Synthesis of [Pt(η^5-C_5Me_5)(η^4-C_8H_{12})]BF_4 (2). Treatment of 1 (0.1 g, 0.17 mmol) with $HBF_4\cdot Et_2O$ (2–3 drops) in pentane at −78 °C gives an instantaneous pale yellow precipitate. The suspension was allowed to warm to room temperature, and the solid was collected by filtration. Recrystallization from THF diethyl ether (1:1; 10 cm^3) gave a yellow microcrystalline solid (0.063 g, 0.12 mmol, 70%).

Synthesis of [Pt(PMe_3)$_2${σ^2-C_8H_{12}(Cp*)$_2$}] (3). To a solution of [Pt(η-C_5Me_5){σ:η^2-C_8H_{12}(Cp*)}] (0.05 g, 0.087 mmol) in pentane (30 cm^3) was added trimethylphosphine (1 cm^3) by vacuum transfer. The mixture was allowed to stir at room temperature for 24 h. The solvent and unreacted PMe_3 were removed in vacuo, yielding a colorless oily residue. The residue was extracted with pentane (2 × 20 cm^3), and the solution was filtered and concentrated to ca. 10 cm^3. Cooling initially to −20 °C and then −80 °C gave colorless crystals (0.5 g, 0.068 mmol, 80%).

Synthesis of [Pt(η-C_8H_{12})(η^1-C_9H_7)Cl] (4). To a suspension of [Pt(η-C_8H_{12})Cl_2](0.2 g, 0.53 mmol) in THF (50 cm^3) was added NaInd (0.073 g, 0.53 mmol) in THF (20 cm^3). The mixture was stirred for 12 h during which time the solution turned yellow. The suspension was allowed to settle and the solution filtered. The filtrate was reduced to dryness in vacuo, yielding a yellow solid. The oily solid was extracted with toluene (2 × 50 cm^3). The toluene extracts were concentrated under reduced pressure. Cooling to −20 °C and then to −80 °C overnight gave yellow crystals of [Pt(η-C_8H_{12})(η^1-C_9H_7)Cl] (0.16 g, 0.37 mmol, 70%).

Synthesis of [Pt(η-C_8H_{12})(η^1-C_9H_7)$_2$] (5). To a suspension of [Pt(η-C_8H_{12})Cl_2] (0.1 g, 0.26 mmol) in THF (50 cm^3) was added NaInd (0.096 g, 0.7 mmol) in THF (20 cm^3). The mixture was stirred for 12 h during which time the solution turned yellow in color. The suspension was allowed to settle and the solution filtered. The filtrate was reduced to dryness in vacuo, yielding a waxy red solid. The waxy solid was extracted with toluene (2 × 50 cm^3) giving a dark orange solution. The toluene extracts were concentrated under reduced pressure. Cooling to −20 °C and then to −80 °C overnight gave orange microcrystalline [Pt(η-C_8H_{12})(η^1-C_9H_7)$_2$] (0.097 g, 0.18 mmol, 71%).

Synthesis of [Pt(η^5-C_9H_7)(η^4-C_8H_{12})]BF_4 (6). Method A. Treatment of mixture of **5a** and **5b** (1:1; 0.2 g, 0.53 mmol) with $HBF_4\cdot Et_2O$ (2–3 drops) in diethyl ether at −78 °C gives an instantaneous pale yellow precipitate. The suspension was allowed to warm to room temperature. The precipitate was collected, washed with diethyl ether (2 × 10 cm^3), and dried in vacuo. Recrystallization from THF/diethyl ether (1:1; 10 cm^3) gave a yellow microcrystalline solid (0.23 g, 0.47 mmol, 90%).

Method B. To a solution of 4 (0.75 g, 0.14 mmol) in CH_2Cl_2 (20 cm^3) was added a solution of $AgBF_4$ (0.027 g, 0.14 mmol) in CH_2Cl_2 at room temperature. The solution was stirred at room temperature for 5–10 min and the solvent removed under reduced pressure to give a yellow waxy solid. Extraction with THF/diethyl ether (1:1; 2 × 10 cm^3) gives an orange solution which on cooling to −20 °C and then −80 °C gives a yellow microcrystalline solid (0.056 g, 0.11 mmol, 80%).

Acknowledgment. I wish to thank Dr. M. L. H. Green and Dr. A. E. Derome for their helpful discussions and the Royal Commission for the Exhibition of 1851 for a Research Fellowship.

Registry No. 1, 108818-18-4; 2, 108818-20-8; 3, 108834-57-7; 4, 108818-21-9; 5a, 108818-22-0; 5b, 108942-24-1; 6, 108818-24-2; NaCp*, 40585-51-1; NaInd, 23181-84-2; [Pt(η-C_8H_{12})Cl_2], 12080-32-9.

Supplementary Material Available: Listings of the hydrogen atom positions and anisotropic thermal parameters for all non-hydrogen atoms (2 pages); a listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

Reactivity and Mechanism in the Formation of (μ-Hydrocarbyl)diplatinum(IV) Complexes by Oxidative Addition of α,α'-Dibromoxylenes to Dimethylplatinum(II) Complexes

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Received February 7, 1987

A study of the formation of binuclear complexes with μ-hydrocarbyl ligands by double oxidative addition of the organic dihalides, α,α'-dibromoxylene (ortho and para isomers), and $I(CH_2)_nI$ to binuclear platinum complexes has been made. In bridged 2,2'-bipyrimidine (bipym) systems it is found that [Me_2Pt(μ-bipym)$PtMe_2$(4-$CH_2C_6H_4CH_2Br$)Br] undergoes rapid intramolecular oxidative addition to give [Me_2BrPt(μ-bipym)(μ-4-$CH_2C_6H_4CH_2$)$PtBrMe_2$] but the analogous complexes [Me_2Pt(μ-bipym)$PtMe_2$(2-$CH_2C_6H_4CH_2Br$)Br] and [Me_2Pt(μ-bipym)$PtMe_2${(CH_2)$_n$I}I] were long-lived and rearranged slowly to tetranuclear complexes. Reasons for these differences are suggested, based on conformational or ring strain effects. Binuclear complexes with μ-hydrocarbyl groups were formed more easily from [Pt_2Me_4(μ-pyen)] (pyen = bis(2-pyridyl)ethylenediimine) as a result of the flexibility of the μ-pyen ligand, but the reagents $I(CH_2)_nI$ failed to give μ-polymethylene derivatives. Kinetic studies of several of these reactions have been carried out, and it is shown that the para isomer of α,α'-$C_6H_4(CH_2Br)_2$ is more reactive than the ortho isomer and that a platinum center can activate a remote C–Br bond by a neighboring group effect. The apparent intermolecular oxidative additions of binuclear complexes to give tetranuclear complexes are shown to follow first-order kinetics and probably involve an intramolecular reaction followed by rapid dimerization. The intramolecular reaction is thought to involve dissociation of platinum(IV) from the diimine ligand.

