

Stereoselective Oxidative-addition Reactions of Dihalogens and Copper(II) Halides to Square-Planar Organoplatinum(II) Complexes containing Hard N and C Donor Atoms. Molecular Structures of [*bc,de*-Bis(8-dimethylamino-1-naphthyl)]-*af*-diiodoplatinum(IV) and *ab*-Dibromo[*cf,de*-bis(8-dimethylamino-1-naphthyl)]platinum(IV) ‡

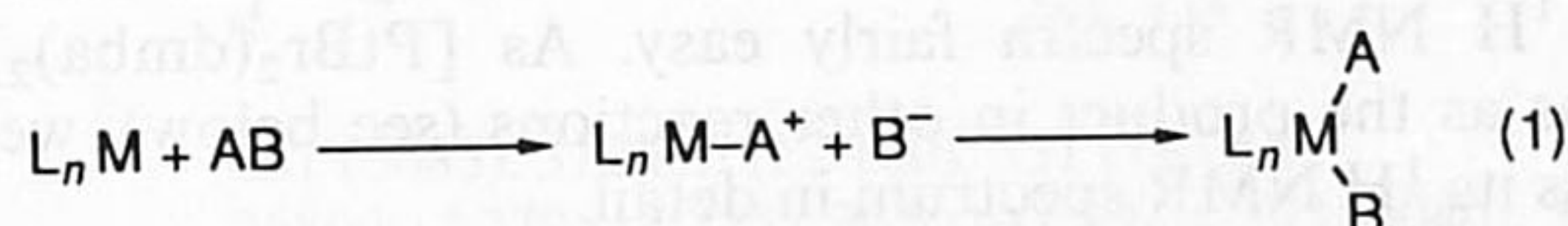
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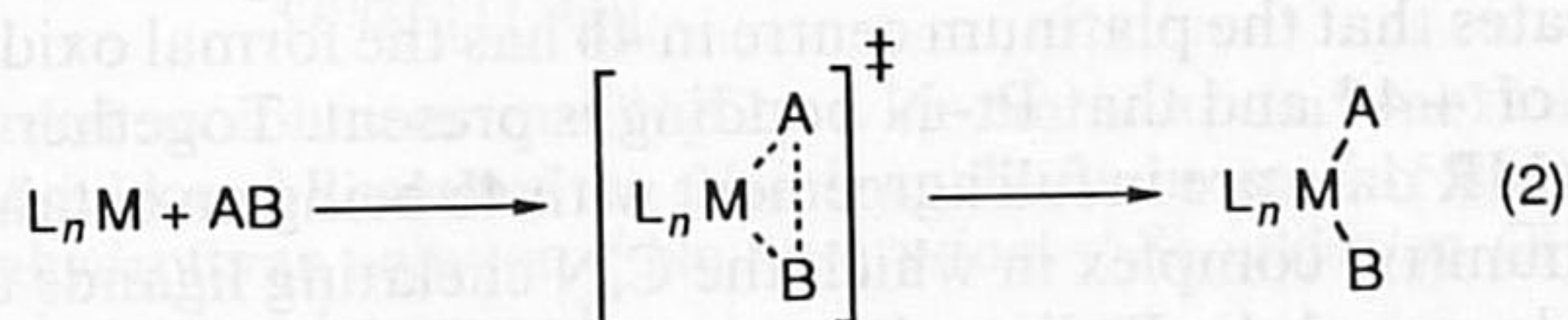
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Oxidative additions of electrophiles X_2 ($X = \text{Br}$ or I) and $\text{Cu}X_2$ ($X = \text{Cl}$ or Br) to the complexes *cis*-bis[2-(dimethylaminomethyl)phenyl]platinum(II) **1** and *cis*-bis(8-dimethylamino-1-naphthyl)platinum(II) **3** have been investigated. Those with X_2 afford the respective *trans*- X_2 platinum(IV) products, whereas with $\text{Cu}X_2$ the *cis*- X_2 platinum(IV) products are obtained, except for the reaction of **1** with CuBr_2 which yields the *trans*-dibromo product. There is no evidence for *cis-trans* or *trans-cis* isomerizations of these octahedral platinum(IV) products in solution. On the basis of these stereoselective product formations (and earlier results) the proposed mechanisms are an S_N2 type for the reactions with dihalogens and an inner-sphere ligand-transfer oxidation for the reactions with copper(II) halides. The mechanisms of the reactions of X_2 and $\text{Cu}X_2$ with *trans*-bis[2-(dimethylaminomethyl)phenyl]platinum(II) **2** are the same as with **1** (and **3**) but lead to other geometrical isomers. The stereochemistry of two of the oxidative addition products, *i.e.* [*bc,de*-bis(8-dimethylamino-1-naphthyl)]-*af*-diiodoplatinum(IV) **5c** and *ab*-dibromo[*cf,de*-bis(8-dimethylamino-1-naphthyl)]platinum(IV) **5e**, have been established by X-ray crystal structure determinations. Crystals of **5c** are orthorhombic, space group *Pbca*, with $a = 7.825(3)$, $b = 17.803(2)$, $c = 37.873(6)$ Å, $Z = 8$ and $R = 0.032$ for 2962 reflections with $I > 2.5\sigma(I)$. Crystals of **5e** are monoclinic, space group *P2₁/c*, with $a = 9.696(2)$, $b = 9.722(6)$, $c = 26.81(3)$ Å, $\beta = 90.46(4)^\circ$, $Z = 4$ and $R = 0.083$ for 3060 reflections with $I > 2.5\sigma(I)$.

The study of oxidative-addition reactions has been a major research topic in organometallic chemistry during the last two decades. The results obtained are important because oxidative addition is a synthetically valuable reaction that also occurs as one of the key steps in homogeneous catalysis. Oxidative-addition reactions with square-planar d^8 metal complexes are of special interest, and so far three main mechanisms have been proposed:^{1,2} (1) S_N2 type [equation (1)]. Here the metal centre of



square-planar L_nM acts as the nucleophile for the substrate $A-B$ in which B represents the leaving group. In the final octahedral product $L_nMA(B)$, A and B can be positioned either *cis* or *trans* to each other. (2) Concerted addition [equation (2)]. In this



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mechanism the oxidative addition invariably affords *cis* positioning of A and B in the product. (3) Radical type. Oxidative-addition reactions based on free-radical chain or non-chain processes can afford both *cis*- and *trans*- AB products.

Which of these mechanisms is valid for a specific oxidative-addition reaction is, of course, dependent on the electrophile $A-B$, the metal complex and the reaction conditions. In general, halocarbons $R-X$ are considered to react *via* either the S_N2 type of mechanism ($R = \text{Me}$, PhCH_2 or allyl) or *via* a radical mechanism ($R = \text{vinyl}$ or aryl) whereas dihydrogen reacts by a concerted addition mechanism.^{1,2} Although the oxidative-addition reactions of dihalogens to organometallic complexes are frequently used in synthesis, relatively few mechanistic studies have appeared; these reactions are generally too fast for kinetic measurements.^{1c,3} Interestingly, there are proposals for all three of the above-mentioned mechanisms for dihalogen oxidative-addition reactions with organometallic or inorganic species.⁴⁻⁶

Our first study of the mechanism of dihalogen oxidative-addition reactions involved platinum(II) complexes containing the terdentate, monoanionic ligand $\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6^-$.⁷ In these complexes the platinum centre possesses an enhanced nucleophilicity resulting from the co-ordination of two hard N donor atoms, which are fixed in mutually *trans* positions, and the hard C donor atom. The study of the stereochemistry of the reactions of these complexes is facilitated by two factors. First, the vacant metal co-ordination sites are restricted to those in a plane perpendicular to the aryl ring plane of the $\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2$ ligand, and secondly the rigid structure of the ligand

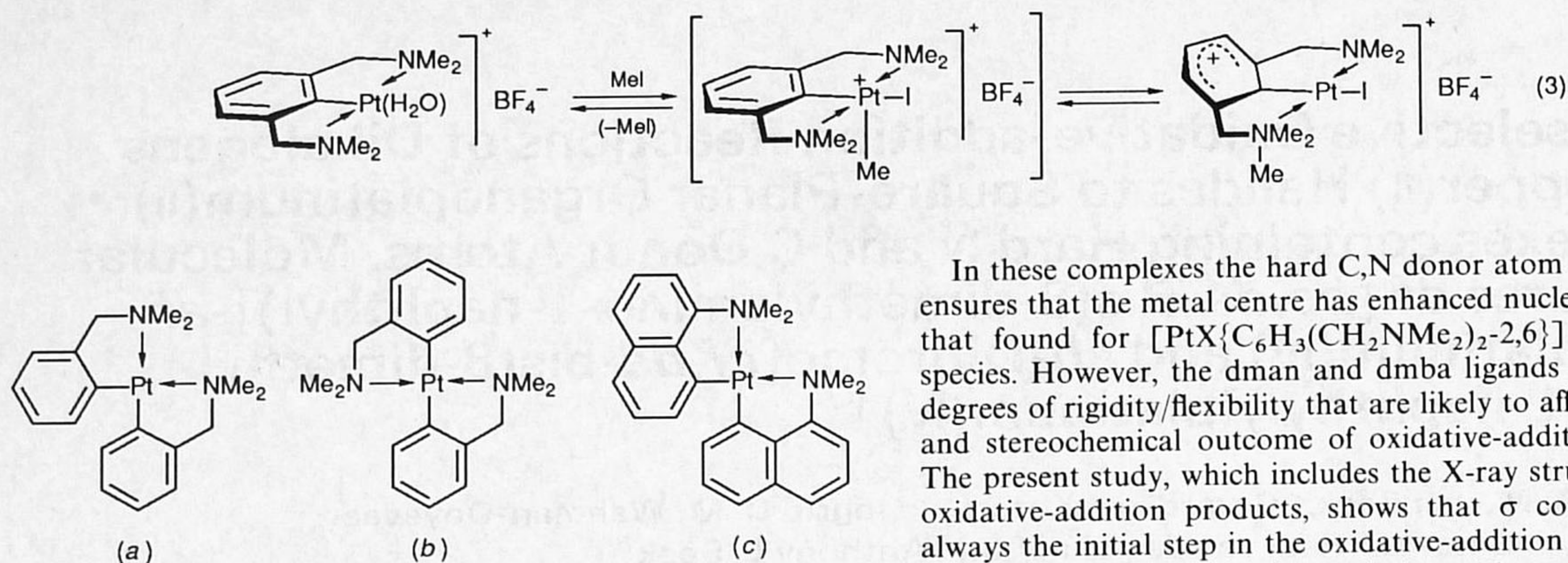
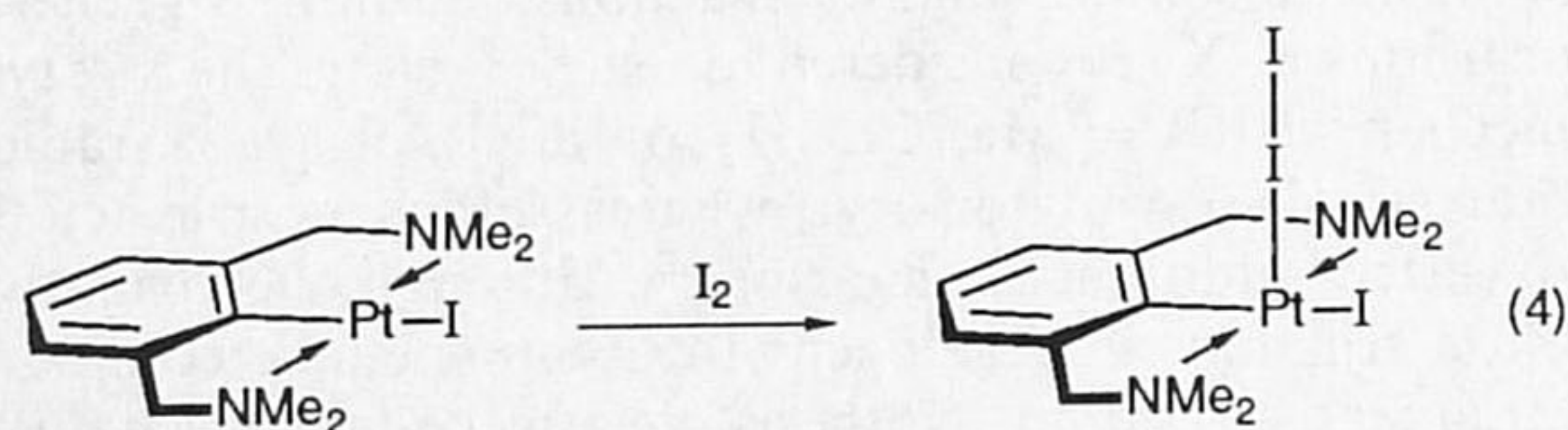


