Stabilization of High Oxidation States by Rigid Bidentate Nitrogen Ligands: Synthesis and Characterization of Diorgano- and Triorganopalladium(IV) and Cationic Triorganoplatinum(IV) Complexes[1]

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Dimethylpalladium(II) and (di)methylplatinum(II) complexes containing the rigid bidentate nitrogen ligands bis(*p*-tolylimino)acenaphthene (*p*Tol-BIAN) and bis(phenylimino)camphane (Ph-BIC) readily undergo oxidative addition of a variety of (organic) halides, to give the corresponding octahedral diorgano- and triorganopalladium(IV) and -platinum(IV) complexes. The palladium complexes $PdMe_2(R)X(NN)$ (RX = MeI, $PhCH_2Br$; NN = *p*Tol-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 triorganopalladium(IV) complexes. The new diorganopalladium(IV) complexes $PdMe_2I_2(NN)$, synthesized via oxidative addition of diiodine to $PdMe_2(NN)$ are much less stable than the triorganopalladium(IV) complexes studied. $PtMe_2(R)X$(*p*Tol-BIAN) (RX = MeI, $PhCH_2Br$, EtI, PhCH(Me)Br, MeC(O)Cl, I_2) and Pt(Me)I(R)X(*p*Tol-BIAN) (RX = MeI, $PhCH_2Br$, I_2) were obtained via oxidative addition to $PtMe_2$(*p*Tol-BIAN) and Pt(Me)I(*p*Tol-BIAN), respectively. Reaction of $PtMe_2(R)X$(*p*Tol-BIAN) with $AgSO_3CF_3$ led to the formation of remarkably stable five-coordinate $[PtMe_2(R)$*p*Tol-BIAN$)]SO_3CF_3$ complexes (R = Me, CH_2-Ph, 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 $CDCl_3$ and CD_3CN $[PtMe_2(CH_2$-Ph)(*p*Tol-BIAN)$]SO_3CF_3$ was stable for at least 7 days at 20 °C or 40 h at 50 °C. The analogous complex $[PtMe_2(CH_2Ph)(phen)]SO_3CF_3$ was also stable at 50 °C in CD_3CN for at least 40 h, whereas $[PtMe_2(CH_2Ph)$(*p*Tol-DAB)$]SO_3CF_3$ 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 *p*Tol-BIAN and Ph-BIC ligands appears to be the major factor in determining the stability of these complexes.

Introduction

The existence of triorganopalladium(IV) complexes, as intermediates in the reductive elimination from dimethylbis(phosphine)palladium(II) complexes in the presence of iodomethane, was proposed by Stille and Milstein in 1979 (Scheme 1).[2] Stable triorganopalladium(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.[3] This complex contained the bidentate nitrogen ligand 2,2′-bipyridine (bpy), and after this report other examples of (stable) triorganopalladium(IV) complexes with bidentate[4] and tridentate nitrogen ligands[4e,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.[4a,c]

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 phosphine[6] and (bidentate) nitrogen[7] ligands

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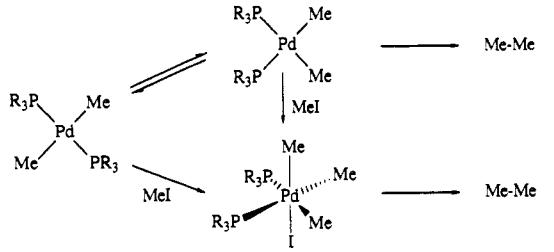
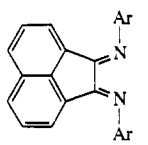
Scheme 1

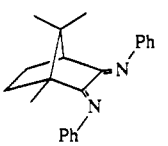


are known. Reductive elimination of ethane from $PtMe_3X(PR_3)_2$ complexes was shown to occur via loss of one coordinated phosphine prior to reductive elimination,[8] whereas decomposition of $PtMe_3I(bpy)$ occurred at higher temperatures and resulted in the formation of methane via α-elimination.[4a] 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.[9]

In view of the observed catalytic activity of Pd(Ar-BIAN) complexes, i.e. complexes containing the *cis*-fixed bidentate nitrogen ligand bis(arylimino)acenaphthene, in cross-coupling reactions between organic halides and organo-



Ar-BIAN



Ph-BIC

metallic reagents,[10] and the possible intermediacy of triorganopalladium(IV) complexes in this process,[2] 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 $Pd^{IV}R_2R'X(L)_2$ can in principle lead to the formation of cross-coupled (R–R′) or homocoupled (R–R) products.[4f,11] 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),[12] from which relatively slow β-H elimination takes place. Furthermore, the Ar-BIAN and Ph-BIC ligands are better σ-donors than bpy and phen due to the presence of exocyclic imine functionalities.[13] 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-butadiene (R-DAB) ligands,[13] which have often been used to stabilize metals in a low oxidation state because of their π-accepting properties.[14] 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. ^1H 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. ^{19}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_3PO_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),[15] $PdCl_2(SMe_2)_2$,[16] Ar-BIAN,[17] and Ph-BIC[17] were synthesized by following reported procedures.

Kinetic measurements of reductive eliminations from Pd(IV) complexes were carried out by ^1H 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(*p*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 35 °C, which were followed during ca. 2 half-lives.

$PdMe_2$(*p*Tol-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 methyllithium 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 *p*Tol-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 (calcd) for $C_{28}H_{26}N_2Pd$: C, 67.19 (67.68); H, 4.83 (5.28); N, 5.20 (5.64).

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$PdMe_2$(*o,o'-i*$Pr_2C_6H_3$-BIAN), 2, was synthesized in the same way (73%). Anal. Found (calcd) for $C_{38}H_{46}N_2Pd$: C, 70.66 (71.63); H, 7.23 (7.28); N, 4.53 (4.40).

$PdMe_2$(Ph-BIC), 3, was synthesized as described above for 1 (80%). Anal. Found (calcd) for $C_{24}H_{30}N_2Pd$: C, 63.25 (63.65); H, 6.78 (6.68); N, 6.10 (6.19). ^1H NMR ($CDCl_3$), δ: 2.65 d (4.5 Hz), H_4; 2.1 m (1 H), 1.9 m (2 H), 1.7 m (1 H), $H_{5,6}$; 0.99 s, 0.87 s, 0.58 s, $H_{8,9,10}$; 7.3–7.5 m (4 H), 7.1–7.3 m (2 H), 6.9–7.1 m (2 H), 7.01 d (8.1 Hz, 2 H), Ph; –0.01 s, –0.12 s, Pd–Me. ^{13}C NMR ($CDCl_3$), δ: 49.6, C_1; 179.9, 179.3, $C_{2,3}$; 50.9, C_4; 33.2, 24.6, $C_{5,6}$; 57.1, C_7; 21.7, 17.8, 12.3, $C_{8,9,10}$; 146.6, 146.2, C_i; 129.4, 128.8, C_o; 126.8, 126.2, C_p; 122.4, C_m; –6.4, –7.1, Pd–Me.

[*OC*-6-33]-$PdMe_3I$(*p*Tol-BIAN), 4a. To a solution of 0.10 g of $PdMe_2$(*p*Tol-BIAN), 1 (0.20 mmol), in 10 mL of THF was added 20 μL iodomethane (0.32 mmol) at 20 °C. After 15 min the product was filtered through Celite filter aid, the residue washed with THF (2 × 5 mL), and the solvent evaporated to approximately 1 mL. the product was precipitated by the addition of hexane (10 mL), washed with diethyl ether–hexane (1:1, 2 × 5 mL), and dried in vacuo, yielding 92 mg of an orange-red product (72%). Anal. Found (calcd) for $C_{29}H_{29}IN_2Pd$: C, 54.99 (54.52); H, 3.91 (4.58); N, 4.53 (4.38).

$PdBrMe_2(CH_2Ph)$(*p*Tol-BIAN), 4b, was synthesized similarly to **4a** (orange, 86%). Anal. Found (calcd) for $C_{35}H_{33}BrN_2Pd$: C, 62.50 (62.93); H, 5.41 (4.98); N, 4.76 (4.19).

$PdMe_2I_2$(*p*Tol-BIAN), 4f (red/brown) was characterized in situ and not isolated (see text).

$PdMe_3I$(Ph-BIC), 5a, was synthesized similarly to **4a** (off-white, 76%). Anal. Found (calcd) for $C_{25}H_{33}IN_2Pd$: C, 49.52 (50.48); H, 5.86 (5.59); N, 4.64 (4.71). ^1H NMR (two isomers, $CDCl_3$), δ: 2.70 d (4.3 Hz), 2.67 d (4.6 Hz), H_4; 2.0 m (1 H), 1.9 m (2 H), 1.7 m (1 H), $H_{5,6}$; 1.13 s, 1.08 s, 0.89 s, 0.83 s, 0.63 s, 0.62 s, $H_{8,9,10}$; 7.85 d (7.8 Hz), 7.63 d (7.8 Hz), 6.85 d (7.6 Hz), 6.76 d (7.6 Hz), H_o(Ph); 7.2–7.5 m (6 H), $H_{m,p}$(Ph); 1.44 s, 1.39 s, 1.35 s, 1.29 s, 1.26 s, Pd–Me. ^{13}C NMR (two isomers, $CDCl_3$), δ: 51.4, 49.6, C_1; 179.6, 179.5, 179.2, 179.0, $C_{2,3}$; 51.2, 51.1, C_4; 33.9, 31.8, 25.5, 23.0, $C_{5,6}$; 57.5, 57.2, C_7; 25.2, 23.3, 22.1, 21.9, 18.8, 18.3, 17.7, 17.5, 17.0, 12.7, 12.2, $C_{8,9,10}$, Pd–Me; 146.0, 145.8, 145.3, 145.2, C_i; 129.9, 129.8, 129.7, 128.8, C_o; 123.7, 122.6, 121.9, 120.0, 119.7, C_m; 127.6, 127.3, 127.0, 126.8, C_p.

$PdBrMe_2(CH_2Ph)$(Ph-BIC), 5b, was synthesized similarly to **4a** (off-white, 71%). Anal. Found (calcd) for $C_{31}H_{37}BrN_2Pd$: C, 59.46 (59.67); H, 6.15 (5.98); N, 4.48 (4.49). ^1H NMR (major isomer, $CDCl_3$), δ: 2.48 d (4.6 Hz), H_4; 2.0 m (1 H), 1.9 m (2 H), 1.7 m (1 H), $H_{5,6}$; 1.15 s, 0.81 s, 0.55 s, $H_{8,9,10}$; 7.83 d (8.6 Hz, 1 H), 7.0–7.5 m (13 H), 6.18 m (1 H), Ph (*Ph*-BIC + *Ph*CH_2); 1.63 s, 1.46 s, Pd–Me; 2.93 s, Pd–CH_2Ph. ^1H NMR minor isomer, $CDCl_3$), 2.53 d (4.3 Hz), H_4; 1.19 s, 0.86 s, 0.59 s, $H_{8,9,10}$; 1.57 s, 1.37 s, Pd–Me; 3.18 d, 3.07 d (7.9 Hz), Pd–CH_2Ph. ^{13}C NMR (major isomer, $CDCl_3$), δ: 51.0, C_1; 179.6, 179.3, $C_{2,3}$; 51.4, C_4; 33.3, 24.7, $C_{5,6}$; 57.2, C_7; 21.8, 18.7, 12.1, $C_{8,9,10}$; 24.5, 23.8, Pd–Me; 41.5, Pd–CH_2Ph. ^1H NMR (minor isomer, $CDCl_3$), δ: 48.9, C_1; 180.4, 180.1, $C_{2,3}$; 51.3, C_4; 32.4, 23.6, $C_{5,6}$; 58.0, C_7; 22.7, 18.0, 12.7, $C_{8,9,10}$; 23.3, 23.1, Pd–Me; 41.6, Pd–CH_2Ph; aromatic region (no further assignments can be made) 129.8, 129.4, 129.3, 129.1, 128.6, 128.3, 127.4, 126.9, 126.6, 126.1, 126.0, 123.4, 122.7, 121.8, 121.7, 120.6, *Ph*-BIC + *Ph*CH_2.

