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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Dimethylpalladium(II) and (dime)thylplatinum(II) complexes containing the rigid bidentate nitrogen ligands bis(p-tolylimino)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)(NN) (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 PdMe2X2(NN), synthesized via oxidative addition of diiodine to PdMe2X2(NN) are much less stable than the triorgano-palladium(IV) complexes studied. PtMe2(R)(X)(pTol-BIAN) (RX = MeI, PhCH2Br, PhCH(Me)Br, MeC(O)Cl, 12) and PtMe(R)(X)(pTol-BIAN) with AgSO3CF3 led to the formation of remarkably stable five-coordinate [PtMe2(R)(pTol-BIAN)]SO3CF3 complexes (R = Me, CH2-Ph, C(O)Me), which were fully characterized and can be isolated and kept at 20 °C. The complexes are very stable towards reductive elimination, e.g. in CDCl3 and CD3CN [PtMe2(CH2-Ph)2(pTol-BIAN)]SO3CF3 was stable for at least 7 days at 20 °C or 40 h at 50 °C. The analogous complex [PtMe2(CH2-Ph)(phen)]SO3CF3 was also stable at 50 °C in CD3CN for at least 40 h, whereas [PtMe2(CH2-Ph)(pTol-DAB)]SO3CF3 gave 30–55% 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.

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).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.2 This complex contained the bidentate nitrogen ligand 2,2'-bipyridine (bpy), and after this report other examples of (stable) triorgano-palladium(IV) complexes with bidentate3 and tridentate nitrogen ligands4,5 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 loss of the coordinated halide, has been demonstrated.6-8

In contrast to the lability of the organopalladium(IV) complexes, the analogous organoplatinum(IV) complexes are by far more kinetically stable and as a consequence numerous examples of organoplatinum(IV) complexes containing phosphine8 and (bidentate) nitrogen2 ligands have been prepared and studied.


are known. Reductive elimination of ethane from PtMe$_3$X-(PR$_3$)$_2$ complexes was shown to occur via loss of one coordinated phosphate prior to reductive elimination, whereas decomposition of PtMe$_3$(bpy) occurred at higher temperatures and resulted in the formation of methane via α-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(aryl-BIAN) complexes, i.e. complexes containing the cis-fixed bidentate nitrogen ligand bis(arylimino)acenaphthene, in cross-coupling reactions between organic halides and organometallic reagents, and the possible intermediary of organopalladium(IV) and -platinum(IV) complexes toward triorganopalladium(1V) 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 MMe$_2$(NN) (M = Pd, Pt; NN = Ar-BIAN, Ph-BIC (=bis(phenylimino)camphane)) and the factors that influence the stability of the M(IV) complexes formed.

We expected that the properties of the Ar-BIAN and Ph-BIC ligands would be favorable for the stabilization of organopalladium(IV) and -platinum(IV) complexes toward reductive elimination. The rigid backbone, which makes these ligands less flexible than bpy and tmeda (N,N,N',N'-tetramethylethylenediamine), will prohibit dissociation of the coordinating N atoms as well as prevent changes of the bonding angles. Enhanced stability has previously been observed for, e.g., Pd(II) complexes containing rigid bidentate nitrogen ligands like phen (1,10-phenanthroline), from which relatively slow β-H elimination takes place. Furthermore, the Ar-BIAN and Ph-BIC ligands are better π-donors than bpy and phen due to the presence of exocyclic imine functionalities. As far as the presence of the two conjugate imine functions is concerned, the Ar-BIAN and Ph-BIC ligands resemble the 1,4-diaza-1,3-butanediene (R-DAB) ligands, which have often been used to stabilize metals in a low oxidation state because of their π-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 of and 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 field shifts positive. $^{19}$F (94.20 Mhz) and $^{31}$P (40.53-MHz) NMR spectra were recorded on a Bruker AC 100 spectrometer, relative to CFC$_3$ 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 Dormis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. Pd(Me)Cl(COD)$_2$, PdCl$_2$(SMe$_2$)$_2$, 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 CDCl$_3$. 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 Me@Tol 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), I. 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 methylmethylthioglycol solution in diethyl ether (1.4 mmol) and the mixture stirred at −70°C. After 1.5 h 100 μL 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 (calded) for C$_{30}$H$_{33}$N$_2$Pd: C, 67.19 (67.68); H, 4.83 (5.28); N, 5.20 (5.64).

(11) van Asselt, R.; Elsevier, C. J. Submitted for publication in Organometallics.
Ph-Me$_2$(o,o'-Pr$_2$C$_6$H$_4$-BIAN), 2, was synthesized in the same way (73%). Anal. Found (calc'd) for C$_{27}$H$_{23}$IN$_2$: C, 78.2 (78.8); N, 3.9 (4.0).

PdMe$_2$(Ph-BIC), 3, was synthesized as described above for 1 (80%). Anal. Found (calc'd) for C$_{33}$H$_{29}$NPd: C, 70.66 (70.72); H, 7.33 (7.28); N, 4.63 (4.70).

**PtCl$_2$(SM$_2$)$_2$** was synthesized by a modified literature procedure. To a solution of 3.43 g of K$_2$PtCl$_6$ (3.86 mmol) in 50 mL of degassed water, 4 mL of dimethyl sulfoxide (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 with MgSO$_4$, filtered, and evaporated to dryness. The product was dried in vacuo, giving 3.01 g of PtCl$_2$(SM$_2$)$_2$ as a yellow powder (93%).

PtMe$_2$(μ-SM$_2$)$_2$, 4a, to a solution of 0.10 g of PtCl$_2$(SM$_2$)$_2$ (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 MeMgBr 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 NH$_4$Cl solution in water. The ether layer was separated and the water layer extracted with diethyl ether. The organic layers were dried on MgSO$_4$, filtered, and evaporated to dryness. The product was dried in vacuo, giving 0.30 g of a brown solid (64%).

