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Synthesis, Characterization, and Protonation Reactions of Ar-BIAN and Ar-BICAT Diimine Platinum Diphenyl Complexes

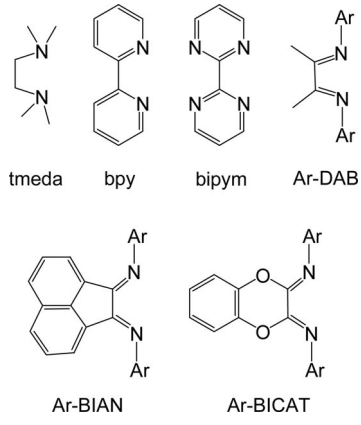
Jerome Parmene,[a] Alexander Krivokapic,[a] and Mats Tilset*[b]

Keywords: Platinum / Hydride ligands / Arene ligands / N ligands / C–H

Pt^{II} diphenyl complexes (N–N)$PtPh_2$ [N–N = diimines Ar–N=C(An)C=N–Ar with Ar = substituted aryl groups] have been prepared and characterized by ^1H, ^{13}C, and ^{195}Pt NMR spectroscopy. The ^{195}Pt NMR spectroscopic data establish the electronic influence exerted by substituents at the backbone of the diimine ligand system to the metal center. When compared to diimines Ar–N=CMe–CMe=N–Ar, the electron-withdrawing ability of the Ar-BIAN ligand and the electron-donating ability of the O,O-heterocyclic Ar-BICAT systems are demonstrated. Trends in ^{195}Pt NMR chemical shifts suggest that electronic tuning of the metal center is better achieved through variations of the diimine backbone substituents rather than variation of the substituents at the N-Aryl groups. Protonation of (N–N)$PtPh_2$ in dichloromethane/acetonitrile at –78 °C furnishes the corresponding Pt^{IV} hydrides (N–N)$PtPh_2H(NCMe)^+$. The Pt^{IV} hydrides liberate benzene with the formation of (N–N)$PtPh(NCMe)^+$ when the temperature is raised. A second protonation and rapid benzene elimination produces the dicationic Pt^{II} species (N–N)$Pt(NCMe)_2^{2+}$ at approximately 50 °C. Protonation of (N–N)$PtPh_2$ in the absence of acetonitrile results in the clean formation of (N–N)$PtPh(\eta^2\text{-}C_6H_6)^+$ at temperatures that depend on the steric hindrance provided by the alkyl substituents at the diimine N-aryl groups. These findings support the notion that the metal is the kinetically preferred site of protonation. The results qualitatively agree with a recent mechanistic study of protonation-induced reactions of (diimine)$PtPh_2$ complexes that bear simple methyl substituents at the diimine backbone. Several compounds have been crystallographically characterized. All complexes have the expected square planar environment at the metal. Modest variations in the metric parameters suggest that the Ar-BICAT system has a weaker *trans* influence than the Ar-BIAN and Ar-DAB systems.

Introduction

Shortly after Garnett and Hodges first reported that acidic solutions of Pt^{II} salts in D_2O were capable of affecting H/D exchange into aromatic hydrocarbons in 1967,[1,2] Shilov extended this reaction to aliphatic hydrocarbons, including methane.[3,4] These early reports of aromatic and aliphatic hydrocarbons C–H activation have been highly influential for the organometallic chemistry community since then. The tremendous industrial and technological implications of effective catalytic C–H activation and functionalization processes have motivated intense research efforts. A wide variety of experimental and theoretical investigations have been published which have helped elucidate the underlying mechanism of what is commonly referred to as "Shilov chemistry"[4–6] and other C–H activating schemes.[7–12] Model systems more amenable to spectroscopic monitoring than the original Pt salts in aqueous media were needed, and the Bercaw group first reported that a tmeda-Pt^{II} complex was capable of activating C–H bonds.[13,14] Variously substituted diimine-Pt^{II} alkyl and aryl complexes have been intensely investigated to gain further insight into the C–H activation mechanisms. In this respect, the most commonly studied diimine-ligand systems (Scheme 1) are those of the DAB (1,4-diaza-1,3-butadiene) type[15–21] and the bpy and bipym systems studied by Puddephatt[22–25] and Periana.[12,26–31]



Scheme 1.

Recent efforts of ours have focused on gaining insight into aromatic C–H activation reactions by looking at a crucial step in the microscopic reverse, i.e. the protonation of Pt^{II} aryl complexes.[15,32] Of particular relevance for this

[a] Department of Chemistry, University of Oslo,
P. O. Box 1033 Blindern, 0315 Oslo, Norway
[b] Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Oslo,
P. O. Box 1033 Blindern, 0315 Oslo, Norway
E-mail: mats.tilset@kjemi.uio.no

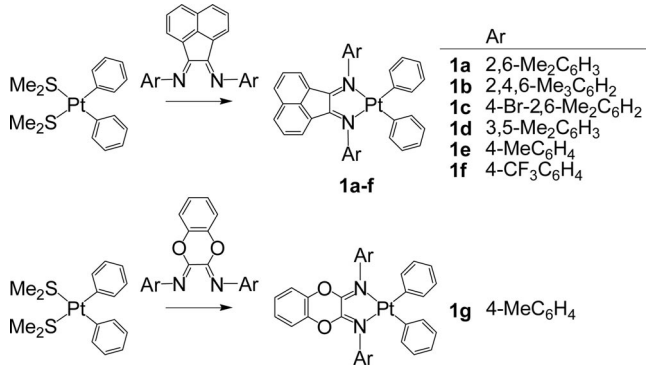
contribution, we have recently[32] conducted detailed kinetic and mechanistic studies of a protonation-induced sequence of reactions that occur from (N–N)$PtPh_2$ with N–N representing the DAB-type ligand Ar–N=CMe-CMe=N–Ar; Ar = 2,6-$Me_2C_6H_3$. Here, low-temperature protonation in CH_2Cl_2/MeCN cleanly yielded the Pt^{IV} hydride (N–N)-$PtPh_2H(NCMe)^+$ which upon heating eliminated benzene to furnish benzene and (N–N)$PtPh(NCMe)^+$ in a reaction for which initial MeCN dissociation was rate limiting. On the other hand, protonation of (N–N)$PtPh_2$ in CH_2Cl_2 in the absence of acetonitrile cleanly furnished (N–N)$PtPh(\eta^2$-$C_6H_6)^+$ which, upon addition of acetonitrile, underwent substitution of benzene by acetonitrile in an associative process. In order to expand the scope of our studies, we have now turned our attention to non-DAB diimine ligands.

The closely related Ar-BIAN [Ar-BIAN = bis(arylimino)-acenaphthene, see Scheme 1] ligand system, pioneered by the Elsevier group,[33–40] has been explored with respect to many catalytic processes, including olefin oligomerization and polymerization[41–45] and olefin/CO copolymerization.[46] The Ar-BIAN system is a highly stable, rigid bidentate spectator ligand with interesting electronic properties.[47,48] Elsevier and co-workers suggested that Ar-BIAN ligands may act as stronger σ-donors toward the metal when compared to bpy, and also proposed that the rigid Ar-BIAN ligands are rather comparable to open chain R-DAB analogues in electronic properties, which would be the case if the diimine system in the Ar-BIAN ligands is electronically isolated from and has no conjugation with the naphthalene backbone.[35] The capacity of this ligand type to support many oxidation states has been amply demonstrated; for example, Pt Ar-BIAN complexes have been reported in oxidation states ranging from Pt^0[35] via Pt^{II}[45] to Pt^{IV}.[38] Ar-BIAN Pt complexes have found uses in catalytic hydrosilylation of styrene[49] and some complexes have interesting photophysical properties.[50–52] Surprisingly to us, to the best of our knowledge no reports have appeared on the use of Ar-BIAN ligand systems in studies of reactions of relevance to C–H bond activation.

In this contribution, we present the synthesis and spectroscopic and structural characterization of a series of new (diimine)Pt^{II} complexes where the diimine is Ar-BIAN with Ar = 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, 4-Br-2,6-$Me_3C_6H_2$, 3,5-$Me_2C_6H_3$, 4-MeC_6H_4, and 4-$CF_3C_6H_4$. In addition, we report the novel bis(arylimino) catechol-based ligand system Ar-BICAT, see Scheme 1. A qualitative description of the protonation reactions of the corresponding (diimine)-$PtPh_2$ complexes is also included and discussed in view of existing knowledge of related reactions.

Results and Discussion

Synthesis and Characterization of Metal Complexes: The air- and moisture-stable platinum complexes **1a**–**g** (Scheme 2) were prepared in good yields by stirring a solution of $(Me_2S)_2PtPh_2$ and the diimine ligand at ambient temperature by adaptation of published procedures.[15] The complexes were characterized by ^1H, ^{13}C, and ^{195}Pt NMR spectroscopy as well as elemental analysis. Complexes **1a**–**f** showed ^{195}Pt signals with chemical shifts in the range δ –2770 to –2851; the chemical shift of **1g** appears at δ –3384 ppm. Within the series **1a**–**1c**, which are 2,6-dimethyl-substituted at Ar and where the substituents within the series change only at the *para* position of Ar, the ^{195}Pt chemical shift increases (to less negative values) with increasing Hammett σ_p substituent parameters.[53] Similarly, within the series **1d**–**1f**, which are 2,6-unsubstituted and where changes occur at the *meta* and *para* positions, there is a trend of increasing chemical shifts with increasing $\Sigma(\sigma_m + \sigma_p)$. Thus, there appears to be a normal substituent electronic effect – higher δ values with increasing electron-withdrawing power – of the Ar substituents on the ^{195}Pt NMR chemical shifts in compounds that may be readily compared. Furthermore, the Ar-BIAN and Ar-BICAT ligand systems appear to have a significant effect on the Pt electronic properties, as seen in a comparison of ^{195}Pt chemical shifts for **1a**–**1g** with those for the corresponding Ar-DAB complexes.[15] The ^{195}Pt NMR signals for the Ar-BIAN series occur at approximately 280 ppm higher (less negative) chemical shift values compared to those of the corresponding compounds in the DAB series. This suggests that the Ar-BIAN ligands are more electron withdrawing than the similarly substituted Ar-DAB ligands, which may be attributed to a greater π acceptor capacity for the extended π systems of the BIAN ligands.[54] On the other hand, the ^{195}Pt NMR signal of the Ar-BICAT ligated complex **1g** is seen at a more than 500 ppm lower (more negative) chemical shift value than that of the corresponding Ar-BIAN complex and thence is located at even more negative chemical shifts, by about 300 ppm, than the Ar-DAB complexes. The catecholate bridge at the backbone therefore appears to exert a considerable electron donating power towards the metal, transmitted through the diimine ligand core. In summary, approximate chemical shifts for the Pt^{II} diphenyl complexes are –2800 for BIAN, –3050 for DAB, and –3380 for BICAT ligand systems.



Scheme 2.

Further support for the apparent electronic effect provided by the diimine backbone structure, as inferred from the ^{195}Pt NMR chemical shifts, were obtained from infrared ν(CO) spectra of (diimine)$PtPh(CO)^+$ complexes which

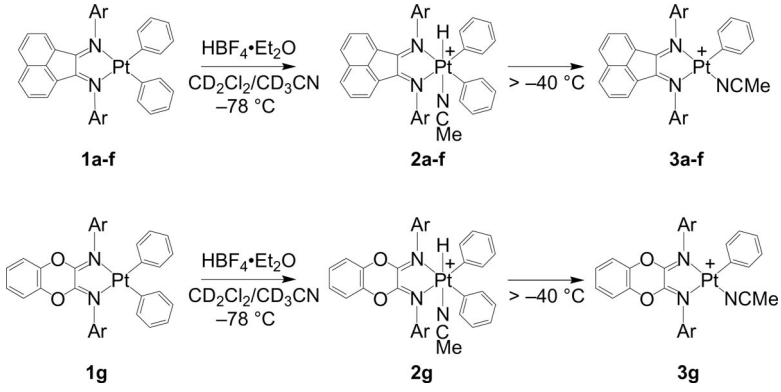
were synthesized by protonolysis of the corresponding (diimine)$PtPh_2$ complexes in trifluoroethanol under CO. This is an adaptation of a published procedure for generation of (Ar-DAB)$PtMe(CO)^+$ complexes (see also Experimental section).[20] The IR ν(CO) spectra of the Ar-BIAN, Ar-DAB, and Ar-BICAT complexes with Ar = 4-MeC_6H_4 exhibited CO stretching bands at 2115.6, 2113.8, and 2113.2 cm^{-1}, respectively. Whereas the differences are small, these data do indeed support the notion that the electronic effect of the Pt center is altered by tuning of the diimine backbone structure. The combined IR and ^{195}Pt NMR spectroscopic data allow us to confidently assert that the BICAT system is a better electron donor than the DAB system, whereas the BIAN system is the poorest donor of the three. We note that the published ν(CO) data for (ArN=CH–CH=NAr)$PtMe(CO)^+$ are approximately 4–5 cm^{-1} higher than those for the corresponding (ArN=CMe-CMe = NAr)$PtMe(CO)^+$ complexes.[20]