$PdMe_2I_2$(Ph-BIC), 5f (purple-red), was analyzed in situ and not isolated. ^1H NMR (major isomer, $CDCl_3$), δ: 2.71 d (4.5 Hz), H_4; 1.7–2.1 m (4 H), $H_{5,6}$; 1.15 s, 0.90 s, 0.65 s, $H_{8,9,10}$; 7.1–7.5 m (10 H), Ph; 2.31 s, 2.18 s, Pd–Me. ^1H NMR (minor isomer (24%), $CDCl_3$), δ: 2.59 d (4.5 Hz), H_4; 1.10 s, 0.86 s, 0.53 s, $H_{8,9,10}$.

Oxidative Additions to $PdMe_2$(*o,o'-i*$Pr_2C_6H_3$-BIAN), 2. To a solution of 15.6 mg of **2** (0.024 mmol) in 0.5 mL of $CDCl_3$ at 20 °C was added 10 μL of $PhCH_2Br$ (0.084 mmol) or 4.0 μL of MeI (0.064 mmol) and NMR spectra were recorded at certain intervals (5 min to 5 h).

Dehalogenation of $PdMe_3I$(Ph-BIC), 5a. To a solution of 18.4 mg of **5a** (0.041 mmol) in 0.5 mL of $CDCl_3$ was added 12.0 mg of $AgSO_3CF_3$ (0.047 mmol) and the mixture stirred in the dark at 20 °C. After 5 min excess NaI was added and the mixture stirred for 1 min. The solution was filtered and analyzed directly by ^1H NMR spectroscopy.

$PtCl_2(SMe_2)_2$ was synthesized by a modified literature procedure.[18] To a solution of 3.43 g of K_2PtCl_4 (8.26 mmol) in 60 mL of degassed water was added 1.70 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 $MgSO_4$, filtered, and evaporated to dryness. The product was dried in vacuo, giving 3.01 g of $PtCl_2(SMe_2)_2$ as a yellow powder (93%).

$[PtMe_2(\mu\text{-}SMe_2)]_2$ was synthesized from $PtCl_2(SMe_2)_2$ and MeLi, as reported before.[19]

$Pt(Me)I(SMe_2)_2$. To a solution of 0.40 g of $PtCl_2(SMe_2)_2$ (1.02 mmol) in 50 mL of diethyl ether, cooled in ice/water, was added dropwise 4 mL of a 0.58 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 NH_4Cl solution in water. The ether layer was separated and the water layer extracted with pentane (3 × 30 mL). The combined 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%).

$PtMe_2$(*p*Tol-BIAN), 6. A mixture of 0.55 g of $[PtMe_2(\mu\text{-}SMe_2)]_2$ (0.96 mmol) and 0.75 g of *p*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). The product was redissolved in 50 mL of dichloromethane, the solution was filtered through Celite filter aid, and the residue was washed with dichloromethane (2 × 20 mL). The combined filtrates were evaporated to approximately 5 mL and the product precipated by the addition of 20 mL of hexane. The solid was washed with diethyl ether–hexane (1:1, 15 mL) and dried in vacuo, yielding a 0.92 g of a green solid (82%). Anal. Found (calcd) for $C_{28}H_{26}N_2Pt$: C, 57.11 (57.43); H, 4.04 (4.48); N, 4.82 (4.78).

$PtMe_2$(*o,o'-i*$Pr_2C_6H_3$-BIAN), 7, synthesized in the same way as **6**, was obtained in 81% yield. Anal. Found (calcd) for $C_{38}H_{46}N_2Pt$: C, 62.78 (62.68); H, 6.46 (6.39); N, 3.92 (3.86).

$PtMe_2$(*p*Tol-DAB) (78%) and **$PtMe_2$(phen)** (84%) were obtained in the same way as **6**.

Pt(Me)I(*p*Tol-BIAN), 8. To a solution of 162.2 mg of Pt(Me)I$(SMe_2)_2$ (0.35 mmol) in 10 mL of dichloromethane was added 139.2 mg of *p*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 washed with dichloromethane (3 × 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 (calcd) for $C_{27}H_{23}IN_2Pt$: C, 46.80 (46.50); H, 3.56 (3.32); N, 3.61 (4.02).

[*OC*-6-33]-$PtMe_3I$(*p*Tol-BIAN), 9a. To a solution of 0.39 g of $PtMe_2$(*p*Tol-BIAN), **6** (0.67 mmol), in 30 mL of dichloromethane was added 100 μL of iodomethane (1.61 mmol), and the solution turned red within 1 min. After 15 min the solution was filtered through Celite filter aid and evaporated to 5 mL. The product was precipitated by the addition of 20 mL of hexane, washed with diethyl ether (10 mL), and dried in vacuo, to yield 0.37 g of an orange product (76%). Anal. Found (calcd) for $C_{29}H_{29}IN_2Pt$: C, 47.94 (47.87); H, 4.05 (4.02); N, 3.79 (3.85).

[*OC*-6-34]- and [*OC*-6-43]-$PtBrMe_2(CH_2Ph)$(*p*Tol-BIAN), 9b (orange, 72%). Anal. Found (calcd) for $C_{35}H_{33}BrN_2Pt$: C, 54.94 (55.56); H, 4.45 (4.40); N, 3.97 (3.70).

[*OC*-6-43]- and [*OC*-6-34]-$PtMe_2(Et)I$(*p*Tol-BIAN), 9c (orange 80%), was synthesized from **6** in THF at 20 °C in 2 h. Anal. Found (calcd) for $C_{30}H_{31}IN_2Pt$: C, 48.64 (48.59); H, 4.29 (4.22); N, 3.73 (3.78).

[*OC*-6-34]-$PtBrMe_2(CH(Me)Ph)$(*p*Tol-BIAN), 9d (yellow, 68%), was synthesized from **6** in THF at 20 °C in 16 h. Anal. Found (calcd) for $C_{36}H_{35}BrN_2Pt$: C, 55.88 (56.10); H, 4.56 (4.58); N, 3.71 (3.63).

(18) Cox, E. G.; Saenger, H.; Wardlaw, W. *J. Chem. Soc.* **1934**, 182.
(19) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643.

[*OC*-6-34]-PtMe$_2$(C(O)Me)Cl(*p*Tol-BIAN), 9e (orange, 75%). Anal. Found (calcd) for $C_{30}H_{29}ClN_2OPt$: C, 53.48 (54.26); H, 4.18 (4.40); N, 4.62 (4.22).

[*OC*-6-13]-PtMe$_2$I$_2$(*p*Tol-BIAN), 9f (brown, 82%). Anal. Found (calcd) for $C_{28}H_{26}I_2N_2Pt$: C, 39.64 (40.06); H, 3.26 (3.12); N, 3.20 (3.34).

[*OC*-6-34]-PtBrMe$_2$(CH$_2$Ph)(*p*Tol-DAB) (orange, 71%) was synthesized in the same way as **9a**. ^{1}H NMR ($CDCl_3$), δ: 8.32 (^3J(Pt—H) = 27.4 Hz), N=C*H*; 7.0–7.2 m (11 H), C_6H_4 + *Ph*CH$_2$; 6.68 d (2 H, 7.0 Hz), H$_o$(*p*Tol); 2.53 s, Me (*p*Tol); 2.51 s (^2J(Pt—H) = 93.8 Hz), Pt—C*H*$_2$Ph; 1.37 (^2J(Pt—H) = 71.7 Hz), Pt—Me; ^{13}C NMR ($CDCl_3$), δ: 161.7, N=CH; 144.3, C$_i$, 123.5, C$_o$, 130.1, C$_m$, 140.5, C$_p$ (*p*Tol); 145.1, C$_i$, 129.0, 128.8, C$_{o,m}$, 125.4, C$_p$ (*Ph*CH$_2$); 21.8 Me (*p*Tol); 22.9 (^1J(Pt—C) = 641 Hz), Pt—C*H*$_2$Ph; 1.1 (^1J(Pt—C) = 675 Hz), Pt—Me.

Oxidative Addition to PtMe$_2$(*o,o'*-*i*Pr$_2$C$_6$H$_3$-BIAN), 7. To a solution of 16.2 mg of **7** (0.022 mmol) in 0.5 mL of $CDCl_3$ at 20 °C was added 10 μL of $PhCH_2Br$ (0.084 mmol) or 4.0 μL of MeI (0.064 mmol), and the reaction was monitored by ^{1}H NMR spectroscopy (10 min to 4 days). ^{1}H NMR of [*OC*-6-33]-PtMe$_3$I(*o,o'*-*i*Pr$_2$C$_6$H$_3$-BIAN) ($CDCl_3$), δ: 8.03 d (8.3 Hz), H$_3$; 6.56 d (7.3 Hz), H$_5$; 7.3–7.5 m (8 H), H$_{4,10,11}$; 4.75 sept (6.7 Hz), 2.92 sept (6.7 Hz), CH (*i*Pr); 1.42 d, 1.22 d, 1.06 d, 0.46 d (6.7 Hz), CH$_3$ (*i*Pr); 1.50 s (^2J(Pt-H) = 73.7 Hz), Pt-Me$_{eq}$; 1.05 s (^2J(Pt-H) = 73.8 Hz), Pt-Me$_{ax}$.

[*OC*-6-32]-PtMe$_2$I$_2$(*p*Tol-BIAN), 10a. To a solution of 0.15 g of Pt(Me)I(*p*Tol-BIAN), **8** (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 × 10 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 (calcd) for $C_{28}H_{26}I_2N_2Pt$: C, 39.12 (40.06); H, 3.57 (3.12); N, 3.38 (3.34).

PtBr(Me)(CH$_2$Ph)I(*p*Tol-BIAN), 10b, was obtained from the reaction of **8** with benzyl bromide (75%). Anal. Found (calcd) for $C_{34}H_{30}BrIN_2Pt$: C, 46.98 (47.02); H, 3.58 (3.48); N, 3.34 (3.23).

[*OC*-6-21]-PtMeI$_3$(*p*Tol-BIAN), 10f. To a solution of 0.10 g of Pt(Me)I(*p*Tol-BIAN), **8** (0.14 mmol), in 10 mL of dichloromethane was added a solution of 50 mg of diiodine (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 (calcd) for $C_{27}H_{23}I_3N_2Pt$: C, 33.88 (34.09); H, 2.37 (2.44); N, 2.93 (2.94).