**PtMe$_2$(tol-BIAN), 6.** A mixture of 0.55 g of PtMe$_2$(μ-SM$_2$)$_2$ (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 15 h the green solution was evaporated to dryness and the product washed with diethyl ether–hexane (1:1, 20 mL), and the residue was washed with the addition of hexane (10 mL), washed with diethyl ether–hexane (1:1, 20 mL), and dried in vacuo, yielding 92 mg of an orange-red product (72%). Anal. Found (calc'd) for C$_{25}$H$_{35}$IN$_2$: C, 54.99 (54.52); H, 3.91 (4.58); N, 4.53 (4.38).

PdMe$_2$(CH$_2$Ph)(Pt(tol-BIAN), 7b, was synthesized by the synthetic route to Pt(tol-DAB) (78%) and PtMe$_2$(phen) (84%) were obtained in the same way as 6.

PtMe$_2$(tol-DAB), 8. To a solution of 162.2 mg of PtMe$_2$(SM$_2$)$_2$ (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. 8. After 5 h the solution was filtered through Celite filter aid and the residue washed with dichloromethane (5 × 5 mL). Evaporation of the solvent to about 2 mL and addition of 10 mL of hexane precipitated the product, which was washed with 5 mL of diethyl ether and dried in vacuo, yielding 210 mg of a dark green complex (86%). Anal. Found (calc'd) for C$_{27}$H$_{23}$IN$_2$: C, 4.82 (4.78).

PtMe$_2$(o,o'-Pr$_2$C$_6$H$_4$-BIAN), 7, synthesized in the same way as 6, was obtained in 81% yield. Anal. Found (calc'd) for C$_{29}$H$_{27}$NPd: C, 62.78 (62.68); H, 6.46 (6.39); N, 3.92 (3.86).

PtBr$_2$(Me$_2$(CH$_2$)$_n$) (Br-Pt-BIC), 5b, was synthesized similarly to 4a (orange, 86%). Anal. Found (calc'd) for C$_{25}$H$_{29}$IN$_2$: C, 67.92 (68.93); H, 5.41 (4.98); N, 4.76 (4.19).

**PdMe$_2$(Ph-BIC), 5a, was synthesized similarly to 4a (light yellow, 71%).** Anal. Found (calc'd) for C$_{33}$H$_{29}$NPd: C, 70.57 (70.77); H, 7.38 (7.32); N, 4.59 (4.70).

**Ph-Me$_2$(o,o'-Pr$_2$C$_6$H$_4$-BIAN), 2, was synthesized in the same way (73%).** Anal. Found (calc'd) for C$_{27}$H$_{23}$IN$_2$: C, 78.2 (78.8); N, 3.9 (4.0).

**PdMe$_2$(Ph-BIC), 3, was synthesized as described above for 1 (80%).** Anal. Found (calc'd) for C$_{33}$H$_{29}$NPd: C, 70.66 (70.72); H, 7.33 (7.28); N, 4.63 (4.70).

**PdBr$_2$(Me$_2$(CH$_2$)$_n$) (Br-Pt-BIC), 5b, was synthesized similarly to 4a (orange, 86%).** Anal. Found (calc'd) for C$_{25}$H$_{29}$IN$_2$: C, 67.92 (68.93); H, 5.41 (4.98); N, 4.76 (4.19).

**PdMe$_2$(Ph-BIC), 5a, was synthesized similarly to 4a (light yellow, 71%).** Anal. Found (calc'd) for C$_{33}$H$_{29}$NPd: C, 70.57 (70.77); H, 7.38 (7.32); N, 4.59 (4.70).

**Ph-Me$_2$(o,o'-Pr$_2$C$_6$H$_4$-BIAN), 2, was synthesized in the same way (73%).** Anal. Found (calc'd) for C$_{27}$H$_{23}$IN$_2$: C, 78.2 (78.8); N, 3.9 (4.0).

**PdMe$_2$(Ph-BIC), 3, was synthesized as described above for 1 (80%).** Anal. Found (calc'd) for C$_{33}$H$_{29}$NPd: C, 70.66 (70.72); H, 7.33 (7.28); N, 4.63 (4.70).

**PdMe$_2$(Ph-BIC), 3, was synthesized as described above for 1 (80%).** Anal. Found (calc'd) for C$_{33}$H$_{29}$NPd: C, 70.66 (70.72); H, 7.33 (7.28); N, 4.63 (4.70).

**PdMe$_2$(Ph-BIC), 3, was synthesized as described above for 1 (80%).** Anal. Found (calc'd) for C$_{33}$H$_{29}$NPd: C, 70.66 (70.72); H, 7.33 (7.28); N, 4.63 (4.70).

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Organopalladium(IV) and -platinum(IV) Complexes

[OC-6-34] PtMe₂(CO)MeCl(pTol-BIAN), 9a (orange, 75%). Anal. Found: C, 58.31 (58.28); H, 4.18 (4.40); N, 6.42 (6.22).

[OC-6-15] PtMe₂(pTol-BIAN), 9f (brown, 82%). Anal. Found: C, 58.31 (58.28); H, 4.18 (4.40); N, 6.42 (6.22).

[OC-6-34] PtBrMe₂(Ph₂CH)₃(pTol-DAB) (orange, 71%), was synthesized in the same way as 9a. 'H NMR (CDCl₃), δ: 8.32 (J(Pt-Pt) = 27.4 Hz), N = CH; 7.0 - 7.2 (11 H), C₈H₉⁺; 6.58 (2 H), 7.0 Hz, H₃(pTol); 2.63 (Me, pTol); 2.51 (J(Pt-Pt) = 93.8 Hz), Pt - C(CH₃)₂; 1.37 (J(Pt-H) = 71.7 Hz), Pt - Me; 13C NMR (CDCl₃), δ: 161.7, N = CH; 144.3, C₈H₉; 123.5, C₆H₄; 130.1, C₆H₄; 140.5, C₅(pTol); 145.1, C₅, 129.0, 128.8, 128.5, 124.5, C₆(Me₃(Ph₀)); 21.8 (Me); 22.9 (J(Pt-C) = 641 Hz), Pt - CH₂Ph; 1.1 (J(VP - C) = 675 Hz), Me - Pt.