Low-Temperature Protonation of (N–N)$PtPh_2$ in the Presence of Acetonitrile: In situ protonation of **1a**–**g** was performed in NMR tubes at –78 °C with HBF_4·Et_2O (see Exp. Sect.). Protonation in the presence of [D_3]acetonitrile in [D_2]dichloromethane led to the immediate formation of the hexacoordinate Pt^{IV} hydrides (N–N)$PtPh_2H(NCCD_3)^+$ (**2a**–**g**) (Scheme 3). The ^1H NMR spectra of these hexacoordinate Pt^{IV} hydrides exhibit characteristic Pt–H singlets at $\delta \approx -21$ with the expected ^{195}Pt satellites, $^1J(^{195}Pt\text{-}H)$ of approximately 1600 Hz. The ^1H NMR spectra show that the two halves of the diimine ligands are symmetry equivalent. We infer that the hydride and MeCN ligands occupy the two apical, mutually *trans*, coordination sites. For the Ar-BIAN complexes, the signals that arise from *ortho* and *meta* Ar–H and Ar–Me groups (when sufficiently resolved) have split into two sets of signals of equal intensity. Such duplication is not seen for any other signals. This phenomenon is most likely due to restricted rotation around the N–C(aryl) bond, where the rotational barrier is imposed by the nearby *ortho* protons at the BIAN skeleton. This renders the aryl hydrogens or methyl groups located at the "top" (hydride side, see Scheme 3) and "bottom" (MeCN side) of the square plane chemically non-equivalent. Such a hindrance to rotation was also observed with Ar-DAB complexes.[15] In the case of the Ar-BICAT complex **2g**, such "top-bottom" non-equivalence was not observed, and the ^1H NMR signals appeared more broadened – possibly indicating somewhat slowed rotation at –78 °C. This suggest less severe steric repulsions between the *N*-aryl methyl protons and the catechol backbone.

As is commonly seen, Pt^{IV} hydrides require stabilization[25] by an additional axial ligand, in our case, acetonitrile. When the NMR samples were heated, **2a**–**g** gradually eliminated benzene starting at approximately –40 °C to furnish the corresponding Pt^{II} acetonitrile complexes **3a**–**g** (Scheme 3), for which the spectroscopic data reveal that the "top-bottom" symmetry has been restored. These complexes have been independently synthesized (vide infra).

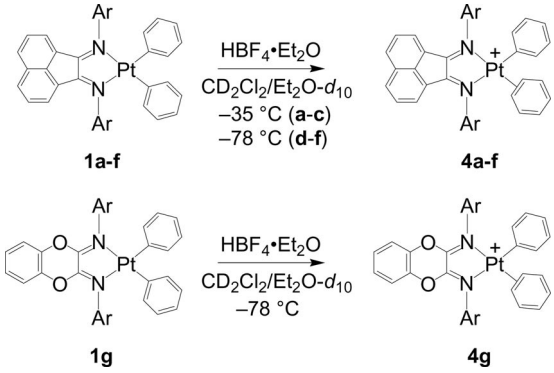
Similar behavior involving protonation at the metal and subsequent hydrocarbon elimination has been reported for (Ar-DAB)$PtMe_2$[16–18,55] and (Ar-DAB)$PtPh_2$[15,32] complexes. The formation of **2a**–**g** is fully consistent with protonation at Pt to give a coordinately unsaturated, five-coordinate Pt^{IV} hydride intermediate that is trapped by acetonitrile, in agreement with mechanistic studies on the mentioned diimine-Pt dimethyl and diphenyl complexes.[16,32]

Low-Temperature Protonation of (N–N)$PtPh_2$ in the Absence of Acetonitrile: Protonation of **1a**–**g** with HBF_4·Et_2O in [D_2]dichloromethane in the presence of [D_{10}]Et_2O (see Experimental section) leads to the quantitative formation of the Pt^{II} π-benzene complexes (N–N)$Pt(C_6H_5)(\eta^2\text{-}C_6H_6)^+$ (**4a**–**g**, Scheme 4) at sub-ambient temperatures. The ^1H NMR spectra of these complexes exhibit a characteristic singlet arising from the η^2-C_6H_6 ligand at approximately δ = 7.1 (**4a**–**f**) or 6.9 (**4g**); the lower chemical shift value of the latter may again reflect the better donor capacity of the BICAT system when compared to BIAN. These signals exhibit a somewhat broadened base, which sometimes can be resolved to reveal broadened ^{195}Pt satellites where the broadening is presumed to arise from spin relaxation caused by chemical shift anisotropy.[56–58] Compounds **1a**–**c** underwent facile protonation at –30 °C, in the sense that the reaction was complete by the time that an NMR spectrum could be recorded. At this temperature the products **4a**–**c** are only partially stable, as slow liberation of benzene is seen. At temperatures of –50 °C and below, the protonations of the Ar-BIAN complexes **1a**–**c** (which are 2,6-Me_2 substituted at Ar) were surprisingly slow (30 min or more



Scheme 3.

was required for complete reaction), compared to the corresponding Ar-DAB complexes (complete reaction by the time NMR spectra could be recorded).[15] The slower protonation of these Ar-BIAN complexes than of analogously substituted Ar-DAB complexes with comparable steric requirements may be a result of the poorer electron donating power of the Ar-BIAN system, as inferred from IR and ^{195}Pt NMR spectroscopic data in a previous paragraph. By contrast, compounds **1d**–**f** (2,6-unsubstituted at Ar) were immediately protonated even at –70 °C, and the corresponding benzene complexes **4d**–**f** started to slowly lose benzene already at –50 °C. The Pt-containing products of these reactions have not been identified. The differences in reactivity between the **a**–**c** and **d**–**f** series presumably arise from the steric influence of the substituents at Ar in the Ar-BIAN ligands. Since the Ar groups are expected to be more or less perpendicularly oriented with respect to the Pt coordination plane, the 2,6-Me_2 substituents will cause a congestion of the space immediately above and below the coordination plane. Thus, protonation by the external acid will be inhibited in these complexes. On the other hand, the η^2-benzene complexes will be stabilized by the 2,6-dimethyl groups because the displacement of benzene (and other hydrocarbons) from these and related diimine-Pt complexes has been demonstrated to be associative reactions.[32,59,60]



Scheme 4.

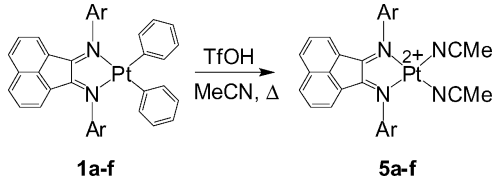
It has been demonstrated that the kinetically preferred site of protonation is the Pt center for (Ar-DAB)$PtMe_2$ complexes.[17,18] We have recently presented experimental evidence that this is also the case for (Ar-DAB)$PtPh_2$ analogues,[32] a scenario that had already been predicted by DFT calculations.[61] The distinct difference in protonation rates between **1a**–**c** and **1d**–**f** may indirectly support the notion of a metal-centered protonation followed by a rapid C(phenyl)/H reductive coupling to furnish the π-benzene ligand: A metal-based protonation in which the acid approaches from above or below the coordination plane should be considerably inhibited by the 2,6-Me_2-substituted aryl groups. On the other hand, a ligand-centered protonation might be less dependent on the nature of these substituents, especially if the putative approach of the acid towards the phenyl ligand occurs more or less in the coordination plane.

In the case of the BICAT complex **1g**, protonation to furnish **4g** is immediate at –78 °C. Monitoring of this product showed no degradation after more than 1 h at that temperature. Decomposition and liberation of benzene was observed from approximately –60 °C, indicating that the BICAT ligand appears to activate the neutral complex toward protonation (as might be expected for a better donor ligand), and the π-benzene complex toward benzene loss, when compared to the BIAN systems.

Protonation of 1a–g in the Presence of Acetonitrile at Ambient Temperature: Treatment of the (N–N)$PtPh_2$ complexes **1a**–**g** with triflic acid (TfOH) or HBF_4·Et_2O in acetonitrile at ambient temperature led to rapid conversion to the corresponding monophenyl solvento cations (N–N)PtPh(NCMe)$^+$ (**3a**–**g**, Scheme 3). The BF_4^- salts of **3a**–**g** were isolated and characterized spectroscopically as well as by elemental analysis and, in some cases, by X-ray diffraction (vide infra). The C_{2v} symmetry of the precursors **1a**–**g** was clearly broken in **3a**–**g** as evidenced by the two sets of signals arising from the two halves of the diimine ligands. The coordinated acetonitrile ligands in the isolated compounds **3a**–**g** were seen as NMR singlets at δ = 2.06–2.21 ppm; for complexes **3a** and **3g**, a $^4J(^{195}Pt\text{-}H)$ coupling of 10.3 and 13.9 Hz respectively were seen in this signal. Species **3** are presumed to form by protonation at Pt with concomitant elimination of benzene, as reported for Ar-DAB analogues.[15,32]

Quantitative production of benzene was seen when the protonation reactions were monitored by NMR spectroscopy (done for **1a**, **e**, and **g**). Complexes **3** were also generated by addition of acetonitrile to solutions of preformed π-benzene complexes (N–N)Pt(C_6H_5)(π-C_6H_6)$^+$ **4** (done for **4a**, **e**, and **g**). Substitution of benzene by acetonitrile occurred within approximately 15 min to an extent of approximately 10% already at –70 °C for **4a** and **4e**, and even at –78 °C for **4g**. These are temperatures at which the π-benzene species are stable in the absence of acetonitrile, clearly consistent with the notion that the substitution of benzene by acetonitrile occurs associatively.

Protonation of 1a–f in the Presence of Acetonitrile at Elevated Temperatures: Treatment of the (Ar-BIAN)$PtPh_2$ complexes **1a**–**f** with triflic acid (TfOH) in acetonitrile at 50 °C overnight led to clean conversion to the corresponding dicationic Pt^{II} species (Ar-BIAN)Pt$(NCMe)_2^{2+}$ (**5a–f**, Scheme 5) which were characterized spectroscopically and, in part, by elemental analysis. The triflate salt of **5b** was in addition characterized by X-ray crystallography (vide infra).



Scheme 5.

Double protonation of diimine Pt dimethyl complexes to furnish related dicationic species has been reported previously to occur when (Ar-DAB)$PtMe_2$ complexes are treated with TfOH or BF_3 in trifluoroethanol.[21] Complex **5b** appears to be the first structurally characterized (diimine)$Pt(NCMe)_2^{2+}$ complex. We recently have reported that an analogous double protonation of an (Ar-DAB)-$PtPh_2$ complex occurs with TfOH, but not with HBF_4, in MeCN at temperatures above ambient.

The C_{2v} symmetry of the precursor **1a**–**f** was clearly preserved as evidenced by the observation of one set of signals arising for the two halves of the diimine ligands. The coordinated acetonitrile ligands in the isolated compounds **5a**–**b** and **5d**–**e** appeared as singlets at δ = 2.24–2.37 with no discernible $^4J(^{195}Pt\text{-}H)$ couplings. Compounds **5c** and **5f** were characterized in situ due to decomposition during attempted purification. We surmise that the Pt^{II} species **5** are produced by two successive protonation/benzene elimination sequences but have made no attempts at investigating the finer details of the underlying reaction mechanism.

X-ray Crystal Structures: Crystals of **1a**, **1b**, **1e**, **1g**, **3a**, **3b**, **5a**, and **5b** were subjected to structure determinations by X-ray crystallography. Selected bond lengths and angles are summarized in Table 1. Figure 1 shows ORTEP drawings of all solid-state structures.

Certain key features are common to all structurally characterized compounds. They all have the square-planar environment that is expected around Pt^{II}. The deviations from the least-squares planes defined by the central Pt atom and the four Pt-bonded atoms are in the range of 0.0–0.057 Å for Pt and 0.001–0.052 Å for the attached C or N atoms (further details on the metric parameters can be found in the respective crystallographic cif files, see Experimental part). The sum of the four cis L–Pt–L′ angles around platinum is 360 ± 0.3° for all compounds. The acenaphthene backbone lies in the coordination plane defined by Pt, N1 and N2. The backbone plane of the BICAT ligand as defined by the catechol ring is only slightly bent from the coordination plane by a 7.6° angle. The rather slight deviation from coplanarity suggests that electronic communication between the backbone skeleton and the diimine-metal structure may occur through the ligand π system.

Some interesting differences may be found, to be discussed in the following paragraph, when comparisons are made between neutral, monocationic, and dicationic species on one side, and between BIAN, BICAT, and DAB ligated systems of same charge on the other.

The Pt–N(diimine) bond lengths average 2.120 Å for the three neutral Ar-BIAN complexes **1a**, **1b**, and **1e**. The corresponding chelate bite angles average 77.7°. In the

Table 1. Selected bond lengths and angles for **1a**, **1b**, **1e**, **1g**, **3a**, **3b**, and **5b**.