[PtMe$_3$(*p*Tol-BIAN)]SO$_3$CF$_3$, 11a. To a solution of 0.26 g of PtMe$_3$I(*p*Tol-BIAN), **9a** (0.36 mmol), in 40 mL of dichloromethane was added 0.11 g of $AgSO_3CF_3$ (0.43 mmol), and the mixture was 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 vacuo, yielding 0.24 g of a yellow powder (89%). Anal. Found (calcd) for $C_{30}H_{29}F_3N_2O_3PtS$: C, 48.10 (48.06); H, 3.88 (3.90); N, 3.77 (3.74).

[PtMe$_2$(CH$_2$Ph)(*p*Tol-BIAN)]SO$_3$CF$_3$, 11b (86%). Anal. Found (calcd) for $C_{36}H_{33}F_3N_2O_3PtS$: C, 51.88 (52.36); H, 4.14 (4.03); N, 3.52 (3.39).

[PtMe$_2$(C(O)Me)(*p*Tol-BIAN)]SO$_3$CF$_3$, 11e (81%). Anal. Found (calcd) for $C_{31}H_{29}F_3N_2O_4PtS$: C, 47.29 (47.87); H, 3.72 (3.76); N, 3.71 (3.60).

[PtMe$_2$(Et)(*p*Tol-BIAN)]SO$_3$CF$_3$, 11c, and [PtMe$_2$(CH(Me)Ph)(*p*Tol-BIAN)]SO$_3$CF$_3$, 11d, were obtained by the same procedure as yellow solids in good yields (80–90%), whereas **[PtMe$_2$(*p*Tol-BIAN)](SO$_3$CF$_3$)$_2$, 11f**, was synthesized from **9f** or **10a** and 2 equiv of $AgSO_3CF_3$ in $CDCl_3$ and analyzed in situ.

[*OC*-6-33]-[PtMe$_3$(MeCN)(*p*Tol-BIAN)]SO$_3$CF$_3$, 11a'. To a solution of 21.8 mg of **11a** (0.029 mmol) in 10 mL of dichloromethane was added 10 μL of acetonitrile (0.19 mmol) and the mixture was stirred at 20 °C. After 30 min the product was evaporated to approximately 1 mL and hexane was added. The precipitate was dried in vacuo during 10 min.

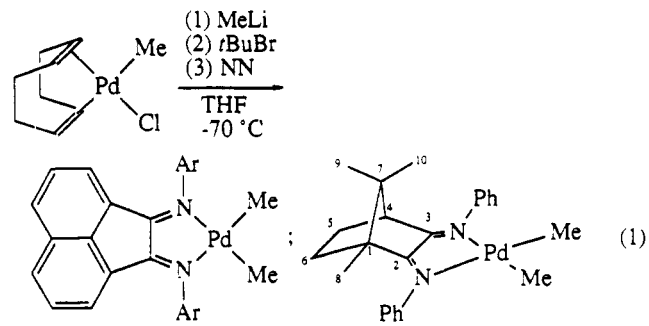
[*OC*-6-33]-[PtMe$_3$(*p*Tol-BIAN)(PPh$_3$)]SO$_3$CF$_3$, 12. To a solution of 53.8 mg of **11a** (0.072 mmol) in 5 mL of dichloromethane was added 20.6 mg of triphenylphosphine (0.078 mmol). After 5 min the solution was filtered through Celite filter aid, the residue washed with 5 mL of dichloromethane, and the solvent evaporated to about 3 mL. Addition of hexane (10 mL) caused the precipitation of the product, which was washed with diethyl ether (5 mL) and dried in vacuo, yielding 68 mg of **12** as a yellow solid (93%). Recrystallization from dichloromethane/hexane gave yellow needles. Anal. Found (calcd) for $C_{48}H_{44}F_3N_2O_3PPtS$): C, 56.60 (56.97); H, 4.64 (4.38); N, 2.61 (2.77). ^{31}P NMR ($CDCl_3$), δ: 0.19 (^1J(Pt-P) = 1038 Hz).

[PtMe$_2$(CH$_2$Ph)(phen)]SO$_3$CF$_3$, 13, was obtained from the reaction of PtBrMe$_2$(CH$_2$Ph)(phen) and $AgSO_3CF_3$ in 88% yield, similar to the synthesis of complexes **11**. ^{1}H NMR (CD_3CN), δ: 9.17 d (5.2 Hz), H$_2$; 8.10 dd (5.2, 8.2 Hz), H$_3$; 8.81 d (8.2 Hz), H$_4$; 8.20 s, H$_5$; 1.58 (^2J(Pt-H) = 68.8 Hz), Pt-Me; 3.06 (^2J(Pt-H) = 95.8 Hz), Pt-C*H*$_2$Ph; 6.57 t (7.5 Hz), H$_p$, 6.34 t (7.5 Hz), H$_m$, 6.10 d (7.5 Hz), H$_o$, Pt-CH$_2$*Ph*. ^{19}F NMR (CD_3CN), δ: -78.10.

[PtMe$_2$(CH$_2$Ph)(*p*Tol-DAB)]SO$_3$CF$_3$, 14 (83%). ^{1}H NMR (major isomer, CD_3CN), δ: 8.84 (^3J(Pt—H) = 29.0 Hz), N=C*H*; 7.43 d, 7.07 d (8.3 Hz), C_6H_4; 2.53 s, Me (*p*Tol); 1.21 (^2J(Pt—H) = 70.4 Hz), Pt—Me; 2.78 s (^2J(Pt—H) = 97.7 Hz), Pt—C*H*$_2$Ph. ^{1}H NMR (minor isomer (34%), CD_3CN), δ: 8.99 (^3J(Pt—H) = 26.9 Hz), 8.93 (^3J(Pt—H) = 27.5 Hz), N=C*H*; 7.62 d, 7.36 d (8.2 Hz), 7.48 d, 7.24 d (8.3 Hz), C_6H_4; 2.60 s, 2.53 s, Me (*p*Tol); 1.08 (^2J(Pt—H) = 70.9 Hz), 0.80 (^2J(Pt—H) = 76.6 Hz), Pt—Me; 3.02 d (^2J(Pt—H) = 69.0 Hz), 3.37 d (^2J(Pt—H) = 113.4 Hz) (9.5 Hz), Pt—C*H*$_2$Ph. ^{1}H NMR (both isomers CD_3CN), δ: all *Ph*CH$_2$ 6.76 m, C$_p$; 6.96 m, 7.18 m, C$_{o,m}$. ^{19}F NMR (CD_3CN), δ: -78.12.

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 methyllithium (eq 1). The reported procedures for the synthesis of PdMe$_2$(NN) complexes starting from PdCl$_2$(SMe$_2$)$_2$ and methyllithium[20] gave low yields of PdMe$_2$(Ar-BIAN) complexes **1** and **2**, due to extensive decomposition, but PdMe$_2$(Ph-BIC), **3**, could be obtained by this procedure in reasonable yield (63%). The method starting from PdMe$_2$(tmeda)[4d] could not be used since tmeda was not substituted by Ar-BIAN or Ph-BIC.



(1)

1, Ar = *p*Tol; **3**
2, Ar = *o,o'*-*i*Pr$_2$C$_6$H$_3$-BIAN

The complexes thus obtained were analyzed by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy (Tables 1 and 2). In ^{1}H (^{13}C) NMR the PdMe$_2$(Ar-BIAN) complexes showed one signal for Pd–Me at low frequency (0.16 (–5.8) and 0.05 (–6.4) ppm for **1** and **2**, respectively),

(20) Byers, P. K.; Canty, A. J. *Organometallics* **1990**, *9*, 210.

Table 1. ^{1}H NMR Data for the Organo-Pd(II) and Organo-Pd(IV) Complexes 1, 2, and 4[a]

	H_3	H_4	H_5	H_9	H_{10}	H_{12}	Pd–R
1	6.94 d 7.2 Hz	7.42 pst	7.99 d 8.2 Hz	7.14 d 8.1 Hz	7.34 d 8.1 Hz	2.47 s	0.16 s, Me
2	6.64 d 7.2 Hz	7.41 pst	8.01 d 8.3 Hz		7.38 s	*b*	–0.08 s, Me
4a[c]	7.0 m (4 H)	7.4 m (4 H)	8.01 d 8.2 Hz	7.82 d 7.4 Hz 7.0 m (4 H)	7.4 m (4 H) 7.33 d 7.4 Hz	2.49 s	1.51 s, Me_{eq} 1.39 s, Me_{ax}
4b[d]	6.89 d 7.3 Hz	7.4–7.5 m (6 H)	8.01 d 8.2 Hz	7.76 d 8.0 Hz 7.4–7.5 m (6 H)	7.4–7.5 m (6 H) 6.22 d 7.9 Hz	2.47 s	1.60 s, Me 3.18 s, CH_2Ph 7.0–7.2 m (5 H), CH_2*Ph*
4f	7.03 d 7.3 Hz	7.53 pst	8.04 d 8.5 Hz	7.43 d 8.1 Hz	7.50 d 8.1 Hz	2.53 s	2.35 s, Me

[a] Recorded at 300.13 MHz in $CDCl_3$ at 20 °C. The adopted numbering scheme for *p*Tol-BIAN is shown in Table 5. [b] 3.43 sep (6.8 Hz), CH (*i*Pr); 1.40 d, 0.93 d (6.8 Hz), CH_3 (*i*Pr). [c] Major isomer. The minor isomer (8%) shows Pd–Me resonances at 1.37 s and 1.12 s. [d] Major isomer. The minor isomer (23%) shows additional resonances at 1.37 s, 1.10 s, Pd–Me; 4.38 d, 3.38 d (7.0 Hz), Pd–CH_2Ph. Furthermore a small Pd–CH_2Ph signal of a rotamer of the major isomer at 3.11 s is observed (about 9% relative to the major isomer).

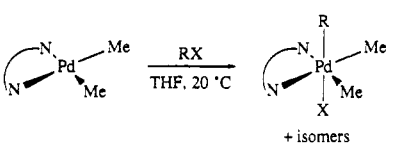
Table 2. ^{13}C NMR Data for the Organo-Pd(II) and Organo-Pd(IV) Complexes 1, 2, and 4[a]

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	Pd–R
1	168.2	127.7	124.8	128.9	130.6	131.9	144.1	145.1	121.1	130.6	136.8	21.8	–5.8
2	168.1	128.6	124.4	129.2	130.5	131.9	143.3	143.5	139.0	124.3	127.3	*b*	–6.4
4a	167.3	127.5	125.4	128.7	131.4	131.6	144.5	144.2	122.9	131.4	137.6	21.9	18.3[c]
									119.3	130.5			25.2
4b[d]	167.7	127.5	125.4	*d*	*d*	131.7	146.0	143.7	122.6	*d*	137.5	21.8	24.2 (Me)
									119.8				41.6 (CH_2)[d]

[a] Recorded at 75.48 MHz in $CDCl_3$ at 20 °C. The adopted numbering scheme is shown in Table 5. [b] 29.2, CH (*i*Pr); 24.4, 24.0, CH_3 (*i*Pr). [c] Pd–Me resonances of the minor isomer at 19.6 and 15.6 ppm. [d] 131.5, 131.4, 130.1, 129.9, 129.6, 129.3, 128.7, 128.6, 128.2, 126.0, $C_{4,5,10}$, $C_{o,m,p}$ (CH_2*Ph*); 144.5, C_i (CH_2*Ph*). The minor isomer gives additional resonances at 167.1, C_1; 122.1, 119.4, C_9; 24.7, 26.2, Pd–Me, 41.0, Pd–CH_2Ph.

