eÅ^{-3} at 1.17 Å from the molybdenum atom. The final fractional coordinates and thermal parameters of the refined atoms are listed in Table VI.

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Supplementary Material Available: Listings of idealized hydrogen atom positions, additional bond distances and angles, thermal parameters, and structure factors for MoO$_2$(dttd) (9 pages). Ordering information is given on any current masthead page.

1,2-Methyl Shift between Pt and the Coordinated Aryl Group in the Reaction of Methyl Iodide with 2,6-Bis[(dimethylamino)methyl]phenyl-*N*,*N'*,*C* Complexes of Platinum(II). X-ray Crystal Structure of the Arenonium–Platinum Compound [Pt(*o*-tolyl)(MeC$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o*,*o'*)]I

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Contribution from the Anorganisch Chemisch Laboratorium, University of Amsterdam, J. H. van't Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands, and Vakgroep Algemene Chemie, Afdeling Kristal- en Struktuurchemie, University of Utrecht, 3584 CH Utrecht, The Netherlands. *Received September 10, 1984*

Abstract: The ionic complexes [PtX(MeC$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o*,*o'*)]OTf (X = Cl, Br, I) prepared from the reaction of [PtX(C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o*,*o'*)] with MeOTf possess a σ-metal-substituted arenonium ion with the Pt–C σ-bond trans to the halide. Synthetic investigations revealed that not only these species with X = Cl, Br, and I trans to the arenonium unit were isolable but also complexes with a more sterically demanding tolyl (ortho or para) group were formed in the reaction of [Pt(tolyl)(C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o*,*o'*)] with MeI. A single-crystal X-ray study has revealed the structure of the complex [Pt(*o*-tolyl)(MeC$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o*,*o'*)]I (see Figure 3): triclinic, space group $P\bar{1}$ with a = 7.295 (2) Å, b = 9.832 (2) Å, c = 15.044 (3) Å, α = 87.47 (2)°, β = 86.24 (2)°, γ = 83.42 (2)°, and Z = 2. The intensities of 3481 independent reflections were used to determine the structure. The structure was solved and refined using standard heavy-atom and least-squares techniques. The approximately square-planar complex has a σ-bonded *o*-tolyl group (Pt–C = 2.005 (9) Å) twisted perpendicular to the coordination plane and trans to the σ-bonded arenonium unit with Pt–C = 2.293 (9) Å. These and other experimental findings provide new evidence regarding oxidative-addition reductive-elimination pathways. It is concluded that attack of the methylating reagent occurs at the metal center. Hereby a five-coordinate cationic Pt$^{\mathrm{IV}}$–Me intermediate is formed that can consequently rearrange via two pathways, either (i) overall reductive elimination of MeX (in the case of X = Cl, Br, I) or (ii) 1,2-methyl shift across the Pt–C bond (Scheme I). Steric hindrance of the trans group and/or the presence of a nucleophile influence the available pathways which are discussed in detail.

In general organometallic complexes have been shown to be the active species in many metal-mediated organic and catalytic synthetic reactions. Extensive efforts have been made in preparing suitable organometallic compexes that, as models for reactive intermediates, can be used to study crucial steps of these processes in detail. In particular, there is a considerable interest in the oxidative addition reactions of organometallic complexes with electrophiles such as alkyl halides, halogens, or metal salts.[1-4] Detailed studies have been undertaken to improve the understanding of the mechanisms of reactions of electrophiles with group 8–10 metals[2,3,33] and of reactions involving C–C bond formation.[5-8] Evidence has been put forward that these reactions of d^8 organometallics may take place either by a direct attack of the electrophile on the carbon atom of the metal–carbon bond or by prior oxidative addition of the electrophile to the transition metal, followed by reductive elimination of the organic product.[4-6] The occurrence of the direct attack mechanism can be proved by detection of the oxidative-addition intermediate, which in a subsequent reaction provides the reductive-elimination product.[9-11] A further mechanism that has been suggested involves attack by the electrophile on the metal–carbon bond itself.[7,12]

In the course of a study of the addition of alkyl halides to the cationic complex [Pt(C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o*,*o'*)(H$_2$O)]BF$_4$ (**1**) we reported that when MeI was used, instead of the expected five-coordinate oxidative addition product [Pt(Me)I(C$_6$H$_3$-

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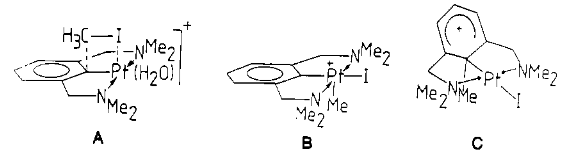
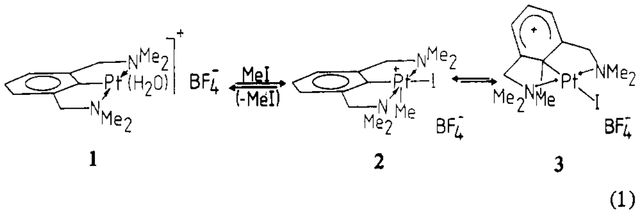


Figure 1. Addition of MeI to $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)]^+$ affording $[PtI(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]^+$; anion is either OTf^- or BF_4^-.

$(CH_2NMe_2)_2\text{-}o,o')]BF_4$ (**2**) the unique complex **3** was formed.[13] In **3** the methyl group of the methyl halide has become bonded to the carbon atom of the aryl ring that was σ bonded to the platinum center (eq 1).



(1)

Surprisingly heating **3** in the presence of halide anion resulted in the reverse reaction, i.e., cleavage of the C(phenyl)–C(methyl) bond and reformation of **1** or neutral $[PtI(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (**4c**).[14] The mechanism of this MeI reaction was not known although various possibilities were envisaged (summarized in Figure 1). For example, the four-center interaction of intermediate A could lead directly to C(phenyl)–C(methyl) bond formation of the final arenonium product C. Another possible route leading to C involves intermediates having an initial Pt^{IV}–CH_3 unit B from which a C(1)–CH_3 bond is formed by a 1,2-methyl shift from Pt to the metal-bonded C(1) atom of the phenyl system of the terdentate ligand.[13b]

In a recent elegant theoretical analysis of the problem of possible mechanisms for the methyl iodide reaction based on our ionic complex $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)]BF_4$ Hoffmann et al. considered various possibilities all employing approach of the MeI along the axis perpendicular to the coordination plane with a Pt–I interaction established first.[15]

In this paper we report the first experimental evidence for the various intermediate stages of this alkyl halide reaction on Pt(II) centers and have observed (i) electrophilic attack at a Pt center, (ii) a (reversible) 1,2-alkyl shift along a Pt–C bond, (iii) the influence that geometric constraints present during C–C bond formation in reductive-elimination processes have on product formation, and (iv) the influence of nucleophiles (anions) on the stability of the cationic intermediates formed. Previous studies of organometallic complexes with the monoanionic terdentate o,o'-$(Me_2NCH_2)_2C_6H_3$ ligand are also discussed and the results used to draw further conclusions.

Experimental Section

General. Compounds of the formula $[PtX(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (X = Cl, Br, I) (**4a–c**) were prepared as previously described.[13] The full synthesis of $[PtR(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (R = *o*-tolyl (**5a**), *p*-tolyl (**5c**)) from $PtBr(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ and *o*- or *p*-tolyllithium, respectively, will be published in a forthcoming paper.[16] Methyl trifluoromethanesulphonate (methyl triflate, MeOTf), was prepared by reacting equimolar quantities of HOTf and Me_2SO_4 according to the method described by Beard et al.[17] MeI and EtI were purified by distillation from KOH and stored over silver wire. AgOTf was commercially available. ^1H NMR spectra were recorded on Varian T60 or Bruker WM250 spectrometers as solutions in $CDCl_3$, C_6D_6, or acetone-d_6. Elemental analyses were carried out by the Analytical Department of the Institute for Applied Chemistry, TNO, Utrecht, The Netherlands.