Compound	**1a**	**1b**	**1e**	**1g**	**3a**	**3b**	**5b**
Bond lengths							
Pt1 N1	2.115(2)	2.122(2)	2.1180(19)	2.1427(17)	2.014(3)	2.014(3)	2.027(5)
Pt1 N2	2.138(2)	2.107(2)	–	2.1492(17)	2.111(3)	2.115(3)	1.997(5)
Pt1 N3	–	–	–	–	1.969(3)	1.965(3)	1.997(7)
Pt1 N4	–	–	–	–	–	–	1.983(6)
Pt1 C31	2.002(3)	1.994(3)	2.001(2)	1.991 (2)	2.010(3)	2.011(4)	–
Pt1 C37	2.020(3)	1.998(3)	–	1.988 (2)	–	–	–
N1 C1	1.287(4)	1.282(3)	1.290(3)	1.280(3)	1.300(4)	1.301(5)	1.308(4)
N2 C2	1.291(4)	1.288(3)	–	1.279(3)	1.286(4)	1.286(5)	1.281(4)
C1 C2	1.489(4)	1.487(4)	–	1.478(3)	1.488(4)	1.490(5)	1.494(4)
C1 C1	–	–	1.482(4)	–	–	–	–
Bond angles							
N1 Pt1 N2	77.86(10)	77.62(8)	77.68(11)	76.75(7)	79.76(11)	80.08(12)	80.76(19)
N1 Pt1 C31	93.04(11)	97.13(9)	97.40(9)	97.85(7)	97.05(12)	97.89(14)	–
N2 Pt1 C37	95.54(11)	95.73(9)	–	97.93(7)	–	–	–
C31 Pt1 C37	93.50(12)	89.52(10)	87.53(13)	87.38(8)	–	–	–
Pt1 N1 C1	114.3(2)	113.89(17)	114.06(15)	114.12(14)	114.5(2)	114.1(3)	113.3(4)
Pt1 N2 C2	113.0(2)	114.47(18)	–	113.75(13)	112.3(2)	112.1(2)	114.3(4)
C1 N1 C22	118.5(2)	118.8(2)	–	120.30(18)	118.5(3)	117.0(3)	122.2(5)
C2 N2 C13	118.9(2)	120.2(2)	–	120.17(17)	121.7(3)	122.5(3)	118.2(5)
C13 N1 C1	–	–	118.46(19)	–	–	–	–
N1 Pt1 N3	–	–	–	–	172.51(12)	171.33(13)	174.6(2)
N2 Pt1 N3	–	–	–	–	93.11(12)	91.81(13)	95.3(2)
N3 Pt1 C31	–	–	–	–	89.93(13)	90.36(14)	–
Torsion angles							
C1 N1 C22 C27	87.5(4)	104.1(3)	–	130.8(3)	82.3(5)	100.5(4)	75.7(8)
C2 N2 C13 C18	–84.3(4)	–84.4(3)	–	–135.7(3)	–93.9(5)	–105.0(4)	–80.0(9)
C1 N1 C13 C18	–	–	63.8(3)	–	–	–	–
C36 C31 Pt1 N1	71.5(2)	120.9(2)	58.7(2)	90.8(2)	52.9(3)	127.2(3)	–
C42 C37 Pt1 N2	–53.4(3)	–72.1(3)	–	–95.2(2)	–	–	–

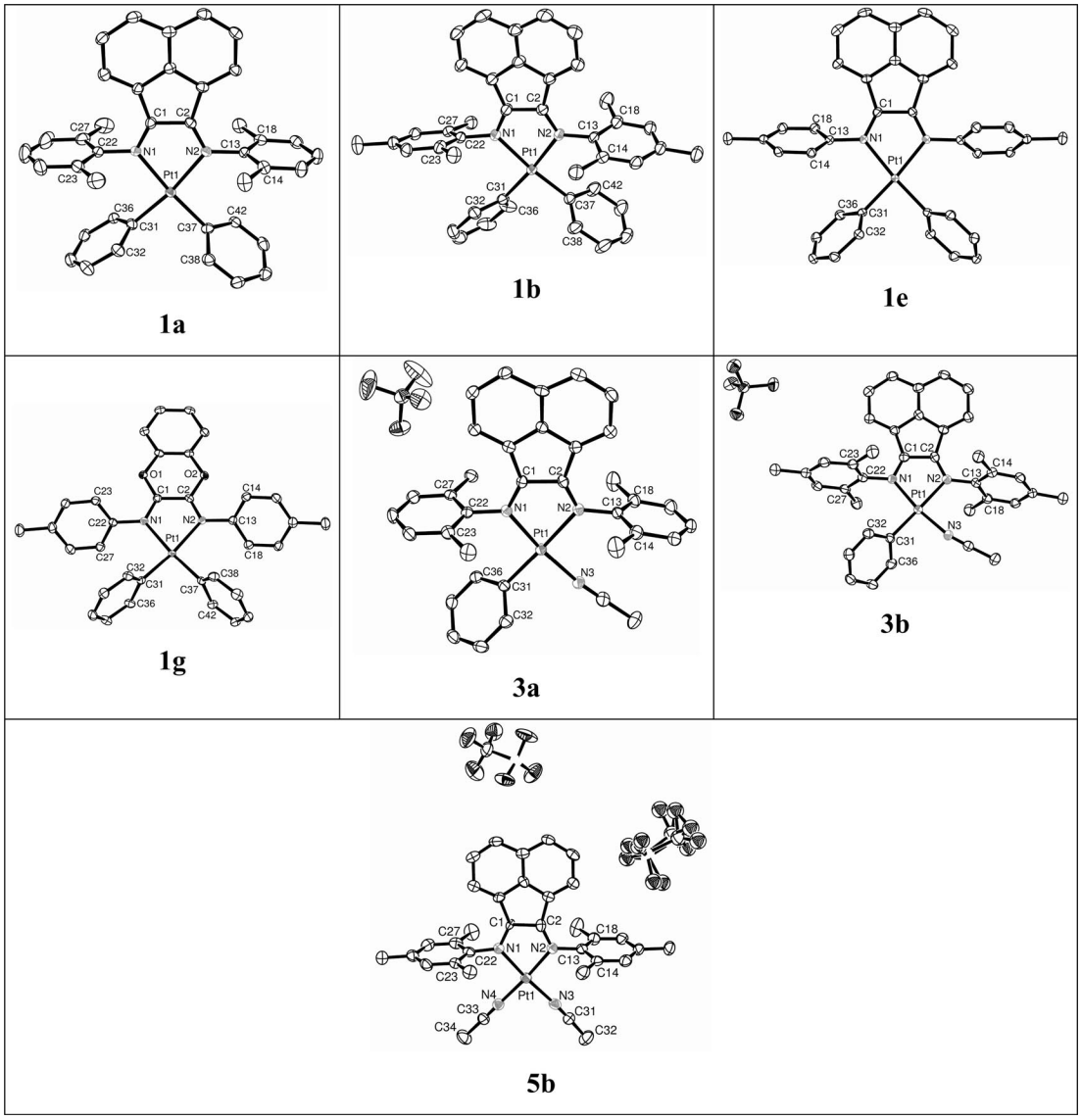


Figure 1. ORTEP drawings of (N–N)Pt^{II} complexes **1a**, **1b**, **1e**, **1g**, **3a**–**b**, and **5b**. 50% probability ellipsoids are shown (hydrogen atoms are removed for clarity. In **5b** there are two molecules in the asymmetric unit, but only one is shown for clarity).

monocationic complexes **3a** and **3b** the Pt–N(diimine) distances average 2.064 Å whereas the bite angles are 79.2°. Finally, in the dicationic complex **5b**, the average Pt–N(diimine) distance is 2.009 Å whereas the bite angle is 80.8°. Thus, Pt–N(diimine) bonds are, as might be expected, shortened when the positive charge increases, and this bond shortening has the consequence of slightly increasing the ligand bite angle. The replacement of a phenyl ligand by MeCN might also contribute to the bite angle increase. For the previously reported[15] (Ar-DAB)$PtPh_2$ and (Ar-DAB)$PtPh(NCMe)^+$ systems, a similar trend towards Pt–N(diimine) bond shortening (from 2.103 Å to 2.053 Å) and chelate bite angle opening (from 75.8 to 77.7°) is also seen when the neutral and charged systems are compared. The average Pt–C(phenyl) bond lengths in neutral Ar-BIAN complexes **1a**, **1b**, and **1e** (2.003 Å) are slightly shorter than in the two cationic counterparts **3a** and **3b** (2.011 Å); a modest change in the same direction was seen in the Ar-DAB systems.[15] When the three ligand systems Ar-BIAN, Ar-BICAT, and Ar-DAB are compared for (diimine)$PtPh_2$ compounds, it is noteworthy that the Pt–N(diimine) bond lengths decrease from Ar-BICAT (2.146) Å via Ar-BIAN (2.120 Å) to Ar-DAB (2.103 Å). The average Pt–C(phenyl) bond lengths show less variation but tend to decrease in the opposite order, i.e. from Ar-DAB (2.011 Å) via Ar-BIAN (2.003 Å) to Ar-BICAT (1.990 Å). Although variations in metric parameters are modest, the data may suggest that the Ar-BICAT system has a somewhat weaker *trans* influence than the Ar-BIAN and Ar-DAB systems. There appears to be no significant differences in the C=N and C–C bond lengths of the ligand backbone when the neutral complexes of Ar-BIAN, Ar-DAB, and Ar-BICAT ligands are compared. In the neutral Ar-BIAN complexes **1a**–**1e**, the N–Pt–N bite an-

Table 2. Crystallographic data for **1a**, **1b**, **1e**, **1g**, **3a**, **3b**, and **5b**.

Compound	**1a**	**1b**	**1e**	**1g**	**3a**	**3b**	**5b**
Formula	$C_{40}H_{34}N_2Pt$	$C_{42}H_{38}N_2Pt$	$C_{38}H_{30}N_2Pt\cdot 2CH_2Cl_2$	$C_{34}H_{28}N_2O_2Pt\cdot 1.5CH_2Cl_2$	$C_{36}H_{32}N_3PtBF_4\cdot 2CH_2Cl_2$	$C_{38}H_{36}N_3PtBF_4\cdot CH_2Cl_2$	$C_{34}H_{28}N_4Pt(CF_3SO_3)_2$
Formula weight	737.8	765.87	879.62	819.10	958.43	901.55	985.84
Color	green	black	black	red	red	red	red
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$C2/c$	$C2/c$	$P\bar{1}$	$P2_1/c$	$C2/c$
a [Å]	7.7564(15)	10.9971(6)	16.250(6)	26.9288(10)	12.470(4)	16.7874(18)	45.443(7)
b [Å]	9.6428(18)	24.7328(15)	23.643(9)	16.3437(6)	13.713(4)	13.0774(14)	15.064(2)
c [Å]	21.685(4)	12.5147(7)	9.052(3)	18.4914(13)	13.834(4)	17.1024(18)	23.998(4)
α	85.280(3)	90	90	90	64.476(3)	90	90
β	79.733(3)	95.378(2)	93.499(4)	128.35	88.788(3)	92.5320(10)	110.685(2)
γ	87.308(3)	90	90	90	67.244(3)	90	90
V [Å^3]	1589.7(5)	3388.9(3)	3471(2)	6382.7(6)	1938.2(10)	3750.9(7)	15369(4)
Z	2	4	4	8	2	4	16
T [K]	105	105	105	103	103	105	105
F(000)	732	1528	1736	3224	944	1784	7742
Radiation				Mo-K_α			
λ				0.71073 Å			
θ range [°]	1.9 to 28.4	1.7 to 28.3	1.52 to 27.56	1.57 to 28.74	1.66 to 28.60	1.96 to 27.13	1.60 to 27.12
Reflection measured	14164	27077	14136	27916	17664	30983	64440
Unique reflections	7260	8357	3985	7718	8986	8269	16927
Number of data/restraint/param.	6484/0/388	6140/0/406	3595/0/214	6291/0/395	7672/0/460	6175/0/451	13564/472/961
Goodness of fit, F	1.0775	1.1030	1.0330	1.1257	1.1055	1.0015	1.221
R_1, w R_2 [I>3 σ (I)]	0.027, 0.03	0.020, 0.022	0.0208, 0.0225	0.0162, 0.0169	0.0286, 0.0296	0.0263, 0.0289	0.0545*, 0.1481*
Largest diff. peak [eÅ^{-3}]	1.47, –1.26	1.33, –0.95	1.06, –0.77	0.80, –0.50	1.07, –0.97	2.07, –0.88	5.956, –1.177

* Refined on F^2. Values are for R_1, w R_2 [I>2 σ (I)].

gle is rather constant at 77.62–77.86° but undergoes a slight decrease to 76.75° in Ar-BICAT complex **1g** and a further decrease to 75.47–75.88° in the previously published[15] Ar-DAB complexes.