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(*p*Tol-BIAN) (100% conversion after 24 h), whereas **2** was much more stable (50% conversion to Pd(Me)Cl(*o,o'*-$iPr_2C_6H_3$-BIAN) after 4 days).

Oxidative Addition to $PdMe_2$(Ar-BIAN), 1 and 2, and $PdMe_2$(Ph-BIC), 3. Addition of 1 equiv of iodomethane or benzyl bromide to a solution of $PdMe_2$(NN) **1** or **3** in THF at 20 °C led to the immediate formation of a triorganopalladium(IV) complex, which could be isolated by evaporation of the solvent (eq 2). The formation

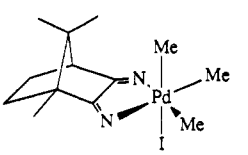


4, NN = *p*Tol-BIAN;
5, NN = Ph-BIC

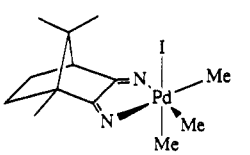
a, RX = MeI;
b, RX = $PhCH_2Br$;
f, RX = I_2 (2)

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 (^{13}C) 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.[3-5] In analogy to the reported triorganopalladium complexes with bidentate nitrogen ligands,[3,4] a *fac* geometry[21a] 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 $PdMe_3I$(*p*Tol-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*-$PdMe_3Y$(*p*Tol-BIAN) complex (where Y is Cl or a solvent molecule) or *mer*-$PdMe_3I$(*p*Tol-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 15.61 ppm in a ratio of approximately 2:1. Reaction of iodomethane with $PdMe_2$(Ph-BIC), **3**, gave a mixture of two isomeric $PdMe_3I$(Ph-BIC) complexes **5a** in a ratio of 54:46, which are most likely the [*OC*-6-44-*A*] and [*OC*-6-44-*C*] isomers, both having a *fac* geometry.

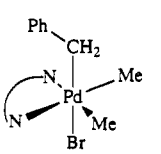


[*OC*-6-44-*A*]-**5a**

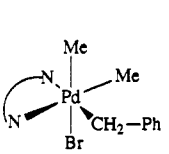


[*OC*-6-44-*C*]-**5a**

$PdBrMe_2(CH_2Ph)$(*p*Tol-BIAN), **4b**, occurs as a mixture of two isomers: the major isomer (77%) has C_s symmetry, [*OC*-6-34]-**4b**, as can be derived from the observation of one Pt–Me resonanceat 1.60 ppm and one singlet for the



major isomer



minor isomer

NN = *p*Tol-BIAN:
major = [*OC*-6-34]-**4b**;
minor = [*OC*-6-43]-**4b**.

NN = Ph-BIC:
major = [*OC*-6-45-*C/A*]-**5b**;
minor = [*OC*-6-55-*C/A*]- or
[*OC*-6-54-*C/A*]-**5b**

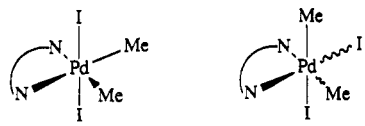
benzylic protons at 3.18 ppm in ^{1}H NMR. The minor isomer gives in ^{1}H NMR two Pd–Me resonances at 1.37

(21) (a) 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. H_9) in the proximity of the axial substituents; cf. references 17c and: van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.*, in press.

and 1.10 ppm and two doublets for the benzylic 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_9 at 7.76 ppm,[21b] 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 $PdBrMe_2(CH_2C_6H_4$-*p*-Br)(phen).[4g] Interestingly, a small Pd–CH_2Ph 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.[4g]

$PdMe_2$(Ph-BIC), **2**, reacted with benzyl bromide to give $PdBrMe_2(CH_2Ph)$(Ph-BIC), **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 $PdMe_2I_2$-(NN) complexes **4** and **5f** which are the first examples of spectroscopically characterized diorganopalladium(IV)



[*OC*-6-13]-**4f**

[*OC*-6-14]-**5f**

[*OC*-6-42]- or [*OC*-6-43]-**5f**

species containing (simple) hydrocarbyl groups (bis-(perfluorophenyl)palladium(IV) compounds are known).[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 $PdMe_2I_2$(*p*Tol-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 $PdMe_2I_2$(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 $PdMe_2$(*p*Tol-BIAN), **1**, did not lead to an observable triorganopalladium(IV) complex, but instead acetone and Pd(Me)Cl-(*p*Tol-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.[4f] $PdMe_2$(*o,o'*-*i*$Pr_2C_6H_3$-BIAN), **2**, reacted much slower than **1** or **3** with benzyl bromide: after 10 min in $CDCl_3$ no reaction had occured 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'*-*i*$Pr_2C_6H_3$-BIAN) and free *o,o'*-*i*$Pr_2C_6H_3$-BIAN. On the other hand, iodomethane reacted instantaneously with **2** in $CDCl_3$ at 20 °C, but the only product observed was Pd(Me)I(*o,o'*-*i*$Pr_2C_6H_3$-BIAN), without observation of a triorganopalladium(IV) intermediate.

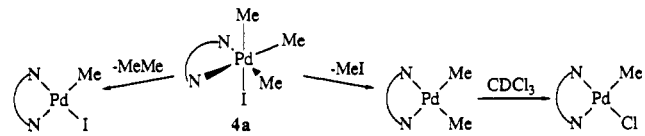
(22) Uson, R.; Forniés, J.; Navarro, R. *J. Organomet. Chem.* **1975**, *96*, 307.

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

complex	T (°C)	10^5k (s^{-1})
$PdMe_3I$(*p*Tol-BIAN)[b] (**4a**)	30	1.2
	35	1.8
	40	2.1
	50	5.2
$PdMe_3I$(Ph-BIC) (**5a**)	40	2.8
$PdBrMe_2(CH_2Ph)$(*p*Tol-BIAN) (**4b**)	50	7.4

[a] 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%. [b] E_a = 60 ± 10 kJ·mol^{-1}.

Scheme 2



Reductive Elimination from $Pd^{IV}Me_2(R)X(NN)$ Complexes 4 and 5. The triorganopalladium(IV) complexes **4** and **5** containing *p*Tol-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^{-5} to 10^{-4} 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 $PdMe_3I$(*p*Tol-BIAN), **4a**, is rather unselective since not only Pd(Me)I(*p*Tol-BIAN), resulting from ethane elimination is formed, but also some Pd(*p*Tol-BIAN)Cl(Me) (10–20%) in all cases. As it was shown that Pd(Me)I(*p*Tol-BIAN) does not react with $CDCl_3$ to give Pd(Me)Cl(*p*Tol-BIAN), the formation of Pd(Me)Cl(*p*Tol-BIAN is most likely due to reductive elimination of iodomethane from $PdMe_3I$(*p*Tol-BIAN), **4a**, followed by reaction of $PdMe_2$(*p*Tol-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(*p*Tol-BIAN) (Scheme 2). Reductive elimination of MeBr, besides ethane, from $PdBrMe_2$-$(CH_2C(O)Ph)$(NN) (NN = bpy, phen) has been observed.[23]

The reductive elimination from $PdMe_3I$(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). $PdBrMe_2(CH_2Ph)$(*p*Tol-BIAN), **4b**, is even more stable than **4a** at 20 °C in $CDCl_3$ solution. After 48 h still 85% of the starting palladium(IV) complex is present and after 7 days a mixture of $Pd^{IV}BrMe_2(CH_2Ph)$(*p*Tol-BIAN), Pd^{II}-Br(Me)(*p*Tol-BIAN), and $PdBr(CH_2Ph)$(*p*Tol-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 60% ethane and 40% ethylbenzene elimination, whereas in all the other cases reported there is a more pronounced preference for ethane elimination from isolated Pd-$BrMe_2(CH_2Ph)$(NN) complexes.[4]

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

(23) Canty, A. J.; Watson, A. A.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1989**, *367*, C25.

Table 4. ^{1}H NMR Data for the Organo-Pt(II) and Organo-Pt(IV)(Ar-BIAN) Complexes 6–10[a]

	H_3	H_4	H_5	H_9	H_{10}	H_{12}	Pt–R
$Pt^{II}Me_2$	7.05 d	7.32 pst	8.18 d	7.25 d	7.38 d	2.50 s	1.47 s (87.8 Hz), Me
6	7.1 Hz		8.2 Hz	8.1 Hz	8.1 Hz		
$Pt^{II}Me_2$	6.76 d	7.29 pst	8.24 d		7.43 s	*b*	1.56 s (88.7 Hz), Me
7	7.1 Hz		8.2 Hz				
$Pt^{II}(Me)I$	7.07 d	7.4 m	8.29 d	7.3 m	7.6 m	2.53 s	1.42 s (77.5 Hz), Me
8	7.2 Hz	(6 H)	8.3 Hz	(4 H)	(6 H)	2.51 s	
	6.82 d		8.15 d				
	7.3 Hz		8.3 Hz				
MeI + **6**	7.03 d	7.47 pst	8.07 d	7.81 d	7.35 d	2.50 s	1.15 s (72.2 Hz), Me_{eq}
9a	7.1 Hz		8.3 Hz	7.42 d	7.01 d		0.97 s (73.4 Hz), Me_{ax}
				8.0 Hz	8.0 Hz		
$PhCH_2Br$[c] + **6**	6.92 d	7.4 m	8.07 d	6.20 d	7.19 m	2.47 s	1.18 s (71.7 Hz), Me[c]
9b	7.2 Hz	(4 H)	8.2 Hz	7.78 d	6.9 Hz		2.93 s (96.8 Hz), CH_2Ph
				6.9 Hz	7.4 m		7.0 m (5 H), CH_2Ph
EtI[d]	7.01 d	7.5 m	8.07 d	7.95 dd	7.07 dd	2.51 s	1.15 s (73.0 Hz), Me
9c	7.1 Hz	(4 H)	8.3 Hz	8.1, 1.9 Hz	8.1, 1.9 Hz		1.64 q (74.3 Hz)
				7.04 d	7.5 m		0.70 t (69.6 Hz), Et[e]
				7.9 Hz			
PhCH(Me)Br + **6**	6.82 d[f]	*f*	*f*	5.65 dd[f]	*f*	2.52 s	1.31 s (72.6 Hz)
9d	7.3 Hz			8.1, 2.0 Hz		2.43 s	1.22 s (73.5 Hz), Me
				7.75 dd			3.24 q (86.7 Hz), PhC*H*(Me)
				8.1, 1.7 Hz			1.15 d (67.7 Hz), PhCH(*Me*)[g]
MeC(O)Cl + **6**	7.02 d	7.48 pst	8.08 d	7.58 dd	7.41 d	2.50 s	1.19 s (72.5 Hz), Me
9e	7.2 Hz		8.3 Hz	8.1, 1.7 Hz	8.1 Hz		2.08 s (16.5 Hz), C(O)Me
				7.11 dd	7.36 d		
				8.1, 1.7 Hz	8.1 Hz		
I_2 + **6**	7.05 d	7.53 pst	8.07 d	7.41 d	7.55 d	2.52 s	1.98 s (74.3 Hz), Me
9f	7.3 Hz		8.3 Hz	8.1 Hz	8.1 Hz		
MeI + **8**	6.80 d	*h*	8.16 d	8.05 dd	7.11 d	2.52 br	1.92 s (69.9 Hz), Me_{eq}
10a	7.3 Hz		8.3 Hz	8.0, 2.0 Hz	8.0 Hz		1.86 s (69.9 Hz), Me_{ax}
	7.18 d		8.11 d	7.87 d	7.3–7.6 m		
	7.3 Hz		8.4 Hz	7.8 Hz[h]			
$PhCH_2Br$ + **8**	6.74 d	*i*	8.17 d	5.76 br.	*i*	2.54 s	1.84 s (69.8 Hz), Me
10b	7.3 Hz		8.3 Hz	(2 H)		2.44 s	4.11 d (94.7 Hz)
	i		8.11 d	7.96 dd			3.58 d (90.6 Hz), CH_2Ph[i]
			8.3 Hz	8.1, 1.7 Hz			8.7 Hz
I_2 + **8**	7.19 d	7.6 m	8.15 d	7.80 d	7.4 m	2.54 s	2.86 s (72.4 Hz), Me
10f	7.3 Hz	(4 H)	8.3 Hz	8.3 Hz	(4 H)	2.53 s	
	6.81 d		8.12 d	7.6 m			
	7.3 Hz		8.3 Hz				

