Oxidative addition - reductive elimination reactions of mono- and bis(aryl)platinum(II) complexes with two amino ligands in fixed trans positions. X-ray crystal structures of (2,6-bis[[dimethylamino]methyl]phenyl)(4-tolyl)platinum(IV) diiodide and (2,6-bis[[dimethylamino]methyl]phenyl)platinum(IV) trichloride

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Oxidative-Addition–Reductive-Elimination Reactions of Mono- and Bis(aryl)platinum(II) Complexes with Two Amino Ligands in Fixed Trans Positions. X-ray Crystal Structures of (2,6-Bis[(dimethylamino)methyl]phenyl)(4-tolyl)platinum(IV) Diiodide and (2,6-Bis[(dimethylamino)methyl]phenyl)platinum(IV) Trichloride

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The mono- and bis(aryl)platinum(II) complexes $[PtX(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (X = halide) and $[PtR(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (R = phenyl, 4-tolyl) react with Cl_2 and Br_2 or $CuCl_2$ to yield the mono- and bis(aryl)platinum(IV) products $[PtX_3(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (**2**) and $[PtRX_2(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (**5**), respectively. The structural features of two representative compounds of **2** and **5** were studied by X-ray crystal structure determinations of **2a** (X = Cl) and of **5d** (R = 4-tolyl, X = I). Crystals of **2a** are monoclinic, space group *Pn*, with $a = 13.759$ (16), $b = 7.950$ (2), $c = 7.244$ (2) Å, $\beta = 103.20$ (4)°, and $Z = 2$. A total of 2050 reflections have been used in the refinement, resulting in a final $R = 0.039$. The platinum center has a distorted octahedral geometry having a mer coordination of the $(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$ (abbreviated NCN) ligand via C(ipso) (1.96 (3) Å) and the two mutually trans positioned NMe_2 groups. There is a significant difference in Pt–Cl bond lengths between the meridial Cl atom (2.446 (7) Å) and the axial Cl atoms (2.324 (4) and 2.329 (5) Å). Crystals of **5d** are hexagonal, space group $R\bar{3}$, with $a = 37.463$ (7), $c = 7.908$ (3) Å, and $Z = 18$. A total of 755 reflections have been used in the refinement, resulting in a final $R = 0.024$. The structure of **5d** shows a mer coordination of the NCN ligand (Pt–C(ipso) 2.00 (2) Å), one axial iodide (Pt–I 2.811 (3) Å), and one meridial iodide (Pt–I 2.813 (3) Å). The remaining axial position is occupied by a 4-tolyl group (Pt–C(ipso) 2.12 (3) Å). The cis orientation of the aryl groups (C(ipso)–Pt–C′(ipso) 94 (1)°) is noteworthy and is the result of the fixed attachment of the NCN ligand to the Pt(IV) center. The NMe_2 groupings of the latter ligand hinder rotation of the 4-tolyl group along the Pt–C(ipso) axis (^1H NMR δ H(2) 6.01 and δ H(6) 8.94). On the basis of extensive product formation studies it is concluded that the oxidative addition reactions of dihalogens to square-planar platinum(II) complexes proceed via the S_N2 type mechanism, usually leading to *trans*-X_2 arrangements in the product. When steric factors prevent this configuration or when the *trans*-X_2 product is thermodynamically unstable, *cis*-X_2 products are found. In the case of formation of **5d**, this reaction is a unique route for synthesizing the complex, as any attempt to prepare this compound by substitution of Br in $[PtBr_3(NCN)]$ by 4-tolyl in reactions with 4-tolyllithium failed.

Introduction

In recent years we have studied the reactivity of organoplatinum(II) complexes with the terdentate, monoanionic ligand $(2,6\text{-}\{Me_2NCH_2\}_2C_6H_3)$ (abbreviated NCN).[1] This NCN ligand system places two N donor atoms mutually trans across the platinum center and restricts therefore the number of available coordination sites at the platinum exclusively to those in a plane perpendicular to that of the ligand; see Figure 1. Consequently, in the square-planar organoplatinum(II) complexes the fourth ligand is always trans to the C(ipso) donor site. We have found that these well-defined organoplatinum complexes are extremely useful for the study of the intimate steps in transmetalation and oxidative addition–reductive elimination reaction sequences. It has been established now that otherwise unstable or even transient stages in these processes are stabilized by the NCN ligand and can be isolated. An example is the isolation of stable square-pyramidal Pt(II)–Hg(II) intermediates from reactions of [PtBr(NCN)] with mercury(II) formamidino, triazenido, and carboxylato compounds, which provides evidence that dinuclear Pt–Hg compounds are key intermediates in reactions between neutral organoplatinum(II) complexes and mercury salts.[2-4]

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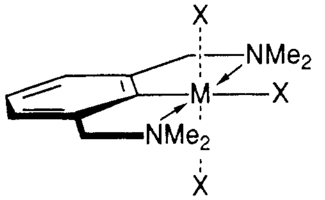

Figure 1. Schematic structure of $[MX(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ showing the available coordination sites X.

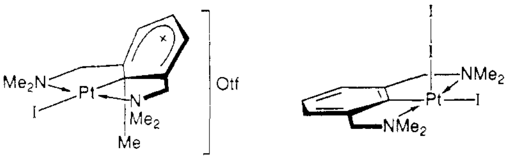

Figure 2. Left: schematic structure of $[PtI(MeC_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]Otf$. Right: schematic structure of $[PtI(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)(\eta^1\text{-}I_2)]$.

As a result of the three hard donor atoms of the NCN monoanion, the platinum(II) center in these [PtX(NCN)] (X = halide) has an enhanced nucleophilic character as compared with the platinum(II) complexes normally used in this type of reactions. To study this aspect in greater detail we set out a study of reactions of both cationic and neutral platinum complexes containing NCN with electrophilic reagents. We already reported reactions of ionic $[Pt(NCN)(H_2O)]Otf$ (Otf is $CF_3SO_3^-$) with methyl iodide. These reactions afforded, rather then the expected six-coordinated oxidative addition product, $[PtI(MeC_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]Otf$, in which the methyl group of the methyl iodide has become bonded to the C(ipso) atom of the aryl ring of NCN (see Figure 2, left). This stable complex can be considered as a frozen "intermediate" that mimicks the situation preceding the release of the newly formed C–C coupled product $2,6\text{-}(Me_2NCH_2)_2C_6H_3Me$ from the metal center in an oxidative addition–reductive elimination sequence taking place at this center. Interestingly, this process appeared to be reversible,[5] and for the first time the 1,2 shift of a methyl group at a platinum–C(ipso) bond could be studied in detail.[1e,6] We have further extended these studies by reacting neutral [PtY(NCN)] (Y = monoanionic ligand; halide or aryl) with reagents like X_2 and CuX_2 (X = Cl, Br; X = I only with I_2), which not only are good electrophiles, known to undergo one-electron-transfer reactions,[7] but also have often been shown to give rise to cleavage of transition metal–carbon σ bonds in organometallic compounds.[8] Recently we found that the reaction of [PtI(NCN)] with I_2 stopped at the stage of the charge-transfer complex $[PtI(NCN)(\eta^1\text{-}I_2)]$ with the diiodine molecule η^1-bonded to Pt(II),[9] and not at the oxidative addition product. This novel complex supports the view that an early step in the oxidative addition reactions of dihalogens to square-planar Pt(II) complexes is the formation of a 1:1 adduct and confirms earlier predictions (see Figure 2, right).[10]

In this paper the synthesis of several mono- and bis(aryl)platinum(IV) complexes will be reported using electrophiles X_2 and CuX_2 without formation of Pt–C bond cleavage reaction products or halogenation of the aryl rings.[11] The structures of *mer*-$[PtCl_3(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ and *cis*-$[Pt(4\text{-tolyl})I_2(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ will be discussed as well as substitution reactions of these platinum(IV) complexes with silver(I) salts and organolithium reagents.

Experimental Section

General Procedures. The proton NMR spectra were recorded on Varian T-60, Bruker AC-100, and Bruker WM-250 spectrometers. Infrared spectra were recorded on Perkin-Elmer 283 and Nicolet 7199 B FT-IR instruments. The Raman spectra were recorded on a Jobin Yvon HG 2S Raman spectrophotometer and excited by the lines of a Spectra-Physics Model 171 argon ion laser. Elemental analyses were carried out at the Institute for Applied Chemistry, TNO, Zeist, the Netherlands. The greater part of the reagents were obtained commercially and used without further purification. The preparation and structural characterization of the platinum(II) complexes $[PtY(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (Y = monoanionic ligand; halide or aryl) are described elsewhere.[12]

A. Reactions with Dihalogens. Synthesis of $[PtCl_3(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, 2a. A stream of dichlorine was bubbled through a solution of $[PtCl(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (0.1 mmol) in benzene (10 mL) during 6 min. During this time the solution developed a yellow color. After the solution was stirred for 1 h, the benzene was evaporated. The resulting orange residue was washed with pentane and dried in vacuo. The yield of **2a** was quantitative. Anal. Calcd for $C_{12}H_{19}N_2PtCl_3$: C, 29.21; H, 3.88; N, 5.68; Cl, 21.55. Found: C, 29.19; H, 3.77; N, 5.59; Cl, 21.17. Pt–Cl: IR 333, 330, and 260 cm^{-1}; res Raman 330 cm^{-1}.