Oxidative Addition to PtMe₂(μ-OCH₂C₄H₈)₂(BIAN), 7. To a solution of 15.2 mg of 7 (0.022 mmol) in 0.5 mL of CDCl₃ at 20 °C was added 10 μL of Ph₂CHBr (0.084 mmol) or 4.0 μL of MeI (0.064 mmol), and the reaction was moniitored by 1H NMR spectroscopy (10 min to 4 days). 'H NMR (CDCl₃), δ: 7.43 d (7.3 Hz), H₂; 7.7 - 7.9 (8 Hz), H₂; 2.7 - 2.9 (6.7 Hz), CH₃; 1.42 - 1.44 (2.4 Hz), 1.06, 0.46 (6.7 Hz), CH₂; 1.50 (J(Pt-H) = 73.7 Hz), Pt - Me₃Me; 1.05 s (J(V(Pt-H) = 73.8 Hz), Pt - Me₃Me.

[OC-6-32] PtMe₂(pTol-BIAN), 10a. To a solution of 0.15 g of Pt(Me)(pTol-BIAN), 0 (0.22 mmol), in 10 mL of THF was added 100 μL of iodomethane (1.61 mmol) and the solution stirred at 20 °C. After 2 h the solution was filtered through Celite filter aid and the residue washed with THF (2 × 1 mL). The solvent was evaporated, the product washed with diethyl ether (2 × 5 mL), and dried in vacuo, yielding 0.13 g of a brown product (70%). Anal. Found: C, 59.2 (59.0); H, 3.57 (3.31); N, 3.38 (3.34).

PtBr(Me)(CH₂Ph)I(pTol-BIAN), 10b, was obtained from the reaction of 8 with benzyl bromide (75%). Anal. Found: C, 58.2 (58.3); H, 3.58 (3.48); N, 3.34 (3.23).

[OC-6-31] PtMe₂(pTol-BIAN), 10f. To a solution of 0.10 g of Pt(Me)(pTol-BIAN), 1 (0.14 mmol), in 5 mL of dichloromethane, was added 8.5 mg of diiodomethane (0.20 mmol) in 5 mL of dichloromethane, and the solution turned brown-red immediately. After 15 min the solution was filtered through Celite filter aid and evaporated to about 2 mL. Addition of diethyl ether (10 mL) caused precipitation of the product, which was washed thoroughly with diethyl ether (3 × 5 mL) and dried in vacuo, yielding 0.10 g of a reddish-brown solid (75%). Anal. Found: C, 58.2 (58.3); H, 3.58 (3.48); N, 3.34 (3.23).

[PtMe₂(pTol-BIAN)]SO₄CF₃, 11a. To a solution of 0.26 g of PtMe₂(pTol-BIAN), 9a (0.36 mmol), in 40 mL of dichloromethane, was added 0.11 g of AgSO₄CF₃ (0.43 mmol), and the mixture stirred in the dark at 20 °C. After 1 h the solution was filtered through Celite filter aid and evaporated to about 5 mL. Addition of hexane precipitated the product, which was dried in vacuum, yielding 0.24 g of a yellow powder (89%). Anal. Found: C, 52.84 (52.36); H, 4.14 (4.03); N, 3.52 (3.39).

[PtMe₂(CO)(Me)(pTol-BIAN)]SO₄CF₃, 11b (86%). Anal. Found: C, 51.85 (52.36); H, 4.14 (4.03); N, 3.52 (3.39).


[PtMe₂(Ph₂PPh₂)(pTol-BIAN)]SO₄CF₃, 11d. Anal. Found: C, 51.85 (52.36); H, 4.14 (4.03); N, 3.52 (3.39).


Results

Synthesis of Dimethyl palladium (II) Complexes

1 - 3. PdMe₂(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 carried out in the presence of BIAN or Ph-BIC ligands.

[MeLi] + 2Pd(Me)Cl(COD) → [Me₂Pd₂(COD)] + 2LiCl

The precipitate was washed thoroughly with diethyl ether (3 × 5 mL) and dried in vacuo during 5 days. The precipitate was dissolved in CDCl₃, and the solution was filtered through Celite filter aid, the residue washed with diethyl ether (3 × 5 mL) and dried in vacuo, yielding 0.13 g of a brown product (70%). Anal. Found: C, 59.2 (59.0); H, 3.57 (3.31); N, 3.38 (3.34).

1. Ar = pTol; 2. Ar = μ-OCH₂C₄H₈; 3.

Recommendations orientated out of the coordination plane, bringing the ortho substituents triorganopalladium(IV) complexes. In analogy to the text 1990; in press. In 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. H) in the proximity of the axial substituents of: references 15c and van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L. Inorg. Chem., in press.

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whereas PdMe$_2$(Ph-BIC), 3, gave two Pd-Me resonances at -0.01 and -0.12 (-6.4 and -7.1 ppm) due to the asymmetry of the Ph-BIC ligand. Upon standing in CDCl$_3$ at 20 °C, 1 reacts to Pd(Me)Cl(pTol-BIAN) (100% conversion after 4 h), whereas 2 was much more stable (50% conversion to Pd(Me)Cl(p,tol-BIC)-Ph) after 4 days.

Oxidative Addition to PdMe$_2$(Ar-BIAN), 1 and 2, and PdMe$_3$(Ph-BIC), 3. Addition of 1 equiv of iodomethane or benzyl bromide to a solution of PdMe$_2$(Ph-BIC), 3, gave two Pd-Me resonances at 1.7 and 1.8 ppm after 4 days.

A mixture of two isomeric PdMe$_3$(Ph-BIC) complexes 5a in a ratio of 8:4:6, which are most likely the [OC-6-44-A] and [OC-6-44-C] isomers, both having a fac geometry.

of PdMe$_2$(R)X(NN) complexes 4 and 5 was apparent from NMR spectroscopic and analytical data (Tables 1 and 2): in $^1$H (13C) NMR spectroscopy the Pd-Me resonances shifted from ca. 0 (-6 ppm) to ca. 1.5 (20-28 ppm), in agreement with the observed NMR data of reported triorganopalladuim(IV) complexes. In analogy to the reported triorganopalladuim complexes with bidentate nitrogen ligands, a fac geometry was assigned to the complexes 4 and 5, on the basis of the comparable $^1$H and $^{13}$C NMR data.

