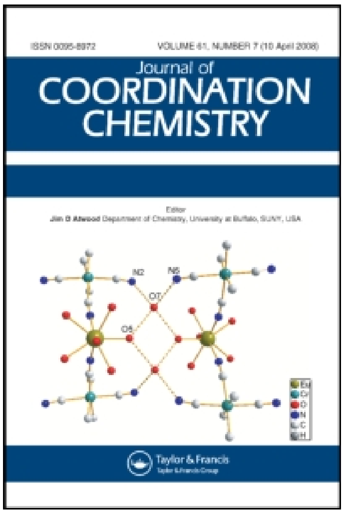

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Pt(II) complexes with diimine and chelating 5-ring iminocarbene ligands: synthesis, characterization, and structural and spectroscopic trends

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Pt(II) complexes with diimine and chelating 5-ring iminocarbene ligands: synthesis, characterization, and structural and spectroscopic trends[#]

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A series of new L_2PtMe_2 and L_2PtPh_2 complexes have been prepared, where L_2 = chelating diimine or NHC iminocarbene ligands with similar substituent patterns. These have been investigated by ^{1}H- and ^{13}C-NMR spectroscopy and single-crystal X-ray structure determinations to assess differences between the two ligand systems. All the three approaches underscore the strong *trans* influence of the *N*-heterocyclic carbene moiety relative to the imine group. This is supported by trends in $J(^{195}\text{Pt–H})$ and $J(^{195}\text{Pt–C})$ coupling constants in the hydrocarbyl NMR resonances as well as in differences in Pt–ligand bond distances *trans* to the imine and carbene moieties. This is paralleled by a clear *trans* effect of the carbene ligand in protonolysis; treatment of the Pt(II) dimethyl or diphenyl iminocarbene complexes with acid causes the elimination of methane and benzene, respectively, with selective loss of the methyl or phenyl groups from the *trans* position relative to the carbene part of the chelating ligand.

Keywords: Platinum; Diimine ligands; NHC ligands; NMR spectroscopy; X-ray structures

1. Introduction

The well-known report of stable *N*-heterocyclic carbenes (NHCs) of the imidazolin-2-ylidene type by Arduengo *et al.* [1, 2] has had a major impact on the design and employment of such compounds as ligands in organometallic catalyst design [3, 4]. Such ligands act as strong σ-donors (comparable to or better than trialkylphosphines) and rather poor π-acceptors [3, 5, 6], and are expected to exert a strong *trans* effect. Metal complexes containing NHC ligands have shown catalytic activity for a large variety of organic reactions. The most well-known examples are the ruthenium metathesis catalysts developed by Grubbs and others [7–9] and numerous palladium-catalyzed reactions including Heck, Suzuki-Miyaura, Stille, and Sonogashira cross-coupling reactions [10–18].

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[#] This contribution is dedicated to Prof. Rudi van Eldik on the occasion of his 65th birthday and retirement.

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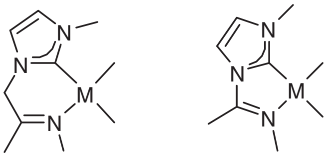
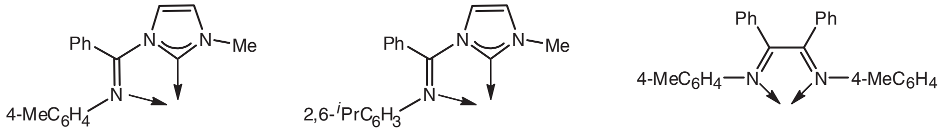


Scheme 1. Iminocarbene complexes with 5- and 6-membered chelate rings.

The use of cationic (N–N)Pt(CH_3)L^+ complexes ((N–N) = α-diimine, L = H_2O, or TFE = 2,2,2-trifluorethanol) for aromatic and aliphatic C–H bond activation has attracted intense interest [19–21]. The Bercaw group has in recent studies [20] established that the ability of these cationic diimine complexes to activate C–H bonds depends highly on the electronic properties of the α-diimine ligands. It has been recently suggested by us that the electronic properties of diimine ligands are more prone to significant variation through adjustment of the backbone structure rather than by varying *N*-aryl substituents [22]. Other possibilities for ligand tuning may arise through replacing the diimine ligand, in full or in part, by another group. Consequently, we envisioned that replacing one imine with the stronger σ-donating group of an NHC carbene might open new possibilities in C–H activation and other processes. General structures of some pertinent hybrid imino-NHC ligands are depicted in scheme 1.

We have recently reported the synthesis and reactivity of a number of imino-NHC-based complexes of the types shown in scheme 1. In particular, a range of non-chelated (κ^1(C)) and/or chelated (κ^2(C,N)) complexes of Ag(I), Rh(I), Pd(II), and Pt(II) have been reported by us [23–27]. At neutral Pd(II), the balance between preference for κ^2(C,N) *versus* κ^1(C) coordination is a function of the exact nature of the imino-NHC ligand: ligands that offer five-membered ring chelates appear to always be ring-closed whereas potential six-membered ring chelates may remain non-chelating, at least at neutral complexes, if steric effects at the imino-NHC chelate rings are severe [23]. The observed hemilabile behavior of the latter species may be of particular interest because the opened coordination site can be employed for substrate binding in catalytic reactions. On the other hand, hemilability may also induce decomposition through the involvement of the same coordination site, or render a particular catalyst system less sensitive towards steric effects as a consequence of imine side-arm dissociation. This was suggested in recent studies on the action of imino-NHC Pd(II) complexes as catalysts in the Suzuki-Miyaura coupling reaction [26]. The catalytic performance of these systems was rather insensitive to changes in the steric properties of the ligand, and it was concluded that the catalytically active species might be a non-chelated (κ^1(C,N))Pd(0) complex or Pd(0) colloids. On the other hand, more recent studies on a related rhodium catalyst [27] demonstrated that it performed well as a cyclopropanation catalyst with exceptionally high *cis* selectivities. In this case, the catalyst selectivity is highly dependent on the steric demands of the imine *N*-aryl group [28], strongly suggesting a κ^2(C,N) coordination mode at Rh(I) in these cases.

Imino-NHC Pt(II) complexes are less well explored than Pd(II) counterparts thus far. Herein, we report the synthesis and characterization of a range of new Pt(II) complexes L_2PtMe_2 and L_2PtPh_2, all of which bear one the three L_2 ligands that are depicted in scheme 2 along with the ligand symbolism to be used in the text. These systems represent two imino-NHC ligands (**a** and **b**) that differ significantly in the steric bulk at



(a) ($^{Tol}N^{Ph}$–C) (b) ($^{Dipp}N^{Ph}$–C) (c) ($^{Tol}N^{Ph}$–$^{Tol}N^{Ph}$)

Scheme 2. Ligand L_2 series **a**–**c**.

the *N*-aryl group, as well as a diimine ligand (**c**) at which the imine-C and imine-N substituents are identical to those in the first imino-NHC ligand. These ligands combined allow assessment and comparison of some steric and electronic effects on the structural and spectroscopic properties of the prepared Pt complexes.

2. Experimental

2.1. *General procedures*

All reactions involving organometallic compounds were carried out with the use of dry box, vacuum line, syringe, and Schlenk techniques unless otherwise noted. Solvents for reactions and NMR studies were dried according to standard procedures. NMR spectra were recorded on Bruker Avance DPX 200, DPX 300, DRX 500, or AV II 600 NMR instruments with QNP or TXI probes. The NMR spectra were recorded at 25°C. Assignment of ^{1}H and ^{13}C signals were aided by DEPT45, HMQC, HMBC, HETCOR, COLOC, COSY 45, and NOESY ^{1}H-NMR spectroscopy. For brevity, the following abbreviations are used for the assignment: Ph = phenyl, Tol = 4-methylphenyl, Dipp = 2,6-diisopropylphenyl; $H_{o/m/p}$ and $C_{ipso/o/m/p}$ denotes the ipso/ortho/meta/para atoms relative to the point of attachment to the iminocarbene or diimine chelate ring. Electrospray ionization mass spectra were obtained from acetonitrile solutions on a Micromass QTOF II spectrometer. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany, or by Mikro Kemi AB, Uppsala, Sweden.

Basic Al_2O_3, triethylamine, triflic acid, and silver triflate were purchased from Aldrich or Fluka and used as received. The diimine $^{Tol}N^{Ph}$–$^{Tol}N^{Ph}$ [29], 2,6-di-*tert*-butylpyridinium triflate [30], silver carbene complexes **1a** and **1b** [25, 26], the Pt complex **2b** [25], $Ph_2Pt(SMe_2)_2$, $[Me_2Pt(\mu\text{-}SMe_2)]_2$, $PtMeCl(SMe_2)_2$, and $PtPhCl(SMe_2)_2$ [31, 32] were prepared as described previously. Dimethylmagnesium was prepared following the procedure of Rickborn *et al.* [33].

