1406 *Organometallics* **1985**, *4*, 1406-1412

partially modelled by including the atoms C(S1)–C(S4) (see Table IV) in the calculations with isotropic temperature factors. The solvent molecules could not be identified crystallographically, although from the method of preparation, it is likely that they are either $CH_2Cl_2$ or MeOH. The closest approach between C(S1)–C(S4) atoms and a non-hydrogen atom of **6** is 3.18 (5) Å to C(3C). The formula for **6** in Table III and quantities calculated directly therefrom contain no allowance for the unidentified solvent.

In the final full-matrix least-squares calculations for **6** the phenyl rings were refined as rigid hexagons of 1.38-Å side. Anisotropic temperature factors were used only for Pt, Cl, P, and methylene C atoms. The structure factors included contributions for the scattering of geometrically positioned hydrogen atoms. The isotropic thermal parameters of the hydrogen atoms were kept equal to those of the carbon atoms to which they were attached. The choice of space group as $P4_32_12$, rather than the enantiomeric $P4_12_12$, was confirmed by refining the Rogers chirality parameter $\eta$; its final value was 1.02 (5), satisfactorily close to +1.[36]

For **5** the X-ray measurements were made with a yellow, irregularly shaped crystal fragment of dimensions ca. 0.40 × 0.30 × 0.20 mm, mounted in air. The intensities of 12940 reflections were measured. Averaging 4802 observations to obtain 2284 independent intensities gave $R_{int} = 0.073$, fairly close to the final value of the conventional $R$ factor (see Table III). The data were not corrected for absorption effects: application of the Gaussian quadrature method was precluded by our inability to define adequately the shape of the crystal fragment used, and an attempt to apply an empirical correction[35] was unsuccessful, presumably because of the serious disorder problems (see below).

In the final full-matrix least-squares calculations for **5** the 11 phenyl rings were treated as rigid hexagons of 1.386-side. Anisotropic temperature factors were applied only to Pt, Cl, and P atoms. No allowance was made for the scattering of the hydrogen atoms. The analysis was hampered and its accuracy diminished by two problems. First, the fluorine atoms of the $[PF_6]^-$ anion are disordered and a satisfactory geometry for the anion could not be obtained. After many attempts the final fluorine atom positions (Table V) were derived from a difference synthesis and not further refined; an isotropic thermal parameter common to all six fluorine atoms was, however, included in the final refinement calculations. The P–F bond lengths are 1.40–1.72 Å, and the F–P–F angles are 71–124° and 148–165°. Secondly, crystals of **5** also contain disordered solvent, believed to be $CH_2Cl_2$ from the method of preparation and confirmed by NMR spectroscopy. The final model included two Cl atoms with occupancies of 0.5 to allow for the scattering of the disordered solvent. As with **6**, the empirical formula and associated quantities in Table III for **5** make no allowance for the disordered solvent. The final difference synthesis contains function values up to 3.7 e $Å^{-3}$, mainly close to the Pt atoms and in the region of the $[PF_6]^-$. The analysis of **5** must therefore be regarded as of limited accuracy, although we consider that the structure of the complex cation has been established without ambiguity.

Anisotropic thermal parameters and assumed hydrogen atom positions for **6** and anisotropic thermal parameters for **5** are presented in Tables VI–VIII, and final $|F_o|$ and $|F_c|$ values in Table IX and X.[37] The calculations were performed on a GOULD SEL 32/27 minicomputer using the locally developed GX program system.[38] Scattering factors and anomalous dispersion corrections were taken from ref 39.

**Acknowledgment.** We thank SERC (U.K.) for help with purchases of the computer and diffractometer, Glasgow University for a studentship (to A.A.F.), and NSERC (Canada) for financial assistance (to R.J.P.) through the operating and strategic grant programs.

**Registry No. 1a**, 74587-82-9; **1b**, 78064-41-2; **1c**, 77275-77-5; **2a**, 83571-85-1; **2b**, 83571-87-3; **4**, 83576-64-1; **5**, 83576-66-3; **6**, 68851-49-0; $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$, 77275-79-7; $[Pt_2Me(CH_2D)(\mu\text{-D})(\pm\text{-dppm-}d_4)_2][PF_6]$, 97042-57-4; $CH_2N_2$, 334-88-3.

**Supplementary Material Available:** Table VI, anisotropic atomic thermal parameters, and Table VII, hydrogen positions for 6; Table VII, anisotropic atomic thermal parameters for 5; Tables IX and X, final $|F_o|$ and $|F_c|$ values for 6 and 5, respectively (49 pages). Ordering information is given on any current masthead page.

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# Synthesis of Binuclear Platinum(IV) Complexes with $Pt(CH_2)_nPt$ Units

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The complex $[PtMe_2(N\frown N)]$, $N\frown N$ = 1,10-phenanthroline, reacts with a series of organic halides to give new platinum(IV) complexes characterized as $[PtXMe_2R(N\frown N)]$ (R = Me, Et, *n*-Pr, *n*-Bu, $CH_2C_6H_4CH_2Br$, $(CH_2)_nX$; $n$ = 0, 1,3, 5; X = Br, I). Complexes $[PtIMe_2\{(CH_2)_nI\}(N\frown N)]$ ($n$ = 3–5) react further with $[PtMe_2(N\frown N)]$ to produce binuclear complexes $[Pt_2I_2Me_4\{\mu\text{-}(CH_2)_n\}(N\frown N)_2]$. The complexes are characterized by elemental analysis and NMR and in the case of the binuclear complexes by pyrolysis.

## Introduction

Fischer and Tropsch[1] originally suggested the polymerization of methylene groups on a metal surface to account for the formation of products in the Fischer–Tropsch reactions. Recent evidence[2] has been found to be consistent with this proposal, and this has resulted in considerable current interest in binuclear complexes containing bridging methylene or polymethylene groups. A possible route to such complexes is by the use of $\alpha,\omega$-dihaloalkanes, annd this paper deals with the formation of platinum(IV) com-

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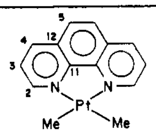
(2) Brady, R. C.; Pettit, R. J. *J. Am. Chem. Soc.* **1980**, *102*, 6181.