Fig. 1 (a) *cis*-[Pt(dmba)₂] **1**, (b) *trans*-[Pt(dmba)₂] **2** and (c) *cis*-[Pt(dman)₂] **3**

does not allow any facile geometrical rearrangements. The usefulness of these characteristics was demonstrated earlier in our study of the reaction of methyl iodide with [Pt{C₆H₃(CH₂NMe₂)₂-2,6}(OH₂)]BF₄ [equation (3)] and [Pt(C₆H₄Me-2){C₆H₃(CH₂NMe₂)₂-2,6}]. We have postulated that this reaction takes place *via* an S_N2 type interaction of Pt^{II} with MeI that is followed by a 1,2-methyl shift from platinum to the coordinated ligand; this results in the formation of a novel type of complex [PtX{MeC₆H₃(CH₂NMe₂)₂-2,6}]Y (X = I, Y = BF₄; X = C₆H₄Me-2, Y = I).^{8a,b} With homologues of MeI this reaction path with [Pt{C₆H₃(CH₂NMe₂)₂-2,6}(OH₂)]O₃SCF₃ is blocked and slow conversion of RI into ROH with concomitant formation of the novel complex [Pt₂I₄{C₆H₃(CH₂NHMe₂)₂-2,6}]₂[O₃SCF₃]₂ occurs.^{7,8c} The reaction here most probably includes nucleophilic assistance (uptake of a proton) by a non-co-ordinated CH₂NMe₂ substituent. The nickel(II) centre in [NiX{C₆H₃(CH₂NMe₂)₂-2,6}] (X = Cl, Br or I) also exhibits enhanced nucleophilicity and is readily oxidized by halogens (in a single electron-transfer reaction) to yield stable [Ni^{III}X₂{C₆H₃(CH₂NMe₂)₂-2,6}] complexes.⁹

The reactions of [PtR{C₆H₃(CH₂NMe₂)₂-2,6}] (R = Ph, C₆H₄Me-4, Cl or Br) with dihalogens result in stereospecific formation of *cis*-X₂ oxidative-addition products.¹⁰ In one case we have isolated an intermediate that mimics the initial stages of the oxidative-addition reaction; the reaction of I₂ with [PtI{C₆H₃(CH₂NMe₂)₂-2,6}] results in the formation of a platinum(II) complex in which the diiodine molecule is σ bonded to the metal centre [equation (4)].¹¹



The S_N2 type mechanism is most probably the one operative in the oxidative-addition reactions of dihalogens X₂ to [Pt^{II}R{C₆H₃(CH₂NMe₂)₂-2,6}]. After initial formation of the platinum(IV) intermediate [PtR(X){C₆H₃(CH₂NMe₂)₂-2,6}]⁺ addition of X⁻ in the next step leads to an oxidative-addition product which, because of steric factors, has a *cis*-halogen atom arrangement. In this system it is difficult to distinguish this process from the one comprising a σ -co-ordination of X₂ that is followed by σ to η^2 rearrangement with cleavage of the X-X bond and formation of Pt-X bonds. For this reason we have now studied the reactions of dihalogens and copper(II) halides with the complexes *cis*- and *trans*-[Pt^{II}(dmba)₂] [dmba = 2-(dimethylaminomethyl)phenyl] **1** and **2**, and *cis*-[Pt^{II}(dman)₂] (dman = 8-dimethylamino-1-naphthyl) **3** which possess C,N chelating ligands (see Fig. 1).

In these complexes the hard C,N donor atom co-ordination ensures that the metal centre has enhanced nucleophilicity like that found for [PtX{C₆H₃(CH₂NMe₂)₂-2,6}] (X = halide) species. However, the dman and dmba ligands have different degrees of rigidity/flexibility that are likely to affect the course and stereochemical outcome of oxidative-addition reactions. The present study, which includes the X-ray structures of two oxidative-addition products, shows that σ co-ordination is always the initial step in the oxidative-addition reactions of a dihalogen with a square-planar platinum(II) complex, and that the stability of the subsequently formed five-co-ordinate cationic complex plays an important role in determining the geometry of the final product.

Results

The platinum(II) complexes *cis*-[Pt(dmba)₂] **1**, *cis*-[Pt(dman)₂] **3** and *trans*-[Pt(dmba)₂] **2** were treated with electrophiles X₂ (X = Cl, Br or I) and CuX₂ (X = Cl or Br). These reactions afford primarily platinum(IV) oxidative-addition products [PtX₂(dmba)₂] **4** and [PtX₂(dman)₂] **5** as summarized in Table 1. The products **4** and **5** were identified by ¹H NMR (Table 2), IR and UV spectroscopy (Table 3), elemental analyses and field desorption/ionization (FD/FI) mass spectroscopic measurements. Elucidation of their stereochemistry is of great importance for establishing the mechanism of the oxidative addition.^{1,2} Their structure in solution could usually be established by ¹H NMR spectroscopy. In two cases, *trans,cis*-[PtI₂(dman)₂] **5c** and *cis,cis*-[PtBr₂(dman)₂] **5e**, structural assignment was supported by an X-ray structure determination.

Reactions with Diiodine and Dibromine.—The reactions of *cis*-[Pt(dmba)₂] **1** and *cis*-[Pt(dman)₂] **3** with I₂ and Br₂ in CH₂Cl₂ afford oxidative-addition products with the bidentate ligands in their original positions and the new halide ligands *trans* to each other, above and below the co-ordination plane of the original complex. These octahedral complexes [Pt(X₂-*af*){(C-N)₂-*bc,de*}] (C-N = dmba, X = Br, **4b**; X = I, **4c**, C-N = dman, X = Br, **5b**; X = I, **5c**) were isolated in 75–85% yield. Complex **4c** was obtained as red crystals which are poorly soluble in tetrahydrofuran (thf) and insoluble in other organic solvents. Orange **5c** and yellow **4b** and **5b** are soluble in CH₂Cl₂, CHCl₃ and toluene. The presence of CH₂NMe₂ groups in **4** and of NMe₂ groups in **5** makes structural assignment based on their ¹H NMR spectra fairly easy. As [PtBr₂(dmba)₂] **4b** returns as the product in other reactions (see below), we will discuss its ¹H NMR spectrum in detail.

The N-methyl and the benzylic protons of complex **4b** appear as singlets, *i.e.* there is chemical and magnetic equivalence of the two NMe groups and of the two CH protons. The ³J(¹⁹⁵Pt-¹H) coupling constants on these signals (10 and 11 Hz, respectively) are smaller than those for the starting complex *cis*-[Pt(dmba)₂] **1** (15 and 19 Hz, respectively). This coupling information indicates that the platinum centre in **4b** has the formal oxidation state of +4* and that Pt-N bonding is present. Together these ¹H NMR data are in full agreement with **4b** being an octahedral platinum(IV) complex in which the C,N chelating ligands are in one plane and the Br ligands are *trans* to each other above and below this plane. On the basis of the ³J(¹⁹⁵Pt-¹H) values it is

* For platinum(IV) compounds the ³J(¹⁹⁵Pt-¹H) coupling constants are reduced to approximately 2/3 of the values for the corresponding platinum(II) compounds.¹²

Table 1 The geometries and isolated yields (%) of platinum(IV) products from oxidation reactions of cyclometallated platinum(II) substrates **1–3** and $[\text{PtR}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6\}]$ with Br_2 , I_2 , CuCl_2 and CuBr_2

| Oxidant | <i>cis</i> -[Pt(dmba) ₂] 1 | | | <i>cis</i> -[Pt(dman) ₂] 3 | | | <i>trans</i> -[Pt(dmba) ₂] 2 | | | $[\text{PtR}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6\}]^a$ | |
|-----------------|---|---------------------------|-----------|---|---------------------------|-----------|---|---------------------------|-----------|---|---|
| | Product | PtX ₂ geometry | Yield (%) | Product | PtX ₂ geometry | Yield (%) | Product | PtX ₂ geometry | Yield (%) | R | Geometry |
| Br_2 | 4b | <i>trans</i> | 76 | 5b | <i>trans</i> | 77 | 4b | <i>trans</i> | 24 | $\text{C}_6\text{H}_4\text{Me-4}$ Br | <i>cis</i> -Br ₂ <i>mer</i> -Br ₃ |
| I_2 | 4c | <i>trans</i> | 80 | 5c | <i>trans</i> | 85 | <i>b</i> | <i>cis</i> + <i>trans</i> | 61 | $\text{C}_6\text{H}_4\text{Me-4}$ I | <i>cis</i> -I ₂ σ -I ₂ ^c |
| CuCl_2 | 4d | <i>cis</i> | 82 | 5d | <i>cis</i> | 76 | 4d | <i>cis</i> | 46 | Cl | <i>mer</i> -Cl ₃ |
| CuBr_2 | 4a | <i>trans</i> | 4 | 5a | <i>trans</i> | <4 | 4b | <i>trans</i> | 64 | Br | <i>mer</i> -Br ₃ |
| | 4b | <i>trans</i> | 85 | 5e | <i>cis</i> | 78 | | | | | |
| | | | | 5b | <i>trans</i> | <4 | | | | | |

^a Products are $[\text{PtR}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6\}\text{X}_2]$; refs. 10 and 11. ^b A mixture of *cis*-I₂ isomers and the *trans*-I₂ isomer **4c**; total yield 61%. ^c See equation (4).

Table 2 Proton NMR data^a

| Compound | N-CH ₃ | CH ₂ | Aromatic H |
|--|----------------------------|----------------------------|-----------------------|
| 1 <i>cis</i> -[Pt(dmba) ₂] | 2.78(15) | 3.87(19) | 6.9–7.7 |
| 2 <i>trans</i> -[Pt(dmba) ₂] | 3.09(43) | 4.03(41) | 7.0–7.6 |
| 4a <i>trans,cis</i> -[PtCl ₂ (dmba) ₂] | 2.81(9) | 4.07(9) | 6.8–7.3 |
| 4b <i>trans,cis</i> -[PtBr ₂ (dmba) ₂] | 2.92(10) | 4.14(11) | 6.9–7.7 |
| 4c <i>trans,cis</i> -[PtI ₂ (dmba) ₂] ^b | 3.16(13) | 4.25(14) | 6.8–7.0 |
| 4d <i>cis,cis</i> -[PtCl ₂ (dmba) ₂] | 2.14(43), | 3.33, 5.13, ^{d,e} | 6.47(d) (34), |
| | 2.95 ^c (9, 12), | 3.75, ^e | 6.8–7.4 |
| | 3.17(27) | 4.43(10) | 7.79 ^e (d) |
| 3 <i>cis</i> -[Pt(dman) ₂] | 3.41(13) | | 7.2–7.8 |
| 5a <i>trans,cis</i> -[PtCl ₂ (dman) ₂] | 3.49 ^e | | 7.1–7.9 |
| 5b <i>trans,cis</i> -[PtBr ₂ (dman) ₂] | 3.55(10) | | 7.3–7.7 |
| 5c <i>trans,cis</i> -[PtI ₂ (dman) ₂] | 3.81(11) | | 7.4–7.7 |
| 5d <i>cis,cis</i> -[PtCl ₂ (dman) ₂] | 2.40(37), | | 5.83(d) (36), |
| | 3.56, ^{c,e} | | 6.9–7.9, |
| | 3.75 ^e | | 8.26(d) (31) |
| | 2.28(37), | | 5.79(d) (34), |
| 5e <i>cis,cis</i> -[PtBr ₂ (dman) ₂] | 3.58(28), | | 6.9–7.7, |
| | 3.76(14), | | 8.57(d) (32) |
| | 3.81 ^e | | |
| | | | |

^a δ in ppm relative to SiMe_4 (internal), recorded in CDCl_3 , ³ $J(^{195}\text{Pt}-^1\text{H})$ in Hz in parentheses; d = doublet. ^b Recorded in $[\text{C}_2\text{H}_5]_2\text{tetrahydrofuran}$. ^c Double intensity with regard to other methyl resonances. ^d AB pattern. ^e ³ $J(^{195}\text{Pt}-^1\text{H})$ not observed.

Table 3 UV^a and IR^b data

| Compound | UV: $\lambda_{\text{max}}(\epsilon)$ | IR: $\nu(\text{Pt-X})$ |
|-----------|--|------------------------|
| 1 | 272(sh) (9115), 284 (10 185) | |
| 4b | 330 (2210) | 168, 185, 216 |
| 4c | 385 (6160), 476(sh) (640) ^c | 153 |
| 4d | <i>d</i> | 284, 334 |
| 3 | 281 (6685), 319(sh) (12 180), 331 (14 065) | |
| 5b | 268(sh), ^e 279 (16 225), 305(sh) (5260), 393 (3040), 366(sh) (880) | |
| 5c | 261(sh), ^e 281 (16 440), 311 (7525), 331 (4725), 379 (3045), 446(sh) (1555) | |
| 5d | 268(sh), ^e 277 (13 825), 305(sh) (5010), 317(sh) (2130), 360 (905) | |
| 5e | 295 (13 220), 310(sh) (10 700), 323 (5485), 336(sh) (2295), 379(sh) (1260) | |

^a Recorded as solutions in CH_2Cl_2 ; λ in nm, ϵ in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$; sh = shoulder. ^b Recorded as Nujol mulls; ν in cm^{-1} . ^c Recorded in tetrahydrofuran solution. ^d No absorptions. ^e Shoulder on CH_2Cl_2 absorption, ϵ not determined.

also possible to deduce that the C,N ligands have a *cis* rather than the alternative *trans* configuration. For *trans*-[Pt(dmba)₂] **2** these coupling constants are 41–43 Hz and for the corresponding *trans*-(dmba)₂ platinum(IV) complex they are

calculated to be *ca.* 27–29 Hz. These calculated values can be seen to be even higher than those for *cis*-[Pt(dmba)₂] **1**. This structural proposal for **4b** in solution, *i.e.* *trans* halide atoms and C,N ligands in one plane in *cis* configuration, can also be made for **4c**, **5b** and **5c** and is confirmed in the solid state by the molecular structure determination of **5c** (see below).

The reactions of Br_2 and I_2 with *trans*-[Pt(dmba)₂] **2** are not so well defined as with **1**. The reaction of dibromine, as with **1**, gave *trans,cis*-[PtBr₂(dmba)₂] **4b**, though the yield (24%) was very low. The reaction also afforded an unidentified off-white precipitate, which is insoluble in CHCl_3 and acetone.