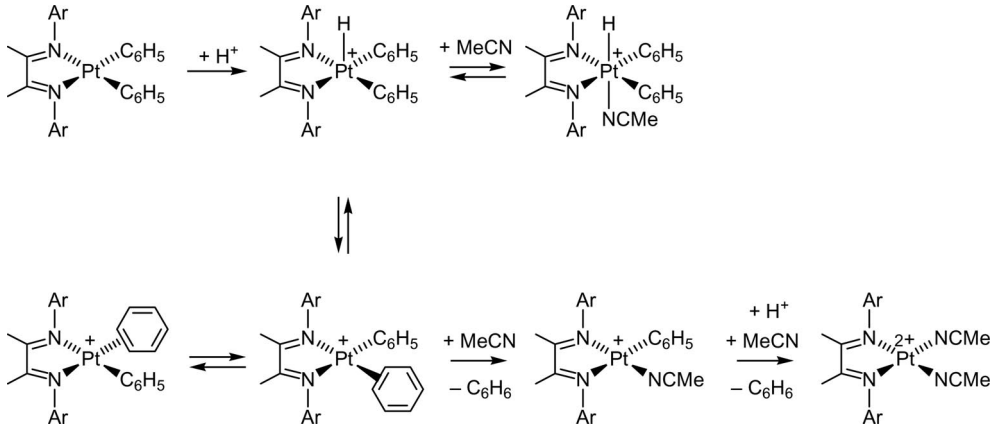
In the cationic compounds **3a** and **3b**, the Pt–N(acetonitrile) distances (1.967 Å) are shorter than the average Pt–N(diimine) distances (2.064 Å) by approximately 0.1 Å. The Pt–N1 bond lengths *trans* to MeCN [2.014(3) Å] are significantly shorter than the Pt–N2 bond lengths *trans* to phenyl (2.113 Å) by approximately 0.1 Å, clearly as a result of the greater *trans* influence of the phenyl compared to the acetonitrile ligand. In the dicationic complex **5b**, the average Pt–N(acetonitrile) distance of 1.997 Å is slightly longer than in the monocationic species **3a** and **3b**. It remains to be seen whether these changes in bond lengths and angles correlate with relative chemical reactivities that are under investigation in our group.

The phenyl ligands and the *N*-aryl groups of the diimines are twisted away from planarity with the Pt coordination plane, as inferred from the torsion angles in Table 2. The aryl groups are twisted out of the coordination plane by 83° and 77–82°, respectively, in complexes **1a** and **1b** which are 2,6-dimethyl-substituted at the aryl. The corresponding twist angles are 64.5° and by 51–54° in complexes **1e** and **1g**, respectively, which are not 2,6-dimethyl-substituted. The torsion angles of the phenyl groups with respect to the coordination plane span 59–78° in compounds **1a** and **1b** and 61–86° in **1e** and **1g**. These differences reflect the increased steric demands of the 2,6-dimethyl-substituted systems and appear to be a common feature for *N*,*N*′-diaryl-substituted (N–N)PtX_2 complexes where similar trends in dihedral angles have been reported.[15,36,44,45,54,60,62–67] This emphasizes the steric hindrance imposed by the 2,6-dimethyl-substituted *N*-aryl groups: The perpendicular orientation of these *N*-aryl groups with respect to the coordination plane causes the methyl groups to sterically block the access to Pt from above and below the coordination plane. This has a pronounced effect on the qualitative protonation rates and on the stabilities of the Pt^{II} π-benzene complexes, as discussed earlier.

Mechanistic Issues: Scheme 6 summarizes the current view of the mechanisms that operate for protonation-induced benzene eliminations from (diimine)$PtPh_2$ complexes.[32]

We have reported that (Ar-DAB)$PtMe_2$ complexes undergo protonation with the metal center as the kinetically preferred site of attack.[18] Recent DFT calculations suggest that this also holds true for protonation of (Ar-DAB)$PtPh_2$ complexes,[61] a conclusion that has been supported by recent kinetic studies in our group.[32] Similarly, the formation of Pt^{IV} hydrides (Ar-BIAN)-$PtPh_2H(NCMe)^+$ and (Ar-BICAT)$Ph_2H(NCMe)^+$ by protonation of square-planar Pt^{II} precursors is in agreement with a metal-centered protonation.

The π-benzene complexes **4a**–**c**, sterically shielded at Pt by the 2,6-Me_2 substituents at the *N*-aryl groups, are formed at approximately –30 °C by protonation with HBF_4 in dichloromethane. Formation of the corresponding complexes **4d**–**f**, sterically less shielded, occurs at much lower temperatures, approximately –60 °C. The consequential difference in protonation rates between **1a**–**c** and **1d**–**f** supports the notion of a metal-centered protonation followed by a rapid phenyl-C/H reductive coupling to furnish the π-benzene ligand: A metal-based protonation in which the



Scheme 6.

acid approaches from above or below the coordination plane should be considerably inhibited by the 2,6-Me_2-substituted aryl groups, leading to a great difference between **1a**–**c** and **1d**–**f**. By contrast, a ligand-centered protonation might be less dependent on the nature of these substituents, especially if the approach of the acid towards the phenyl ligand occurs more or less in the coordination plane: The expected difference between **1a**–**c** and **1d**–**f** will be less striking.

In our recent study of the protonation of (Ar-DAB)$PtPh_2$ (Ar = 2,6-$Me_2C_6H_4$),[32] one issue that was discussed was whether the protonation of the neutral Pt^{II} complex in the presence of acetonitrile to give (Ar-DAB)$PtPh_2H(NCMe)^+$ was a stepwise process, involving initial protonation followed by rapid capture of the putative five-coordinate intermediate (Ar-DAB)$PtPh_2H^+$ by acetonitrile, or a concerted process involving simultaneous protonation and acetonitrile coordination. The same question is relevant here. We note that the series of complexes **1a**–**c** are protonated rather slowly in dichloromethane, requiring temperatures as high as approximately –30 °C for protonation to occur and furnish the π-benzene complexes **4a**–**c** at reasonable rates. By contrast, protonation of **1a**–**c** in dichloromethane containing acetonitrile proceeds rapidly even at –70 °C to produce **2a**–**c**. The considerable difference in protonation rates under these different conditions is certainly consistent with an acetonitrile-assisted protonation event, i.e. a scenario that bypasses the five-coordinate species as discrete intermediates. Alternative explanations should however be considered, in particular because solvent medium effects may strongly influence the kinetics and thermodynamics of the proton transfer.

The π-benzene complex **4a** appears to be thermally more robust in the absence of acetonitrile than the Pt^{IV} hydridodiphenyl complex **3a** is in the presence of acetonitrile. Whereas **4a** decomposes by benzene elimination at approximately –30 °C, **3a** undergoes benzene elimination at –50 °C without observation of the more robust **4a** as an intermediate. The addition of acetonitrile to a solution of **4a** leads to benzene substitution already at –70 °C by what is believed to be an associative process.[15,19,32,60,61] It is likely that the π-benzene complex is an intermediate in the elimination of benzene from **3a**, as discussed in our recent contribution.[32]

Conclusions

A series of new diimine platinum diphenyl complexes has been synthesized and subjected to protonation reactions that are of relevance for our on-going investigation of mechanistic aspects of Pt-mediated C–H activation reactions, which in the past has focused on Ar-DAB supporting ligands. Thus, the well-known Ar-BIAN diimine structures have been used, and a novel Ar-BICAT diimine ligand has been synthesized. Spectroscopic features of the Ar-BIAN, Ar-BICAT, and Ar-DAB systems have been compared and suggest that the donor capacity of the ligands decrease in the order Ar-BICAT > Ar-DAB > Ar-BIAN. Furthermore, crystallographic data suggest that the *trans* influence of the ligands increases in the order Ar-BICAT > Ar-BIAN > Ar-DAB. (N–N)$PtPh_2$ complexes based on the Ar-BIAN and Ar-BICAT ligands were subjected to protonation reactions, as an extension of recently reported work on the kinetics of an (Ar-DAB)$PtPh_2$ complex.[32] Very approximate assessments of the rates of protonation and the ensuing reactions lead to some tentative conclusions regarding the influence of the ligands on the reactivity patterns. First of all, the behavior of all the systems were quite similar in that the entire sequence of reactions proceeded in two well-defined protonation/benzene elimination steps, nicely separated in onset temperatures, independently of the diimine structure. Spectroscopic data suggest that variations of the diimine backbone, i.e. BIAN vs. DAB vs. BICAT, constitute a more powerful way to tune the electronic properties of the ligand system than variations of the *N*-aryl substituents within a given backbone series. However, regardless of the backbone structure, the rate of protonation appears to be primarily controlled by steric factors, best modulated by the presence or absence of *ortho* substituents at the *N*-aryl groups. More details on the influence of the diimine backbone on related processes will be addressed in forthcoming reports.

Experimental Section

General Considerations: Deuteriated solvents were used as received without further drying (CD_2Cl_2, $[D_{10}]Et_2O$, CD_3CN). NMR spectra were recorded with Bruker DPX200, DPX300, and DRX500 instruments. For low-temperature NMR spectroscopic experiments, the temperature calibration was done using a thermocouple situated inside a thin glass tube that was inserted into an NMR tube with methanol. ^1H NMR chemical shifts (δ) are reported in ppm relative to TMS using the residual proton resonances of the solvent as a reference (δ = 1.94 in CD_3CN, 5.32 in CD_2Cl_2). In signal assignments, the terms Ar$H_{o,m,p}$ denotes protons in the *o*, *m*, *p* positions of the diimine *N*-aryl substituents (relative to N-attached carbon), Ph$H_{o,m,p}$ denotes the *o*, *m*, *p* protons of the Pt-phenyl ligands, and An$H_{o,m,p}$ denotes protons in the *o*, *m*, *p* positions of the BIAN skeleton (relative to attachment point of the five-membered ring). 2D ^1H,^1H-COSY and ^1H,^1H-NOESY NMR spectroscopic experiments were recorded on the Bruker DPX300 spectrometer equipped with a 5 mm QNP probe to help the assignments of ^1H NMR signals. ^{19}F NMR shifts (δ) are reported using CCl_3F as an internal reference. ^{195}Pt NMR shifts (δ) are referenced according to the 2001 IUPAC "unified scale" recommendation with Ξ = 21.496784 for 1.2 M Na_2PtCl_6 in D_2O.[68] ^{195}Pt NMR spectra were acquired with a 20 ms acquisition time and a 500 ms relaxation time between pulses. Backward linear prediction to recalculate the 50 first points of the FID gave good baselines (Bruker settings: ME-mod = LPbc, ncoef = 200, Lpbin = 130, TDOFF = 50). IR spectra were recorded with a Perkin–Elmer Spectrum One spectrometer. Elemental analyses were performed by Mikro Kemi AB, Uppsala, Sweden. Mass spectra were recorded on a Waters Micromass Q-TOF2W instrument. MS data are given as *m*/*z* values.

X-ray Crystallographic Structure Determinations: Crystals of **1a**, **1b**, **1e**, **1g**, **3a**–**b**, and **5b** were grown from dichloromethane/pentane. The crystals were mounted on glass fibers with perfluoropolyether. The data were collected at 105 K using graphite-monochromated Mo-K_α radiation on a Siemens 1K SMART CCD diffractometer (**1a** and **1b**) or a Bruker Apex II diffractometer (**1e**, **1g**, **3a**,**b** and **5b**). Data collection method: ω-scan, range 0.3°, crystal to detector distance 5 cm. Data reduction and cell determination were carried out with the SAINT and XPREP programs.[69] Absorption corrections were applied by the use of the SADABS program.[70] All the structures were solved using the Sir92[71] or Sir97[72] programs and refined on *F* using the program Crystals.[73] The non-hydrogen atoms were refined with anisotropic thermal parameters; the H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C–H in the range 0.93–98 Å) and isotropic ADPs [*U*(H) in the range 1.2–1.5 × U_{eq} of the adjacent atom], after which they were refined with riding constraints. Selected crystallographic data for these complexes are listed in Table 2.

CCDC-737961 (for **1a**), -737962 (for **1b**), -737963 (for **1e**), -737964 (for **1g**), -737965, (for **3a**) -737966 (for **3b**), -737967 (for **5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthetic Procedures

The Ar-BIAN ligands,[36,62,74] the Ar-BICAT precursor[75] Ar′N=C(Cl)–C(Cl)=NAr′ with Ar′ = 4-MeC_6H_4, and $Ph_2Pt(SMe_2)_2$[76] were prepared according to published procedures. Because of the limited long-term thermal instability of $Ph_2Pt(SMe_2)_2$ in our hands, this compound was frequently used without purification.