Table I. $^1$H NMR Data for Complexes with General Formula [PtIMe$_2$R($\widehat{N\ N}$)]

| | PtMe | | PtR[b] | | $\widehat{N\ N}$[c] | |
|---|---|---|---|---|---|---|
| complex[a] | δ | $J$(PtH)/Hz | δ | $J$/Hz | δ | $J$/Hz |
|  | 1.15 | 86.5 | | | 9.51 ($H_2$)[d]<br>7.82 ($H_3$)<br>8.63 ($H_4$)<br>7.92 ($H_5$) | 5.2 ($J_{2,3}$)<br>8.0 ($J_{3,4}$)<br>1.3 ($J_{2,4}$) |
| [PtIMe$_3$(phen)] | 1.63 | 71.5 | 0.65 | 73 ($^2J_{PtH}$) | 9.32 ($H_2$)[e]<br>7.92 ($H_3$)<br>8.60 ($H_4$)<br>8.08 ($H_5$) | 5.0 ($J_{2,3}$)<br>8.0 ($J_{3,4}$)<br>1.5 ($J_{2,4}$) |
| [PtIMe$_2$(Et)(phen)] | 1.63 | 71.5 | −0.11 ($CH_3$)<br>1.48 ($CH_2$) | 68.4 ($^3J_{PtH}$<br>72.0 ($^2J_{PtH}$) | 9.25 ($H_2$)[f]<br>7.87 ($H_3$)<br>8.50 ($H_4$)<br>7.97 ($H_5$) | 4.98 ($J_{2,3}$)<br>8.19 ($J_{3,4}$)<br>1.43 ($J_{2,4}$) |
| [PtIMe$_2$(*n*-Pr)(phen)] | 1.60 | 72.5 | 0.43 ($CH_3$ , br)<br>1.4 (Pt-$CH_2$) | | 9.27 ($H_2$)[g]<br>7.97 ($H_3$)<br>8.60 ($H_4$)<br>8.06 ($H_5$) | 5.09 ($J_{2,3}$)<br>8.0 ($J_{3,4}$)<br>1.4 ($J_{2,4}$) |
| [PtIMe$_2$(*n*-Bu)(phen)] | 1.63 | 71.4 | 0.43 ($CH_3$)<br>0.87 ($CH_2CH_2$) | 7.1 ($^3J_{HH}$) | 9.26 ($H_2$)[h]<br>7.89 ($H_3$)<br>8.51 ($H_4$)<br>7.97 ($H_5$) | 5.09 ($J_{2,3}$)<br>8.19 ($J_{3,4}$)<br>1.4 ($J_{2,4}$) |

[a] Solvent $CD_2Cl_2$. [b] R = Me, Et, *n*-Pr, *n*-Bu. [c] $\widehat{N\ N}$ = phen. [d] $J$(PtH) = 21.5 Hz. [e] $J$(PtH) = 18 Hz. [f] $J$(PtH) = 18 Hz. [g] $J$(PtH) = 17 Hz. [h] $J$(PtH) = 18.5 Hz.

plexes (mononuclear and binuclear) by oxidative addition of such reagents to [PtMe$_2$($\widehat{N\ N}$)], 1, where $\widehat{N\ N}$ = 1,10-phenanthroline. Results are also given for the oxidative addition of primary alkyl iodides and $\alpha,\alpha'$-dibromo-*o*-xylene to 1. Among other products these reactions have given a synthesis of the first series of binuclear platinum complexes containing bridging polymethylene groups with no other bridging ligands.

Relevant work includes studies of oxidative addition of primary alkyl halides to platinum(0) and platinum(II) complexes to give new platinum(II) and platinum(IV) complexes,[3-9] and the synthesis of other complexes in which two metal centers are bridged by a hydrocarbyl ligand.[10-14] A common synthetic method involves the reaction between metal carbonyl anions and $\alpha,\omega$-dihaloalkanes. As an extension of this, mixed $\mu$-alkanediyl complexes[14] have been synthesized by reacting a haloalkyl complex of one metal wiith the anionic carbonyl complex of another (eq 1).

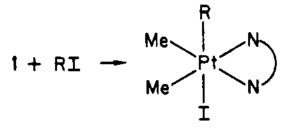
$$[CpFe(CO)_2\{(CH_2)_3Br\}] + [CpMo(CO)_3]^- \rightarrow [CpFe(CO)_2\{\mu\text{-}(CH_2)_3\}Mo(CO)_3Cp] \quad (1)$$

A preliminary account of parts of this work has been published.[16]

## Results

The complex [PtMe$_2$(phen)], 1, is a red solid, the color being due to the presence of a metal to ligand charge-transfer band in the visible region of the spectrum.[15] The complex is electron rich and among the most active of noble-metal complexes in oxidative addition reactions.[5,6,16-18]

**Reactions with Primary Alkyl Iodides.** Complex 1 reacted cleanly with a series of primary alkyl iodides in acetone producing a pale yellow solution, from which the product could be recovered in high yield. The reactions proceeded in all cases with trans addition (eq 2).



(2)

2a-d

R = Me (2a), Et (2b), *n*-Pr (2c), *n*-Bu (2d)

The stereochemistry at platinum was established by $^1$H NMR spectroscopy (Table I). For example, for the complex **2b** only one MePt signal is observed, indicating that the two Me groups remain equivalent in the product. The coupling constant $^2J$(PtMe) decreased from 86.5 Hz in 1 to 71.5 in **2b** consistent with oxidation of the platinum(II) to platinum(IV).[5,19] Likewise the coupling between H2 of the phen ring and the platinum is reduced from 21.5 Hz in 1 to 18 Hz in **2b**. A similar change is noted for all the platinum(IV) complexes. The resonances due to the alkyl groups R are as expected (Table I).[8]

**Reactions of 1 with Methylene Dihalides.** The methylene dihalides $CH_2I_2$, $CH_2Br_2$, $CH_2BrCl$, and $CH_2ClI$ reacted with 1 in acetone. In the case of $CH_2Cl_2$, the reaction was performed by using $CH_2Cl_2$ as solvent and took several hours to go to completion. The reactions with

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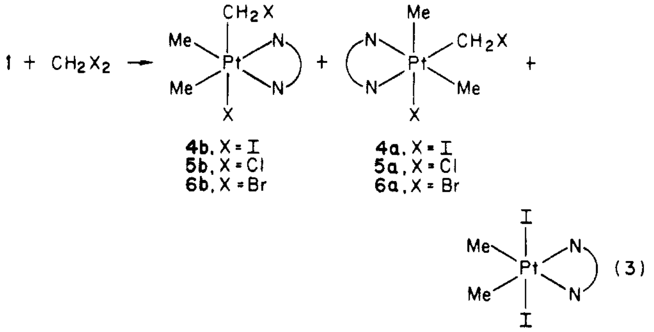
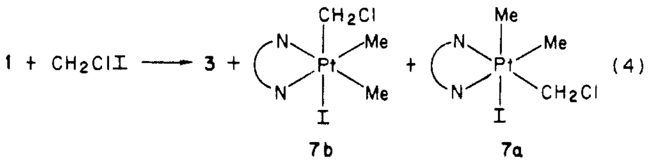
$CH_2I_2$ and $CH_2ClI$ were very fast, while those with $CH_2ClBr$ and $CH_2Br_2$ were considerably slower, taking several hours to go to completion. Each of the compounds produced was isolated as a pale yellow solid. The product formed by oxidative addition was, in all cases, a mixture of cis and trans isomers, and for the reaction with $CH_2ClI$ and $CH_2I_2$ some $[PtI_2Me_2(phen)]$, **3**, was also produced. The products of the reactions and their stereochemistries are shown in eq 3–5.