Apart from a major isomer of PdMe$_3$(pTol-BIAN), 4a, having $^1$H 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-PdMe$_3$Y(pTol-BIAN) complex (where Y is Cl or a solvent molecule) or mer-PdMe$_3$Y(pTol-BIAN). The presence of this second isomer also appeared from the $^{13}$C 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 PdMe$_3$(Ph-BIC), 3, gave a mixture of two isomeric PdMe$_3$(Ph-BIC) complexes 5a in a ratio of 8:4:6, which are most likely the [OC-6-44-A] and [OC-6-44-C] isomers, both having a fac geometry.

<table>
<thead>
<tr>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>Pd-R</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>127.7</td>
<td>124.8</td>
<td>128.9</td>
<td>130.6</td>
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<td>128.6</td>
<td>124.8</td>
<td>129.2</td>
<td>130.5</td>
<td>131.9</td>
</tr>
<tr>
<td>4a</td>
<td>167.3</td>
<td>127.5</td>
<td>125.4</td>
<td>128.7</td>
<td>131.4</td>
<td>131.6</td>
</tr>
<tr>
<td>4b</td>
<td>167.7</td>
<td>127.5</td>
<td>125.4</td>
<td>d</td>
<td>d</td>
<td>131.7</td>
</tr>
</tbody>
</table>

PdBrMe$_2$(CH$_2$Br)(pTol-BIAN), 4b, occurs as a mixture of two isomers: the major isomer (77%) has C$_3$ symmetry, [OC-6-54-C/A]-5b, as can be derived from the observation of one Pt-Me resonance at 1.60 ppm and one singlet for the benzylic protons at 3.18 ppm in $^1$H NMR. The minor isomer gives in $^1$H NMR two Pd-Me resonances at 1.37
and 1.10 ppm and two doublets for the benzyllic protons at 4.38 and 3.38 ppm, indicating $C_1$ symmetry, i.e. [OC-6-43]-4b. The axial position of the bromide was deduced from the high frequency resonance of two of the protons H$_8$ at 7.76 ppm, whereas the other two protons H$_9$ are shifted to low frequency for the major isomer (6.22 ppm), due to shielding by the phenyl ring of the benzyl ligand. The orientation of this phenyl ring toward the NN ligand was also observed for PdBrMe$_2$(CH$_2$C$_6$H$_4$p-Br)(phen) and free O,O'-diphenylacetone. Interestingly, a small Pd–CH$_2$Ph resonance is observed at 3.11 ppm (ca. 9% relative to the major isomer), which might be due to the rotamer complex having the phenyl ring of the benzyl group oriented toward the methyl ligands.\footnote{22} 

PdMe$_2$(phen), 2, reacted with benzyl bromide to give PdBrMe$_2$(CH$_2$Ph)(phen), 5b, which occurred as a mixture of two isomers in a 3:1 ratio. From $^1$H 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 PdMe$_2$(NN) complexes 1 and 3 in CDCl$_3$ at 20 °C led to the formation of PdMe$_2$(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.\footnote{22} 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 $^1$H NMR of PdMe$_2$(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 PdMe$_2$(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 PdMe$_2$(pTol-BIAN), 1, did not lead to an observable triorganopalladium(IV) complex, but instead acetone and Pd(Me)Cl$_2$(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 PdMe$_2$(tmeda) complexes.\footnote{43} PdMe$_2$(o,o'-iPr$_2$C$_6$H$_4$-BIC), 2, reacted much slower than 1 or 3 with benzyl bromide: after 10 min in CDC$_3$ 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$_2$(o,o'-iPr$_2$C$_6$H$_4$-BIC) and free o,o'-iPr$_2$C$_6$H$_4$-BIC. On the other hand, iodomethane reacted instantaneously with 2 in CDC$_3$ at 20 °C, but the only product observed was Pd(Me)I(o,o'-iPr$_2$C$_6$H$_4$-BIC), without observation of a triorganopalladium(IV) intermediate.

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

<table>
<thead>
<tr>
<th>complex</th>
<th>$T$ (°C)</th>
<th>$\log(k)$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdMe$_3$(pTol-BIAN)$^6$ (4a)</td>
<td>30</td>
<td>1.2</td>
</tr>
<tr>
<td>35</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>PdMe$_3$(Ph-BIC) (5a)</td>
<td>40</td>
<td>2.8</td>
</tr>
<tr>
<td>PdBrMe$_2$(CH$_2$Ph)(pTol-BIAN) (4b)</td>
<td>70</td>
<td>7.4</td>
</tr>
</tbody>
</table>

* The reactions were monitored by $^1$H NMR spectroscopy of 0.050–0.10 M solutions in CDCl$_3$, during 15–30 h. The accuracy of the rate constants is ±5%. $^g$ $E_a = 60 ± 10$ kJ·mol$^{-1}$.

Scheme 2

Reductive Elimination from PdIVMe$_2$(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 $^1$H 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 PdMe$_3$(pTol-BIAN), 4a, is rather unselective since not only Pd(Me)I(pTol-BIAN), resulting from ethane elimination is formed, but also some Pd(pTol-BIAN)Cl(Me) (10–20%) in all cases. As it was shown that Pd(Me)I(pTol-BIAN) does not react with CDCl$_3$ to give Pd(Me)Cl(pTol-BIAN), the formation of Pd(Me)Cl(pTol-BIAN) is most likely due to reductive elimination of iodomethane from PdMe$_3$(pTol-BIAN), 4a, followed by reaction of PdMe$_2$(pTol-BIAN), 1, with CDCl$_3$ (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 PdBrMe$_2$(CH$_2$C(O)Ph)(NN) (NN = bpy, phen) has been observed.\footnote{22}

The reductive elimination from PdMe$_3$(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 CDCl$_3$, but after reaction with silver trifluoromethanesulfonate in CDCl$_3$ at 20 °C, followed after 5 min by sodium iodide, the only organometallic product obtained is Pd(Me)I(Ph-BIC). PdBrMe$_2$(CH$_2$Ph)(pTol-BIAN), 4b, is even more stable than 4a at 20 °C in CDC$_3$ solution. After 48 h still 85% of the starting palladium(IV) complex is present and after 7 days a mixture of PdBr$_2$Me$_2$(CH$_2$Ph)(pTol-BIAN), Pd$_2$Br$_2$(Me)(pTol-BIAN), and PdBr$_2$(CH$_2$Ph)(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$^{-5}$ 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 PdBr$_2$Me$_2$(CH$_2$Ph)(NN) complexes.\footnote{43}