Synthesis of $[PtBr_3(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, 2b. $[PtBr(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (1 mmol) was suspended in benzene (8 mL). To this suspension was added dropwise an excess of dibromine (1.3 mmol). After the resultant mixture was stirred for 2 h, the red precipitate was filtered off and washed with diethyl ether (2 × 6 mL) and pentane (2 × 6 mL) and then dried in vacuo. The yield of **2b** was 92%. Anal. Calcd for $C_{12}H_{19}N_2PtBr_3$: C, 23.01; H, 3.05; N, 4.47; Br, 38.31. Found: C, 22.78; H, 3.42; N, 4.00; Br, 38.78. Pt–Br: IR 214, 192, 177, and 165 cm^{-1}; res Raman 204 cm^{-1}.

Synthesis of *cis*-$[Pt(C_6H_5)I_2(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, 5a. A dark violet solution of diiodine (0.29 mmol) in benzene (3 mL) was added dropwise to a stirred solution of $[Pt(C_6H_5)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (0.3 mmol) in benzene (5 mL). After 20 min the orange solution was concentrated to 4 mL. Addition of pentane (10 mL) afforded orange crystals of **5a**, which were washed with pentane (2 × 5 mL), yield 75%. Anal. Calcd for $C_{18}H_{24}N_2PtI_2$: C, 30.14; H, 3.37; N, 3.91. Found: C, 29.96, H, 3.31; N, 3.78.

Synthesis of *cis*-$[Pt(4\text{-tolyl})Br_2(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, 5c. To a stirred suspension of $[Pt(4\text{-tolyl})(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (0.3 mmol) in 10 mL of diethyl ether was added dropwise 4.7 mL of 0.06 M dibromine in toluene. After the yellow mixture was stirred for 2 h, the toluene and diethyl ether were evaporated in vacuo, leaving a red residue, which was washed with pentane (3 × 10 mL) and extracted with CH_2Cl_2 (10 mL). Upon addition of pentane to the CH_2Cl_2 extract, a yellow product precipitated, which was washed with pentane and dried in vacuo. The yield of **5c** was 50%. Anal. Calcd for $C_{19}H_{26}N_2PtBr_2$: C, 35.81; H, 4.11; N, 4.23; Br, 25.07. Found: C, 35.58; H, 4.14; N, 4.23; Br, 25.00.

Synthesis of *cis*-$[Pt(4\text{-tolyl})I_2(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, 5d. A dark violet solution of diiodine (0.29 mmol) in benzene (10 mL)

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[5] This reversible process was found for the complex $[PtX(MeC_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]^+$ (X = Cl, Br, I), which afforded in acetone-/H_2O $[Pt(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)(H_2O)]^+$ and MeX.

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was added dropwise to a stirred solution of $[Pt(4\text{-tolyl})(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (0.3 mmol) in benzene (5 mL). After 20 min the orange solution was concentrated to 4 mL. Addition of pentane (15 mL) afforded a yellow precipitate, which was filtered off and washed with pentane (5 mL). The yellow product was recrystallized from CH_2Cl_2/pentane, yielding 61% of orange crystals of **5d**. Anal. Calcd for $C_{19}H_{26}N_2PtI_2$: C, 31.20; H, 3.58; N, 3.83. Found: C, 31.20; H, 3.63; N, 3.76.

Reaction of Diiodine with $[Pt(2\text{-tolyl})(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, 4b. A dark violet solution of diiodine (0.29 mmol) in benzene (10 mL) was added dropwise to a stirred solution of $[Pt(2\text{-tolyl})(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (0.3 mmol) in benzene (5 mL). The mixture was stirred for 20 min and worked up as described above for **5d**. The ^1H NMR spectrum (250 MHz) of the product (in CD_2Cl_2) showed the patterns of $[PtI(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ and $[PtI(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)(\eta^1\text{-}I_2)]$[10] and presumably 2-tolyl iodide (checked by comparison with ^1H NMR spectra of authentic samples). Low-temperature ^1H NMR spectra (−70 °C, $CDCl_3$) of a freshly prepared mixture of diiodine and $[Pt(2\text{-tolyl})(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ showed a mixture of patterns, of which one could be assigned as the ^1H NMR spectrum of *cis*-$[Pt(2\text{-tolyl})I_2(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, **5b**, by comparison with the pattern of **5d**.

Reaction of Dibromine with $[Pt(O_2CMe)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, 1d. To a solution of $[Pt(O_2CMe)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (0.2 mmol) in benzene (5 mL) was added dropwise a solution of dibromine (0.2 mmol) in benzene (10 mL). After stirring for 2.5 h, the orange solution was concentrated to 5 mL, upon which an orange solid precipitated. This product was filtered off, washed with hexane (2 × 10 mL), and dried in vacuo. A ^1H NMR spectrum of this solid in $CDCl_3$ showed that one of the products was $[PtBr_3(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (**2b**), while a second pattern could be tentatively assigned as that of *trans*-$[Pt(O_2CMe)Br_2(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, **3a**.

B. Reactions with Copper(II) Salts. Reaction of $Cu^{II}Cl_2$ with $[PtCl(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, 1a. $[PtCl(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (0.2 mmol) was dissolved in dichloromethane (5 mL), and this solution was added dropwise to a stirred solution of $CuCl_2{\cdot}2H_2O$ (0.4 mmol) in ethanol (5 mL). The color of the copper solution changed from green to orange. The mixture was stirred for about 60 min. The light green precipitate (CuCl) was filtered off, followed by concentration of the filtrate to 2 mL by evaporation of the solvent in vacuo. Addition of pentane (10 mL) gave a light orange product, which was filtered off, washed with diethyl ether (5 mL), and dried in vacuo, yielding 50% of isolated $[PtCl_3(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, **2a**.

Reaction of $Cu^{II}Br_2$ with $[PtBr(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, 1b. $[PtBr(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (0.2 mmol) was dissolved in dichloromethane (5 mL), and this solution was added dropwise to a stirred suspension of $CuBr_2$ (0.4 mmol) in acetone (5 mL), resulting in a color change of the copper suspension from dark green to orange. The mixture was stirred for about 30 min, after which the white precipitate (CuBr) was filtered off. The filtrate was concentrated to 2 mL by evaporation of the solvent in vacuo. Addition of pentane (10 mL) gave an orange product, which was filtered off, washed with pentane (5 mL), and dried in vacuo, yielding 80% of $[PtBr_3(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, **2b**.

Reaction of $Cu^{II}Cl_2$ with $[Pt(O_2CMe)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, 1d. A solution of $[Pt(O_2CMe)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (0.25 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a suspension of $CuCl_2{\cdot}2H_2O$ (2 equiv) in CH_2Cl_2. The suspension was stirred for 20 min, the resulting precipitate was filtered off, and the filtrate was concentrated in vacuo to 2 mL. Addition of pentane (5 mL) afforded an orange precipitate. This was filtered off and dried in vacuo. The product was identified by ^1H NMR as a mixture of compounds, consisting mainly of $[PtCl_3(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (**2a**) and $[PtCl(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (**1a**; ratio 2:1), yield 0.091 g.

Reaction of $CuCl_2$ with $[Pt((4\text{-tolyl})NC(H)N(4\text{-tolyl}))(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, 1e. To a stirred solution of $[Pt((4\text{-tolyl})NC(H)N(4\text{-tolyl}))(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (0.2 mmol) in acetone (5 mL) was added $CuCl_2{\cdot}2H_2O$ (0.2 mmol). The resulting red solution was allowed to stand for 3 days, during which time orange crystals were formed. These were collected on a sintered glass filter and separated from the green precipitate. The orange crystals were identified by ^1H NMR as **2a**, yield 25%.

Reaction of $CuCl_2$ with $[Pt(4\text{-tolyl})(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, 4c. To a solution of $[Pt(4\text{-tolyl})(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (0.2 mmol) in CH_2Cl_2 (5 mL) was added dropwise a solution of $CuCl_2{\cdot}2H_2O$ (2 equiv) in ethanol. The resulting suspension was stirred for 30 min, the solution was filtered, and the filtrate was concentrated in vacuo to 2 mL. Addition of pentane (5 mL) afforded an orange precipitate. This was filtered off and dried in vacuo. The product was identified by ^1H NMR as a mixture of **2a** and **1a**.

C. Substitution Reactions. Synthesis of $[Pt(O_2CMe)_2Br(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, 3b. Silver(I) acetate (0.91 mmol) and $[PtBr_3(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (0.3 mmol) were mixed and stirred in CH_2Cl_2 (15 mL) for 2 h. The resulting gray precipitate of AgBr was filtered off, and the filtrate concentrated to 3 mL by evaporation of the solvent in vacuo. Addition of pentane (8 mL) gave an orange solid of $[Pt(O_2CMe)_2Br(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, which was filtered off, washed with pentane (5 mL), and dried in vacuo. Recrystallization from CH_2Cl_2/pentane under nitrogen atmosphere gave orange crystals. The yield of **3b** was 57%. Anal. Calcd for $C_{16}H_{25}N_2O_4PtBr$: C, 32.88; H, 4.31; N, 4.79. Found: C, 32.96; H, 4.38; N, 4.73.