4b, X = I
5b, X = Cl
6b, X = Br

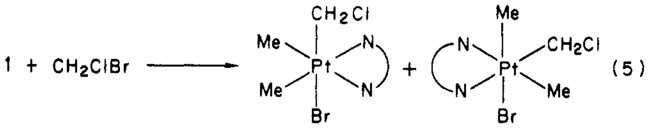
4a, X = I
5a, X = Cl
6a, X = Br

(3)



7b 7a

(4)



8b 8a

(5)

In all cases the cis isomer formed initially, with subsequent isomerization to the trans isomer. This was confirmed, in the case of the reactions with $CH_2I_2$ and $CH_2ClBr$, by following the reactions by NMR. In reaction 4 some of complexes **5a** and **5b** were also formed.

In an attempt to form a binuclear complex, the trans isomer **4b** was added to a solution of **1** in acetone (1:1 mole ratio). No reaction occurred, almost certainly as a result of steric hindrance. The binuclear complex $[Pt_2I_2Me_4(\mu\text{-}CH_2)(phen)]$ that would be formed is not viable due to steric interactions between ligands on the different platinum atoms.

All of these (haloalkyl)platinum(IV) complexes have been characterized by their $^1H$ NMR spectra (Table II). The $^1H$ NMR spectrum of the products from the reaction of **1** with $CH_2Cl_2$ contains a singlet due to the $PtCH_2Cl$ protons of the trans isomer **5b** at 3.62 ppm and an AB quartet due to the nonequivalent $PtCH_2Cl$ protons of the cis isomer **5a** centered at about 5 ppm. These resonances were absent in the corresponding complex obtained from **1** and $CD_2Cl_2$. The complex **5a** also gave two MePt signals while **5b** gave only one. The isomers are easily identified in this way even when present as a mixture.

The $^1H$ NMR spectra of the products from the reactions with $CH_2Br_2$ and $CH_2I_2$ (Table II) were very similar to that in Figure 1. In the case of $CH_2I_2$ however, a peak at 2.53 ppm, with $^{195}Pt$ satellites, was present. This has been assigned to the MePt group of *trans*-$[PtI_2Me_2(phen)]$, **3**, by comparison with an authentic sample.

The $^1H$ NMR spectrum (Figure 1) of the products from the reaction between **1** and $CH_2ClBr$, by comparison with those discussed above, clearly shows that a cis adduct and trans adduct were formed. By comparing the trends in chemical shifts and $^2J_{PtMe}$ values for a methyl group trans to Cl or Br and the chemical shifts for $PtCH_2Cl$ and $PtCH_2Br$ protons, the assignments were made for addition via rupture of the C–Br bond as expected (eq 5).[20] The products from the reaction of $CH_2ClI$ with **1** were identified by NMR spectroscopy in a similar way, and the unexpected products **5a** and **5b** are formed by halogen scrambling, in a similar way as in the reactions studied by Lappert.[20]

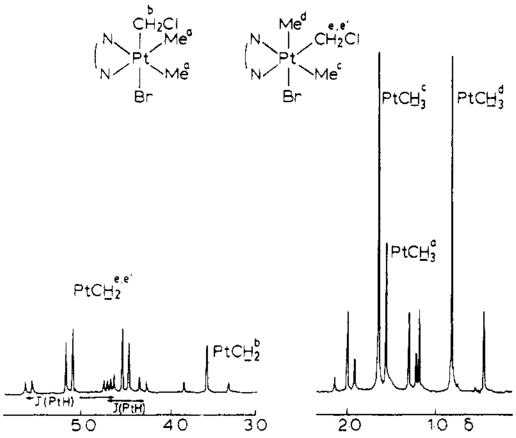
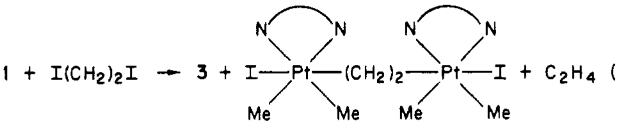


**Figure 1.** $^1H$ NMR spectrum (100 MHz) of the products of eq 5. Assignments are given above.

**Reactions of 1 with α,ω-Dihaloalkanes.** The products from the reaction of **1** with $X(CH_2)_nX$ ($n = 2$, X = I, Br; $n = 3, 5$, X = I) depends upon the length of the carbon chain. The present discussion will be divided into the results for $n = 2$ and those for $n = 3$–5.

In the reactions between complex **1** and $I(CH_2)_2I$ or $Br(CH_2)_2Br$, in acetone, an insoluble product was formed in both cases. The insoluble product for the reaction with $I(CH_2)_2I$ has been characterized as $[Pt_2I_2Me_4(\mu\text{-}(CH_2)_2)(phen)_2]$, **9**. In the reaction with $Br(CH_2)_2Br$ the insoluble product is believed to be $[Pt_2Br_2Me_4\{\mu\text{-}(CH_2)_2\}(phen)_2]$, **10**. Due to the insolubility of these two complexes no NMR spectral data could be obtained. The elemental analyses (Experimental Section) of the complexes are however consistent with the general formula $[Pt_2X_2Me_4\{\mu\text{-}(CH_2)_2\}(phen)_2]$ (X = Br, I).

