Stabilization of high oxidation states by rigid bidentate nitrogen ligands: synthesis and characterization of diorgano- and triorganopalladium(IV) and cationic triorganoplatinum(IV) complexes

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Stabilization of High Oxidation States by Rigid Bidentate Nitrogen Ligands: Synthesis and Characterization of Diorgano- and Triorgano palladium(IV) and Cationic Triorgano platinum(IV) Complexes

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Introduction

The existence of triorgano palladium(IV) complexes, as intermediates in the reductive elimination from dimethylbisis(phosphine)palladium(II) complexes in the presence of iodomethane, was proposed by Stille and Milstein in 1979 (Scheme 1). Stable triorgano palladium(IV) complexes containing phosphine ligands could however not be obtained and it was not before 1986 that the first hydrocarbylpalladium(IV) complex was isolated and characterized. This complex contained the bidentate nitrogen ligand 2,2'-bipyridine (bpy), and after this report other examples of (stable) triorgano palladium(IV) complexes with bidentate and tridentate nitrogen ligands were followed rapidly. The (in situ) synthesis of palladium(IV) complexes allowed a study of reductive elimination from this type of complexes, and a dissociative mechanism, initiated by the loss of the coordinated halide, has been demonstrated.

In contrast to the lability of the organopalladium(IV) complexes, the analogous organoplatinum(IV) complexes are far more kinetically stable and as a consequence numerous examples of organoplatinum(IV) complexes containing phosphine and (bidentate) nitrogen ligands were obtained.

Dimethylpalladium(II) and (dimethyl)platinum(II) complexes containing the rigid bidentate nitrogen ligands bis(p-toly1imino)acenaphthene (pTol-BIAN) and bis(phenylimino)camphane (Ph-BIC) readily undergo oxidative addition of a variety of (organic) halides, to give the corresponding octahedral diorgano- and triorgano palladium(IV) and -platinum(IV) complexes. The palladium complexes PdMe₂(R)X[N] (RX = MeI, PhCH₂Br; NN = pTol-BIAN, Ph-BIC) were synthesized and isolated at 20 °C and were fully characterized. Reductive elimination from these complexes in chloroform obeyed first order kinetics and was slower than for other reported triorgano palladium(IV) complexes. The new diorgano palladium(IV) complexes PdMe₂₁₂(NN), synthesized via oxidative addition of diiodine to PdMe₂₁₁(NN) are much less stable than the triorgano palladium(IV) complexes studied. PtMe₂(R)(pTol-BIAN) (RX = MeI, PhCH₂Br, EtI, PhCH₂(Me)Br, MeCl[O]Cl, I₂) and PtMe₂(R)(pTol-BIAN) (RX = MeI, PhCH₂Br, I₂) were obtained via oxidative addition to PtMe₂(pTol-BIAN) and PtMe[R](pTol-BIAN), respectively. Reaction of PtMe₂(I) with AgSO₃CF₃ led to the formation of remarkably stable five-coordinate [PtMe₂(R)pTol-BIAN]SO₃CF₃ complexes (R = Me, CH₂Ph, C(O)Me), which were fully characterized and can be isolated and kept at 20 °C. The complexes are very stable toward reductive elimination, e.g. in CDCl₃ and CD₃CN [PtMe₂(CH₂Ph)(phen)]SO₃CF₃ was also stable at 50 °C in CD₃CN for at least 40 h, whereas [PtMe₂(CH₂Ph)(pTol-DAB)]SO₃CF₃ gave 30-35% reductive elimination under these conditions. From the observed order of reductive elimination from Pd(IV) and Pt(IV) complexes the rigidity of the pTol-BIAN and Ph-BIC ligands appears to be the major factor in determining the stability of these complexes.


are known. Reductive elimination of ethane from PtMe$_3$X-(PR$_3$)$_2$ complexes was shown to occur via loss of one coordinated phosphine prior to reductive elimination, whereas decomposition of PtMe$_3$(bpy) occurred at higher temperatures and resulted in the formation of methane via $\alpha$-elimination. It was shown that the rate of reductive elimination from organoplatinum(IV) complexes increased when a coordinatively unsaturated species was generated, e.g. by dehalogenation with silver salts.

In view of the observed catalytic activity of Pd(1-BIAN) complexes, i.e. complexes containing the cis-fixed bidentate nitrogen ligand bis(arylmino)acenaphthene, in cross-coupling reactions between organic halides and organo-
metallic reagents, and the possible intermediacy of triorganopalladium(IV) complexes in this process, we were interested in the synthesis and stability of palladium(IV) and platinum(IV) complexes containing such rigid bidentate nitrogen ligands. In several cases homocoupled products were formed in the catalytic reactions and reductive elimination from complexes of the type PdIV. R$_2$R'X(L)$_2$ can in principle lead to the formation of cross-coupled (R-R') or homocoupled (R-R) products. Therefore we investigated oxidative addition of a variety of (organic) halides to the model complexes MMeN($N,N',N'$-tetramethylethylenediamine) and from the ratio of the Pd-Me to the Me@Tol signals (the latter represent 6 H total in any instance). Both methods gave Pd(II):Pd(IV) of these signals and the known initial concentration, complexes were derived from the integrals of the methyl signals of exocyclic imine functionalities. As far as the presence of conjugate imine functionalities is concerned, the Ar-BIAN and Ph-BIC ligands resemble the 1,4-diaza-1,3-butadiene (R-DAB) ligands, which have often been used to stabilize metals in a low oxidation state because of their $\pi$-accepting properties. We report here that Ar-BIAN and Ph-BIC ligands are capable of stabilizing organopalladium(IV) and -platinum(IV) complexes and the first examples of diorganopalladium(IV) complexes and of highly stable five-coordinate cationic triorganoplatinum(IV) complexes will be presented.

Experimental Section

All manipulations were carried out in an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried and distilled before use. $^1$H NMR spectra were recorded on a Bruker AMX 300 (300.13-MHz) and a Bruker AC 100 (100.13-MHz) spectrometer, and $^{13}$C NMR spectra, on a Bruker AMX 300 spectrometer (75.48 MHz). Chemical shift values are in ppm relative to TMS as an external standard with high frequency shifts positive. $^{39}$F (94.20-MHz) and $^{31}$P (40.53-MHz) NMR spectra were recorded on a Bruker AC 100 spectrometer, relative to CFCl$_3$ and 85% H$_3$PO$_4$ as external standards, respectively. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Elemental analyses were carried out by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. Pd(Me)(Cl(COD)), PdCl$_3$(SMes)$_2$, Ar-BIAN, and Ph-BIC were synthesized by following reported procedures.

Kinetic measurements of reductive eliminations from Pd(IV) complexes were carried out by $^1$H NMR in sealed tubes, containing 0.050–0.10 M solutions of the organopalladium complex in CCl$_4$. Relative and absolute concentrations of Pd(IV) and Pd(II) complexes were derived from the integrals of the methyl signals of the Pd–Me groups of the respective compounds from the ratio Pd(II):Pd(IV) of these signals and the known initial concentration, and from the ratio of the Pd–Me to the M(pTol) signals (the latter represent 6 H total in any instance). Both methods gave the same $k$ values within experimental error (see Table 3). All experiments were followed through at least 3 to 4 half-lives, except for 4a at 30 and 55 °C, which were followed during ca. 2 half-lives.

