic |
| 4-$EtOC_6H_4$ | $P^nBu_3$ | Id |
| Ph | $PMe_2Ph$ | Ie |
| 4-$MeOC_6H_4$ | $PMe_2Ph$ | If |
| 4-$EtOC_6H_4$ | $PMe_2Ph$ | Ig |
| 4-$MeC_6H_4$ | $PMe_2Ph$ | Ih |

$$[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2] + 2NaTeAr \longrightarrow \left[\underset{(II)}{Pt_2Cl_2(\mu\text{-}TeAr)_2(PR_3)_2}\right] + 2NaCl \tag{2}$$

| Ar | $PR_3$ | |
|---|---|---|
| 4-$MeOC_6H_4$ | $P^nBu_3$ | IIa |
| 4-$MeOC_6H_4$ | $PMe_2Ph$ | IIb |
| 4-$EtOC_6H_4$ | $PMe_2Ph$ | IIc |

$$[Pt_2(\mu\text{-}Cl)_2(P\text{–}C)_2] + 2NaTeAr \longrightarrow \underset{(III)}{[Pt_2(\mu\text{-}TeAr)_2(P\text{–}C)_2]} + 2NaCl \tag{3}$$

| | |
|---|---|
| Ar = 4-$MeC_6H_4$ | IIIa |
| 4-$MeOC_6H_4$ | IIIb |

P–C = $^tBu_2PCMe_2CH_2$–

When the reaction 3 was carried out in 1 : 1 stoichiometry to obtain complexes of the type $[Pt_2(\mu\text{-}Cl)(\mu\text{-}TeAr)(P\text{–}C)_2]$, the complex III was formed leaving behind the unreacted parent chloro-bridged complex as revealed by $^{31}P$ NMR data. All the complexes I–III are yellow crystalline solids. The yields of II and III were considerably lower than that of I.

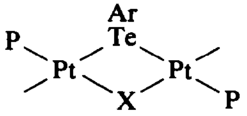
Table 2

Physical and analytical data for aryltellurolato-bridged dinuclear platinum(II) complexes

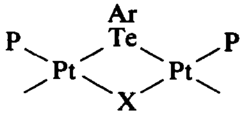
| Compound | Recrystallization solvent (yield %) | m.p. (°C) | Analyses (Found (calc.) (%)) | |
|---|---|---|---|---|
| | | | C | H |
| Ia | $CH_2Cl_2$/hexane | 180–182 | 23.56 | 3.77 |
| | (44) | | (23.58) | (3.85) |
| Ib | $CH_2Cl_2$/hexane | 148–149 | 32.91 | 5.41 |
| | (44) | | (32.58) | (5.38) |
| IC | $CH_2Cl_2$/hexane | 158–160 | 33.02 | 5.31 |
| | (78) | | (32.78) | (5.41) |
| Id | $CH_2Cl_2$/hexane | 174–176 | 33.87 | 5.55 |
| | (81) | | (33.42) | (5.52) |
| Ie | $CH_2Cl_2$/hexane | 230–231 [a] | 27.07 | 2.79 |
| | (51) | | (27.03) | (2.78) |
| If | $CH_2Cl_2$/hexane | 218–220 [a] | 27.13 | 2.91 |
| | (39) | | (27.42) | (2.90) |
| Ig | $CH_2Cl_2$/hexane | 196–198 [a] | 28.76 | 2.89 |
| | (53) | | (28.22) | (3.06) |
| Ih | $CH_2Cl_2$/hexane | 210 [a] | 27.39 | 2.85 |
| | (40) | | (27.86) | (2.95) |
| IIa | Benene/hexane | 118–119 | 33.92 | 5.05 |
| | (26) | | (34.19) | (5.13) |
| IIb | $CH_2Cl_2$/hexane | 160–162 [a] | 30.17 | 3.19 |
| | (42) | | (29.86) | (3.01) |
| IIc | $CH_2Cl_2$/hexane | 161–163 [a] | 30.27 | 3.08 |
| | (39) | | (31.12) | (3.26) |
| IIIa | Benene/hexane | 191–192 [a] | 37.13 | 5.26 |
| | (20) | | (37.10) | (5.41) |
| IIIb | Benene/hexane | 197–198 [a] | 36.64 | 5.22 |
| | (37) | | (36.16) | (5.27) |

[a] Decomposed.