2.2. *Synthesis of compounds*

2.2.1. Preparation of ($^{Tol}N^{Ph}$–C)$PtMe_2$ (2a). Silver carbene complex **1a** (0.414 g, 0.989 mmol) was added to a solution of $[Me_2Pt(\mu\text{-}SMe_2)]_2$ (0.276 g, 0.962 mmol) in acetonitrile (40 mL) at −10°C. The mixture was stirred at −5°C for 2 h, heated to ambient temperature, and stirred for another 1 h. The solution was concentrated to *ca* 1/15 of the original volume and the precipitated AgCl was removed by centrifugation. The concentrate was purified by flash chromatography on a small deactivated (1% Et_3N in acetonitrile) Al_2O_3 column. The product was collected as a red solid (0.300 g, 0.599 mmol, 62%) after evaporation of the volatiles. Crystals of **2a** were grown by slow diffusion of pentane into a 0.015 mol L^{-1} solution of the product in acetonitrile/ether (1 : 3). ^{1}H-NMR (CD_3CN, 500 MHz, 25°C) δ 7.3–7.4 (m, 5H, Ph), 7.02 (d, $^3J = 8.1$ Hz, 2H, $TolH_m$), 6.89 (d, $^3J = 2.3$ Hz, NCHCHN near NMe), 6.81 (d, $^3J = 2.3$ Hz, NCHCHN near C=N), 6.78 (d, $^3J = 8.1$ Hz, 2H, $TolH_o$), 3.74 (s, 3H, NMe), 2.24 (s, 3H, TolMe), 1.31 (s, $^2J(^{195}Pt–H) = 93.2$ Hz, 3H, PtMe *cis* to carbene), 0.07 (s, $^2J(^{195}Pt–H) = 62.9$ Hz, 3H, PtMe *trans* to carbene). $^{13}C\{H\}$-NMR (CD_3CN, 50 MHz, 25°C) δ 190.7 ($^1J(^{195}Pt–C) = 862$ Hz, C(carbene)), 161.7 (C=N), 144.0 ($^2J(^{195}Pt–C) = 12$ Hz, $TolC_{ipso}$), 135.7 ($TolC_p$), 131.5 (PhC_p), 130.4 ($^3J(^{195}Pt–C) = 8.2$ Hz, PhC_{ipso}), 129.5 (Ph), 129.3 ($TolC_m$), 129.2 (Ph), 125.3 ($^3J(^{195}Pt–C) = 6$ Hz, $TolC_o$), 124.8 ($^3J(^{195}Pt–C) = 23$ Hz, NCHCHN near NMe), 118.2 ($^3J(^{195}Pt–C) = 16$ Hz, NCHCHN near C=N), 37.5 (NMe), 20.8 (TolMe), 6.1 ($^1J(^{195}Pt–C) = 623$ Hz, PtMe *trans* to carbene), −22.0 ($^1J(^{195}Pt–C) = 812$ Hz, PtMe *cis* to carbene). MS–ESI: *m/z* 526 ($[M(^{195}Pt)]^+ + CH_3CN - CH_3$, 85%), 525 ($[M(^{194}Pt)]^+ + CH_3CN - CH_3$, 55%), 485 ($[M(^{195}Pt)]^+ - CH_3$, 100%), 484 ($[M(^{194}Pt)]^+ - CH_3$, 68%). HRMS–ESI: Calcd for $C_{21}H_{23}N_4^{194}Pt$ ($[M(^{194}Pt)]^+ + CH_3CN - CH_3$), 525.1549. Found: 525.1533. Calcd for $C_{19}H_{20}N_3^{194}Pt$ ($[M(^{194}Pt)]^+ - CH_3$), 484.1284. Found: 484.1281. Anal. Calcd for $C_{20}H_{23}N_3Pt$: C, 47.83; H, 4.81; N, 8.38. Found: C, 48.00; H, 4.63; N, 8.40.

2.2.2. Preparation of ($^{Tol}N^{Ph}$–C)PtMe(NCMe)$^+$ OTf$^-$ (3a). A 0.150 mol L^{-1} solution of triflic acid in acetonitrile (1.06 mL, 0.159 mmol) was added to a solution of **2a** (0.0796 g, 0.159 mmol) in acetonitrile (8 mL). The mixture was stirred for 2 h at ambient temperature before removal of the volatiles under vacuum. The crude product was repeatedly washed with ether. The product was dried under vacuum and isolated as an orange solid in quantitative yield (0.108 g, 0.159 mmol). ^{1}H-NMR (CD_2Cl_2, 600 MHz, 25°C) δ 7.55 (m, 1H, PhH_p), 7.46 (m, 2H, PhH_m), 7.34 (m, 2H, PhH_o), 7.15 (d, $^3J = 2.2$ Hz, 1H, NCHCHN near NMe), 7.14 (m, 2H, $TolH_m$), 7.05 (d, $^3J = 2.2$ Hz, 1H, NCHCHN near C=N), 6.88 (m, 2H, $TolH_o$), 3.89 (s, 3H, NMe), 2.32 (s, 3H, TolMe), 2.01 (s, 3H, NCMe), 1.31 (s, $^2J(^{195}Pt–H) = 79.4$ Hz, 3H, PtMe). $^{13}C\{H\}$-NMR (CD_2Cl_2, 50 MHz, 25°C) δ 160.6 ($^2J(^{195}Pt–C) = 27.2$ Hz, C=N), 154.9 ($^1J(^{195}Pt–C) = 1723$ Hz, C(carbene)), 141.1 ($TolC_{ipso}$), 137.6 ($TolC_p$), 132.5 (PhC_p), 129.8 ($TolC_m$), 129.6 (PhC_m), 129.0 (PhC_o), 126.1 (PhC_{ipso}), 126.0 ($^3J(^{195}Pt–C) = 59$ Hz, NCHCHN near NMe), 123.9 ($TolC_o$), 119.3 ($^3J(^{195}Pt–C) = 36$ Hz, NCHCHN near C=N), 119.3 (NCMe), 38.3 ($^3J(^{195}Pt–C) = 15$ Hz, NMe), 20.9 (TolMe), 3.0 ($^3J(^{195}Pt–C) = 8$ Hz, NCMe), –22.1 ($^1J(^{195}Pt–C) = 683$ Hz, PtMe). MS–ESI: *m/z* 526 ($[M(^{195}Pt)]^+$, 100%), 525 ($[M(^{194}Pt)]^+$, 71%), 485 ($[M(^{195}Pt)]^+ - CH_3CN$, 39%), 484 ($[M(^{194}Pt)]^+ - CH_3CN$, 31%). HRMS–ESI: Calcd for $C_{21}H_{23}N_4^{194}Pt$ ($[M(^{194}Pt)]^+$), 525.1549. Found: 525.1537. Anal. Calcd for $C_{22}F_3H_{23}N_4O_3PtS$: C, 39.11; H, 3.43; N, 8.29. Found: C, 39.11; H, 3.46; N, 8.33.

2.2.3. Preparation of $(^{\mathrm{Dipp}}\mathrm{N}^{\mathrm{Ph}}$–C)PtMe(NCMe)$^{+}$OTf^{-} (3b). Solutions of **2b** (0.0543 g, 0.0952 mmol) in acetonitrile (10 mL) and of 2,6-di-*tert*-butylpyridinium triflate (0.0325 g, 0.0952 mmol) in acetonitrile (1 mL) were combined and stirred for 30 min. The volatiles were removed under vacuum, and the crude product was washed with dichloromethane/pentane mixtures. The product was dried under vacuum and collected as an orange solid in 99% yield (0.0705 g, 0.0945 mmol). ^{1}H-NMR (CD_2Cl_2, 500 MHz, 25°C) δ 7.58 (tt, $^3J = 7.6$, 3.0 Hz, 1H, PhH$_p$), 7.46 (m, 2H, PhH$_m$), 7.34 (m, 2H, PhH$_o$), 7.27 (m, 1H, NCHCHN near NMe), 7.26 (m, 1H, DippH$_p$), 7.22 (m, 1H, NCHCHN near C=N), 7.21 (m, 2H, DippH$_m$), 3.91 (s, 3H, NMe), 2.97 (sept., $^3J = 6.8$ Hz, 2H, CHMe$_2$), 1.82 (s, $^4J(^{195}$Pt–H$) = 7.1$ Hz, 3H, NCMe), 1.29 (s, $^2J(^{195}$Pt–H$) = 79.0$ Hz, 3H, PtMe), 1.28 (d, $^3J = 6.8$ Hz, 6H, CHMe$_2$), 0.94 (d, $^3J = 6.8$ Hz, 6H, CHMe$_2$). ^{13}C{H}-NMR (CD_2Cl_2, 50 MHz, 25°C) δ 159.7 ($^2J(^{195}$Pt–C$) = 26$ Hz, C=N), 154.9 ($^1J(^{195}$Pt–C$) = 1739$ Hz, C(carbene)), 141.0 (DippC$_o$), 138.4 (Dipp C$_{ipso}$), 133.1 (PhC$_p$), 129.6 (PhC$_m$), 128.8 (PhC$_o$), 128.4 (DippC$_p$), 126.1 ($^3J(^{195}$Pt–C$) = 59$ Hz, NCCN near NMe), 125.8 ($^3J(^{195}$Pt–C$) = 11$ Hz, PhC$_{ipso}$), 124.4 (DippC$_m$), 119.9 ($^3J(^{195}$Pt–C$) = 36$ Hz, NCCN near C=N), 118.6 (NCMe), 38.3 ($^3J(^{195}$Pt–C$) = 16$ Hz, NMe), 28.4 (CHMe$_2$), 24.9 (CHMe$_2$), 23.0 (CHMe$_2$), 2.1 ($^3J(^{195}$Pt–C$) = 8$ Hz, NCMe), –22.1 ($^1J(^{195}$Pt–C$) = 683$ Hz, PtMe). MS–ESI: *m*/*z* 596 ([M(^{195}Pt)]$^+$, 100%), 595 ([M(^{194}Pt)]$^+$, 59%). HRMS–ESI: Calcd for $C_{26}H_{33}N_4^{194}Pt$ ([M(^{194}Pt)]$^+$), 595.2332. Found: 595.2314. Anal. Calcd for $C_{27}F_3H_{33}N_4O_3PtS$: C, 43.5; H, 4.5; N, 7.5. Found: C, 43.0; H, 4.5; N, 7.3.

2.2.4. Preparation of $(^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$–C)PtPh$_2$ (4a). Solid PtPh$_2$(SMe$_2$)$_2$ (0.116 g, 0.245 mmol) was added to a solution of silver carbene complex **1a** (0.103 g, 0.245 mmol) in acetonitrile (8 mL) at −18°C. The temperature was slowly raised to ambient over a period of 16 h, at which point precipitated AgCl was removed by centrifugation. The product was isolated as yellow crystals in 99% yield (0.152 g, 0.243 mmol) after the removal of volatiles under vacuum. ^{1}H-NMR (CD_2Cl_2, 500 MHz, 25°C) δ 7.5 (m, $^3J(^{195}$Pt–H$) = 80.6$ Hz, 2H, PtPhH$_o$ *cis* to carbene), 7.46 (m, 1H, imine-PhH$_p$), 7.38 (m, 2H, imine-PhH$_m$), 7.31 (m, 2H, imine-PhH$_o$), 6.94 (m, $^3J(^{195}$Pt–H$) = 50.2$ Hz, 2H, PtPhH$_o$ *trans* to carbene), 6.92 (m, 2H, PtPhH$_m$ *cis* to carbene), 6.86 (m, 1H, NCHCHN near C=N), 6.73 (m, 1H, PtPhH$_p$ *cis* to carbene), 6.68 (m, 1H, NCHCHN near NMe), 6.67 (m, 2H, TolH$_m$), 6.61 (m, 2H, PtPhH$_m$ *trans* to carbene), 6.54 (m, 2H, TolH$_o$), 6.48 (m, 1H, PtPhH$_p$ *trans* to carbene), 3.14 (s, 3H, NMe), 2.13 (s, 3H, TolMe). ^{13}C{H}-NMR (CD_2Cl_2, 125 MHz, 25°C) δ 189.3 ($^1J(^{195}$Pt–C$) = 832$ Hz, C(carbene)), 165.1 ($^1J(^{195}$Pt–C$) = 859$ Hz, PtPhC$_{ipso}$ *trans* to carbene), 161.9 (C=N), 142.6 ($^1J(^{195}$Pt–C$) = 1104$ Hz, PtPhC$_{ipso}$ *cis* to carbene), 142.4 (TolC$_{ipso}$), 137.8 ($^2J(^{195}$Pt–C$) = 22$ Hz, PtPhC$_o$ *trans* to carbene), 137.6 ($^2J(^{195}$Pt–C$) = 44$ Hz, PtPhC$_o$ *cis* to carbene), 135.2 (TolC$_p$), 131.3 (imine-PhC$_p$), 129.2 (imine-PhC$_m$), 129.0 (imine-PhC$_o$), 128.9 (imine-PhC$_{ipso}$), 128.2 (TolC$_m$), 127.4 ($^3J(^{195}$Pt–C$) = 86$ Hz, PtPhC$_m$ *cis* to carbene), 126.1 ($^3J(^{195}$Pt–C$) = 58$ Hz, PtPhC$_m$ *trans* to carbene), 124.6 (TolC$_o$), 123.8 ($^3J(^{195}$Pt–C$) = 21$ Hz, NCCN near NMe), 121.1 (PtPhC$_p$ *cis* to carbene), 121.0 (PtPhC$_p$ *trans* to carbene), 118.5 ($^3J(^{195}$Pt–C$) = 15$ Hz, NCCN near C=N), 37.8 (NMe), 20.8 (TolMe). MS–ESI: *m*/*z* 588 ([M(^{195}Pt)]$^+$ + MeCN – C_6H_5, 100%), 587 ([M(^{194}Pt)]$^+$ + MeCN – C_6H_5, 64%). HRMS–ESI: Calcd for $C_{26}H_{25}N_4^{194}Pt$ ([M(^{194}Pt)]$^+$ + MeCN – C_6H_5), 587.1706. Found: 587.1701. Anal. Calcd for $C_{30}H_{27}N_3Pt$: C, 57.69; H, 4.36; N, 6.73. Found: C, 57.73; H, 4.37; N, 6.65.