PdMe$_2$(pTol-BIAN), 1. To a solution of 0.26 g of Pd(Me)-Cl(COD) (0.98 mmol) in 30 mL of THF, cooled to −70 °C, was added dropwise a mixture of 10 mL of THF and 0.90 mL of a 1.6 M methylmethylbenzene solution in diethyl ether (1.4 mmol) and the mixture stirred at −70 °C. After 1.5 h 100 mL of tert-butyl bromide (0.89 mmol) was added and the mixture stirred 30 min at −70 °C. Then 0.37 g of pTol-BIAN (1.03 mmol) was added, and the mixture was stirred at −70 °C for 5 min and then slowly warmed to 20 °C (ca. 1 h). The solution was filtered through Celite filter aid, the residue washed with THF (2 × 15 mL), and the solution evaporated to 5 mL. The product was precipitated by the addition of hexane (20 mL), washed with hexane (3 × 10 mL), and dried in vacuo, yielding 0.40 g of a greenish-brown solid (82%). Anal. Found (cared) for C$_{22}$H$_{39}$N$_2$Pd: C, 67.19 (67.68); H, 4.83 (5.28); N, 5.20 (5.64).
PtMe₂(SMe₂)₂ was synthesized by a modified literature procedure. To a solution of 3.43 g of K₂PtCl₆ (8.39 mmol) in 60 mL of degassed water, the solution was added 1.7 mL of dimethyl sulfide (23.3 mmol) and the mixture heated to 80 °C. After 45 min the yellow suspension was cooled to room temperature and extracted with dichloromethane (3 × 50 mL). The combined dichloromethane layers were dried on MgSO₄, filtered, and evaporated to dryness. The product was dried in vacuo, giving 3.01 g of PtCl₃(SMe₂)₂ as a yellow powder (93%).

PtMe₂(μ-SMe₂)₂ was synthesized from PtCl₃(SMe₂)₂ and MeLi, as reported before.

Pt(Me)(SMe₂)₂. To a solution of 0.40 g of PtCl₃(SMe₂)₂ (1.02 mmol) in 50 mL of diethyl ether, cooled in ice/water, was added dropwise 4 mL of a 0.88 M solution of MeMgI in diethyl ether (2.32 mmol) and the mixture was stirred at 0 °C. After 2 h the colorless solution was hydrolyzed with 20 mL of saturated NH₄Cl solution in water. The ether layer was separated and the water layer extracted with dichloromethane (3 × 50 mL). The combined dichloromethane layers were dried on MgSO₄, filtered, and evaporated to dryness. The product was dried in vacuo, giving 0.30 g of a brown solid (64%).

PtMe₂(tol-BIAN), 6. A mixture of 0.55 g of PtMe₂(SMe₂)₂ (0.96 mmol) and 0.75 g of Pt(tol-BIAN) (2.03 mmol) in 50 mL of acetone was stirred overnight at 20 °C. After 16 h the green solution was evaporated to dryness and the product washed with diethyl ether/hexane (1:1, 20 mL), and dried in vacuo, yielding 192 mg of an orange-red product (72%).

Anal. Found (calcd) for C₃₅H₃₆BrN₂Pt: C, 51.2, 51.1, 51.0, 50.9; H, 4.75, 4.76, 4.76, 4.75.

PtMe₂(tol-DAB) (78%) and PtMe₂(phen) (84%) were obtained in the same way as 6.

Pt(Me)(SMe₂)₂. To a solution of 16.22 mg of Pt(Me)(SMe₂)₂ (0.35 mmol) in 10 mL of dichloromethane was added 139.2 mg of Pt(tol-BIAN) (0.39 mmol) and the mixture was stirred at 20 °C. After 5 h the solution was filtered through Celite filter aid and the residue was washed with dichloromethane (3 × 5 mL). The combined dichloromethane layers were washed with 5 mL of diethyl ether and dried in vacuo, yielding 210 mg of a dark green complex (86%).

Anal. Found (calcd) for C₃₀H₂₉BrN₂Pt: C, 57.11 (57.43); H, 4.04 (4.48); N, 4.82 (4.78).

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Organopalladium (IV) and Platinum (IV) Complexes

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\[ \text{[OC-6-34]} \text{PtMe}_2\text{(CO)}\text{MeCl(pTol-BIAN), 9a (orange, 75%)} \]  
Anal. Found (calcd) for C_{16}H_{20}ClN_{2}Pt: C, 53.48 (54.28); H, 4.18 (4.40); N, 6.42 (6.22).

\[ \text{[OC-6-15]} \text{PtMe}_2\text{(pTol-BIAN), 9f (brown, 82%)} \]  
Anal. Found (calcd) for C_{16}H_{20}N_{2}Pt: C, 73.8 (73.8); N, 9.6 (9.6); S, 3.8 (3.8); NMR (CDCl_3), \( \delta \): 8.32 (J(Pt-H) = 27.4 Hz), N=C-H 7.0-7.5 m (8 H), CH_3 2.18 d (8 J(Pt-H) = 17.7 Hz), Pt-CH_3 1.37 s (6 J(Pt-H) = 27.4 Hz), Pt-CH_2 CO 3.52 d (8 J(Pt-H) = 76.7 Hz), H_2 7.48 d (8 J(Pt-H) = 76.7 Hz), Pt-C 129.0, 128.8, 128.4, 124.5, 87.3 NMR (CDCl_3), \( \delta \): 8.32 (J(Pt-H) = 27.4 Hz), N=C-H 7.0-7.5 m (8 H), CH_3 2.18 d (8 J(Pt-H) = 17.7 Hz), Pt-CH_3 1.37 s (6 J(Pt-H) = 27.4 Hz), Pt-CH_2 CO 3.52 d (8 J(Pt-H) = 76.7 Hz), H_2 7.48 d (8 J(Pt-H) = 76.7 Hz), Pt-C 129.0, 128.8, 128.4, 124.5, 87.3

[PtBrMe_2(PhCH_2)(pTol-DAB), 10a], was obtained from the reaction of BrMe_2(pTol-DAB) and AgSO_3CF_3 in 88% yield, similar to the synthesis of complexes 11. \( \text{H} \) NMR (CDCl_3), \( \delta \): 8.37 (J(Pt-H) = 27.4 Hz), N=C-H 7.0-7.5 m (8 H), CH_3 2.18 d (8 J(Pt-H) = 17.7 Hz), Pt-CH_3 1.37 s (6 J(Pt-H) = 27.4 Hz), Pt-CH_2 CO 3.52 d (8 J(Pt-H) = 76.7 Hz), H_2 7.48 d (8 J(Pt-H) = 76.7 Hz), Pt-C 129.0, 128.8, 128.4, 124.5, 87.3

Results

Synthesis of Dimethylpalladium (II) Complexes 1–3. PdMe_2(NN) complexes 1–3 containing Ar-BIAN or Ph-BIC ligands were synthesized in good yields (73–82%), starting from Pd(Me)Cl(COD) (COD = (Z,Z)-1,5-cyclooctadiene) and halide-free methyl lithium (eq 1). The reaction was monitored by \( ^1H \) NMR and lH NMR spectroscopy (Tables 1–3).

\[ \text{(1)} \]  
\[ \text{(2)} \]  
\[ \text{(3)} \]  

of PdMe₂(R)X(NN) complexes 4 and 5 was apparent from NMR spectroscopic and analytical data (Tables 1 and 2): in ¹H (¹³C) NMR spectroscopy the Pd–Me resonances shifted from ca. 0 (–6 ppm) to ca. 1.5 (20–25 ppm), in agreement with the observed NMR data of reported triorganopalladium(IV) complexes. In analogy to the reported triorganopalladium complexes with bidentate NN ligands, a fac geometry was assigned to the complexes 4 and 5, on the basis of the comparable ¹H and ¹³C NMR data.

Apart from a major isomer of PdMe₂(Ph-BIAN), 4a, having ¹H NMR resonances at 1.51 and 1.39 ppm, a small amount (5–10%) of another isomer was present, which appeared from the observation of resonances at 1.37 and 1.12 ppm in a 2:1 ratio. This product can either be the fac-PdMe₂Y(pTol-BIAN) complex (where Y is Cl or a solvent molecule) or mer-PdMe₂(pTol-BIAN). The presence of this second isomer also appeared from the ¹³C NMR spectrum, where two small resonances are observed at 19.56 and 18.61 ppm in a ratio of approximately 2:1. Reaction of iodomethane with PdMe₂(Ph-BIC), 3, gave a mixture of two isomeric PdMe₂(Ph-BIC) complexes 5a in a ratio of 84:16, which are most likely the [OC-6-44-A] and [OC-6-44-C] isomers, both having a fac geometry.