The reaction of **1** with these two α,ω-dihaloalkanes also gave a more soluble product. In the reaction with $I(CH_2)_2I$ this more soluble product was identified as $[PtI_2Me_2(phen)]$, **3**, by its $^1H$ NMR spectrum. The new reaction of **1** with $I(CH_2)_2I$ is thus shown in eq 6. The evolution of ethylene during reaction 6 was confirmed by analysis of the gaseous products from the reaction using GC. Evidence for the bridging $-(CH_2)_2-$ group was obtained by pyrolysis of complex **9**. The major gas thus produced was ethene. Furthermore a mass balance experiment showed that the relative number of moles of **1** used to the moles of **3** and **9** produced was 4:2:1. This gives a good mass balance for platinum and indicates the stoichiometry shown in eq 7. A similar reaction, using $[Co(CN)_5]^{3-}$, has been reported by Halpern.[21,22]



9

(6)

$$4[PtMe_2(phen)] + 3I(CH_2)_2I \rightarrow 2[PtI_2Me_2(phen)] + [Pt_2I_2Me_4(\mu\text{-}(CH_2)_2)(phen)_2] + 2C_2H_4 \quad (7)$$

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**Table II. $^1$H and $^{13}$C NMR Data for Complexes of General Formula [PtXMe$_2${(CH$_2$)$_n$X}(phen)]$^a$ and [Pt$_2$I$_2$Me$_4${$\mu$-(CH$_2$)$_n$}(phen)$_2$]$^b$**

| | Pt–Me | | (CH$_2$)$_n$ | | NN$^d$ | |
|---|---|---|---|---|---|---|
| complex$^c$ | $\delta$ | $^2J$(PtH)/Hz | $\delta$ | $J$/Hz | $\delta$ | $J$/Hz |
| **3** | 2.53 | 74.0 | | | 9.25 (H$_2$)$^f$ | 5.0 ($J_{2,3}$) |
| | | | | | 8.01 (H$_3$) | 8.0 ($J_{3,4}$) |
| | | | | | 8.58 (H$_4$) | 1.6 ($J_{2,4}$) |
| | | | | | 8.10 (H$_5$) | |
| **4a** | 1.80 (trans to N) | 72 | 4.50 | 80 ($^2J_{PtH}$) | | |
| | 0.84 (trans to I) | 72 | 4.21 | 26 ($^2J_{PtH}$) | | |
| **4b** | 1.68 | 70.5 | 2.86 | 40 ($^2J_{PtH}$) | 9.18 (H$_2$)$^e$ | 5.0 ($J_{2,3}$) |
| | | | | | 8.05 (H$_3$) | 8.0 ($J_{3,4}$) |
| | | | | | 8.63 (H$_4$) | 1.3 ($J_{2,4}$) |
| | | | | | 8.11 (H$_5$) | |
| **5a** | 1.57 (trans to N) | 70 | 4.98 | 91 ($^2J_{PtH}$) | 9.75 (H$_2$) | 5.0 ($J_{2,3}$) |
| | 0.81 (trans to Cl) | 74 | 4.72 | 39 ($^2J_{PtH}$) | | 2.0 ($J_{2,4}$) |
| **5b** | 1.47 | 69 | 3.62 | 53 ($^2J_{PtH}$) | 9.18 (H$_2$) | 5.0 ($J_{2,3}$) |
| | | | | | 7.93 (H$_3$) | 8.0 ($J_{3,4}$) |
| | | | | | 8.54 (H$_4$) | 1.0 ($J_{2,4}$) |
| | | | | | 7.98 (H$_5$) | |
| **6a** | 1.82 (trans to N) | 69 | 4.96 | 84 ($^2J_{PtH}$) | 9.18 (H$_2$) | 8.0 ($J_{3,4}$) |
| | 0.96 (trans to Br) | 71 | | | 7.92 (H$_3$) | 1.5 ($J_{3,4}$) |
| | | | 4.48 | 36 ($^2J_{PtH}$) | 8.50 (H$_4$) | |
| | | | | | 8.01 (H$_5$) | |
| **6b** | 1.70 | 68 | 3.50 | 43.25 ($^2J_{PtH}$) | 8.97 (H$_2$) | 5.0 ($J_{2,3}$) |
| | | | | | 7.78 (H$_3$) | 8.0 ($J_{3,4}$ |
| | | | | | 8.41 (H$_4$) | 1.5 ($J_{2,4}$) |
| | | | | | 7.85 (H$_5$) | |
| **7a** | 1.85 | 70 | 5.41 | 92 ($^2J_{PtH}$) | | |
| | 0.98 | 72 | 4.66 | 32 ($^2J_{PtH}$) | | |
| **7b** | 1.73 | 66 | 3.53 | 49 ($^2J_{PtH}$) | | |
| **8a** | 1.65 | 70 | 5.13 | 92.9 ($^2J_{PtH}$) | | |
| | 0.81 | 73.5 | 4.51 | 40.1 ($^2J_{PtH}$) | | |
| **8b** | 1.55 | 70 | 3.58 | 51.6 ($^2J_{PtH}$) | | |
| **10a**$^g$ | 1.61 | 71 | 2.73 (C$H_2$I) | 7 ($^3J_{HH}$) | 9.25 (H$_2$)$^h$ | 5.0 ($J_{2,3}$) |
| | | | 0.4 (H$_\alpha$) | | 7.99 (H$_3$) | 8.5 ($J_{3,4}$) |
| | | | | | 8.62 (H$_4$) | |
| | | | | | 8.09 (H$_5$) | 1.6 ($J_{2,4}$) |
| **10a**$^s$ | 1.63 (trans to N) | 72 | 3.41 (C$H_2$I) | | | |
| | 0.65 (trans to I) | 72 | | | | |
| **10b** | 1.64 | 71.5 | 2.92 (C$H_2$I) | 6.5 ($^3J_{HH}$) | 9.27 (H$_2$)$^i$ | 6.0 ($J_{2,3}$) |
| | | | 0.87 (H$_\alpha$) | | 7.91 (H$_3$) | 8.5 ($J_{3,4}$) |
| | | | | | 8.51 (H$_4$) | 1.7 ($J_{2,4}$) |
| | | | | | 7.99 (H$_5$) | |
| **10b**$^s$ | 1.66 (trans to N) | 72 | 3.35 (CH$_2$I) | 6.5 ($^3J_{HH}$) | | |
| | 0.59 (trans to I) | 73 | | | | |
| **10c**$^{j,k}$ | 1.60 | 71.5 | 2.90 ($H_2$I) | 6.9 ($^3J_{HH}$) | 9.25 (H$_2$)$^l$ | 6.0 ($J_{2,3}$) |
| | | | 1.45 (H$_\alpha$) | | 7.92 (H$_3$) | 8.0 ($J_{3,4}$) |
| | | | 0.40 (H$_\beta$) | | 8.51 (H$_4$) | 1.7 ($J_{2,4}$) |
| | | | 0.99 (H$_\gamma$) | | 8.0 (H$_5$) | |
| | | | 1.39 (H$_\delta$) | | | |
| **11a**$^m$ | 1.22 | 72 | not assigned | | | |
| **11b**$^n$ | 1.58 | 72 | not assigned | | 9.21 (H$_2$)$^o$ | 5.0 ($J_{2,3}$) |
| | | | | | 8.07 (H$_3$) | 8.5 ($J_{3,4}$) |
| | | | | | 8.76 (H$_4$) | |
| | | | | | 8.16 (H$_5$) | 1.0 ($J_{2,4}$) |
| **11c**$^{p,q}$ | 1.34 | 70 | 0.96 (H$_\alpha$) | 64 ($^2J_{PtH}$) | 9.02 (H$_2$)$^r$ | |
| | | | −0.07 (H$_\beta$) | | 7.84 (H$_3$) | |
| | | | −0.4 (H$_\gamma$) | | 8.49 (H$_4$) | |
| | | | | | 7.98 (H$_5$) | |
| **12** | 1.36 (trans to N) | 72 | | | | |
| | 0.45 (trans to I) | 73 | | | | |
| | 1.64 (trans to N) | 66 | | | | |