The product of the reaction of complex **2** with I_2 is a light brown solid (yield 61%) that is soluble in CHCl_3 and CH_2Cl_2 . Its FI-MS spectrum gives an m/z value of 717 that points to an empirical formula of $\text{C}_{18}\text{H}_{24}\text{I}_2\text{N}_2\text{Pt}$. The ¹H NMR spectrum reveals that the product consists of a mixture of *cis*-I₂ oxidative-addition isomers, together with a small amount of known *trans,cis*-[PtI₂(dmba)₂] **4c**. The identification of the *cis*-I₂ stereochemistry of the major products comes principally from the aromatic signals at δ 6.7 and 8.3 {see below, *cis,cis*-[PtCl₂(dmba)₂] **4d**}.

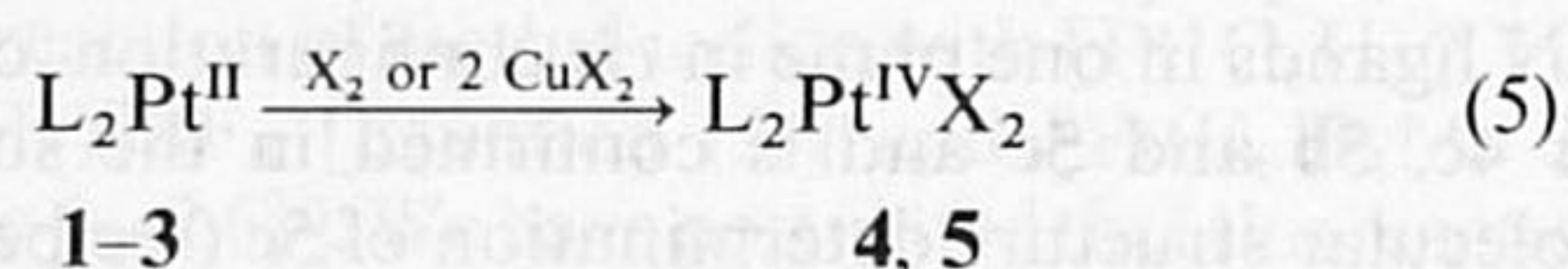
It is important to note that the reactions of Br_2 and I_2 with *trans*-[Pt(dmba)₂] **2** both afford products in which the dmba ligands have *cis* positioning of the N (and C) donor atoms whereas **2** has *trans* positioning of these atoms. The reasons why these particular product geometries are obtained will be dealt with in detail in the Discussion.

Reactions with Dichlorine.—The reactions of complexes **1–3** with dichlorine, carried out as described for the synthesis of octahedral $[\text{PtCl}_3\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6\}]$,¹⁰ afford in all cases yellow solids that are soluble in CHCl_3 and CH_2Cl_2 . The ¹H NMR spectrum of the product from the reaction of *cis*-[Pt(dmba)₂] **1** with Cl_2 shows, apart from signals in the aromatic region, singlets at δ 2.83 and 4.13 with ³ $J(^{195}\text{Pt}-^1\text{H})$ of 9 Hz. These data are consistent with the material being a *trans* oxidative-addition product like *trans,cis*-[PtBr₂(dmba)₂] **4b** and *trans,cis*-[PtI₂(dmba)₂] **4c** (Table 2). However, the FI-MS spectrum of such a product with empirical formula $\text{C}_{18}\text{H}_{24}\text{Cl}_2\text{N}_2\text{Pt}$ would be expected to show a peak at m/z 534, but the actual spectrum has peaks at m/z = 533, 567 and 602; *i.e.* there are more than two chlorine atoms in the product. This conclusion is supported by data from elemental analyses, although no satisfactory formula could be found. The yellow products of the reactions of *trans*-[Pt(dmba)₂] **2** and *cis*-[Pt(dman)₂] **3** with dichlorine also contain more than two chlorine atoms per platinum; the ¹H NMR spectra show the products to be mixtures of compounds.

Since the reactions of complexes **1–3** with Cl_2 all produce unidentified products with more than the expected amount of halide present it is clear that the use of excess of dihalogen in such reactions is not advisable. When *cis*-[Pt(dmba)₂] **1** was

treated with a ten-fold excess of dibromine (instead of an equivalent amount) a solid was isolated with showed similar spectroscopic data to those found for the product from the Cl₂ reaction above, *i.e.* a clear ¹H NMR spectrum (singlets at δ 2.92 and δ 4.11 with small ¹⁹⁵Pt-¹H couplings of 10 Hz on both signals) and a FI mass spectrum showing peaks at *m/z* = 543, 623, 703 and 783 (expected value for C₁₈H₂₄Br₂N₂Pt: *m/z* = 623). An explanation for these results is that reactions with dihalogens can afford products originating from (besides oxidative addition) Pt-C bond cleavage¹³ and halogenation of the aromatic ligand.¹⁴ In our case the use of excess of dihalogen could lead to a combination of such a reaction with an oxidative addition of 1 equivalent of X₂ to the metal centre.¹⁵ The selective and straightforward formation of [PtCl₃{C₆H₃(CH₂-NMe₂)_{2-2,6}}]¹⁰ by treating [PtCl{C₆H₃(CH₂-NMe₂)_{2-2,6}}] with dichlorine is therefore the more surprising and is a demonstration of the bis *ortho* chelate effect exerted by the monoanionic terdentate ligand.

Reactions with Copper(II) Halides.—All reactions involving copper(II) halides CuX₂ (X = Cl or Br) [see equation (5)] were



carried out by adding a solution of 2 equivalents of the copper salt in methanol to a solution of the starting platinum(II) complex in dichloromethane under a dry, inert nitrogen atmosphere. The reactions of *cis*-[Pt(dmba)₂] **1** with CuCl₂ and of *cis*-[Pt(dman)₂] **3** with CuBr₂ were also carried out in open vessels, and the latter reaction was also performed in the presence and absence of daylight. These different conditions did not exert any noticeable influence on either the reaction products or the yields.

The reactions of complexes **1** and **2** with CuBr₂ afford the same octahedral platinum(IV) product **4b**, *trans,cis*-[PtBr₂(dmba)₂], in 85 and 64% yield, respectively. As already seen this platinum(IV) compound is also obtained in the reactions of **1** and **2** with Br₂ in 76 and 24% yield, respectively. Accordingly, in these oxidation reactions of **1** and **2**, CuBr₂ is a better, more selective, brominating agent than dibromine. With both reagents it is the complex *cis*-[Pt(dmba)₂] which provides the higher yield of **4b**. It should be noted that [PtBr₃{C₆H₃(CH₂-NMe₂)_{2-2,6}}], which like **2** has the two N ligands in *trans* positions, gives the platinum(IV) product [PtBr₃{C₆H₃(CH₂-NMe₂)_{2-2,6}}]¹⁰ with both dibromine (92% yield) and CuBr₂ (80% yield).

The reactions of complexes **1-3** with CuCl₂ and of **3** with CuBr₂ all afford oxidative-addition products (Table 1) according to elemental analyses and FD/FI-MS. The ¹H NMR of the product of the reaction of **2** with CuCl₂, *i.e.* [PtCl₂(dmba)₂] **4d**, shows three singlets at δ 2.14, 2.95 and 3.17 in an integral ratio of 1:2:1; that at δ 2.95 somewhat broadened and showing two different ³J(¹⁹⁵Pt-¹H) of 9 and 12 Hz. The ³J(¹⁹⁵Pt-¹H) on the peaks at δ 2.14 and 3.17 are 43 and 27 Hz, respectively. Thus, there are four different N-bonded methyl groups in the complex, two of which have the same chemical shift. Furthermore, the four benzylic protons are also inequivalent. Two AB patterns are present in the spectrum; the signals occurring at δ 5.13 and 3.33 have ²J(¹H-¹H) = 13 Hz and those at δ 4.43 and 3.75 have ²J(¹H-¹H) = 14 Hz. Of these signals only the one at δ 4.43 shows a resolved coupling to platinum [³J(¹⁹⁵Pt-¹H) = 10 Hz]. These NMR data are consistent with a structure in which the two NMe₂ groups are bonded to platinum and both the CH₂ and NMe₂ groups are diastereotopic, *i.e.* **4d** is a *cis*-Cl₂ oxidative-addition product. Although in principle eight *cis*-X₂ stereoisomers (four pairs of enantiomers) are possible,¹⁶ the ¹H NMR spectrum only shows one set of resonances and hence **4d** represents only one diastereomer or one pair of enantiomers. Careful examination

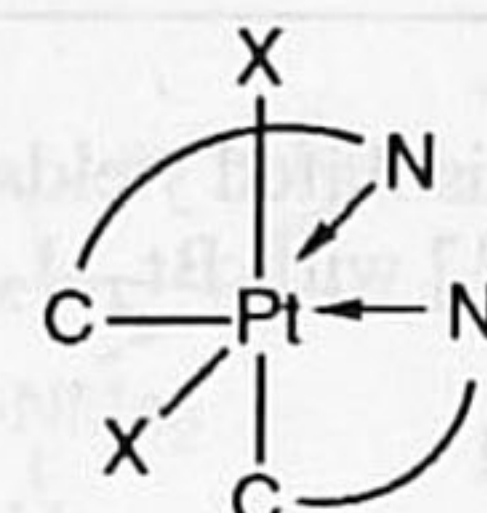


Fig. 2 Schematic structures of **4d**, **5d** and **5e** in solution

of the NMR data can provide extra information on the actual diastereomer formed. In the aromatic region there is a doublet signal at δ 6.47 with ³J(¹H-¹H) = 8 Hz and ³J(¹⁹⁵Pt-¹H) = 34 Hz that can only be attributed to the *ortho* proton of one of the dmba ligands. Its upfield shift, *i.e.* extra shielding, indicates that it is held near the aromatic ring of the second dmba ligand.¹⁷ There is also a doublet signal at δ 7.79 [³J(¹H-¹H) = 6 Hz] for which ³J(¹⁹⁵Pt-¹H), although present, is not well resolved. [The ³J(¹⁹⁵Pt-¹H) are well resolved on the downfield-shifted aromatic signals in the spectra of **5d** and **5e**, see Table 2.] This signal must be attributed to that of the *ortho* proton of the second dmba ligand and its downfield chemical shift is brought about by the anisotropy of one of the chloride ligands in whose neighbourhood it is held.¹⁸ These data restrict the possible structures for **4d** to only one diastereomer (two enantiomers): [Pt(X₂-*ab*){(dmba)₂-*cf,de*}] (Fig. 2). A similar diastereomer was encountered in the X-ray analysis of the analogous dman complex **5e** (see below).

The ¹H NMR spectrum of the product mixture obtained from the reaction of complex **1** with CuCl₂ shows principally **4d** (95%) as well as one additional pattern with a singlet at δ 2.81 [³J(¹⁹⁵Pt-¹H) = 9 Hz] and a singlet at δ 4.07 [³J(¹⁹⁵Pt-¹H) = 9 Hz]. These resonances can be ascribed to the N-methyl and benzylic protons, respectively, of the *trans*-Cl₂ oxidative-addition product *trans,cis*-[PtCl₂(dmba)₂] **4a** (by comparison with the analogous spectra of *trans,cis*-[PtX₂(dmba)₂] **4b** (X = Br) and **4c** (X = I) (see above).

The ¹H NMR spectra of the reaction products of *cis*-[Pt(dman)₂] **3** with CuCl₂ and CuBr₂ show features that are similar to those described above for **4d** (see Table 2), but now without the benzylic protons. The reaction of **3** with CuCl₂ affords *cis,cis*-[PtCl₂(dman)₂] **5d** and a minor amount of *trans,cis*-[PtCl₂(dman)₂] **5a** (<5%). The reaction of **3** with CuBr₂ gives as the products *cis,cis*-[PtBr₂(dman)₂] **5e** and less than 5% of *trans,cis*-[PtBr₂(dman)₂] **5b**. In the spectrum of **5e** the resonances of the NMe groupings are well resolved and four separate singlets are observed with equal integrals.

A crucial difference in this chemistry is that *cis*-[Pt(dmba)₂] **1** reacts with CuBr₂ to afford a *trans* oxidative-addition product **4b** whereas with **3** a *cis* product **5e** is obtained.

Description of the Structures of [bc,de-Bis(8-dimethylamino-1-naphthyl)]-af-diiodoplatinum(IV) 5c and ab-Dibromo[cf,de-bis(8-dimethylamino-1-naphthyl)]platinum(IV) 5e.—Figs. 3 and 4 show the ORTEP drawings of the molecular structures of complexes **5c** and **5e**, respectively, along with the adopted numbering schemes. Positional parameters are listed in Tables 4 and 5 and the relevant bond lengths and angles in Tables 6 and 7 for **5c** and **5e**, respectively.

In *trans,cis*-[PtI₂(dman)₂] **5c** the platinum(IV) centre is six-coordinate with the two C atoms and the two N atoms mutually *cis* positioned, and the two I atoms situated *trans* to each other. This stereochemistry is the same as the one proposed for **5c** in solution (see above). The octahedral arrangement around the platinum centre is distorted, as can be seen from the I(1)-Pt-I(2) angle of 170.40(3) as well as from N(1)-Pt-N(2) 101.7(3), C(1)-Pt-C(13) 100.4(3), N(1)-Pt-C(1) 79.7(3) and N(2)-Pt-C(13) 78.4(3)°.