Reaction of 4-Tolyllithium and $[PtBr_3(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, 2b. $[PtBr_3(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (0.94 mmol) was suspended in diethyl ether (5 mL) and allowed to react with 1 equiv of 4-tolyllithium (in 4 mL of diethyl ether). After 4 h the solvent was evaporated in vacuo. The resulting orange solid was extracted with CH_2Cl_2, and the extract filtered over Celite. Concentration of the filtrate to 2 mL followed by addition of pentane afforded a red–brown product, which was identified by ^1H NMR as a mixture of $[PtBr_3(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ and $[PtBr(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$. Reaction of $[PtBr_3(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ with an excess of 4-tolyllithium (3 equiv) afforded also a small amount of $[Pt(4\text{-tolyl})(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (less than 5%, checked by ^1H NMR).

Data Collection and Structure Determination of $[PtCl_3(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, 2a. Crystals of **2a** are monoclinic. The systematic absences, $h0l$ for $h + l$ odd, are consistent with the space groups $P2/n$ and Pn. The choice of Pn was suggested by the number of molecule in the unit cell ($Z = 2$) and was justified by the structure determination. The cell constants are $a = 13.759$ (16), $b = 7.950$ (2), $c = 7.244$ (2) Å, $\beta = 103.20$ (4)°, $V = 771.4$ (10) $Å^3$, $Z = 2$, D(calcd) = 2.12 g/cm^3, and $F(000) = 468$ electrons. From the total of 2232 reflections, measured on an Enraf-Nonius CAD 4 diffractometer using graphite-monochromated Mo Kα radiation, 182 were less than $2{,}5\sigma(I)$ and were treated as unobserved. For details see Table I. The position of Pt was derived from a Patterson synthesis. The other non-hydrogen atoms were found from a subsequent ΔF synthesis. The hydrogen atoms were poorly indicated in a ΔF Fourier transform and were kept fixed at their calculated positions. Refinement proceeded by means of anisotropic block-diagonal least-squares calculations, using a weighting scheme $w = (10 + F_o + 0.005F_o^2)^{-1}$. An empirical absorption correction[13] has been applied and the anomalous dispersion of Pt and Cl has been taken into account. The final R value was 0.027 ($R_w = 0.037$). The programs used were from XRAY76.[14]

Data Collection and Structure Determination of $[Pt(4\text{-tolyl})I_2(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, 5d. Crystals of **5d** are hexagonal. The systematic absences ($-h + k + l \neq 3n$) and the Laue symmetry $\bar{3}$ are consistent with the space groups $R\bar{3}$ and $R3$. The number of molecules in the unit cell ($Z = 18$) suggested $R\bar{3}$, the choice of which was confirmed by the structure determination. The cell constants are $a = 37.463$ (7), $c = 7.908$ (3) Å, $V = 9612$ (7) $Å^3$, D(calcd) = 2.27 g/cm^3, and $F(000) = 6084$ electrons. A total of 4360 reflections were measured on an Enraf-Nonius CAD 4 diffractometer using graphite-monochromated Mo Kα radiation, from which 1450 unique data were derived; 695 were less than $2.5\sigma(I)$ and were treated as unobserved. For details see Table I. The positions of Pt and I were derived from a Patterson synthesis. The other non-hydrogen atoms were found in a subsequent ΔF synthesis. The hydrogen atoms were not indicated in ΔF syntheses and were left out of consideration. Refinement

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[13] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

[14] Stewart, J. M. 1976, Editor; The X-Ray System, Tecn. Rep. TR. 466; Computer Science Center, University of Maryland, College Park, MD.

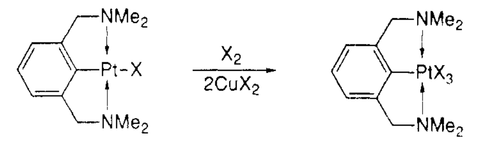
Table I. Crystal Data and Details of the Structure Determinations of [PtCl$_3$(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6)], 2a, and [Pt(4-tolyl)I$_2$(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6)], 5d

	2a	**5d**
	Crystal Data	
formula	$C_{12}H_{19}N_2PtCl_3$	$C_{19}H_{26}N_2PtI_2$
mol wt	492.73	731.39
space group	*Pn*	$R\bar{3}$
cryst syst	monoclinic	hexagonal
a, Å	13.759 (16)	37.463 (7)
b, Å	7.950 (2)	
c, Å	7.244 (2)	7.908 (3)
β	103.20 (4)	
V, Å^3	771.4 (10)	9612 (7)
Z	2	18
D(calcd), g/cm^3	2.12	2.27
F(000), electrons	468	6084
μ(Mo Kα), cm^{-1}	97.0	95.1
cryst vol, mm^3	0.004	0.0012
abs corr, max/min	1.229/0.681	1.109/0.900
	Data Collection	
θ min, max, deg	1.1, 30	1.1, 18
radn, Å	Mo Kα, λ = 0.71069	Mo Kα, λ = 0.71069
ref reflns	604, 533	491
total reflns data	2232	4360
total unique reflns	2232	1450
obsd data ($I > 2.5\sigma(I)$)	2050	755
	Refinement	
no. of refined parameters	163	217
weighting scheme	$(10 + F_o + 0.005F_o^2)^{-1}$	$(3.7 + F_o + 0.058F_o^2)^{-1}$
final R_F, R_{wF}	0.027, 0.037	0.024, 0.034
max shift/error	0.45	0.39
res density, max/min	1.1/−1.4	0.4/−0.4

proceeded by means of anisotropic block-diagonal least-squares calculations employing a weighting scheme $w = (3.7 + F_o + 0.058F_o^2)^{-1}$. An empirical absorption correction[13] has been applied, and the anomalous dispersion of Pt and I has been taken into account. The final *R* value was 0.024 (R_w = 0.034). The programs used were from XRAY76.[14] Crystal data and details of the structure determination are collected in Table I.

Results

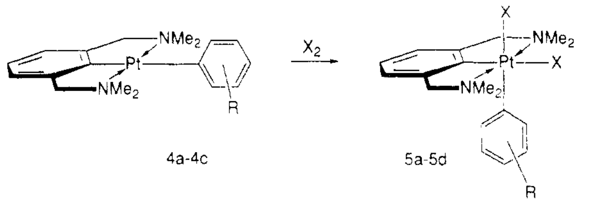
The organoplatinum(II) complexes [PtX(NCN)] (NCN = (C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6)) (X = Cl (**1a**), X = Br (**1b**)) react in benzene with dihalogens to give the organoplatinum(IV) complexes [PtX$_3$(NCN)] (X = Cl (**2a**), Br (**2b**)) as summarized in eq 1. Products have been identified by elemental analyses, IR (see Experimental Section), and ^{1}H NMR spectroscopy (Table II). Both Cl$_2$ and Br$_2$ could be used in excess without any effect on the yield or purity of the respective trihaloplatinum(IV) complexes. The formation of the air-stable products **2a** (orange) and **2b** (red) was nearly quantitative, and products originating from Pt–C bond cleavage were not formed. The two products are slightly soluble in dichloromethane, chloroform, benzene, and acetone.



1a-b 2a-b (1)

Complexes **2a** and **2b** are also obtainable from the ligand-transfer oxidation reaction of **1a** and **1b** with Cu^{II}Cl$_2$ and Cu^{II}Br$_2$, respectively, in a 1/2 molar ratio (see eq 1). Though this latter reaction also afforded the organoplatinum(IV) complexes the yields appeared to be lower (50% for **2a** and 80% for **2b**) than in the reactions with the corresponding dihalogens (100 and 92%, respectively).

The reactions of the bis(aryl)platinum(II) complexes *trans*-[PtR(NCN)][12] (R = phenyl (**4a**), 2-tolyl (**4b**), 4-tolyl (**4c**)) with dibromine or diiodine gave rise to the formation of the stable bis(aryl)platinum(IV) complexes *cis*-[PtRX$_2$(NCN)] (R = phenyl, X = I (**5a**); R = 4-tolyl, X = Br (**5c**); R = 4-tolyl, X = I (**5d**)) (see eq 2). The orange crystalline products are air-stable and soluble in dichloromethane, chloroform, benzene, and acetone. The complexes were identified and characterized by elemental analyses and ^{1}H NMR spectroscopy (Table II). Attempts to obtain the analogous complex with R = 2-tolyl, **5b**, failed, though the orange color of the reaction mixture when adding dihalogen dropwise to **4b** pointed to an initially formed organoplatinum(IV) complex. A ^{1}H NMR spectrum recorded at low temperature directly after addition of a less than equivalent amount of diiodine to a solution of **4b** in a NMR tube showed a mixture of patterns, of which one could be identified as the pattern belonging to *cis*-[Pt(2-tolyl)I$_2$(NCN)] (see Table II). Using an excess of dihalogen did not lead to Pt–C bond cleavage in any of the bis(aryl)platinum(IV) dihalide complexes **5a**, **5c**, and **5d**, in contrast to observations made in the reactions of [Pt(C$_6$F$_5$)$_2$L$_2$] (L = 1,10-phenanthroline) with Cl$_2$ or Br$_2$, which gave complexes [Pt^{IV}X$_2$(C$_6$F$_5$)$_2$L$_2$] but which was followed by a subsequent reaction with dihalogen to give as the product [PtX$_4$L$_2$].[15] It is noteworthy that



4a-4c 5a-5d (2)