[a] Cl, Br, I. $n$ = 0, 1, 3–5. [b] $n$ = 3, 4, 5. [c] Solvent CD$_2$Cl$_2$; cis and trans refer to mode of addition. [d] $\widehat{NN}$ = phen. [e] $J$(PtH) = 20 Hz. [f] $J$(PtH) = 18 Hz. [g] Notation for carbon chain: PtC$^\alpha$H$_2$C$^\beta$H$_2$. [h] $J$(PtH) = 20 Hz. [i] $J$(PtH) = 18 Hz. [j] Spectrum run on Bruker AM250. [k] $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$) $\delta$ −5.41 ($^1J$(PtC) = 695.8 Hz, MePt), 26. 14 ($^1J$(PtC) = 662.8 Hz, C$^\alpha$), 31.67 ($^2J$(PtC) = 87.6 Hz, C$^\beta$), 33.39 ($^3J$(PtC) = 70 Hz, C$^\gamma$), 29.07 ($^4J$(PtC) = 28.7 Hz, C$^\delta$), 7.34(C$^\omega$). [l] $J$(PtH) = 17 Hz. [m] Solvent DMF-$d_7$. [n] Solvent acetone-$d_6$. [o] $J$(PtH) = 18 Hz. [p] Solvent CD$_2$Cl$_2$; spectrum run on Bruker AM250. [q] $^{13}$C{$^1$H}NMR (CD$_2$Cl$_2$) $\delta$ −5.45 ($^1J$(PtC) = 700 Hz, MePt), 26.403 ($^1J$(PtC) = 670 Hz, C$^\alpha$), 29.18 (C$^\beta$), 30.53 (C$^\gamma$), 147.56 (C$^2$), 125.62 (C$^3$), 138.25 (C$^4$), 128.097 (C$^5$), 146.76 (C$^{11}$), 131.54 (C$^{12}$). [r] $J$(PtH) = 18 Hz. [s] Cis isomer.

A solution of complex **1**, in acetone, reacted with excess of I(CH$_2$)$_n$I ($n$ = 3–5) to form a pale yellow solution, from which solid products having the general formula [PtIMe$_2${(CH$_2$)$_n$I}(phen)] were obtained. If insufficiently large excess of the $\alpha,\omega$-diiodoalkane is used some precipitation is observed due to the formation of the insoluble binuclear complexes [Pt$_2$I$_2$Me$_4${$\mu$-(CH$_2$)$_n$}(phen)$_2$]. The new reactions, for the formation of the mononuclear complexes, are shown in eq 8. The product of each reaction is predominantly that for trans addition of the $\alpha,\omega$-diiodides, but very small traces of the cis isomers were observed.

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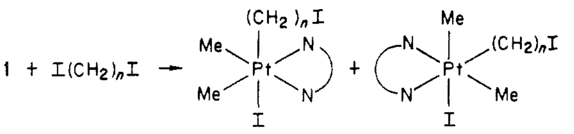
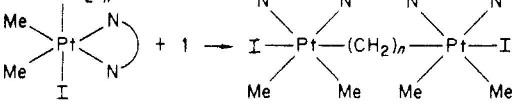


(8)

10a, $n = 3$
b, $n = 4$
c, $n = 5$

Characterization of the complexes was achieved by elemental analysis and $^{1}$H and NMR spectroscopy (Table II) and in the case of complex **10c** by $^{13}$C NMR spectroscopy. Assignments were straightforward based on comparison with the simple model compounds[23-25] and are discussed only briefly. The 250-MHz $^{1}$H NMR spectrum of **10c** gave a single MePt resonance as expected for a trans isomer, two triplets at 2.90 and 1.45 ppm due to the $CH_2I$ and $CH_2Pt$ protons, respectively, and three quintets due to the internal $CH_2$ groups. The $\beta$-$CH_2$ protons occur at 0.40 ppm, the $\gamma$-protons at 0.99 ppm, and the $\delta$-protons at 1.39 ppm. In addition, traces of a cis isomer could be detected by the characteristic MePt resonances at 0.65 and 1.62 ppm and a $CH_2I$ resonance at 3.22 ppm. The $^{13}$C NMR spectrum of the most soluble complex **10c** was recorded and is shown in Figure 2. The high field peak at −5.41 ppm is assigned to the carbon of a MePt group, by comparison with similar complexes.[23] The presence of only one such siignal also indicates the symmetrical stereochemistry of complex **10**. Iodine shields the carbon atom to which it is bonded, and the high-field peak at 7.34 ppm is therefore assigned to the $\omega$-carbon atom. The peak at 26.14 ppm has $^{195}$Pt satellites, with coupling to carbon of 662.8 Hz. This indicates direct bonding to platinum, and the resonance is assigned to the $\alpha$-carbon atom. The remaining assignments, for the alkyl chain, are made, very tentatively, on the basis of the magnitude of $^{195}$Pt–C coupling constants, assuming the coupling decreases the further the carbon atom is from the platinum. Thus the $\beta$-carbon signal occurs at 31.67 ppm, the $\gamma$-carbon at 33.39 ppm, and the $\delta$-carbon at 29.07 ppm. The assignments for the phenanthroline ring were based on literature precedents.[24,25]

Complexes **10** were reacted with $[PtMe_2(phen)]$, **1**, in acetone to give pale yellow, insoluble solids characterized as binuclear bridging polymethylene complexes of general formula $[Pt_2I_2Me_4(\mu\text{-}(CH_2)_n](phen)_2]$(eq 9). Complexes **11a** and **11b** can also be synthesized by reacting **1** with a slight excess of the corresponding $\alpha,\omega$-diiodoalkane but this method also produces some of the mononuclear complex **10a** or **10b**.



