

Experimental Section

General Procedures. Acetonitrile was distilled from P_2O_5 , and dichloromethane and dichloromethane- d_2 were distilled from CaH_2 . Trifluoroethanol (TFE) and TFE- d_3 were distilled from $CaSO_4$ and a small amount of $NaHCO_3$. 1H , $^{13}C\{^1H\}$ and ^{19}F NMR spectra were recorded on a Bruker Advance DXP 200 instrument.

1H and ^{13}C chemical shifts are reported in ppm relative to tetramethylsilane, with the residual solvent proton resonance as internal standards. ^{19}F chemical shifts are reported in ppm relative to $CFCl_3$. For TFE- d_3 , the solvent fluorine resonance was used as internal standard ($\delta -77.72$). Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany. $Pt(CH_3)_4(\mu-SMe_2)_2$ ¹ and $Pt(C_6H_5)_2(SMe_2)_2$ ² were prepared as described in the literature.

N-N = ArN=CMeCMe=NAr, Ar = 3,5-(CF₃)₂C₆H₃. To a solution of 3,5-bis(trifluoromethyl)aniline (37.20 g, 162.4 mmol) and 2,3-butanedione (6.99 g, 81.2 mmol) in methanol (10 mL) was added formic acid (1 mL). The mixture was stirred for 4 days under slow precipitation of an off-white material. After filtration and washing with cold methanol, the crude product was recrystallized from an ether/pentane mixture to yield the product as pale yellow crystals (10.89 g, 26 %). 1H NMR (200 MHz, chloroform- d) δ 2.16 (s, 6 H, NCM₂MeN), 7.22 (s, 4 H, ArH_o), 7.65 (s, 2 H, ArH_p). $^{13}C\{^1H\}$ NMR (50 MHz, chloroform- d) δ 15.7 (NCMeCMeN), 117.8 ($^3J(^{19}F-C) = 3.8$ Hz, ArC_p), 118.9 (ArC_o), 123.1 ($^1J(^{19}F-C) = 273$ Hz, CF₃), 132.7 ($^2J(^{19}F-C) = 33.5$ Hz, ArC_m), 151.6 (ArC_{ipso}), 169.7 (NCMeCMeN). ^{19}F NMR (188 MHz, chloroform- d) δ -63.5 (s, ArCF₃). Anal. Calcd for C₂₀H₁₂F₁₂N₂: C, 47.26; H, 2.38; N, 5.51. Found: C, 47.84; H, 3.43; N, 6.03. HRMS: m/z 508.0797 (M^+); calcd for C₂₀H₁₂F₁₂N₂, 508.0809.

(N-N)Pt(CH₃)₂ (1). The diimine ligand (1.782 g, 3.505 mmol) was added to a solution of $Pt(CH_3)_4(\mu-SMe_2)_2$ (1.007 g, 1.753 mmol) in toluene (180 mL) and the mixture was stirred overnight. The solvent was removed and the residue was recrystallized from a dichloromethane/pentane mixture. The product was obtained after drying *in vacuo*. Dark violet microcrystals (2.351 g, 91%). 1H NMR (200 MHz, dichloromethane- d_2) δ 1.14 (s, $^2J(^{195}Pt-H) = 87.2$ Hz, 6 H, PtMe), 1.35 (s, 6 H, NCM₂MeN), 7.57 (s, 4 H, ArH_o), 7.89 (s, 2 H, ArH_p). ^{19}F NMR (188 MHz, dichloromethane- d_2) δ -63.14 (s, ArCF₃). Anal. Calcd for C₂₂H₁₈F₁₂N₂Pt: C, 36.03; H, 2.47; N, 3.82. Found: C, 37.21; H, 3.49; N, 4.04.

[(N-N)Pt(CH₃)(OH₂)]⁺(BF₄⁻) (2(BF₄⁻)). To a solution of **1** (123 mg, 0.168 mmol) in dichloromethane (50 mL) was added H₂O (9 μ L, 0.5 mmol). The solution was cooled to -40 °C and a 54% solution of HBF₄ in ether (23 μ L, 0.17 mmol) was added with a syringe. The reaction mixture was stirred for 15 min, during which the dark purple solution was transformed to an orange suspension. The solvent was slowly removed by vacuum transfer while the solution was maintained at -40 °C. The residue was dried *in vacuo* for 15 min at ambient temperature to give the product as an orange powder, more than 95 % pure according to NMR. ¹H NMR (200 MHz, TFE-*d*₃) δ 0.79 (s, ²*J*(¹⁹⁵Pt-H) = 73.3 Hz, 3 H, PtMe), 1.80 (s, 3 H, NCMeC'MeN), 2.05 (s, 3 H, NCMeC'MeN), 7.58 (s, 2 H, ArH_o), 7.71, (s, 2 H, Ar'H_o) 8.00 (s, 2 H, ArH_p and Ar'H_p). ¹H NMR (200 MHz, dichloromethane-*d*₂ with ca. 250 of TFE added, -20 °C) δ 0.62 (s, ²*J*(¹⁹⁵Pt-H) = 73.5 Hz, 3 H, PtMe), 1.81 (s, 3 H, NCMeC'MeN), 2.07 (s, 3 H, NCMeC'MeN), 6.51 (br s, PtOH₂), 7.58 (s, 2 H, ArH_o), 7.70, (s, 2 H, Ar'H_o) 7.96 (s, 2 H, ArH_p and Ar'H_p). ¹⁹F NMR (188 MHz, TFE-*d*₃) δ -151.83 (s, 4 F, BF₄⁻), -63.64 (s, 6 F, ArCF₃), -63.52 (s, 6 F, Ar'CF₃). Anal. Calcd for C₂₁H₁₇BF₁₆N₂OPT: C, 30.64; H, 2.08; N, 3.40. Found: C, 30.89; H, 2.68; N, 3.65.