Table 1. ¹H NMR Data for the Organo–Pd(II) and Organo–Pd(IV) Complexes 1, 2, and 4

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Table 2. ¹³C NMR Data for the Organo–Pd(II) and Organo–Pd(IV) Complexes 1, 2, and 4

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* Recorded at 300.13 MHz in CDC1₃ at 20 °C. The adopted numbering scheme for Pd-Tol-BIAN is shown in Table 5. According to IUPAC rules the isomer designators fac and mer should not be used for nomenclature. Throughout this paper the systematic names will be given in the figures, but for convenience in the text fac and mer will be used when this does not cause any confusion: Leigh, G. J., Ed. IUPAC Nomenclature of Inorganic Chemistry. Recommendations 1990; Blackwell Scientific Publications: Oxford, U.K., 1990; pp 143–206. (b) The aromatic groups of Ar-BIAN ligands are orientated out of the coordination plane, bringing the ortho substituents (e.g. H₃) in the proximity of the axial substituents: cf. references 15c and 16. van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L. Inorg. Chem., in press.
was also observed for Hg at PdBrMe(CH2=CH2-p-Br)(phen). Interestingly, a small Pd–CH2Ph resonance is observed at 3.11 ppm (ca. 9% relative to the major isomer), which might be due to the rotameric complex having the phenyl ring of the benzyl group oriented toward the methyl ligands.

PdMe2(Ph-BIC), 2, reacted with benzy1 bromide to give PdBrMe2(CH2Ph)(Ph-BIC), 5b, which occurred as a mixture of two isomers in a 3:1 ratio. From 1H NMR data it appears that the benzyl group occupies an axial position in the major isomer and the minor isomer contains a benzyl group in the equatorial plane, in analogy to complexes 4b. There are two possible isomers for the major product and four for the minor product, but the spectroscopic data give no further evidence as to which of the isomers are formed.

Oxidative addition of diiodine to PdMe2(NN) complexes 1 and 3 in CDCl3 at 20 °C led to the formation of PdMe2(NN) complexes 4 and 5f which are the first examples of spectroscopically characterized diorganopalladium(IV) species containing (simple) hydrocarbyl groups (bis-(perfluorophenyl)palladium(IV) compounds are known). The complexes are rather unstable and decompose within 2 h at 20 °C in solution or upon attempted isolation by evaporation of the solvent. From the observed symmetrical pattern in 1H NMR of PdMe2I(pTol-BIAN), 4f, formation of the OC-6-13 isomer, via trans oxidative addition of diiodine, was derived. The same structure is assigned to the major isomer of PdMe2(Ph-BIC), 5f, but 24% of another isomer [(OC-6-42)- or (OC-6-43)-5f] was also formed in this case.

Oxidative addition of acetyl chloride to PdMe2(pTol-BIAN), 1, did not lead to an observable triorganopalladium(IV) complex, but instead acetone and Pd(Me)Cl(pTol-BIAN) were observed as the only products. This finding suggests oxidative addition of acetyl chloride to 1 followed by rapid reductive elimination, analogous to the observations made for PdMe2(tmeda) complexes. PdMe2(o,o′-iPr2C6H4-BIAN), 2, reacted much slower than 1 or 3 with benzyl bromide: after 10 min in CDCl3 no reaction had occurred and after 1.5 h 2 was still present as the main species in solution (>80%). After 5 h a lot of decomposition had occurred (precipitate) and the major products in solution were PdBrMe(o,o′-iPr2C6H4-BIAN) and free o,o′-iPr2C6H4-BIAN. On the other hand, iodomethane reacted instantaneously with 2 in CDCl3 at 20 °C, but the only product observed was Pd(Me)I(o,o′-iPr2C6H4-BIAN), without observation of a triorganopalladium(IV) intermediate.

Table 3. First Order Rate Constants for the Reductive Elimination from Triorganopalladium(IV) Complexes 4 and 5

<table>
<thead>
<tr>
<th>Complex</th>
<th>T (°C)</th>
<th>log k (s-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdMe2(pTol-BIAN)</td>
<td>4a</td>
<td>5.2</td>
</tr>
<tr>
<td>PdMe2(Ph-BIC)</td>
<td>5a</td>
<td>7.4</td>
</tr>
<tr>
<td>PdBrMe2(CH2Ph)(pTol-BIAN)</td>
<td>4b</td>
<td>7.4</td>
</tr>
</tbody>
</table>

* The reactions were monitored by 1H NMR spectroscopy of 0.05–0.10 M solutions in CDCl3, during 15–30 h. The accuracy of the rate constants is ±5%. k = 60 × 10 kJ-mol-1.

Scheme 2

Reductive Elimination from PdIVMe2(R)X(NN) Complexes 4 and 5. The triorganopalladium(IV) complexes 4 and 5 containing pTol-BIAN and Ph-BIC ligands are quite stable in solution at 20 °C. The reductive elimination reactions, as monitored by 1H NMR spectroscopy, obeyed first order kinetics and the observed rate constants were in the range 10⁻⁴ to 10⁻² s⁻¹ (Table 3). Chloroform was used as solvent, because both the starting material and the expected products were soluble in this solvent, whereas in acetone or benzene the palladium(II) complexes were not very soluble.

The reductive elimination from PdMe2(pTol-BIAN), 4a, is rather unselective since not only Pd(Me)I(pTol-BIAN), resulting from ethane elimination is formed, but also some Pd(µCl)(Me)pTol-BIAN) in (10–20%) in all cases. As it was shown that Pd(Me)I(pTol-BIAN) does not react with CDCl3 to give Pd(Me)Cl(pTol-BIAN), the formation of Pd(µCl)(pTol-BIAN) is most likely due to reductive elimination of iodomethane from PdMe2(pTol-BIAN), 4a, followed by reaction of PdMe2(pTol-BIAN), 1, with CDCl3 (vide supra). When the reductive elimination of 4a was carried out at 20 °C, iodomethane was indeed observed in the spectrum, in an amount approximately equal to Pd(Me)Cl(pTol-BIAN) (Scheme 2). Reductive elimination of MeBr, besides ethane, from PdBrMe2(CH2C(0)Ph)(NN)(NN = biphenyl) has been observed.

The reductive elimination from PdMe2(Ph-BIC), 5a, proceeds at 40 °C with a rate constant comparable to that of 4a. The complex is quite stable at 20 °C in CDCl3, but after reaction with silver trifluoromethanesulfonate in CDCl3 at 20 °C, followed after 5 min by sodium iodide, the only organometallic product obtained is Pd(µCl)(Ph-BIC). PdBrMe2(CH2Ph)(pTol-BIAN), 4b, is even more stable than 4a at 20 °C in CDCl3 solution. After 48 h still 85% of the starting palladium(IV) complex is present and after 7 days a mixture of Pd(µBr)(µ-CH2Ph)(pTol-BIAN), Pd(µBr)(Me)(pTol-BIAN), and PdBr(CH2Ph)(pTol-BIAN) in a ratio of 40:35:25 is obtained. At 50 °C the reductive elimination occurs with a first order rate constant of 7.4 × 10⁻³ s⁻¹ and is rather unselective, giving about 80% ethane and 40% ethylbenzene elimination, whereas in all the other cases reported there is a more pronounced preference for ethane elimination from isolated PdBrMe2(CH2Ph)(NN) complexes.