Synthesis of $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)]OTf$ (7). A stirred suspension of $[PtBr(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ in acetone (5 mL) was treated with 1 equiv of AgOTf at room temperature. After 20 min the AgBr was filtered off and washed with 5 mL of acetone. The combined filtrate and washings were evaporated to dryness in vacuo. The resultant solid was extracted with CH_2Cl_2. Concentration of this solution followed by addition of pentane resulted in precipitation of a white product. Recrystallization of this product from CH_2Cl_2/pentane afforded the pure complex $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)]OTf$ (**7**), yield 70%. Anal. Calcd for $C_{13}H_{21}N_2PtSO_4F_3$: C, 28.21; H, 3.82; N, 5.06. Found: C, 28.73; H, 3.82; N, 5.02.

Reaction of 7 with MeI. To a solution of **7** (1 mmol) in acetone (5 mL) was added an excess of freshly distilled MeI. The clear solution was then allowed to stand undisturbed for 24 h, during which time the solution became dark red. Concentration of the solvent and slow addition of pentane afforded a dark red precipitate of $[PtI(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]OTf$ (**6c**). Recrystallization from CH_2Cl_2/pentane gave the pure product, yield 91%. Anal. Calcd for $C_{14}H_{22}N_2PtIO_3SF_3$: C, 24.82; H, 3.27; N, 4.13; I, 18.74. Found: C, 24.87; H, 3.35; N, 4.10; I, 17.77.

Reaction of 7 with CD_3I. A stirred solution of **7** (0.35 mmol) in acetone (5 mL) was reacted with an excess of CD_3I (1 mL, 99% CD_3I). The reaction mixture was worked up as described above for MeI resulting the pure product $[PtI(CD_3C_6H_3(CH_2NMe_2)_2\text{-}o,o')]OTf$ (**6d**). This product was identified with ^1H and ^{13}C NMR spectroscopy by comparison with the nondeuterated analogue, see above. The abscence of the resonance at 3.12 ppm (i.e., of the CH_3 in **6c**) in the ^1H NMR was established.

Reaction of 7 with MeBr. To a solution of **7** (0.3 mmol) in acetone (5 mL) was added an excess of MeBr. The clear solution was then allowed to stand undisturbed for 24 h, during which time the solution became dark orange. Concentration of the solvent and slow addition of pentane afforded orange red $[PtBr(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]OTf$ (**6b**). Recrystallization from CH_2Cl_2/pentane gave the pure product, yield 54%.

Syntheses of $[PtX(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]OTf$ (X = Cl, Br, I) (6a–c) (via the MeOTf Route). To a solution of $[PtX(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (**4a–c**) (0.3 mmol) in acetone (5 mL) was added 2 equiv of MeOTf. After several minutes the solution became colored, orange (Cl), red (Br), or dark red (I). Diethyl ether was added carefully to the reaction mixture to obtain a two-layer system which was allowed to stand undisturbed for 24 h. During this time crystals of **6a–c** were formed and were collected by filtration, washed with 5 mL of diethyl ether, and dried in vacuo, yield 40–60%. Concentration of the combined filtrate and washings gave an oily residue which contained the cationic complex $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)]OTf$ (**7**) (checked by ^1H NMR). Anal. Calcd for the orange complex **6a**, $C_{14}H_{22}N_2ClPtO_3SF_3$: C, 28.70; H, 3.79; N, 4.78; Cl, 6.05. Found: C, 28.36; H, 3.77; N, 4.64; Cl, 5.77. Calcd for the red complex **6b**, $C_{14}H_{22}N_2BrPtO_3SF_3$: C, 26.67; H, 5.52; N, 4.44; Br, 12.67. Found: C, 26.40; H, 3.57; N, 4.26; Br, 12.15. Calcd for the dark red complex **6c**, $C_{14}H_{22}N_2PtIO_3SF_3$: C, 24.82; H, 3.27; N, 4.13. Found: C, 25.67; H, 3.70; N, 4.11.

Synthesis of [Pt(*o*-tolyl)($MeC_6H_3(CH_2NMe_2)_2\text{-}o,o'$)]I (5b). To [Pt(*o*-tolyl)($C_6H_3(CH_2NMe_2)_2\text{-}o,o'$)] (**5a**) (477 mg, 1 mmol) was added an excess of freshly distilled MeI (3 mL). The mixture was stirred for 2 h, during which time it became light yellow. Evaporation of the resulting suspension to dryness followed by washing the residue with diethyl ether (5 mL) and benzene (5 mL) gave the crude product. Recrystallization from CH_2Cl_2/pentane afforded bright yellow crystals of **5b**, yield 82%. Anal. Calcd for $C_{20}H_{29}N_2IPt$: C, 38.78; H, 4.72; N, 4.52; I, 20.49. Found: C, 38.44; H, 4.66; N, 4.58; I, 20.97.

Synthesis of [Pt(*p*-tolyl)($MeC_6H_3(CH_2NMe_2)_2\text{-}o,o'$)]I (5d). To [Pt(*p*-tolyl)($C_6H_3(CH_2NMe_2)_2\text{-}o,o'$)] (**5c**) (143 mg, 0.3 mmol) in acetone (5 mL) was added an excess of freshly distilled MeI (0.1 mL). The mixture was stirred for 20 min during which time it became yellow. Evaporating of the acetone and unreacted MeI followed by washing the residue with diethyl ether (4 × 5 mL) and benzene (2 × 5 mL) afforded the yellow product, yield 52%. Anal. Calcd for $C_{20}H_{29}N_2IPt$: C, 38.78; H, 4.72; N, 4.52; I, 20.49; Pt, 31.50. Found: C, 36.71; H, 4.31; N, 3.87; I, 21.24; Pt, 32.54.

Synthesis of [Pt(*p*-tolyl)($MeC_6H_3(CH_2NMe_2)_2\text{-}o,o'$)]OTf (5e). To a stirred solution of AgOTf (77 mg, 0.31 mol) in acetone (5 mL) was added 1 equiv of **5d** (187 mg). Immediately a solid precipitated (AgI) which was filtered off and washed with 2 mL of acetone. The combined filtrate and washings were evaporated to dryness in vacuo. The resultant solid was extracted with CH_2Cl_2. Concentration of these extracts fol-

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lowed by addition of pentane (15 mL) resulted in precipitation of a light yellow product, which was filtered off and dried in vacuo, yield 51%. Anal. Calcd for $C_{21}H_{29}N_2O_3SF_3Pt$: C, 37.67; H, 4.37; N, 4.18. Found: C, 38.26; H, 4.64; N, 4.00.

Reaction of MeI with [PtBr($C_6H_3(CH_2NMe_2)_2$-*o,o′*)] (4b). A stirred solution of **4b** (0.3 mmol) in acetone was reacted with 1 equiv of MeI (0.3 mmol) at room temperature. After 24 h the solvent was evaporated in vacuo and the solid isolated. Crystallization from CH_2Cl_2/pentane afforded a mixture of two compounds, identified by ^1H NMR as [PtBr($C_6H_3(CH_2NMe_2)_2$-*o,o′*)] (**4b**) (36%) and [PtI($C_6H_3(CH_2NMe_2)_2$-*o,o′*)] (**4c**) (64%), respectively. When another equivalent of MeI (0.3 mmol) was added to this mixture of products in acetone there was complete conversion to **4c** which was isolated in 84% yield.