[a] Recorded at 300.13 MHz in $CDCl_3$ at 20 °C. See Table 5 for the adopted numbering scheme of *p*Tol-BIAN. For *o,o'*-$iPr_2C_6H_3$-BIAN the same numbering scheme is applied. Coupling constants (Hz) are given below the chemical shifts, and ^{195}Pt–^1H coupling constants for Pt–R groups are in parentheses. [b] 3.51 sep (6.8 Hz), CH (*i*Pr); 1.38 d, 0.91 d (6.8 Hz), CH_3 (*i*Pr). [c] Minor isomer: 0.96 (73.4 Hz), Me_{eq}; 0.68 (76.6 Hz), Me_{ax}; 3.8 d and 4.0 d (^2J(H–H) ≈ 8 Hz), Pt–CH_2Ph. [d] Minor isomer: 6.90 d (7.2 Hz), H_3; 8.06 d (8.2 Hz), H_5; 7.84 dd, 7.80 dd (8.1, 1.9 Hz), H_9; 1.13 s (^2J(Pt–H) = 74.0 Hz), Me_{eq}; 0.98 s (^2J(Pt–H) = 74.1 Hz), Me_{ax}; 2.10 dq (1 H, 7.6, 9.8 Hz, ^2J(Pt–H) = 97.5 Hz), other signal overlapped by those of the major isomer, CH_2CH_3; 0.71 t (7.6 Hz, ^2J(Pt–H) = 56.5 Hz), CH_2CH_3. [e] ^3J(H–H) = 7.6 Hz. [f] 8.05 m (3 H), $H_{5,9}$; 7.3–7.5 m (6 H) and 6.9–7.2 m (7 H), $H_{3,4,9,10}$, *Ph*CH(Me). [g] ^3J(H–H) = 7.2 Hz. [h] 7.3–7.6 m (6 H), $H_{4,9,10}$. [i] 7.3–7.5 m (4 H), 7.1–7.3 m (4 H), 6.9–7.1 m (4 H), $H_{3,4,10}$, *Ph*CH_2.

BIAN, *p*Tol-DAB, and phen ligands were conveniently synthesized from $[PtMe_2(\mu\text{-}SMe_2)]_2$ (eq 3). The $PtMe_2$(Ar-BIAN) complexes (Ar = *p*Tol, **6**; *o,o'*-$iPr_2C_6H_3$-BIAN, **7**) are dark green solids and were analyzed by elemental analysis and ^1H and ^{13}C NMR spectroscopy (Tables 4 and 5).

$$PtCl_2(SMe_2)_2 \xrightarrow[Et_2O]{\text{(1) MeLi, (2) } H_2O} 1/2\ [PtMe_2(\mu\text{-}SMe_2)]_2 \xrightarrow[\text{acetone}]{\text{Ar-BIAN}} PtMe_2(\text{Ar-BIAN}) \quad (3)$$

6, Ar = *p*Tol
7, Ar = *o,o'*-$iPr_2C_6H_3$

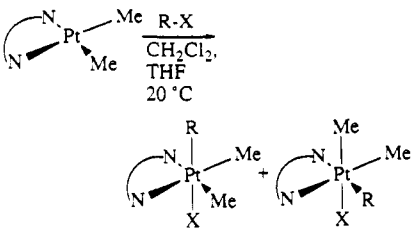
Pt(Me)I(*p*Tol-BIAN), **8**, was synthesized from Pt(Me)I-$(SMe_2)_2$ (eq 4), which was in turn obtained via the reaction of $PtCl_2(SMe_2)_2$ and methylmagnesium iodide, in a way similar to the reaction of $PtCl_2(SEt_2)_2$ with MeMgI.[24] The

$$PtCl_2(SMe_2)_2 \xrightarrow[Et_2O]{\text{(1) MeMgI, (2) } H_2O} Pt(Me)I(SMe_2)_2 \xrightarrow[CH_2Cl_2]{p\text{Tol-BIAN}} Pt(Me)I(p\text{Tol-BIAN}) \quad (4)$$

8

product **8** could easily be purified and was obtained analytically pure, which shows that isolated Pt(Me)I-$(SMe_2)_2$ can be successfully used as starting material for the synthesis of $Pt(Me)IL_2$ complexes, despite the fact that some decomposition might occur during its isolation as was reported previously.[19]

Oxidative Addition of (Organic) Halides to $PtMe_2$(*p*Tol-BIAN), 6. $PtMe_2$(*p*Tol-BIAN), **6**, reacted with a variety of (organic) halides to give stable diorgano- and triorganoplatinum(IV) complexes **9** (eq 5).



RX:
9a, MeI;
9b, $PhCH_2Br$;
9c, EtI;
9d, PhCH(Me)Br;
9e, MeC(O)Cl;
9f, I_2 (5)

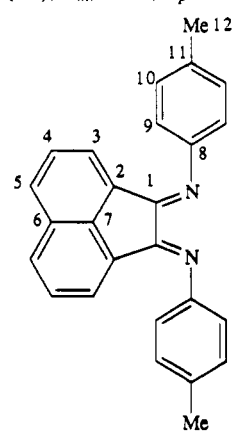
The reactions with iodomethane, benzyl bromide, acetyl chloride, and diiodine were completed within 15 min, as

(24) Kuyper, J.; van der Laan, R.; Jeanneaus, F.; Vrieze, K. *Transition Met. Chem.* **1976**, *1*, 199.

Table 5. ^{13}C NMR Data for the Organo-Pt(II) and Organo-Pt(IV)(Ar-BIAN) Complexes 6–12[a]

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	Pt–R
6	170.6	n.o.	122.9	129.1	130.0	133.1	144.6	144.9	122.3	130.4	137.4	21.8	–14.4 (808), Me
7	170.6	131.3	122.3	128.8	130.3	133.4	143.6	143.7	140.7	124.3	127.8	*b*	–15.4, Me
8	173.3	129.1	124.2	*c*	*c*	132.9	145.6	144.9	123.4	*c*	138.7	21.9	–15.9, Me
	171.1	127.9	123.9					143.3	122.6		138.1		
9a	170.7	127.7	125.2	129.0	130.4	131.9	145.4	143.4	123.5	131.4	138.3	21.9	–4.3 (668), Me_{eq}
									120.0				7.5 (677), Me_{ax}
9b	171.1	127.6	125.1	129.8	131.4	131.9	146.9	145.3	123.0	*d*	138.2	21.8	–0.7 (678), Me
									120.7				21.9 (668), CH_2Ph[d]
9c	171.1	127.7	125.2	129.0	130.2	131.9	145.4	143.9	124.0	*e*	*e*	21.9	–2.4 (694), Me
									120.6				20.0 (679)
													15.9 (35), Et
minor	170.9	127.8	125.3		130.5	131.8	145.2	143.6	123.3				–1.7 (702), Me_{eq}
		127.6			130.4			143.3	122.8				6.9 (723), Me_{ax}
									120.0				9.1 (661)
									119.9				18.9 (19), Et
9d	171.6	127.9	125.3	129.5	131.5	131.9	145.3	142.9	124.0	131.1	138.5	21.9	2.1 (706)
	171.4	127.8	125.2		131.2			142.8	123.1	130.7	137.9	21.8	2.0 (708), Me
									122.3	129.1			28.9 (685), PhCH(Me)
									120.8	128.5			23.0 (38), PhCH(*Me*)[f]
9e	172.3	127.5	125.5	129.0	131.7	131.9	146.0	142.9	122.3	131.1	138.3	21.9	–1.4 (700), Me
									120.7	130.4			35.0 (224), C(O)*Me*[g]
9f	172.1	127.7	125.6	129.1	131.9	132.0	145.8	143.3	121.5	131.0	138.5	21.9	–10.9 (505), Me
10a	174.6	127.0	126.1	129.4	*h*	132.9	146.3	143.2	123.8	*h*	140.2	22.0	–2.3 (528), Me_{eq}
	170.7	126.7	125.8	129.3				141.5	121.3		139.1	21.9	9.3 (524), Me_{ax}
									120.6				
									118.8				
11a[i]	173.4	126.9	126.1	129.3	131.7	132.0	146.4	142.4	122.5	132.2	138.7	22.2	–1.4 (685), –12.2, Me
									120.6	130.8			
minor			125.9	129.1	131.9	131.8	146.6	142.3	122.1	132.1	138.5	22.1	–2.6 (679), –13.4, Me
									120.5	130.7			
11b[i]	174.4	127.0	126.1	*j*	*j*	131.9	147.0	*k*	122.8	*j*	139.3	22.3	3.3, 1.4
	174.2	126.7	126.2			131.8	146.4		122.3		138.7	22.2	–2.3, –10.0, Me
	173.5	126.6					146.3		121.1		138.6	22.1	19.2, 11.1, CH_2[j,k]
	173.4								120.4		136.5		
12	173.3	127.0	126.2	129.6	133.6	138.5	145.9	142.2	121.6	131.6	140.2	21.8	15.5, Me_{ax}[l]

[a] Recorded at 75.48 MHz in $CDCl_3$ at 20 °C, unless noted otherwise. For the carbon numbering, see the structure below. J(Pt–H) (Hz) in parentheses. [b] 28.5, CH (*i*Pr); 24.6, 24.1, CH_3 (*i*Pr). [c] 130.9, 130.5, 130.3, 129.9, $C_{4,5,10}$. [d] 131.0, 129.3, 129.2, 128.9, C_{10}, $C_{o,m,p}$ (*Ph*CH_2); 142.8, C_i (*Ph*CH_2). [e] 131.4, 131.3, 131.2, C_{10}; 138.4, 138.2, 138.1, C_{11}. [f] *Ph*CH(Me): 151.6, C_i; 129.0, 128.8, 125.5, $C_{o,m,p}$. [g] 195.0, *C*(O)Me. [h] 132.8, 132.0, 131.9, 131.3, 131.1, 129.8, $C_{5,10}$. [i] Recorded at –40 °C. [j] 132.4, 132.3, 132.0, 131.9, 131.5, 131.3, 130.8, 130.3, 130.1, 129.9, 129.6, 129.3, 129.2, 129.0, $C_{4,5,10}$, $C_{o,m,p}$ (*Ph*CH_2). [k] 144.5, 143.7, 142.9, 142.2, 141.7, 141.6, C_8, C_i (*Ph*CH_2). [l] Me_{ax}: ^2J(P–C) = 104 Hz. Me_{eq}: ^2J(P–C) n.o. PPh_3 (J(P–C) in parentheses): 127.6 (38.5), C_i; 143.3 (9.8), C_o; 129.5 (9.8), C_m; 132.1, C_p.