2.2.5. Preparation of (^{Dipp}N^{Ph}–C)PtPh$_2$ (4b). Silver carbene complex **1b** (0.223 g, 0.456 mmol) was added to a solution of PtPh$_2$(SMe$_2$)$_2$ (0.217 g, 0.458 mmol) in CH$_2$Cl$_2$ (10 mL) at −30°C. The mixture was allowed to warm to ambient temperature after 17 h before filtration of AgCl and removal of volatiles under vacuum. The solid was washed with several portions of ether/pentane to yield the product as yellow orange crystals. Yield: 0.240 g (76%). ^{1}H-NMR (CD$_2$Cl$_2$, 500 MHz, 25°C) δ 7.48–7.51 (m, ^{3}J(^{195}Pt–H) = 80.1 Hz, 2H, PtPhH$_o$ *cis* to carbene), 7.45–7.48 (m, 1H, imine-PhH$_p$), 7.30–7.37 (m, 4H, imine-PhH$_{o,m}$), 7.06 (t, ^{3}J = 7.7 Hz, 1H, DippH$_p$), 7.05 (d, ^{3}J = 1.9 Hz, 1H, NCHCHN near C=N), 6.93 (d, ^{3}J = 7.7 Hz, 2H, DippH$_m$), 6.91 (m, 2H, PtPhH$_m$ *cis* to carbene), 6.87 (d, ^{3}J = 7.4 Hz, ^{3}J(^{195}Pt–H) = 50.4 Hz, 2H, PtPhH$_o$ *trans* to carbene), 6.72 (d, ^{3}J = 1.9 Hz, 1H, NCHCHN near NMe), 6.71 (m, 1H, PtPhH$_p$ *cis* to carbene), 6.56 (t, ^{3}J = 7.4 Hz, 2H, PtPhH$_m$ *trans* to carbene), 6.45–6.48 (m, 1H, PtPhH$_p$ *trans* to carbene), 3.14 (sept., J = 6.8 Hz, 2H, CHMe$_2$), 3.13 (s, 3H, NMe), 1.05 (d, J = 6.8 Hz, 6H, CHMe$_2$), 0.78 (d, J = 6.9 Hz, 6H, CHMe$_2$). ^{13}C{H}-NMR (CD$_2$Cl$_2$, 125 MHz, 25°C) δ 189.5 (^{1}J(^{195}Pt–C) = 849 Hz, C(carbene)), 162.6 (^{1}J(^{195}Pt–C) = 864 Hz, PtPhC$_{ipso}$ *trans* to carbene), 160.7 (C=N), 142.6 (^{1}J(^{195}Pt–C) = 1114 Hz, PtPhC$_{ipso}$ *cis* to carbene), 140.9 (DippC$_{ipso}$), 140.9 (DippC$_o$), 138.3 (^{2}J(^{195}Pt–C) = 23 Hz, PtPhC$_o$ *trans* to carbene), 137.9 (^{2}J(^{195}Pt–C) = 44 Hz, PtPhC$_o$ *cis* to carbene), 131.9 (imine-PhC$_p$), 129.7 (imine-PhC$_m$), 129.0 (imine-PhC$_o$), 128.3 (imine-PhC$_{ipso}$), 127.3 (^{3}J(^{195}Pt–C) = 88 Hz, PtPhC$_m$ *cis* to carbene), 127.1 (DippC$_p$), 125.6 (^{3}J(^{195}Pt–C) = 57 Hz, PtPhC$_m$ *trans* to carbene), 123.9 (^{3}J(^{195}Pt–C) = 22 Hz, 1C, NCCN near NMe), 123.6 (DippC$_m$), 121.2 (PtPhC$_p$ *trans* to carbene), 121.1 (PtPhC$_p$ *cis* to carbene), 118.9 (^{3}J(^{195}Pt–C) = 16 Hz, NCCN near C=N), 37.9 (NMe), 28.5 (CHMe$_2$), 24.0 (CHMe$_2$), 23.7 (CHMe$_2$). MS–ESI: *m*/*z* 658 ([M(^{195}Pt)]$^{+}$ + MeCN – C$_6$H$_5$, 100%), 657 ([M(^{194}Pt)]$^{+}$ + MeCN – C$_6$H$_5$, 78%). HRMS–ESI: Calcd for C$_{31}$H$_{35}$N$_4^{194}$Pt([M(^{194}Pt)]$^{+}$ + MeCN – C$_6$H$_5$), 657.2483. Found: 657.2518. Anal. Calcd for C$_{35}$H$_{37}$N$_3$Pt: C, 60.51; H, 5.37; N, 6.05. Found: C, 61.09; H, 5.45; N, 5.97.

2.2.6. Preparation of (^{Tol}N^{Ph}–C)PtPh(NCMe)$^{+}$OTf^{-} (5a). Triflic acid (19.0 µL, 0.216 mmol) was added to a solution of **4a** (0.136 g, 0.218 mmol) in acetonitrile (6 mL) at ambient temperature. The mixture was stirred for 30 min before the removal of volatiles under vacuum. The solid was washed with CH$_2$Cl$_2$/pentane and then with CH$_2$Cl$_2$/ether to yield the pure product as a pale yellow solid in 80% yield (0.128 g, 0.175 mmol). ^{1}H-NMR (CD$_2$Cl$_2$, 600 MHz, 25°C) δ 7.57 (m, 1H, imine-PhH$_p$), 7.48 (m, 2H, imine-PhH$_m$), 7.44 (m, 2H, PtPhH$_o$), 7.39 (m, 2H, imine-PhH$_o$), 7.18 (m, 2H, TolH$_m$), 7.10 (m, 2H, PtPhH$_m$), 7.06 (d, ^{3}J = 2.3 Hz, 1H, NCHCHN near C=N), 7.04 (d, ^{3}J = 2.3 Hz, 1H, NCHCHN near NMe), 6.99 (m, 1H, PtPhH$_p$), 6.97 (m, 2H, TolH$_o$), 3.12 (s, 3H, NMe), 2.32 (s, 3H, TolMe), 1.90 (s, 3H, NCMe). ^{13}C{H}-NMR (CD$_3$CN, 50 MHz, 25°C) δ 161.8 (^{2}J(^{195}Pt–C) = 27 Hz, C=N), 154.2 (^{1}J(^{195}Pt–C) = 1748 Hz, C(carbene)), 140.9 (TolC$_{ipso}$), 137.8 (TolC$_p$), 137.6 (^{2}J(^{195}Pt–C) = 32 Hz, PtPhC$_o$), 132.6 (imine-PhC$_p$), 130.8 (^{1}J(^{195}Pt–C) = 944 Hz, PtPhC$_{ipso}$), 129.9 (TolC$_m$), 129.7 (imine-PhC$_m$), 129.2 (imine-PhC$_o$), 128.5 (^{3}J(^{195}Pt–C) = 64 Hz, PtPhC$_m$), 125.7 (^{3}J(^{195}Pt–C) = 58 Hz, NCCN near NMe), 125.6 (imine-PhC$_{ipso}$), 124.7 (^{4}J(^{195}Pt–C) = 11 Hz, PtPhC$_p$), 123.8 (TolC$_o$), 119.8 (^{3}J(^{195}Pt–C) = 37 Hz, NCCN near C=N), 119.1 (NCMe), 38.7 (^{3}J(^{195}Pt–C) = 22 Hz, NMe), 20.9 (TolMe), 2.95 (^{3}J(^{195}Pt–C) = 8 Hz, NCMe). MS–ESI: *m*/*z* 587 ([M]$^{+}$ (C$_{26}$H$_{25}$N$_4^{194}$Pt), 100%). HRMS–ESI: Calcd for C$_{26}$H$_{25}$N$_4^{194}$Pt, 587.1696. Found: 587.1682. Anal. Calcd for C$_{27}$F$_3$H$_{25}$N$_4$O$_3$PtS: C, 44.0; H, 3.4; N, 7.6.

Found: C, 41.4; H, 3.3; N, 7.2 (the discrepancy may be due to residual CH_2Cl_2 in the crystalline product, observed by ^{1}H-NMR).