Reaction of MeBr with [PtI($C_6H_3(CH_2NMe_2)_2$-*o,o′*)] (4c). A stirred solution of **4c** (0.1 mmol) in acetone was reacted with a tenfold excess of MeBr at room temperature. After 3 h the solvent was evaporated in vacuo. The resulting white product was identified as pure **4b**.

The reactions of [PtBr($C_6H_3(CH_2NMe_2)_2$-*o,o′*)] with either MeI or EtI were monitored by ^1H NMR. Standard solutions containing 0.05 mmol of [PtBr($C_6H_3(CH_2NMe_2)_2$-*o,o′*)] in acetone-d_6 (0.5 mL) were used and MeI or EtI were added with a microsyringe. The reaction progress was followed by measuring the increase in intensity of the NMe_2 signal of [PtI($C_6H_3(CH_2NMe_2)_2$-*o,o′*)] and the decrease in intensity of the NMe_2 signal of the starting complex [PtBr($C_6H_3(CH_2NMe_2)_2$-*o,o′*)]. These signals have only a slightly different chemical shift (0.06 ppm) and they overlap mutually the ^{195}Pt satellites of each others resonances. As a result of this overlap good quantitative measurements were not possible and only qualitative conclusions will be drawn.

Reactions of [Pt(*o*-tolyl)($MeC_6H_3(CH_2NMe_2)_2$-*o,o′*)]I (5b) with Some Weak Nucleophiles: Reaction of 5b with H_2O. A solution of 100 mg of **5b** in H_2O (5 mL) was boiled for 90 min. The water was evaporated with a N_2 stream (ca. 18 h) and the resulting residue was extracted with CH_2Cl_2. The clear solution was concentrated and upon addition of pentane a yellow product precipitated which was identified by ^1H NMR spectroscopy as unreacted starting material **5b**.

Reaction of 5b with NaI. To a solution of 50 mg of **5b** in acetone/water was added a tenfold excess of NaI. After stirring the mixture for about 10 min at 90–100 °C the solvent was evaporated with a N_2 stream and the resulting residue was extracted with CH_2Cl_2. The clear solution was concentrated and addition of pentane afforded a yellow product. This product was identified by ^1H NMR spectroscopy as unreacted starting material **5b**.

Reaction of 5b with Na[CH($COOCH_3$)$_2$]. To a solution of 124 mg of **5b** in THF/H_2O was added 2 equiv of Na[CH($COOCH_3$)$_2$]. The mixture was stirred for 3 h. The solvent was evaporated with a N_2 stream and the resulting residue was extracted with CH_2Cl_2. Upon addition of pentane a yellow solid precipitated. This product was identified by ^1H NMR spectroscopy as unreacted starting material **5b**.

Reaction of 5b with KCN. To a stirred solution of **5b** (50 mg) in acetone/H_2O (5 mL) was added a tenfold excess of KCN. After 2 h the solvent was evaporated with a N_2 stream and the resulting residue was extracted with CH_2Cl_2 (3 mL). The isolated organic species was identified by ^1H NMR spectroscopy as *o,o′*-$(Me_2NCH_2)_2C_6H_3Me$.

Collection and Treatment of X-ray Diffraction Data of [Pt(*o*-tolyl)($MeC_6H_3(CH_2NMe_2)_2$-*o,o′*)]I (5b). A yellow crystal (0.35 × 0.35 × 0.13 mm) of **5b** preliminarily examined with a Weissenberg photograph was glued on top of a glass fiber and mounted on an Enraf-Nonius CAD-4F diffractometer for data collection. Unit cell dimensions, their corresponding standard deviations, and a complete data set were obtained via a previously described standard procedure using Zirconium filtered Mo Kα radiation.[18] The crystal data and details of the data collection and structure refinement are summarized in Table I. The intensities of two reflections were monitored every hour of X-ray exposure time. They indicated a slight decay of 1% during data collection and fluctuations less than 3%. The data were subsequently corrected for the decay, absorption, Lorentz, and polarization effects and averaged into a unique data set in the previously described way. The empirical absorption correction[19] was based on the results of a preliminary isotropic refinement and resulted in corrections up to 20%.

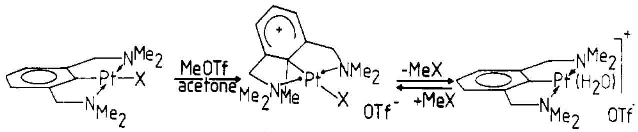
Structure Determination and Refinement of [Pt(*o*-tolyl)($MeC_6H_3(CH_2NMe_2)_2$-*o,o′*)]I (5b). The structure was solved by standard Patterson techniques and subsequently refined by blocked full-matrix least-squares techniques.[20] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were introduced on calculated positions and refined in the riding mode on the corresponding non-hydrogen atom positions, with separate temperature factors for hydrogen atoms in methyl groups and the remaining hydrogen atoms. Weights based on counting statistics were introduced in the final stage of the refinement. Convergence was reached at $R = 0.043$ for 3481 reflections. Apart from residual density up to 1 e $Å^{-3}$ concentrated around the platinum and iodine atoms the final difference Fourier map showed no significant features. The final values of the refined parameters are given in Table I. Neutral scattering factors were taken from ref 21 and corrected for anomalous dispersion effects.[22] All calculations were carried out on the Cyber-175 of the University of Utrecht Computer Centre with the programs of the SHELX-76[20] and Euclid packages (molecular geometry and pictures).[23]

Table I. Crystal Data and Details of the Structure Determination of [Pt(*o*-tolyl)($MeC_6H_3(CH_2NMe_2)_2$-*o,o′*)]I

Crystal Data	
formula	$C_{20}H_{29}IN_2Pt$
M_r	619.46
space group	$P\bar{1}$
cryst sys	triclinic
a, Å	7.295 (2)
b, Å	9.832 (2)
c, Å	15.044 (3)
α, deg	87.47 (2)
β, deg	86.24 (2)
γ, deg	83.42 (2)
V, $Å^3$	1068.9 (5)
Z	2
D(calcd), g cm^{-3}	1.925
F(000) electrons	588
μ(Mo Kα), cm^{-1}	83.7
cryst size, mm	0.35 × 0.35 × 0.13
Data Collection	
θ min, max	1.36, 25.0
radiatn, Å	Mo Kα (Zr filtered), 0.71069
ω, 2θ scan, deg	1.00 + 0.35 tan θ
horiz and vert aperture, mm	3.0, 3.0
max time/reflcn, s	60
ref reflcn	131, 01-1
total reflcn data	3924
total unique reflcns	3778
obsd data ($I > 2.5\sigma(I)$)	3481
Refinement	
no. refined params	219
weighting scheme	$w^{-1} = (\sigma^2(F) + 0.00649F^2)$
final R_F and R_{wF}	0.0428, 0.0490
variance (rms dev of a reflcn of unit wt)	1.99

Results

The neutral complex [PtX($C_6H_3(CH_2NMe_2)_2$-*o,o′*)] (X = Cl (**4a**), Br (**4b**), I (**4c**)), reacts in acetone with MeOTf to give the arenonium type of complex [PtX($MeC_6H_3(CH_2NMe_2)_2$-*o,o′*)]OTf (X = Cl (**6a**), Br (**6b**), I (**6c**)) and traces of the cationic complex [Pt($C_6H_3(CH_2NMe_2)_2$-*o,o′*)(H_2O)]OTf (**7**) (eq 2). Products were identified by elemental analysis and comparison of ^1H NMR spectra with those of authentic samples (Table II). The air-stable products **6a–c** are orange (Cl), red (Br), and dark red (I), re-