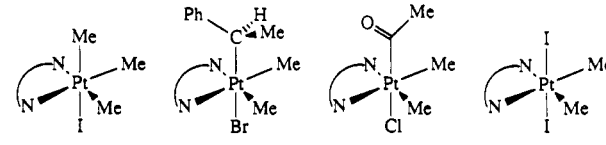


could be judged from the color change of the solution from dark green to orange-red. Reactions with iodoethane and 1-phenyl-1-bromoethane were slower and required several hours to go to completion. The Pt(IV) complexes **9** all showed correct analytical data and were analyzed by ^1H and ^{13}C NMR spectroscopy (Tables 4 and 5).

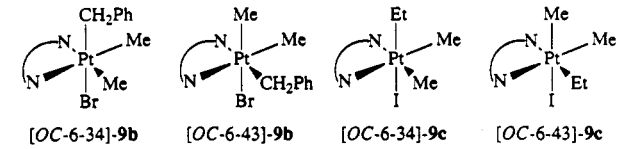
The products formed have a *fac* geometry,[21a] as can be derived from the observed Pt–Me coupling constants, which are in the range 71–77 Hz,[25] and from comparison with known triorganoplatinum(IV) complexes that all have a *fac* geometry. Furthermore, in ^1H NMR of all complexes the doublet due to two of the protons H_9 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) 56–59 Hz, Me (*trans* to carbon ligand) 43–44 Hz, and Me (*trans* to imine-N) 66–73 Hz: (a) Clegg, D. E.; Hall, J. R.; Swile, G. A. *J. Organomet. Chem.* **1972**, *38*, 403. (b) Reference 6b.

The complexes $PtMe_3I$(*p*Tol-BIAN), **9a**, $PtMe_2$(C(O)Me)Cl(*p*Tol-BIAN), **9e**, and $PtMe_2I_2$(*p*Tol-BIAN), **9f**, are



[*OC*-6-33]-**9a** [*OC*-6-34]-**9d** [*OC*-6-34]-**9e** [*OC*-6-13]-**9f**



[*OC*-6-34]-**9b** [*OC*-6-43]-**9b** [*OC*-6-34]-**9c** [*OC*-6-43]-**9c**

formed as a single isomer: in ^1H and ^{13}C NMR a single

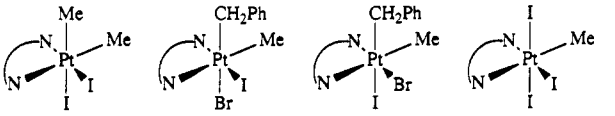
Pt–Me resonance isobserved for **9e** and **9f** and two signals in a ratio of 2:1 for **9a**. In ^{13}C (^1H) NMR of **9a** and **9e** two resonances are observed for $C(H)_9$ and $C(H)_{10}$, due to the inequivalence on both sides of the coordination plane, whereas the atoms that lie in the coordination plane (e.g. $C(H)_{3,4,5,12}$ and $C_{1,8,11}$) give one resonance. All these data are in agreement with the formation of a C_s-symmetric isomer. For $PtBrMe_2(CH(Me)Ph)$(*p*Tol-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 H_9 by the phenyl ring of 1-phenylethyl, point at the coordination of the 1-phenylethyl group in an axial position.

The complexes $PtBrMe_2(CH_2Ph)$(*p*Tol-BIAN), **9b**, and $PtMe_2(Et)I$(*p*Tol-BIAN), **9c**, occur as mixtures of two isomers, in ratios of 87:13 and 68:32, respectively. In these cases the C_s 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–CH_2Ph and one quartet for Pt–CH_2CH_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 quartets is observed for one of the protons ($AA'B_3X$ 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 ^3J(Pt–H) coupling constants observed for Pt–$CH(R)CH_3$ (R = H, Ph) (69.6 Hz and 67.7 Hz for the major and the minor isomer of **9c** and 67.7 Hz for **9d**) are in the range of those observed for $[PtEt_3Cl]_4$ (72.0 Hz),[26] $PtMe_2$(Et)I(phen) (68.4 Hz),[7c] and $PtMe_2$(*i*Pr)I(phen) (63 Hz).[7d] An 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**, $PtMe_2$(*o,o'*-$iPr_2C_6H_3$-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'*-$iPr_2C_6H_3$-BIAN had formed together with unknown Pt complexes. There was no evidence for the formation of a $Pt^{IV}BrMe_2(CH_2Ph)$(*o,o'*-$iPr_2C_6H_3$-BIAN) complex during any stage of the reaction. However, **7** reacted readily with iodomethane and $PtMe_3I$(*o,o'*-$iPr_2C_6H_3$-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 $Pt(oTol)_2$(bpy) and $Pt(o,o'\text{-}Me_2C_6H_3)_2$(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(*p*Tol-BIAN), 8. Pt(Me)I(*p*Tol-BIAN), **8**, readily reacted with several (organic) halides to give mono- and diorganoplatinum(IV) complexes **10**. Oxidative addition of diiodine gave $PtMeI_3$(*p*Tol-BIAN), **10f**, instantaneously,



[*OC*-6-32]-**10a** [*OC*-6-34]-**10b** [*OC*-6-43]-**10b** [*OC*-6-21]-**10f**

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 *p*Tol-BIAN ligand in ^1H NMR. Iodomethane also added rapidly to **8**, and in 15 min 80% conversion to Pt(*p*Tol-BIAN)Me_2I_2, **10a**, had occurred when a 10-fold excess of iodomethane was used, which contrasts to the much longer reaction times in the reaction of $Pt(Me)I(PMe_2Ph)_2$ 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 *p*Tol-BIAN ligand, the formation of C_1-symmetric [*OC*-6-32]-**10a** was deduced. The formation of a mixture of two C_s-symmetric isomers **10a** (*OC*-6-13 and *OC*-6-22) in a ratio of 1:1 can be excluded by the observed differences with **9f** and from the ^2J(Pt–Me) coupling constants, which exclude mutually *trans* methyl groups.[25] Oxidative addition of benzyl bromide to **8** resulted in the formation of one isomer of PtBrMe(CH_2Ph)I(*p*Tol-BIAN), **10b**. From the observed chemical shifts of H_9 (5.76 ppm (2 H) and 7.96 ppm (2 H)) and the ^2J(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 $PtMe_2(R)X$(*p*Tol-BIAN), **9**, are very stable in solution at 20 °C. In all cases the complexes 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 $PtMe_2$(C(O)Me)Cl(*p*Tol-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 $PtMe_2(C(O)Me)ClL_2$ complexes (L = phosphine).[6c,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.

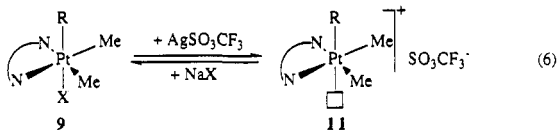
Dehalogenation of the Platinum(IV) Complexes 9 with Silver Salts. The triorganoplatinum(IV) complexes **9a–e** all react readily with silver salts like silver trifluoromethanesulfonate in noncoordinating solvent (CH_2Cl_2, $CDCl_3$), to give the cationic complexes $[PtMe_2(R)$(*p*Tol-BIAN)$]SO_3CF_3$, **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).

(26) Kettle, S. F. A. *J. Chem. Soc.* **1965**, 6664.
(27) (a) van Baar, J. F.; Vrieze, K.; Stufkens, D. J. *J. Organomet. Chem.* **1974**, *81*, 247. (b) van Vliet, M. R. P.; van Koten, G.; van Beek, J. A. M.; Vrieze, K.; Muller, F.; Stam, C. H. *Inorg. Chim. Acta* **1986**, *112*, 77. (c) Balacco, G.; Natile, G. *J. Chem. Soc., Dalton Trans.* **1990**, 3021. (d) Pregosin, P. S.; Wombacher, F. *Magn. Reson. Chem.* **1991**, *29*, S106.
(28) (a) Jawad, J. K.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1466. (b) Klein, A.; Hausen, H. D.; Keim, W. *J. Organomet. Chem.* **1992**, *440*, 207.
(29) (a) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1974**, *65*, 275. (b) Hall, J. R.; Swile, G. A. *J. Organomet. Chem.* **1974**, *76*, 257.

Table 6. ^{1}H NMR Data for the [$PtMe_2$(R)(*p*Tol-BIAN)] SO_3CF_3 Complexes 11 and 12[a]

R	H_3	H_4	H_5	H_9	H_{10}	H_{12}	Pt–R
Me[b]	7.04 d	7.48 pst	8.08 d	6.98 d	7.37 d	2.51 s	1.03 s (84.8 Hz), Me_{ax}
11a	7.3 Hz		8.3 Hz	7.7 Hz	7.7 Hz		0.98 br (67.8 Hz), Me_{eq}
				7.64 br	7.5 br[c]		
$PhCH_2$[d]	6.7–7.2 m	7.47 pst	8.08 d	6.20 br	7.5 m[c]	2.49 s	1.16 br (67.2 Hz), Me
11b	(9 H)		8.2 Hz	7.61 br	(4 H)		3.24 br (107.8 Hz), CH_2Ph
				6.7–7.2 m			6.7–7.2 m (9H), CH_2Ph
Et	7.0 m	7.48 pst	8.07 d	7.64 br	7.4 br	2.52 s	0.99 br (72.3 Hz), Me
11c	(4 H)		8.3 Hz	7.0 m	7.5 m[c]		1.4–2.0 vbr, 0.7 br, Et
C(O)Me	7.0 m	7.2–7.6 m	8.09 d	7.2–7.6 m	7.2–7.6 m	2.51 s	1.18 s (71.0 Hz), Me
11e	(4 H)	(8 H)	8.2 Hz	(8 H)	(8 H)		2.12 s (21.1 Hz), C(O)Me
SO_3CF_3	6.74 d	7.1–7.7 m	8.21 d	7.1–7.7 m	7.1–7.7 m	2.52 s	2.00 s (78.5 Hz), Me
11f	7.3 Hz	(11 H)	8.1 Hz	(11 H)	(11 H)		1.68 s (81.0 Hz), Me
	7.1–7.7 m		8.15 d				
			8.1 Hz				
Me/PPh_3	6.99 d	7.61 pst	8.31 d	8.08 d	7.4 m	2.55 s	0.83 (68.9 Hz), Me_{eq}[e]
12	7.4 Hz		8.3 Hz	8.3 Hz	(6 H)		1.24 (58.4 Hz), Me_{ax}
				7.4 m			7.1 m (9H), 7.2 m (6H), PPh_3
Me[f]	7.06 d	7.61 pst	8.28 d	7.21 pst	7.53 pst	2.52 s	0.75 s (69.9 Hz), Me_{eq}
11a	7.3 Hz		8.3 Hz				0.90 s (77.6 Hz), Me_{ax}

[a] Recorded at 300.13 MHz, in $CDCl_3$ 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 H_{12} at 2.51 and 2.50 ppm. [c] Overlapped by the signal of H_4. [d] At –40 °C two isomers are observed. The major isomer shows resonances at 1.09 (81.9 Hz), Me_{ax}; 0.96 (67.2 Hz), Me_{eq}; and 2.99 d, 2.89 d, ^2J(H–H) = 9.4 Hz, CH_2Ph, and the minor isomer, at 1.14 (69.3 Hz), Me_{eq} and 3.19 s (107 Hz), CH_2Ph. [e] Me_{eq}, ^3J(P–H) = 8.1 Hz; Me_{ax}, ^3J(P–H) = 6.6 Hz. [f] In CD_3CN at 20 °C.