2.2.7. Preparation of ($^{Dipp}N^{Ph}$–C)PtPh(NCMe)$^+$OTf$^-$ (5b). Triflic acid (7.0 µL, 0.079 mmol) was added to a solution of **4b** (0.0543 g, 0.0786 mmol) in acetonitrile (10 mL). The mixture was stirred for 15 min at ambient temperature. The volatiles were removed under vacuum, and the residue was recrystallized from an acetonitrile/toluene mixture. The product was obtained as a fine yellow powder in 80% yield after drying in vacuum (0.0508 g, 0.0629 mmol). ^{1}H-NMR (CD_2Cl_2, 600 MHz, 25°C) δ 7.61 (m, 1H, imine-PhH$_p$), 7.50 (m, 2H, imine-PhH$_m$), 7.43 (m, 2H, PtPhH$_o$), 7.41 (m, 2H, imine-PhH$_o$), 7.29 (m, 1H, DippH$_p$), 7.24 (d, $^3J = 2.4$ Hz, 1H, NCHCHN near C=N), 7.23 (m, 2H, DippH$_m$), 7.17 (d, $^3J = 2.4$ Hz, 1H, NCHCHN near NMe), 7.09 (m, 2H, PtPhH$_m$), 6.98 (m, 1H, PtPhH$_p$), 3.18 (s, 3H, NMe), 3.09 (sept., $J = 6.8$ Hz, 2H, CHMe$_2$), 1.72 (s, 3H, NCMe), 1.39 (d, $J = 6.8$ Hz, 6H, CHMe$_2$), 1.02 (d, $J = 6.8$ Hz, 6H, CHMe$_2$). ^{13}C{H}-NMR (CD_2Cl_2, 50 MHz, 25°C) δ 161.1 ($^2J(^{195}$Pt–C$) = 27$ Hz, C=N), 154.2 ($^1J(^{195}$Pt–C$) = 1749$ Hz, C(carbene)), 141.0 (DippC$_o$), 138.3 (DippC$_{ipso}$), 137.7 ($^2J(^{195}$Pt–C$) = 33$ Hz, PtPhC$_o$), 133.5 (imine-PhC$_p$), 130.9 ($^1J(^{195}$Pt–C$) = 942$ Hz, PtPhC$_{ipso}$), 129.7 (imine-PhC$_m$), 129.0 (imine-PhC$_o$), 128.7 (DippC$_p$), 128.5 ($^3J(^{195}$Pt–C$) = 64$ Hz, PtPhC$_m$), 125.9 ($^3J(^{195}$Pt–C$) = 58$ Hz, NCCN near NMe), 125.4 ($^3J(^{195}$Pt–C$) = 11$ Hz, imine-PhC$_{ipso}$), 124.9 ($^4J(^{195}$Pt–C$) = 10$ Hz, PtPhC$_p$), 124.6 (DippC$_m$), 120.3 ($^3J(^{195}$Pt–C$) = 38$ Hz, NCCN near C=N), 118.4 (NCMe), 38.9 ($^3J(^{195}$Pt–C$) = 23$ Hz, NMe), 28.6 (CHMe$_2$), 24.6 (CHMe$_2$), 23.1 (CHMe$_2$), 2.3 ($^3J(^{195}$Pt–C$) = 8$ Hz, NCMe). MS–ESI: m/z 658 ([M(^{195}Pt)]$^+$, 100%), 657 ([M(^{194}Pt)]$^+$, 57%). HRMS–ESI: Calcd for $C_{31}H_{35}N_4^{194}Pt$ ([M(^{194}Pt)]$^+$), 657.2488. Found: 657.2486. Anal. Calcd for $C_{32}F_3H_{35}N_4O_3PtS$: C, 47.58; H, 4.37; N, 6.94. Found: C, 50.74; H, 4.58; N, 6.32 (the discrepancy may be due to residual toluene in the crystalline product, observed by ^{1}H-NMR).

2.2.8. Preparation of ($^{Tol}N^{Ph}$–$^{Tol}N^{Ph}$)PtMeCl. A solution of the diimine $^{Tol}N^{Ph}$–$^{Tol}N^{Ph}$ (0.581 g, 1.50 mmol) in toluene (7 mL) was added to a solution of PtMeCl(SMe$_2$)$_2$ (0.269 g, 0.727 mmol) in toluene (7 mL) at ambient temperature, and the mixture was then stirred under argon at 45°C. Stirring was continued for 3 days during which the contents of the flask were purged repeatedly to remove liberated SMe$_2$. The solvent was removed under vacuum and the crude product was washed repeatedly with toluene/pentane to yield the product as a dark purple powder in 83% yield (0.384 g, 0.606 mmol). ^{1}H-NMR (CD_3CN, 500 MHz, 25°C) δ 6.9–7.1 (m, 18H, all aromatic H's), 2.25 (s, 6H, TolMe), 1.01 (s, $^2J(^{195}$Pt–H$) = 80.0$ Hz, 3H, PtMe). ^{13}C{H}-NMR (CD_3CN, 50 MHz, 25°C) δ 177.7 (C=N), 174.7 ($^2J(^{195}$Pt–C$) = 57$ Hz, C=N), 146.3 ($J(^{195}$Pt–C$) = 45$ Hz), 145.4 ($J(^{195}$Pt–C$) = 18$ Hz), 137.4 ($J(^{195}$Pt–C$) = 12$ Hz), 137.1, 136.5, 135.4 ($J(^{195}$Pt–C$) = 18$ Hz), 129.8, 129.7, 129.3 ($J(^{195}$Pt–C$) = 9$ Hz), 129.0, 128.9, 128.5, 128.3, 127.7, 125.0 ($J(^{195}$Pt–C$) = 15$ Hz), 124.6, 21.0, 20.9, –10.0 ($^1J(^{195}$Pt–C$) = 723$ Hz, PtMe). MS–ESI: m/z 639 ([M(^{195}Pt)]$^+$ + CH_3CN – Cl, 100%), 638 ([M(^{194}Pt)]$^+$ + CH_3CN – Cl, 61%). HRMS–ESI: Calcd for $C_{31}H_{30}N_3^{194}Pt$ ([M(^{194}Pt)]$^+$ + CH_3CN – Cl), 638.2061. Found: 638.2071. Anal. Calcd for $C_{29}H_{27}N_2PtCl$: C, 54.93; H, 4.29; N, 4.42. Found: C, 55.02; H, 4.43; N, 4.26.

2.2.9. Preparation of ($^{Tol}N^{Ph}$–$^{Tol}N^{Ph}$)$PtMe_2$ (2c). A dark purple solution of ($^{Tol}N^{Ph}$–$^{Tol}N^{Ph}$)PtMeCl (0.103 g, 0.163 mmol) in THF (90 mL) was cooled to −35°C under argon. A 0.18 mol L^{-1} solution of Me_2Mg in 3 : 1 THF/dioxane (1.5 mL, 0.28 mmol) was slowly added (*ca* 15 min) until the first appearance of a dark green solution. The reaction mixture was immediately quenched by the addition of water (0.3 mL), warmed to –3°C, and stirred for 1 h before the volatiles were removed under vacuum. The remaining solids were dissolved in 20 mL of a 1 : 1 toluene/pentane mixture and stored in a dry box for slow precipitation of unreacted starting material. The pure product was isolated as a dark green solid in 70% yield (0.070 g, 0.114 mmol) after removal of solvent and drying under vacuum. ^{1}H-NMR (C_6D_6, 500 MHz, 25°C) δ 7.10 (d, $^3J = 7.6$ Hz, 4H, TolH$_o$), 6.81 (d, $^3J = 7.6$ Hz, 4H, TolH$_m$), 6.77 (d, $^3J = 6.9$ Hz, 4H, PhH$_o$), 6.6 (m, 6H, PhH$_{m/p}$), 2.77 (s, $^2J(^{195}Pt–H) = 76.9$ Hz, 6H, PtMe), 1.92 (s, 6H, TolMe). ^{13}C{H}-NMR (C_6D_6, 50 MHz, 25°C) δ 171.6 (C=N), 146.8 (TolC$_{ipso}$), 137.8 (PhC$_{ipso}$), 135.4 (TolC$_p$), 128.8 (TolC$_m$), 127.8 (PhC$_p$), 127.7 (PhC$_m$), 126.6 (PhC$_o$), 123.8 (TolC$_o$), 20.8 (TolMe), –8.8 ($^1J(^{195}Pt–C) = 806$ Hz, PtMe). MS–ESI: *m/z* 639 ($[M(^{195}Pt)]^+ + CH_3CN - CH_3$, 100%), 638 ($[M(^{194}Pt)]^+ + CH_3CN - CH_3$, 59%), 389 ($[C_{28}H_{25}N_2]^+$, 6%). HRMS–ESI: Calcd for $C_{31}H_{30}N_3^{194}Pt$ ($[M(^{194}Pt)]^+ + CH_3CN - CH_3$), 638.2066. Found: 638.2051. Anal. Calcd for $C_{30}H_{30}N_2Pt$: C, 58.72; H, 4.93; N, 4.56. Found: C, 58.66; H, 4.96; N, 4.61.