Ar-BICAT with Ar = 4-MeC_6H_4: To a solution of pyrocatechol (277 mg, 2.51 mmol) in THF (20 mL) was added NaH (181 mg, 7.6 mmol). After 45 min and the end of gas evolution, the resulting solution was added dropwise to a solution of Ar′N=C(Cl)–C(Cl)=NAr′ (640 mg, 2.10 mmol) in THF (40 mL), upon which a progressive green coloration appeared. The mixture was stirred overnight at room temperature. Solid ammonium chloride (400 mg, 7.5 mmol) was added and the mixture was stirred for an additional 15 min. After filtration, the solution was concentrated, and the resulting solid was stirred in pentane for 1 h. The extracts were evaporated to give a white solid (450 mg, 63%) that was sufficiently pure (ca. 95% by ^1H NMR) for the following coordination at Pt. The ligand itself revealed difficult to purify due to decomposition on silica gel (attempted purification of the ligand by chromatography on silica, filtration through Celite, or extraction were unsuccessful). ^1H NMR (200 MHz, CD_2Cl_2): δ = 7.24 (br., 8 H, Ar$H_{o,m}$), 7.10–7.07 (m, AA′BB′ pattern, 4 H, catechol-*H*), 2.39 (s, 6 H, Ar*Me*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = 139.4, 135.9, 129.7, 124.9, 123.7, 116.8, 98.9, 21.2 ppm. EI-MS: *m*/*z* (%) = 342 (62) [M^+], 327 (22), 225 (100).

General Procedure for Preparation of (Ar–BIAN)$PtPh_2$ (1a–f) and (Ar-BICAT)$PtPh_2$ (1g): The complexes (diimine)$PtPh_2$ were prepared from $Ph_2Pt(SMe_2)_2$ and the appropriate diimine ligand by adapting a literature procedure.[15] A mixture of $Ph_2Pt(SMe_2)_2$ (ca. 300 mg, 63 mmol) and the diimine (ca. 250 mg, 63 mmol) was stirred overnight at room temperature in toluene (15 mL). The solution was concentrated and dichloromethane (ca. 15 mL) was added. The solution was filtered, and concentrated again. The resulting solid was washed with pentane and dried in air to afford the desired complex as a deep green solid in 63–92% yields.

(2,6-$Me_2C_6H_3$-BIAN)$PtPh_2$ (1a): From $Ph_2Pt(SMe_2)_2$ (300 mg, 0.63 mmol) and the corresponding diimine (246 mg, 0.63 mmol); yield 380 mg (82%); green microcrystals. ^1H NMR (200 MHz, CD_2Cl_2): δ = 8.21 (d, *J* = 8.0 Hz, 2 H, AnH_p), 7.40 (dd, *J* = 7.2, 7.1, *J* = 7.2 Hz, 2 H, AnH_m), 7.08 (br., 6 H, Ar$H_{m,p}$), 7.03 [d, *J* = 6.6; $^3J(^{195}Pt\text{-}H)$ = 54.2 Hz, 4 H, PhH_o], 6.79 (d, *J* = 7.3 Hz, 2 H, AnH_o), 6.62–6.45 (m, 6 H, Ph$H_{m,p}$), 2.30 (s, 12 H, Ar*Me*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ = 145.3, 137.6, 130.0, 128.4, 126.9, 125.8, 122.6, 121.5, 98.9, 98.8, 17.8 ppm. $^{195}Pt\{^1H\}$ NMR (107 MHz, CD_2Cl_2): δ = –2770 ppm. $C_{40}H_{34}N_2Pt$ (737.79): calcd. C 65.12, H 4.64, N 3.80; found C 64.92, H 4.54, N 3.84.

(2,4,6-$Me_3C_6H_2$-BIAN)$PtPh_2$ (1b): From $Ph_2Pt(SMe_2)_2$ (500 mg, 1.05 mmol) and the corresponding diimine (438 mg, 1.05 mmol); yield 705 mg (87%); green microcrystals. ^1H NMR (300 MHz, CD_2Cl_2): δ = 8.20 (d, *J* = 8.4 Hz, 2 H, AnH_p), 7.40 (dd, *J* = 7.4, 7.3 Hz, 2 H, AnH_m), 7.01 [dd, *J* = 7.2, 1.4, $^3J(^{195}Pt\text{-}H)$ = 66.6 Hz, 4 H, PhH_o], 6.86 (br. s, 4 H, ArH_m), 6.82 (d, *J* = 7.2 Hz, 2 H, AnH_o), 6.59 (br. t, *J* = 7.2 Hz, 4 H, PhH_m), 6.50 (tt, *J* = 7.0, 1.4 Hz, 2 H, PhH_p), 2.32 (s, 6 H, ArMe_p), 2.23 (s, 12 H, ArMe_o) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ = 171.5, 143.0, 137.8, 136.6, 132.5, 130.0, 129.9, 129.0, 128.8, 125.7, 122.6, 121.5, 21.0, 17.7 ppm. $^{195}Pt\{^1H\}$ NMR (107 MHz, CD_2Cl_2): δ = –2777 ppm. $C_{42}H_{40}N_2Pt$ (767.86): calcd. C 65.70, H 5.25, N 3.65; found C 65.25, H 5.0, N 3.75.

(4-Br-2,6-$Me_2C_6H_2$-BIAN)$PtPh_2$ (1c): From $Ph_2Pt(SMe_2)_2$ (300 mg, 0.63 mmol) and the corresponding diimine (344 mg, 0.63 mmol); yield 443 mg (78%); green microcrystals. ^1H NMR (300 MHz, CD_2Cl_2): δ = (d, *J* = 8.2 Hz, 2 H, AnH_p), 7.46 (dd, *J* = 8.3, 7.3 Hz, 2 H, AnH_m), 7.22 (br. s, 4 H, ArH_m), 7.01 [dd, *J* = 7.5,

3.3, $^3J(^{195}$Pt-H) = 70.8 Hz, 4 H, PhH_o], 6.96 (d, J = 7.1 Hz, 2 H, AnH_o), 6.64 (br. t, J = 7.0 Hz, 4 H, PhH_m), 6.56 (tt, J = 7.2, 2.4 Hz, 2 H, PhH_p), 2.27 (s, 12 H, Ar*Me*) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 171.5, 144.3, 141.3, 137.4, 132.7, 131.6, 131.1, 130.5, 128.7, 126.1, 122.8, 121.9, 119.9, 17.7 ppm. ^{195}Pt{^{1}H} NMR (107 MHz, CD_2Cl_2): δ = –2750 ppm. $C_{40}H_{34}Br_2N_2Pt$ (897.60): calcd. C 53.52, H 3.82, N 3.12; found C 53.30, H 3.65, N 3.20.

(3,5-Me$_2$C$_6$H$_3$-BIAN)PtPh$_2$ (1d): From $Ph_2Pt(SMe_2)_2$ (300 mg, 0.63 mmol) and the corresponding diimine (246 mg, 0.63 mmol); yield 422 mg (91%); green microcrystals. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.18 (d, J = 7.7 Hz, 2 H, AnH_p), 7.42 (dd, J = 7.2, 7.2 Hz, 2 H, AnH_m), 7.23 (d, J = 7.2 Hz, 2 H, AnH_o), 6.97 [dd, J = 8.1, 1.4, $^3J(^{195}$Pt-H) = 71.8 Hz, 4 H, PhH_o], 6.87 (br. s, 2 H, ArH_p), 6.70 (br. s, 4 H, ArH_o), 6.65 (br. t, J = 7.5 Hz, 4 H, PhH_m), 6.53 (tt, J = 7.2, 1.5 Hz, 2 H, PhH_p), 2.21 (s, 12 H, Ar*Me*) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 138.9, 137.8, 129.9, 129.4, 128.8, 126.1, 123.8, 121.7, 120.3, 21.2 ppm. ^{195}Pt{^{1}H} NMR (107 MHz, CD_2Cl_2): δ = –2849 ppm. $C_{40}H_{34}N_2Pt$ (737.79): calcd. C 65.12, H 4.64, N 3.80; found C 64.85, H 4.70, N 3.90.

(4-MeC$_6$H$_4$-BIAN)PtPh$_2$ (1e): From $Ph_2Pt(SMe_2)_2$ (264 mg, 0.56 mmol) and the corresponding diimine (200 mg, 0.56 mmol); yield 270 mg (68%); green microcrystals. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.18 (d, J = 8.2 Hz, 2 H, AnH_p), 7.40 (t, J = 7.2 Hz, 2 H, AnH_m), 7.12 (app d, J = 7.8 Hz, 6 H, ArH and AnH_o), 6.98 (d, J = 8.3 Hz, 4 H, ArH), 6.92 [dd, J = 8.3, 1.3, $^3J(^{195}$Pt-H) = 40.1 Hz, 4 H, PhH_o], 6.62 (br. t, J = 6.9 Hz, 4 H, PhH_m), 6.54 (tt, J = 7.3, 1.4 Hz, 2 H, PhH_p), 2.39 (s, 6 H, Ar*Me*) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 138.2, 137.5, 129.9, 129.5, 129.4, 126.2, 123.8, 122.3, 121.6, 21.2 ppm. ^{195}Pt{^{1}H} NMR (107 MHz, CD_2Cl_2): δ = –2851 ppm. $C_{38}H_{32}N_2Pt$ (711.75): calcd. C 64.12, H 4.53, N 3.94; found C 64.00, H 4.20, N 4.00.

(4-CF$_3$C$_6$H$_4$-BIAN)PtPh$_2$ (1f): From $Ph_2Pt(SMe_2)_2$ (370 mg, 0.78 mmol) and the corresponding diimine (365 mg, 0.78 mmol). The product was purified by chromatography on silica with dichloromethane/pentane (1:1). Yield 370 mg (92%); green microcrystals. ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 8.24 (d, J = 8.1 Hz, 2 H, AnH_p), 7.54 (d, J = 8.3 Hz, 4 H, ArH_m), 7.44 (d, J = 7.2, 7.2 Hz, 2 H, AnH_m), 7.20 (app d, J = 7.5 Hz, 6 H, AnH_o and ArH_o), 6.86 [dd, J = 8.0, 1.6, $^3J(^{195}$Pt-H) = 64.7 Hz, 4 H, PhH_o], 6.67–6.55 (m, 6 H, Ph$H_{m,p}$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 141.4, 137.7, 130.8, 129.7, 128.0, 126.5, 126.3, 124.0, 123.0, 122.1 ppm. ^{19}F NMR (188 MHz, CD_2Cl_2): δ = –62.57 ppm. ^{195}Pt{^{1}H} NMR (107 MHz, CD_2Cl_2): δ = –2782 ppm. $C_{38}H_{24}F_6N_2Pt$ (817.68): calcd. C 55.82, H 2.96, N 3.43; found C 55.70, H 3.00, N 3.50.

(4-MeC$_6$H$_4$-BICAT)PtPh$_2$ (1g): The diimine (350 mg, 1 mmol) was added to a toluene suspension of $Ph_2Pt(SMe_2)_2$ (485 mg, 1 mmol) and stirred overnight under inert atmosphere. Filtration and concentration gave a red mixture that was purified by chromatography on silica with dichloromethane/pentane (1:1). Yield 488 mg (69%); red microcrystals. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.19 and 7.11 (two m, AA′BB′ pattern, 2 H each, catechol-H), 6.98 (br. d, J = 8.3 Hz, 4 H, ArH), 6.92–6.86 (m, 8 H, ArH and PhH_o), 6.57–6.53 (m, 6 H, Ph$H_{m,p}$), 2.30 (s, 3 H, Ar*Me*) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 140.9, 138.3, 138.2, 138.0, 137.4, 128.7, 126.7, 126.2, 124.0, 121.5, 117.4, 21.1 ppm. ^{195}Pt{^{1}H} NMR (107 MHz, CD_2Cl_2): δ = –3384 ppm. $C_{34}H_{28}N_2O_2Pt\cdot H_2O$ (709.69): calcd. C 57.54, H 4.26, N 3.96; found C 57.65, H 4.17, N 4.10.

General Procedure for in Situ Generation of (N–N)PtPh$_2$H(NCCD$_3$)$^+$ (2a–g) as BF$_4^-$ Salts: The appropriate (N–N)$PtPh_2$ complex **1** (ca. 4 mg, 5 μmol) was dissolved in CD_2Cl_2 (400 μL) and kept under inert atmosphere at –78 °C in an NMR tube. A premade mixture of $HBF_4\cdot Et_2O$ (5 μL, ca. 40 μmol) in CD_3CN (100 μL) and CD_2Cl_2 (200 μL) was then carefully layered on top of the solution of **1** in CD_2Cl_2 and the tube with contents was maintained at –78 °C in a dry ice/acetone bath without mixing of the layers. This procedure was used to minimize premature protonation of the Pt complex **1**. The tube was shaken to mix the layers immediately before it was transferred to the pre-cooled NMR probe at the desired temperature. The low-temperature ^{1}H NMR spectra indicated clean conversion of compounds **1** into the corresponding Pt^{IV} hydrides **2**. No traces of the Pt^{II} species (N-N)PtPh(NCCD$_3$)$^+$ (**3**) were seen.