[(N-N)Pt(CH₃)(NCMe)]⁺(BF₄⁻). To a solution of **1** (300 mg, 0.409 mmol) in 40 mL dichloromethane and 3 mL acetonitrile was added a 54% solution of HBF₄ in ether (56 μ L, 0.41 mmol), and the reaction mixture was stirred for 15 min. The solvent was removed and the residue was washed with several portions of diethyl ether. The product was obtained as an orange powder (301 mg, 87 %) after recrystallization from acetone/diethyl ether and drying *in vacuo*. ¹H NMR (200 MHz, TFE-*d*₃) δ 0.71 (s, ²*J*(¹⁹⁵Pt-H) = 74.5 Hz, 3 H, PtMe), 2.02 (s, 3 H, NCMeC'MeN), 2.10 (s, 3 H, PtNCMe), 2.13 (s, 3 H, NCMeC'MeN), 7.59 (s, 2 H, ArH_o), 7.74, (s, 2 H, Ar'H_o) 8.01 (s, 1 H, ArH_p) 8.04 (s, 1 H, Ar'H_p). ¹⁹F NMR (188 MHz, TFE-*d*₃) δ -152.06 (s, 4 F, BF₄⁻), -63.64 (s, 6 F, ArCF₃), -63.41 (s, 6 F, Ar'CF₃). Anal. Calcd for C₂₃H₁₈BF₁₆N₃Pt: C, 32.64; H, 2.14; N, 4.97. Found: C, 32.77; H, 6.35; N, 5.40.

(N-N)Pt(C₆H₅)₂. A solution of Pt(C₆H₅)₂(SMe₂)₂ (452 mg, 0.954 mmol) and **1** (485 mg, 0.954 mmol) in toluene (50 mL) was stirred at 45 °C for 20 h. The solution was removed and the residue was recrystallized from a dichloromethane/pentane mixture. The product was obtained as dark purple microcrystals (755 mg, 92%). ¹H NMR (200 MHz, dichloromethane-*d*₂) δ 1.82 (s, 6 H, NCMeCMeN), 6.42-6.63 (m, 6H, PhH_m and PhH_p), 6.73 ("d", ³*J*(H-H) = 8.3 Hz, ³*J*(¹⁹⁵Pt-H) = 71.0 Hz, 4H, PhH_o), 7.26 (s, 4 H, ArH_o), 7.60 (s, 2 H, ArH_p). ¹⁹F NMR

(188 MHz, dichloromethane- d_2) δ -63.21 (s, ArCF_3). Anal. Calcd for $\text{C}_{32}\text{H}_{22}\text{F}_{12}\text{N}_2\text{Pt}$: C, 44.82; H, 2.59; N, 3.27. Found: C, 45.10; H, 2.97; N, 4.13.

$[(\text{N-N})\text{Pt}(\text{C}_6\text{H}_5)(\text{NCMe})]^+(\text{BF}_4^-)$. To a solution of $(\text{N-N})\text{Pt}(\text{C}_6\text{H}_5)_2$ (199.2 mg, 0.232 mmol) in acetonitrile (15 mL) was a 54% solution of HBF_4 in ether (35 μL , 0.26 mmol) added with a syringe. The mixture was stirred for 20 minutes. The solvent was removed, and the solid was washed with diethyl ether portions and dissolved in a minimum amount of acetone. The product was obtained as orange crystals (192.5 mg, 91 %) by the addition of diethyl ether. ^1H NMR (200 MHz, $\text{TFE-}d_3$) δ 2.01 (s, 3 H, PtNCMe), 2.14 (s, 3 H, $\text{NCMeC}'\text{MeN}$), 2.28 (s, 3 H, $\text{NCMeC}'\text{MeN}$), 6.65-6.75 (m, 5 H, PhH), 7.27 (s, 2 H, ArH_o), 7.65 (s, 1 H, ArH_p), 7.81 (s, 2 H, $\text{Ar}'\text{H}_o$), 8.07 (s, 1 H, $\text{Ar}'\text{H}_p$). ^{19}F NMR (188 MHz, $\text{TFE-}d_3$) δ -152.01 (s, 4 F, BF_4^-), -63.63 (s, 6 F, ArCF_3), -63.37 (s, 6 F, $\text{Ar}'\text{CF}_3$). Anal. Calcd for $\text{C}_{28}\text{H}_{20}\text{BF}_{16}\text{N}_3\text{Pt}$: C, 37.02; H, 2.22; N, 4.63. Found: C, 37.75; H, 2.58; N, 4.74.

¹ Scott, J.D.; Puddephatt, R.J. *Organometallics* **1983**, 2, 1643.

² Hadj-Bagheri, N.; Puddephatt, R.J. *Polyhedron* **1988**, 7, 2695.