4a, X = Cl
b, X = Br
c, X = I

6a, X = Cl
b, X = Br
c, X = I

7

(2)

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Table II. ^{1}H NMR Data for the Cationic Complexes **7** and the Arenonium Complexes **3**, **5b,d,e**, and **6a–d**

compd	ppm[a] C_6H_3 H(4)	 H(3,5)[b]	 CH_2[c]	 NMe_2[d]	 Me
$[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)]OTf$[g] (**7**)	6.98 t	6.76 d	3.99[e] (50)	3.03[e] (37)	
$[PtI(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]BF_4$[f] (**3**)	8.70 (42)	7.60 (15)	5.08, 3.97 (21, 40)	3.15, 2.69 (36, 28)	3.27 (8)
$[Pt(o\text{-tolyl})(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]I$[g,h] (**5b**)	7.85	7.54	4.99, 4.05 (–, 44)	2.61, 2.42 (58, 52)	3.39 (9)
$[Pt(p\text{-tolyl})(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]I$[f,i] (**5d**)	7.80 t	7.48 d	5.00, 4.13 (–, 43)	2.54, 2.46 (64, 54)	3.32 (8)
$[Pt(p\text{-tolyl})(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]OTf$[g,j] (**5e**)	7.76 t	7.10 d	4.90, 3.86 (–, 46)	2.78, 2.68 (60, 56)	3.32 (8)
$[PtCl(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]OTf$[g] (**6a**)	8.38 t	7.33 d	4.81, 3.84 (21, 44)	2.88, 2.51 (29, 25)	3.12 (9)
$[PtBr(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]OTf$[g] (**6b**)	8.38 t	7.33	4.82, 3.85 (21, 44)	2.88, 2.52 (30, 24)	3.13 (11)
$[PtI(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]OTf$[g] (**6c**)	8.48 t (43)	7.38 t (13)	4.83, 4.13 (21, 48)	3.05, 2.61 (30, 26)	3.12 (10)
$[PtI(CD_3C_6H_3(CH_2NMe_2)_2\text{-}o,o')]OTf$[f] (**6d**)	8.74 t (44)	7.64 d (18)	5.11, 4.01 (24, 40)	3.18, 2.73 (36, 30)	

[a] Chemical shifts are relative to Me_4Si and coupling constants are in Hz; $^nJ(^{195}Pt,^1H)$ values are in parentheses; t = triplet, d = doublet. [b] Relative intensity ratio H(4)/H(3,5) is 1:2. [c] Diastereotopic benzylic protons $^2J(H,H)$ = 13 Hz. [d] Diastereotopic Me groups. [e] Enantiotopic protons. [f] In acetone. [g] In $CDCl_3$. [h] o-Tolyl group: δ_{aryl} 7.31 (ortho H; $^3J(^{195}Pt,^1H)$ = 57 Hz), 6.82 (multiplet, δ_{CH_3} 2.36 ($^4J(^{195}Pt,^1H$ = 15 Hz). [i] p-Tolyl group: δ_{aryl} 7.12 (ortho H; $^3J(^{195}Pt,H)$ not observed), 6.70 (multiplet), $\delta(CH_3)$ 2.20. [j] p-Tolyl group: δ_{aryl} 7.42 (ortho H; $^3J(^{195}Pt,H)$ not observed), 6.65 (multiplet), δ_{CH_3}, 2.16.

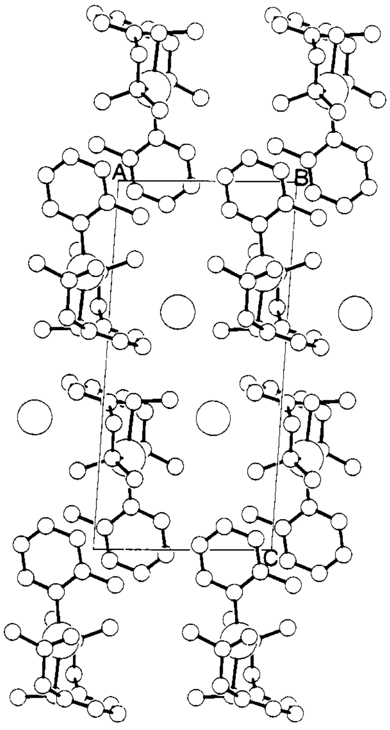
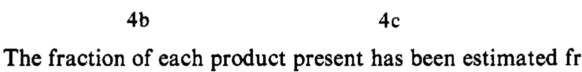


Figure 2. Projection of the structure down the *b* axis of **5b** illustrating the unit-cell contents and packing.

spectively. They are soluble in $CHCl_3$, CH_2Cl_2, and acetone, but decompose slightly in these solvents into the cationic water complex **7** and the corresponding methyl halide (see eq 2; detected by ^{1}H NMR). The complexes $[PtX(Me(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]OTf$ (X = Br, I) could also be prepared in high yield by reacting the cationic water complex **7** with an excess of MeX (X = Br, I) (cf. eq 1). In a separate experiment with CD_3I the corresponding deuterated complex **6d** was obtained.

Reaction of the neutral complex $[PtBr(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ with MeI did not give the arenonium type of compound $[PtBr(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]I$ but instead gave products originating from overall substitution of the halide. Reaction of $[PtBr(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ with 1 equiv of methyl iodide in acetone afforded the equilibrium shown in eq 3.



(3)

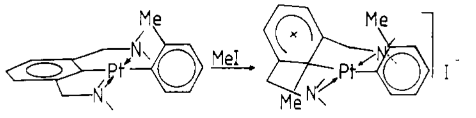
4b 4c

The fraction of each product present has been estimated from the integrals of the respective resonances in the ^{1}H NMR spectrum of this solution. With an excess of MeI the equilibrium of eq 3 shifts to the right and pure $[PtI(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ was isolated from these solutions. Applying similar conditions we found for the 1:1, 1:2, and 1:10 mixtures of $[PtBr(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ and MeI after 1 day 60%, 79%, and 99% of $[PtI(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$, respectively. Consequently the equilibrium shifts to the left upon addition of MeBr to pure $[PtI(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$.

If either dry benzene or chloroform were used as solvents (in N_2 atmosphere) the equilibrium 3 was not observed even after 1 day, while in the case of benzene $[PtI(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ was detected after 7 days but only in small quantities (<10%). Furthermore compared to MeI there was a striking drop in reaction rate when EtI was used as the electrophilic reagent. Reaction with a tenfold excess of EtI with $[PtBr(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ in acetone gave after 5 days only 50% of the platinum iodide product **4c**.

In the above MeI reaction no trace of the six-coordinate oxidative addition product $[Pt(Me)IBr(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (with Pt^{IV}–Me) was found, substitution of the halide always being observed instead. These experimental facts indicate a S_N2 type of mechanism for this reaction since (i) the reaction progresses more rapidly in polar solvents, (ii) the reaction is in equilibrium, and (iii) the reaction with MeI is much faster than with EtI. These observations are of importance for the discussion of the mechanistic pathways in the reaction of alkyl halides with our platinum complexes.