Synthesis of (Di)methylplatinum(II) Complexes 6–8. Dimethylplatinum(II) complexes containing Ar-
Table 4. \(^1\)H NMR Data for the Organo–Pt(II) and Organo–Pt(IV)(Ar-BIAN) Complexes 6–10*  

<table>
<thead>
<tr>
<th></th>
<th>H1</th>
<th>H4</th>
<th>H5</th>
<th>H6</th>
<th>H10</th>
<th>H12</th>
<th>Pt–R</th>
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<tbody>
<tr>
<td>PtMe₂</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>6</td>
<td>7.05 d</td>
<td>7.32 pst</td>
<td>8.18 d</td>
<td>7.25 d</td>
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<td>2.50 s</td>
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<td>7</td>
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<td>7.3 m</td>
<td>7.6 m</td>
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<td>10</td>
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<td>8.3 Hz</td>
<td>(4 H)</td>
<td>(6 H)</td>
<td>2.51 s</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>7.47 pst</td>
<td>8.07 d</td>
<td>7.81 d</td>
<td>7.35 d</td>
<td>2.50 s</td>
<td>1.15 s (72.2 Hz), Meeq</td>
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<td>9e</td>
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<td>8.0 Hz</td>
<td>8.0 Hz</td>
<td>0.97 s (73.4 Hz), Meex</td>
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<td></td>
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<tr>
<td>PhCH₂Br + 6</td>
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<td>7.4 m</td>
<td>8.07 d</td>
<td>6.20 d</td>
<td>7.19 m</td>
<td>2.47 s</td>
<td>1.18 s (71.7 Hz), Me</td>
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<tr>
<td>9b</td>
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<td>(4 H)</td>
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<tr>
<td>Et³</td>
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<td>7.5 m</td>
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<td>7.07 dd</td>
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<td>1.15 s (73.0 Hz), Me</td>
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<td>(4 H)</td>
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<td>1.64 q (74.3 Hz), Me</td>
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<tr>
<td>PhCH(Me)Br + 6</td>
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<td>f</td>
<td>f</td>
<td>5.65 dd'</td>
<td>f</td>
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<td>1.31 s (72.6 Hz), Me</td>
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<td>8.07 d</td>
<td>7.41 d</td>
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<td>8.1 Hz</td>
<td>8.1 Hz</td>
<td></td>
<td></td>
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<td>h</td>
<td>8.16 d</td>
<td>8.05 dd</td>
<td>7.11 d</td>
<td>2.52 br</td>
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<td>8.0 Hz</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10b</td>
<td>7.18 d</td>
<td>8.1 d</td>
<td>8.1 d</td>
<td>7.3–7.6 m</td>
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<td></td>
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<tr>
<td>PhCH₂Br + 8</td>
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<td>i</td>
<td>8.17 d</td>
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<td>1.84 s (69.8 Hz), Me</td>
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<tr>
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<td>2.53 m</td>
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</table>

* Recorded at 300.13 MHz in CDCl₃ at 20 °C. See Table 5 for the adopted numbering scheme of pTol-BIAN. For o,o′-i-Pr₂C₂H₄-BIAN the same numbering scheme is applied. Coupling constants (Hz) are given below the chemical shifts, and \(^{191}\)Pt–H coupling constants for (Ar-BIAN) complexes (Ar = Ph, BIAN) were conveniently measured, as was reported previously.  

BIAN, pTol-DAB, and phen ligands were conveniently synthesized from [PtMe₂(μ-SMe₂)₂] (eq 3). The PtMe₂-(Ar-BIAN) complexes (Ar = pTol, 6; o,o′-i-Pr₂C₂H₄-BIAN, 7) are dark green solids and were analyzed by elemental analysis and \(^{1}H\) and \(^{13}C\) NMR spectroscopy (Tables 4 and 5).

The reactions with iodomethane, benzyl bromide, acetyl chloride, and diiodine were completed within 15 min, as was reported previously.  

Oxidative Addition of (Organic) Halides to PtMe₂-(pTol-BIAN), 6. PtMe₃(pTol-BIAN), 6, reacted with a variety of (organic) halides to give stable diorgano- and triorgano-iodine (IV) complexes 9 (eq 5).  

The product 8 could easily be purified and was obtained analytically pure, which shows that isolated PtMe₂(SMe₂)₂ can be successfully used as starting material for the synthesis of PtMeᴵᴵᴵ₃ complexes, despite the fact that some decomposition might occur during isolation as was reported previously.
could be judged from the color change of the solution from dark green to orange-red. Reactions with iodoethane and 1-phenyl-1-bromoethane were slower and required several hours to go to completion. The Pt(IV) complexes 9 all showed correct analytical data and were analyzed by ¹H and ¹³C NMR spectroscopy (Tables 4 and 5).

The products formed have a fac geometry,²¹b as can be seen from the observed Pt–Me coupling constants, which are in the range 71–77 Hz,²⁵ and from comparison with known triorganoplatinum(IV) complexes that all have a fac geometry. Furthermore, in ¹H NMR of all complexes the doublet due to two of the protons H₂ has shifted to approximately 7.8 ppm, which is indicative of a neighboring halide atom.²¹b

(²⁵) Pt–Me coupling constants are strongly influenced by the ligand trans to the methyl group: Me (trans to halogen) 67–75 Hz, Me (trans to P) 56–69 Hz, Me (trans to carbon ligand) 49–44 Hz, and Me (trans to imine-N) 68–73 Hz. (a) Clegg, D. E.; Hall, J. R.; Swie, G. A. J. Organomet. Chem. 1972, 38, 403. (b) Reference 6b.

The complexes PtMe₂I(pTol-BIAN), 9a, PtMe₂Cl(O)-Me(pTol-BIAN), 9e, and PtMe₂I(pTol-BIAN), 9f, are formed as a single isomer: in ¹H and ¹³C NMR a single
Pt–Me resonance is observed for 9e and 9f and two signals in a ratio of 2:1 for 9a. In $^{13}$C $(H)$ NMR of 9a and 9e two resonances are observed for $\text{C}(H)_2$ and $\text{C}(H)_{10}$ due to the inequivalence on both sides of the coordination plane, whereas the atoms that lie in the coordination plane (e.g. $\text{C}(H)_{8,4,12}$ and $\text{C}(H)_{8,11}$) give one resonance. All these data are in agreement with the formation of a $C_1$-symmetric isomer. For $\text{PtBrMe}_2(\text{CH(Me)}_2\text{Ph})(\text{pTol-BIAN})$, 9d, the observation of two sets of signals for the ligand and two Pt–Me resonances in $^1H$ and $^{13}$C NMR and a doublet at 5.65 ppm, due to anisotropic shielding of $\text{H}_2$ by the phenyl ring of 1-phenylethyl, point at the formation of the 1-phenylethyl group in an axial position.

The complexes $\text{PtBrMe}_2(\text{CH(Me)}_2\text{Ph})(\text{pTol-BIAN})$, 9b, and $\text{PtMe}_2(\text{Et})(\text{pTol-BIAN})$, 9c, occur as mixtures of two isomers, in ratios of 57:13 and 68:32, respectively. In these cases the $C_1$ symmetry of the major $[OC-6-34]$ isomers is also reflected in the observation of one resonance for both methylene protons in $^1H$ NMR (i.e. one singlet for Pt–$\text{CH}_2\text{Ph}$ and one quartet for Pt–$\text{CH}_2\text{CH}_3$), with Pt satellites.

For the $C_1$-symmetric $[OC-6-43]$ isomers the methylene protons are diastereotopic and for 9b two doublets are observed (AA'X spin system), while for complex 9c a doublet of quadruplets is observed for one of the protons (AA'B3X spin system) and the signal of the other proton is overlapped by the methylene signal of the major isomer at 1.64 ppm.

The large $\beta$(H–C1)2 resonance of $\text{PtMe}_2(o,o'$-$\text{iPr}_2\text{C}_6\text{H}_3$-BIAN), 10, reacted slowly with benzyl bromide. No observable reaction occurred within 1 h and after 4 h still mainly 7 was present in the reaction mixture ($>75\%$). After 2 days all of the starting complex had remained intact ($>90\%$). The product could not be isolated, and the only product detected was a mixture of two C1-symmetric isomers 10a (OC-6-13 and OC-6-22) in a ratio of 1:1. After both reactions 9e is regained without any observable reaction within 1 h from analogous $\text{PtMe}_2(\text{C}(\text{O})\text{Me})\text{Cl}(\text{pTol-BIAN})$, 9e, gave some uncharacterized products after 75 h in CDCl$_3$ at 20 °C, but the majority of the complex had retained intact ($>90\%$). The product is even stable at 170 °C in vacuo for 2 h and in refluxing methanol for 3 h, conditions which have been reported to lead to quantitative reductive elimination of acetone within 1 h from analogous $\text{PtMe}_2(\text{C}(\text{O})\text{Me})\text{Cl}_2$ complexes (L = phosphine). After both reactions 9e is regained without any reductive elimination or decarbonylation and there was no evidence for the formation of other (insoluble) decomposition products such as polymers or metallic platinum.