Synthesis of (D1)methylplatinum(II) Complexes 6–8. Dimethylplatinum(II) complexes containing Ar-

Bian, ptol-DAB, and phen ligands were conveniently synthesized from \( \text{PtMe}_2(\mu-\text{SMe}_2) \) (eq 3). The PtMe\(_2\) (Ar-BIAN) complexes (Ar = ptol, 6; o,o'-iprC\(_2\)H\(_4\)-BIAN, 7) are dark green solids and were analyzed by elemental analysis and \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy (Tables 4 and 5).

\[ \text{PtMe}_2(\mu-\text{SMe}_2) + \text{MeLi} \rightarrow \text{MePtMe}_2(\mu-\text{SMe}_2) \text{ar-BIAN} + \text{EtCl} \]  

(1) MeLi

\[ \text{PtCl}_2(\text{SMe})_2 + \text{H}_2\text{O} \rightarrow \text{PtMe}_2(\mu-\text{SMe}_2) \text{ar-BIAN} + \text{HCl} \text{acetone} \]  

(2) H\(_2\)O

The reactions with iodonium, benzyl bromide, acetyl chloride, and diiodine were completed within 15 min, as

\[ \text{Pt}(\text{Me})\text{I}(\text{ptol-BIAN}), 8, \text{was synthesized from Pt(Me)I-} \]  

\[ \text{SMe}_2 \text{eq 4}, \text{which was in turn obtained via the reaction of PtCl}_2(\text{SMe})_2 \text{and methylmagnesium iodide, in a way similar to the reaction of PtCl}_2(\text{SE})_2 \text{with MeMgI}. \]  

(3)
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 $^1$H and $^{13}$C NMR spectroscopy (Tables 4 and 5).

The products formed have a fac geometry, as can be obtained from the observed P–Me coupling constants, which are in the range 71–77 Hz, and from comparison with known triorganoplatinum(IV) complexes that all have a fac geometry. Furthermore, in $^1$H NMR of all complexes the doublet due to two of the protons H$_2$ has shifted to approximately 7.8 ppm, which is indicative of a neighboring halide atom.

(25) P–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) 66–69 Hz, Me (trans to carbon ligand) 69–44 Hz, and Me (trans to imine)-N 68–78 Hz: (a) Clegg, D. E.; Hall, J. R.; Swile, G. A. J. Organomet. Chem. 1972, 38, 403. (b) Reference 6b.

The complexes PtMe$_3$I(pTol-BIAN), 9a, PtMe$_3$(C(O)-Me)Cl(pTol-BIAN), 9e, and PtMe$_3$I(pTol-BIAN), 9f, are formed as a single isomer: in $^1$H and $^{13}$C NMR a single
Platinum, which shield axial positions. 28 Balacco, G.; Natile, G. Pregosin, P. S.; Wombacher, F.

-containing ortho substituted aryl groups bonded to from the observed unreactivity toward iodomethane of of steric factors on oxidative addition is also apparent through space interaction between the Pt center and the.

After 2 days all of the starting complex A explanation for these large coupling constants has not been given, but there might be a contribution from a through space interaction between the Pt center and the β-H atoms of the pendant alkyl group. 27

In analogy to the palladium complex 2, PtMe2(o,o'; iPr2C6H3-BIAN), 7, 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 7 had disappeared and uncoordinated o,o'-iPr2C6H3-BIAN had formed together with unknown Pt complexes. There was no evidence for the formation of a PtBr2Me2(CH2Ph)(o,o'-iPr2C6H3-BIAN) complex during any stage of the reaction. However, 7 reacted readily with iodomethane and PtMe2(o,o'-iPr2C6H3-BIAN) was obtained. The proximity of the isopropyl groups to the axial ligands is apparent from the high frequency shift of the septet due to two of the methyne protons to 4.75 ppm, which is caused by the interaction of these protons with the axial iodide. 21b The influence of steric factors on oxidative addition is also apparent from the observed unreactivity toward iodomethane of Pt(tol)(bpy) and Pt(o,o'-Me2C6H3-BIAN)(bpy), i.e. complexes containing ortho substituted aryl groups bonded to platinum, which shield axial positions. 28

Oxidative Addition of (Organic) Halides to Pt-(Me)I(pTol-BIAN), 8. Pt(Me)I(pTol-BIAN), 8, readily reacted with several (organic) halides to give mono- and dirganoplatinum(IV) complexes 10. Oxidative addition of diiodine gave PtMe2(pTol-BIAN), 10f, instantaneously, in which the methyl group is situated in the equatorial plane, i.e. trans to an imine N atom, as can be derived from the asymmetric pattern for the pTol-BIAN ligand in 1H NMR. Iodomethane also added rapidly to 8, and in 15 min 80% conversion to Pt(pTol-BIAN)Me2, 10a, had occurred when a 10-fold excess of iodomethane was used, which contrasts to the much longer reaction times in the reaction of Pt(Me)I(PMe2Ph)2 with iodomethane (several days to weeks in neat MeI). 29 From the observation of two Pt–Me resonances at 1.92 and 1.86 ppm and an asymmetric pattern for the pTol-BIAN ligand, the formation of C1-symmetric [OC-6-341-10a was deduced. The formation of a mixture of two C2-symmetric isomers 10a (OC-6-13 and OC-6-22) in a ratio of 1:1 can be excluded from the observed differences with 9f and from the J(Pt–Me) coupling constants, which exclude mutually trans methyl groups. 26 Oxidative addition of benzyl bromide to 8 resulted in the formation of one isomer of PtBrMe2(CH2Ph)I(pTol-BIAN), 10b. From the observed chemical shifts of H5 (5.76 ppm (2H) and 7.96 ppm (2H)) and the J(Pt–Me) coupling constants, a geometry with an axial benzyl and halide ligand and a methyl group in the equatorial position is derived, but whether an [OC-6-34] or an [OC-6-43] isomer is formed, cannot be determined on the basis of these data.