(6)

The new complexes 11 are characterized by elemental analysis, IR spectroscopy, and ^{1}H, ^{13}C, and ^{19}F 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.[30] [$PtMe_3$(*p*Tol-BIAN)]SO_3CF_3, **11a**, was also obtained by the oxidative addition of $MeSO_3CF_3$ to $PtMe_2$(*p*Tol-BIAN), **6**.

The chemical shifts in the ^{19}F 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,[31] but for complexes of the type M(η^5-C_5Me_5)(SO_3CF_3)$_2$(PMe_3) (M = Rh, Ir) containing coordinated trifluoromethanesulfonate (based on IR spectroscopy), ^{19}F NMR chemical shifts of –78.36 and –78.12 ppm have been reported.[32] Thus ^{19}F 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 C_{3v} symmetry of SO_3CF_3 is lowered by coordination, as has been elaborated for Cu(SO_3CF_3) complexes.[33] Indeed, [Pd(η^3-PhCH—CH=CH_2)(*p*Tol-BIAN)]SO_3CF_3,[34] which is included for comparison, and [$PtMe_3$(*p*Tol-BIAN)(PPh_3)]SO_3CF_3, **12** (vide infra), both containing ionic SO_3CF_3, 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,[35] indicates that the Pt—SO_3CF_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 diffraction.

Table 7. IR and ^{19}F NMR Data for the [$PtMe_2$(R)(NN)] SO_3CF_3 Complexes 11–14[a]

	IR				^{19}F NMR
11a, R = Me	1295, 1231	1174	1022	635	–78.8 br
11b, R = CH_2Ph	1304, 1233	1170	1015	n.o.	–79.0 br
11e, R = C(O)Me	1294, 1231	1165	1020	633	–78.73
12, R = Me; PPh_3	1270	1145	1031	632	–78.51
13, NN = phen	1275, 1230	1175	1030	n.o.	–78.10[b]
14, NN = *p*Tol-DAB	1265, 1230	1175	1030	n.o.	–78.12[b]
Pd(allyl)SO_3CF_3[c]	1278, 1265	1112	1031	633	

[a] IR as Nujol mull and ^{19}F NMR in $CDCl_3$ at 20 °C. [b] In CD_3CN. [c] [Pd^{II}(η^3-PhC_3H_4)(*p*Tol-BIAN)]SO_3CF_3.

[$PtMe_3$(*p*Tol-BIAN)]SO_3CF_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) in a ratio of 1:2:1:2 in ^{1}H NMR and at –1.36 (685 Hz), –2.62 (679 Hz), –12.16, and –13.38 ppm in a ratio of about 2:2:1:1 in ^{13}C NMR, together with the observation of two resonances for all *p*Tol-BIAN protons and C atoms, except $C(H)_9$ and $C(H)_{10}$ which both give four resonances, indicates that two isomers of [$PtMe_3$(*p*Tol-BIAN)]SO_3CF_3, **11a**, are present in solution, in a ratio of 1:1. The observed values of the ^2J(Pt–Me) coupling constants exclude isomers with two mutually *trans* oriented methyl groups[25] and are characteristic of complexes with two methyl groups *trans* to the *p*Tol-BIAN ligand and one methyl group *trans* to a weakly coordinating ligand. Upon warming (to 20 and 50 °C) the two isomers interconvert,

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

(31) (a) Modder, J. F.; Ernsting, J. M.; Vrieze, K.; de Wit, M.; Stam, C. H.; van Koten, G. *Inorg. Chem.* **1991**, *30*, 1208. (b) van Stein, G. C.; van Koten, G.; Vrieze, K.; Brevard, C.; Spek, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 4486.

(32) Stang, P. J.; Huang, Y. H.; Arif, A. M. *Organometallics* **1992**, *11*, 231.

(33) Dedert, P. L.; Thompson, J. S.; Ibers, J. A.; Marks, T. J. *Inorg. Chem.* **1982**, *21*, 969.

(34) van Asselt, R.; Vrieze, K.; Elsevier, C. J. Submitted for publication in *J. Organomet. Chem.*

(35) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

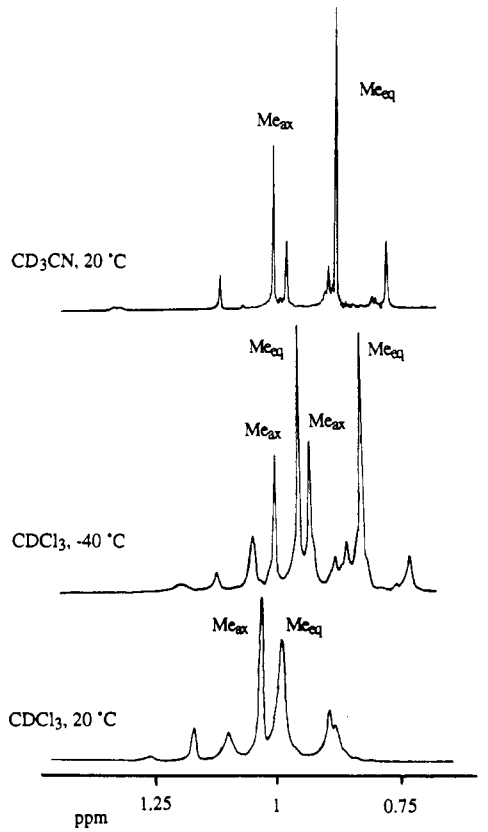
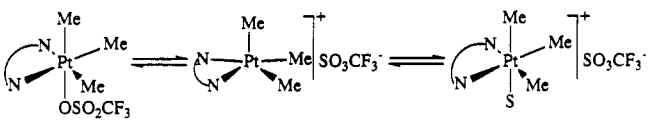


Figure 1. ^{1}H NMR spectra of [PtMe$_3$(*p*Tol-BIAN)]SO$_3$CF$_3$, **11a**, in CDCl$_3$ and CD$_3$CN.

Scheme 3



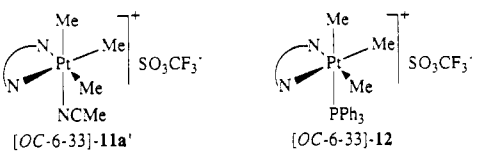
but no exchange between the axial and the equatorial methyl groups is observed (Figure 1).

The presence of two isomers is also apparent from ^{19}F NMR recorded in CDCl$_3$ where at −40 °C two resonances are observed at −78.81 and −79.33 ppm, whereas at 20 °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 °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 *p*Tol-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 °C is only slightly broadened in ^{1}H and ^{13}C NMR, indicating that there is fast exchange. Only the signals of C(H)$_9$ 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)$_9$), 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 ^{19}F 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$_3$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



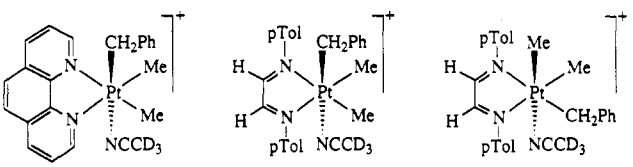
acetonitrile is present. The observed large coupling constant for the axial methyl group indicates that acetonitrile is a weak ligand which is in agreement with the observation that coordinated acetonitrile is lost from **11a′** when the product is kept in vacuo at 20 °C for several hours and with our observations that acetonitrile coordinates weakly to Pd^{II}(Ar-BIAN) complexes.[36]

Reaction of **11a** with ligands that require π-back-donation 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,

(36) (a) van Asselt, R.; Gielens, E. E. C. G.; Rülke, R. E.; Elsevier, C. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1203. (b) van Asselt, R.; Gielens, E. E. C. G.; Rülke, R. E.; Vrieze, K.; Elsevier, C. J. *J. Am. Chem. Soc.*, in press.

due to anisotropic shielding of two protons H_9 by one of the phenyl rings of the triphenylphosphine ligand.

[$PtMe_2(CH_2Ph)(NN)$]SO_3CF_3 Complexes 11b, 13, and 14. [$PtMe_2(CH_2Ph)$(*p*Tol-BIAN)]SO_3CF_3, **11b**, in $CDCl_3$ at 20 °C shows in ^1H NMR one broadened Pt–Me resonance at 1.16 ppm (67 Hz), one broadened Pt–CH_2Ph resonance at 3.24 ppm (108 Hz), and a broad signal at 6.20 ppm (H_9), 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 1:4. 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–CH_2Ph 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 ca. 1:2:2. Analogous to [$PtMe_3$(*p*Tol-BIAN)]SO_3CF_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 an η^3-coordinated benzyl moiety, as has been observed for [$Pd(\eta^3$-$CH_2Ph)$(*p*Tol-BIAN)]SO_3CF_3[34] (the chemical shift of CH_2 and C_{ipso} has hardly changed as compared to η^1-CH_2Ph in the platinum(IV) bromide complex **9b**). In CD_3CN also a mixture of two isomers is observed and the slightly different chemical shifts, as compared to $CDCl_3$ solutions, indicate that acetonitrile is coordinated to the platinum(IV) center. The C_1-symmetric complex is the major isomer (65%) and there is no indication for any exchange on the NMR time scale at 20 °C. In ^{19}F NMR one sharp resonance is observed at −78.10 ppm. The analogous [$PtMe_2(CH_2Ph)(NN)$]SO_3CF_3 complexes (NN = phen, **13**; *p*Tol-DAB, **14**) did not dissolve well enough



[*OC*-6-34]-**13** [*OC*-6-34]-**14** [*OC*-6-43]-**14**

in $CDCl_3$ to allow characterization by ^1H NMR. In CD_3CN the phen complex **13** occurs as a single C_s-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 (68.8 Hz), one singlet for Pt–CH_2Ph at 3.06 ppm (95.8 Hz), and a symmetrical pattern for the phen ligand in ^1H NMR. The observed shift of the $PhCH_2$ resonances to low frequency are characteristic of a benzyl group oriented toward the phen ligand and concomitant anisotropic shielding. In ^{19}F NMR one resonance is found at −78.10 ppm.

The cationic *p*Tol-DAB complex **14** exists in CD_3CN as a mixture of isomers (66% of a C_s-symmetric isomer and 34% of a C_1-symmetric isomer). The C_1-symmetric isomer exhibits in ^1H NMR two doublets for the Pt–CH_2Ph moiety with large differences in the observed Pt–CHH' coupling constants: 3.37 (^2J(Pt–H) = 113.4 Hz) and 3.02 ppmm (^2J(Pt–H′) = 69.0 Hz). Probably, there is some interference of the benzyl group with the *p*-tolyl substituent of *p*Tol-DAB, which might be in the coordination plane[37] (contrary to *p*Tol-BIAN[17c]), hindering rotation around the Pt–benzyl bond and bringing both benzyl protons into a different orientation relative to platinum.