Table II. ^{1}H NMR Data of the Organoplatinum(IV) Complexes 2a,b, 3a,b, and 5a–d[a,b]

	(NCN) ligand			R group					
compound	C$_6$H$_3$	CH$_2$	NCH$_3$	H(6)	H(5)	H(4)	H(3)	H(2)	CH$_3$
[PtCl$_3$(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6)], **2a**	7.0	4.36[c] (30)	3.02[c] (29)						
[PtBr$_3$(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6)], **2b**	7.0	4.51[c] (32)	3.30[c] (32)						
[Pt(O$_2$CMe)Br$_2$(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6)], **3a**	7.0	4.34 (*e*)	2.94 (24)						2.01
[Pt(O$_2$CMe)$_2$Br(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6)], **3b**	6.99, 6.92	4.45 (28), 4.12[d] (28)	3.21 (30), 2.87 (23)						2.17, 1.96
[Pt(C$_6$H$_5$)I$_2$(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6)], **5a**	7.20, 6.98	4.60 (30), 4.09[d] (30)	3.78 (31), 2.38 (43)	9.11 (40)	6.94	*f*	*f*	6.15 (41)	
[Pt(2-tolyl)I$_2$(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6)], **5b**	*g*	4.68, 4.18[d] (35)	3.86 (31), 2.39 (39)	9.46 (37)	*g*		*g*	*g*	2.46
[Pt(4-tolyl)Br$_2$(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6)], **5c**	7.21, 7.00	4.48 (30), 4.02[d] (31)	3.46 (30), 2.36 (42)	8.90 (35)	6.85		6.55	6.10 (42)	2.22
[Pt(4-tolyl)I$_2$(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6)], **5d**	7.19, 6.98	4.58 (30), 4.09[d] (31)	3.77 (30), 2.39 (43)	8.94 (37)	6.83		6.55	6.01 (38)	2.33

[a] Recorded in CDCl$_3$; chemical shifts (ppm) relative to TMS; $^3J(^{195}Pt,^1H)$ (hertz) in parentheses. [b] For **3a,b** and **5a,c,d** the protons of C$_6$H$_3$ occur as an AB$_2$ multiplet, $^3J(^1H,^1H)$ = 8 Hz. [c] Enantiotopic protons or methyl groups. [d] Diastereotopic benzylic protons, $^2J(^1H,^1H)$ = 13 Hz. [e] $^3J(^{195}Pt,^1H)$ not resolved. [f] Multiplet of H(3) and H(4) centered at 6.73 ppm. [g] This part of the spectrum was not resolved.

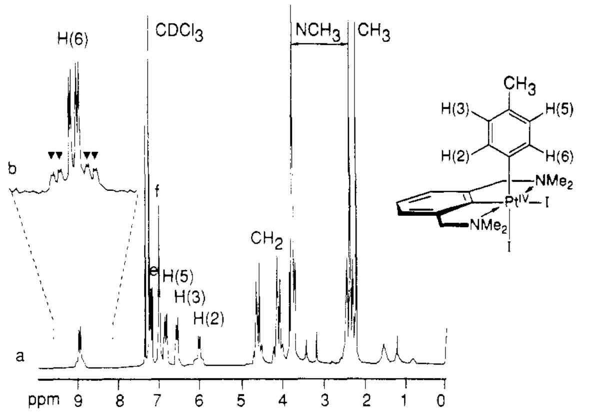


Figure 3. (a) ^{1}H NMR spectrum (250 MHz) of *cis*-[Pt(4-tolyl)$I_2(C_6H_3\{CH_2NMe_2\}_2$-2,6)], **5d**, in $CDCl_3$. (b) Detail of the spectrum showing $J(^1H,^1H)$ and $^3J(^{195}Pt,^1H)$.

heating pure **5c** or **5d** in $CHCl_3$ for several hours did not lead to Pt–C cleavage reaction products either.

The reaction of **4c** with $CuCl_2$ resulted in the formation of a mixture of [PtCl(NCN)] (**1a**) and [$PtCl_3$(NCN)] (**2a**), which were identified by their respective ^{1}H NMR patterns.

The reaction of [$PtBr_3$(NCN)] (**2b**) with 1 equiv of 4-tolyllithium was expected to afford substitution of the bromine atom trans to C(ipso). Instead a mixture of products was isolated that could not be separated. The mixture was identified by ^{1}H NMR spectroscopy as [$PtBr_3$(NCN)], [PtBr(NCN)], and in minor amounts, some unknown products. Excess of 4-tolyllithium (more than 2 mol equiv) afforded also [Pt^{II}(4-tolyl)(NCN)], **4c**.

[$Pt(O_2CMe)_2$Br(NCN)] (**3b**) was obtained via a substitution reaction of [$PtBr_3$(NCN)] (**2b**) with 2 equiv of silver(I) acetate. Reaction of **2b** with only 1 equiv of silver(I) acetate gave rise to formation of a mixture of unreacted platinum(IV) tribromide **2b** and the platinum(IV) bis(acetato) bromide compound **3b**. It is important to note that an excess of silver(I) acetate did not lead to the displacement of all three bromide ligands. Thus the reaction stops at the stage of the platinum(IV) bis(acetato) bromide complex.

Reaction of [$Pt(O_2CMe)$(NCN)] with 1 equiv of dibromine in benzene led to a mixture of compounds that could not be separated. The ^{1}H NMR spectrum showed the main products to be [$PtBr_3$(NCN)] (**2b**) and presumably [$Pt(O_2CMe)Br_2$(NCN)] (**3a**); other products could not be identified.

Oxidation of the Pt(II) center and cleavage of the Y group were found in reactions of [PtY(NCN)] (Y = acetate or bis(4-tolyl)formamidine) with $CuCl_2$. Though **2a** and CuCl were isolated, the expected products Cu(I) acetate and Cu(I) bis(4-tolyl)formamidine, respectively, were not found.

Spectroscopic Measurements. Evidence for rigid donor atom arrangement in the coordination sphere of the platinum(IV) center in **2a,b** comes from the ^{1}H NMR patterns of the CH_2 and NMe_2 groups (see Table II). The spectra show singlets for the CH_2 and CH_3 protons with sharp ^{195}Pt ($I = {}^1/_2$, 34% abundance) satellites of magnitude 29–32 Hz. These values are much lower than those observed for the platinum(II) complexes **1a,b**, which fall in the range 38–40 Hz.[16] Both ranges for the $^3J(^{195}Pt,^1H)$ values are characteristic for trans positioned N atoms bonded to Pt(IV) and Pt(II), respectively, and moreover establish that the platinum atom is coordinated in **2a** and **2b** to both CH_2NMe_2 side chains. The fact that the CH_2 protons and the NMe_2 groups in the ^{1}H NMR spectra of **2a** and **2b** are singlets, which appear in narrow ranges of 4.36–4.51 and 3.02–3.30 ppm, respectively, establishes the *mer*-[PtX_3] arrangement of the halide ligands in **2a** and **2b**.[17]

The ^{1}H NMR spectra of **5a,c,d** in $CDCl_3$ show a complex pattern of chemical shifts and ^{195}Pt–^{1}H couplings. Assignment of these patterns has been achieved by homodinuclear decoupling experiments. As an illustration the assignment of the proton NMR spectrum of *cis*-[Pt(4-tolyl)I_2(NCN)], **5d**, in terms of the proposed structure will be discussed.

The ^{1}H NMR spectrum (250 MHz) of the terdentate NCN ligand in **5d** (see Figure 3) shows for the aryl protons a typical AB_2 multiplet at 7.19 and 6.98 ppm with relative intensity ratio 1:2 and $^3J(^1H,^1H) = 8$ Hz. Furthermore, the spectrum shows inequivalent chemical shifts and magnetic couplings for the CH_2 protons and NMe_2 methyl groups, which establishes that the CH_2 protons and NMe_2 methyl groups are diastereotopic. This diastereotopicity of the CH_2 protons and the NMe_2 methyl groupings within the CH_2NMe_2 side chain indicates that different groups reside above and below the (NCN)Pt coordination plane, which thus excludes the *trans*-I_2 isomer as a possible structure for **5d**. The remaining part of the ^{1}H NMR spectrum shows signals due to the 4-tolyl groups: four separated multiplets at low field with proton–proton and platinum–proton couplings and a singlet at high field without couplings. The latter singlet, which was found at 2.33 ppm, has been assigned to the 4-methyl group. On the basis of the results of homodinuclear decoupling experiments the respective multiplets could be assigned to the respective aryl protons in the complex. Irradiation of the doublet at 8.94 ppm (H(6)) caused collapse of the doublet at 6.83 ppm (H(5)) to one peak while the irradiation of the doublet at 6.55 ppm (H(3)) resulted in collapse of the doublet at 6.01 ppm (H(2)) to one peak. On the basis of these results the system could be unambigously assigned as two AX patterns (AA′XX′, see ref 18) (H(5)-H(6) and H(2)H(3)) with a $^3J(^1H,^1H)$ of 9 and $^4J(^1H,^1H)$ of 2 Hz.