Stability of Triorganoplatinum(IV) Complexes 9 toward Reductive Elimination. All complexes of the type $\text{PtMe}_2(R)(\text{pTol-BIAN})$, 9, are very stable in solution at 20 °C. In all cases the complex can be kept in CDCl$_3$ solution in air at 20 °C for several days without any detectable decomposition, i.e. reductive elimination, β-elimination or decarbonylation. The acyl complex $\text{PtMe}_2(\text{C}(\text{O})\text{Me})\text{Cl}(\text{pTol-BIAN})$, 9e, gave some uncharacterized products after 75 h in CDCl$_3$ at 20 °C, but the majority of the complex had remained intact ($>90\%$). The product is even stable at 170 °C in vacuo for 2 h and in refluxing methanol for 3 h, conditions which have been reported to lead to quantitative reductive elimination of acetone within 1 h from analogous $\text{PtMe}_2(\text{C}(\text{O})\text{Me})\text{Cl}_2$ complexes (L = phosphine). After both reactions 9e is regained without any reductive elimination or decarbonylation and there was no evidence for the formation of other (insoluble) decomposition products such as polymers or metallic platinum.

Dehalogenation of the Platinum(IV) Complexes 9 with Silver Salts. The triorganoplatinum(IV) complexes 9a–e all react readily with silver salts like silver trifluoromethanesulfonate in noncoordinating solvent ($\text{CH}_2\text{Cl}_2$, CDCl$_3$), to give the cationic complexes $\text{PtMe}_2(R)(\text{pTol-BIAN})\text{SO}_2\text{CF}_3$, 11a–e. This reaction is reversible and stereospecific, as upon addition of the appropriate sodium salt to 11a–e the starting complex 9a–e with the same isomeric distribution is regenerated (eq 6).
The new complexes 11-14 are characterized by elemental analysis, IR spectroscopy, and 1H, 13C, and 19F NMR spectroscopy (Tables 5-7) and represent the first examples of dehalogenated triorganoplatinum(IV) complexes, which are stable toward reductive elimination in the absence of added ligands.\textsuperscript{30} \([\text{PtMe}_3(\text{pTol-BIAN})] \text{SO}_3\text{CF}_3\), 11a, was also obtained by the oxidative addition of \(\text{MeSO}_2\text{CF}_3\) to \(\text{PtMe}_3(\text{pTol-BIAN})\).\textsuperscript{6}

The chemical shifts in the 19F NMR are in the range -78 to -80 ppm for all complexes 11 (Table 7). It has been noted that this is in the region of noncoordinating trifluoromethanesulfonate anions,\textsuperscript{31} but for complexes of the type \(\text{M}(_2\text{C}6\text{H}_{12})(\text{SO}_2\text{CF}_3)\) (\(\text{M} = \text{Rh, Ir}\) containing coordinated trifluoromethanesulfonate (based on IR spectroscopy), 19F NMR chemical shifts of -78.36 and -78.12 ppm have been reported.\textsuperscript{32} Thus 19F NMR gives ambiguous results and cannot generally be used as a reliable tool for determining whether the trifluoromethanesulfonate group is coordinated to the metal or is present as an anion.

In the IR spectra (Nujol) all complexes 11-14 show the expected vibrations of the trifluoromethanesulfonate group (Table 7). The observation of a S=O stretching frequency in the region 1200-1250 cm\(^{-1}\) for the complexes 11, 13, and 14, apart from one at 1250-1300 cm\(^{-1}\), indicates that the \(\text{C}_\text{S} \text{O}\) symmetry of \(\text{SO}_2\text{CF}_3\) is lowered by coordination, as has been elaborated for \(\text{Cu(SO}_2\text{CF}_3\) complexes.\textsuperscript{38} Indeed, \([\text{Pt}(\eta^5\text{PhCH-CH=CH}_2)(\text{pTol-BIAN})] \text{SO}_2\text{CF}_3\)]

\begin{table}[h]
\centering
\caption{IR and 19F NMR Data for the \([\text{PtMe}_2(\text{R})(\text{pTol-BIAN})] \text{SO}_3\text{CF}_3\) Complexes 11-14\textsuperscript{a}}
\begin{tabular}{cccccccc}
\hline
 & R & & & & & & & \\
 & \text{IR} & & & & & & & 19F NMR \\
\hline
11a & R = \text{Me} & & & & & & & 1295, 1231 & 1174 & 1022 & 635 & -78.8 br \\
11b & R = \text{CH}_3\text{Ph} & & & & & & & 1304, 1233 & 1170 & 1015 & n.o. & -79.0 br \\
11c & R = \text{C(O)}\text{Me} & & & & & & & 1294, 1231 & 1165 & 1020 & 633 & -78.73 \\
12 & R = \text{Me} & \text{PPh}_3 & & & & & & 1270 & 1145 & 1031 & 632 & -78.51 \\
13 & R = \text{Me} & \text{PPh}_3 & \text{phen} & & & & & 1275, 1230 & 1175 & 1030 & n.o. & -78.10\textsuperscript{b} \\
14 & R = \text{Me} & \text{PPh}_3 & \text{pTol-DAB} & & & & & 1265, 1230 & 1175 & 1030 & n.o. & -78.12\textsuperscript{b} \\
\hline
\end{tabular}
\end{table}

\textsuperscript{a} IR as Nujol mull and 19F NMR in CDC\(_3\) at 20 °C. \textsuperscript{b} In CDC\(_3\). 

\(\text{CF}_3\) which is included for comparison, and \([\text{PtMe}_2(\text{pTol-BIAN})(\text{PPh}_3)] \text{SO}_2\text{CF}_3\), 12 (vide infra), both containing ionic \(\text{SO}_2\text{CF}_3\), show no S=O stretching frequency in the region 1320-1380 cm\(^{-1}\), which was reported to be characteristic of bound trifluoromethanesulfonate.\textsuperscript{35} indicates that the Pt—SO\(_2\text{CF}_3\) interaction is only weak. Unfortunately, we have not been able to obtain crystals of any of the complexes 11 that were suitable for X-ray diffractometry.

\([\text{PtMe}_2(\text{pTol-BIAN})] \text{SO}_2\text{CF}_3\), 11a, in Noncoordinating Solvents in the Absence of Added Ligands. At -40 °C the observation of four Pt—Me resonances at 1.00 (85.5 Hz), 0.95 (67.3 Hz), 0.92 (82.0 Hz), and 0.80 ppm (67.6 Hz) (1:2:1:2) and two resonances of \(\text{H}_2\) at 2.51 and 2.50 ppm.\textsuperscript{4} At -40 °C two isomers are observed. The major isomer shows resonances at 1.09 (81.9 Hz), \(\text{Me}_{\text{eq}}\) 0.96 (67.2 Hz), \(\text{Me}_{\text{ax}}\) and 2.99 ppm, 2.89 ppm, 1\(\text{H}—\text{H} = 9.4 \text{ Hz}\), \(\text{CH}_2\text{Ph}\), and the minor isomer, at 1.14 (69.3 Hz), \(\text{Me}_{\text{eq}}\) and 3.19 ppm (107 Hz), \(\text{CH}_2\text{Ph}\).\textsuperscript{4} \(\text{Me}_{\text{eq}}\)

\(1\text{H} = 8.1 \text{ Hz}\); \(\text{Me}_{\text{ax}}\) 1\(\text{H} = 8.6 \text{ Hz}\). /n CD\(_3\text{CN}\) at 20 °C.

\textsuperscript{30} Cationic platinum(IV) complexes have been reported before, but a stabilizing sixth ligand is necessary to prevent reductive elimination: refs 9 and 35a.


\textsuperscript{34} van Asselt, R.; Vrieze, K.; Elsevier, C. J. Submitted for publication in J. Organomet. Chem.