The neutral complex $[Pt(o\text{-tolyl})(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (**5a**) reacts with MeI to give the arenonium type of complex $[Pt(o\text{-tolyl})(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]I$ (**5b**) (eq 4). This light-yellow



(4)

5a 5b

compound is air stable and soluble in polar solvents such as CH_2Cl_2, $CHCl_3$, acetone, and warm water. In contrast to the high reactivity of **3** with nucleophiles complex **5b** is inert to weak nucleophilic reagents like sodium malonate, sodium iodide, and water. With an excess of potassium cyanide a solution of **5b** decolorized readily as a result of the formation of the free organic ligand $o,o'\text{-}(Me_2NCH_2)_2C_6H_3Me$. No attempt was made to identify the inorganic platinum species presumably $[Pt(CN)_4]^{2-}$ or $[Pt(CN)_3I]^{2-}$.

The complex $[Pt(p\text{-tolyl})(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (**5c**) reacts in acetone with MeI to give the complex $[Pt(p\text{-tolyl})(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]I$ (**5d**). The yellow complex decomposed slowly in acetone (and faster in chloroform; decomposition products were already detected immediately after dissolution) into the species $o,o'\text{-}(Me_2NCH_2)_2C_6H_3Me$ and presumably toluene and an unknown platinum salt. Substitution of iodide in complex **5d** by the triflate anion afforded the complex $[Pt(p\text{-tolyl})(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]OTf$ (**5e**). It is noteworthy that complex **5e**,

Table III. Relevant Bond Distances, Bond Angles, and Torsion Angles for $[Pt(o\text{-tolyl})(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]I$

	Bond Distances (Å)		
Pt–N(1)	2.094 (7)	C(1)–C(2)	1.44 (1)
Pt–N(2)	2.090 (7)	C(1)–C(6)	1.35 (1)
Pt–C(1)	2.293 (9)	C(1)–C(20)	1.51 (1)
Pt–C(13)	2.005 (9)	C(2)–C(3)	1.37 (1)
N(1)–C(7)	1.49 (1)	C(2)–C(10)	1.44 (1)
N(1)–C(8)	1.51 (1)	C(3)–C(4)	1.36 (2)
N(1)–C(9)	1.52 (1)	C(4)–C(5)	1.37 (2)
N(2)–C(10)	1.53 (1)	C(5)–C(6)	1.41 (1)
N(2)–C(11)	1.51 (2)	C(6)–C(7)	1.54 (1)
N(2)–C(12)	1.52 (2)		
	Bond Angles (deg)		
N(1)–Pt–N(2)	171.1 (3)	C(7)–N(1)–C(8)	109.5 (8)
N(1)–Pt–C(1)	85.4 (3)	C(7)–N(1)–C(9)	109.5 (7)
N(1)–Pt–C(13)	95.3 (3)	C(8)–N(1)–C(9)	109.3 (8)
N(2)–Pt–C(1)	85.7 (3)	Pt–N(2)–C(10)	103.8 (5)
N(2)–Pt–C(13)	93.3 (3)	Pt–N(2)–C(11)	107.7 (7)
C(1)–Pt–C(13)	167.8 (3)	Pt–N(2)–C(12)	115.7 (8)
Pt–N(1)–C(7)	106.6 (5)	C(10)–N(2)–C(11)	108.4 (8)
Pt–N(1)–C(8)	109.4 (6)	C(10)–N(2)–C(12)	112.8 (9)
Pt–N(1)–C(9)	112.5 (6)	C(11)–N(2)–C(12)	108 (1)
Pt–C(1)–C(2)	87.0 (5)	C(3)–C(2)–C(10)	123.0 (9)
Pt–C(1)–C(6)	89.1 (6)	C(2)–C(3)–C(4)	121 (1)
Pt–C(1)–C(20)	101.4 (6)	C(3)–C(4)–C(5)	120.2 (9)
C(2)–C(1)–C(6)	114.8 (7)	C(4)–C(5)–C(6)	117.9 (9)
C(2)–C(1)–C(20)	120.7 (8)	C(5)–C(6)–C(7)	116.8 (8)
C(6)–C(1)–C(20)	123.9 (8)	C(1)–C(6)–C(5)	123.2 (9)
C(1)–C(2)–C(3)	120.6 (9)	C(1)–C(6)–C(7)	118.1 (8)
C(1)–C(2)–C(10)	115.4 (8)	N(1)C(7)–C(6)	104.7 (7)
		N(2)–C(10)–C(2)	107.5 (8)
	Torsion Angles		
C(1)–Pt–N(1)–C(7)	1.2 (6)	C(2)–C(1)–C(6)–C(5)	−15 (1)
C(1)–Pt–N(1)–C(8)	119.4 (7)	C(2)–C(1)–C(6)–C(7)	148.5 (8)
C(1)–Pt–N(1)–C(9)	−118.9 (7)	C(3)–C(2)–C(10)–N(2)	−98 (1)
Pt–N(1)–C(7)–C(6)	25.9 (7)	C(10)–C(2)–C(3)–C(4)	164.2 (9)
Pt–N(2)–C(10)–C(2)	−23.6 (8)	C(1)–C(2)–C(3)–C(4)	−4 (1)
Pt–C(1)–C(2)–C(3)	102.8 (8)	C(1)–C(2)–C(10)–N(2)	71 (1)
Pt–C(1)–C(6)–C(7)	62.2 (8)	C(2)–C(3)–C(4)–C(5)	−9 (1)

in contrast to **5d**, is stable in acetone and chloroform. After 2 days still no decomposition product could be detected by ^{1}H NMR.

Spectroscopic Measurements

The ^{1}H NMR spectra of the complexes $[PtX(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]OTf$ (**6**), $[Pt(R)(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]I$ (**5b,d**), and $[Pt(p\text{-tolyl})(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]OTf$ (**5e**) have resonance patterns that are analogous to the characteristic arenonium type of pattern of the complex $[PtI(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]BF_4$ (**3**) that has been discussed in a previous paper.[13b] ^{1}H NMR data for **3,5b,d,e,6a–d**, and **7** are in Table II.

The ^{13}C NMR data of the complexes $[PtI(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]OTf$ (**6c**) and $[Pt(o\text{-tolyl})(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]I$ (**5b**) as regards the unique methyl group are comparable (δ_{CH_3} = 18.8 (**6c**) and 20.85 (**5b**) Hz). In addition both signals possess ^{195}Pt satellites ($^2J_{PtC}$ = 59 and 56 Hz, respectively) suggesting that the methyl group is coupled to the metal via a σ skeleton. The chemical shift of the phenyl carbon (C1) bonded to the methyl group is at 102.6 (**6c**) and 115.6 (**5b**) ppm, respectively (cf. the chemical shift of C(1) bonded directly to Pt in $PtBr(C_6H_3(CH_2NMe_2)_2\text{-}o,o')$], 145.7 ppm[16]).