Introduction

There is considerable interest in μ-hydrocarbyl complexes of transition metals, partly since such compounds can act as models for proposed catalytic intermediates, and this area of chemistry has been reviewed.[1-4] Platinum complexes with $Pt(CH_2)_nPt$ units have been prepared by oxidative addition of $I(CH_2)_nI$ to complexes such as the 2,2'-bipyrimidine derivative [$PtMe_2$(bipym)] (1c).[5,6] The

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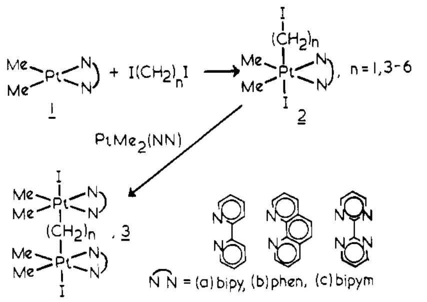
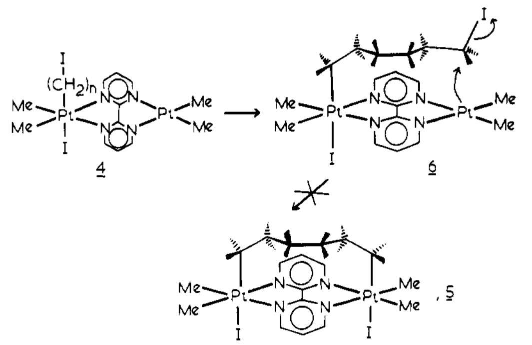
Scheme I



Scheme II

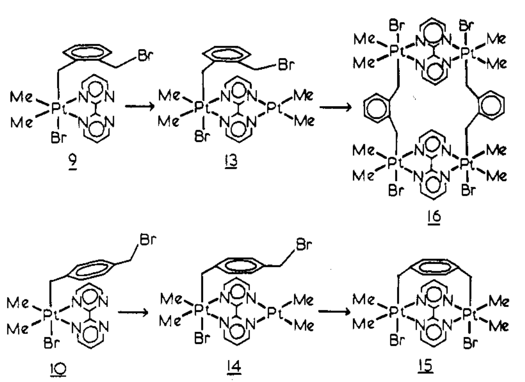


first product was **2c**, containing a $Pt(CH_2)_nI$ group, but further reaction between **2c** and **1c** gave **3c**, containing the desired $Pt(CH_2)_nPt$ units with n = 3–6 (Scheme I).

Although this intermolecular oxidative addition occurred readily, intramolecular oxidative addition of the C–I bond of **4** to the dimethylplatinum center did not occur. This observation was interpreted in terms of the difficulty of arranging the $(CH_2)_nI$ chain into the conformation required for oxidative addition to the second platinum center since, when n = 6, the $(CH_2)_n$ chain is certainly long enough to bridge between the platinum centers (separated by about 5.7 Å).[6] In this case, an 11-membered ring would be formed in complex **5**, Scheme II, and the problem may be related to the difficulty, which is well-known in organic chemistry,[7] of forming medium-sized rings. Hydrogen atoms of the central methylene groups of **5**, and especially of the hypothetical transition state **6** leading to **5**, must be directed toward the bipyrimidine ring, and unfavorable steric effects result from this. In addition, there are unfavorable eclipsed conformations of carbon–carbon bonds in **6**.

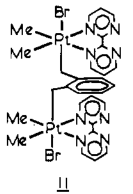
These problems should be largely overcome by use of a planar aromatic ring bridging two $-CH_2X$ groups, and this paper reports a study of the reactions of the ortho and para isomers of α,α′-dibromoxylene with dimethylplatinum(II) derivatives of 2,2′-bipyrimidine. In addition, reactions with the binuclear complex $[Pt_2Me_4(\mu\text{-pyen})]$ (**7**) having a flexible bridge between the two diimine chelates are described. The flexible CH_2CH_2 bridge allows the orientation of the coordination planes and the distance between the two platinum(II) centers to vary, in contrast with the rigidly coplanar 2,2′-bipyrimidine complexes. This leads to significant differences in reactivity. The formation of chelate or bridging complexes with $CH_2C_6H_4CH_2$ ligands has been observed in several other systems.[2,5,8-12]

Scheme III

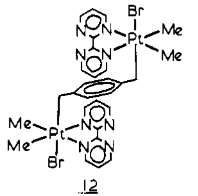


Results and Discussion

The 2,2′-Bipyrimidine System. Because the binuclear complex $[Pt_2Me_4(\mu\text{-bipym})]$ (**8**) is highly insoluble,[6] the mononuclear complex $[PtMe_2(bipym)]$ (**1**) was used in synthesis. The reaction of **1c** with excess α,α′-dibromo-*o*-xylene or α,α′-dibromo-*p*-xylene to give $[PtBrMe_2(2\text{-}CH_2C_6H_4CH_2Br)(bipym)]$ (**9**) or $[PtBrMe_2(4\text{-}CH_2C_6H_4CH_2Br)(bipym)]$ (**10**), respectively has been reported earlier.[6] Further reaction of **9** and **10** with **1** then gave the binuclear derivatives $[\{PtBrMe_2(bipym)\}_2(\mu\text{-}2\text{-}CH_2C_6H_4CH_2)]$ (**11**) and $[\{PtBrMe_2(bipym)\}_2(\mu\text{-}4\text{-}CH_2C_6H_4CH_2)]$ (**12**), respectively.



11



12

Reaction of **9** or **10** with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ should give initially the Pt(IV)–Pt(II) derivative **13** or **14**, respectively, by displacement of SMe_2 ligands by the free nitrogen donors present in **9** or **10** (Scheme III).