2.2.10. Preparation of ($^{Tol}N^{Ph}$–$^{Tol}N^{Ph}$)PtMe(NCMe)$^+$OTf$^-$ (3c). A solution of silver triflate (0.0446 g, 0.173 mmol) in acetonitrile (4 mL) was added to a solution of ($^{Tol}N^{Ph}$–$^{Tol}N^{Ph}$)PtMeCl (0.116 g, 0.183 mmol) in acetonitrile (6 mL), and the mixture was stirred in a drybox for 30 h. The precipitated silver chloride was removed by centrifugation and the volatiles were removed under reduced pressure. The crude product was washed with 4 × 8 mL 1 : 3 dichloromethane/pentane to yield the product as a dark red solid in 98% yield (0.134 g, 0.169 mmol). ^{1}H-NMR (CD_2Cl_2, 600 MHz, 25°C) δ 7.20 (m, 1H, PhH$_p$ *trans* to PtMe), 7.19 (m, 2H, TolH$_m$ *trans* to PtMe), 7.16 (m, 1H, PhH$_p$ *cis* to PtMe), 7.10 (m, 2H, TolH$_m$ *cis* to PtMe), 7.09 (m, 2H, PhH$_m$ *trans* to PtMe), 7.06 (m, 2H, PhH$_m$ *cis* to PtMe), 7.04 (m, 2H, TolH$_o$ *trans* to PtMe), 6.96 (m, 2H, PhH$_o$ *trans* to PtMe), 6.94 (m, 2H, TolH$_o$ *cis* to PtMe), 6.93 (m, 2H, PhH$_o$ *cis* to PtMe), 2.33 (s, 3H, TolMe *trans* to PtMe), 2.28 (s, 3H, TolMe *cis* to PtMe), 2.27 (s, 3H, NCMe), 0.94 (s, $^2J(^{195}Pt–H) = 71.8$ Hz, 3H, PtMe). ^{13}C{H}-NMR (CD_2Cl_2, 50 MHz, 25°C) δ 182.7 (C=N *cis* to PtMe), 172.9 ($^2J(^{195}Pt–C) = 61$ Hz, C=N *trans* to PtMe), 143.5 ($^2J(^{195}Pt–C) = 47$ Hz, TolC$_{ipso}$ *cis* to PtMe), 143.4 ($^2J(^{195}Pt–C) = 18$ Hz, TolC$_{ipso}$ *trans* to PtMe), 138.8 (TolC$_p$ *trans* to PtMe), 138.3 ($^5J(^{195}Pt–C) = 11$ Hz, TolC$_p$ *cis* to PtMe), 133.3 ($^3J(^{195}Pt–C) = 51$ Hz, PhC$_{ipso}$ *cis* to PtMe), 132.7 ($^3J(^{195}Pt–C) = 19$ Hz, PhC$_{ipso}$ *trans* to PtMe), 130.5 (PhC$_p$ *trans* to PtMe), 130.4 (PhC$_p$ *cis* to PtMe), 129.8 (TolC$_m$ *trans* to PtMe), 129.3 ($^4J(^{195}Pt–C) = 9$ Hz, TolC$_m$ *cis* to PtMe), 128.8 (PhC$_o$ *trans* to PtMe), 128.6 (PhC$_m$ *trans* to PtMe), 128.4 (PhC$_m$ *cis* to PtMe), 128.2 (PhC$_o$ *cis* to PtMe), 123.7 ($^3J(^{195}Pt–C) = 16$ Hz, TolC$_o$ *cis* to PtMe), 123.1 (TolC$_o$ *trans* to PtMe), 120.6 (NCMe), 21.1 (TolMe *trans* to PtMe), 21.0 (TolMe *cis* to PtMe), 3.8 ($^3J(^{195}Pt–C) = 16$ Hz, NCMe), –16.2 ($^1J(^{195}Pt–C) = 667$ Hz, PtMe). MS–ESI: *m/z* 639 ($[M(^{195}Pt)]^+$, 100%), 638 ($[M(^{194}Pt)]^+$, 56%). HRMS–ESI: Calcd for $C_{31}H_{30}N_3^{194}Pt$ ($[M(^{194}Pt)]^+$), 638.2066. Found: 638.2053. Anal. Calcd for $C_{32}F_3H_{30}N_3O_3PtS$: C, 48.73; H, 3.83; N, 5.33. Found: C, 47.78; H, 3.83; N, 5.02 (The discrepancy may be due to residual CH_2Cl_2 in the crystalline product, observed by ^{1}H-NMR).

2.2.11. Preparation of ($^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$–$^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$)$\mathrm{PtPh_2}$ (4c). Inside the drybox, ether solutions (11 mL of each) of $\mathrm{PtPh_2(SMe_2)_2}$ (0.113 g, 0.239 mmol) and the diimine $^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$–$^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$ (0.116 g, 0.299 mmol) were mixed, shaken, and stored for 2 days to yield dark green shimmering crystals. The volatiles were removed under vacuum and the dark green crystals were washed with ether (2 × 5 mL) to yield the product in 68% yield (0.120 g, 0.163 mmol) after drying under vacuum. ^{1}H-NMR ($\mathrm{CD_2Cl_2}$, 600 MHz, 25°C) δ 7.12 (m, 2H, imine-PhH$_\mathrm{p}$), 7.01 (m, 4H, imine-PhH$_\mathrm{m}$), 6.88 (m, 4H, imine-PhH$_\mathrm{o}$), 6.75 (m, 4H, PtPhH$_\mathrm{o}$), 6.69 (m, 4H, TolH$_\mathrm{m}$), 6.59 (m, 4H, PtPhH$_\mathrm{m}$), 6.58 (m, 4H, TolH$_\mathrm{o}$), 6.53 (m, 2H, PtPhH$_\mathrm{p}$), 2.15 (s, 3H, TolMe). ^{13}C{H}-NMR ($\mathrm{CD_2Cl_2}$, 50 MHz, 25°C) δ 174.0 ($^2J(^{195}\mathrm{Pt–C}) = 16$ Hz, C=N), 145.4 ($^2J(^{195}\mathrm{Pt–C}) = 26$ Hz, TolC$_\mathrm{ipso}$), 144.9 ($^1J(^{195}\mathrm{Pt–C}) = 1102$ Hz, PtPhC$_\mathrm{ipso}$), 137.8 ($^2J(^{195}\mathrm{Pt–C}) = 32$ Hz, PtPhC$_\mathrm{o}$), 136.2 ($^5J(^{195}\mathrm{Pt–C}) = 32$ Hz, TolC$_\mathrm{p}$), 136.1 (imine-PhC$_\mathrm{ipso}$), 129.1 (imine-PhC$_\mathrm{p}$), 128.3 (imine-PhC$_\mathrm{o}$), 128.2 (imine-PhC$_\mathrm{m}$), 128.1 (TolC$_\mathrm{m}$), 126.2 ($^3J(^{195}\mathrm{Pt–C}) = 81$ Hz, PtPhC$_\mathrm{m}$), 123.8 ($^3J(^{195}\mathrm{Pt–C}) = 7$ Hz, TolC$_\mathrm{o}$), 121.6 ($^4J(^{195}\mathrm{Pt–C}) = 13$ Hz, PtPhC$_\mathrm{p}$), 21.0 (TolMe). MS–ESI: *m/z* 701 ($[\mathrm{M}(^{195}\mathrm{Pt})]^+ + \mathrm{MeCN} - \mathrm{C_6H_5}$, 36%), 700 ($[\mathrm{M}(^{194}\mathrm{Pt})]^+ + \mathrm{MeCN} - \mathrm{C_6H_5}$, 19%), 389 ($[\mathrm{C_{28}H_{25}N_2}]^+$, 100%). HRMS–ESI: Calcd for $\mathrm{C_{36}H_{32}N_3^{194}Pt}$ ($[\mathrm{M}(^{194}\mathrm{Pt})]^+ + \mathrm{MeCN} - \mathrm{C_6H_5}$), 700.2223. Found: 700.2191. Anal. Calcd for $\mathrm{C_{40}H_{34}N_2Pt}$: C, 65.12; H, 4.64; N, 3.80. Found: C, 65.05; H, 4.75; N, 3.70.

2.2.12. Preparation of ($^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$–$^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$)$\mathrm{PtPh(NCMe)^+OTf^-}$ (5c). A solution of **4c** (0.118 g, 0.160 mmol) in acetonitrile (30 mL) was treated with 2,6-di-*tert*-butylpyridinium triflate (0.066 g, 0.193 mmol). The resulting mixture was held at 50°C for 6 h. After the removal of volatiles under vacuum, the crude product was washed thrice with dichloromethane/ether mixtures to yield the product as red crystals in 80% yield (0.109 g, 0.128 mmol) after drying under vacuum. ^{1}H-NMR ($\mathrm{CD_2Cl_2}$, 600 MHz, 25°C) δ 7.22 (m, 1H, imine-PhH$_\mathrm{p}$ *trans* to PtPh), 7.21 (m, 2H, TolH$_\mathrm{m}$ *trans* to PtPh), 7.16 (m, 1H, imine-PhH$_\mathrm{p}$ *cis* to PtPh), 7.12 (m, 2H, TolH$_\mathrm{o}$ *trans* to PtPh), 7.11 (m, 2H, imine-PhH$_\mathrm{m}$ *trans* to PtPh), 7.04 (m, 2H, imine-PhH_m *cis* to PtPh), 7.0 (m, 2H, imine-PhH$_\mathrm{o}$ *trans* to PtPh), 6.94 (m, 2H, imine-PhH$_\mathrm{o}$ *cis* to PtPh), 6.77 (m, 2H, PtPhH$_\mathrm{o}$), 6.71 (m, 2H, PtPhH$_\mathrm{m}$), 6.70 (m, 1H, PtPhH$_\mathrm{p}$), 6.67 (m, 2H, TolH$_\mathrm{m}$ *cis* to PtPh), 6.59 (m, 2H, TolH$_\mathrm{o}$ *cis* to PtPh), 2.34 (s, 3H, TolMe *trans* to PtPh), 2.14 (s, 3H, NCMe), 2.09 (s, 3H, TolMe *cis* to PtPh). ^{13}C{H}-NMR ($\mathrm{CD_3CN}$, 50 MHz, 25°C) δ 181.5 (C=N *cis* to PtPh), 174.7 ($^2J(^{195}\mathrm{Pt–C}) = 61$ Hz, C=N *trans* to PtPh), 143.8 ($^2J(^{195}\mathrm{Pt–C}) = 48$ Hz, TolC$_\mathrm{ipso}$ *cis* to PtPh), 143.5 ($^2J(^{195}\mathrm{Pt–C}) = 17$ Hz, TolC$_\mathrm{ipso}$ *trans* tp PtPh), 138.8 (TolC$_\mathrm{p}$ *trans* to PtPh), 137.9 ($^5J(^{195}\mathrm{Pt–C}) = 11$ Hz, TolC$_\mathrm{p}$ *cis* to PtPh), 135.7 (PtPhC$_\mathrm{o}$), 134.0 ($^1J(^{195}\mathrm{Pt–C}) = 889$ Hz, PtPhC$_\mathrm{ipso}$), 133.3 ($^3J(^{195}\mathrm{Pt–C}) = 53$ Hz, imine-PhC$_\mathrm{ipso}$ *cis* to PtPh), 132.5 ($^3J(^{195}\mathrm{Pt–C}) = 19$ Hz, imine-PhC$_\mathrm{ipso}$ *trans* to PtPh), 130.7 (imine-PhC$_\mathrm{p}$ *trans* to PtPh), 130.5 (imine-PhC$_\mathrm{p}$ *cis* to PtPh), 129.8 (TolC$_\mathrm{m}$ *trans* to PtPh), 129.0 (imine-PhC$_\mathrm{o}$ *trans* to PtPh), 128.7 (imine-PhC$_\mathrm{m}$ *trans* to PtPh), 128.6 (imine-PhC$_\mathrm{o}$ *cis* to PtPh), 128.5 (TolC$_\mathrm{m}$ *cis* to PtPh), 128.4 (imine-PhC$_\mathrm{m}$ *cis* to PtPh), 127.1 ($^3J(^{195}\mathrm{Pt–C}) = 49$ Hz, PtPhC$_\mathrm{m}$), 124.2 ($J(^{195}\mathrm{Pt–C}) = 20$ Hz, TolC$_\mathrm{o}$ *cis* to PtPh), 124.2 (PtPhC$_\mathrm{p}$), 123.1 (TolC$_\mathrm{o}$ *trans* to PtPh), 119.9 (NCMe), 21.1 (TolMe), 20.9 (TolMe), 3.8 ($^3J(^{195}\mathrm{Pt–C}) = 14$ Hz, NCMe). MS–ESI: *m/z* 701 ($[\mathrm{M}(^{195}\mathrm{Pt})]^+$, 100%), 700 ($[\mathrm{M}(^{194}\mathrm{Pt})]^+$, 62%). HRMS–ESI: Calcd for $\mathrm{C_{36}H_{32}N_3^{194}Pt}$ ($[\mathrm{M}(^{194}\mathrm{Pt})]^+$), 700.2223. Found: 700.2231. Anal. Calcd for $\mathrm{C_{37}F_3H_{32}N_3O_3PtS}$: C, 52.23; H, 3.79; N, 4.94. Found: C, 50.6; H, 3.7; N, 4.5. (The discrepancy from calculated values may be due to considerable amounts of $\mathrm{CH_2Cl_2}$ in the crystalline product, seen by ^{1}H-NMR).