Furthermore, the aromatic region at 20 °C is only slightly broadened in $^1$H and $^{13}$C NMR, indicating that there is fast exchange. Only the signals of (C(H)$_3$)$_2$ are broad, in agreement with a variation of the axial substituent which has a large influence on the ortho-position of the $p$-tolyl substituent of the $p$Tol-BIAN ligand (C(H)$_3$)$_2$, but has much less influence on the other C atoms.$^{21b}$

Reactions of [PtMe$_3$($p$Tol-BIAN)]SO$_3$CF$_3$, 11a, with Coordinating Molecules. After reaction of [PtMe$_3$($p$Tol-BIAN)]SO$_3$CF$_3$, 11a, in dichloromethane with 6.5 equiv of acetonitrile and evaporation of the solvent, the isolated product dissolved in CDCl$_3$ occurs in two forms: 70% 11a and 30% [PtMe$_3$(MeCN)($p$Tol-BIAN)]SO$_3$CF$_3$, 11a', showing in $^1$H NMR Pt–Me resonances at 0.79 and 0.90 ppm (2:1) and a very broad signal at 1.8 ppm of coordinated acetonitrile in exchange with free acetonitrile. Upon cooling to −40 °C the amount of 11a decreases and the signals at 0.79 and 0.90 ppm increase in intensity. The Pt–Me region shows a complex set of signals, indicating the presence of several isomers. Two resonances are observed in $^{19}$F NMR (−40 °C) at −78.83 and −79.30 ppm.

When an excess of acetonitrile (6 equiv relative to Pt$^{IV}$) is added to a solution of 11a in CDCl$_3$ only one isomer is observed, which gives at 20 °C in $^1$H NMR resonances at 0.77 (69.0 Hz) and 0.88 ppm (77.0 Hz). In $^{13}$C NMR one sharp resonance at −79.06 ppm is observed. No spectral changes occur upon cooling to −40 °C. One single isomer is also observed when 11a is dissolved in CD$_2$CN, giving in $^1$H NMR Pt–Me resonances at 0.75 (69.6 Hz) and 0.90 ppm (77.6 Hz) (Figure 1) and a $^{19}$F resonance at −78.13 ppm. These results show that the tendency of acetonitrile to coordinate to the cationic Pt$^{IV}$ complex 11a is rather low and that fac-[PtMe$_3$(MeCN)($p$Tol-BIAN)]SO$_3$CF$_3$, 11a', is only formed quantitatively when an excess of acetonitrile is present. The observed large coupling constant for the axial methyl group indicates that acetonitrile is a weak ligand which is in agreement with the observation that coordinated acetonitrile is lost from 11a' when the product is kept in vacuo at 20 °C for several hours and with our observations that acetonitrile coordinates weakly to Pd$^{II}$(Ar-BIAN) complexes.$^{36}$

Reaction of 11a with ligands that require π-backdonation from the metal to obtain stable complexes, such as carbon monoxide, ethene, and (E)-2-butene, did not lead to a [PtMe$_3$L($p$Tol-BIAN)]SO$_3$CF$_3$ complex observable by $^1$H NMR spectroscopy. On the other hand, with the donor ligand PPh$_3$ an adduct [PtMe$_3$($p$Tol-BIAN)(PPh$_3$)]SO$_3$CF$_3$, 12, is formed instantaneously and the coordination of PPh$_3$ to platinum appears unambiguously from the Pt satellites in $^{31}$P NMR. Complex 12 has a fac geometry, with the triphenylphosphine ligand coordinating in an axial position, as is clear from the observed $^1$H NMR resonances and coupling constants of the Pt–Me groups, the symmetrical pattern for the $p$Tol-BIAN ligand, and the low frequency doublet at 5.98 ppm.

due to anisotropic shielding of two protons H₂ by one of the phenyl rings of the triphenylphosphine ligand.

\[ \text{[PtMe₂(CH₂Ph)(NN)SO₂CF₃ Complexes} \]

11b, 13, and 14. [PtMe₂(CH₂Ph)(pTol-BIAN)SO₂CF₃, 11b, in CDCl₃ at 20 °C shows in ¹H NMR one broadened Pt-Me resonance at 1.16 ppm (67 Hz), one broadened Pt-CH₂Ph resonance at 3.24 ppm (108 Hz), and a broad signal at 6.20 ppm (H₅), indicative of a complex with an axial benzyl group. In ¹⁹F NMR a broad signal at -79.0 ppm is observed. Upon cooling to -40 °C in ¹⁹F NMR two trifluoromethanesulfonate resonances are observed at -78.82 and -79.48 ppm in a ratio of 1:4. In ¹H NMR three Pt–Me resonances are observed at 1.14 (69.3 Hz), 1.09 (81.9 Hz), and 0.96 ppm (67.2 Hz) (about 1:2:2) and for the Pt-CH₂Ph moiety one singlet at 3.19 ppm (²J(Pt–H) ~ 107 Hz) and two doublets at 2.99 and 2.89 ppm (²J(Pt–H) not resolved) in a ratio of 1:2:2. Analogous to [PtMe₂(pTol-BIAN)SO₂CF₃, 11a, these isomers are assigned to a fac octahedral or a square pyramidal structure. The NMR data indicate that at -40 °C the major product (80%) has a C₁-symmetric structure, with the benzyl group in an equatorial position. The C₁ symmetry of the major isomer and the presence of the minor isomer gives rise to a very complex ¹³C NMR spectrum. From these ¹³C NMR data there is no evidence for an η⁵-coordinated benzyl moiety, as has been observed for [Pd(η⁵-CH₂Ph)(pTol-BIAN)SO₂CF₃ (the chemical shift of CH₂ and C₆H₅ has changed as compared to η¹-CH₂Ph in the platinum(IV) bromide complex 9b)]. In CD₂CN also a mixture of two isomers is observed and the slightly different chemical shifts, as compared to CDCl₃ solutions, indicate that acetonitrile is coordinated to the platinum(IV) center. The C₁-symmetric complex is the major isomer (55%) and there is no indication for any exchange on the NMR time scale at 20 °C. In ¹⁹F NMR one sharp resonance is observed at -78.10 ppm. The analogous [PtMe₂(CH₂Ph)(NN)SO₂CF₃ complexes (NN = phen, 13; pTol-DAB, 14) did not dissolve well enough in CDCl₃ to allow characterization by ¹H NMR. In CD₃CN the phen complex 13 occurs as a single C₁-symmetric isomer containing the benzyl and an acetonitrile ligand in the axial positions, which can be derived from the observation of one Pt–Me resonance at 1.58 ppm (65.8 Hz), one singlet for Pt–CH₂Ph at 3.06 ppm (95.8 Hz), and a symmetrical pattern for the phen ligand in ¹H NMR. The observed shift of the PhCH₂ resonances to low frequency are characteristic of a benzyl group oriented toward the phen ligand and concomitant anisotropic shielding. In ¹⁹F NMR one resonance is found at -78.10 ppm.

The cationic pTol-DAB complex 14 exists in CD₃CN as a mixture of isomers (66% of a C₁-symmetric isomer and 34% of a C₁-symmetric isomer). The C₁-symmetric isomer exhibits in ¹H NMR two doublets for the Pt–CH₂Ph moiety with large differences in the observed Pt–CH₂ coupling constants: 3.37 ²J(Pt–H) = 113.4 Hz and 3.02 ppm ²J(Pt–H) = 69.0 Hz. Probably, there is some interference of the benzyl group with the p-tolyl substituent of pTol-DAB, which might be in the coordination plane contrary to pTol-BIAN, hindering rotation around the Pt–benzyl bond and bringing both benzyl protons into a different orientation relative to platinum.

Other [PtMe₂(R)(pTol-BIAN)]SO₂CF₃ Complexes 11c–f in CDCl₃. The acyl complex [PtMe₂(C(O)Me)(pTol-BIAN)]SO₂CF₃ 11e, at 20 °C in CDCl₃ is present as one C₁-symmetric isomer. The ¹H NMR spectrum has hardly changed compared to the platinum(IV) chloride complex 9e, only the ²J(Pt–H) coupling to the acetyl group has increased somewhat (to 20.5 Hz). The small differences might indicate that the chloride was already weakly coordinated due to the high trans influence of the acetyl group. In ¹⁹F NMR one sharp resonance is observed at -78.73 ppm is observed. At 20 °C the complexes [PtMe₂(Et)(pTol-BIAN)]SO₂CF₃, 11c, and [PtMe₂(CH(Me)Ph)(pTol-BIAN)]SO₂CF₃, 11d, gave a very complex spectrum with several broad and overlapping signals, from which no valuable structural information could be derived. Therefore the structure of these complexes in solution was not further investigated. At 20 °C in CDCl₃ the ¹H NMR spectra of [PtMe₂(pTol-BIAN)]SO₂CF₃, 11f, obtained by addition of two equiv of Ag₂SO₃CF₃ to [OC-6-13]-Pt(pTol-BIAN)Me₂, 9f, showed the presence of two Pt–Me resonances at 2.00 (78.5 Hz) and 1.68 ppm (81.0 Hz) and two doublets of H₂. Cooling to -20 or -50 °C did not bring about any changes in the ¹H NMR spectra. In ¹⁹F NMR a broad signal is observed at 20 °C at -78.7 ppm, which sharpens to one signal at -79.13 ppm upon cooling to -20 °C. The complex 11f most likely has a C₁-symmetric structure with one equatorial and one axial methyl group, instead of being a mixture of two C₁-symmetric isomers, since upon addition of sodium iodide [OC-6-23]-Pt(pTol-BIAN)Me₂, 10a, is obtained as the only product.