(2,6-Me$_2$C$_6$H$_3$-BIAN)PtPh$_2$H(NCCD$_3$)$^+$BF$_4^-$ (2a·BF$_4^-$): ^{1}H NMR (500 MHz, CD_2Cl_2, –78 °C): δ = 8.24 (d, J = 8.3 Hz, 2 H, AnH_p), 7.56 (t, J = 7.8 Hz, 2 H, AnH_m), 7.19 (t, J = 7.6 Hz, 2 H, ArH_p), 7.13 (d, J = 7.5 Hz, 2 H, ArH_m), 7.06 (d, J = 7.3 Hz, 2 H, ArH_m), 6.89–6.60 (m, 8 H, Ph$H_{o,p}$ and AnH_o), 6.61 (t, J = 7.6 Hz, 4 H, PhH_m), 2.19 (s, 6 H, Ar*Me*), 2.00 (s, 6 H, Ar*Me*), –20.89 [s, $^1J(^{195}$Pt-H) = 1598 Hz, 1 H, PtH] ppm.

(2,4,6-Me$_3$C$_6$H$_2$-BIAN)PtPh$_2$H(NCCD$_3$)$^+$BF$_4^-$ (2b·BF$_4^-$): ^{1}H NMR (500 MHz, CD_2Cl_2, –78 °C): δ = 8.23 (d, J = 8.2 Hz, 2 H, AnH_p), 7.55 (t, J = 7.9 Hz, 2 H, AnH_m), 6.86 (s, 2 H, ArH_m), 6.80 (s, 2 H, ArH_m), 6.80–6.68 (m, 8 H, AnH_o, Ph$H_{o,p}$), 6.62 (br. t, J = 7.5 Hz, 4 H, PhH_m), 2.28 (s, 6 H, Ar*Me*), 2.12 (s, 6 H, Ar*Me*), 1.93 (s, 6 H, Ar*Me*), –20.99 [s, $^1J(^{195}$Pt-H) = 1605 Hz, 1 H, PtH] ppm.

(4-Br-2,6-Me$_2$C$_6$H$_2$-BIAN)PtPh$_2$H(NCCD$_3$)$^+$BF$_4^-$ (2c·BF$_4^-$): ^{1}H NMR (500 MHz, CD_2Cl_2, –78 °C): δ = 8.28 (d, J = 8.3 Hz, 2 H, AnH_p), 7.61 (t, J = 7.8 Hz, 2 H, AnH_m), 7.31 (s, 2 H, ArH_m), 7.22 (s, 2 H, ArH_m), 6.92 (d, J = 7.4 Hz, 2 H, AnH_o), 6.84–6.70 (m, 6 H, Ph$H_{o,p}$), 6.66 (br. t, ^3J = 7.4 Hz, 4 H, PhH_m), 2.18 (s, 6 H, Ar*Me*), 1.97 (s, 6 H, Ar*Me*), –20.90 [s, $^1J(^{195}$Pt-H) = 1593 Hz, 1 H, Pt-H] ppm.

(3,5-Me$_2$C$_6$H$_3$-BIAN)PtPh$_2$H(NCCD$_3$)$^+$BF$_4^-$ (2d·BF$_4^-$): ^{1}H NMR (500 MHz, CD_2Cl_2, –78 °C): δ = 8.22 (d, J = 8.3 Hz, 2 H, AnH_p), 7.58 (t, J = 7.9 Hz, 2 H, AnH_m), 7.27 (d, J = 7.3 Hz, 2 H, AnH_o), 7.00–6.83 (m, 6 H, PhH_o and ArH_o), 6.75 (br. t, J = 7.2 Hz, 2 H, PhH_p), 6.69–6.64 (m, 6 H, PhH_m and ArH_o), 6.51 (s, 2 H, ArH_p), 2.18 (s, 6 H, Ar*Me*), 2.10 (s, 6 H, Ar*Me*), –21.46 [s, $^1J(^{195}$Pt-H) = 1608 Hz, 1 H, PtH] ppm.

(4-MeC$_6$H$_4$-BIAN)PtPh$_2$H(NCCD$_3$)$^+$BF$_4^-$ (2e·BF$_4^-$): ^{1}H NMR (500 MHz, CD_2Cl_2, –78 °C): δ = 8.22 (d, J = 8.3 Hz, 2 H, AnH_p), 7.56 (t, J = 7.9 Hz, 2 H, AnH_m), 7.14–7.09 (m, 6 H, ArH and AnH_o), 6.95 (d, J = 7.9 Hz, 2 H, ArH), 6.93–6.84 (m, 6 H, ArH and PhH_o), 6.76 (t, J = 7.3 Hz, 2 H, PhH_p), 6.62 (t, J = 7.5 Hz, 4 H, PhH_m), 2.33 (s, 6 H, Ar*Me*), –21.37 [s, $^1J(^{195}$Pt-H) = 1608 Hz, 1 H, PtH] ppm.

(4-CF$_3$C$_6$H$_4$-BIAN)PtPh$_2$H(NCCD$_3$)$^+$BF$_4^-$ (2f·BF$_4^-$): ^{1}H NMR (500 MHz, CD_2Cl_2, –78 °C): δ = 8.27 (d, J = 8.3 Hz, 2 H, AnH_p), 7.62 (d, J = 8.5 Hz, 2 H, ArH), 7.60 (t, J = 7.9 Hz, 2 H,AnH_m), 7.55 (d, J = 8.3 Hz, 2 H, ArH), 7.35 (d, J = 7.9 Hz, 2 H, ArH), 7.17 (d, J = 7.3 Hz, 2 H, AnH_o), 7.10 (d, J = 8.0 Hz, 2 H, ArH), 6.84 [d, J = 7.5, $^3J(^{195}$Pt-H) = 60.3 Hz, 4 H, PhH_o], 6.75 (br. t, J = 7.3 Hz, 2 H, PhH_p), 6.60 (br. t, J = 7.4 Hz, 4 H, PhH_m), –21.15 [s, $^1J(^{195}$Pt-H) = 1592 Hz, 1 H, PtH] ppm.

(4-MeC$_6$H$_4$-BICAT)PtPh$_2$H(NCCD$_3$)$^+$BF$_4^-$ (2g·BF$_4^-$): ^{1}H NMR (500 MHz, CD_2Cl_2, –78 °C): δ = 7.21–7.19 (m, 2 H, catechol-H), 7.11–7.09 (m, 2 H, catechol-H), 6.95 (br. d, J = 7.9 Hz, 4 H, ArH), 6.82–6.79 (m, 8 H, ArH and PhH_o), 6.74 (br. t, J = 7.5 Hz, 2 H, PhH_p), 6.59 (br. t, J = 7.9 Hz, 4 H, PhH_m), 2.23 (s, 6 H, Ar*Me*), –21.61 [s, $^1J(^{195}$Pt-H) = 1594 Hz, 1 H, PtH] ppm.

General Procedure for the Synthesis of (N–N)PtPh(NCMe)$^+$ (3a–g) as BF$_4^-$ Salts: $HBF_4\cdot Et_2O$ (22 μL, 0.16 mmol) was added dropwise

to a stirred solution of (N–N)$PtPh_2$ (ca. 100 mg, depending on the diimine, 0.14 mmol) in acetonitrile at 0 °C under an argon atmosphere. The solution was stirred and gradually warmed to ambient temperature. After 1 h the solvent was removed under vacuum, and the resulting red-orange solid was washed several times with ether. The product was recrystallized from a dichloromethane solution layered with ether.

(2,6-$Me_2C_6H_3$-BIAN)PtPh(NCMe)$^+BF_4^-$ (3a·BF_4^-): From **1a** (113 mg, 0.15 mmol). Yield 88 mg (73%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.35 (d, J = 7.1 Hz, 1 H, AnH_p), 8.33 (d, J = 7.1 Hz, 1 H, AnH_p), 7.64 (dd, J = 8.3, J = 8.3 Hz, 1 H, AnH_m), 7.54 (dd, J = 8.3, J = 8.3 Hz, 1 H, AnH_m), 7.44 (br., 3 H, ArH), 7.22 (t, J = 8.3 Hz, 1 H, ArH_p), 7.16 (d, J = 7.0 Hz, 1 H, AnH_o), 7.09 (d, J = 7.7 Hz, 2 H, ArH_m), 6.89–6.87 (m, 2 H, PhH_o), 6.74–6.71 (m, 3 H, Ph$H_{m,p}$), 6.69 (d, J = 7.2 Hz, 1 H, AnH_o), 2.50 (s, 6 H, ArMe), 2.24 (s, 6 H, ArMe), 2.06 [s, ^4J(Pt-H) = 10.3 Hz, 3 H, NCMe] ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 148.2, 142.2, 135.1, 133.7, 133.0, 132.2, 130.5, 130.4, 140.0, 129.6, 129.4, 129.1, 127.0, 125.6, 125.5, 125.2, 124.9, 18.0, 17.9, 3.2 ppm. ^{19}F NMR (188 MHz, CD_2Cl_2): δ = –153.02, –153.07 ($^{10}BF_4^-$ and $^{11}BF_4^-$) ppm. ^{195}Pt NMR (107 MHz, CD_2Cl_2): δ = –3170 ppm. $C_{36}H_{32}BF_4N_3Pt$ (788.54): calcd. C 54.8, H 4.1, N 5.3; found C 54.0, H 4.3, N 5.3. ESI MS: m/z = 701.1 [M$^+$].

(2,4,6-$Me_3C_6H_2$-BIAN)PtPh(NCMe)$^+BF_4^-$ (3b·BF_4^-): From **1b** (100 mg, 0.13 mmol). Yield 90 mg (85%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.35 (d, J = 7.9 Hz, 1 H, AnH_p), 8.33 (d, J = 7.6 Hz, 1 H, AnH_p), 7.64 (dd, J = 7.4, 7.3 Hz, 1 H, AnH_m), 7.54 (dd, J = 7.5, 7.2 Hz, 1 H, AnH_m), 7.24 (br. s, 2 H, ArH_m), 7.18 (d, J = 7.2 Hz, 1 H, AnH_o), 6.89 (br. s, 2 H, ArH_m), 6.89–6.85 (m, 2 H, PhH_o), 6.75–6.72 (m, 4 H, AnH_o and Ph$H_{m,p}$), 2.47 (s, 3 H, Ar-Me_p), 2.45 (s, 6 H, ArMe_o), 2.30 (s, 3 H, ArMe_p), 2.16 (s, 6 H, ArMe_o), 2.07 (s, 3 H, NCMe) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 178.9, 148.0, 140.2, 139.9, 139.4, 139.1, 135.3, 133.5, 132.8, 130.4, 130.3, 130.1, 129.9, 129.6, 128.8, 126.9, 125.7, 125.5, 124.9, 21.2, 21.1, 17.9, 17.2, 3.2 ppm. ^{19}F NMR (188 MHz, CD_2Cl_2): δ = –153.11, –153.16 ($^{10}BF_4^-$ and $^{11}BF_4^-$) ppm. ^{195}Pt NMR (107 MHz, CD_2Cl_2): δ = –3164 ppm. $C_{38}H_{36}BF_4N_3Pt$ (816.60): calcd. C 55.9, H 4.4, N 5.2; found C 55.0, H 4.5, N 5.0. ESI MS: m/z = 729.1 [M$^+$].

(4-Br-2,6-$Me_2C_6H_2$-BIAN)PtPh(NCMe)$^+BF_4^-$ (3c·BF_4^-): From **1c** (100 mg, 0.11 mmol). Yield 71 mg (68%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.41 (d, J = 8.4 Hz, 1 H, AnH_p), 8.38 (d, J = 8.4 Hz, 1 H, AnH_p), 7.69 (dd, J = 8.3, 8.3 Hz, 1 H, AnH_m), 7.62 (br. s, 2 H, ArH_m), 7.60 (dd, J = 8.3, 8.3 Hz, 1 H, AnH_m), 7.24 (br. s, 2 H, ArH_m), 7.21 (d, J = 7.1 Hz, 1 H, AnH_o), 6.86–6.77 (m, 6 H, AnH_o and Ph$H_{o,m,p}$), 2.49 (s, 6 H, ArMe), 2.21 (s, 6 H, ArMe), 2.19 (br. s, 3 H, NCMe) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 178.9, 172.7, 148.4, 141.5, 134.9, 134.2, 133.5, 132.4, 132.3, 132.1, 131.5, 130.6, 130.5, 127.3, 125.6, 125.2, 125.1, 124.9, 122.6, 122.2, 17.9, 17.8, 3.5 ppm. ^{19}F NMR (188 MHz, CD_2Cl_2): δ = –152.61, –152.65 ($^{10}BF_4^-$ and $^{11}BF_4^-$) ppm. ^{195}Pt NMR (107 MHz, CD_2Cl_2): δ = –3177 ppm. $C_{36}H_{30}BBr_2F_4N_3Pt$ (946.33): calcd. C 45.7, H 3.2, N 4.4; found C 44.7, H 3.2, N 4.2. ESI MS: m/z = 857.9, 859.9 [M$^+$].