Table 1. Crystallographic data and refinement parameters for **2a**, **2c**, **4a**, and **4b**.

Complex	**2a**	**2c**	**4a**	**4b**
Empirical formula	$C_{20}H_{23}N_3Pt$	$C_{30}H_{30}N_2Pt$	$C_{30}H_{27}N_3Pt$	$C_{35}H_{37}N_3Pt$
Formula weight	500.51	613.67	624.65	694.79
Temperature (K)	105	105	105	105
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)				
a	9.6413(7)	9.851(2)	7.6191(8)	11.5963(5)
b	15.5169(11)	24.103(6)	28.859(3)	23.3643(9)
c	20.0733(14)	11.971(3)	11.7462(12)	21.9125(9)
α	103.5160(10)	90	90	90
β	96.2490(10)	96.368(4)	98.102(2)	90.7490(10)
γ	101.8750(10)	90	90	90
Volume (Å^3), Z	2818.2(3), 6	2824.8(11), 4	2557.0(5), 4	5936.5(4), 8
Absorption coefficient (mm^{-1})	7.473	4.985	5.510	4.755
Reflections measured	25,134	5777	23,267	42,146
Unique reflection	13,049	5777	6150	14,199
R_1, wR_2 $[I > 3\sigma(I)]$	0.0321, 0.0357	0.0484, 0.0464	0.0200, 0.0207	0.0258, 0.0264
wR_2 (all data)	0.0574	0.0562	0.0234	0.0321

2.3. *X-ray crystallography*

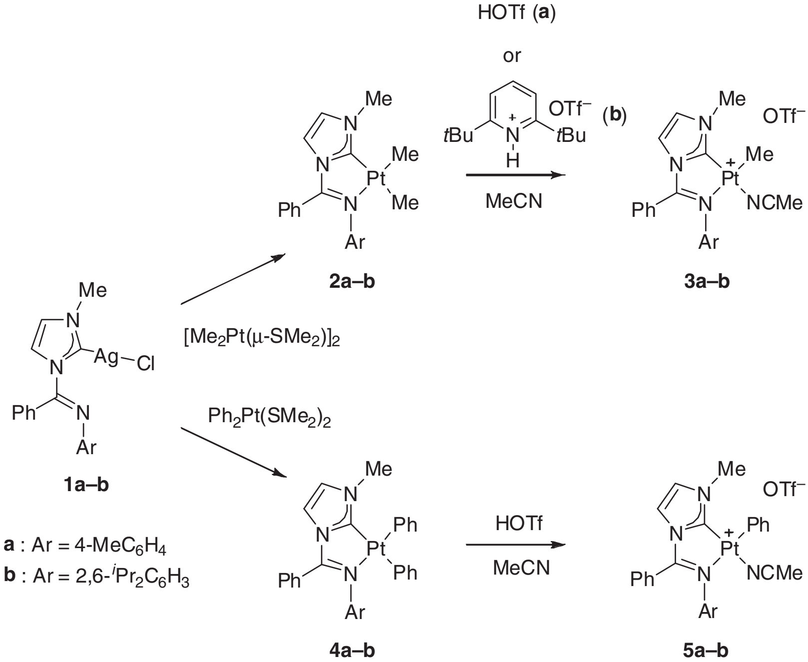
Pertinent parameters for data collection and refinement for all compounds are provided in table 1. The crystals were mounted on glass fibers with perfluoropolyether, and the data collected at 105 K on a Siemens 1K SMART CCD diffractometer using graphite-monochromated Mo-Kα radiation. Data collection method: ω-scan; range is 0.3° and crystal to detector distance is 5 cm. Data reduction and cell determination were carried out with SAINT and XPREP [34] programs. Absorption corrections were applied by using SADABS (G.M. Sheldrick, Private communication, 1996). All structures were solved using the Sir92 program [35], and refined on F using the program Crystals [36]. The non-hydrogen atoms were refined with anisotropic thermal parameters; all hydrogens were located in a difference map, but those attached to carbon were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C–H distances in the range 0.93–0.98 Å) and isotropic adsorptions (U(H) in the range $1.2–1.5 \times U_{\text{equiv.}}$ of the adjacent atom), after which they were refined with riding constraints.

3. Results and discussion

3.1. *Synthesis of compounds*

In the following section, the preparative work will be briefly described. Characterization methods, in particular the wide range of NMR techniques used, and the pertinent data are given in Section 2 and will not be emphasized here.

3.1.1. Synthesis of platinum complexes with iminocarbene ligands. The silver carbene complexes **1a** and **1b**, whose syntheses from Ag_2O and corresponding imidazolium salt



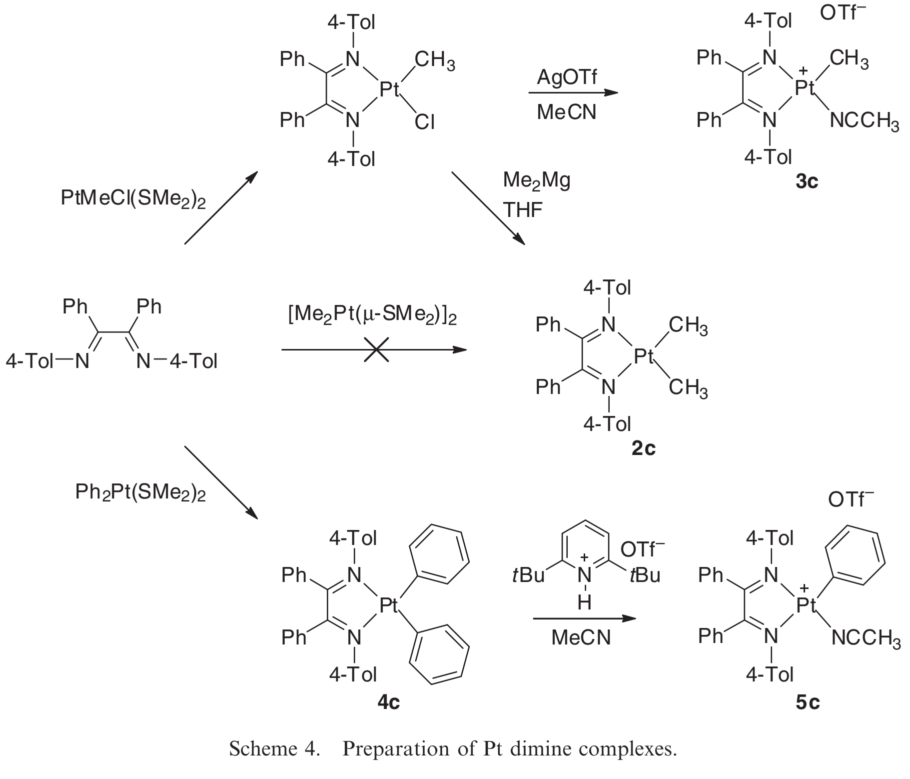
Scheme 3. Preparation of Pt iminocarbene complexes.

precursors have been previously described by us [25, 26], underwent reasonably smooth transfer of the carbene moiety to Pt upon treatment with $[Me_2Pt(\mu\text{-}SMe_2)]_2$ to furnish the Pt complexes $(^{Tol}N^{Ph}\text{–}C)PtMe_2$ (**2a**) and $(^{Dipp}N^{Ph}\text{–}C)PtMe_2$ (**2b**) [25] (scheme 3). A similar carbene transfer to Pt has been previously done with other Ag iminocarbene sources. During the synthesis of **2a**, it became apparent that the new Pt complex **2a** slowly reacted with the Pt precursor $[Me_2Pt(\mu\text{-}SMe_2)]_2$ to yield minor quantities of unidentified Pt–Me containing impurities (as inferred from ^{1}H-NMR spectra of the crude product mixtures). We did not succeed in separating these impurities from the desired product and therefore the preparation of **2a** was done by employing a slight molar excess of **1a** relative to $[Me_2Pt(\mu\text{-}SMe_2)]_2$. The separation of unreacted **1a** from the product **2a** could be accomplished by rapid chromatography on alumina, albeit with significant product losses (62% isolated yield). Upon treatment of **2a** and **2b** with triflic acid (**a**) or 2,6-*tert*-butylpyridinium triflate (**b**) in acetonitrile, the methyl group that was located *trans* to the carbene moiety was selectively removed to produce the cationic complexes **3a** and **3b** (scheme 3) [37].

Carbene transfer from silver to $Ph_2Pt(SMe_2)_2$ successfully produced the analogous diphenylplatinum complexes **4a** and **4b** without complications arising from difficult separations or work-up. The diphenyl complexes **4a** and **4b** were in turn converted to the cationic complexes **5a** and **5b** by careful treatment with triflic acid in acetonitrile (scheme 3). Again, protonolysis led to the selective loss of the phenyl group located *trans* to the carbene. The protonation presumably generates (unobserved) cationic η^2-C_6H_6 complexes which under the reaction conditions undergo benzene substitution by acetonitrile; the large *trans* effect of the carbene ligand relative to the imine causes selective substitution at the *trans* location.