In **5c**, as in bis(2,2'-bipyridyl)- and bis(1,10-phenanthroline)-metal complexes,¹⁹ there is a steric interference between the *ortho* protons [on C(2) and C(14)] of the two naphthyl systems. This is alleviated to some degree by the angle of 5.6(3)° between the chelate ring planes PtC(1)C(10)C(9)N(1) and

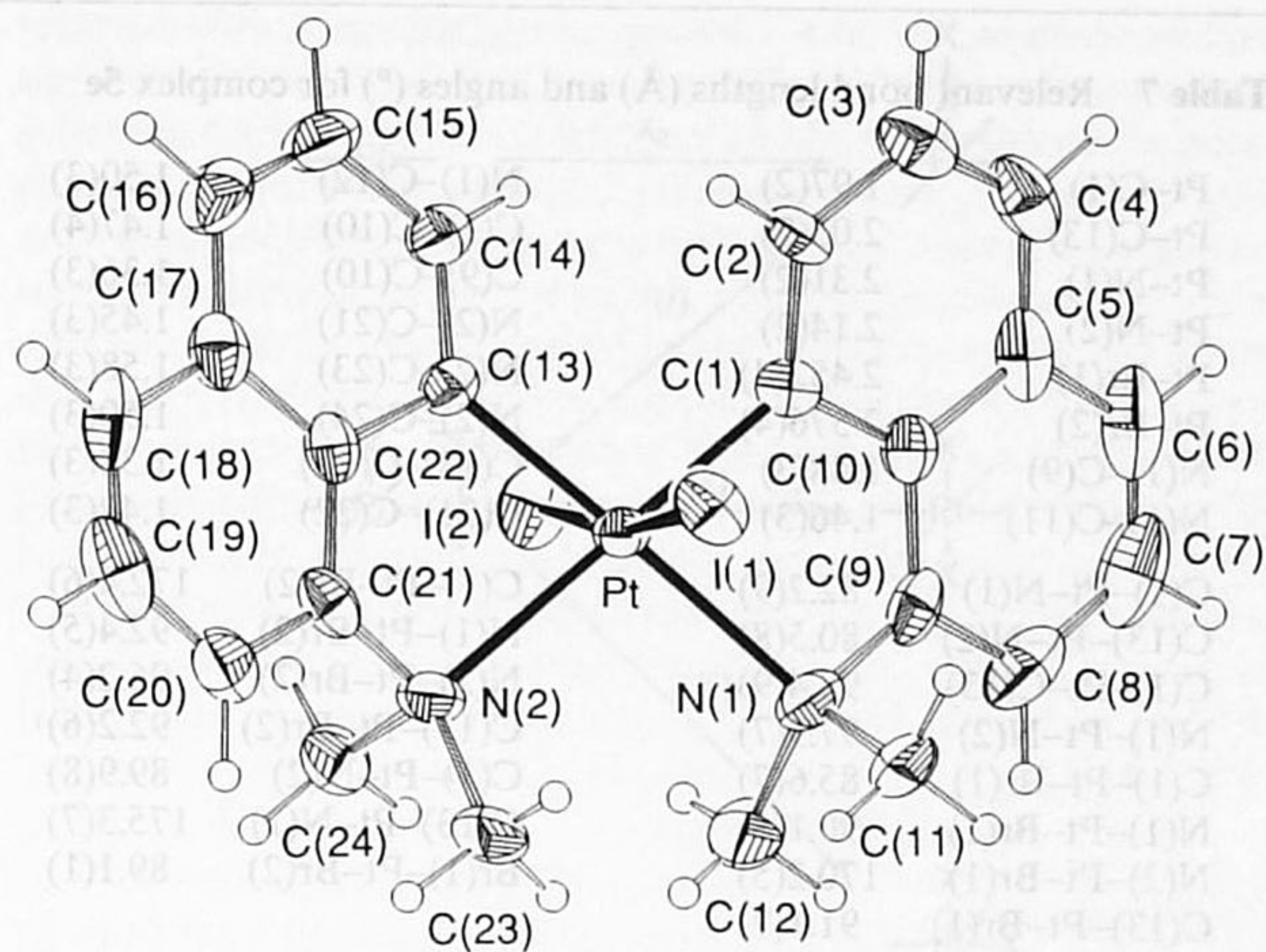


Fig. 3 ORTEP drawing (40% probability level) and adopted numbering scheme for *trans*-[PtI₂(dman)₂] **5c**

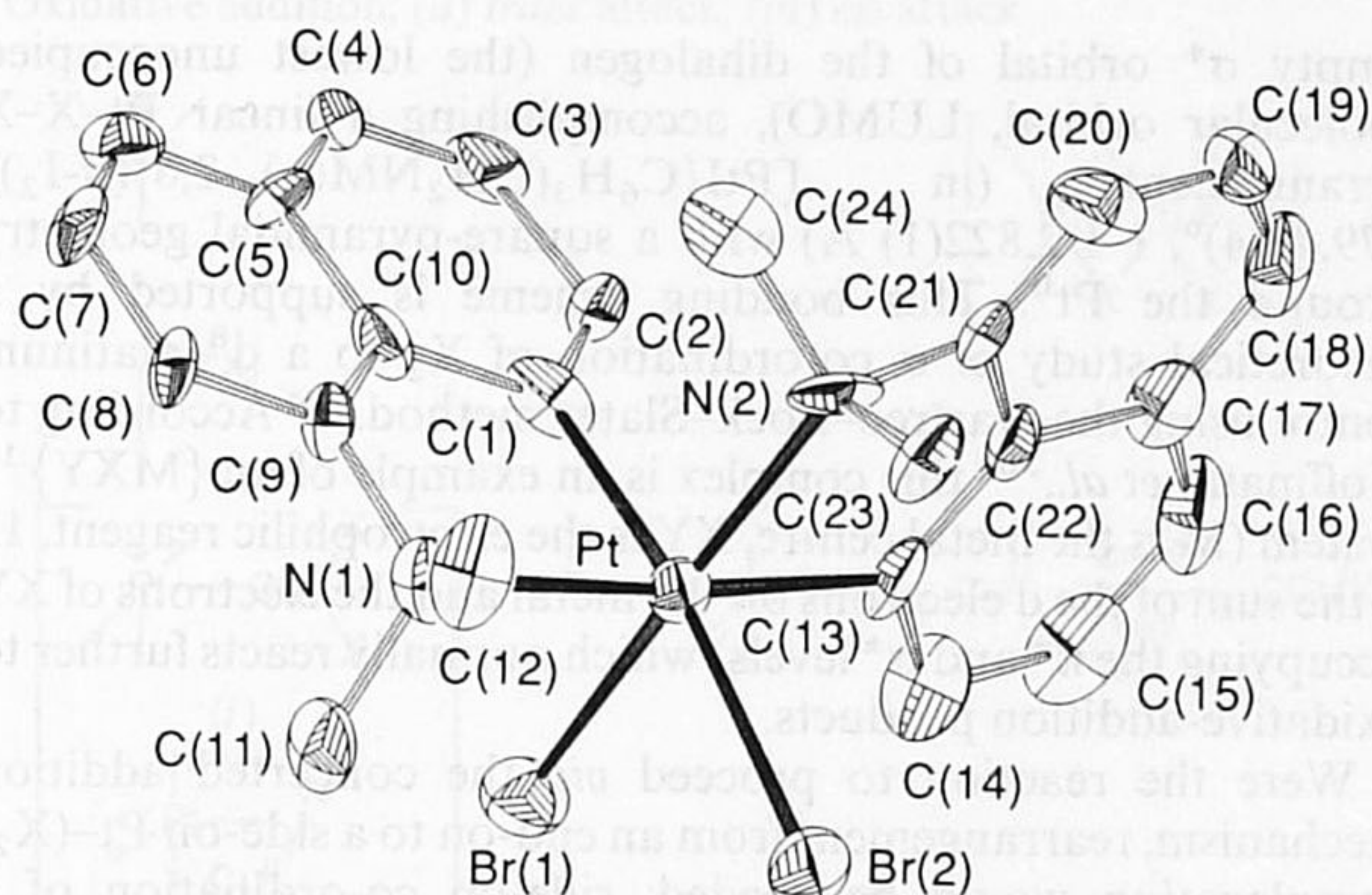


Fig. 4 ORTEP drawing (40% probability level) and adopted numbering scheme for *cis*-[PtBr₂(dman)₂] **5e**

PtC(13)C(22)C(21)N(2) (*anti* twist conformation). Moreover, there is noticeable bending of the naphthyl skeletons: the angle between the two six-membered rings in the naphthyl ligand containing C(1) is 4.3(4)°, in the other naphthyl ligand containing C(13) this angle amounts to 4.5(4)°. Similar deviations from planarity are also found in the molecular structure of [Pt(dman)₂] **3**.²⁰

The Pt–C(1) and Pt–C(13) bond lengths of 2.015(8) and 2.028(7) Å are comparable to the value of 2.05(3) Å found for the Pt–C bond in [NH₄][PtCl₄(C₁₀H₇)(NH₃)]·2Me₂CO, in which a NH₃ group is *trans* to the monodentate naphthyl ligand.¹⁸ The Pt–N bond distances of 2.290(7) and 2.312(7) Å in complex **5c** reflect the influence of the *trans* positioned C ligands and are longer than, for example, the Pt–N bonds of 2.15(2) and 2.21(2) Å encountered in [PtI₂(C₆H₄Me-4){C₆H₃(CH₂NMe₂)₂-2,6}].^{10b} The Pt–I(1) and Pt–I(2) bond lengths of 2.635(1) and 2.655(1) Å are comparable to those in other platinum(IV) complexes with *trans* iodide geometries; for example Pt–I 2.641(1) Å in [Pt{CH₂(CH₂)₂CH₂}I₂(PMe₂-Ph)₂]²¹ and 2.667(1) Å in [PtI₂(acac)₂] (acac = acetylacetonate).²²

The X-ray structure of [PtBr₂(dman)₂] **5e** shows a platinum(IV) centre which, like that in **5c**, is six-co-ordinate. In this structure there is mutual *cis* positioning of each pair of co-ordinated nitrogen, carbon and bromine atoms.

The distortions in **5e** from a perfect octahedral geometry are noticeable; the most significant deviations are seen in the Br(1)–Pt–N(2) angle of 170.2(5)° and the small angles N(1)–Pt–C(1) and N(2)–Pt–C(13) [82.2(9) and 80.5(8)°, respectively]. Steric interference between *ortho* protons, as

Table 4 Positional parameters for complex **5c**

| Atom | x | y | z |
|-------------------------|--------------|-------------|-------------|
| Pt | 0.090 62(4) | 0.254 63(2) | 0.144 31(1) |
| I(1) | 0.274 93(8) | 0.207 76(4) | 0.090 40(2) |
| I(2) | –0.139 85(8) | 0.296 42(4) | 0.191 88(2) |
| N(1) | 0.248 9(9) | 0.362 8(4) | 0.145 5(2) |
| N(2) | 0.224 2(9) | 0.183 4(4) | 0.187 2(2) |
| C(1) | –0.039(1) | 0.317 1(5) | 0.108 9(2) |
| C(2) | –0.201(1) | 0.304 6(5) | 0.096 4(2) |
| C(3) | –0.267(1) | 0.350 0(6) | 0.069 1(2) |
| C(4) | –0.176(2) | 0.406 3(6) | 0.054 4(2) |
| C(5) | –0.014(1) | 0.423 6(5) | 0.067 7(2) |
| C(6) | 0.090(2) | 0.482 3(6) | 0.054 4(3) |
| C(7) | 0.241(2) | 0.498 7(7) | 0.068 9(3) |
| C(8) | 0.304(1) | 0.458 9(6) | 0.097 9(3) |
| C(9) | 0.208(1) | 0.401 2(5) | 0.112 0(2) |
| C(10) | 0.051(1) | 0.380 6(4) | 0.096 1(2) |
| C(11) | 0.204(1) | 0.415 5(5) | 0.174 5(2) |
| C(12) | 0.438(1) | 0.347 5(6) | 0.148 8(3) |
| C(13) | –0.039(1) | 0.156 2(4) | 0.140 7(2) |
| C(14) | –0.142(1) | 0.133 6(5) | 0.113 3(2) |
| C(15) | –0.239(1) | 0.067 3(5) | 0.116 3(3) |
| C(16) | –0.237(1) | 0.024 7(5) | 0.146 5(3) |
| C(17) | –0.127(1) | 0.044 1(5) | 0.174 0(3) |
| C(18) | –0.111(2) | 0.001 7(5) | 0.205 7(3) |
| C(19) | 0.002(2) | 0.021 7(6) | 0.230 9(3) |
| C(20) | 0.112(1) | 0.083 4(5) | 0.226 2(2) |
| C(21) | 0.100(1) | 0.125 0(5) | 0.196 3(2) |
| C(22) | –0.021(1) | 0.108 4(5) | 0.170 5(2) |
| C(23) | 0.276(1) | 0.228 2(5) | 0.219 6(2) |
| C(24) | 0.384(1) | 0.144 4(5) | 0.174 5(3) |
| Dichloromethane solvate | | | |
| Cl(1) | 0.604 0(4) | 0.167 0(2) | 0.023 69(9) |
| Cl(2') | 0.932 8(7) | 0.102 6(5) | 0.010 0(1) |
| C(25) | 0.791(2) | 0.175 3(8) | 0.001 0(3) |
| Cl(3'') | 0.979(2) | 0.157(2) | 0.019 9(8) |

Single prime indicates disordered atom with s.o.f. = 0.88(1), double primes atom with s.o.f. = 0.12(1).

observed in **5c**, is absent in this structure of **5e**, but the naphthyl ligands are not perfectly planar. The angle between the two aromatic six-membered rings in the naphthyl ligand containing C(1) amounts to 2.9(1)° while in the second dman ligand this angle is 1.3(1)°. This geometrical strain in the naphthyl ring systems is less than in the ring systems of **5c**, as one would expect.