(3,5-$Me_2C_6H_3$-BIAN)PtPh(NCMe)$^+BF_4^-$ (3d·BF_4^-): From **1d** (100 mg, 0.14 mmol). Yield 82 mg (76%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.30 (d, J = 8.2 Hz, 1 H, AnH_p), 8.28 (d, J = 8.1 Hz, 1 H, AnH_p), 7.62 (dd, J = 7.4, 8.2 Hz, 1 H, AnH_m), 7.52 (dd, J = 7.5, 8.3 Hz, 1 H, AnH_m), 7.47 (d, J = 7.1 Hz, 1 H, AnH_o), 7.24 (br. s, 1 H, ArH_p), 7.15 (br. s, 2 H, ArH_o), 7.02 (d, J = 7.1 Hz, 1 H, AnH_o), 6.93 (br. s, 1 H, ArH_p), 6.89–6.86 (m, 2 H, PhH_o), 6.77–6.71 (m, 3 H, Ph$H_{m,p}$), 6.61 (br. s, 2 H, ArH_o), 2.50 (s, 6 H, ArMe), 2.20 (s, 6 H, ArMe), 2.19 (s, 3 H, NCMe) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 144.4, 140.8, 139.9, 135.5, 133.0, 132.5, 131.2, 130.5, 129.7, 126.3, 125.6, 124.7, 120.5, 119.2, 21.5, 21.1, 3.7 ppm. ^{19}F NMR (188 MHz, CD_2Cl_2): δ = –153.04, –153.10 ($^{10}BF_4^-$ and $^{11}BF_4^-$) ppm. ^{195}Pt NMR (107 MHz, CD_2Cl_2): δ = –3216 ppm. $C_{36}H_{32}BF_4N_3Pt$ (788.54): calcd. C 54.8, H 4.1, N 5.3; found C 53.8, H 4.3, N 5.7. ESI MS: m/z = 701.1 [M$^+$].

(4-MeC_6H_4-BIAN)PtPh(NCMe)$^+BF_4^-$ (3e·BF_4^-): From **1e** (100 mg, 0.14 mmol). Yield 58 mg (54%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.30 (d, J = 8.2 Hz, 1 H, AnH_p), 8.28 (d, J = 7.8 Hz, 1 H, AnH_p), 7.62 (t, J = 7.8 Hz, 1 H, AnH_m), 7.57–7.45 (m, 6 H, An$H_{o,m}$ and ArH), 7.11 (d, J = 8.0 Hz, 2 H, ArH), 6.93–6.85 (m, 5 H, ArH, AnH_o and PhH_o), 6.74–6.72 (m, 3 H, Ph$H_{m,p}$), 2.57 (s, 3 H, ArMe), 2.36 (s, 3 H, ArMe), 2.20 (br. s, 3 H, NCMe) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 178.6, 171.4, 147.9, 142.4, 142.0, 140.5, 139.7, 135.8, 133.1, 132.5, 132.2, 130.9, 130.7, 130.2, 129.6, 127.2, 126.2, 125.9, 125.5, 125.1, 124.5, 122.8, 121.9, 21.4, 21.6, 3.8 ppm. ^{19}F NMR (188 MHz, CD_2Cl_2): δ = –152.88, –152.93 ($^{10}BF_4^-$ and $^{11}BF_4^-$) ppm. ^{195}Pt NMR (107 MHz, CD_2Cl_2): δ = –3216 ppm. $C_{34}H_{28}BF_4N_3Pt$ (760.49): calcd. C 53.7, H 3.7, N 5.5; found C 51.3, H 3.8, N 5.1. ESI MS: m/z = 673.1 [M$^+$].

(4-$CF_3C_6H_4$-BIAN)PtPh(NCMe)$^+BF_4^-$ (3f·BF_4^-): From **1f** (100 mg, 0.12 mmol). Yield 60 mg (56%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.34 (d, J = 6.8 Hz, 1 H, AnH_p), 8.32 (d, J = 7.0 Hz, 1 H, AnH_p), 8.06 (d, J = 8.4 Hz, 2 H, ArH), 7.82 (d, J = 6.2 Hz, 2 H, ArH), 7.64 (dd, J = 7.5, 8.2 Hz, 1 H, AnH_m), 7.58–7.51 (m, 3 H, AnH_m and ArH), 7.39 (d, J = 7.3 Hz, 1 H, AnH_o), 7.24 (d, J = 8.3 Hz, 2 H, ArH), 6.92 (d, J = 8.3 Hz, 1 H, AnH_o), 6.86–6.84 (m, 2 H, PhH_o), 6.72–6.70 (m, 3 H, Ph$H_{m,p}$), 2.21 (s, 3 H, NCMe) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 135.5, 133.7, 133.1, 132.3, 129.9, 127.9, 127.6, 127.0, 126.3, 125.9, 125.6, 124.8, 124.0, 123.0, 3.8 ppm. ^{19}F NMR (188 MHz, CD_2Cl_2): δ = –62.65 (s, Ar-CF_3), –63.02 (s, Ar-CF_3), –152.35 and –152.40 ($^{10}BF_4^-$ and $^{11}BF_4^-$) ppm. ^{195}Pt NMR (107 MHz, CD_2Cl_2): δ = –3240 ppm. $C_{34}H_{22}BF_{10}N_3Pt$ (868.43): calcd. C 47.0, H 2.6, N 4.8; found C 46.2, H 2.7, N 4.9. ESI MS: m/z = 781.0 [M$^+$].

(4-MeC_6H_4-BICAT)PtPh(NCMe)$^+BF_4^-$ (3g·BF_4^-): From **1g** (100 mg, 0.15 mmol). Yield 89 mg (83%). ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 7.43 (br., 4 H, ArH), 7.31–7.20 (m, 3 H, catechol-H), 7.14–7.08 (m, 1 H, catechol-H), 6.95 (br. d, J = 7.9 Hz, 2 H, ArH), 6.87 (br. d, J = 8.1 Hz, 2 H, ArH), 6.83–6.78 (m, 2 H, PhH_o), 6.69–6.63 (m, 3 H, Ph$H_{m,p}$), 2.47 (s, 3 H, ArMe), 2.26 (s, 3 H, ArMe), 2.08 [s, ^4J(^{195}Pt-NCMe) = 13.9 Hz, 3 H, NCMe] ppm. ^{19}F NMR (188 MHz, CD_2Cl_2): δ = –152.15, 152.20 ($^{10}BF_4^-$ and $^{11}BF_4^-$) ppm. ESI MS: m/z = 655.2 [M$^+$].

General Procedure for in situ Generation of (N–N)PtPh(η^2-C_6H_6)$^+$ (4a–g) as BF_4^- Salts: The appropriate (N-N)$PtPh_2$ complex (ca. 5 mg, 7 μmol) was dissolved in CD_2Cl_2 (400 μL) and kept under an inert atmosphere at –78 °C in an NMR tube. A pre-made mixture of HBF_4·Et_2O (5–10 μL) in [D_{10}]Et_2O (80 μL) and CD_2Cl_2, for a total volume of 300 μL, was then carefully layered on top of the solution of **1** in CD_2Cl_2 and the tube with contents was maintained at –78 °C in a dry ice/acetone bath without mixing of the layers. This procedure was used to minimize premature protonation of the Pt complex **1**. The tube was shaken to mix the layers immediately before it was transferred to the pre-cooled NMR probe at the desired temperature. The low-temperature ^{1}H NMR spectra indicated clean conversion of compounds **1a**–**g** into the corresponding Pt^{II} phenyl π-benzene complexes **4a**–**g**.

(2,6-$Me_2C_6H_3$-BIAN)PtPh(η^2-C_6H_6)$^+BF_4^-$ (4a·BF_4^-): ^{1}H NMR (500 MHz, CD_2Cl_2, –35 °C): δ = 8.29 (d, J = 8.3 Hz, 1 H, AnH_p), 8.24 (d, J = 8.4 Hz, 1 H, AnH_p), 7.51 (t, J = 7.9 Hz, 1 H, AnH_m), 7.46 (t, J = 7.9 Hz, 1 H, AnH_m), 7.40–7.37 (m, 3 H, ArH), 7.07 (s,

6 H, C_6H_6), 7.02 (t, J = 7.6 Hz, 1 H, ArH_p), 6.92 (d, J = 6.7 Hz, 2 H, ArH_m), 6.74 (br. d, J = 7.0 Hz, 2 H, PhH_o), 6.52–6.36 (m, 5 H, AnH_o and Ph$H_{m,p}$), 2.29 (s, 6 H, Ar*Me*), 2.20 (s, 6 H, Ar*Me*) ppm.

(2,4,6-$Me_3C_6H_2$-BIAN)PtPh(η^2-C_6H_6)$^+BF_4^-$ (4b·BF_4^-): ^{1}H NMR (500 MHz, CD_2Cl_2, –35 °C): δ = 8.28 (d, J = 8.3 Hz, 1 H, AnH_p), 8.23 (d, J = 8.4 Hz, 1 H, AnH_p), 7.55 (t, J = 8.2 Hz, 1 H, AnH_m), 7.46 (t, J = 8.1 Hz, 1 H, AnH_m), 7.16 (s, 2 H, ArH_m), 7.05 (s, 6 H, C_6H_6), 6.68 (br. s, 4 H, ArH_m and PhH_o), 6.57 (d, J = 8.2 Hz, 1 H, AnH_o), 6.46–6.38 (m, 4 H, AnH_o and Ph$H_{m,p}$), 2.42 (s, 3 H, ArMe_p), 2.25 (s, 6 H, ArMe_o), 2.14 (s, 3 H, ArMe_p), 2.12 (s, 6 H, ArMe_o) ppm.

(4-Br-2,6-$Me_2C_6H_2$-BIAN)PtPh(η^2-C_6H_6)$^+BF_4^-$ (4c·BF_4^-): ^{1}H NMR (500 MHz, CD_2Cl_2, –35 °C): δ = 8.33 (d, J = 8.4 Hz, 1 H, AnH_p), 8.28 (d, J = 8.4 Hz, 1 H, AnH_p), 7.58–7.49 (m, 4 H, AnH_m and ArH_m), 7.10 (s, 6 H, C_6H_6), 7.06 (s, 2 H, ArH_m), 6.74 (br., 2 H, PhH_o), 6.62 (d, J = 6.4 Hz, 1 H, AnH_o), 6.57–6.55 (m, 2 H, AnH_o and PhH_p), 6.49 (br. t, J = 7.1 Hz, 2 H, PhH_m), 2.24 (s, 6 H, Ar*Me*), 2.17 (s, 6 H, Ar*Me*) ppm.

(3,5-$Me_2C_6H_3$-BIAN)PtPh(η^2-C_6H_6)$^+BF_4^-$ (4d·BF_4^-): ^{1}H NMR (500 MHz, CD_2Cl_2, –55 °C): δ = 8.27 (d, J = 7.3 Hz, 1 H, AnH_p), 8.23 (d, J = 7.4 Hz, 1 H, AnH_p), 7.55 (t, J = 7.5 Hz, 1 H, AnH_m), 7.46 (t, J = 7.7 Hz, 1 H, AnH_m), 7.18 (s, 1 H, ArH_p), 7.12 (s, 6 H, C_6H_6), 7.08 (s, 2 H, ArH_o), 6.77 (d, J = 9.4 Hz, 1 H, AnH_o), 6.71 (s, 1 H, ArH_p), 6.64 (d, J = 7.7 Hz, 1 H, AnH_o), 6.40 (s, 2 H, ArH_o), 6.30–6.22 (m, 5 H, Ph$H_{o,m,p}$), 2.44 (s, 6 H, Ar*Me*), 2.06 (s, 6 H, Ar*Me*) ppm.

(4-MeC_6H_4-BIAN)PtPh(η^2-C_6H_6)$^+BF_4^-$ (4e·BF_4^-): ^{1}H NMR (500 MHz, CD_2Cl_2, –78 °C): δ = 8.25 (d, J = 8.3 Hz, 1 H, AnH_p), 8.21 (d, J = 8.4 Hz, 1 H, AnH_p), 7.54–7.49 (m, 3 H, AnH_m and 2 Ar*H*), 7.45–7.38 (m, 3 H, AnH_m and Ar*H*), 7.09 (br. s, 6 H, C_6H_6), 6.89 (d, J = 8.1 Hz, 2 H, Ar*H*), 6.73–6.71 (m, 3 H, AnH_o and Ar*H*), 6.42 (d, J = 7.4 Hz, 1 H, AnH_o), 6.30–6.26 (m, 3 H, Ph$H_{o,p}$), 6.19 (br. t, J = 7.2 Hz, 2 H, PhH_m), 2.46 (s, 3 H, Ar*Me*), 2.18 (s, 3 H, Ar*Me*) ppm.