Stability of Triorganoplatinum(IV) Complexes 9 toward Reductive Elimination. All complexes of the type PtMe2(R)X(pTol-BIAN), 9, are very stable in solution at 20 °C. In all cases the complexes can be kept in CDC13 solution in air at 20 °C for several days without any detectable decomposition, i.e. reductive elimination, β-elimination or decarbonylation. The acyl complex PtMe2(C(O)Me)Cl(pTol-BIAN), 9e, gave some uncharacterized products after 75 h in CDC13 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 PtMe2(C(O)Me)Cl2 complexes (L = phosphine). 44, 9a 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.

Dihalogenation 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 (CH3Cl2, CDC13), to give the cationic complexes [PtMe2(R)(pTolBIAN)]SO3CF3, 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).

References

The new complexes are stable toward reductive elimination in the absence of a stabilizing sixth ligand is necessary to prevent reductive elimination: as has been elaborated for Cu(SO₃CF₃) complexes.  

Indeed, the C₃v symmetry of SO₃CF₃ is lowered by coordination (Table 7). The observation of a 19F NMR chemical shift of -78.36 ppm for all complexes (vide infra), both containing ionic SO₃CF₃, show no S=O stretching frequency in the region 1200–1250 cm⁻¹. The fact that for the complexes 11,13, and 14 no absorption is observed in the region 1320–1380 cm⁻¹, which was reported to be characteristic of bound trifluoromethanesulfonate, indicates that the Pt–SO₃CF₃ 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 diffraction.

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 the region of noncoordinating trifluoromethanesulfonate anions, but for complexes of the type M(C₆H₄M)₂(SO₃CF₃)(PMe₃) (M = Rh, Ir) containing coordinated trifluoromethanesulfonate (based on IR spectroscopy), 19F NMR chemical shifts of -78.36 and -78.12 ppm have been reported. 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 C₃v symmetry of SO₃CF₃ is lowered by coordination, as has been elaborated for Cu(SO₃CF₃) complexes. Indeed, [Pd(η²-PhCH=CH=CH₂)(pTol-BIAN)]SO₃C₃F₃, which is included for comparison, and [PtMe₂(pTol-BIAN)]SO₃C₃F₃, 12 (vide infra), both containing ionic SO₃CF₃, show no S=O stretching frequency in the region 1200–1250 cm⁻¹. The fact that for the complexes 11,13, and 14 no absorption is observed in the region 1320–1380 cm⁻¹, which was reported to be characteristic of bound trifluoromethanesulfonate, indicates that the Pt–SO₃CF₃ 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 diffraction.

Table 6. ¹H NMR Data for the [PtMe₂(R)(pTol-BIAN)]SO₃C₃F₃ Complexes 11 and 12a

<table>
<thead>
<tr>
<th>R</th>
<th>H₂</th>
<th>H₃</th>
<th>H₄</th>
<th>H₅</th>
<th>H₆</th>
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<tbody>
<tr>
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<td>8.08 d</td>
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</tr>
<tr>
<td>11a</td>
<td>7.3 Hz</td>
<td>8.3 Hz</td>
<td>7.7 Hz</td>
<td>7.7 Hz</td>
<td>7.64 br</td>
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<tr>
<td>PhCH₃</td>
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<td>6.20 br</td>
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<tr>
<td>11b</td>
<td>(9 H)</td>
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<td>4 (H)</td>
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<td>C(O)Me</td>
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<td>12</td>
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<td>8.3 Hz</td>
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<td>8.3 Hz</td>
<td>8.3 Hz</td>
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<td>8.3 Hz</td>
<td>0.90 s (77.6 Hz), Me⁺</td>
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</table>

Table 7. IR and ¹⁹F NMR Data for the [PtMe₂(R)(NN)]SO₃C₃F₃ Complexes 11-14b

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<thead>
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<th>R</th>
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<th>¹⁹F NMR</th>
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<tbody>
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<tr>
<td>11b, R = CH₃Ph</td>
<td>1304, 1233</td>
<td>1170 1015 n.o. -79.0 br</td>
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<tr>
<td>11c, R = C(O)Me</td>
<td>1294, 1231</td>
<td>1165 1020 633 -78.73</td>
</tr>
<tr>
<td>12, R = Me; PPh₃</td>
<td>1270 1145 1031</td>
<td>632 -78.51</td>
</tr>
<tr>
<td>13, NN = phen</td>
<td>1275, 1230</td>
<td>1175 1030 n.o. -78.10b</td>
</tr>
<tr>
<td>14, NN = pTol-DAB</td>
<td>1265, 1230</td>
<td>1175 1030 n.o. -78.12b</td>
</tr>
<tr>
<td>Pd(allyl)SO₃C₃F₃</td>
<td>1278, 1265</td>
<td>1112 1031 633</td>
</tr>
</tbody>
</table>

a: Recorded at 300.13 MHz, in CDCl₃ at 20 °C, unless noted otherwise. See Table 5 for the adopted numbering scheme. b: At -40 °C four Pt–Me resonances are observed 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 H₂ at 2.51 and 2.50 ppm. c: Overlapped by the signal of H₂. d: At -40 °C two isomers are observed. The major isomer shows resonances at 1.09 (81.9 Hz), Me⁺, 0.96 (67.2 Hz), Me⁺ₗ and 2.99 d, 2.89 d, 1/H(H–H) = 9.4 Hz, CH₂Ph, and the minor isomer, at 1.14 (69.3 Hz), Me⁺, and 3.19 s (107 Hz), CH₂Ph. * Me⁺, 1/H(P–P) = 8.1 Hz; Me⁺ₗ, 1/H(P–P) = 6.6 Hz. In CDCl₃ at 20 °C.

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(30) Cationic platinum(IV) complexes have been reported before, but a stabilizing sixth ligand is necessary to prevent reductive elimination: refs 9 and 25a.


but no exchange between the axial and the equatorial methyl groups is observed (Figure 1).