Other [$PtMe_2$(R)(*p*Tol-BIAN)]SO_3CF_3 Complexes 11c–f in $CDCl_3$. The acyl complex [$PtMe_2(C(O)Me)$(*p*Tol-BIAN)]SO_3CF_3, **11e**, at 20 °C in $CDCl_3$ is present as one C_s-symmetric isomer. The ^1H NMR spectrum has hardly changed compared to the platinum(IV) chloride complex **9e**, only the ^3J(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.[38] In ^{19}F NMR one sharp resonance at −78.73 ppm is observed. At 20 °C the complexes [$PtMe_2(Et)$(*p*Tol-BIAN)]SO_3CF_3, **11c**, and [$PtMe_2(CH(Me)Ph)$(*p*Tol-BIAN)]SO_3CF_3, **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 $CDCl_3$ the ^1H NMR spectra of [$PtMe_2$(*p*Tol-BIAN)]$(SO_3CF_3)_2$, **11f**, obtained by addition of 2 equiv of $AgSO_3CF_3$ to [*OC*-6-13]-Pt(*p*Tol-BIAN)Me_2I_2, **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 H_5. Cooling to −20 or −50 °C did not bring about any changes in the ^1H 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_s-symmetric isomers, since upon addition of sodium iodide [*OC*-6-23]-Pt(*p*Tol-BIAN)Me_2I_2, **10a**, is obtained as the only product.

Thermal Stability of the [$PtMe_2$(R)(*p*Tol-BIAN)]SO_3CF_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 $CDCl_3$ 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 [$PtMe_2(C(O)Me)$(*p*Tol-BIAN)]SO_3CF_3, **11e**, does not show any decarbonylation (after 75 h). The complexes [$PtMe_2(Et)$(*p*Tol-BIAN)]SO_3CF_3, **11c**, and [$PtMe_2(CH(MePh)$(*p*Tol-BIAN)]SO_3CF_3, **11d**, did not reveal any sign of reductive elimination or β-elimination after several hours in $CDCl_3$ (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 [$PtMe_3$(*p*Tol-BIAN)]SO_3CF_3, **11a**, and [$PtMe_2(CH_2Ph)$(*p*Tol-BIAN)]SO_3CF_3, **11b**, were stable toward reductive elimination at 20 °C in $CDCl_3$ and in CD_3CN for at least 1 week and in $CDCl_3$ or CD_3CN at 50 °C for at least 40 h. [$PtMe_2(CH_2Ph)$(phen)]SO_3CF_3, **13**, was also stable toward decomposition in CD_3CN at 50 °C for at least 40 h, but [$PtMe_2(CH_2Ph)$(*p*Tol-DAB)]SO_3CF_3, **14**, showed 30–35% decomposition after 40 h in CD_3CN 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 Pt^{II}–Me complex. Unfortunately, the other signals of

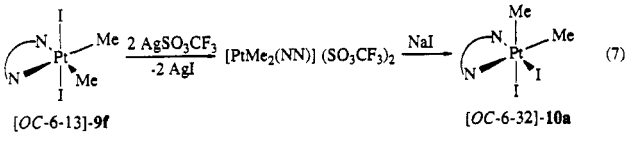
(37) See for example: de Lange, P. P. M.; Kraakman, M. J. A.; van Wijnkoop, M.; Frühauf, H.-W.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chim. Acta* **1992**, *196*, 151.

(38) Dent, S. P.; Eaborn, C.; Pidcock, A.; Ratcliff, B. *J. Organomet. Chem.* **1972**, *42*, C68.

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 $MMe_2(NN)$ (M = Pd, Pt; NN = *p*Tol-BIAN, Ph-BIC), **1**, **3**, and **6**, undergo facile oxidative addition of a variety of (organic) halides. Oxidative addition to $PtMe_2$(*p*Tol-BIAN), **6**, and Pt(Me)I(*p*Tol-BIAN), **7**, complexes is much faster as compared to phosphine analogues and is probably more like that of the bpy and phen complexes $PtMe_2$(NN), which have been reported to be among the most reactive species for oxidative addition reactions.[7] The high reactivity of the MMe_2(*p*Tol-BIAN) and $PdMe_2$(Ph-BIC) complexes is due to the donative character of the *p*Tol-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]-$PtMe_2I_2$(*p*Tol-BIAN), **9f**, via *trans* oxidative addition of I_2 to $PtMe_2$(*p*Tol-BIAN), **6**, and the formation of [*OC*-6-32]-$PtMe_2I_2$(*p*Tol-BIAN), **10a**, via *trans* oxidative addition of iodomethane to Pt(Me)I(*p*Tol-BIAN), **8**. These complexes did not isomerize in solution at 50 °C (16 h), but upon reaction with silver trifluoromethanesulfonate in $CDCl_3$ followed by reaction with sodium iodide [*OC*-6-13]-**9f** is completely converted to [*OC*-6-32]-**10a** (eq 7), which



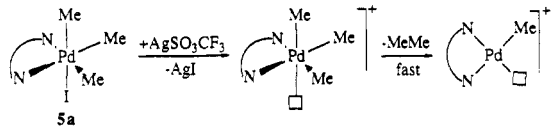
[*OC*-6-13]-**9f** [*OC*-6-32]-**10a** (7)

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,[3,4] $(py)_2CHMe$, and $(py)(pz)CH_2$ (py = pyridin-2-yl, pz = pyrazol-1-yl).[39] Although several of these could be isolated and X-ray crystallographic studies have been reported,[3,4] 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.[4a,c] The observed rapid elimination of ethane after reaction of $PdMe_3I$(Ph-BIC) with $AgSO_3CF_3$ is in agreement with such a mechanism (Scheme 4). Furthermore, the calculated activation energy of 60 kJ·mol^{-1} for reductive elimination from $PdMe_3I$(*p*Tol-BIAN) in $CDCl_3$ is in the same range as that found for $PdMe_3I$(bpy) in acetone (65 kJ·mol^{-1}),[4a] which indicates that reductive elimination might occur via a similar pathway in both cases.

(39) Byers, P. K.; Canty, A. J.; Honeyman, R. T.; Watson, A. A. *J. Organomet. Chem.* **1990**, *385*, 429.

Scheme 4



5a

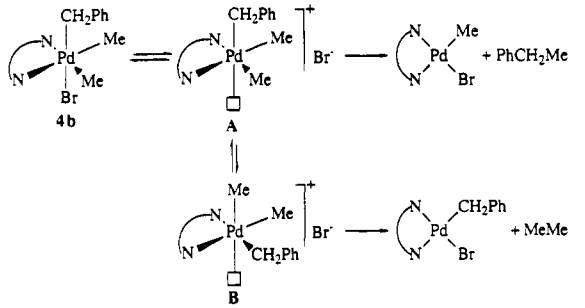
The observed first order rate constants for reductive elimination from the $PdMe_3I$(NN) complexes **4**,**5a** in chloroform are 2 or 3 orders of magnitude smaller than those of $PdMe_3I$(bpy) in acetone or benzene.[4a] From comparison with other reported triorganopalladium(IV) complexes containing bidentate nitrogen ligands it appears that the stability decreases in the order *p*Tol-BIAN, Ph-BIC > phen, bpy > tmeda, $(py)_2CHMe$, $(py)(pz)CH_2$, 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.[4d,j,39] The higher stability of the triorganopalladium(IV) complexes $PdMe_2$(R)X(NN) containing *p*Tol-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 *p*Tol-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 $PdMe_2$(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 PdI_2(NN). Comparable diorganopalladium(IV) complexes are likely intermediates in the reactions of organopalladium(II) complexes with organic halides, yielding finally Pd^{II}–dihalide complexes and organic coupling products.[34]

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 $PdMe_2$(*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN) with iodomethane, which did not lead to an observable trimethylpalladium(IV) intermediate, but instead reductive elimination occurred immediately to give only Pd(Me)I(*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN). The low stability of $PdMe_3I$(*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN) is due to the orientation of the aromatic groups perpendicular

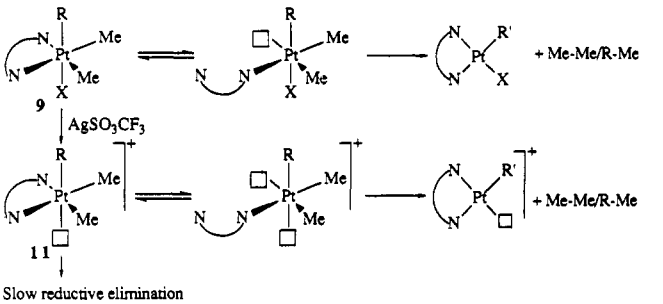
(40) Flexible chelating ligands which are capable of varying the L–M–L angle might facilitate reductive elimination reactions, as calculations have shown that opening of the P–Pd–P angle during reductive elimination from Pd(Me)(CH=CH_2)$(PH_3)_2$ lowers the activation energy: Calhorda, M. J.; Brown, J. M.; Cooley, N. A. *Organometallics* **1991**, *10*, 1431.

(41) From an investigation of the available crystal structure data of Pd(NN) and Pt(NN) complexes it appeared that typical N–M–N angles are 77–80° (*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN), 74–80° (phen), 82–85° (tmeda), and 84–90° (ligands forming six-membered chelate rings). For bpy N–M–N angles typically lie in the range 75–80°, but angles of 84.3(8)° 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.

Scheme 5



Scheme 6



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 (*i*Pr) groups to 4.75 ppm in $PtMe_3I$(*o,o'*-$iPr_2C_6H_3$-BIAN) and might facilitate reductive elimination from $PdMe_3I$(*o,o'*-$iPr_2C_6H_3$-BIAN). Alternatively, reductive elimination might occur from the intermediate $[PdMe_3$(*o,o'*-$iPr_2C_6H_3$-BIAN)$]^+I^-$ formed during oxidative addition, because coordination of I^- to Pd(IV) is hindered by the *o,o'*-$iPr_2C_6H_3$-BIAN ligand.[42]

A remarkable aspect is the unselective reductive elimination from $PdBrMe_2(CH_2Ph)$(*p*Tol-BIAN), **4b**, in $CDCl_3$, giving 60% $PdBr(CH_2Ph)$(*p*Tol-BIAN) and 40% PdBr(Me)(*p*Tol-BIAN). In all reported cases of reductive elimination from $PdBrMe_2(CH_2Ph)$(NN) complexes, studied in acetone and 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 (75%) > *p*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 *p*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,[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 *p*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(*p*Tol-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 *p*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.[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 $[PtMe_2(R)$(*p*Tol-BIAN)$]SO_3CF_3$, **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 $[PtMe_2(CH_2Ph)$(*p*Tol-DAB)$]SO_3CF_3$ in acetonitrile at 50 °C emphasizes the importance of the ridigity 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 $PtMe_3X(P)_2$ 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 *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.[3,4,23,39] The employed Ar-BIAN and Ph-BIAN ligands are good σ-donors and activate the divalent complexes to undergo oxidative addition, as also appeared from the reactions of monoorganopalladium(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 *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 $PdMe_2$(NN). The importance of the rigidity of the ligands in kinetically stabilizing high oxidation states became also apparent from the observed stability of the

(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.; Canty, A. J.; Skelton, B. W.; Traill, P. R.; Watson, A. A.; White, A. H. *Organometallics* **1992**, *11*, 3085.

acyl–platinum(IV) complex $PtMe_2(C(O)Me)Cl(p$Tol-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 $PtMe_2(R)X(p$Tol-BIAN) complexes with $AgSO_3CF_3$. The observed order of stability for $[PtMe_2(CH_2Ph)(NN)]SO_3CF_3$ 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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