3.1.2. Synthesis of platinum complexes with diimine ligands. In order to facilitate a direct comparison of structural and spectroscopic features between closely related diimine and iminocarbene complexes, we also undertook the preparation of several new diimineplatinum complexes with phenyl substituents at the diimine backbone, i.e., ligand system **c** (${}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}\_{}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$) in scheme 1. Unfortunately, all attempts to selectively prepare the simple derivative (${}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}\_{}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$)PtMe$_2$ (**2c**, scheme 4) by reacting the required diimine [29] ${}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}\_{}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$ with [Me$_2$Pt(μ-SMe$_2$]$_2$ led to intractable product mixtures, although ^{1}NMR spectra of crude products showed **2c** to be one major constituent. A more selective route to **2c** was therefore sought. It was found that, contrary to [Me$_2$Pt(μ-SMe$_2$)]$_2$, chloromethyl complex PtMeCl(SMe$_2$)$_2$ underwent facile reaction with ${}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}\_{}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$ to yield the corresponding (${}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}\_{}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$)PtMeCl in good yields, by analogy with related systems [38]. The desired dimethyl complex (${}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}\_{}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$)PtMe$_2$ (**2c**) was then obtained in 70% yield from the reaction between a slight excess dimethylmagnesium and (${}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}\_{}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$)PtMeCl in THF at −35°C. In this synthesis, it was important to suppress undesired side reactions by adding water to the reaction mixture at the first hint of development of a dark green color. The cationic methylplatinum complex (${}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}\_{}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$)PtMe(NCMe)$^+$ (**3c**) was readily produced when (${}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}\_{}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$)PtMeCl was treated with silver triflate in acetonitrile.

The phenylplatinum complexes based on ${}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}\_{}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$ were prepared straightforwardly. Thus, neutral (${}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}\_{}^{\mathrm{Tol}}\mathrm{N}^{\mathrm{Ph}}$)PtPh$_2$ (**4c**) was obtained from the diimine and Ph$_2$Pt(SMe$_2$)$_2$ in ether. Its cationic derivative **5c** was obtained by protonation of **4c** with



Scheme 4. Preparation of Pt dimine complexes.

2,6-di-*tert*-butylpyridinium triflate accompanied by benzene substitution by acetonitrile solvent at 50°C (scheme 4).

3.2. *Crystal structure determinations*

Crystals of the neutral complexes **2a**, **2c**, **4a**, and **4b** were subjected to structure determination by single crystal X-ray crystallography (see Section 2 for crystallographic data). Selected bond distances and angles are summarized in table 2. Figure 1 shows ORTEP drawings of the four molecular structures.

All structurally characterized compounds show the expected square-planar environment around Pt(II) that is expected for four-coordinate d^8 species. The sum of the four *cis* L–Pt–L′ angles around platinum are $360 \pm (0.1–0.7)^\circ$ for all compounds. Deviations from the ideal 90° L–Pt–L′ angles are however significant, ranging from 75.9–78.5° for the chelate bite angles to 96.0–99.2° for the *cis* N(imine)–Pt–C(Me/Ph) or *cis* C(carbene)–Pt–C(Me/Ph) angles. These observations are expected and consistent with previous structural studies on diimine (N–N)$PtMe_2$ complexes [39–41], as well as the structure of **2b** [25].

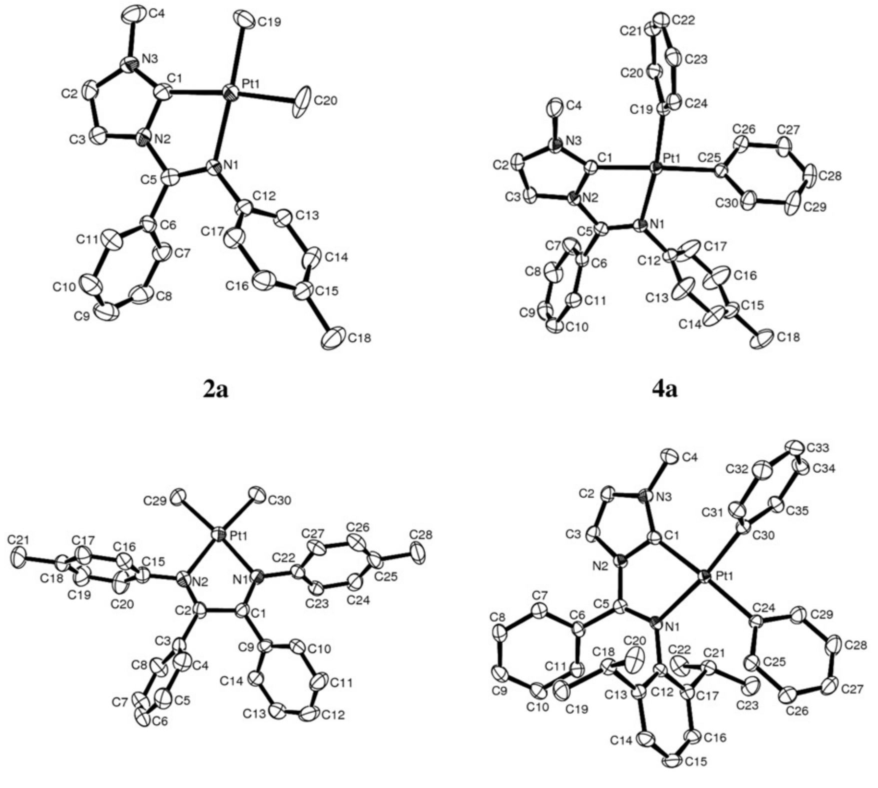
3.3. *Discussion of some trends in the NMR and metric data for Pt complexes*

All new platinum complexes were thoroughly characterized by ^1H- and ^{13}C-NMR spectroscopy methods and the complete assignments are given in Section 2. Selected shifts and coupling constants to the spin = ½ ^{195}Pt nucleus are summarized in tables 3 and 4 (spectroscopic data for the previously reported **2b** [25] are included for comparison). In all relevant cases, the position of the methyl/phenyl group *cis* to the carbene *versus cis* to the imine in the iminocarbene complexes were unambiguously determined by ^1H-NMR NOESY spectroscopy as discussed in an already published work [25].

Table 2. Selected bond lengths (Å) and angles (°) in **2a**, **2c**, **4a**, and **4b**.

	2a[a]	**2c**	**4a**	**4b**
Distances				
Pt–C(*trans* to carbene)	2.085(11)	–	2.046(2)	2.066(3)
Pt–C(*trans* to imine)	2.046(2)	2.056(9), 2.070(9)	1.998(3)	2.005(3)
Pt–C(carbene)	2.034(23)	–	2.021(3)	2.027(3)
Pt–N(imine)	2.123(3)	2.085(7), 2.090(7)	2.157(2)	2.152(2)
C=N(imine)	1.300(3)	1.263(11), 1.307(11)	1.292(3)	1.283(4)
Angles				
N(imine)–Pt–C(*trans* to imine)	177.1(11)	173.9(4), 174.4(4)	172.32(9)	171.25(11)
N(imine)–Pt–C(*cis* to imine)	94.7(17)	98.1(4), 98.9(4)	97.56(9)	97.69(10)
C(carbene)–Pt–C(*cis* to carbene)	100.1(10)	–	95.95(10)	97.32(12)
C(carbene)–Pt–C(*trans* to carbene)	172.0(10)	–	173.04(10)	171.27(11)
N(imine)–Pt–C(carbene)	77.7(13)	–	77.17(10)	76.86(11)
N(imine)–Pt–N(imine)	–	75.9(3)	–	–
C(Me/Ph)–Pt–C(Me/Ph)	87.5(12)	87.0(5)	89.01(10)	88.84(12)

[a] The asymmetric unit of **2a** contains three molecules and the average bond lengths and angles are reported.



2a **4a**

2c **4b**

Figure 1. ORTEP drawings of Pt(II) iminocarbene complexes **2a**, **4a**, and **4b** and diimine Pt(II) complex **2c** with 50% ellipsoids. Hydrogen atoms have been omitted for clarity.

3.3.1. ***Trans* influence of carbene *versus* imine.**

The *trans* influence is defined as the tendency of a ligand to weaken the bond *trans* to itself [42, 43]. This ground-state phenomenon is distinct from the kinetic *trans* effect [44] since it addresses the thermodynamic strength of the *trans* bond rather than on the kinetic labilization of the *trans* ligand. Consequently, the *trans* influence is commonly assessed by structural (ground-state) studies, i.e., by X-ray analysis [43], and in some cases, as with platinum complexes, by nuclear magnetic resonance techniques [42]. In this regard, for the sake of spectroscopic measurements, the scalar *trans* coupling constants $^1J(^{195}\mathrm{Pt}$–ligand) have been shown to be inversely correlated to the *trans* Pt–ligand bond distance for complexes with a given coordination number [42, 43, 45–47].

In the iminocarbene complexes **4a** and **4b**, this correlation is clearly demonstrated by the bond distances and $^1J(^{195}\mathrm{Pt{-}C_{ipso}})$ coupling constants to the Pt-bonded phenyl groups: The shorter Pt–C bonds (1.998(3) and 2.005(3) Å) of $\mathrm{C_{ipso}}$ *trans* to N(imine) correlate with strong $^1J(^{195}\mathrm{Pt{-}C})$ couplings (1104 and 1114 Hz), whereas the longer Pt–C bonds (2.046(2) and 2.066(3) Å) of the $\mathrm{C_{ipso}}$ *trans* to C(carbene) correlate with significantly weaker $^1J(^{195}\mathrm{Pt{-}C})$ couplings (859 and 864 Hz, table 3). The same trend is also seen for the Pt-bonded methyl groups in **2a** ($d_{\mathrm{Pt{-}C}} = 2.046(2)$ Å and

Table 3. NMR data and Pt–R distances for Pt-bonded R groups (R=Me, Ph) in neutral Pt complexes.