This well-resolved ^{1}H NMR pattern of the aromatic 4-tolyl protons points to a fixed orientation of the 4-tolyl ring and is in accordance with the structure found for **5d** in the solid, i.e., a geometry with its plane perpendicular to both the aryl plane of the terdentate ligand and the N–Pt–N axis; see Figure 5, right. The H(6) and H(2) absorptions show platinum satellites with $^3J(^{195}Pt,^1H)$ of 37 and 38 Hz, respectively, and therefore can be assigned as the protons ortho to the Pt–C bond. As a result of the fixed orientation one of the ortho protons of the 4-tolyl group, H(2), is held above the aryl ring of the terdentate ligand whereas the other proton is close to the iodide ligand. In fact, H(2) undergoes some influence of the π electrons of the aryl ring that account for extra shielding of this proton, resulting in an upfield shift to 6.01 ppm, while the anisotropy excerted by the iodide ligand results in a downfield shift of H(6) to 8.94 ppm.[18] This assign-

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[15] Uson, R.; Fornies, J.; Espinet, P. *J. Organomet. Chem.* **1976**, *116*, 353.

[16] The ratio of $^3J(^{195}Pt,^1H)$ values for [PtX(NCN)] and [PtX_3(NCN)] is 0.76; this ratio is typical; cf.: Ruddick, J. D.; Shaw, B. L. *J. Chem. Soc.* **1969**, 2801.

[17] van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L. *Inorg. Chem.* **1982**, *21*, 2014.

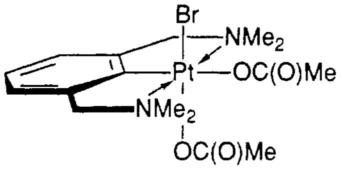

Figure 4. Schematic structure of *cis*-[Pt$(O_2CMe)_2$Br$(C_6H_3\{CH_2NMe_2\}_2$-2,6)], **3b**.

ment is tentative because comparison of δ(H(6)) and δ(H(2)) values in **5c** and **5d** show not only an expected change of δ(H(6)) on going from Br to I but also one for δ(H(2)) (in the opposite direction) which in both compounds is invariably near C(ipso); see Table II.[18b]

The proton NMR spectrum of [Pt$(O_2CMe)_2$Br(NCN)], **3b**, in $CDCl_3$ likewise shows an AB_2 multiplet (δ(A) = 6.92 (2 H) and δ(B) = 6.99 (1 H)) for the aryl protons of NCN. The CH_2 and NMe_2 protons show anisochronous chemical shifts and magnetic couplings (see Table II), which points to inequivalency of the space above and below the *mer*-[(NCN)Pt] plane. Moreover, the ^1H NMR data of the acetato groups show two inequivalent CH_3 groups at 2.17 and 1.96 ppm, therefore supporting a proposed structure for **3b** with a cis coordination of the two acetato groups; see Figure 4.

The Raman spectra of [PtX_3(NCN)], **2a**,**b**, show strong bands at 330 (Cl) and 204 (Br) cm^{-1}, respectively, which can be assigned as arising from the symmetric Pt–X stretching vibrations. For the trichloride compound, in the IR spectra three absorption bands due to the asymmetric and symmetric Pt–X stretching vibrations are observed. These data (viz. for **2a** 333, 330 and 260 cm^{-1} (IR), 330 cm^{-1} (Raman)) are consistent with a *mer*-PtX_3 unit and can be compared with the Pt–Cl stretching vibrations of 344, 325, and 281 cm^{-1} (IR) and 326 cm^{-1} (Raman) in *mer,cis*-[Pt$Cl_3(C_6F_5)(PEt_3)_2$].[19] The low value (260 cm^{-1}) of the stretching frequency of the Pt–Cl bond trans to the C(ipso) atom in **2a** points to a strong trans effect of the C(ipso) atom of the terdentate ligand.[20] In general high values for metal–chloride stretching frequencies have been found for mutually trans positioned chloride ligands, whereas low values have been found for chloride ligands trans to carbon ligands.

Molecular Geometries of [Pt$Cl_3(C_6H_3\{CH_2NMe_2\}_2$-2,6)] and [Pt(4-tolyl)$I_2(C_6H_3\{CH_2NMe_2\}_2$-2,6)]. The structures in the solid state of [Pt$Cl_3(C_6H_3\{CH_2NMe_2\}_2$-2,6)], **2a**, and of *cis*-[Pt(4-tolyl)$I_2(C_6H_3\{CH_2NMe_2\}_2$-2,6)], **5d**, have been established by single-crystal X-ray structure determinations, crystal data and details of which are summarized in Table I. In both structures there is one independent molecule. The molecular geometries of **2a** and **5d** along with the adopted numbering schemes are shown in Figure 5. Bond lengths and angles of the nonhydrogen atoms are given in Table III. Fractional atomic coordinates for **2a** and **5d** are listed in Table IV.

Both complexes show a Pt center with a distorted octahedral geometry having a mer coordination of the $(C_6H_3\{CH_2NMe_2\}_2$-2,6) ligand via C(ipso) and two mutually trans positioned NMe_2 groups. The principal distortion of the octahedral geometry in both compounds results from the N(1)–Pt–N(2) angle of 160.3 (5)° (**2a**) and 162.5 (8)° (**5d**), which is due to the intrinsically small N–Pt–C(1) bit angles of the two neighboring five-membered chelate rings.

Table III. Bond Distances (angstroms) and Bond Angles (degrees) of 2a and 5d

Bond Distances of **2a**

Pt–Cl1	2.446 (7)	C3–C4	1.391 (23)
Pt–Cl2	2.324 (4)	C4–C5	1.370 (24)
Pt–Cl3	2.329 (5)	C5–C6	1.399 (18)
Pt–C1	1.948 (12)	C6–C8	1.501 (19)
Pt–N1	2.152 (12)	C7–N1	1.528 (18)
Pt–N2	2.143 (9)	C8–N2	1.523 (16)
C1–C2	1.386 (16)	C9–N1	1.466 (16)
C1–C6	1.384 (16)	C10–N1	1.517 (20)
C2–C3	1.406 (20)	C11–N2	1.487 (14)
C2–C7	1.480 (17)	C12–N2	1.520 (18)

Bond Angles of **2a**

Cl1–Pt–Cl2	89.8 (2)	C2–C3–C4	118.8 (14)
Cl1–Pt–C13	89.9 (2)	C3–C4–C5	122.6 (13)
Cl1–Pt–C1	179.2 (4)	C4–C5–C6	119.9 (13)
Cl1–Pt–N1	99.0 (4)	C1–C6–C5	116.8 (12)
Cl1–Pt–N2	100.7 (3)	C1–C6–C8	115.7 (10)
C12–Pt–C13	179.2 (2)	C5–C6–C8	127.3 (12)
C12–Pt–C1	90.1 (4)	C2–C7–N1	107.9 (10)
Cl2–Pt–N1	93.5 (4)	C6–C8–N2	106.9 (10)
Cl2–Pt–N2	86.2 (3)	Pt–N1–C7	106.1 (7)
C13–Pt–C1	90.2 (3)	Pt–N1–C9	113.7 (9)
C13–Pt–N1	87.3 (3)	Pt–N1–C10	114.2 (9)
Cl3–Pt–N2	93.1 (3)	C7–N1–C9	108.0 (11)
C1–Pt–N1	80.2 (5)	C7–N1–C10	108.1 (11)
C1–Pt–N2	80.0 (4)	C9–N1–C10	106.4 (10)
N1–Pt–N2	160.3 (5)	Pt–N2–C8	106.9 (7)
Pt–C1–C2	117.4 (8)	Pt–N2–C11	114.4 (7)
Pt–C1–C6	117.8 (9)	Pt–N2–C12	114.4 (7)
C2–C1–C6	124.8 (11)	C8–N2–C11	106.8 (8)
C1–C2–C3	117.0 (11)	C8–N2–C12	108.3 (9)
C1–C2–C7	116.3 (10)	C11–N2–C12	105.7 (9)
C3–C2–C7	126.7 (12)		

Bond Distances of **5d**

Pt–I1	2.811 (3)	C6–C8	1.57 (4)
Pt–I2	2.813 (3)	C7–N1	1.56 (4)
Pt–C1	1.99 (2)	C8–N2	1.57 (3)
Pt–C13	2.15 (2)	C9–N1	1.52 (3)
Pt–N1	2.15 (2)	C10–N1	1.50 (3)
Pt–N2	2.21 (2)	C11–N2	1.54 (4)
C1–C2	1.34 (3)	C12–N2	1.54 (4)
C1–C6	1.38 (2)	C13–C14	1.39 (3)
C2–C3	1.45 (4)	C13–C18	1.36 (4)
C2–C7	1.54 (3)	C14–C15	1.41 (4)
C3–C4	1.38 (3)	C15–C16	1.38 (5)
C4–C5	1.40 (4)	C16–C17	1.43 (3)
C5–C6	1.42 (4)	C16–C19	1.56 (5)
C6–C11	1.40 (5)	C17–C18	1.45 (4)