Molecular Geometry of $[Pt(o\text{-tolyl})(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]I$ (5b). The novel complex **5b** has an ionic crystal structure with two centrosymmetrically related asymmetric units in the triclinic unit cell (Figure 2). The structure of complex **5b** along with the adopted numbering scheme is shown in the PLUTO drawings in Figure 3a,b. Relevant interatomic bond distances, angles, and torsion angles are listed in Table III. The four-coordinate platinum center has a distorted square-planar coordination geometry by virtue of the N,N′,C donor atoms of the terdentate ligand $o,o'\text{-}(Me_2NCH_2)_2C_6H_3$ and one C atom of the *o*-tolyl group. The Pt–C(13) and Pt–C(1) distances amount to 2.005 (9) and 2.293 (9) Å, respectively, with the latter bond length being particularly large for a normal Pt–phenyl σ bond (average Pt–phenyl 2.00 Å[24]). The unique C(1)–Me separation of 1.51 (1) Å is that expected for a Me–phenyl bond.[25]

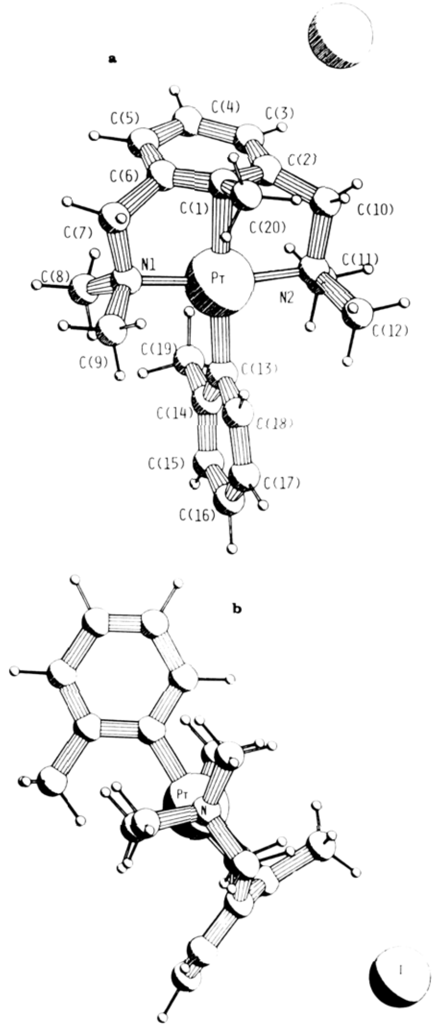


Figure 3. PLUTO drawings of the complex **5b** with the adopted numbering scheme.

A striking feature of **5b** is the orientation of the aryl groups with respect to the coordination plane. The plane of the *o*-tolyl group is perpendicular both to that of the square coordination plane of the complex and to the ring of the terdentate N,N′,C ligand. The slightly puckered ring of the latter ligand makes a dihedral angle of 70.7° with the coordination plane of the complex. A crystal structure of the related tetrafluoborato complex $[PtI(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]BF_4$ (**3**) has previously been published and shows a similar structural feature.[13b] The most significant difference between **3** and **5b** is the Pt–C(1) separation, which in **3** was found to be 2.18 Å. This almost certainly reflects the large difference in electronic properties of the ligand trans (I vs. *o*-tolyl) to the phenyl C(1) of the terdentate ligand.[26]

Discussion

It has now been shown that the syntheses of complexes **6a–d** containing the unusual Pt σ-bonded arenonium unit may be easily accomplished by addition of MeOTf to the appropriate $[PtX(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ species or by addition of either MeBr, MeI, or CD_3I to $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)]OTf$. The conclusions drawn in a previous paper[13b] regarding the σ-bonding of this structural unit to Pt in **3** are in good agreement with the

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(24) Wilkinson, G.; Stone, F. G. A.; Abel, E. W. "Comprehensive Organometallic Chemistry"; Pergamon Press: London, 1982; Vol. 6.

(25) Values taken from: "Inter-atomic Distances Supplement"; The Chemical Society: London, 1965; Special Publication no. 18.

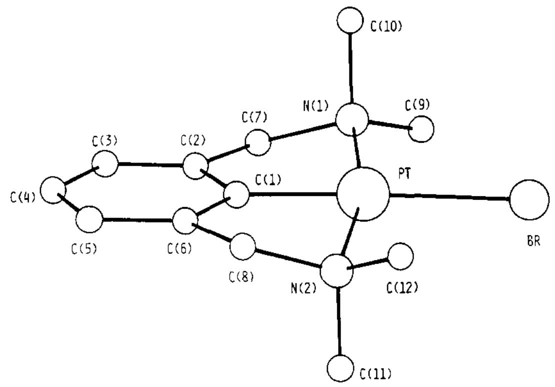

Figure 4. PLUTO drawing of **4b** showing the special N,C,N′ arrangement and the adopted numbering scheme.[29]

new spectroscopic data on **5b,d** and **6a–d** of which the latter have a much better solubility resulting from the presence of the OTf anion. In particular the ^{13}C NMR data shows that the C(1) has a strong interaction with Pt; vide supra the $^2J[^{195}Pt,^{13}C(H_3)]$ values of **3** and **5b**.

The synthetic investigations also revealed that not only species with X = Cl, Br, or I trans to the arenonium unit were isolable but also, more interestingly, complexes **5b** and **5d** having a trans *o*-tolyl and *p*-tolyl substituent, respectively. Surprisingly, whereas the halo species show similar reactivities the *o*-tolyl complex **5b** was found to be inert in many cases to the reagents. The basic structural features (see Results) found by X-ray structure determination are retained. The X-ray structure of **5b** has proven useful for the following reasons.

It confirms the coordination geometry anticipated from ^{1}H and ^{13}C NMR measurements and in particular the specific stereochemistry of the complex wherein the *o*-tolyl and the arenonium methyl groups are positioned in opposite directions. The other possible stereoisomer was not found. As a result of the relative positioning of these methyl groups a Pt center is present (Figure 3a,b) that is particularly well shielded.

Evidence has been put forward that an important mechanism for oxidative addition of alkyl halides to organometallic complexes involves S_N2 displacement of the halide by the metal nucleophile.[3,5,7] Other possibilities that have been proved to be operative in the case of substrates or electrophiles with special contraints include free-radical chain or nonchain mechanisms with the latter being characterized by one-electron transfer from the metal to the alkyl halide.[27,28]

Our monoanionic terdentate ligand system can be expected to strongly influence the mechanisms operative during reactions of its metal complexes. In the complexes **4**, **5a**, **5c**, and **7** the rigid N,C,N′ arrangement restricts the number of active coordination sites about the platinum exclusively to those in a plane perpendicular to the terdentate ligand plane. Another unique feature of the Pt(II) species is that the aryl ring of the terdentate ligand is held almost coplanar with the platinum coordination plane (see Figure 4)[29] and furthermore the strongly donating nitrogen ligands will cause a blooming of the d_{z^2} orbital making this a better nucleophile. In view of these geometric considerations together with the experimental results concerning $[PtX(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$, **4b** and **4c**, with alkyl halides it seems plausible that in the case of these neutral complexes the S_N2 reaction involves attack of the CH_3X molecule at the platinum center. During a reaction with these substances it is likely therefore that incoming ligands approach (along the *z*-axis) from above or below the virtually flat square coordination plane. Using the neutral species **5a** and **5c** we have now obtained results (vide supra) which provide new and interesting information on the path of the alkyl halide addition to Pt(II). Furthermore the reaction of the neutral species **4b** and **4c** with MeOTf is an alternative synthetic route to the unusual arenonium type of complexes **6b** and **6c**.

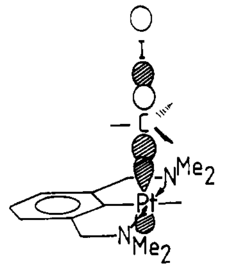

Figure 5. Interaction of the LUMO of MeI with the d_{z^2} orbital of the platinum.

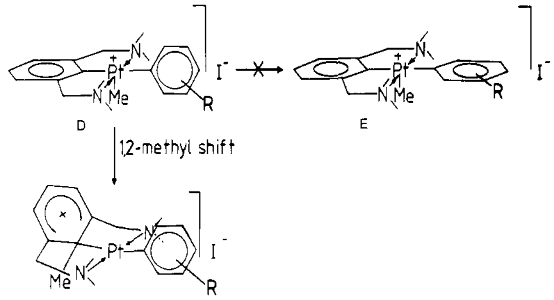

Figure 6. Reaction pathways as suggested for the reaction of MeI with **5a** and **5c**.