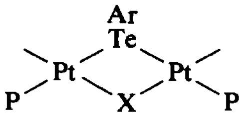
The aryltellurolato-bridged dinuclear complexes, like their thiolato and selenolato-bridged analogues, may exist in the following three configurations A–C, which can be readily identified from their NMR spectra.



(A)



(B)



(C)

*trans* isomer

*cis* isomers

The mixed chloro-aryltellurolato bridged complexes (I) like their RS$^-$ or RSe$^-$ bridged derivatives [3,5,13], exclusively exist in *cis* configuration **B** with phosphines *trans* to bridging chloride. The $^{31}$P NMR spectra of these complexes displayed a single Pt–P resonance with $^{1}J$(Pt–P) ~ 3900 Hz which is comparable to that of the corresponding PhSe$^-$ or PhS$^-$ bridged derivatives. In none of the spectra could the $^{3}J$(Pt–P) be resolved. The magnitude of $^{1}J$(Pt–P) for isomer C is expected to be

~ 3000 Hz as observed for II. The $^1H$ NMR spectra of these complexes showed a single type of ArTe proton resonance. The dimethylphenylphosphine complexes exhibited two doublets for P–Me protons indicating non-equivalence of the methyl groups. The two phosphine ligands in $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SEt)(PMe_2Ph)_2]$ are non-equivalent as shown by X-ray studies [5] showing two doublets for P–Me protons [3]. The $^{13}C\{^1H\}$ NMR spectrum of Ib in $C_6D_6$ displayed a singlet for Te–C carbon at $\delta$ 138.7 ppm with $^2J(^{195}Pt\text{–}Te\text{–}^{13}C)$ 25 Hz.

The $^{125}Te$ and $^{195}Pt$ NMR spectra of Ib were recorded in $C_6D_6$. The $^{195}Pt$ NMR spectrum exhibited a doublet due to coupling with phosphorus nuclei ($\delta(^{195}Pt)$ $-4239$ ppm; $^1J(^{195}Pt\text{–}^{31}P)$ 3803 Hz, $^2J(Pt\text{–}Pt)$ 845 Hz). The spectral features were consistent with the spectra expected for $[Pt_2Cl_2(\mu\text{-}X)(\mu\text{-}Y)(PR_3)_2]$. The $^{125}Te\{^1H\}$ NMR spectrum showed a triplet at $\delta$ $-802$ ppm with $^1J(Pt\text{–}Te)$ 402 Hz. Because of line broadening the $^2J(^{125}Te\text{–}^{31}P)_{cis}$ could not be resolved. Our preliminary X-ray results [18] on $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TePh)(PBu_3)_2]$ confirmed the conclusions drawn from NMR data.

All the complexes of the types II and III (Fig. 1) exist in the *cis* form (X = TeAr) in a freshly prepared solution, except IIa which exists as a mixture of *cis* and *trans* isomers. The $^1H$ NMR spectra of these complexes showed two sets of resonances for the ArTe groups. In the $^{31}P$ NMR spectra, a single line with platinum satellites is observed. The $^1H$ NMR spectrum of IIa, however, displayed three sets of resonances for ArTe moiety. Two of these having the same intensity are assigned to the *cis* isomer which is present in smaller concentration. The third set is assigned to the *trans* isomer. The $^{31}P$ NMR spectrum of this complex showed two resonances attributable to the *cis* and *trans* isomers (Table 1).