Complexes **13** and **14** are expected to be characterized by a metal to ligand charge-transfer band [Pt^{II} (dπ) → bipym (π*)] in the region 500–600 nm.[6] The species **13** was formed, as shown by the growth of the expected band in the UV–visible spectrum (Figure 1, supplementary material), but the complex slowly reacted further as shown by the subsequent decay of this band (Figure 1, supplementary material). An examination of a molecular model of **13** shows that intramolecular oxidative addition of the C–Br bond to the platinum(II) center is impossible due to ring strain (see structure **13** which is drawn approximately to scale), and the nature of the final product will be discussed later. In contrast, reaction of **10** with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ gave a product with no band in the region 500–600 nm. Models show that **14** can undergo intramolecular oxidative addition by the S_N2 mechanism to give **15** (Scheme III), and this reaction is clearly much faster than the rate of formation of **14**. The difference between these two systems is illustrated in Figure 2, which

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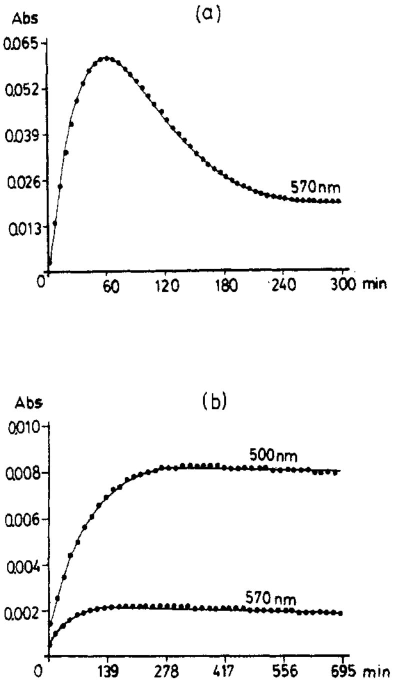


Figure 2. Absorbance vs. time plots: above, at λ = 570 nm for the reaction **9** → **13** → **16**; below, (a) at λ = 500 nm and (b) at λ = 570 nm for the reaction **10** → **15**.

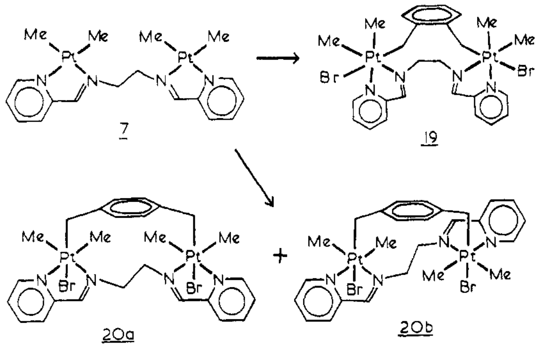
shows the changes in UV–visible absorption at 570 nm during the reactions. The growth and subsequent decay of the 570-nm band can be used to monitor the reaction **9** → **13** → final product (Figure 2a), whereas the similar reaction of **10** → **15** shows no buildup of the proposed intermediate **14** (Figure 2b). The complete set of UV–visible spectra in the latter case show only the growth of a band at 480 nm, typical of binuclear Pt(IV)–Pt(IV) complexes with μ-bipym ligands.[6]

The final product from the α,α'-dibromo-*o*-xylene system was identified as the tetranuclear derivative **16**. The initial evidence for the tetranuclear formulation was based on the mass spectrum which gave the highest mass peak at m/e 1424, with the expected isotope pattern for a Pt_4 species, corresponding to the loss of four bromine atoms from the molecular ion. Since the other spectroscopic data did not define the nuclearity of the complex and crystals suitable for X-ray studies could not be grown, a confirmation of the proposed structure by an independent synthesis was made. Complexes **11** and $[Pt_2(\mu\text{-}Br)_2Me_4(\mu\text{-}o\text{-}CH_2C_6H_4CH_2)(SMe_2)_2]$ (**17**)[13] already contain the μ-$PtCH_2C_6H_4CH_2Pt$ units proposed in **16**. It was found that the free nitrogen donors present in **11** displaced dimethyl sulfide ligands from **17** to yield **16**, identical (IR, MS) with the complex prepared earlier. Since this reaction, by analogy with many others,[6] is expected to give **16**, the proposed structure is strongly supported.

It has since been discovered that the complexes **4**, with n = 3–6, slowly (3–5 days) react in dilute acetone solution to give insoluble orange solids which, by analogy with the above reaction, are suggested to be tetranuclear derivatives **18**. These complexes **18** gave satisfactory elemental analyses but were too insoluble to give NMR spectra.

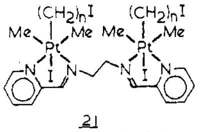
The Bis(2-pyridyl)ethylenediimine System. The two platinum centers in the pyen complex **7** have much flexibility, unlike the bipym system described above. The dimer **7** is also soluble enough for direct study. Reaction of **7** with α,α'-dibromo-*o*-xylene gave **19** by double oxidative addition (Scheme IV). The structure of **19** is deduced from the NMR spectra. Examination of molecular models shows that the structure with methylplatinum units syn as shown is the only viable form and that the angle between the coordination planes of the two platinum centers is likely to be ~100°. Clearly the difference from the bipym system, in which a long-lived Pt(IV)–Pt(II) intermediate was formed, is due to the flexibility of the pyen ligand, which allows the $o\text{-}CH_2C_6H_4CH_2$ to bridge between the two platinum centers without severe angle strain.

Scheme IV

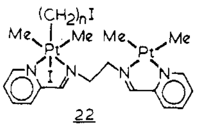


α,α'-Dibromo-*p*-xylene also reacted readily with **7** to give **20**, again by double oxidative addition. Two isomers of **20** with the dimethylplatinum units syn (**20a**) or anti (**20b**) are possible, depending on which face of the second dimethylplatinum(II) unit the second, rapid oxidative addition occurs. One of these isomers was formed in much higher yield than the other (product ratio ~4:1) but, since suitable crystals for X-ray diffraction were not obtained, the two isomers could not be distinguished. In this case, molecular models suggest that the two dimethylplatinum units should be approximately coplanar in **20**.

On the basis of the above results, it appeared likely that the reagents $I(CH_2)_nI$ would yield $Pt_2\{\mu\text{-}(CH_2)_n\}$ complexes on reaction with **7**. However this was not the case and the products **21a–d** were obtained instead. These complexes were identified by the ^1H NMR spectra and analytical data. All showed prominent triplets in the ^1H NMR spectra due to the dangling CH_2I groups, though the remaining CH_2 resonances of the $Pt(CH_2)_nI$ groups gave complex, overlapping peaks which would not be assigned. Confirmation of the structure was obtained by recording the ^{13}C NMR spectrum of complex **21c**, for which the expected five CH_2 resonances of the $Pt(CH_2)_5I$ unit were readily identified (Experimental Section). Only one isomer of each complex **21** was observed.