The presence of two isomers is also apparent from $^{19}$F NMR recorded in CDCl$_3$ where at $-40^\circ$C two resonances are observed at $-78.81$ and $-79.33$ ppm, whereas at $20^\circ$C one broad resonance is observed at $-78.8$ ppm. The basic geometries that agree with the observed data are a square pyramidal geometry and a fac octahedral geometry with a weakly coordinating trifluoromethanesulfonate or a solvent molecule in an axial position. The differences between these isomers are marginal, and they only differ in the relative distances between the platinum center and the solvent or the trifluoromethanesulfonate molecules. The fluxional behavior can be described by interconversion between these isomers, but it is not clear which isomers are present in solution (Scheme 3).

The fact that the other possible isomers, having trans methyl groups (mer octahedral and trigonal bipyramidal), do not play a role in the fluxional behavior is supported by two observations. Firstly, at all temperatures studied ($-40$ to $+50^\circ$C) the equatorial and the axial methyl groups remain inequivalent, whereas scrambling would be expected in the case of interconversion between, e.g., a fac and a mer octahedral complex. Secondly, the observed data for the pTol-BIAN ligand are not in agreement with two mutually trans methyl groups: in that case in $^{13}$C NMR one signal for C$_9$ and one signal for C$_{10}$ would be expected, whereas for each isomer two signals are observed.

Furthermore, the aromatic region at $20^\circ$C is only slightly broadened in $^1$H and $^{13}$C NMR, indicating that there is fast exchange. Only the signals of C(H)$_2$ 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 pTol-BIAN ligand (C(H)$_3$), but has much less influence on the other C atoms.\(^{21b}\)

Reactions of $[\text{PtMe}_3(p\text{Tol-BIAN})]$SO$_3$CF$_3$, 11a, with Coordinating Molecules. After reaction of $[\text{PtMe}_3(p\text{Tol-BIAN})]$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% $[\text{PtMe}_3(\text{MeCN})](p\text{Tol-BIAN})$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 $-40^\circ$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 ($-40^\circ$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 $20^\circ$C in $^1$H NMR resonances at 0.77 (69.0 Hz) and 0.88 ppm (77.0 Hz). In $^{19}$F NMR one sharp resonance at $-79.06$ ppm is observed. No spectral changes occur upon cooling to $-40^\circ$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-$[\text{PtMe}_3(\text{MeCN})](p\text{Tol-BIAN})$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 $20^\circ$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 $\tau$-back-donation from the metal to obtain stable complexes, such as carbon monoxide, ethene, and (E)-2-butene, did not lead to a $[\text{PtMe}_3(\text{L})(p\text{Tol-BIAN})]$SO$_3$CF$_3$ complex observable by $^1$H NMR spectroscopy. On the other hand, with the donor ligand PPh$_3$ an adduct $[\text{PtMe}_3(p\text{Tol-BIAN})(\text{PPh}_3)]$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 tripênylphosphate ligand coordinating in an axial position, as is clear from the observed $^3$H NMR resonances and coupling constants of the Pt–Me groups, the symmetrical pattern for the pTol-BIAN ligand, and the low frequency doublet at 5.98 ppm.

due to anisotropic shielding of two protons H$_3$ by one of the phenyl rings of the triphenylphosphine ligand.

[PtMe$_2$(CH$_2$Ph)(NN)]SO$_2$CF$_3$ Complexes 11b, 13, and 14. [PtMe$_2$(CH$_2$Ph)(pTol-BIAN)]SO$_2$CF$_3$, 11b, in CDCl$_3$ at 20 °C shows in $^1$H NMR one broadened Pt–Me resonance at 1.16 ppm (67 Hz), one broadened Pt–CH$_2$Ph resonance at 3.24 ppm (108 Hz), and a broad signal at 6.20 ppm (H$_3$), indicative of a complex with an axial benzyl group. In $^{19}$F NMR a broad signal at 79.0 ppm is observed. Upon cooling to −40 °C in $^{19}$F NMR two trifluoromethanesulfonate resonances are observed at −78.82 and −79.48 ppm in a ratio of 1:2. In $^1$H 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–CH$_2$Ph moiety one singlet at 3.19 ppm ($^2$J(Pt–H) ≈ 107 Hz) and two doublets at 2.99 and 2.89 ppm ($^2$J(Pt–H) not resolved) in a ratio of 1:2:2. Analogous to [PtMe$_2$(pTol-BIAN)]SO$_2$CF$_3$, 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 C$_1$-symmetric structure, with the benzyl group in an equatorial position. The C$_1$ symmetry of the major isomer and the presence of the minor isomer gives rise to a very complex $^{13}$C NMR spectrum. From these $^{13}$C NMR data there is no evidence for a C$_1$-symmetric isomer and the benzyl group is not coordinated due to the high trans influence of the acetyl group.

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The acyl complex [PtMe$_2$(C(O)Me)(pTol-BIAN)]SO$_2$CF$_3$, 11f, obtained by addition of 2 equiv of AgSO$_2$CF$_3$ to [OC-6-13]-Pt(pTol-BIAN)Me$_2$, 9f, showed the presence of two Pt–Me resonances at 2.06 (75.8 Hz) and 1.68 ppm (81.0 Hz) and two doublets of H$_3$. Cooling to −20 or −50 °C did not bring about any changes in the $^1$H NMR spectra. In $^{19}$F 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 C$_1$-symmetric structure with one equatorial and one axial methyl group, instead of being a mixture of two C$_1$-symmetric isomers, since upon addition of sodium iodide [OC-6-23]-Pt(pTol-BIAN)Me$_2$, 10a, is obtained as the only product.