Bridge cleavage reactions of Ib with triphenylarsine and excess pyridine have been studied by $^{31}P$ NMR spectroscopy. The spectra obtained immediately after mixing showed the formation of $[PtCl_2(L)(P^nBu_3)]$ (L = pyridine or $AsPh_3$) and $[Pt_2Cl_2(\mu\text{-}TePh)_2(PBu_3)_2]$ as a mixture of *cis* and *trans* isomers. The latter complex reacts slowly with the free ligand (L) over a period of 2 weeks at room temperature to establish an equilibrium with the mononuclear complex $[PtCl(TePh)(L)(P^nBu_3)]$.

When I–III were left in $CH_2Cl_2$ or $CDCl_3$ solutions for some time (~ 10 h), a colour change from yellow to brown was noticed; the colour change in I was slower however. Thus, when a chloroform solution of IIb was refluxed for 20 h, the $^{31}P$ NMR spectrum showed that it contained mainly $[PtCl_2(PMe_2Ph)_2]$ ($\delta$ $-15.3$ ppm; $^1J(Pt\text{–}P)$ 3547 Hz) (~ 90%) as the phosphorus containing species. The analogous $RS^-$ or $RSe^-$ bridged complex showed no apparent change when left in $CH_2Cl_2$ or $CDCl_3$ for several days.

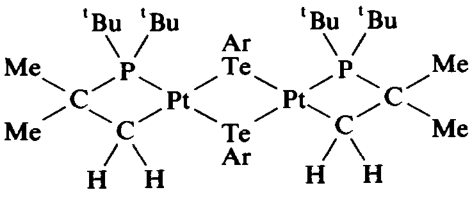


Fig. 1. Structure of III.

## Experimental

The phosphines were obtained from Strem Chemicals, USA. $K_2PtCl_4$ and $PtCl_2$ were prepared in the laboratory from platinum metal. The diarylditellurides [19] and the platinum compounds, $[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ ($PR_3 = PEt_3$, $P^nBu_3$, $PMe_2Ph$) [20,21] and $[Pt_2(\mu\text{-}Cl)_2(P\text{–}C)_2]$ [22] were prepared according to the literature methods. Analytical grade solvents were used through out. The $^1H$ NMR spectra were recorded using freshely prepared $CDCl_3$ solutions on a Varian FT-80A or Bruker AC-200 spectrometer operating at 80 and 200 MHz, respectively. Chemical shifts shown are relative to $Me_4Si$ as 0.0 ppm which were calculated from the data obtained with the internal chloroform peak ($\delta$ 7.26 ppm). The $^{13}C$, $^{31}P$, $^{125}Te$ and $^{195}Pt$ spectra were obtained on a Varian FT-80 NMR spectrometer operating at 20.0, 32.2, 25.129 and 17.01 MHz, respectively. Chemical shifts for $^{13}C$ are obtained using an internal $C_6D_6$ peak ($\delta$ 128.0 ppm) and calculated relative to $Me_4Si$ as 0.0 ppm. Chemical shifts for other elements are relative to external 85% $H_3PO_4$ for $^{31}P$, $Te(DTC)_2$ (DTC = diethyldithiocarbamate) in $CDCl_3$ for $^{125}Te$ and $Na_2PtCl_6$ in $D_2O$ for $^{195}Pt$. Microanalyses of these compounds were performed by the Analytical Chemistry Division and Bio-Organic Division, B.A.R.C. Melting points were determined in capillary tubes and are uncorrected.

### *Preparation of* $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TeC_6H_4OEt\text{-}4)(P^nBu_3)_2]$

Di(*p*-ethoxyphenyl)ditelluride (56 mg, 0.113 mmol) was dissolved in a benzene/methanol mixture (1 : 3, v/v; 5 ml) and a dilute methanolic solution of $NaBH_4$ was added dropwise under a nitrogen atmosphere with vigorous stirring. Addition of methanolic $NaBH_4$ solution was continued until a pale yellow coloured solution was obtained as distinct from the red colour of the parent ditelluride.