21
n = a,3; b,4; c,5; d,6



22
n = 5

For the reaction with $I(CH_2)_5I$ with **7** in acetone-d_6, monitoring by ^1H NMR showed that the 1:1 adduct **22** was formed at an intermediate stage and reacted further with $I(CH_2)_5I$ to give **21c**. The reactions of **7** and **22** with $I(CH_2)_5I$ occurred at about the same rate, and it was therefore not possible to isolate the intermediate **22**, which was characterized by the observation of two $MePt^{II}$ resonances [δ 1.14 (^2J(PtH) = 88 Hz), 1.22, (^2J(PtH) = 88 Hz)], two $MePt^{IV}$ resonances [δ 1.43 (^2J(PtH) = 70 Hz), 1.48 (^2J(PtH) = 72 Hz)], and a triplet due to the CH_2I resonance [δ 3.14 (^3J(HH) = 7 Hz)]. The failure of **22** to undergo intramolecular oxidative addition is presumably due to unfavorable conformational effects in the transition state

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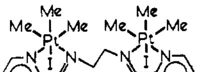
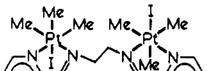
Table I. Second-Order Rate Constants for Reactions of α,α'-Dibromoxylene and Derivatives in Acetone at 25 °C

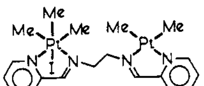
complex	reagent	product	k_2/L mol^{-1} s^{-1}
[PtMe$_2$(bipym)] (1)	1,2-$C_6H_4(CH_2Br)_2$	**9**	2.75
1	1,4-$C_6H_4(CH_2Br)_2$	**10**	17.5
1	**9**	**11**	1.33
1	**10**	**12**	21.0
[Pt$_2$Me$_4$(μ-pyen) (7)	1,2-$C_6H_4(CH_2Br)_2$	**19**	2.08
7	1,4-$C_6H_4(CH_2Br)_2$	**20**	18.1
7	$I(CH_2)_3I$	**21a**	3.2×10^{-2}
7	$I(CH_2)_4I$	**21b**	2.0×10^{-2}
7	$I(CH_2)_5I$	**21c**	2.0×10^{-2}
7	$I(CH_2)_6I$	**21d**	2.2×10^{-2}

for the S_N2 mechanism, although examination of molecular models suggested that such effects should be less severe than in **6** and related complexes with the 2,2′-bipyrimidine ligand.

In an attempt to gain further insight into these reactions, a more detailed study of the reaction of methyl iodide with complex **7** was made. It was earlier reported that the two isomers **23a** and **23b** were formed in this reaction.[14] This has been confirmed, but, on standing, one isomer decays and the other grows until, after 1 day, only one isomer was present. The NMR data do not define which isomer is the more stable. It is suggested that the isomerization of the less stable to the more stable isomer occurs by partial dissociation of a PtMe$_3$I unit from the diimine ligand, followed by rearrangement and recoordination. Because of the complexity of the NMR spectra of the initial product mixture, it was particularly difficult to identify intermediates in this system. However, by using only a small excess of methyl iodide and monitoring the early stages of the reaction by NMR at -80 °C, we observed new resonances presumed to be due to intermediate **24**: δ(MePt) 0.55 (trans to I), 0.96, 0.98 (MePt^{II}), 1.12, 1.34 (MePt^{IV} trans N). However, **24** was always a minor component in the presence of **7** and **23** and clearly reacts more rapidly with MeI than does the parent **7**, for reasons which are not understood.


23a


23b


24

Kinetic Studies. The kinetics of several of the above reactions were studied, in order to compare the reactivities of the ortho and para isomers of α,α'-dibromoxylene and to compare the reactivities of the different platinum complexes. Some of the results, obtained at 25 °C in acetone solution, are given in Table I and Figure 3.

The mononuclear complex [PtMe$_2$(bipym)] (**1**) reacted with excess of the ortho and para isomers of α,α'-dibromoxylene to give **9** and **10**, respectively. The reactions were first order in each reagent, and the second-order rate constants were 2.75 and 17.5 L mol^{-1} s^{-1}, respectively. The corresponding rate constants for the oxidative addition reaction of the remaining C–Br bond of **9** and **10** to **1** were 1.33 and 21.0 L mol^{-1} s^{-1}, respectively. For the *p*-xylene derivatives, complex **10**, which has only one C–Br bond, reacts slightly faster than α,α'-dibromo-*p*-xylene which has two C–Br bonds. The remote platinum atom in **10** therefore has a modest activating effect. In contrast, **9** reacts more slowly than α,α'-dibromo-*o*-xylene with **1**, but this is probably a result of greater steric hindrance in the ortho derivative **9**. It is likely that steric effects are responsible for the lower rate of reaction of the ortho derivatives in all the systems studied here.

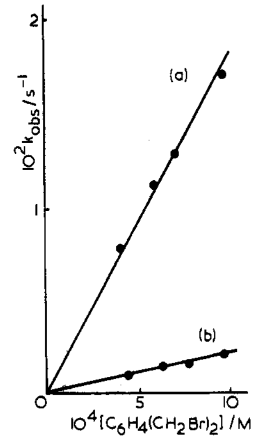


Figure 3. Plots of observed first order rate constants vs. concentration of α,α'-dibromoxylene for reaction with complex **7** in acetone at 25 °C: (a) para isomer; (b) ortho isomer.

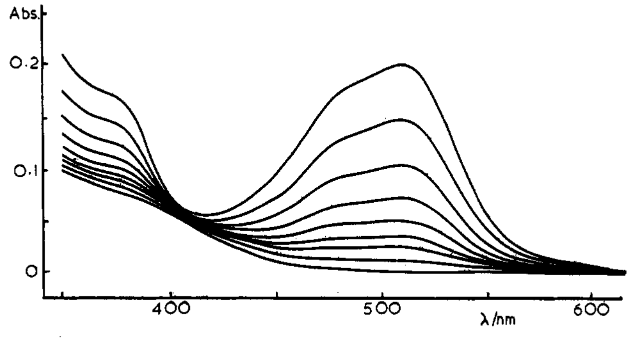


Figure 4. Changes in absorption spectra during the reaction of complex **7** with $I(CH_2)_3I$ in acetone to give **22a** and then **21a**. Absorbance decreases with time.