(4-$CF_3C_6H_4$-BIAN)Pt(η^2-C_6H_6)Ph$^+BF_4^-$ (4f·BF_4^-): ^{1}H NMR (500 MHz, CD_2Cl_2, –55 °C): δ = 8.31 (d, J = 8.3 Hz, 1 H, AnH_p), 8.28 (d, J = 9.0 Hz, 1 H, AnH_p), 8.02 (d, J = 7.3 Hz, 2 H, Ar*H*), 7.79 (d, J = 8.3 Hz, 2 H, Ar*H*), 7.56 (t, J = 7.3 Hz, 1 H, AnH_m), 7.47 (t, J = 7.3 Hz, 1 H, AnH_m), 7.36 (d, J = 7.3 Hz, 2 H, Ar*H*), 7.10–7.08 (m, 8 H, C_6H_6 and 2 Ar*H*), 6.72 (d, J = 7.7 Hz, 1 H, AnH_o), 6.57 (d, J = 7.7 Hz, 1 H, AnH_o), 6.31–6.29 (m, 3 H, Ph$H_{o,p}$), 6.19 (t, J = 7.2 Hz, 2 H, PhH_m) ppm.

(4-MeC_6H_4-BICAT)Pt(η^2-C_6H_6)Ph$^+BF_4^-$ (4g·BF_4^-): ^{1}H NMR (500 MHz, CD_2Cl_2, –78 °C): δ = 7.36–7.32 (m, 4 H, Ar*H*), 7.22–7.17 (m, 2 H, catechol-*H*), 7.11 (br. d, J = 7.8 Hz, 1 H, catechol-*H*), 7.04 (br. d, J = 7.9 Hz, 1 H, catechol-*H*), 6.90 (br. s, 6 H, C_6H_6), 6.72 (d, J = 8.1 Hz, 2 H, Ar*H*), 6.66 (d, J = 7.2 Hz, 2 H, Ar*H*), 6.25–6.21 (m, 3 H, Ph$H_{o,p}$), 6.08 (br. t, J = 7.0 Hz, 2 H, PhH_m), 2.34 (s, 3 H, Ar*Me*), 2.07 (s, 3 H, Ar*Me*) ppm.

General Procedure for Synthesis of (N–N)Pt(NCMe)$_2^{2+}$ (5a–f) as TfO$^-$ Salts: TfOH (ca. 150 μL, 1 mmol) was added dropwise to a stirred solution of (N–N)$PtPh_2$ (ca. 100 mg, 0.10 mmol) in acetonitrile (3 mL) under argon. The solution was heated to 50 °C and stirred overnight. The solvent was removed under vacuum, producing an orange solid which was washed several times with ether.

(2,6-$Me_2C_6H_3$-BIAN)Pt(NCMe)$_2^{2+}$(TfO$^-$)$_2$ [5a·(TfO$^-$)$_2$]: From **1a** (80 mg, 0.10 mmol) and TfOH (40 μL, 0.46 mmol). Yield 78 mg (75%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.44 (d, J = 8.3 Hz, 2 H, AnH_p), 7.71 (dd, J = 7.4, 7.5 Hz, 2 H, AnH_m), 7.58–7.44 (m, 6 H, Ar$H_{m,p}$), 7.04 (d, J = 7.3 Hz, 2 H, AnH_o), 2.50 (s, 12 H, Ar*Me*), 2.24 (s, 6 H, NC*Me*) ppm. ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = 136.2, 131.6, 131.1, 130.5, 127.4, 18.0, 3.0 ppm. ^{19}F NMR (188 MHz, CD_2Cl_2): δ = –78.83 ppm. ^{195}Pt NMR (107 MHz, CD_2Cl_2): δ = –2391 ppm. $C_{34}H_{30}F_6N_4O_6PtS_2$ (963.82): calcd. C 42.4, H 3.1, N 5.8; found C 43.7, H 3.6, N 6.2. ESI MS: m/z = 332.6 [M^{2+}], 312.0 [M^{2+} – MeCN].

(2,4,6-$Me_3C_6H_2$-BIAN)Pt(NCMe)$_2^{2+}$(TfO$^-$)$_2$ [5b·(TfO$^-$)$_2$]: From **1b** (100 mg, 0.13 mmol) and TfOH (40 μL, 0.46 mmol). Yield 102 mg (79%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.44 (d, J = 8.2 Hz, 2 H, AnH_p), 7.70 (dd, J = 7.8, 7.7 Hz, 2 H, AnH_m), 7.24 (br. s, 4 H, ArH_m), 7.08 (d, J = 7.3 Hz, 2 H, AnH_o), 2.46 (br. s, 12 H, ArMe_o), 2.45 (s, 6 H, ArMe_p), 2.34 (s, 6 H, NC*Me*) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 182.1, 152.4, 145.8, 141.9, 138.7, 135.8, 132.3, 130.8, 130.5, 127.1, 122.7, 21.3, 18.0, 3.6 ppm. ^{19}F NMR (188 MHz, CD_2Cl_2): δ = –78.85 ppm. ^{195}Pt NMR (107 MHz, CD_2Cl_2): δ = –2391 ppm. $C_{36}H_{34}F_6N_4O_6PtS_2$ (991.88): calcd. C 43.6, H 3.5, N 5.7; found C 43.3, H 3.5, N 5.3. ESI MS: m/z = 346.6 [M^{2+}], 326.0 [M^{2+} – MeCN].

(4-Br-2,6-$Me_2C_6H_2$-BIAN)Pt(NCCD$_3$)$_2^{2+}$(TfO$^-$)$_2$ [5c·(TfO$^-$)$_2$]: On top of a solution of **1c** (8 mg, 9 μmol) in [D_2]dichloromethane (400 μL) was layered 50 μL of [D_2]dichloromethane. Then a premixed solution of TfOH (3 μL, 0.035 mmol) in [D_3]acetonitrile (200 μL) was added, and the tube was shaken and kept overnight at 50 °C at which point a bright orange solution was obtained. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.43 (d, J = 8.1 Hz, 2 H, AnH_p), 7.70 (dd, J = 8.2, 8.2 Hz, 2 H, AnH_m), 7.59 (br. s, 4 H, ArH_m), 7.07 (d, J = 7.3 Hz, 2 H, AnH_o), 2.46 (s, 12 H, Ar*Me*) ppm.

(3,5-$Me_2C_6H_3$-BIAN)Pt(NCMe)$_2^{2+}$(TfO$^-$)$_2$ [5d·(TfO$^-$)$_2$]: From **1d** (100 mg, 0.13 mmol) and TfOH (40 μL, 0.47 mmol). Yield 85 mg (65%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.23 (d, J = 8.2 Hz, 2 H, AnH_p), 7.62 (dd, J = 8.2, 8.1 Hz, 2 H, AnH_m), 7.40 (br. s, 4 H, ArH_o), 7.30 (br. s, 2 H, ArH_p), 7.17 (d, J = 7.3 Hz, 2 H, AnH_o), 2.48 (s, 12 H, Ar*Me*), 2.37 (s, 6 H, NC*Me*) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 141.4, 134.4, 132.7, 128.9, 127.2, 120.2, 21.4, 3.8 ppm. ^{19}F NMR (188 MHz, CD_2Cl_2): δ = –78.8 ppm. ^{195}Pt NMR (107 MHz, CD_2Cl_2): δ = –2397 ppm. $C_{34}H_{30}F_6N_4O_6PtS_2$ (963.82): calcd. C 42.4, H 3.1, N 5.8; found C 41.3, H 3.2, N 5.4. ESI MS: m/z = 346.6 [M^{2+}], 326.0 [M^{2+} – MeCN].

(4-MeC_6H_4-BIAN)Pt(NCMe)$_2^{2+}$(TfO$^-$)$_2$ [5e·(TfO$^-$)$_2$]: From **1e** (100 mg, 0.14 mmol) and TfOH (50 μL, 0.56 mmol). Yield 80 mg (61%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.35 (d, J = 8.1 Hz, 2 H, AnH_p), 7.65 (dd, J = 7.5, 7.3 Hz, 2 H, AnH_m), 7.54 (br., 8 H, Ar*H*), 7.21 (d, J = 7.3 Hz, 2 H, AnH_o), 2.54 (s, 6 H, Ar*Me*), 2.29 (s, 6 H, NC*Me*) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 141.1, 134.5, 134.1, 131.3, 129.8, 127.1, 123.0, 21.6, 3.9 ppm. ^{19}F NMR (188 MHz, CD_2Cl_2): δ = –78.7 ppm. ^{195}Pt NMR (107 MHz, CD_2Cl_2): δ = –2407 ppm. $C_{32}H_{26}F_6N_4O_6PtS_2$ (935.77): calcd. C 41.1, H 2.8, N 6.0; found C 39.4, H 2.9, N 5.4. ESI MS: m/z = 318.5 [M^{2+}], 298.0 [M^{2+} – MeCN].

(4-$CF_3C_6H_4$-BIAN)Pt(NCCD$_3$)$_2^{2+}$(TfO$^-$)$_2$ [5f·(TfO$^-$)$_2$]: On top of a solution of **1f** (8 mg, 0.01 mmol) in [D_2]dichloromethane (400 μL) was layered 50 μL of [D_2]dichloromethane. Then a premixed solution of TfOH (3 μL, 0.035 mmol) in [D_3]acetonitrile (200 μL) was added, and the tube was shaken and kept overnight at 50 °C at which point a bright orange solution was obtained ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 8.37 (d, J = 8.2 Hz, 2 H, AnH_p), 8.02 (dd, J = 9.4, 9.3 Hz, 8 H, Ar*H*), 7.65 (dd, J = 6.8, 7.9 Hz, 2 H, AnH_m), 7.10 (d, J = 7.4 Hz, 2 H, AnH_o) ppm. ^{19}F NMR (188 MHz, CD_2Cl_2): δ = –62.48 (s, ArCF_3), –78.66 (s, OTf) ppm.

General Procedure for the Preparation and Characterization of (diimine)Pt(CO)Ph$^+BF_4^-$ (diimine = 4-MeC_6H_4-DAB, 4-MeC_6H_4-

BIAN, 4-MeC$_6$H$_4$-BICAT): (4-MeC$_6$H$_4$-DAB)PtPh$_2$ was prepared according to the published procedure.[20] These compounds were prepared solely for IR and ^{1}H NMR characterization by adaptation of a published procedure.[20] HBF_4·Et_2O (3–6 μL, 0.02–0.04 mmol) was added to a solution of (diimine)PtPh$_2$ complex (15–30 mg, 0.02–0.04 mmol) in trifluoroethanol (2 mL). After 18 h under a CO atmosphere, the solution was concentrated to give an oily residue. Part of the product was dissolved in CD_2Cl_2 for NMR characterization whereas another part was dissolved in CH_2Cl_2 for IR characterization.

(4-MeC$_6$H$_4$-DAB)Pt(CO)Ph$^+$BF$_4^-$: ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 7.39 (d, J = 8.1 Hz, 2 H, Ar*H*), 7.25 (d, J = 8.5 Hz, 2 H, Ar*H*), 6.92–6.86 (m, 4 H, Ar*H*, PhH_o), 6.86–6.72 (m, 3 H, Ar*H*, PhH_p), 6.63–6.59 (m, 2 H, PhH_m), 2.46 (s, 3 H, DAB*Me*), 2.44 (s, 3 H, DAB*Me*), 2.38 (s, 3 H, Ar*Me*), 2.21 (s, 3 H, Ar*Me*) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = ν(CO) 2113.8 cm^{-1}.

(4-MeC$_6$H$_4$-BIAN)Pt(CO)Ph$^+$BF$_4^-$: ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 8.29 (br. d, J = 8.2 Hz, 2 H, AnH_p), 7.68 (t, J = 7.4 Hz, 2 H, AnH_m), 7.61 (d, J = 7.6 Hz, 1 H, AnH_o), 7.55 (br., 4 H, Ar*H*), 7.51 (d, J = 7.8 Hz, 1 H, AnH_o), 7.09 (d, J = 8.6 Hz, 2 H, Ar*H*), 7.08–7.02 (m, 2 H, PhH_o), 6.99–6.80 (m, 3 H, Ph$H_{m,p}$), 6.84 (d, J = 7.6 Hz, 2 H, Ar*H*), 2.56 (s, 3 H, Ar*Me*), 2.35 (s, 3 H, Ar*Me*) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = ν(CO) 2115.6 cm^{-1}.

(4-MeC$_6$H$_4$-BICAT)Pt(CO)Ph$^+$BF$_4^-$: ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 7.54 (br. d, J = 8.4 Hz, 2 H, Ar*H*), 7.39 (br. d, J = 8.3 Hz, 2 Ar*H*), 7.35–7.25 (m, 3 H, catechol-*H*), 7.19–7.16 (m, 1 H, catechol-*H*), 7.05–7.00 (m, 2 H, PhH_o), 6.95–6.75 (m, 7 H, ArH and Ph$H_{m,p}$), 2.47 (s, 3 H, Ar*Me*), 2.25 (s, 3 H, Ar*Me*) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = ν(CO) 2113.2 cm^{-1}.

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