The bond distances in complex **5e** reflect the usual *trans* influence order: (a) Pt–Br(2) [2.576(4) Å] is larger than Pt–Br(1) [2.452(4) Å] due to the greater *trans* influence of a carbon ligand than of a nitrogen ligand; (b) Pt–N(1) is larger than Pt–N(2) [2.31(2) vs. 2.14(2) Å] because carbon ligands have a greater *trans* influence than bromide; (c) Pt–C(1) and Pt–C(13) are similar in length because the *trans* influences of N and Br are comparable. The bond distances involving platinum are in the usual range for platinum(IV) complexes.^{23,24}

Discussion

Mechanism of the Oxidative-addition Reactions of Dihalogens to Square-planar d⁸ Organoplatinum Complexes.—Despite the limited number of studies various mechanisms have been proposed for the oxidative-addition reactions of dihalogens. Morgan and Jones showed that the chlorination^{4a} and bromination^{4b} of [Pt(CN)₄]²⁻ in aqueous solutions proceed *via* an S_N2 type mechanism. The reaction of diiodine can also follow the S_N2 route as has been proposed for reactions of binuclear compounds of Pt²⁵ and Mn and Re.²⁶ The concerted addition mechanism has been suggested for the reactions of [Rh{P(OMe)₃}₅]⁺ with Cl₂²⁷ and [Rh(β-diketonate)-{P(OPh)₃}]₂ with I₂.⁵ Hopgood and Jenkins⁶ proposed a radical chain mechanism for the oxidative addition of I₂ to

Table 5 Positional parameters for complex **5e**

| Atom | x | y | z |
|------------------------------------|-------------|-------------|-------------|
| Pt | 0.102 29(8) | 0.135 57(9) | 0.141 57(3) |
| Br(1) | 0.086 4(3) | 0.012 9(3) | 0.061 83(9) |
| Br(2) | -0.141 2(2) | 0.049 0(3) | 0.163 05(9) |
| N(1) | 0.017(2) | 0.332(2) | 0.103 9(7) |
| N(2) | 0.147(2) | 0.222(2) | 0.213 3(7) |
| C(1) | 0.278(2) | 0.208(3) | 0.116 4(8) |
| C(2) | 0.409(2) | 0.150(3) | 0.119 2(8) |
| C(3) | 0.524(2) | 0.222(3) | 0.099 6(9) |
| C(4) | 0.514(2) | 0.342(2) | 0.077 7(7) |
| C(5) | 0.388(2) | 0.409(2) | 0.074 2(8) |
| C(6) | 0.369(2) | 0.548(3) | 0.054 5(9) |
| C(7) | 0.245(2) | 0.605(2) | 0.052 4(9) |
| C(8) | 0.128(2) | 0.539(2) | 0.068 4(8) |
| C(9) | 0.142(2) | 0.409(2) | 0.089 1(7) |
| C(10) | 0.266(2) | 0.344(3) | 0.092 5(8) |
| C(11) | -0.070(2) | 0.299(3) | 0.061(1) |
| C(12) | -0.077(2) | 0.414(3) | 0.136 9(9) |
| C(13) | 0.193(2) | -0.030(2) | 0.174 7(9) |
| C(14) | 0.204(3) | -0.160(3) | 0.154(1) |
| C(15) | 0.281(3) | -0.260(3) | 0.181(1) |
| C(16) | 0.339(3) | -0.233(4) | 0.226(1) |
| C(17) | 0.331(2) | -0.104(2) | 0.247(1) |
| C(18) | 0.389(3) | -0.069(4) | 0.293(1) |
| C(19) | 0.373(3) | 0.060(4) | 0.310(1) |
| C(20) | 0.293(2) | 0.157(4) | 0.285 2(9) |
| C(21) | 0.236(2) | 0.132(2) | 0.242 2(8) |
| C(22) | 0.251(2) | -0.001(3) | 0.220 6(9) |
| C(23) | 0.019(2) | 0.245(3) | 0.248 3(9) |
| C(24) | 0.217(3) | 0.360(3) | 0.211 5(9) |
| Disordered dichloromethane solvate | | | |
| Cl(1) | 0.766(2) | 0.692(1) | 0.047(1) |
| Cl(2') | 0.535(2) | 0.867(2) | 0.064(1) |
| Cl(3') | 0.572(2) | 0.860(1) | 0.091(1) |
| Cl(4'') | 0.534(2) | 0.870(1) | 0.038(1) |
| C(25) | 0.709(2) | 0.860(1) | 0.049(1) |

Single prime indicates disordered atom with s.o.f. = 0.35(2), double primes atom with s.o.f. = 0.30(2).

Table 6 Relevant bond lengths (Å) and angles (°) for complex **5c**

| | | | |
|---------------|----------|---------------|-----------|
| Pt-C(1) | 2.015(8) | N(1)-C(12) | 1.51(1) |
| Pt-C(13) | 2.028(7) | C(1)-C(10) | 1.42(1) |
| Pt-N(1) | 2.290(7) | C(9)-C(10) | 1.42(1) |
| Pt-N(2) | 2.312(7) | N(2)-C(21) | 1.47(1) |
| Pt-I(1) | 2.635(1) | N(2)-C(23) | 1.52(1) |
| Pt-I(2) | 2.655(1) | N(2)-C(24) | 1.51(1) |
| N(1)-C(9) | 1.48(1) | C(13)-C(22) | 1.42(1) |
| N(1)-C(11) | 1.49(1) | C(21)-C(22) | 1.39(1) |
| C(1)-Pt-N(1) | 79.7(3) | C(1)-Pt-I(2) | 87.4(2) |
| C(13)-Pt-N(2) | 78.4(3) | N(1)-Pt-I(2) | 96.8(2) |
| C(1)-Pt-C(13) | 100.4(3) | N(2)-Pt-I(2) | 89.1(2) |
| N(1)-Pt-N(2) | 101.7(3) | C(13)-Pt-I(2) | 87.1(2) |
| C(1)-Pt-I(1) | 86.3(2) | C(1)-Pt-N(2) | 176.3(3) |
| N(1)-Pt-I(1) | 89.2(2) | C(13)-Pt-I(1) | 176.1(3) |
| N(2)-Pt-I(1) | 97.1(2) | I(1)-Pt-I(2) | 170.40(3) |
| C(13)-Pt-I(1) | 87.0(2) | | |

[Pt(acac)₂]. Dihalogen reactivity in oxidative-addition reactions increases in the order Cl₂ > Br₂ > I₂²⁸ and in the products the geometry of the MX₂ unit is far more likely to be *trans* than *cis*.^{10b,29} Strikingly, in all three possible mechanisms the first step in the oxidative-addition process has been proposed to be σ complexation of the dihalogen X₂ to the metal centre.⁴⁻⁶ We have demonstrated that this complexation indeed is feasible with I₂ as the dihalogen and Pt^{II} as the metal centre.¹¹ The bonding in such a 1:1 Pt(σ-X₂) adduct is provided for by overlap of the filled d_{z²} orbital (or d_{z²-s} or -p_z mixtures) on Pt^{II} (the highest occupied molecular orbital, HOMO) with the

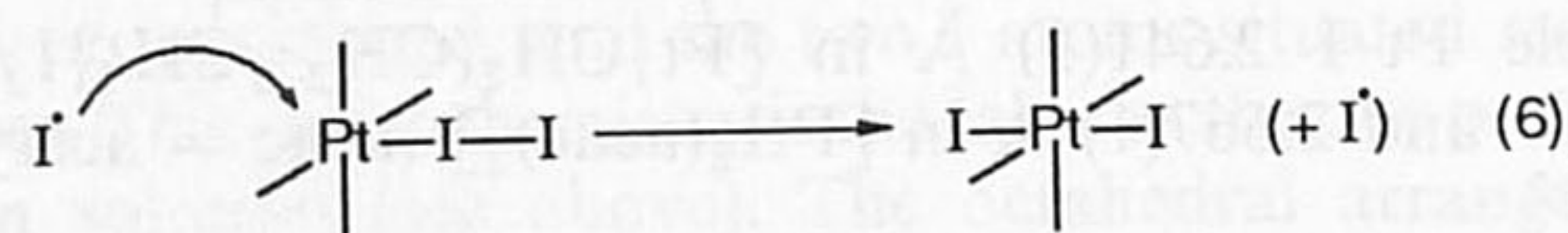
Table 7 Relevant bond lengths (Å) and angles (°) for complex **5e**

| | | | |
|----------------|----------|----------------|----------|
| Pt-C(1) | 1.97(2) | N(1)-C(12) | 1.50(3) |
| Pt-C(13) | 2.03(2) | C(1)-C(10) | 1.47(4) |
| Pt-N(1) | 2.31(2) | C(9)-C(10) | 1.36(3) |
| Pt-N(2) | 2.14(2) | N(2)-C(21) | 1.45(3) |
| Pt-Br(1) | 2.452(4) | N(2)-C(23) | 1.58(3) |
| Pt-Br(2) | 2.576(4) | N(2)-C(24) | 1.50(3) |
| N(1)-C(9) | 1.48(3) | C(13)-C(22) | 1.38(3) |
| N(1)-C(11) | 1.46(3) | C(21)-C(22) | 1.42(3) |
| C(1)-Pt-N(1) | 82.2(9) | C(1)-Pt-Br(2) | 172.4(6) |
| C(13)-Pt-N(2) | 80.5(8) | N(1)-Pt-Br(2) | 92.4(5) |
| C(1)-Pt-C(13) | 93.4(9) | N(2)-Pt-Br(2) | 96.2(4) |
| N(1)-Pt-N(2) | 97.9(7) | C(13)-Pt-Br(2) | 92.2(6) |
| C(1)-Pt-Br(1) | 85.6(7) | C(1)-Pt-N(2) | 89.9(8) |
| N(1)-Pt-Br(1) | 90.1(5) | C(13)-Pt-N(1) | 175.3(7) |
| N(2)-Pt-Br(1) | 170.2(5) | Br(1)-Pt-Br(2) | 89.1(1) |
| C(13)-Pt-Br(1) | 91.1(7) | | |

empty σ* orbital of the dihalogen (the lowest unoccupied molecular orbital, LUMO), accomplishing a linear Pt-X-X arrangement (in [PtI{C₆H₃(CH₂NMe₂)_{2-2,6}}(σ-I₂)] 179.43(4)°, I-I 2.822(1) Å) with a square-pyramidal geometry around the Pt^{II}. This bonding scheme is supported by a theoretical study of σ co-ordination of X₂ to a d⁸ platinum centre using the Hartree-Fock-Slater method.^{30a} According to Hoffmann *et al.*,^{30b} this complex is an example of an {MXY}¹² system (M is the metal centre, XY is the electrophilic reagent, 12 is the sum of the d electrons on the metal and the electrons of XY occupying the π* and σ* levels) which normally reacts further to oxidative-addition products.

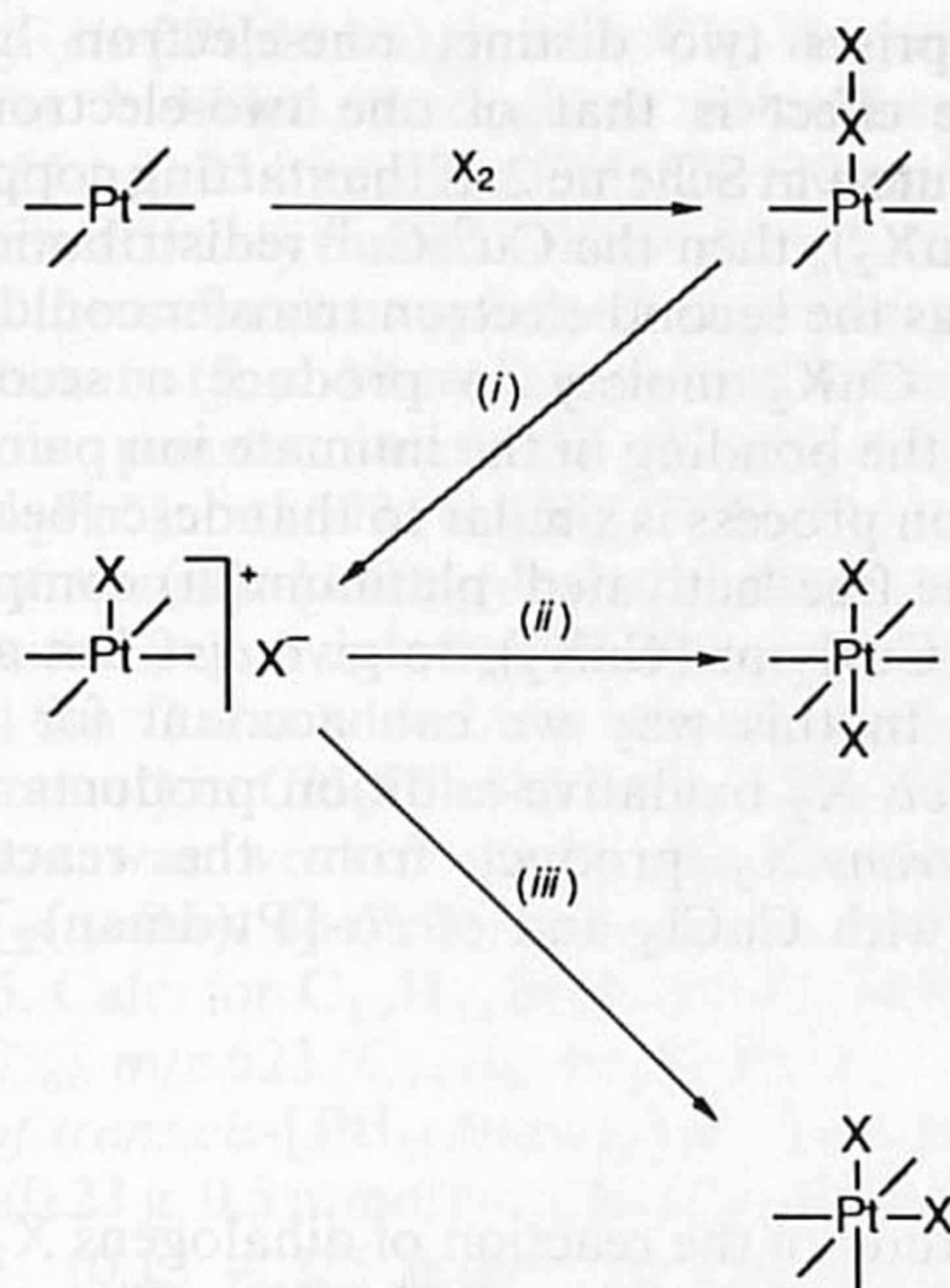
Were the reaction to proceed *via* the concerted addition mechanism, rearrangement from an end-on to a side-on Pt-(X₂) complexation would be needed; side-on co-ordination of a dihalogen molecule can be compared to the side-on co-ordination of dihydrogen. The two interactions that are responsible for the M-(H₂) interaction (and the following oxidative addition) are:³¹ (a) σ donation from the filled σ orbital of H₂ into a vacant metal orbital of p_z hybrid character and (b) a back-bonding interaction involving overlap between a filled orbital of π symmetry of the metal centre and σ* of H₂. After the first end-on interaction between Pt^{II} and I₂ just described, interactions similar to (a) and (b) are not to be expected. In particular, the filled p_y and p_z orbitals of I₂ would cause a strong repulsive interaction with the filled d_{z²} orbital of the metal centre.