For the reactions with [Pt$_2$Me$_4$(μ-pyen)] (**7**), the products, even with a large excess of α,α'-dibromoxylene, were always **19** and **20**. The measured rate constants are therefore for the first oxidative addition to give the Pt(IV)–Pt(II) intermediate, which then undergoes very fast intramolecular oxidative addition to give **19** or **20**. However, in the reactions of **7** with $I(CH_2)_nI$ the observed rate constant is an average of the values for the first and second oxidative addition to give **21**. It is remarkable that the UV–visible spectra indicate a single proces and good first-order kinetics were observed in all cases. This is expected only if the rate constants for the first and second oxidative additions are very similar and if the intermediates **22** have very similar UV–visible spectra to the starting complex **7**. A set of UV–visible spectra for a typical reaction is shown in Figure 4. The diiodoalkane $I(CH_2)_nI$ with $n = 3$ was more reactive than when $n = 4$–6, consistent with previous studies on oxidative addition to the mononuclear complex [PtMe$_2$(1,10-phen)] (phen = phenanthroline).[5]

A brief kinetic study has also been made of the reactions of **9** and **10** with [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] in acetone at 25 °C, by analysis of the UV–visible spectral changes illustrated in Figures 1 and 2. The reaction of **10** with [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] to give **15** followed overall first-order kinetics, with $k_{obsd} = 3.5 \times 10^{-4}$ s^{-1}. The rate-determining step is the ligand displacement to give **14**, and the observation of

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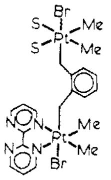
[14] Scott, J. D.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 2522.

first-order kinetics suggests a mechanism similar to that for displacement of dimethyl sulfoxide from *cis*-[PtMe$_2$(Me$_2$SO)$_2$] by 2,2′-bipyridine or 1,10-phenanthroline, which was suggested to involve rate determining loss of Me$_2$SO from *cis*-[PtMe$_2$(Me$_2$SO)$_2$].[15] In the present case, rate-determining dissociation or solvolysis of [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] to give *cis*-[PtMe$_2$(SMe$_2$)] or *cis*-[PtMe$_2$(SMe$_2$)(acetone)], followed by rapid attack by **10** can be invoked. However, we have not studied the kinetics in detail and this conclusion is tentative. The first step of the reaction of **9** with [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] to give **13** also followed overall first-order kinetics, with $k_{obsd} = 3.4 \times 10^{-4}$ s^{-1}. The close similarity in magnitudes of these two rate constants lends support to the mechanism of formation of **13** and **14** proposed above and also supports the suggestion that the ligand substitution step is rate determining in the reaction of **10** with [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$].

More surprising was the observation that the slow reaction of the binuclear complex **13** to give the tetranuclear product **16** also followed first-order kinetics, with $k_{obsd} = 2.8 \times 10^{-4}$ s^{-1}. Clearly a true intermolecular oxidative addition, which we had expected, involving the C–Br bond of one molecule of **13** adding to the Pt(II) center of a second molecule of **13** should lead to second-order kinetics. We suspect that, in the rate-determining step, the platinum(IV) center of **13** must partly dissociate from the bipym ligand, thus allowing the C–Br bond to approach the platinum(II) center and undergo intramolecular oxidative addition. the initial product would then be **25** (S = solvent acetone), which must rapidly dimerize to give the observed product **16**. The ability of platinum to dissociate (presumably with solvent assistance) from the chelate diimine ligand is at first surprizing. However, we have observed similar steps in the disproportionation of Pt(IV)–Pt(II) complexes with binucleating bis(diimine) ligands to give the Pt(IV)–Pt(IV) and Pt(II)–Pt(II) analogues,[14,16] as well as in the isomerization of complexes **23a** and **23b** discussed above. Presumably the trans-labilizing effect of the methylplatinum groups is responsible for this effect.



25

Conclusions

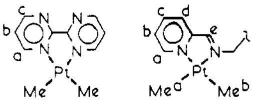
This work has demonstrated two significant effects in the formation of (μ-alkanediyl)dimetal complexes by double oxidative addition.

Firstly, the observation that **6** does not undergo rapid intramolecular oxidative addition whereas **14** does demonstrate the importance of conformational effects in oxidative addition by the S$_N$2 mechanism. In the above two compounds the chain lengths are similar but steric effects involving the (CH$_2$)$_6$ chain hinder the approach of the CH$_2$I group of **6** to platinum(II), whereas no such problem arises with the bridging CH$_2$C$_6$H$_4$CH$_2$ group of **14**.

Secondly, the flexibility of the pyen ligand in [Pt$_2$Me$_4$(μ-pyen)] (**7**) allows the orientation of the coordination planes of the two platinum centers to vary and the distance between the platinum atoms to vary. This greatly enhances the ability to form (μ-hydrocarbyl)diplatinum complexes when compared to the bipym system. The comparison of the complexes **19**, formed by double oxidative addition, and **13** illustrates this point clearly. However, the reactions of I(CH$_2$)$_n$I with **7** failed to give μ-hydrocarbyl derivatives, and it is clear that conformational effects are still unfavorable even in this case.

Experimental Section

^{1}H NMR spectra were recorded on a Varian XL200 spectrometer in CD$_2$Cl$_2$ solvent. Chemical shifts are given with respect to Me$_4$Si. Peaks are labeled as follows:



IR spectra were recorded on a Beckman IR4250 spectrometer as Nujol mulls between NaCl plates. Mass spectra were recorded on a Varian MAT Bremen mass spectrometer MAT311A. UV-visible spectra were recorded, and kinetic studies were performed in acetone solution at 25.0 °C on a Varian Cary 2290 spectrometer equipped with a PolyScience Series 900 constant temperature fluid circulator and a DS-15 data station. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario.

Complexes **1**–**4** and **9**–**11** were prepared as previously described.[6,14]

Kinetic Studies. The reactions of **2** and **7** with *o*- or *p*-BrCH$_2$(C$_6$H$_4$)CH$_2$Br were carried out by using an excess of BrCH$_2$C$_6$H$_4$CH$_2$Br, monitoring the decay of the MLCT band of **1** or **7** (see Figure 4). For example, a 10.0-mL aliquot of a solution of 4-C$_6$H$_4$(CH$_2$Br)$_2$ (9.09×10^{-4} M) was added to 10.0 mL of a solution of [Pt$_2$Me$_4$(μ-pyen)] (7.26×10^{-5} M) in acetone at 25.0 °C. A sample of the combined solutions was transferred to a cuvette and placed in a cell compartment thermostated to 25.0 °C. The DS-15 was engaged, and data points (absorbance at 510 nm) were collected every 10 s by using the Varian Kinetics Storage program. With use of the Varian Kinetics Calculation program, treatment of the data gave good first-order kinetics and linear plots of k_{obsd} vs. [4-C$_6$H$_4$(CH$_2$Br)$_2$] then gave the second-order rate constants k_2 (Figure 3). The same method was used for reaction of **1** in acetone with [C$_6$H$_4$(CH$_2$Br)$_2$].