To the above $NaTeC_6H_4OEt$-4 solution, a benzene solution of $[Pt_2Cl_2(\mu\text{-}Cl)_2(P^nBu_3)_2]$ (200 mg, 0.214 mmol) was added and the mixture stirred at room temperature for 4 h. The solvents were evaporated under vacuum leaving a yellow orange mass. The residue was extracted with dichloromethane and filtered. The filtrate was concentrated to 3 ml and 1 ml of methanol was added to give a yellow solid after a few hours. This was filtered and recrystallized twice from a dichloromethane hexane mixture as a yellow crystalline solid (Table 2).

Other complexes of this series were prepared similarly. In the case of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$, its benzene suspension was used. The products $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TeC_6H_4X\text{-}4)(PMe_2Ph)_2]$ (X = H or Me) were separated out from the reaction mixture and filtered off, then washed with water and ethanol, and dried. They were finally recrystallized from a dichloromethane/hexane mixture.

### *Preparation of* $[Pt_2Cl_2(\mu\text{-}TeC_6H_4OMe\text{-}4)_2(P^nBu_3)_2]$

A solution of $NaTeC_6H_4OMe$-4 was prepared from dianisylditelluride (91 mg, 0.194 mmol) and $NaBH_4$ as described above. A benzene solution of $[Pt_2Cl_2(\mu\text{-}Cl)_2(P^nBu_3)_2]$ (180 mg, 0.192 mmol) was added to the $NaTeC_6H_4OMe$ solution under a nitrogen atmosphere. The reactants were stirred for 4 h. The solvents were evaporated under vacuum. The orange-brown residue was extracted with benzene and filtered. The filtrate was concentrated *in vacuo*. The residue was dissolved in a minimum quantity of ethanol (2 ml) and ~ 5 ml of hexane was added, and kept in a freezer for 2 weeks to give a yellow crystalline solid. This was filtered off by a sintered disc, then washed with hexane and dried. The product was recrystallized twice from a benzene/hexane mixture as a yellow crystalline solid in 26% yield.

In cases of complexes IIb and IIc the product precipitated out from the reaction mixture which was filtered, washed with water and ethanol, and dried. It was then recrystallized two or three times from a benzene/hexane mixture.

### *Preparation of* $[Pt_2(\mu\text{-}TeC_6H_4OMe\text{-}4)_2(P\text{-}C)_2]$

To a solution of $NaTeC_6H_4OMe$-4 (prepared from dianisylditelluride [82 mg, 0.174 mmol] and $NaBH_4$ as described above) a benzene solution of $[Pt_2(\mu\text{-}Cl)_2(P\text{-}C)_2]$ (150 mg, 0.174 mmol) was added under a nitrogen atmosphere. It was stirred for 6 h. The solvents were evaporated under reduced pressure. The residue was dissolved in benzene and filtered to remove NaCl. The filtrate was concentrated *in vacuo*. One millilitre of methanol containing > 5% benzene was added and crystallization was initiated by scratching with a spatula. The yellow product that separated out was filtered off, washed with methanol, and dried. The product was recrystallized from benzene/hexane. $[Pt_2(\mu\text{-}TeC_6H_4Me\text{-}4)_2(P\text{-}C)_2]$ was prepared similarly.

### *Reaction of* $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TePh)(P^nBu_3)_2]$ *with pyridine*

A solution of pyridine (0.5 ml) in $C_6D_6$ was added to a solution of $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TePh)(P^nBu_3)_2]$ (80 mg) in an NMR tube and progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. A reaction with triphenylarsine was carried out similarly.

### *Reaction of* $[Pt_2Cl_2(\mu\text{-}TeC_6H_4OMe\text{-}4)_2(PMe_2Ph)_2]$ *with* $CHCl_3$

A chloroform solution (10 ml) of $[Pt_2Cl_2(\mu\text{-}TeC_6H_4OMe\text{-}4)_2(PMe_2Ph)_2]$ (100 mg) was refluxed for 20 h during which the colour changed from yellow to brown. The solvent was removed under reduced pressure. The residue was dissolved in $CDCl_3$ and studied by $^{31}P$ NMR spectroscopy.

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