**Thermal Stability of the [PtMe₂(R)(pTol-BIAN)]SO₂CF₃ Complexes 11.** In the solid state the cationic Pt(IV) complexes 11–14 can be stored at 20 °C without any detectable decomposition for at least 2 months. Complexes 11a,b,e,f can be kept in CDCl₃ solution at 20 °C for at least 3 days without any decomposition. This means that none of the complexes gives any reductive elimination in solution at 20 °C and, furthermore, that the acyl complex [PtMe₂(C(O)Me)(pTol-BIAN)]SO₂CF₃, 11e, does not show any decarbonylation (after 75 h). The complexes [PtMe₂(ET)(pTol-BIAN)]SO₂CF₃, 11c, and [PtMe₂(CH(Me)Ph)(pTol-BIAN)]SO₂CF₃, 11d, did not reveal any sign of reductive elimination or β-elimination after several hours in CDCl₃ (monitored by ¹H NMR) and the halide complexes 9c,d were recovered with complete retention of configuration upon addition of sodium iodide or sodium bromide to the cationic complexes.

The methyl and benzyl complexes [PtMe₂(pTol-BIAN)]SO₂CF₃, 11a, and [PtMe₂(CH₂Ph)(pTol-BIAN)]SO₂CF₃, 11b, were stable toward reductive elimination at 20 °C in CDCl₃ and in CD₃CN for at least 1 week and in CDCl₃ or CD₃CN at 50 °C for at least 40 h. [PtMe₂(CH₂Ph)(phen)]SO₂CF₃, 13, was also stable toward decomposition in CD₃CN at 50 °C for at least 40 h, but [PtMe₂(CH₂Ph)(pTol-DAB)]SO₂CF₃, 14, showed 30% decomposition after 40 h in CD₃CN at 50 °C. Some metallic precipitate was present and in the ¹H NMR a new Pt–Me signal was observed at 1.23 ppm (76.1 Hz), characteristic of a Pt¹–Me complex. Unfortunately, the other signals of

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the complex and of the organic products formed after reductive elimination were overlapped by the signals of unreacted 14.

**Discussion**

**Oxidative Addition Reactions.** Complexes of the type MMMe₂(NN) (M = Pd, Pt; NN = pTol-BIAN, Ph-BIC), 1, 3, and 6, undergo facile oxidative addition of a variety of (organic) halides. Oxidative addition to PtMe₂(pTol-BIAN), 6, and Pt(Me)I(pTol-BIAN), 7, complexes is much faster as compared to phosphine analogues and is probably more like that of the bpy and phen complexes PtMe₂(NN), which have been reported to be among the most reactive species for oxidative addition reactions. The high reactivity of the MMMe₂(pTol-BIAN) and PtMe₂(Ph-BIC) complexes is due to the donative character of the pTol-BIAN and Ph-BIC ligands, which renders the metal center electron rich and capable of efficient nucleophilic attack of the substrate. Net trans oxidative addition occurs, as appeared from the formation of [OC-6-13]-PtMe₂(pTol-BIAN), 9f, via trans oxidative addition of I₂ to PtMe₂(pTol-BIAN), 6, and the formation of [OC-6-32]-PtMe₂(pTol-BIAN), 10a, via trans oxidative addition of iodomethane to Pt(Me)I(pTol-BIAN), 8. These complexes did not isomerize in solution at 50 °C (18 h), but upon reaction with silver trifluoromethanesulfonate in CDCl₃ followed by reaction with sodium iodide [OC-6-32]-10a (eq 7), which indicates that the latter is the thermodynamically more stable product. Products from a trans oxidative addition were also observed for the (1-phenylethyl)- and acetylplatinum(IV) complexes 9d and 9e, but a mixture of isomers, formed via isomerization after oxidative addition, was observed for the benzyl- and the ethylplatinum(IV) complexes 9b and 9c.

**Reductive Elimination from the Triorganopalladium(IV) and -platinum(IV) Complexes in Solution.** The organopalladium(IV) complexes 4 and 5 show unprecedented thermal stability in solution toward reductive elimination in contrast to the much greater lability of other triorganopalladium(IV) complexes containing bidentate nitrogen ligands such as bpy, phen, tmdea, (py)₂CHMe, and (py)(pz)CH₂ (py = pyridin-2-yl, pz = pyrazol-1-yl). Although several of these could be isolated and X-ray crystallographic studies have been reported, these complexes in solution must be studied spectroscopically at temperatures usually below 0 °C. Reductive elimination from triorganopalladium(IV) halide complexes has been demonstrated to proceed via initial dissociation of the halide. The observed rapid elimination of ethane after reaction of PdMe₂I(Ph-BIC) with Ag₂SO₄CF₃ is in agreement with such a mechanism (Scheme 4). Furthermore, the calculated activation energy of 60 kJ-mol⁻¹ for reductive elimination from PdMe₂I(pTol-BIAN) in CDCl₃ is in the same range as that found for PdMe₂I(bpy) in acetone (65 kJ-mol⁻¹), which indicates that reductive elimination might occur via a similar pathway in both cases.

The observed first order rate constants for reductive elimination from the PdMe₂I(NN) complexes 4,5a in chloroform are 2 or 3 orders of magnitude smaller than those of PdMe₂I(bpy) in acetone or benzene. From comparison with other reported triorganopalladium(IV) complexes containing bidentate nitrogen ligands it appears that the stability decreases in the order pTol-BIAN, Ph-BIC > phen, bpy > tmeda, (py)₂CHMe, (py)(pz)CH₂, which means that the rigidity of the bidentate nitrogen ligand is the major factor in determining the stability of the triorganopalladium(IV) complexes. Flexible ligands allow the formation of intermediates from which reductive elimination is favorable, e.g. by variation of the N—Pd—N angle. Alternatively, when flexible ligands are coordinated to palladium, five-coordinate intermediates might be more readily accessible by loss of a coordinated N atom or by more facile dissociation of the halide. The higher stability of the triorganopalladium(IV) complexes PdMe₂(R)(X)(NN) containing pTol-BIAN and Ph-BIC ligands as compared to phen can be ascribed to the better σ-donating capabilities of the Ar-BIAN and Ph-BIC ligands as compared to phen. These results show that good σ-donor ligands do have a stabilizing effect on triorganopalladium(IV) and (cationic) platinum(IV) complexes but that these electronic properties are less important than the rigidity of the ligand. The stabilizing effect of the pTol-BIAN and Ph-BIC ligands on palladium(IV) complexes, as reflected in the thermal stability of the triorganopalladium(IV) complexes, has allowed us to study for the first time diorganopalladium(IV) complexes obtained via oxidative addition of diiodine to PdMe₂(NN). These diorganopalladium(IV) complexes were shown to be less stable than triorganopalladium(IV) complexes, as they decomposed within 2 h at 20 °C in the solid state as well as in solution, with formation of ethane, methyl iodide, and an unsoluble complex, probably PdI₂(NN). Comparable diorganopalladium(IV) complexes are likely intermediates in the reactions of organopalladium(IV) complexes with organic halides, yielding finally PdH₂-dihalide complexes and organic coupling products.