(9)

11a, $n = 3$
b, $n = 4$
c, $n = 5$

The solubility of the binuclear complexes increases as "$n$" increases, and a good $^{1}$H NMR spectrum (Table II) could be obtained only for **11c**. The 250-MHz $^{1}$H NMR spectrum is shown in Figure 3. The very strong peak at 1.34 ppm is assigned to the MePt protons and is good evidence that complex **11c** retains the methyl groups trans to the phenanthroline ligand. The protons ($H_\alpha$) of the methylene group directly bonded to platinum should appear as a triplet with $^{195}$Pt satellites. The distorted triplet at 0.96 ppm is assigned to these protons with $^{2}J_{PtH}$ equal to 64 Hz. A somewhat similar distortion was observed for the signal due to the $H_\alpha$ protons of the mononuclear complex **10c**. The protons of the two remaining methylene groups should appear as quintets, and these resonances are observed at −0.07 and 0.40 ppm, respectively.

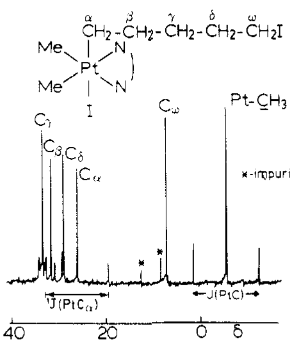


**Figure 2.** $^{13}C\{^{1}H\}$ NMR spectrum (50 MHz) of complex **10c**.

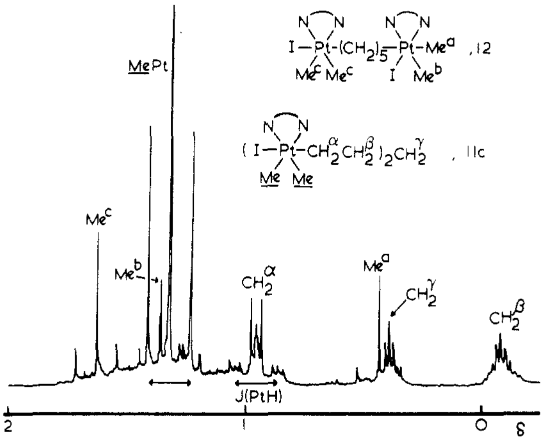


**Figure 3.** $^{1}$H NMR spectrum (250 MHz) of complex **11c**. Tentative assignments of resonances due to the methyl groups of the minor isomer **12** are given.

A small amount of the binuclear complex **12** is also present, and its structure is illustrated in Figure 3. The singlet at 0.45 ppm ($^{2}J_{PtMe}$ = 73 Hz) is assigned to the protons of the MePt group above the plane of the aromatic rings. The peak at 1.36 ppm ($^{2}J_{PtMe}$ = 72 Hz), of equal intensity to that at 0.45 ppm, is assigned to the protons of the MePt group, trans to nitrogen, on the same platinum atom as the methyl group at 0.45 ppm. The remaining two MePt groups of **12** are not equivalent and thus should produce two singlets, with $^{195}$Pt satellites. If however their resonances are accidentally degenerate, a peak twice the intensity of the one at 0.45 ppm would be observed. The peak at 1.64 ppm is believed to be due to these two MePt groups.

Each of the binuclear complexes **11** was pyrolyzed, and the gaseous products were analyzed by GC/mass spectrometry. For $n = 3$ the major gaseous product was propene with smaller traces of cyclopropane. For $n = 4$ the product was a mixture of butenes, and, for $n = 5$, the major products were 1,3-pentadiene and 1-pentene.

**Reaction of 1 with $\alpha,\alpha$-Dibromo-*o*-xylene.** There has been much interest in the use of the *o*-xylylidene ligand $o\text{-}C_6H_4(CH_2^-)_2$ as a bridging[26-28] or chelating ligand.[29]

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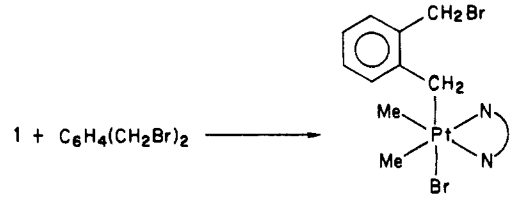
Complex 1 was reacted with an excess of $C_6H_4(CH_2Br)_2$ in acetone. The reaction was very fast, and a pale yellow solid was recovered from the solution. The product is that of trans oxidative addition (eq 10). The complex was fully



13

(10)

characterized by its $^1H$ NMR spectrum. Complex 13 reacted with 1 in acetone to give a pale yellow precipitate. This new complex 14 was too insoluble to obtain good NMR data, but, by analogy with previous work,[26-30] it is believed to be the bridging *o*-xylylene complex $[Pt_2Br_2Me_4(\mu\text{-}C_6H_4(CH_2)_2)(phen)_2]$.

## Discussion

Complex 1 undergoes clean oxidative addition with primary alkyl halides to give stable alkylplatinum(IV) compounds. This property has been exploited to give a simple synthesis of binuclear complexes with $Pt(CH_2)_nPt$ bridging units, where $n$ = 2–5. Pyrolysis of these complexes did not give coupling of the $(CH_2)_n$ unit with methyl groups on platinum but usually gave alkenes of formula $C_nH_{2n}$. This type of reaction has been observed previously in dimetallacycloalkanes, which have a metal–metal bond in addition to the $M(CH_2)_nM$ unit.[31,32] However, in Complex 11c, with the $Pt(CH_2)_5Pt$ unit, the major $C_5$ product was 1,3-pentadiene. It is probable that the hydride, presumed to be formed in the first β-elimination, is too far removed from the second platinum center to transfer to the $PtCH_2$ group to give pentene, and hence a second β-elimination occurs.

## Experimental Section

$^1H$ and $^{13}C(^1H)$NMR spectra were recorded by using Varian XL100 or Bruker AM-250 spectrometers, using $CD_2Cl_2$ or $CDCl_3$ as solvent unless otherwise stated.

Gas–liquid chromatography was carried out by using a Varian Aerograph Series 1400 system. The columns variously used were molecular sieve 5A, Porapak Q, and 10% SE-30, each aas 6 ft × $^1/_8$ in. columns.

Mass spectra were recorded on a Varian Mat Bremen mass spectrometer Mat 311A.