Before discussing the individual reactions in detail it is relevant to note that recently it was demonstrated that the d_{z^2} orbital is able to function as a donative interaction with a second metal being able to accept electron density.[30] Taking this into account it seems plausible to propose that in the reaction of $[PtBr(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ with MeI it is the metal complex that attacks the alkyl halide via the d_{z^2} orbital which is perpendicular to the coordination plane and so produces a polar transition state (cf. solvent effect). We consider that approach of the MeI will therefore most likely be in such a way as to first produce a Pt–C interaction. As the attack of the d_{z^2} orbital is progressing the C–I bond is weakened and polarized because the LUMO of MeI is an antibonding C–I σ orbital that is largely centered on the carbon atom. The barrier for this reaction is breaking of the C–I bond which generates a Pt^{IV}–Me bond in a five-coordinate cationic intermediate and an iodide anion that can subsequently move to the sixth site of the platinum center (Figure 5). However, the latter is not a prerequisite for the occurrence of the subsequent MeBr elimination reaction since Ettore et al. have suggested that elimination reactions from neutral Pt(IV) species can occur from a five-coordinate cationic intermediate.[31] Accordingly Pt–I formation may take place at a latter stage of the reaction. After formation of cationic B (see Figure 1) the steric constraints of the N,C,N′ ligand system now prevent subsequent stereoisomerization reactions and allow only either elimination of MeBr or reformation of MeI (the forward or backward reaction of eq 3).

The results of the reactions of both the *o*- and the *p*-tolyl platinum complexes with MeI, which in both cases afforded the exclusive formation of $[Pt(o\text{- or } p\text{-tolyl})(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]I$ as well as the observation that the *p*-tolyl derivation is unstable in solution, support the above mechanistic pathway. Again the first step is attack of the Pt d_{z^2} at the methyl carbon atom, which generates, after the C–I bond has been broken,

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[26] Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 423.

[27] Hall, T. L.; Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Dalton Trans.* **1980**, 1448.

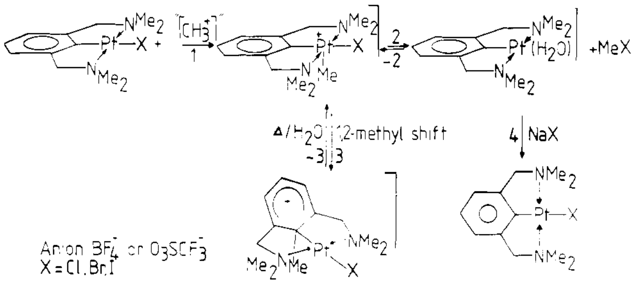
[28] Ferguson, G.; Pavez, M.; Monaghan, P. K.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1983**, 267.

[29] Terheijden, J.; van Koten, G.; Mul, P. W., unpublished results.

[30] van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *Inorg. Chem.* **1982**, *21*, 2026.

[31] Ettore, R. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 45.

Scheme I. Reaction Pathways of $[PtX(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (X = Cl, Br, I) and $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)]^+$ with MeOTf, MeX or CD_3I Explaining the Observed C–C Bond Making and Breaking Processes



the five-coordinate intermediate D (see Figure 6).

The possible reductive elimination of xylene (cf. MeBr in the above reaction) does not occur and instead the 1,2-methyl shift between Pt and the metal-bonded C(1) of the phenyl system of the terdentate ligand takes place, thus providing **5b** and **5d**. A reasonable explanation for the lack of xylene (ortho or para) elimination may be the fact that the rotation of the tolyl group around the Pt–C(13) axis is hindered.[16] Such a rotation by 90°, i.e., production of intermediate E (Figure 6), would be necessary in order to bring the tolyl LUMO in a favorable position for the methyl group to migrate from Pt to C(13)(tolyl) (cf. Figure 3a). Naturally therefore migration of the methyl group in the opposite direction across the Pt–C(1) bond is favored. As mentioned earlier, the aryl plane of the N,C,N′ terdentate ligand coincides with the platinum coordination plane and accordingly Me–C(1) bond formation with concomitant tilting of the aryl ring (vide infra) is a low-energy process. Elimination of $o,o'\text{-}(Me_2NCH_2)_2C_6H_3Me$ should then be the next step if it was not blocked because of the anchoring of the product by the coordination of the two side arms with nitrogen donor sites to platinum.

The importance of the nature of the anion in these arenonium complexes as well as the accessibility of a coordination site at the platinum center is demonstrated by difference in stability of the *o*- and *p*-tolyl derivatives. In the case of the *o*-tolyl derivative **5b**, which is very stable both in the solid and in solution ($CHCl_3$ or acetone), the ortho methyl and C(20)–methyl groups (see Figure 3) screen the platinum center for attack by the iodide anion.

In contrast in the *p*-tolyl derivatives **5d** and **5e** the platinum atoms are less well screened for such an attack. This is reflected in the difference in stability of both complexes in solution, i.e., the complex **5e** with the OTf anion, which is a poor nucleophile, is stable in both $CHCl_3$ and acetone whereas the corresponding I^- complex **5d** decomposes under elimination of the C–C coupled product $o,o'\text{-}(Me_2NCH_2)_2C_6H_3Me$. A plausible explanation for the elimination of the latter product is attack of the platinum center by I^- which destabilizes the Pt–N coordination. The observation that the reaction occurs faster in apolar solvents ($CHCl_3$) than in the polar solvents (acetone) is in line with the proposed mechanism which involves an apolar transition state.

So far we can explain our results of the reactions of the neutral platinum complexes with MeI with the aid of initially formed five-coordinate cationic intermediate which can rapidly react further via two pathways, either (1) reductive elimination (of MeBr in the case of **4b**) assisted by nucleophiles either in this stage or stabilizing the cationic species by forming the neutral derivatives or (2) 1,2-methyl shift across the Pt–C bond (favored in the case of **5b** and **5d** where (1) is blocked).

The reaction of **4a–c** with MeOTf provides evidence for both mechanisms being operative. Again the five-coordinate cationic intermediate B is formed. Reductive elimination of MeX afford the cationic complex **7** in minor amounts but the main product is the arenonium complex **6** suggesting that under these circumstances pathway (1) is favored. There is ample experimental evidence that the proposed five-coordinate intermediate and the arenonium species are in equilibrium with each other with the equilibrium position depending on temperature, the amount of alkyl halide, and the nature of the anions present. For example, excess of alkyl halide is necessary to push the equilibrium completely to the left (reactions −2, 3; Scheme I). In a separate experiment the arenonium complex **6c** was dissolved in an acetone-d_6/water mixture. Within 1 h small amounts of **7** and methyl iodide could be detected by ^1H NMR spectroscopy. This result further established earlier observations[13b] that the reversed reaction (reactions −3, 2) in which the arenonium species was refluxed for 48 h in acetone/H_2O afforded the cationic complex and MeI.[34] Furthermore heating the solution of the arenonium species in the presence of a good nucleophile (NaX, X = Cl, Br, I) gave, via the cationic intermediate, the neutral complex (reactions 3, 2, 4).[14] It is important to note that reaction 4 is an irreversible reaction. A solution of the *o*-tolyl platinum product **5b** is inert toward this latter reaction because the elimination of *o*-xylene is a blocked process. Finally, the isolation of the methyl-deuterated arenonium complex **6d** confirmed that the transferred methyl group originated from the methyl iodide reagent. The observation that the reaction of pure **6d** with nondeuterated MeI afforded the slow formation of the nondeuterated arenonium complex **6c** is further proof of the existence of equilibrium 2 and 3.