Apart from the rigidity and the electronic properties of the ligands, the steric properties of the ligands also influence the stability of the triorganopalladium(IV) complexes formed. This appears from the reaction of PdMe₂(0,0'-iPr₂C₆H₄-BIAN) with iodomethane, which did not lead to an observable trimethylpalladium(IV) intermediate, but instead reductive elimination occurred immediately to give only Pd₂(Me)I(0,0'-iPr₂C₆H₄-BIAN). The low stability of PdMe₂I(0,0'-iPr₂C₆H₄-BIAN) is due to the orientation of the aromatic groups perpendicular to the M-M-L angle. Flexible chelating ligands which are capable of varying the L-M-L angle might facilitate reductive elimination reactions, as calculations have shown that opening of the P—Pd—P angle during reductive elimination from Pd₂(Me)I(0,0'-CH₂C₆H₄-BIAN) in hexane is 78° (α-β-Pd₂I₂C₆H₄-BIAN), 79° (α-β-Pd₂I₂C₆H₄-BIAN), 80° (α-β-Pd₂I₂C₆H₄-BIAN), 81° (α-β-Pd₂I₂C₆H₄-BIAN), 82° (α-β-Pd₂I₂C₆H₄-BIAN), 83° (α-β-Pd₂I₂C₆H₄-BIAN), 84° (α-β-Pd₂I₂C₆H₄-BIAN), and 85° (α-β-Pd₂I₂C₆H₄-BIAN) ligands forming six-membered chelate rings. For bpy N—Pd—N angles typically lie in the range 75°–95°, but angles of 84.3° have been reported for M(CN)₂(bpy) (M = Pd, Pt), indicating that bpy is more flexible than phen or Ar-BIAN, see: Che, C. M.; He, L. Y.; Poon, C. K.; Mak, T. C. W. Inorg. Chem. 1989, 28, 3081.
to the coordination plane, leading to steric interference of the isopropyl groups with the axial ligands on the palladium(IV),\textsuperscript{17c,19} The interaction of these isopropyl groups with the axial iodide appeared also from the high frequency shift of two CH (iPr) groups to 4.75 ppm in PtMe\(_2\)(I,o'-iPr\(_2\)C\(_6\)H\(_5\)-BIAN) and might facilitate reductive elimination from PdMe\(_2\)(I,o'-iPr\(_2\)C\(_6\)H\(_5\)-BIAN). Alternatively, reductive elimination might occur from the intermediate [PdMe\(_2\)(o,o'-iPr\(_2\)C\(_6\)H\(_5\)-BIAN)]\(^+\)I\(^-\) formed during oxidative addition, because coordination of I\(^-\) to Pd(IV) is hindered by the o,o'-iPr\(_2\)C\(_6\)H\(_5\)-BIAN ligand.\textsuperscript{42}

A remarkable aspect is the unsselective reductive elimination from PdBrMe\(_2\)(CH\(_2\)Ph)(o Tol-BIAN), \textsuperscript{4b} in CDCl\(_3\), giving 60% PdBr(CH\(_2\)Ph)(o Tol-BIAN) and 40% PdBrMe(Me)(o Tol-BIAN). In all reported cases of reductive elimination from PdBrMe\(_2\)(CH\(_2\)Ph)(NN) complexes, studied in acetone and benzene solution, there is a preference for the elimination of ethane over ethylbenzene,\textsuperscript{4} and the selectivity for ethane elimination decreases in the order bpy, tmeda (85-100%) > phen (75%) > o Tol-BIAN (60%), i.e. the order of increasing ligand rigidity. A reason for the increased amount of ethylbenzene elimination in the case of the o Tol-BIAN complexes might be the decreased rate of alkyl group scrambling in the cationic intermediate formed after bromide dissociation when a rigid ligand is coordinated to palladium (Scheme 5). As the conversion from A to B is expected to be slower for rigid bidentate ligands and the reductive elimination of organic groups occurs preferentially from an axial and an equatorial position,\textsuperscript{4a,c} the reductive elimination of ethylbenzene from A becomes competitive with alkyl group scrambling.

Similarly to what has been observed for the triorganopalladium(IV) complexes, triorganoplatinum(IV) complexes containing the rigid o Tol-BIAN ligands were also remarkably stable. The formed organoplatinum(IV) complexes did not undergo reductive elimination at 20 °C in solution or in the solid state. The acyl complex PtMe\(_2\)(C(O)Me)Cl(o Tol-BIAN), \textsuperscript{9e} was also stable under conditions where the analogous phosphine complexes gave facile reductive elimination of acetone, i.e. refluxing methanol or pyrolysis at 170 °C in vacuo in the solid state.\textsuperscript{6c,9a} The high stability of these complexes is due to the rigidity of the o Tol-BIAN ligand which prevents dissociation of one of the coordinating nitrogen atoms, as reductive elimination from organoplatinum(IV)-phosphine complexes was reported to be initiated by loss of coordinated phosphine.\textsuperscript{5} The stabilizing effect of the rigid ligands on M(IV) complexes has allowed the isolation and characterization of dehalogenated platinum(IV) complexes of the type [PtMe\(_2\)(R)(o Tol-BIAN)]SO\(_2\)CF\(_3\), \textsuperscript{11} and to our knowledge these complexes represent the first examples of platinum(IV) complexes that are stable toward reductive elimination in the presence of only a very weakly coordinating or even noncoordinating triflate ion as the sixth ligand. The observed reductive elimination of ethylbenzene from [PtMe\(_2\)(CH\(_2\)Ph)(p Tol-DAB)]SO\(_2\)CF\(_3\) in acetonitrile at 50 °C emphasizes the importance of the rigidity of the NN ligand for the stabilization of organoplatinum(IV) complexes, as the analogous complexes containing p Tol-BIAN and phen ligands were stable under similar conditions. Thus, dissociation of a N atom from platinum is more effective in inducing reductive elimination from triorganoplatinum(IV) complexes than dissociation of the coordinated halide (Scheme 6), in agreement with the reported dissociation of a phosphine ligand prior to reductive elimination from PtMe\(_2\)X(P)\(_2\) complexes.\textsuperscript{6} The stabilizing effect of rigid Ar-BIAN ligands by retarding dissociation of one of the imine N atoms has also been observed for acyl-palladium complexes.\textsuperscript{36}

**Conclusion**

The rigid bidentate nitrogen donor ligands p Tol-BIAN and Ph-BIC are very effective in stabilizing organopalladium(IV) and -platinum(IV) complexes. Triorganopalladium(IV) complexes could be synthesized and isolated at 20 °C, which contrasts to hitherto reported triorganopalladium(IV) complexes containing other bidentate nitrogen ligands, that were generally prepared and characterized at lower temperatures.\textsuperscript{3,4,23,29} The employed Ar-BIAN and Ph-BIC ligands are good \(\sigma\)-donors and activate the divalent complexes to undergo oxidative addition, as also appeared from the reactions of monooorganopalladium(II) complexes with organic halides.\textsuperscript{34} Furthermore, the palladium(IV) complexes are kinetically stabilized due to the rigidity of the ligands; i.e. pathways for reductive elimination such as formation of a five-coordinate intermediate by dissociation of a coordinated halide or N atom are not readily available. The stabilizing effect of the p Tol-BIAN and Ph-BIC ligands on palladium(IV) complexes has allowed us to study for the first time diorganopalladium(IV) complexes, formed by oxidative addition of diiodine to PtMe\(_2\)(NN). The importance of the rigidity of the ligands in kinetically stabilizing high oxidation states became also apparent from the observed stability of the
acyl–platinum(IV) complex PtMe₂(C(O)Me)Cl(pTol-BIAN), which was much more stable than its phosphine analogues. Furthermore, stable cationic five-coordinate triorganoplatinum(IV) complexes, without a stabilizing sixth ligand, were obtained by reaction of PtMe₂(R)X-(pTol-BIAN) complexes with AgSO₃CF₃. The observed order of stability for [PtMe₂(CH₂Ph)(NN)]SO₃CF₃ complexes, i.e. pTol-BIAN, phen > pTol-DAB emphasizes the fact that the rigidity of the bidentate nitrogen ligand is more important than its electronic properties for the stabilization of high oxidation states.

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