**[PtMe$_2$(phen)].** This was prepared according to the previous literature method.[18]

**[PtIMe$_3$(phen)].** To a solution of $[PtMe_2(phen)]$ (0.08 g) in acetone (20 mL) was added an excess of MeI (0.5 mL). The solution immediately turned pale yellow. The solvent was removed under vacuum and the solid residue redissolved in $CH_2Cl_2$ (10 mL). Pentane (20 mL) was added to this solution, and the product precipitated as a pale yellow solid: yield 84%; mp 284 °C. Anal. Calcd for $C_{15}H_{17}N_2IPt$: C, 32.9; H, 3.1; N, 5.1; I, 23.2. Found: C, 32.9; H, 3.2; N, 5.0; I, 21.8. The following were prepared in a similar way: [PtIMe$_2$(Et)(phen)]. [Anal. Calcd for $C_{16}H_{19}N_2IPt$: C, 34.2; H, 3.4; N, 4.99; I, 22.6. Found: C, 33.8; H, 3.1; N, 4.94; I, 22.9.]; [PtIMe$_2$(*n*-Pr)(phen)] [Anal. Calcd for $C_{17}H_{21}N_2IPt$: C, 38.6; H, 3.97; N, 5.30. Found: C, 38.5; H, 4.1; N, 5.35.]; [PtIMe$_2$(*n*-Bu)(phen)] [Anal. Calcd for $C_{18}H_{23}N_2IPt$: C, 36.7; H, 3.9; N, 4.8; I, 21.6. Found: C, 36.4; H, 3.8; N, 4.9; I, 21.7.].

**[PtI$_2$Me$_2$(phen)].** To a solution of $[PtMe_2(phen)]$ (0.13 g) in acetone (20 mL) was added a very slight excess of iodine (0.056 g) in acetone (10 mL). The intense colour of the iodine immediately disappeared, and the solvent was removed under vacuum. Excess iodine was removed by washing the product with a small volume of $CCl_4$; yield 80%. Anal. Calcd for $C_{12}H_{14}N_2I_2Pt$: C, 25.49; H, 2.1; N, 4.25. Found: C, 25.44; H, 2.1; N, 3.95.

***cis*- and *trans*-[PtClMe$_2$(CH$_2$Cl)(phen)].** A solution of $[PtMe_2(phen)]$ (0.07 g) in the $CH_2Cl_2$ (20 mL) was left to react for 1 day producing a pale yellow solution. The volume of solvent was reduced (3 mL), and pentane (20 mL) was added to precipitate the product, yield 85%.

***cis*- and *trans*-[PtClMe$_2$(CD$_2$Cl)(phen)].** A solution of $[PtMe_2(phen)]$ (0.03 g) in $CD_2Cl_2$ (4.0 mL) was left to react till a pale yellow solution was formed. The solid product was recovered by precipitation using pentane (15 mL); yield 75%.

***cis*- and *trans*-[PtBrMe$_2$(CH$_2$Br)(phen)].** To a solution of $[PtMe_2(phen)]$ (0.08 g) in acetone (8.0 mL) was added $CH_2Br_2$ (1.0 mL), and the reaction mixture was left to stand for 4 h. The solvent volume was reduced and the product recovered by precipitation using pentane (15 mL). Anal. Calcd for: $C_{15}H_{16}N_2Br_2Pt$: C, 31.1; H, 2.76; N, 4.83; Br, 27.64. Found: C, 32.1; H, 2.72; N, 3.83; Br, 27.41. In a similar fashion was prepared *cis*- and *trans*-[PtIMe$_2$(CH$_2$I)(phen)]. This product was separated from an impurity of $[PtI_2Me_2(phen)]$ by recrystallization from $CH_2Cl_2$. Anal. Calcd for $C_{15}H_{16}N_2I_2Pt$: C, 26.8; H, 2.4; N, 4.16; I, 37.8. Found: C, 27.2; H, 2.2; N, 4.0; I, 33.4.

***cis*- and *trans*-[PtBrMe$_2$(CH$_2$Cl)(phen)].** To a solution of $[PtMe_2(phen)]$ (0.103 g) in acetone (20 mL) was added an excess of $CH_2ClBr$ (1.25 mL). The reaction went to completion in 4 h. The solvent was removed under vacuum and the pale yellow residue redissolved in $CH_2Cl_2$ (5 mL). The product was recovered by precipitation using pentane (20 mL).

**Reaction between [PtMe$_2$(phen)] and CH$_2$ClI.** To a solution of $[PtMe_2(phen)]$ (0.144 g) in acetone (20 mL) was added $CH_2ClI$ (0.02 mL, 1:1 mole ratio). The reaction mixture was left for 15 min after which time a pale yellow solution had developed along with a small amount of precipitate. The solution was filtered and the solvent removed under vacuum. The solid residue was redissolved in a little $CH_2Cl_2$ and recovered by precipitation using pentane (15 mL).

**[Pt$_2$I$_2$Me$_4$(μ-C$_2$H$_4$)(phen)$_2$].** The 1,2-diiodoethane was recrystallized from $CCl_4$ before use.

To a solution of $[PtMe_2(phen)]$ (0.2 g) in acetone (20 mL) was added a solution of $I(CH_2)_2I$ (0.14 g) in acetone (10 mL). The desired product appeared as a brown precipitate after several minutes. The product was recovered by filtration and dried under vacuum. Anal. Calcd for $C_{30}H_{32}N_4I_2P_2$: C, 32.8; H, 2.97; N, 5.1. Found: C, 33.4; H, 2.92; N, 5.1. Similarily was prepared $[Pt_2Br_2Me_4(\mu\text{-}C_2H_4)(phen)_2]$ using excess $Br(CH_2)_2Br$. Anal. Calcd for $C_{30}H_{32}N_4Br_2Pt_2$: C, 36.07; H, 3.21; N, 5.61; Br, 16.03. Found: C, 35.84; H, 3.20; N, 5.61; Br, 16.89.

**[PtIMe$_2${(CH$_2$)$_3$I}(phen)].** To a solution of $[PtMe_2(phen)]$ (0.09 g) in acetone (30 mL) was added a large excess of 1,3-diiodopropane (1.0 mL). The reaction mixture was left to stand for 2 h after which time a yellow solution had developed. The solvent was removed under vacuum and the solid residue redissolved in a little $CH_2Cl_2$. The product was recovered by precipitation using pentane: yield 81%; mp 335 °C dec. Anal. Calcd for $C_{17}H_{20}N_2I_2Pt$: C, 29.1; H, 2.85; N, 3.99; I, 36.2. Found: C, 29.1; H, 2.80; N, 4.24; I, 36.1. In a similar way was prepared [PtIMe$_2${(CH$_2$)$_4$I}(phen)] [Anal. Calcd for $C_{18}H_{22}N_2I_2Pt$: C, 30.2; H, 3.08; N, 3.9; I, 35.5. Found: C, 29.4; H, 3.16; N, 3.3; I, 35.8.] and [PtIMe$_2${(CH$_2$)$_5$I}(phen)] [Anal. Calcd for $C_{19}H_{24}N_2I_2Pt$: C, 31.3; H, 3.3; N, 3.8. Found: C, 31.3; H, 3.3; N, 3.8 (yield 84%; mp 212 °C.)].