Rate constants for reaction of **9** and **10** with **1** were determined similarly but with [**9** or **10**] = [**1**]. Second-order treatment then gave straight-line plots from which values of k_2 were calculated.

Rate constants for reaction **9** or **10** with [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] were also determined similarly but with [**9** or **10**] = 2 [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] such that [**9** or **10**] = [Me$_2$Pt^{II}]. Due to the extreme insolubility of **15**, very low concentrations were used to study the kinetics of the reaction of **10** and standard solutions were prepared by dilution of stronger solutions to minimize error. In all cases the temperature was 25 °C.

Synthesis. [Pt$_2$Br$_2$Me$_4${μ-*p*-CH$_2$C$_6$H$_4$CH$_2$}(bipym)$_2$] (12). [PtMe$_2$(bipym)] (0.050 g) was dissolved in CH$_2$Cl$_2$ (5 mL) and diluted to 20 mL with acetone. To this solution was added a solution containing 1 equiv of [PtBrMe$_2${*p*-CH$_2$C$_6$H$_4$CH$_2$Br}(bipym)] (0.085 g) in acetone (50 mL). After 1 h the red solution had turned bright yellow, and after 4 h the solvent was removed. The product was precipitated as a yellow solid from a minimum of CH$_2$Cl$_2$ with pentane and dried under vacuum: yield 81%; mp 218 °C dec. Anal. Calcd for C$_{28}$H$_{32}$N$_8$Br$_2$Pt$_2$: C, 32.6; H, 3.1; N, 10.9. Found: C, 32.3; H, 3.5; N, 10.5. ^{1}H NMR: 1.42 [s, 12 H, ^2J(PtH) = 72 Hz, MePt], 2.52 [s, 4 H, ^2J(PtH) = 90 Hz, ^7J(PtH) = 5 Hz, *H*$_2$*CPt*], 5.66 [s, 4 H, ^4J(PtH) = 6 Hz, C$_6$*H*$_4$(CH$_2$)$_2$], 7.47 [dd, 4 H, ^3J(H^{b}H^a) = 5.5 Hz, ^3J(H^{b}H^c) = 5.0 Hz, *H*^{b}], 8.68 [dd, 4 H, ^3J(H^{a}H^b) = 5.5 Hz, ^4J(H^{a}H^c) = 2.5 Hz, ^3J(PtH^a) = 11.5 Hz, *H*^{a}], 8.98 ppm [dd, 4 H, ^3J(H^{c}H^b) = 5.0 Hz, ^4J(H^{c}H^a) = 2.5 Hz, *h*^{c}]. IR: ν(C=N) 1568 and 1552 cm^{-1}.

[Pt$_2$Br$_2$Me$_4${μ-*p*-CH$_2$C$_6$H$_4$CH$_2$}(μ-bipym)] (15). [PtBrMe$_2${4-CH$_2$C$_6$H$_4$CH$_2$Br}(bipym)] (0.096 g) was dissolved in acetone (100 mL), and to this solution was added 0.5 equiv of [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] (0.043 g) as an acetone solution (50 mL). The yellow solution turned orange after 10 min, and the product precipitated as an orange solid. After 6 h the solvent was removed and the orange solid was washed with CH$_2$Cl$_2$ and dried under vacuum:

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(15) Lanza, S.; Minniti, D.; Romeo, R.; Moore, P.; Sachinidis, J.; Tobe, M. L., *J. Chem. Soc., Chem. Commun.* **1984**, 542.

(16) Hux, J. E.; Puddephatt, R. J., unpublished work.

yield 96%; mp 268 °C dec. Anal. Calcd for C$_{20}$H$_{26}$N$_4$Br$_2$Pt$_2$: C, 27.5; H, 3.0; N, 6.4. Found: C, 27.6; H, 3.2; N, 6.1. IR: ν(C=N) 1569 cm^{-1}.

[Pt$_4$Br$_4$Me$_8${μ-*o*-CH$_2$C$_6$H$_4$CH$_2$}$_2$(μ-bipym)$_2$] (16). To a solution of [PtBrMe$_2${2-CH$_2$C$_6$H$_4$CH$_2$Br(bipym)] (0.60 g) in acetone (75 mL) was added 0.5 equiv of [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] (0.026 g) as an acetone solution (25 mL). In the first 0.5 h the yellow solution turned deep brownish red (UV–vis: λ_{max} ~570 nm (MLCT) due to intermediate formation of [PtBrMe$_2${2-CH$_2$C$_6$H$_4$CH$_2$Br}(μ-bipym)PtMe$_2$]), and after 1 h it began to turn orange and the product precipitated as an orange solid. After 6 h the solvent was removed, and the orange solid was washed with CH$_2$Cl$_2$ and dried under vacuum: yield 88%; mp 280 °C dec. Anal. Calcd for C$_{40}$H$_{52}$N$_8$Br$_4$Pt$_4$: C, 27.5; H, 3.0; N, 6.4. Found: C, 27.6; H, 3.0; N, 6.6. ^{1}H NMR (C$_5$D$_5$N): 1.78 ppm [s, ^2J(PtH) = 76 Hz, MePt]. The product is only sparingly soluble in pyridine and reacted slowly; the spectrum must be obtained immediately after dissolution. IR: ν(C=N) 1570 cm^{-1}. Mass spectrum: see text. The following complexes were prepared similarly. Maximum yields of [Pt$_4$I$_4$Me$_8${μ-(CH$_2$)$_n$}$_2$(μ-bipym)$_2$] (**18a–d**) are obtained after 3 days for n = 3 and increasing through to 5 days for n = 6, with the reactions performed in the dark to minimize side reactions. All complexes **18a–d** were insoluble orange solids that were collected by filtration, washed with CH$_2$Cl$_2$, and dried under vacuum. [Pt$_4$I$_4$Me$_8${μ-(CH$_2$)$_3$}$_2$(μ-bipym)$_2$] (**18a**): yield 63%; mp 165 °C dec. Anal. Calcd for C$_{30}$H$_{48}$N$_8$I$_4$Pt$_4$: C, 19.9; H, 2.7; N, 6.2. Found: C, 20.0; H, 2.7; N, 6.0. IR: ν(C=N) 1568 cm^{-1}. [Pt$_4$I$_4$Me$_8${μ-(CH$_2$)$_4$}$_2$(μ-bipym)$_2$] (**18b**): yield 57%; mp 155 °C dec. Anal. Calcd for C$_{32}$H$_{52}$N$_8$I$_4$Pt$_4$: C, 20.9; H, 2.9; N, 6.1. Found: C, 21.3; H, 3.0; N, 6.0. IR: 1567 ν(C=N) cm^{-1}. [Pt$_4$I$_4$Me$_8${μ-(CH$_2$)$_5$}$_2$(μ-bipym)$_2$] (**18c**): yield 41%; mp 155 °C dec. Anal. Calcd for C$_{34}$H$_{56}$N$_8$I$_4$Pt$_4$: C, 21.9; H, 3.0; N, 6.0. Found: C, 22.2; H, 3.1; N, 6.2. IR: 1568 ν(C=N) cm^{-1}. [Pt$_4$I$_4$Me$_8${μ-(CH$_2$)$_6$}$_2$(μ-bipym)$_2$] (**18d**): yield 37%; mp 145 °C. Anal. Calcd for C$_{36}$H$_{60}$N$_8$I$_4$Pt$_4$: C, 22.8; H, 3.2; N, 5.9. Found: C, 23.0; H, 3.2; N, 5.8. IR: ν(C=N) 1568 cm^{-1}.