For a radical mechanism there are two routes from the σ bonded metal-X₂ complex. (i) A one-electron transfer, resulting in a five-co-ordinate platinum(III) complex and a halogen radical. Although examples of platinum(III) complexes exist,³² the +3 oxidation state is not favourable, particularly for mononuclear complexes.^{32b} (ii) Attack of a halogen radical X• on the platinum centre from the site opposite to the co-ordinated dihalogen, as proposed earlier [equation (6)].⁶ We

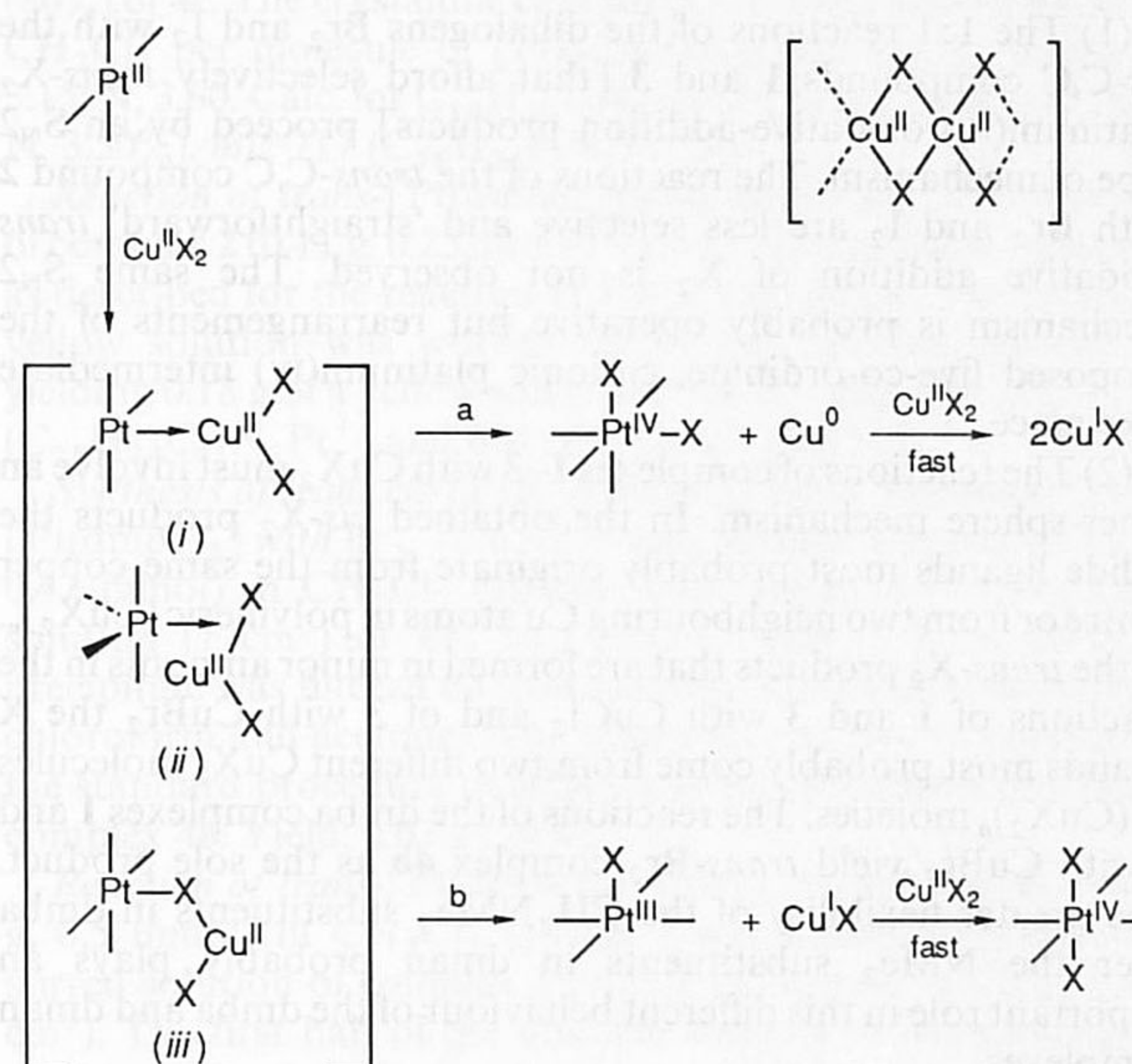


have no indication that radicals participate in the reactions we have carried out: whether in light or in dark, kept under nitrogen or exposed to air, the reaction products and their yields were always the same.

Actually, the linear Pt-X-X arrangement of the σ-X₂ adduct is a good starting point for the S_N2 type mechanism since some electron transfer from the metal centre to the co-ordinated



Scheme 1 S_N2 type of mechanism for the oxidative-addition reactions of dihalogens with square-planar organoplatinum(II) complexes. (i) Oxidative addition; (ii) *trans* attack; (iii) *cis* attack



Scheme 2 Inner-sphere mechanism for the reactions of copper(II) halides with organoplatinum(II) complexes leading to dihalogenoplatinum(IV) products (other ligands to Cu^{II} , either MeOH or X, are not shown)

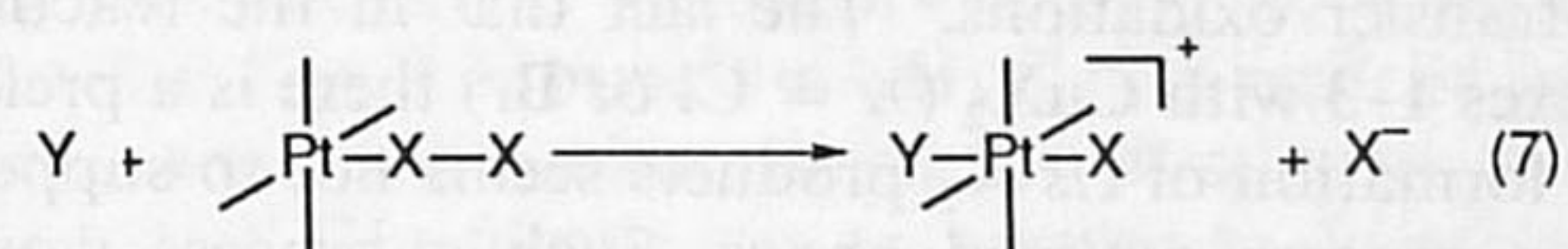
dihalogen has already taken place.* The donation of two electrons, as a logical continuation, results in the formation of a five-co-ordinate, cationic platinum(IV) complex and a halide anion. This complex can, in principle, retain a square-pyramidal configuration (like that of the $\sigma-X_2$ adduct) or rearrange in the direction of a trigonal-bipyramidal structure. In the square-pyramidal cationic intermediate, the open co-ordination site for approach of X^- is *trans* to the Pt-X bond that has just been formed; this affords a *trans* oxidative-addition product. *cis* Oxidative-addition products can be formed only when steric constraints in the cationic platinum(IV) intermediate prevent attack at this site, or a rearrangement of this intermediate has occurred. The reaction mechanism outlined above is shown schematically in Scheme 1.

It is evident that the stability of the five-co-ordinate, cationic platinum(IV) intermediate will strongly influence the outcome of the oxidative-addition reaction. The *cis*-C,C compounds **1** and **3**

* Evidence for electron transfer from the metal centre to the halogen is found in the lengthening of the I-I bond of $[PtI\{C_6H_3(CH_2NMe_2)_2-2,6\}(\sigma-I_2)]$ by 0.107 Å compared to that in free diiodine; see refs. 9 and 11.

both react with Br_2 and I_2 to yield one *trans*- X_2 oxidative-addition product as expected for reactions which smoothly proceed by the S_N2 mechanism just described. This route represents a low-energy pathway for the reaction. However, when the *trans*-C,C complex **2** reacts with a dihalogen, the first-formed five-co-ordinate, cationic intermediate has the C donor atoms in *trans* positions and this is a less-stable configuration. Therefore, rearrangement to a geometry with the C atoms in *cis* positions is likely to occur and in the reaction of **2** with Br_2 this obviously happens. The intermediate is identical to the one from the reaction of **1** with Br_2 and hence the same *trans*- Br_2 product **4b** is obtained. In the reaction of **2** with I_2 there is apparently no discrimination between the various reaction channels of this higher-energy reaction path and a number of rearrangements occur, evidenced by the formation of a mixture of *cis*- I_2 oxidative-addition products together with a minor amount of *trans*- I_2 , *cis*-C,C product.

The electron-transfer step (*i.e.* donation overall of two electrons by Pt^{II} to the co-ordinated dihalogen) can be accelerated by attack of an extra nucleophilic agent Y (a solvent molecule or other Lewis base present in the solution) on the Pt- X_2 adduct, as shown in equation (7). This has been proposed



for the chlorination and bromination of $[Pt(CN)_4]^{2-}$ in aqueous solution; here H_2O attacks the Pt^{II} of the dihalogen adduct to afford a $HO-Pt^{IV}-X$ complex which can then react with X^- to provide the $[PtX_2(CN)_4]^{2-}$ product.⁴

In the present reactions of complexes **1–3** with dihalogens the solvent CH_2Cl_2 could act as a base by attacking the Pt^{II} with one of its chlorine atoms. This seems unlikely since in related reactions of, for example, Br_2 with $[PtR\{C_6H_3(CH_2NMe_2)_2-2,6\}]$ ($R = Br, Ph$ or C_6H_4Me-4) oxidative addition occurs as readily in CH_2Cl_2 as in benzene.¹⁰

Isolation of exclusively *trans* oxidative-addition products is in principle not a good test for excluding the possibility of the concerted addition mechanism. It could be possible, and has indeed been proposed⁵ for the reaction of diiodine with $[Rh(\beta\text{-diketonate})\{P(OPh)_3\}_2]$, that the concerted addition mechanism is valid for the reactions which afford *cis*- X_2 products, which then undergo a very fast rearrangement to *trans* products; the latter are isolated. We can exclude this possibility in our case. If the first-formed product of the reaction of, for example, $[Pt(dman)_2]$ with Br_2 were to be the *cis*- Br_2 oxidative-addition product **5e** it would have been isolated. This stereoisomer, *cis,cis*- $[PtBr_2(dman)_2]$ **5e**, is stable and can be isolated from the reaction of **3** with $CuBr_2$ (see above)!