**[PtBrMe$_2$(CH$_2$C$_6$H$_4$CH$_2$Br)(phen)].** To a solution of $[PtMe_2(phen)]$ (0.044 g) in acetone (25 mL) was added a solution of α,α′-dibromo-*o*-xylene (0.06 g) in acetone (10 mL). An immediate reaction occurred producing a pale yellow solution. The solvent was removed under vacuum, and the solid residue was washed with ether to remove any excess α,α′-dibromo-*o*-xylene. The solid product was redissolved in $CH_2Cl_2$ (3 mL) and precipitated from solution by using pentane (15 mL): yield 60%;

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mp 280 °C dec; $^1$H NMR data solvent $CD_2Cl_2$ $\delta$ 1.69 ($J$(PtH) = 71 Hz, MePt), 2.99 ($J$(PtH) = 94 Hz, $CH_2Pt$), 3.76 ($CH_2Br$). Anal. Calcd for $C_{22}H_{22}Br_2N_2Pt$: C, 39.5; H, 3.3; Br, 23.9. Found: C, 39.8; H, 3.4; Br, 23.0.

**[$Pt_2I_2Me_4\{\mu\text{-}(CH_2)_3\}(phen)_2$].** This complex was prepared by two different routes, described below.

(a) To a solution of [$PtMe_2$(phen)] (0.112 g) in acetone (20 mL) was added $I(CH_2)_3I$ (0.032 mL, 1:1 mole ratio). The solution rapidly turned pale yellow with the formation of a cream precipitate. The precipitate was the required binuclear complex and was removed by filtration and dried under vacuum; mp 195 °C dec. Anal. Calcd for $C_{31}H_{34}N_4I_2Pt_2$: C, 33.6; H, 3.1; N, 5.1; I, 22.97. Found: C, 33.4; H, 2.9; N, 5.2; I, 22.80.

(b) To a solution of [$PtMe_2$(phen)] (0.19) in acetone (15 mL) was added a solution of [$PtIMe_2\{(CH_2)_3I\}$(phen)] (0.032 g) in acetone (25.0 mL, 1:1 mole ratio). The reaction solution was left to stand for a day after which time some precipitate had formed and the solution had become a pale yellow color. Both the precipitate and the product left in solution were found to be the desired binuclear complex. In a similar fashion were prepared [$Pt_2I_2Me_4\{\mu\text{-}(CH_2)_4\}(phen)_2$] [Anal. Calcd for $C_{32}H_{36}N_4I_2Pt_2$: C, 34.3; H, 3.2; N, 5.0. Found: C, 33.5; H, 3.4; N, 4.6 (yield 85%: mp 269 °C.)] and [$Pt_2I_2Me_4\{\mu\text{-}(CH_2)_5\}$(phen)] [Anal. Calcd for $C_{33}H_{38}N_4I_2Pt_2$: C, 34.9; H, 3.4; N, 4.9; I, 22.4. Found: C, 34.9; H, 3.5; N, 4.8; I, 22.8.].

**Reaction of [$PtMe_2$(phen)] with [$PtBrMe_2(CH_2C_6H_4CH_2Br)$(phen)].** To a solution of [$PtMe_2$(phen)] (0.012 g) in acetone (20 mL) was added a solution of [$PtBrMe_2(CH_2C_6H_4CH_2Br)$(phen)] (0.019 g) in acetone (15 mL, 1:1 mole ratio). The reaction solution was left to stand for 3 days in which time a yellow precipitate formed. Anal. Calcd for $C_{36}H_{36}Br_2N_4Pt_2$: C, 40.2, H, 3.35. Found: C, 39.9, H, 3.2%.

**Analysis of the Gaseous Product from the Reaction between $I(CH_2)_2I$ and [$PtMe_2$(phen)].** A solution of [$PtMe_2$(phen)] (0.04 g) in $CH_2Cl_2$ (3 mL) was transferred to a glass vessel and frozen by use of liquid $N_2$. A sample of $I(CH_2)_2I$ (0.028 g, 1:1 mole ratio) in $CH_2Cl_2$ (1 mL) was then introduced into the vessel, and the apparatus was sealed and evacuated. The apparatus was allowed to return to room temperature and the solution left to react for 1 h. With use of gas-tight syringe (1 mL) a sample of the gas was removed from the vessel and analyzed by gas chromatography. The gas chromatogram showed a large peak due to ethene, confirmed by comparison of the retention time with an authentic sample of ethene.

**Mass Balance Experiment.** To a solution of [$PtMe_2$(phen)] (0.187 g) in acetone (20 mL) was added an excess of $I(CH_2)_2I$ (0.210 g) in acetone (10 mL). A brown precipitate rapidly formed along with a pale yellow solution. The brown precipitate was removed by filtration, dried, and weighed (0.122 g). The solvent was removed under vacuum from the filtrate and thoroughly dried and then weighed (0.128 g).

**Isomerization of *cis*-[$PtIMe_2(CH_2I)$(phen)].** To a solution of [$PtMe_2$(phen)] (0.015 g) in $CH_2Cl_2$ (1 mL) in an NMR tube was added $CH_2I_2$ (0.003 mL, 1:1 mole ratio). The solution was shaken vigorously and placed in the probe of a Varian XL100 spectrometer. The probe was at ambient temperature. NMR spectra were recorded at regular intervals over a period of 15 min and finally after about 2 h. A similar experiment was performed for the reaction between [$PtMe_2$(phen)] and $CH_2ClBr$.

**Pyrolysis of [$Pt_2I_2Me_4\{\mu\text{-}(CH_2)_n\}(phen)_2$] ($n$ = 2, 3, 4, 5).** A sample of [$Pt_2I_2Me_4\{\mu\text{-}(CH_2)_2\}$(phen)] (0.03 g) was placed in a glass reaction vessel fitted with a serum cap. The vessel was sealed and evacuated. The sample was heated till it melted and charred. With use of a gas-tight syringe (1 mL) a sample of the gaseous product was removed and analyzed by gas chromatography. The gas chromatogram showed the presence of large amounts of ethene.

The same procedure was used to pyrolyze the gaseous products from the complexes with $n$ = 3, 4, and 5. However, in these cases analysis of the gaseous products was performed by MS/GC. A temperature program was used ranging from 20 to 150 °C and set at 15 °C min$^{-1}$.

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