All our experimental results for reactions MeBr, MeI, and MeOTf with the neutral complexes **4a–c**, **5a**, and **5c** can be explained in terms of an S_N2 type of reaction with Pt–Me interaction established first. However, as suggested above, those reactions involving cationic $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)]OTf$ could proceed via initial oxidative addition to provide a five-coordinate intermediate with a Pt–X interaction established first. This is the route considered by Hoffmann et al. for which they calculated that the proposed methyl migration across the Pt–C(1) bond is assisted by tilting of the ring.[15] Although the general consideration of these calculations for the 1,2-methyl shift are likely to be valid for all intermediates related to B, it is apparent that for the *o*- and *p*-tolyl species formation of $[Pt(o\text{- or }p\text{-tolyl})(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]I$ cannot occur via initial Pt–I interaction as demanded by these author's mechanism. It should be noted, however, that their theoretical description of formation of a five-coordinate intermediate by attack of Me^+ on $[PtI(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ is analogous to our reaction of this latter complex with MeOTf and this reaction does in fact result in formation of the arenonium species.

In summary the reactions of **4a–c**, **5a**, and **5c** with various methylating reagents has provided new evidence regarding oxidative-addition and/or reductive-elimination pathways. In particular steric constraints both of the terdentate ligand and ligands trans to the Pt–C(1) bond strongly influence the available pathways for both these processes and as consequence these constraints lead to stabilization of the arenonium structures that may be visualized as reductive-elimination intermediates. Furthermore the terdentate nature of the ligand system has allowed us to draw conclusions concerning the mechanism of MeX addition of which the following are the most important aspects: (1) MeI (or MeOTf, MeBr) addition for the neutral complexes occurs via Pt–Me interaction, (2) reaction of our complexes with MeI (or MeOTf, MeBr) occurs via an S_N2 type of mechanism, (3) a 1,2-methyl shift is possible across a Pt–C(1) bond.

In a forthcoming paper we will describe further reactions of $[PtR(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (R = aryl derivatives) or $[PtX(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (X = Cl, Br, I) with oxidants like halogens or Cu(II) salts,[32] where the stability of the Pt(IV) product is shown to depend on the nature of the R group trans to the phenyl C(1) atom of the terdentate ligand.

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(32) A short communication has already been published: Terheijden, J.; van Koten, G.; de Booys, J. L.; Ubbels, H. J. C.; Stam, C. H. *Organometallics* **1983**, *2*, 1882.

(33) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(34) Under these reaction conditions MeI is removed from the reaction mixture.

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Registry No. 3, 83311-98-2; **4a**, 82112-96-7; **4b**, 67507-09-9; **4c**, 82112-97-8; **5a**, 95532-50-6; **5b**, 95532-53-9; **5c**, 95532-51-7; **5d**, 95532-54-0; **5e**, 95552-59-3; **6a**, 95532-56-2; **6b**, 95532-58-4; **6c**, 95532-59-5; **6d**, 95532-61-9; **7**, 95532-52-8; *o,o'*-$(Me_2NCH_2)_2C_6H_3Me$, 95532-49-3; MeI, 74-88-4; CD_3I, 865-50-9; MeBr, 74-83-9; MeOTf, 333-27-7; *o*-tolyllithium, 6699-93-0; *p*-tolyllithium, 2417-95-0.

Supplementary Material Available: Observed and calculated structure factors for **5b**, Tables I–IV and VI for positional and thermal parameters, bond distances, bond angles, and torsion angles for **5b**, and Figure 7, an ORTEP drawing giving a view of **5b** (27 pages). Ordering information is given on any current masthead page.

Investigations of the Mechanism of the Rh/Cu- and Rh-Catalyzed Oxidation of Terminal Olefins with O_2

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Abstract: The mechanism of the Rh(III)-catalyzed oxidation of 1-hexene to 2-hexanone, both with and without a Cu(II) co-catalyst, is investigated. In the absence of Cu(II), only one oxygen atom of dioxygen is found to be incorporated into ketone product. This contrasts with the previously reported observation that in the presence of the Cu(II) co-catalyst both oxygen atoms of O_2 are incorporated into product. Similarly, the Rh(III) catalyst without Cu(II) isomerizes 1-hexene to a large extent, in contrast to the previously reported Rh/Cu catalyst system. Both acetone and water are found to be produced continuously when isopropyl alcohol is the solvent in the absence of Cu(II), while neither are formed continuously when Cu(II) is present. Furthermore, it is shown that H_2O_2 and *t*-BuOOH may be used as the 1-hexene oxidant under anaerobic conditions in the presence or absence of Cu(II), producing 2-ketone. These observations are incorporated into tentative mechanisms which specify key roles for copper that lead to differences in reactivity.

Transition-metal-catalyzed oxidations of hydrocarbons generally exhibit poor product specificity due to free radical mechanisms predominating in these reactions. Very often the only role of the metal complex is to initiate free radical autoxidation by decomposing trace quantities of peroxides.[1] Improved product specificity may be obtained when free radical processes are avoided, as evidenced by the groups 5 and 6 metal-catalyzed olefin epoxidation reactions[2] (using peroxides) and the Pd/Cu-cocatalyzed Wacker process.[3] These latter reactions are more specific because the principle bond-breaking and -reforming steps occur at the metal catalyst center. A relatively new class of transition-metal-catalyzed olefin oxidations with O_2 have been reported which also appear to involve the metal-centered reaction between oxidant and olefin,[4,5] while avoiding the Wacker-type hydroxometalation process. The mechanism suggested for these oxidations involves the consecutive coordination of olefin and O_2 to a rhodium(I) catalyst, a rearrangement to a peroxymetallocycle, and a decomposition to primarily 2-ketone. Most noteworthy among these is the homogeneous oxidation studied by Mimoun and co-workers,[5] which utilizes 98% of the oxygen atoms in dioxygen for 2-ketone production. This system is unique for its extraordinary selectivity as well as its activity, stability, and dependence on alcohol solvents. Another feature of the Rh(III)/Cu(II) systems is the zero-order dependence of its rate law on P_{O_2}.

We have recently reported a new characterization of the rhodium catalyst for this Rh/Cu olefin oxidation at 40 °C and implicated the rhodium(III) chloride complex produced in eq 1.[6]

$$RhCl_3 + Cu^{2+} + {}^1/_2(CH_3)_2CHOH \rightarrow RhCl_2^+ + CuCl(s) + {}^1/_2(CH_3)_2CO + H^+ \quad (1)$$

This is evidenced by the stoichiometry of eq 1 in acetone, the observation of an induction period in the 1-hexene oxidation when employing $[Rh(CO)_2Cl]_2$ as the catalyst precursor, and the need for 3 or more equivalents of chloride in the initial mixtures for maximum activity (at both 40 °C[5] and 70 °C[6]). Equation 1 is not meant to suggest the only role for Cu(II) in this system is the precipitation of chloride. In fact, the familar redox chemistry of copper ion requires consideration of its role in any oxidation occurring in its presence.

We have studied the $RhCl_3{\cdot}3H_2O$-catalyzed olefin oxidation in the presence and absence of Cu(II) in an attempt to more completely elucidate the roles of this co-ion in the more complex Rh(III)/Cu(II) system. This reaction without Cu(II) was reported to proceed at vastly reduced rates, with only a few turnovers and with only 6% selectivity.[5] Our characterization of the $RhCl_3$-catalyzed reaction includes an examination of peroxides as olefin oxidants. The results are incorporated in specific proposals for the mechanisms of the $RhCl_3$- and Rh(III)/Cu(II)-catalyzed oxidations of olefins by O_2.

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