		Pt–Me *trans* to carbene			Pt–Me *trans* to imine		
		X-ray $d_{\mathrm{Pt-C}}$ (Å)	^{1}H-NMR δ ($J_{\mathrm{Pt-H}}$, Hz)	^{13}C-NMR δ ($J_{\mathrm{Pt-C}}$, Hz)	X-ray $d_{\mathrm{Pt-C}}$ (Å)	^{1}H-NMR δ ($J_{\mathrm{Pt-H}}$, Hz)	^{13}C-NMR δ ($J_{\mathrm{Pt-C}}$, Hz)
($^{\mathrm{Tol}}$N$^{\mathrm{Ph}}$–C)PtMe$_2$ (**2a**)		2.085	0.07 (63)	6.1 (623)	2.046	1.31 (93)	−22.0 (812)
($^{\mathrm{Dipp}}$N$^{\mathrm{Ph}}$–C)PtMe$_2$ (**2b**) [25]		2.071	0.21 (63)	5.6 (618)	2.051	1.50 (92)	−22.7 (799)
($^{\mathrm{Tol}}$N$^{\mathrm{Ph}}$–$^{\mathrm{Tol}}$N$^{\mathrm{Ph}}$)PtMe$_2$ (**2c**)		NA	NA	NA	2.056, 2.070	2.77 (77)	−8.8 (806)
		Pt–Ph *trans* to carbene			Pt–Ph *trans* to imine		
($^{\mathrm{Tol}}$N$^{\mathrm{Ph}}$–C)PtPh$_2$ (**4a**)	C_{ipso}	2.046	NA	165.1 (859)	1.998	NA	142.6 (1104)
	C_{ortho}		6.94 (50)	137.8 (22)		7.50 (81)	137.6 (44)
	C_{meta}		6.61	126.1 (58)		6.92	127.4 (86)
	C_{para}		6.48	121.0		6.73	121.1
($^{\mathrm{Dipp}}$N$^{\mathrm{Ph}}$–C)PtPh$_2$ (**4b**)	C_{ipso}	2.066	NA	162.6 (864)	2.005	NA	142.6 (1114)
	C_{ortho}		6.87 (50)	138.3 (23)		7.50 (80)	137.9 (44)
	C_{meta}		6.56	125.6 (57)		6.91	127.3 (88)
	C_{para}		6.47	121.2		6.71	121.1
($^{\mathrm{Tol}}$N$^{\mathrm{Ph}}$–$^{\mathrm{Tol}}$N$^{\mathrm{Ph}}$)PtPh$_2$ (**4c**)	C_{ipso}	NA	NA	NA	NA	NA	144.9 (1102)
	C_{ortho}					6.75	137.8 (32)
	C_{meta}					6.59	126.2 (81)
	C_{para}					6.53	121.6 (13)

$^1J(^{195}\mathrm{Pt{-}C}) = 812$ Hz for methyl *trans* to N(imine) *versus* $d_{\mathrm{Pt-C}} = 2.085(11)$ Å and $^1J(^{195}\mathrm{Pt{-}C}) = 623$ Hz for methyl *trans* to C(carbene)). These values are comparable with the previously reported values of **2b** [25] (table 3).

The data from the detailed NMR investigation (table 3) also include $^2J(^{195}\mathrm{Pt{-}C}H_3)$ couplings, 3-bond couplings to *ortho* phenyl protons, and 2- and 3-bond couplings to *ortho* and *meta* phenyl carbons of the Pt-bonded phenyl groups. In all cases, couplings are significantly greater *trans* to imine than *trans* to carbene. As an interesting detail, couplings to $\mathrm{C_{meta}}$ are always greater than to $\mathrm{C_{ortho}}$. Finally, the data for the diimine compound **4c** reveal that the magnitudes of the observed couplings are essentially the same as those seen in the phenyl group *trans* to the imine of the iminocarbene in **4a**.

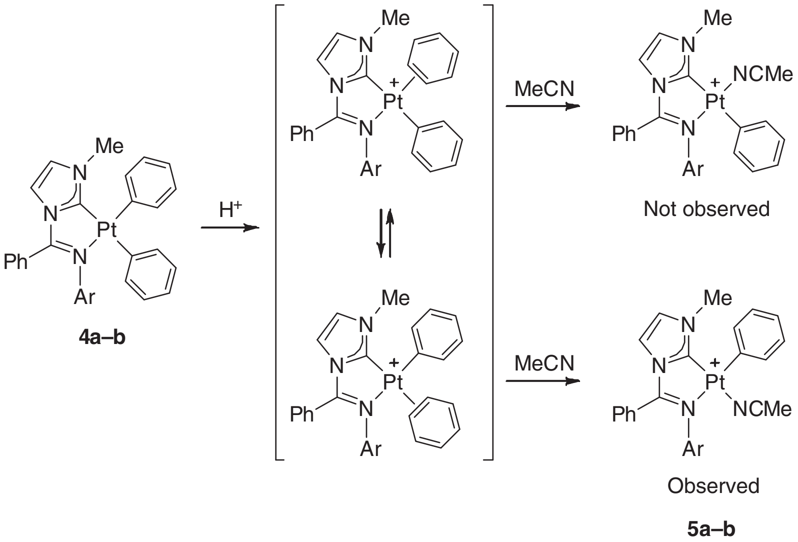
The combination of relatively long $d_{\mathrm{Pt-C}}$ distances and weak $^1J(^{195}\mathrm{Pt{-}C})$ couplings for the ligands *trans* to the carbene is consistent with weaker Pt–C bond strengths of the ligand *trans* to the carbene, and attests to the great *trans* influence [42, 43] of the carbene ligand relative to the imine.

There are significant differences between the Pt–C(carbene) distances in the dimethyl and diphenyl complexes **2a**, **2b** [25], **4a**, and **4b**. However, the Pt–N(imine) bonds of the diphenyl complexes **4a** and **4b** are slightly longer (0.027–0.032 Å) than the corresponding Pt–N(imine) bonds in the corresponding dimethyl complexes **2a** (2.123(3) Å, table 2) and **2b** (2.126(3) Å [25]). This increase reflects the stronger *trans* influence of the phenyl ligand relative to the methyl ligand. Similar differences have been previously seen in diimine complexes [41, 48].

Thus, the accumulated NMR and structural data support the notion that the carbene exerts a dominating ground-state *trans* influence on the Pt center in the iminocarbene complexes. This is paralleled by observation of preferential loss of the methyl groups from the positions *trans* to the carbene upon protonation of **2a** and **2b** resulting in products **3a** and **3b**, as well as the analogous loss of the phenyl groups *trans* to the carbene upon protonation of **4a** and **4b** to yield **5a** and **5b**. These findings demonstrate that the carbene moiety also exerts a dominating kinetic *trans* effect [37]. Similar selective cleavage of a Pt-methyl group *trans* to carbene, rather than *trans* to a pyridine, was seen in a *bis*(2-pyridylmethyl)-substituted NHC dimethylplatinum complex [49]. For the phenyl cleavage reactions presented here, we presume that protonation (which is likely to occur at Pt [22, 50]) yields $\mathrm{Pt}(\eta^2\text{-}\mathrm{C_6H_6})$ complexes that are responsible for benzene loss. By analogy to what has been observed by us in diimine complexes [22, 48, 50], it is possible that two isomeric Pt benzene complexes may coexist and interconvert in solution, with the benzene ligand located *trans* with respect to the imine and carbene moieties, respectively (scheme 5). The strong *trans* effect of the carbene ligand relative to the imine will then preferentially labilize the benzene ligand in the *trans* benzene complex, ultimately leading to the observed stereochemistry in the product (scheme 5, bottom reaction).

3.3.2. Metal charge effects.

Additional spectroscopic features are also noteworthy when the cationic complexes are compared with the neutral ones. Some relevant data are summarized in table 4. The $^1J(^{195}\mathrm{Pt{-}C_{methyl}})$ value of *ca* 800 Hz for the methyl group that is *trans* to the imine in the neutral dimethyl complexes **2a** and **2b** is diminished by 15–16% to *ca* 680 Hz for the methyl group (still *trans* to the imine) in the cationic derivatives **3a** and **3b**. A similar decrease is seen in the ^{13}C-NMR spectra for the phenyl complexes: the neutral complexes **4a** and **4b** exhibit a $^1J(^{195}\mathrm{Pt{-}C_{ipso}})$ value of *ca* 1110 Hz



Scheme 5. Protonolysis of iminocarbene-Pt diphenyl complexes.

Table 4. Selected ^{13}C chemical shifts and coupling constants in neutral and cationic iminocarbene and diimine complexes.

δ ($J_{\text{Pt–C}}$ Hz)						
	L_2PtMe_2			$L_2PtMe(NCMe)^+$		
	2a	**2b** [25]	**2c**	**3a**	**3b**	**3c**
C(carbene)	190.7	190.7	–	154.9	154.9	–
	(862)	(837)		(1723)	(1739)	
C(Pt–Me)	−22.0	−22.7	−8.8	−22.1	−22.1	−16.2
	(812)[a]	(799)[a]	(806)	(683)[a]	(683)[a]	(667)
	L_2PtPh_2			$L_2PtPh(NCMe)^+$		
	4a	**4b**	**4c**	**5a**	**5b**	**5c**
C(carbene)	189.3	189.5	–	154.2	154.2	–
	(832)	(849)		(1748)	(1749)	
C(Pt–Ph$_{\text{ipso}}$)	142.6	142.6	144.9	130.8	130.9	134.0
	(1104)[a]	(1114)[a]	(1102)	(944)[a]	(942)[a]	(889)

[a] Data for the Me or Ph group located *trans* to the imine N of the iminocarbene ligand.

for the phenyl group that is *trans* to the imine; this coupling is reduced to *ca* 940 Hz in the cationic complexes **5a** and **5b**. Furthermore, this trend is not unique to the imonocarbene ligand systems: the diimine complexes, **2c** *versus* **3c** and **4c** *versus* **5c**, exhibit analogous reductions in the $^1J(^{195}\text{Pt–C}_{\text{methyl}})$ and $^1J(^{195}\text{Pt–C}_{\text{ipso}})$ values. The origin of this trend is not clear and probably should not be taken as strong evidence for a weakening of the Pt–Me or Pt–Ph bonds in the cationic complexes. In addition to the effect of altering the charge at Pt (which will affect differently σ and π components in the bonding), the neutral and cationic complexes significantly differ in the identity of the additional ligand (acetonitrile *versus* Me/Ph) that is *cis* to the one being scrutinized.

In contrast, the data in table 4 show that the $^1J(^{195}\text{Pt–C}_{\text{carbene}})$ couplings in cationic **3a** and **3b** and **5a** and **5b** (1723–1749 Hz) are twice as great as those in neutral **2a** and **2b** and **4a** and **4b** (832–862 Hz). Again, caution should be exerted when these trends are discussed because the additional ligand (acetonitrile *vs*. Me/Ph) *trans* to the carbene is changed. However, the observations are at least consistent with a strengthening of the Pt–C(carbene) bond in the cationic complexes **3a** and **3b** and **5a** and **5b**. This is expected for the bonding of a σ-donor ligand when the positive charge at the metal increases with a concomitant reduction of the ionic radius. Preliminary X-ray structure data for **3a** establishes the suggested geometry and gives a Pt–C(carbene) bond distance of 1.950(3) Å in cationic **3a** [37] to be compared with 2.034(23) Å in neutral **2a**.

4. Conclusion

The combination of NMR and X-ray crystallographic structural data for Pt(II) complexes of closely related iminocarbene and diimine chelating ligands establish beyond doubt the strong *trans* influence of the NHC carbene moiety, compared with the imino group. This is manifested by significant differences in Pt–C bond distances and Pt–H and Pt–C coupling constants in Pt-methyl and Pt–Ph complexes. The carbene ligand also exerts a clear kinetic *trans* effect in the outcome of protonolysis reactions of these Pt(II) species. The observed differences may have significant implications in the further development of Pt-mediated C–H activation reactions and other processes.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center and are available free of charge under the CCDC numbers 770375 (**2a**), 770376 (**2c**), 770377 (**4a**), and 770378 (**4b**).

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