Bond Angles of **5d**

I1–Pt–I2	84.27 (7)	C3–C2–C7	126 (2)
I1–Pt–C1	170.2 (7)	C2–C3–C4	120 (2)
I1–Pt–C13	95.6 (7)	C3–C4–C5	121 (3)
I1–Pt–N1	100.5 (6)	C4–C5–C6	116 (2)
I1–Pt–N2	97.0 (6)	C1–C5–C6	120 (2)
I2–Pt–C1	87.0 (7)	C1–C6–C8	118 (2)
I2–Pt–C13	178.4 (5)	C5–C6–C8	121 (2)
I2–Pt–N1	88.4 (5)	C2–C7–N1	107 (7)
I2–Pt–N2	94.6 (5)	C5–C8–N2	107 (2)
C1–Pt–C13	94.1 (9)	Pt–C13–C14	121 (2)
C1–Pt–N1	80.6 (8)	Pt–C13–C18	118 (1)
C1–Pt–N2	82.5 (8)	C14–C13–C18	120 (2)
C13–Pt–N1	90.1 (8)	C13–C14–C15	120 (3)
C13–Pt–N2	86.9 (7)	C14–C15–C16	119 (2)
N1–Pt–N2	162.5 (8)	C15–C16–C17	121 (3)
Pt–C1–C2	119 (1)	C15–C16–C19	121 (2)
Pt–C1–C6	117 (2)	C17–C16–C19	117 (3)
C2–C1–C6	124 (2)	C16–C17–C18	111 (2)
C1–C2–C13	116 (2)	C13–C18–C17	122 (2)
C1–C2–C7	115 (2)		

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[18] (a) Gunther, H. *NMR Spectroscopy*; Georg Thieme Verlag: Stuttgart, 1973. (b) In **5c** and **5d** the distance between H(2) and the arene C atoms (including C(ipso)) is a result of the balanced interactions of H(6) with the cis-halogen atom and H(2) with the arene ring atoms. Accordingly it seems plausible to expect that increase of the size of the halogen atom, i.e., replacement of Br in **5c** by I in **5d**, causes a tilting of the ring (C(ipso)–C(4) axis) in the direction of the arene and consequently a movement of H(2) in the direction of the electron cloud.

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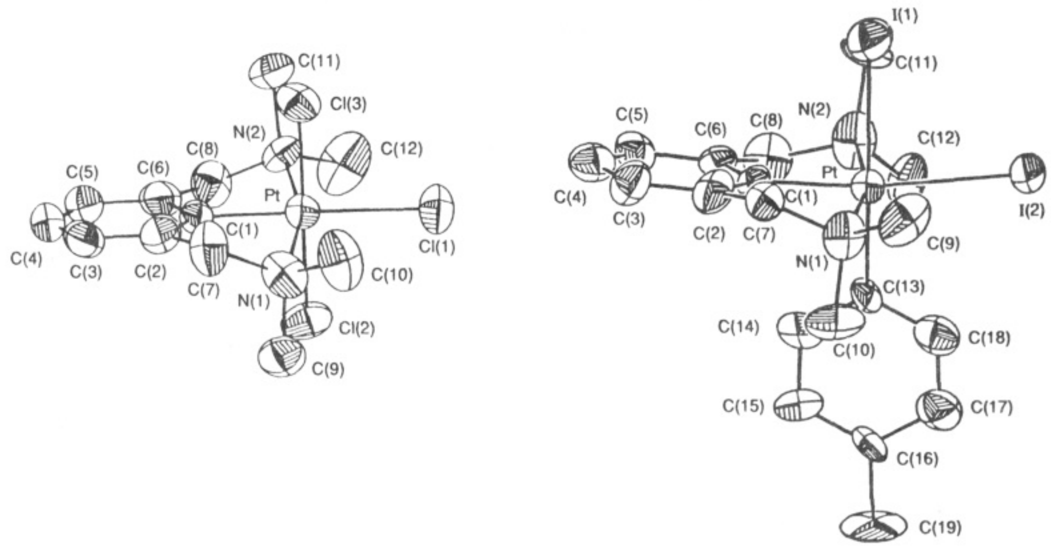

Figure 5. ORTEP drawings and adopted numbering schemes of (left) $[PtCl_3(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, **2a**, and (right) $[Pt(4\text{-tolyl})I_2(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, **5d**.

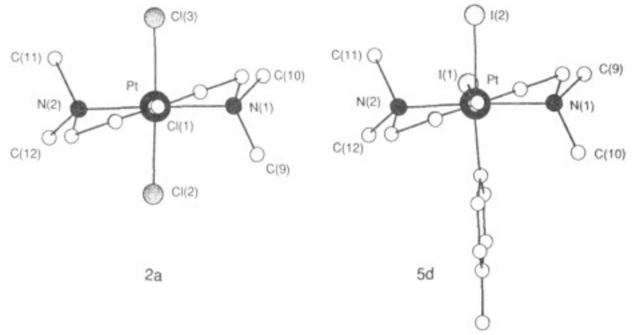

Figure 6. Projection along the Pt–C(ipso) axis showing the puckering of the five-membered cyclometalated rings for **2a** and **5d**.

The puckering in the cyclometalated ring that is observed in these and other octahedral or square-planar compounds with the terdentate NCN ligand, viz. $[Pd_2(NCN)_2(\mu\text{-Cl})]BF_4$ and $[Ni(O_2CH)(NCN)]$,[1b,21] is of the "2-fold axis" type of puckering (see Figure 6).[22]

A significant difference in **2a** is observed between the Pt–Cl bond lengths with the axial (2.324 (4) and 2.329 (5) Å) and meridial (2.446 (7) Å) Cl ligands. This difference reflects the strong trans influence of C(ipso) of NCN on the *trans*-Cl–Pt interaction, which results in weakening of this bond; see also the IR results.

The complex *cis*-$[Pt(4\text{-tolyl})I_2(NCN)]$ has one axial (Pt–I(1) 2.811 (3) Å) and one meridial iodide (Pt–I(2) 2.813 (3) Å). The remaining axial position is occupied by the 4-tolyl group. The two long Pt–I distances in **5d** are in agreement with the fact that both iodide ligands are now trans to the C(ipso) atoms of the terdentate ligand (cf. **2a**, vide supra) and of the 4-tolyl group, respectively. Previously reported values for Pt–I distances in bis- and tris(organo)platinum(IV) iodide complexes comprise 2.64 (2)–2.65 (1) Å for an I trans to an I (e.g., in $[PtMe_2I_2(\{Me_2pz\}_2CH_2)]$) and 2.843 (1) Å for an I trans to CH_3 with C(ipso) (e.g., in $[PtMe_3I(\{Me_2pz\}_2CH_2)]$).[23,24]

Table IV. Fractional Atomic Coordinates for 2a[a] and 5d

	x	y	z
		2a	
Pt	0.50000	0.47707 (3)	0.50000
Cl1	0.3464 (3)	0.4325 (6)	0.6093 (6)
Cl2	0.4622 (2)	0.2444 (4)	0.3023 (5)
Cl3	0.5382 (3)	0.7076 (4)	0.7020 (5)
C1	0.6213 (7)	0.5142 (13)	0.4099 (14)
C2	0.6233 (8)	0.6522 (15)	0.2939 (14)
C3	0.7109 (11)	0.6776 (22)	0.2287 (16)
C4	0.7885 (10)	0.5624 (25)	0.2795 (16)
C5	0.7841 (8)	0.4275 (22)	0.3950 (18)
C6	0.6990 (8)	0.4014 (19)	0.4663 (14)
C7	0.5338 (10)	0.7614 (15)	0.2571 (16)
C8	0.6782 (8)	0.2554 (16)	0.5830 (17)
C9	0.4043 (9)	0.5737 (20)	0.0910 (16)
C10	0.3635 (10)	0.7694 (19)	0.3119 (20)
C11	0.6561 (9)	0.3970 (17)	0.8657 (16)
C12	0.5515 (10)	0.1604 (19)	0.7523 (21)
N1	0.4446 (8)	0.6534 (16)	0.2751 (16)
N2	0.6006 (6)	0.3145 (12)	0.6887 (13)
		5d	
Pt1	0.20352 (3)	−0.01501 (3)	−0.1475 (1)
I1	0.21393 (6)	0.04993 (6)	−0.3584 (2)
I2	0.26754 (5)	−0.01256 (5)	−0.3423 (2)
C1	0.2025 (6)	−0.0620 (6)	−0.024 (2)
C2	0.2317 (6)	−0.0537 (6)	0.093 (2)
C3	0.2310 (7)	−0.0892 (7)	0.173 (3)
C4	0.2001 (7)	−0.1287 (7)	0.134 (3)
C5	0.1690 (6)	−0.1362 (6)	0.013 (2)
C6	0.1706 (7)	−0.1014 (6)	−0.062 (2)
C7	0.2661 (7)	−0.0091 (7)	0.103 (3)
C8	0.1353 (6)	−0.1053 (7)	−0.181 (2)
C9	0.2834 (7)	0.0615 (6)	−0.006 (3)
C10	0.2313 (7)	0.0260 (7)	0.206 (3)
C11	0.1173 (7)	−0.0590 (7)	−0.340 (3)
C12	0.1699 (8)	−0.0726 (8)	−0.457 (3)
C13	0.1567 (6)	−0.0157 (6)	0.004 (2)
C14	0.1355 (6)	−0.0463 (6)	0.123 (2)
C15	0.1041 (6)	−0.0457 (6)	0.219 (3)
C16	0.0953 (7)	−0.0143 (7)	0.202 (2)
C17	0.1165 (8)	0.0176 (8)	0.081 (3)
C18	0.1482 (7)	0.0155 (7)	−0.017 (2)
C19	0.0589 (8)	−0.0152 (9)	0.298 (4)
N1	0.2480 (5)	0.0188 (5)	0.046 (2)
N2	0.1537 (5)	−0.0657 (5)	−0.295 (2)

[a] The origin has been defined by fixing x and z of Pt at $^1/_2$.