Reactions with Copper(II) Halides.^{7b}—Like the reactions with dibromine and diiodine, the reactions of *cis*- $[Pt(dmba)_2]$ **1**, *trans*- $[Pt(dmba)_2]$ **2** and *cis*- $[Pt(dman)_2]$ **3** with $CuCl_2$ and $CuBr_2$ afford oxidative-addition products. Products originating from Pt-C bond cleavage were not found.¹⁰ Recently, further examples of oxidative-addition reactions of cyclometallated compounds with copper(II) halides have been reported.³³ The results with **1–3** indicate that the reactions probably take place *via* an inner-sphere redox mechanism.³⁴

In Scheme 2 various possibilities for the initial contact of the reactions are envisaged: (i) the formation of a complex with a $Pt^{II}-Cu^{II}$ bond, (ii) side-on attack on the Pt^{II} by a $Cu-X$ bond, and (iii) the formation of a halide-bridged $Pt^{II}-X-Cu^{II}$ complex. Each of these possibilities has stable precedents in the chemistry of cyclometallated d^8 metal compounds. The formation of heterodinuclear complexes with a $Pt \rightarrow Hg$ bond and their role as intermediates in the redox reactions between platinum and mercury compounds have been demonstrated and discussed.³⁵ Side-on (η^2) co-ordination of metal-halide bonds to Ir^I has been established by the isolation and characterization of $[Ir\{C_6H_4(CH_2NMe_2)_2\}(cod)(\eta^2-BrSnMe_2Br)]$ ($cod = cyclo-$

octa-1,5-diene), which contains an η^2 -co-ordinated Sn-Br bond brought about by $d_{xz}(\text{Ir}) \rightarrow \sigma^* \text{sp}^2(\text{Br}-\text{Sn})$ contribution to the bonding.³⁶ Finally, bridged complexes and their role as intermediates in redox reactions are well known.^{2b,34}

If we assume that the first-formed complex has a general formula $[\text{Pt}^{\text{II}}(\text{dman})_2(\text{Cu}^{\text{II}}\text{X}_2)_n]$ then this is likely to react further by electron transfer from Pt^{II} to Cu^{II} . The question then arises as to whether the reaction proceeds *via* one overall two-electron step or as a process with two separate one-electron steps to yield the isolated products, see Scheme 2. The mechanism involving two separate one-electron steps (route b in Scheme 2) would result in the initial formation of a five-coordinate platinum(III) intermediate. The second electron transfer would then require the reaction of the platinum(III) complex with another CuX_2 molecule to afford the observed platinum(IV) complex. Formation of a platinum(III) intermediate has been proposed in the oxidation of $[\text{PtMe}_2(\text{PMe}_2\text{Ph})_2]$ by hexachloroiridate (the Pt^{III} here being four-co-ordinate).³⁷ Furthermore, $[\text{Ni}^{\text{II}}\text{X}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}\}]$ react with CuX_2 to afford almost quantitatively the d^7 organometallic square-pyramidal compounds $[\text{Ni}^{\text{III}}\text{X}_2\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}\}]$ ($\text{X} = \text{Cl}$ or Br), *i.e.* products resulting from one-electron ligand-transfer oxidations.⁹ The fact that in the reactions of complexes **1–3** with CuX_2 ($\text{X} = \text{Cl}$ or Br) there is a preference for the formation of *cis*- X_2 products seems not to support the two-step process outlined above. Such a process would be expected to lead to *cis*- and *trans*- X_2 products.

Before discussing the alternative mechanism it is important to recall that complexes **1–3** react with CuCl_2 to give *cis*- Cl_2 platinum(IV) products while the amounts of *trans*- Cl_2 products in the reactions of **1** and **3** are less than 5%, see Table 1. In the reactions with the less-reactive reagent CuBr_2 a clear distinction arises between the *dmba* and *dman* complexes: both **1** and **2** yield the *trans*- Br_2 product **4b** while **3** affords one *cis*- Br_2 product, **5e** (and less than 5% of *trans*- Br_2 compound **5b**). The only difference between the *dmba* and *dman* complexes is the ability of the NMe_2 group to move away from the metal centre after Pt-N bond cleavage to provide an open co-ordination site. This means that the formation of *trans*- Br_2 products is the result of a rearrangement [in the intermediate complex or in a first-formed *cis*- Br_2 platinum(IV) oxidative-addition product] which cannot take place in a complex with *dman* ligands.

The alternative mechanism, comprising one two-electron transfer in the first formed Pt-Cu complex [(i)–(iii)], could account for the formation of *cis*- X_2 products from the reactions of **1–3** with CuX_2 , as now the two new X ligands of the final platinum(IV) centre now come from the same CuX_2 molecule (Scheme 2, route a). The Cu^0 formed in this mechanism would react in a fast subsequent reaction with CuX_2 to afford CuX .

Most likely the reactions of CuX_2 ($\text{X} = \text{Cl}$ or Br) with complexes **1–3** take place *via* a mechanism which lies in between the two extreme possibilities discussed above. One problem is that the nature of the CuX_2 species in solution is uncertain. Earlier studies have shown that these species can be polynuclear $(\text{CuX}_2)_n$ with halide bridges, as schematically shown in Scheme 2. Anchoring of the platinum(II) centre to $(\text{CuX}_2)_n$ could occur by all three modes (i)–(iii) outlined in Scheme 2 for mononuclear CuX_2 . The reactions were carried out in a mixture of methanol and dichloromethane, so (some) CuX_2 could also have been present as mononuclear MeOH solvated species. We believe the most likely mechanistic path for the oxidative-addition reactions of Pt^{II} with CuX_2 is as follows. A one-electron transfer from Pt^{II} to Cu^{II} takes place to give an intimate pair consisting of a five-co-ordinate platinum(III) species and $\text{Cu}^{\text{I}}\text{X}$ or $\text{Cu}^{\text{I}}\text{X}(\text{CuX}_2)_{n-1}$. As the +3 oxidation state is not favoured (see above), a fast second electron/ligand transfer is likely to occur in the intimate pair. This leads to a *cis*- X_2 platinum(IV) product because in the ion pair the second X is held near the first transferred halide. When the starting CuX_2 species is monomeric, the redistribution reaction between Cu^0 and CuX_2 , as mentioned above, must then follow. Although the electron

transfer comprises two distinct one-electron halide-transfer reactions, the effect is that of one two-electron transfer as outlined in route a in Scheme 2. If the starting copper material is polymeric $(\text{CuX}_2)_n$ then the $\text{Cu}^0/\text{Cu}^{\text{II}}$ redistribution reaction is not required as the second electron transfer could occur with a neighbouring CuX_2 moiety to produce a second copper(I) centre. When the bonding in the intimate ion pair vanishes, the overall reaction process is similar to that described in route b in Scheme 2. The free 'activated' platinum(III) complex can react with another CuX_2 or $(\text{CuX}_2)_n$ to give *cis*-, but also to *trans*-, X_2 products. In this way we can account for the observed formation of *cis*- X_2 oxidative-addition products with a minor amount of *trans*- X_2 product from the reactions of *cis*- $[\text{Pt}(\text{dmba})_2]$ with CuCl_2 and of *cis*- $[\text{Pt}(\text{dman})_2]$ with CuCl_2 and CuBr_2 .

Conclusion

The present study of the reaction of dihalogens X_2 ($\text{X} = \text{Cl}$, Br or I) and copper(II) halides CuX_2 ($\text{X} = \text{Cl}$ or Br) with the organoplatinum(II) complexes *cis*- $[\text{Pt}(\text{dmba})_2]$ **1**, *trans*- $[\text{Pt}(\text{dmba})_2]$ **2** and *cis*- $[\text{Pt}(\text{dman})_2]$ **3** leads us to the following conclusions.

(1) The 1:1 reactions of the dihalogens Br_2 and I_2 with the *cis*-C,C compounds **1** and **3** [that afford selectively *trans*- X_2 platinum(IV) oxidative-addition products] proceed by an $\text{S}_{\text{N}}2$ type of mechanism. The reactions of the *trans*-C,C compound **2** with Br_2 and I_2 are less selective and 'straightforward' *trans* oxidative addition of X_2 is not observed. The same $\text{S}_{\text{N}}2$ mechanism is probably operative but rearrangements of the proposed five-co-ordinate, cationic platinum(IV) intermediate take place.

(2) The reactions of complexes **1–3** with CuX_2 must involve an inner-sphere mechanism. In the obtained *cis*- X_2 products the halide ligands most probably originate from the same copper centre or from two neighbouring Cu atoms in polymeric $(\text{CuX}_2)_n$. In the *trans*- X_2 products that are formed in minor amounts in the reactions of **1** and **3** with CuCl_2 and of **3** with CuBr_2 the X ligands most probably come from two different CuX_2 molecules or $(\text{CuX}_2)_n$ moieties. The reactions of the *dmba* complexes **1** and **2** with CuBr_2 yield *trans*- Br_2 complex **4b** as the sole product. The greater flexibility of the CH_2NMe_2 substituents in *dmba* over the NMe_2 substituents in *dman* probably plays an important role in this different behaviour of the *dmba* and *dman* complexes.

In a separate paper we will describe the results of the reactions of *cis*- $[\text{Pt}(\text{dman})_2]$ **3** with various electrophiles including alkyl halides and organo tin(IV) compounds.²⁰

Experimental

General.—All syntheses involving organolithium compounds were carried out in a dry, inert nitrogen atmosphere using Schlenk-tube techniques. Other syntheses were carried out in the presence of air, unless stated otherwise. Solvents were distilled before use and kept under nitrogen. The complexes *cis*- and *trans*- $[\text{Pt}(\text{dmba})_2]$, **1** and **2**, *cis*- $[\text{Pt}(\text{dman})_2]$ **3** and *trans*,*cis*- $[\text{PtI}_2(\text{dman})_2]$ **5c** were synthesized by literature methods.^{38,39} Proton NMR spectra were recorded on Bruker AC 100 and WM 250 spectrometers, infrared spectra on Perkin-Elmer 283 and Nicolet 7199B FT-IR spectrophotometers, UV spectra on a Perkin-Elmer Lambda 5 UV-VIS spectrophotometer and FD and FI mass spectra on a Varian MAT 711 double-focused mass spectrometer. Elemental analyses were carried out at the Institute for Applied Chemistry, T.N.O., Zeist, The Netherlands.

Reactions of Complexes 1–3 with Dihalogens.—**Standard work-up procedure.** The reaction mixture/solution was concentrated to 4 cm³ *in vacuo* and hexane (30 cm³) added. The resulting precipitate was collected by filtration, washed with hexane (2 × 10 cm³) and dried *in vacuo*.

Reaction of *cis*-[Pt(dmab)₂] with Cl₂. A gentle stream of dichlorine was bubbled through a colourless solution of complex **1** (0.11 g, 0.23 mmol) in CH₂Cl₂ (30 cm³), whereupon the solution immediately turned yellow. After 5 min the reaction was stopped, the solvent evaporated, and the yellow residue washed with hexane (2 × 10 cm³) and dried *in vacuo*. Yield: 0.10 g of a yellow powder. *m/z* 533 (C₁₈H₂₃Cl₂N₂Pt⁺), 567 (C₁₈H₂₂Cl₃N₂Pt⁺) and 602 (C₁₈H₂₁Cl₄N₂Pt⁺).

Synthesis of *trans,cis*-[PtBr₂(dmab)₂] **4b by reaction of *cis*-[Pt(dmab)₂] with Br₂.** A solution of dibromine in CH₂Cl₂ (0.7 cm³, 0.57 mol dm⁻³) was added to a stirred solution of complex **1** (0.18 g, 0.4 mmol) in CH₂Cl₂ (10 cm³). After 1 h the resultant yellow solution was worked up by the standard procedure. Yield: 0.19 g of yellow **4b** (76%) (Found: C, 34.55; H, 3.95; Br, 25.85; N, 4.45. Calc. for C₁₈H₂₄Br₂N₂Pt: C, 34.70; H, 3.90; Br, 25.65; N, 4.50%). *m/z* 623 (C₁₈H₂₄Br₂N₂Pt⁺).

Synthesis of *trans,cis*-[PtI₂(dmab)₂] **4c.** To a stirred solution of complex **1** (0.23 g, 0.5 mmol) in CH₂Cl₂ (10 cm³) was added a solution of I₂ (0.13 g, 0.5 mmol) in CH₂Cl₂ (15 cm³). The product immediately crystallized, and after 10 min of additional stirring the red crystals were collected by filtration, washed with dichloromethane (2 × 10 cm³) and dried *in vacuo*. Yield: 0.32 g (80%) of **4c**. The crystalline compound contains one molecule of CH₂Cl₂ per molecule of [PtI₂(dmab)₂] (Found: C, 28.20; H, 3.15; N, 3.60. Calc. for C₁₈H₂₄I₂N₂Pt·CH₂Cl₂: C, 28.45; H, 3.25; N, 3.50%). *m/z* 717 (C₁₈H₂₄I₂N₂Pt⁺).

Reaction of *trans*-[Pt(dmab)₂] with dichlorine. This reaction of complex **2** (0.11 g, 0.23 mmol) was carried out in the same way as described for the reaction of **1** with dichlorine. The resultant yellow solution was worked up by the standard procedure, yielding 0.18 g of a yellow solid. *m/z* 498 (C₁₈H₂₃ClN₂Pt⁺), 569 (C₁₈H₂₄Cl₃N₂Pt⁺) and 604 (C₁₈H₂₃Cl₄N₂Pt⁺).

Synthesis of *trans,cis*-[PtBr₂(dmab)₂] **4b by reaction of *trans*-[Pt(dmab)₂] with Br₂.** To a stirred solution of complex **2** (0.22 g, 0.47 mmol) in CH₂Cl₂ (10 cm³) was added a 0.5 mol dm⁻³ solution (1 cm³) of Br₂ in CH₂Cl₂. After 3 d an off-white precipitate was filtered off (this white solid was also insoluble in chloroform and acetone). The yellow filtrate was worked up by the standard procedure to afford a yellow product identified as complex **4b**. Yield: 0.07 g (24%).

Reaction of *trans*-[Pt(dmab)₂] with I₂. A solution of I₂ (0.13 g, 0.5 mmol) in CH₂Cl₂ (15 cm³) was added dropwise to a stirred solution of complex **2** (0.23 g, 0.5 mmol) in CH₂Cl₂ (10 cm³). The first half of the diiodine solution discoloured upon addition; after 1 equivalent had been added the reaction mixture was clear dark brown. After 48 h of stirring the reaction mixture was worked up by the standard procedure. Yield: 0.22 g of a pale brown solid. *m/z* 717 (C₁₈H₂₄I₂N₂Pt⁺).

Reaction of *cis*-[Pt(dman)₂] with Cl₂. A gentle stream of dichlorine was bubbled through a solution of complex **3** (0.29 g, 0.54 mmol) in CH₂Cl₂ (15 cm³) for 10 min, during which time the solution changed from pale to dark yellow. After stirring for 17 h the solution was worked up by the standard procedure. Yield: 0.46 g of a yellow solid.