Reaction of 11 with [Pt$_2$(μ-Br)$_2$Me$_4${μ-*o*-CH$_2$C$_6$H$_4$CH$_2$}(SMe$_2$)$_2$]. To a solution of [Pt$_2$Br$_2$Me$_4${μ-*o*-CH$_2$C$_6$H$_4$CH$_2$}(bipym)$_2$] (0.040 g) in CH$_2$Cl$_2$ (25 mL) was added 1 equiv of [Pt$_2$(μ-Br)$_2$Me$_4${μ-*o*-CH$_2$C$_6$H$_4$CH$_2$}(SMe$_2$)$_2$] (0.033 g) as a CH$_2$Cl$_2$ solution (10 mL). After 6 h the product [Pt$_4$Br$_4$Me$_8${μ-*o*-CH$_2$C$_6$H$_4$CH$_2$}$_2$(μ-bipym)$_2$] (**16**) had precipitated and was collected by filtration, washed with CH$_2$Cl$_2$, and dried under vacuum: yield 96%. Analysis and spectral parameters of the orange product were the same as for **11** prepared as described above.

[Pt$_2$Br$_2$Me$_4${μ-*o*-CH$_2$C$_6$H$_4$CH$_2$}(μ-pyen)] (19). [Pt$_2$Me$_4$(μ-pyen)] (0.050 g) was dissolved in acetone (150 mL), and to this solution was added 1 equiv of *o*-BrCH$_2$C$_6$H$_4$CH$_2$Br (0.020 g) as an acetone solution (50 mL). Over 6 h the red solution turned bright yellow. After 8 h the solvent was removed. The product was precipitated from a minimum of CH$_2$Cl$_2$ with Et$_2$O washed with Et$_2$O and dried under vacuum: yield 81%; mp 210 °C dec. Anal. Calcd for C$_{26}$H$_{34}$N$_4$Br$_2$Pt$_2$: C, 32.8; H, 3.6; N, 5.9. Found: C, 32.7; H, 4.0; N, 5.6. ^{1}H NMR: 1.46 [s, 6 H, ^2J(PtH) = 70 Hz, *Me*^{a} *or Me*^{b}*Pt*], 1.54 [s, 6 H, ^2J(PtH) = 68 Hz, *Me*^{a} *or Me*^{b}*Pt*], 2.98–5.00 [m, 8 H, Pt*CH*$_2$ and *CH*$_2$N], 9.57 [s, 2 H, ^3J(PtH) = 30 Hz, *H*C=N], 8.61 [d, br, ^3J(HH) = 5 Hz, ^3J(PtH) = 10 Hz, *H*^{a}], 6.54–7.80 ppm [m, aromatic H]. [Pt$_2$Br$_2$Me$_4${μ-*p*-CH$_2$C$_6$H$_4$CH$_2$}(μ-pyren)] (**20**) was prepared in a similar manner; however the reaction was complete after 4 h: yield 91%; mp 225 °C dec. Anal. Calcd for C$_{26}$H$_{34}$N$_4$Br$_2$Pt$_2$: C, 32.8; H, 3.6; N, 5.9. Found: C, 32.5; H, 3.8; N, 5.4. ^{1}H NMR: 1.36 [s, 6 H, ^2J(PtH) = 70 Hz, *Me*^{a} *or Me*^{b}*Pt*], 1.45 [s, 6 H, ^2J(PtH) = 72 Hz, *Me*^{a} *or Me*^{b}*Pt*], 2.64 [d, 2 H, ^2J(HH) = 10 Hz, ^2J(PtH) = 75 Hz, ^7J(PtH) = 2 Hz, PtC*H*^{a}H^b], 2.88 [d, 2 H, ^2J(HH) = 10 Hz, ^2J(PtH) = 108 Hz, ^7J(PtH) = 2 Hz, PtCH^a*H*^{b}], 3.26–4.76 [m, br, 4 H, C*H*$_2$N], 8.60 [s, 2 H, ^{3}J(PtH) = 30 Hz, *H*C=N], 8.94 [d, 2 H, ^3J(H^{a}H^b) = 5 Hz, ^3J(PtH) = 10 Hz, *H*$^{\circ}$], 5.92–8.84 ppm [m, aromatic H]. The other possible isomer occurs as a very minor product and is identifiable only by its distinct MePt resonances at 1.23 [s, ^{2}J(PtH) = 72 Hz] and 1.46 ppm [s, ^2J(PtH) = 72 Hz].