The structure of **5d** shows an interesting structural orientation of the two aryl groups. As a consequence of

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(22) The puckering in cyclometalated rings that is observed in complexes with the terdentate ligand NCN may be either of the 2-fold axis symmetry or the mirrow plane type. Examples of the latter type are found in square-pyramidal complexes with the NCN ligand (see ref 53).

the rigid conformation of the NCN ligand as well as the distinct puckering of the two five-membered chelate rings, the 4-tolyl ring is forced into a fixed arrangement being orientated perpendicularly to both the plane of the aryl ring and the N–Pt–N axis (viz., C(13)–Pt–N(1) = 90.1 (8)°). The presence of *N*-methyl groups of the NCN ligand on both sides of the 4-tolyl group (see Figure 6) hinders rotation of the 4-tolyl group along the Pt–C(ipso) axis. As a result the "ortho" protons of the tolyl ring are held in the neighborhood of either the aryl ring of the NCN ligand or the equatorial iodide ligand (see also NMR results, vide supra).

Discussion

Many studies concerning the oxidation of organoplatinum(II) complexes have been reported. The greater part of these investigations involved the synthesis of organoplatinum complexes with a Me_3Pt^{IV} or a Me_2Pt^{IV} unit.[23-26] Platinum(IV) complexes with aryl ligands were obtained from oxidation reactions of Pt(II)–aryl complexes with dihalogens or methyl iodide,[4,27-30] while anionic complexes of platinum(IV) were found to be formed in transmetalation reactions between $PtCl_6^{2-}$ and aryl derivatives of non-transition metals.[31]

The synthesis of organoplatinum(IV) compounds by reacting platinum(II) precursors with electrophiles can be unsuccessful because of the occurrence of concurrent or subsequent reactions leading to Pt–C bond cleavage. In general the latter type of reactions may take place by either (i) a direct attack of the electrophile on the carbon atom of the Pt–C bond,[32] (ii) a one-electron-transfer mechanism,[7,8b,c] or (iii) prior oxidative addition of the electrophile to the platinum center, followed by reductive elimination of the organic product.[33,34]

Although it has only recently been demonstrated clearly in two cases,[35,36] it has been accepted for a long time that reaction sequence iii represents the valid mechanism in many C–C coupling reactions via palladium(II) complexes.[37] This assumption was partly based on the fact that in spite of the failure to observe or isolate the intermediate organopalladium(IV) species, a number of related organoplatinum(IV) complexes were known. The stability of these oxidative addition Pt(IV) products depends on the nature of the coordinated groups and on the possibility of these species to undergo subsequent stereoisomerization to give intermediates from which reductive elimination can occur.

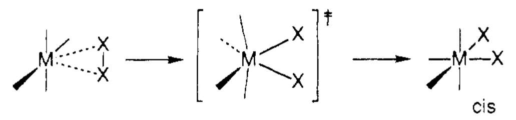

Figure 7. Concerted mechanism with the metal atom inserting into the X–X bond.

The monoanionic, terdentate ligand system we used in this study restricts the available coordination sites while this ligand is firmly bonded to the platinum metal via a σ Pt–C bond and the two hard N donor atoms in a fixed trans position across the metal center. Because the "CH_2NMe_2" site arms are connected to the rigid planar aryl ring, possible stereoisomerization reactions of platinum(IV) reaction products can be disregarded. Accordingly it may be expected that a subsequent reductive elimination step can be prevented and the oxidative addition product be isolated. The special structural and electronic features of the NCN ligand have already been shown to be important for the stabilization of the kinetic organometallic products formed in transmetalation and oxidative addition reactions (see Introduction). From those reactions it became clear that cationic Pt(IV) species like $[Pt(Me)I(NCN)]BF_4$ are not stable and rearrange to the thermodynamically more stable arenoniumplatinum(II) complex $[PtI(MeC_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]BF_4$.[1e]

Reactions with Dihalogens. Addition of dichlorine and dibromine to the square-planar Pt(II) complexes **1a** and **1b**, respectively, affords exclusively the stable, monomeric Pt(IV) complexes $[PtX_3(NCN)]$ (X = Cl, Br), while the reaction of **4a,c** with I_2 provides only $[PtRI_2(NCN)]$ (R = phenyl, 4-tolyl) products with *cis*-I_2 stereochemistry. The fact that in all cases products arising from Pt–C bond cleavage reactions were not found makes a pathway involving free radicals less probable for these reactions. This pathway has been found to be the predominant route in several other cases.[7,38,39]

Two other mechanistic possibilities then remain open to discussion: the concerted addition and the S_N2 type mechanisms. For both processes the metal basicity is of importance. We have found that the electrochemical oxidation of [PtBr(NCN)] (E_p = 1.32 V vs an Ag/AgCl electrode) is a straightforward process,[40] and this result is in line with the easy chemical oxidation of the organoplatinum complexes.[1f] Furthermore, a recent study of the ultraviolet photoelectron spectroscopy (UPS) of [MX(NCN)] (M = Ni, Pd, Pt; X = Cl, Br, I) showed that the d_{xz} and the d_{z^2} orbitals have a low ionization energy.[41] The presence of a d_{z^2} orbital with a low energy seems a general feature in square-planar complexes of Pd and Pt.[42] The above results give an indication that these orbitals, which serve both to weaken the X–X bond and strengthen the Pt–X bond, may be very active in reactions of the above square-planar Pt(II) complexes with electrophiles.

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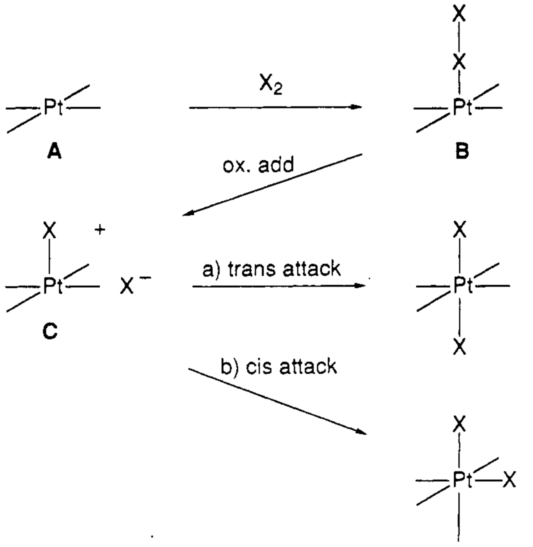
Scheme I. S_N2 Type Mechanism for the Oxidative-Addition Reactions of Dihalogens to Square-Planar Organoplatinum(II) Complexes



Our finding that in the reactions of Br_2 and I_2 with [PtR(NCN)] (R = phenyl, 4-tolyl) exclusively *cis*-X_2 oxidative addition products are formed could suggest that these reactions proceed via the concerted addition mechanism. In this symmetry-allowed process[43,44] the metal would insert into the X–X bond via a concerted addition of the X_2 electrophile; see Figure 7. The bonding scheme for this attack would be similar to that discussed theoretically[45] for the oxidative addition of H_2 to d^8 metals; i.e., one interaction comprising donation from the σ_b type orbital of X_2 into either a vacant metal acceptor hybrid (mixing p_z and d_{z^2}) or the p_z orbital and a second one involving back-bonding from the filled metal d_{xy} or d_{yz} orbital into the antibonding σ combination of X_2. Computational studies,[46] however, reveal that in particular the $3\sigma_u$ orbital of I_2 is the LUMO which actually makes initial η^1-coordination of the I_2 to the d^8 metal more likely than the η^2-coordination necessary for the concerted process. It remains to be seen whether η^1 to η^2 rearrangement of the Pt–I_2 interaction could be a viable route to a cis product.

The experimental evidence is that oxidative addition reactions of dihalogens X_2 to square-planar complexes usually yield *trans*-X_2 products,[29,47-50] and the *cis*-[Pt(R)X_2(NCN)] complexes belong rather to exceptional cases[27] than to the expected products. Indeed, related complexes *cis*-[PtL_2] (L = 2-[(dimethylamino)methyl]phenyl and 8-(dimethylamino)-1-naphthyl) react with Br_2 and I_2 to give the *trans*-X_2Pt(IV) complexes [PtX_2L_2].[51] Therefore we propose that the mechanism of these reactions is of the S_N2 type, by which both cis and trans oxidative addition products can be formed. The details of this mechanism are shown in Scheme I. Actually, this mechanism parallels that presented by Morgan and Jones, which was based on kinetic studies of the halogenation reactions of anionic $Pt(CN)_4^{2-}$ by dichlorine and dibromine in aqueous solutions.[10b,c]

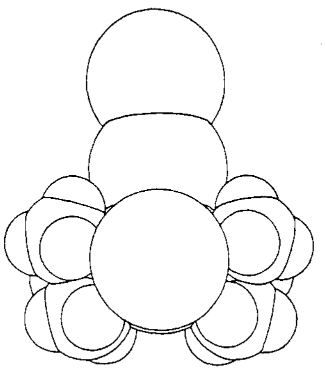
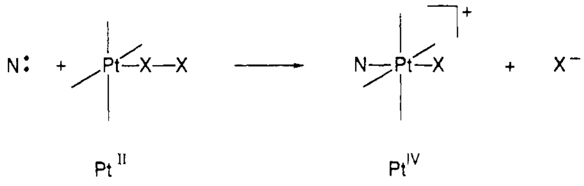


Figure 8. Space-filling model of [PtI($C_6H_3\{CH_2NMe_2\}_2$-2,6)(η^1-I_2)] projected along the I–Pt–C(ipso) axis showing the effective screening of the Pt site opposite to the coordinated halogen by the two axially positioned Me groupings.