Thermal Stability of the [PtMe$_2$(R)(pTol-BIAN)]SO$_2$CF$_3$ 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 CD$_3$CN 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 [PtMe$_2$(C(O)Me)(pTol-BIAN)]SO$_2$CF$_3$, 11e, does not show any decarboxylation (after 75 h). The complexes [PtMe$_2$(Et)(pTol-BIAN)]SO$_2$CF$_3$, 11c, and [PtMe$_2$(CH(Me)Ph)(pTol-BIAN)]SO$_2$CF$_3$, 11d, did not reveal any sign of reductive elimination or $\beta$-elimination after several hours in CD$_3$CN (monitored by $^1$H NMR) and the halide complexes 9e,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 [PtMe$_2$(pTol-BIAN)]SO$_2$CF$_3$, 11a, and [PtMe$_2$(CH$_2$Ph)(pTol-BIAN)]SO$_2$CF$_3$, 11b, were stable toward reductive elimination at 20 °C in CD$_3$CN and in CD$_2$CF$_3$ for at least 1 week and in CD$_3$O or CD$_2$CN at 50 °C for at least 40 h. [PtMe$_2$(CH$_2$Ph)(phen)]SO$_2$CF$_3$, 13, was also stable toward decomposition in CD$_3$CN at 50 °C for at least 40 h, but [PtMe$_2$(CH$_2$Ph)(pTol-DAB)]SO$_2$CF$_3$, 14, showed some broadening of the Pt–Me signal after 40 h in CD$_3$CN at 50 °C. Some metallic precipitate was present and in the $^1$H NMR a new Pt–Me signal was observed at 1.23 ppm (76.1 Hz), characteristic of a Pt$_2$Me$_3$ complex. Unfortunately, the other signals of


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 MM(II)(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)(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.7 The high reactivity of the MM(II)(pTol-BIAN) and PdMe₃(II)(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), 9f, and the formation of [OC-6-32]-PtMe₂(pTol-BIAN), 10a, via trans oxidative addition of iodomethane to Pt(Me)(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]-9f is completely converted to [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, tmeda,34 (py)(pz)CHMe, and (py)(pz)CH₂ (py = pyridin-2-yl, pz = pyrazol-1-yl).82 Although several of these could be isolated and X-ray crystallographic studies have been reported,33,34 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.43 The observed rapid elimination of ethane after reaction of PdMe₃(II)(Ph-BIC) with AgSO₃CF₃ is in agreement with such a mechanism (Scheme 4). Furthermore, the calculated activation energy of 60 kJ·mol⁻¹ for reductive elimination from PdMe₃(II)(pTol-BIAN) in CDCl₃ is in the same range as that found for PdMe₃(I)(bpy) in acetonitrile (65 kJ·mol⁻¹),44 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 PdMe₃(II)(NN) complexes 4,5a in chloroform are 2 or 3 orders of magnitude smaller than those of PdMe₃(I)(bpy) in acetone or benzene.44 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 > tmdea, (py)(pz)CHMe, (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.40,41 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.42,43 The higher stability of the triorganopalladium(IV) complexes PdMe₃(II)(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.17c,21b 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 PdMe₃(II). 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(II). Comparable diorganopalladium(IV) complexes are likely intermediates in the reactions of organopalladium(IV) complexes with organic halides, yielding finally Pd₃(III)-dihalide complexes and organic coupling products.24

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 PdMe₃(II)(O₂/C₆H₅)₂(BIAN) with iodomethane, which did not lead to an observable trimethylplatinum(IV) intermediate, but instead reductive elimination occurred immediately to give only PdMeI(II)(O₂/C₆H₅)₂(BIAN). The low stability of PdMe₃(II)(O₂/C₆H₅)₂(BIAN) is due to the orientation of the aromatic groups perpendicular to the metal center.44 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 Pd(II)(Me)(CH₃)(CH₃)₂(P₂Me₅) allows the complex to adopt a more favorable conformation for reaction with another molecule of MeI.44


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(41) From an investigation of the available crystal structure data of PdMe₂(II)(bpy) and Pt(NN) complexes, it was observed that typical M=N–N angles are 77–80° (α = Pt²⁺(P₂Me₅)₂CH₃), 74–93° (phen), 62–89° (imidazole), and 84–90° (ligands forming six-membered chelate rings). For bpy N–N angles typically lie in the range 75–95°, but angles of 84.3(8)° have been reported for (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, 3061.
to the coordination plane, leading to steric interference of the isopropyl groups with the axial ligands on the palladium(IV),17c,21b 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 PtMe2Cl[O,O'-iPr2C6H5-BIAN] and might facilitate reductive elimination from PdMe2I[O,O'-iPr2C6H5-BIAN]. Alternatively, reductive elimination might occur from the intermediate [PdMe2(O,O'-iPr2C6H5-BIAN)]+I- formed during oxidative addition, because coordination of I- to Pd(IV) is hindered by the o,o'-iPr2C6H5-BIAN ligand.42

A remarkable aspect is the unsselective reductive elimination from PdBrMe2(CH2Ph)(pTol-BIAN), 4b, in CDCl3, giving 60% PdBr(CH2Ph)(pTol-BIAN) and 40% PdBr2(Me)(pTol-BIAN). In all reported cases of reductive elimination from PdBrMe2(CH2Ph)(NN) complexes, studied in acetonitrile or benzene solution, there is a preference for the elimination of ethane over ethylbenzene,4 and the selectivity for ethane elimination decreases in the order bpy, tmeda (85-100%) > phen > pTol-BIAN (60%), i.e. the order of increasing ligand rigidity. A reason for the increased amount of ethylbenzene elimination in the case of the pTol-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,4ac 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 pTol-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 PtMe2(ClOMe)Cl(pTol-BIAN), 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.6c,9a The high stability of these complexes is due to the rigidity of the pTol-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.8 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 [PtMe2R(pTol-BIAN)]SO2CF3, 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 [PtMe2(CH2Ph)(pTol-DAB)]SO2CF3 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 pTol-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 PtMe2X(P)2 complexes.8 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.36

Conclusion

The rigid bidentate nitrogen donor ligands pTol-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.3,4,23,29 The employed Ar-BIAN and Ph-BIC ligands are good σ-donors and activate the divalent complexes to undergo oxidative addition, as also appeared from the reactions of monooorganopalladium(II) complexes with organic halides.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 pTol-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 PdMe2(NN). The importance of the rigidity of the ligands in kinetically stabilizing high oxidation states became also apparent from the observed stability of the

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(42) Cationic complexes have been observed in oxidative addition reactions to dimethylplatinum and -palladium complexes: (a) Puddephatt, R. J.; Scott, J. D. Organometallics 1985, 4, 1221. (b) Crespo, M.; Puddephatt, R. J. Organometallics 1987, 6, 2548. (c) Byers, P. K.; Catty, A. J.; Skelton, B. W.; Traill, P. R.; Watson, A. A.; White, A. H. Organometallics 1992, 11, 3085.
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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