[Pt$_2$I$_2$Me$_4${(CH$_2$)$_n$I}$_2$(μ-pyen)] (21). To a solution of [Pt$_2$Me$_4$(μ-pyen)] (0.07 g) in acetone (10 mL) was added 1,4-diiodobutane (0.6 mL), and the mixture was allowed to stand for 16 h. The solution was evaporated, and the product was washed with ether and purified by precipitation from a concentrated solution in CH$_2$Cl$_2$ using hexane. [Pt$_2$I$_2$Me$_4${(CH$_2$)$_4$I}$_2$(μ-pyen)]: yield 72%; mp 188 °C dec. Anal. Calcd for C$_{26}$H$_{42}$N$_4$I$_4$Pt$_2$: C, 23.9; H, 3.2; N, 4.3. Found: C, 24.1; H, 3.3; N, 4.3%. ^{1}H NMR: 1.35 [s, 6 H, ^{2}J(PtH) = 68 Hz, *Me*^{a} or *Me*^{b}*Pt*], 1.46 [s, 6 H, ^2J(PtH) = 70 Hz, *Me*^{a} or *Me*^{b}*Pt*], 3.00 [t, ^3J(HH) = 7 Hz, *CH*$_2$I], 4.52, 4.79 [m, 4 H, *CH*$_2$N], 7.67 [m, 2 H, H^c], 7.90 [d, 2 H, ^3J(HH) = 7 Hz, H^d], 8.02 [t, ^3J(HH) = 7 Hz, H^b], 8.90 [d, 2 H, ^3J(HH) = 7 Hz, H^a], 10.15 [s, 2 H, ^3J(PtH) = 29 Hz, H^e].

Similarly were prepared the following complexes: [Pt$_2$I$_2$Me$_4${(CH$_2$)$_3$}$_2$(μ-pyen)]: mp 216 °C dec. Anal. Calcd for C$_{24}$H$_{38}$N$_4$I$_4$Pt$_2$: C, 22.5; H, 3.0; N, 4.4. Found: C, 23.7; H, 3.3; N, 4.8. ^{1}H NMR: 1.35 [s, ^2J(PtH) = 70 Hz, *Me*Pt], 1.38 [s, ^2J(PtH) = 72 Hz, *Me*Pt], 3.00 [t, ^3J(HH) = 7, *CH*$_2$I], 4.54 and 4.77 ppm [m, *CH*$_2$N]. [Pt$_2$I$_2$Me$_4${(CH$_2$)$_5$I}$_2$(μ-pyen)]: mp 182 °C dec. Anal. Calcd for C$_{28}$H$_{46}$N$_4$I$_4$Pt$_2$: C, 25.2; H, 3.5; N, 4.2. Found: C, 25.1; H, 3.6; N, 4.6. ^{1}H NMR: 1.32 [s, 6 H, ^2J(PtH) = 72 Hz, *Me*Pt], 1.43 [s, 6 H, ^2J(PtH) = 72 Hz, *Me*Pt], 3.04 [t, 4 H, ^3J(HH) = 7 Hz *CH*$_2$I], 4.53, 4.84 [m, 4 H, CH$_2$N], 7.66 [m, 2 H, *H*^{c}], 7.86 [d, 2 H, *H*^{d}], 8.02 [m, 2 H, *H*^{b}]; 8.89 [d, 2 H, *H*^{a}], 10.13 ppm [s, ^3J(PtH) = 30 Hz, H^e]. ^{13}C NMR: −7.05 [^1J(PtC) = 690 Hz, *Me*Pt], −3.70 [^1J(PtC) = 685 Hz, *Me*Pt], 25.93 [^1J(PtC) = 665 Hz, CH$_2$$^{\alpha}$Pt], 31.69 [$^2J$(PtC) = 91 Hz, CH$_2$$^{\beta}$], 28.98 [$^3J$(PtC) = 29 Hz, CH$_2$$^{\gamma}$], 33.47 [$^4J$(PtC) = 8 Hz, CH$_2$$^{\delta}$], 7.54 [CH$_2$$^{\epsilon}$I], 54.55 [$^2J$(PtC) = 14 Hz, CH$_2$N], 128.4 [$J$(PtC) = 12 Hz, C^a], 129.4 [J(PtC) = 7 Hz, C^b], 139.4 [C^c], 148.1 [J(PtC) = 15 Hz, *C*N], 154.3 [J(PtC) = 7 Hz, C^d], 170.1 ppm [C^e]. [Pt$_2$I$_2$Me$_4${(CH$_2$)$_6$I}$_2$(μ-pyen)]. Anal. Calcd for C$_{30}$H$_{50}$N$_4$I$_4$Pt$_2$: C, 26.4; H, 3.7; N, 4.1. Found: C, 26.9; H, 3.7; N, 4.3. ^{1}H NMR: 1.34 [s, 6 H, ^2J(PtH) = 72 Hz, *Me*Pt], 1.44 [s, 6 H, ^2J(PtH) = 72 Hz, *Me*Pt], 3.10 [t, 4 H, ^3J(HH) = 7 Hz, *CH*$_2$I], 4.60, 4.84 ppm [m, 4 H, *CH*$_2$N].

Acknowledgment. We thank NSERC (Canada) for financial support.

Registry No. **4** (n = 3), 93708-98-6; **4** (n = 4), 93708-99-7; **4** (n = 5), 93709-00-3; **4** (n = 6), 102615-02-1; **7**, 105040-56-0; **9**, 93709-02-5; **10**, 102614-97-1; **11**, 102615-08-7; **12**, 108971-22-8; **13**, 108971-23-9; **15**, 108971-25-1; **16**, 93709-03-6; **18a**, 108971-31-9; **18b**, 108971-32-0; **18c**, 108971-33-1; **18d**, 108971-34-2; **19**, 108971-26-2; **20a**, 109062-31-9; **20b**, 108971-24-0; **21a**, 108971-27-3; **21b**, 108971-28-4; **21c**, 109011-16-7; **21d**, 109011-17-8; **22**, 108971-30-8; **23a/23b**, 105040-58-2; **24**, 108971-29-5; PtMe$_2$(bipym), 90144-57-3; Pt$_2$Me$_4$(μ-SMe$_2$)$_2$, 79870-64-7; Pt$_2$(μ-Br)$_2$Me$_4${μ-*o*-CH$_2$C$_6$H$_4$CH$_2$}(SMe$_2$)$_2$, 96413-70-6; *p*-BrCH$_2$C$_6$H$_4$CH$_2$Br, 623-24-5; I(CH$_2$)$_5$I, 628-77-3; CH$_3$I, 74-88-4; *o*-BrCH$_2$C$_6$H$_4$CH$_2$Br, 91-13-4; I(CH$_2$)$_4$I, 628-21-7; I(CH$_2$)$_3$I, 627-31-6; I(CH$_2$)$_6$I, 629-09-4.

Supplementary Material Available: Figure 1, spectral changes during the reaction of **9** with [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] to give **13** and then **16** (solid lines show the growth of the absorption at 570 nm due to **13**, and broken lines show the subsequent decay of this band on formation of **16**) (1 page). Ordering information is given on any current masthead page.