Synthesis of *trans,cis*-[PtBr₂(dman)₂] **5b.** A solution of complex **3** (0.24 g, 0.45 mmol) in CH₂Cl₂ (15 cm³) and a 0.5 mol dm⁻³ solution of dibromine in CH₂Cl₂ (0.9 cm³) were combined and stirred for 3 d, after which the resultant yellow solution was worked up by the standard procedure. Yield: 0.24 g (77%) of complex **5b** as a yellow solid. *m/z* 695 (C₂₄H₂₄Br₂N₂Pt⁺).

Reactions with Copper(II) Halides.—The reactions of the platinum(II) compounds with CuX₂ (X = Cl or Br) were carried out under a nitrogen atmosphere.

Reaction of *cis*-[Pt(dmab)₂] with CuCl₂. A green solution of CuCl₂ (0.15 g, 1.1 mmol) in methanol (10 cm³) was added to a stirred solution of complex **1** (0.24 g, 0.52 mmol) in CH₂Cl₂ (10 cm³). Immediately a white precipitate of Cu^ICl was formed and after 30 min of additional stirring the solution was filtered. The filtrate was worked up with the standard procedure affording 0.24 g (86%) of a mixture of *cis,cis*-[PtCl₂(dmab)₂] **4d** and

trans,cis-[PtCl₂(dmab)₂] **4a** (Found: C, 40.15; H, 4.65; Cl, 13.20; N, 5.10. Calc. for C₁₈H₂₄Cl₂N₂Pt: C, 40.45; H, 4.55; Cl, 13.25; N, 5.25%). *m/z* 534 (C₁₈H₂₄Cl₂N₂Pt⁺).

Synthesis of *trans,cis*-[PtBr₂(dmab)₂] **4b by reaction of *cis*-[Pt(dmab)₂] with CuBr₂.** A brown solution of CuBr₂ (0.18 g, 0.8 mmol) in methanol (10 cm³) was added to a solution of complex **1** (0.19 g, 0.4 mmol) in CH₂Cl₂ (10 cm³). After stirring the solution for 0.5 h the white precipitate of CuBr was filtered off. The filtrate was evaporated to dryness and the residue extracted with CH₂Cl₂ (2 × 10 cm³). Work-up of the combined CH₂Cl₂ extracts using the standard procedure afforded complex **4b** as a yellow solid. Yield: 0.21 g (85%). *m/z* 623 (C₁₈H₂₄Br₂N₂Pt⁺).

Synthesis of *cis,cis*-[PtCl₂(dmab)₂] **4d by reaction of *trans*-[Pt(dmab)₂] with CuCl₂.** To a stirred solution of complex **2** (0.19 g, 0.41 mmol) in CH₂Cl₂ (10 cm³) was added a green solution of CuCl₂ (0.11 g, 0.82 mmol) in methanol (10 cm³) whereupon a white precipitate formed. After 30 min of stirring this solid was filtered off and the filtrate was worked up using the standard procedure. Yield: 0.10 g (46%) of yellow-green complex **4d**. *m/z* 534 (C₁₈H₂₄Cl₂N₂Pt⁺).

Synthesis of *trans,cis*-[PtBr₂(dmab)₂] **4b by reaction of *trans*-[Pt(dmab)₂] with CuBr₂.** Addition of a brown solution of CuBr₂ (0.18 g, 0.81 mmol) in methanol (10 cm³) to a solution of complex **2** (0.17 g, 0.37 mmol) in CH₂Cl₂ (10 cm³) immediately afforded a white solid. After stirring for 30 min the precipitate was filtered off. The filtrate was evaporated to dryness and the residue extracted with CH₂Cl₂ (2 × 15 cm³). The combined CH₂Cl₂ solutions were worked up by the standard procedure to afford 0.15 g, of yellow complex **4b** (64%). *m/z* 623 (C₁₈H₂₄Br₂N₂Pt⁺).

Reaction of *cis*-[Pt(dman)₂] with CuCl₂. A green solution of CuCl₂ (0.11 g, 0.82 mmol) in methanol (10 cm³) was added to a stirred solution of complex **3** (0.22 g, 0.41 mmol) in CH₂Cl₂ (15 cm³). After 30 min a white precipitate was filtered off and the filtrate reduced in volume to 4 cm³. Hexane was added (40 cm³) and the resultant greenish yellow precipitate was collected by filtration. The impure product(s) was extracted with CH₂Cl₂ (2 × 15 cm³) and after concentration of the combined CH₂Cl₂ extracts to 4 cm³ hexane (30 cm³) was added. This afforded a yellow precipitate which was filtered off, washed with hexane (2 × 10 cm³) and dried *in vacuo*. Yield: 0.20 g (80%) of a mixture of *trans,cis*-[PtCl₂(dman)₂] **5a** and *cis,cis*-[PtCl₂(dman)₂] **5d**. *m/z* 606 (C₂₄H₂₄Cl₂N₂Pt⁺).

Reaction of *cis*-[Pt(dman)₂] with CuBr₂. A brown solution of CuBr₂ (0.20 g, 0.89 mmol) in methanol (10 cm³) was added to a solution of complex **3** (0.21 g, 0.39 mmol) in CH₂Cl₂ (15 cm³). Immediately a white precipitate formed. This yellow, turbid reaction mixture was stirred for 3 d during which time it turned green. The precipitate was filtered off and the filtrate evaporated to dryness. Extraction of the solid residue with CH₂Cl₂ (3 × 15 cm³), reduction of the volume of the combined CH₂Cl₂ solutions to 4 cm³ and addition of hexane (30 cm³) afforded a precipitate which was filtered off, washed with hexane (2 × 10 cm³) and dried *in vacuo*. Yield: 0.25 g, (82%) of a yellow-brown solid, consisting primarily of *cis,cis*-[PtBr₂(dman)₂]·CH₂Cl₂ **5e** (>95%) and a trace of *trans,cis*-[PtBr₂(dman)₂] **5b**. Recrystallization from CH₂Cl₂-hexane (1:4) afforded yellow crystals of pure complex **5e** as its dichloromethane solvate (Found: C, 38.10; H, 3.35; N, 3.50. Calc. for C₂₄H₂₄Br₂N₂Pt·CH₂Cl₂: C, 38.50; H, 3.35; N, 3.60%). *m/z* 695 (C₂₄H₂₄Br₂N₂Pt⁺).

Structure Determination of *trans,cis*-[PtI₂(dman)₂] **5c.**—Crystals were grown by vapour diffusion of pentane into a dichloromethane solution. A suitable orange, rod-shaped crystal was mounted in a Lindemann-glass capillary to prevent loss of dichloromethane solvate and was transferred to an Enraf-Nonius CAD-4 diffractometer for data collection. Unit-cell parameters were determined from a least-squares treatment of the setting angles of 25 SET4 reflections with 8.0 < θ < 14.0°. They were checked for the presence of higher lattice symmetry.^{40a} Data were corrected for Lorentz polarisation, for

Table 8 Crystal data and details of the structure determinations of *trans*-[PtI₂(dman)₂] **5c** and *cis*-[PtBr₂(dman)₂] **5e***

| (a) Crystal data | 5c | 5e |
|---|--|---|
| Formula | C ₂₄ H ₂₄ I ₂ N ₂ Pt·CH ₂ Cl ₂ | C ₂₄ H ₂₄ Br ₂ N ₂ Pt·CH ₂ Cl ₂ |
| <i>M</i> | 874.29 | 780.29 |
| Space group | <i>Pbca</i> (no. 61) | <i>P2₁/c</i> (no. 14) |
| Crystal system | Orthorhombic | Monoclinic |
| <i>a</i> /Å | 7.825(3) | 9.696(2) |
| <i>b</i> /Å | 17.803(2) | 9.722(6) |
| <i>c</i> /Å | 37.873(6) | 26.81(3) |
| β/° | | 90.46(4) |
| <i>U</i> /Å ³ | 5276(2) | 2527(3) |
| <i>Z</i> | 8 | 4 |
| <i>D_c</i> /g cm ⁻³ | 2.201 | 2.051 |
| <i>F</i> (000) | 3264 | 1488 |
| μ(Mo-Kα)/cm ⁻¹ | 79.1 | 89.7 |
| Crystal size/mm | 0.68 × 0.16 × 0.14 | 0.50 × 0.33 × 0.15 |
| (b) Data collection | | |
| <i>T</i> /K | 294 | 294 |
| Minimum, maximum θ/° | 0.54, 25.0 | 0.76, 27.5 |
| Δω/° | 0.60 + 0.35tanθ | 0.70 + 0.35tanθ |
| Horizontal, vertical aperture/mm | 2.0, 6.0 | 3.0, 4.0 |
| Reference reflections | 102, 026 | $\bar{1}\bar{1}1$ |
| Data set | <i>h</i> 0–9, <i>k</i> 0–21, <i>l</i> 0–45 | <i>h</i> 0–12, <i>k</i> –12 to 0, <i>l</i> –34 to 34 |
| Total data | 5261 | 6485 |
| Total unique data | 4627 | 5783 |
| Observed data | 2962 | 3060 |
| [<i>I</i> > 2.5σ(<i>I</i>)] | | |
| Absorption correction range | 0.92–1.09 (DIFABS) | 4.68–18.12 (ABSORB) |
| (c) Refinement | | |
| No. of refined parameters | 307 | 299 |
| Weighting scheme | 1.0/[σ ² (<i>F</i>) + 0.000 072 <i>F</i> ²] | 1.0/[σ ² (<i>F</i>) + 0.002 795 <i>F</i> ²] |
| Final <i>R</i> , <i>R'</i> , <i>S</i> | 0.032, 0.026, 4.36 | 0.083, 0.103, 7.94 |
| (Δ/σ) _{av} in final cycle | 0.021 | 0.018 |
| Maximum, minimum residual density/e Å ⁻³ | 0.74, –0.97 | 4.86, –3.09 |

* Details in common: zirconium-filtered Mo-Kα radiation (λ = 0.710 73 Å); scan type ω–2θ; distance from crystal to detector 173 mm.

a small linear increase (2.2%) of the intensities during the 96 h of X-ray exposure time. An empirical correction for absorption (DIFABS:^{40b} because of poorly defined crystal shape mounted inside a capillary) was carried out. Standard deviations obtained by counting statistics were increased according to an analysis of the excess variance of the two reference reflections: σ²(*I*) = σ²_{cs}(*I*) + (0.008*I*)².^{40c} The Pt and I atoms were found with standard Patterson methods (SHELXS 86^{40d}), the remaining non-hydrogen atoms from subsequent Fourier difference syntheses. Refinement on *F* was carried out by full-matrix least-squares techniques. Hydrogen atoms were introduced in calculated positions (C–H 0.98 Å) and included in the refinement riding on their carrier atoms. The Cl(2) atom of the dichloromethane solvent molecule is disordered over two sites [site occupancy factor (s.o.f.) = 0.88(1) and 0.12(1), respectively]. The Cl atom with s.o.f. = 0.12(1) was included in the refinement with an isotropic thermal parameter. All remaining non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined with one common isotropic thermal parameter [*U* = 0.061(5) Å²]. Weights were introduced in the final refinement cycles; convergence was reached at *R* = 0.032. Residual densities in the final difference Fourier synthesis were located within 1 Å of Pt

and are therefore interpreted as residual absorption artefacts. Neutral atom scattering factors were taken from ref. 40e and corrected for anomalous dispersion.^{40f} All calculations were performed with SHELX 76^{40g} and the EUCLID package^{40h} (geometrical calculations and illustrations) on a MicroVAX-II computer. Crystal data and numerical details of the structure determination are given in Table 8.

Structure determination of cis,cis-[PtBr₂(dman)₂] **5e**.—A suitable yellow, plate-shaped crystal was mounted in a Lindemann-glass capillary to prevent loss of dichloromethane solvent and was transferred to an Enraf-Nonius CAD-4 diffractometer for data collection. Unit-cell parameters were determined from a least-squares treatment of the setting angles of 12 SET4 reflections with 8.2 < θ < 10.8°. Reflection profiles were relatively broad, indicating the rather poor quality of the crystals. Data were collected at optimum ψ values, minimizing Δω following the *A*-vector method.⁴⁰ⁱ The unit-cell parameters were checked for the presence of higher lattice symmetry.^{40a} Data were corrected for Lorentz polarization, for a small linear decay (<0.5%) of the intensities during the 124 h of X-ray exposure time and for absorption (Gaussian integration, grid 10 × 10 × 8). Standard deviations obtained by counting statistics were increased according to an analysis of the excess variance of the reference reflection: σ²(*I*) = σ²_{cs}(*I*) + (0.004*I*)².^{40c} The Pt and Br atoms were found with standard Patterson methods (SHELXS 86^{40d}), the remaining non-hydrogen atoms from subsequent Fourier difference syntheses. One of the Cl atoms of the dichloromethane solvent molecule was found to be disordered over three sites. Refinement on *F* was carried out by full-matrix least-squares techniques. Hydrogen atoms were introduced in calculated positions (C–H 0.98 Å) and included in the refinement riding on their carrier atoms. The solvent molecule was refined with bond restraints. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined with one common isotropic thermal parameter [*U* = 0.06(2) Å²]. Weights were introduced in the final refinement cycles; convergence was reached at *R* = 0.083. Residual densities in the final Fourier difference synthesis were located within 1 Å from Pt and are therefore interpreted as absorption artefacts. For neutral atom scattering factors, calculations and crystal data see complex **5c**.

Additional material available for both structures comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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