An early step of the reaction is the end-on, η^1-complexation of the dihalogen molecule X_2 to the Pt(II) center. This suggestion was made by Morgan and Jones[10b,c] based upon UV measurements of their system, which indicated a rapid preequilibrium before the real oxidative addition reaction took place. Considering the possible orbital interactions, it was concluded that the first product had to be a dihalogen coordination complex like B (with X = Cl or Br; see Scheme I). Hopgood and Jenkins[10d] also expected such a complex to be formed in the photochemically initiated oxidative addition reaction of diiodine to platinum bis(acetylacetonate), for which process they suggested a free radical chain pathway. Recently, we could confirm these suggestions about the first step in the process, as we have been able to isolate the η^1-I_2 complex shown in Figure 2, right.[9]

The intermediate dihalogen coordination complex B reacts further by an overall two-electron transfer from the platinum center to the coordinated dihalogen. The question arises whether or not this step is assisted by attack of an additional nucleophilic agent N, i.e., the solvent or another, in the solution present, nucleophile, from the side opposite to the coordinated dihalogen, as shown in eq 3. Two observations from the literature seem to support this assistance. First, in the chlorination and bromination of $Pt(CN)_4^{2-}$ in aqueous solution the initially formed oxidative addition product is the halo–aquo–Pt(IV) complex *trans*-[Pt(halide)(OH_2)$(CN)_4$], which is converted in a next step to the final dihalo–Pt(IV) product by halide anation. Second, in the oxidative addition reactions of RX to [PtMe_2L_2] (L_2 = 2,2′-bipyridine, RX = MeI, $PhCH_2Br$; L = PMe_2Ph, RX = MeI) cationic Pt(IV) intermediates [Pt(S)Me_2RL_2]$^+X^-$ (S = CD_3CN) could be observed at low temperature by ^1H NMR.[52] However, both observations do not exclude the possibility that first electron transfer takes place in the η^1-dihalogen complex, followed by rapid coordination of a solvent molecule to the vacant sixth coordination site of the Pt(IV) center. In summary, it is



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plausible that the electron transfer from the Pt center to the η^1-coordinated dihalogen can be accelerated by an additional nucleophile N but not that the attack of such a nucleophile is needed for the electron transfer to take place, except, perhaps, in some cases.

The molecular structure of $[PtI(NCN)(\eta^1\text{-}I_2)]$[9] shows that the site of the Pt center opposite the coordinated dihalogen is effectively screened by two axially positioned Me groupings (see Figure 8). This situation must exist in all intermediate $[Pt(R)(NCN)(\eta^1\text{-}I_2)]$ complexes (B in Scheme I).[53] In spite of the fact that the Pt center in our complexes is hindered for attack of an additional nucleophile, the oxidative addition takes place and Pt(IV) products are formed. Moreover, the oxidative addition reactions with [Pt(R)(NCN)] can be carried out in benzene, which is not a very good Lewis base to attack Pt(II). In addition, the reactions were carried out by adding dropwise a solution of the dihalogen in benzene to a solution of the Pt complex in benzene. On the basis of the present data it seems therefore most likely that the second step in the reaction mechanism is an intramolecular (overall) two-electron transfer from the Pt(II) center to the coordinated dihalogen molecule, i.e., a donation of two electrons from the filled d_{z^2} orbital on Pt to the empty $\sigma_u{}^*$ of the dihalogen, leading to the intermediate, five-coordinated cationic Pt(IV) complex C and the halide anion X^-. The process can be accelerated by attack of an additional nucleophile as described above, but this does not seem to be a prerequisite for the forward reaction.

The last step in the oxidative addition mechanism involves the attack of the halide anion X^- on complex C. Reactions between coordinatively unsaturated, cationic metal complexes and anionic reagents are expected to be fast. Attack of X^- will therefore be on the vacant coordination site, trans to the other halide ligand (Scheme I, path a). When sterical hindrance prevents attack from this side, the halide will react with C to a *cis*-X_2 arranged product (Scheme I, path b). These are, off course, the routes leading to the kinetic products. When these products are not stable, either intra- or intermolecular rearrangements can take place: the latter involve cleavage of one of the Pt–X bonds, topological rearrangement of the cationic Pt(IV) complexes, and formation of a new Pt–X bond. Rearrangements can be facilitated, e.g., by addition of a silver(I) salt to the Pt(IV) complex to abstract a halide and subsequently adding the appropriate sodium halide salt.[28]

Reactions with Copper Salts. The reactions of [PtY(NCN)] (Y = halide, aryl, O_2CMe, formamidino) with copper(II) chloride afforded the organoplatinum(IV) complexes $[PtCl_3(NCN)]$, copper(I) chloride, and either arylcopper(I), copper(I) acetate, or copper(I) formamidine, respectively. As no intermediate stages in these ligand-transfer and Pt–Y bond-breaking processes could be detected or isolated, each mechanistic proposal remains speculative. Considerations on possible reaction mechanisms will be given in another paper,[51] where the results of some reactions of bis(organo)platinum(II) complexes with CuX_2 (X = Cl, Br) will be reported.

Substitution Reactions of the Organoplatinum(IV) Trihalide Compounds. An alternative route for the synthesis of the substituted organoplatinum(IV) compounds $[PtY_{3-n}X_n(NCN)]$ (X = halide, Y = aryl, O_2CR) would comprise the replacement of halides in the complexes **2a**,**b** with either suitable Ag^IY salts or organolithium reagents LiY. It appeared, however, that attempts to substitute the halide in $[PtBr_3(NCN)]$ with Ag^IY (Y = acetate, nitrate, nitrite) gave rise to the replacement of two bromide ligands irrespective of the molar ratio of the ligands; the reaction with 1 equiv of silver(I) acetate yielded a mixture of unreacted $[PtBr_3(NCN)]$ and the disubstituted complex $[Pt(O_2CMe)_2Br(NCN)]$. Moreover, the reaction mixtures were not clean, and only in the case of the reaction with 2 (!) equiv of silver(I) acetate could pure, well-defined $[Pt(O_2CMe)_2Br(NCN)]$, **3b**, be isolated. This finding contrasts with recent observations that the halides in $[Ni^{III}Br_2(NCN)]$ can be easily substituted by NCS, NO_2, NO_3, I, or Cl following the same synthetic route with the corresponding Ag salt.[54]

It is interesting to observe that attempts to synthesize $[Pt(4\text{-tolyl})Br_2(NCN)]$ or related compounds via the reaction of $[PtBr_3(NCN)]$ with 4-tolyllithium failed. A mixture of $[PtBr_3(NCN)]$ and [PtBr(NCN)] was obtained, while excess 4-tolyllithium also afforded [Pt(4-tolyl)(NCN)]. These results indicate that the bromide compound is reduced by 4-tolyllithium, most probably via an electron-transfer process taking place in early stages of the reaction. This observation further supports that $[Pt(4\text{-tolyl})I_2(NCN)]$, which is a stable compound (vide supra), is available only via a distinct kinetic route, i.e., via the attack of I_2 on the *trans*-bis(aryl)platinum(II) compound [Pt(4-tolyl)(NCN)].

Conclusions

The monoanionic, terdentate ligand $(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)^-$ enforces the platinum metal in a fixed ligand arrangement. This is reflected by the observation that the complexes $[PtY(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (Y = halide or aryl) react via specific pathways with the electrophiles X_2 (X = Cl, Br, I) and $Cu^{II}X_2$.

In the present study involving reactions with dihalogens and copper(II) halides we concluded that (i) metal oxidation is preferred over metal–carbon bond cleavage and (ii) attack of dihalogen on the platinum(II) center occurs via a S_N2 type mechanism leading to a *cis*-X_2 arrangement in the case of the $[Pt(aryl)X_2(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ complexes because of steric constraints.

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Registry No. **1a**, 82112-96-7; **1b**, 67507-09-9; **1d**, 80484-98-6; **1e**, 125637-10-7; **2a**, 87555-29-1; **2b**, 87555-30-4; **3a**, 125542-09-8; **3b**, 82180-00-5; **4a**, 111101-57-6; **4b**, 95532-50-6; **4c**, 95532-51-7; **5a**, 125542-10-1; **5b**, 125542-11-2; **5c**, 125542-12-3; **5d**, 125542-13-4.

Supplementary Material Available: For **2a**, listings of fractional coordinates and bond distances and bond angles of the hydrogen atoms, and for **2a** and **5d**, listings of anisotropic thermal parameters and PLUTO drawings (5 pages); for **2a** and **5d**, listings of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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[53] In the related complex $[Pt(C_6H_3\{CH_2N(t\text{-}Bu)Me\}_2\text{-}2,6)(I_3)(\eta^1\text{-}I_2)]$, two *t*-Bu groupings are placed in the axial positions and screen the platinum(II) center even more effectively from attack of any nucleophile: van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681.

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