Supplementary Material for Chemical Communications

Unusual Fragmentation of CH_2Cl_2 by an Ir(III) Centre Bonded to a Doubly Metalated Tp^{Ms} Ligand (Tp^{Ms} = Hydrotris(3-mesitylpyrazol-1-yl)borate)

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Supplementary Information

$Tp^{Ms}Ir(\eta^4\text{-}CH_2{=}CHC(Me){=}CH_2)$ (1).

A solution of $[IrCl(coe)_2]_2$ in CH_2Cl_2 (0.116 g, 0.13 mmol, 10 mL) is treated at 20 ºC with an excess of 2-methylbutadiene (0.5 mL) and subsequently with $TlTp^{Ms}$ (0.200 g, 0.26 mmol). Following stirring at room temperature for 36 h, and separation of insoluble TlCl by centrifugation, all volatile components were removed *in vacuo*. Extraction with hexane and crystallization at -20 ºC gave **1** as a yellow microcrystalline solid (0.170 g, 85% yield). The X-ray structure of **1** has been determined and will be reported elsewhere. Selected spectroscopic data: IR(nujol): ν(B-H) 2455 cm^{-1}. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ 86.7 (Cq), 73.2 (CH), 18.0 (Me), 8.0, 5.6 (CH_2) (isoprene

ligand). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ -3.3. Anal. Calcd. For $C_{41}H_{48}BN_6Ir \cdot 1/2\ CH_2Cl_2$: C, 57.6; H, 5.6; N, 9.6. Found: C, 57.9; H, 5.9; N, 9.0.

$Tp^{Ms''}Ir(NCMe)$ (3).

UV photolysis of a solution of 0.25 g (0.3 mmol) of **1** in 10 mL of C_6H_6 for 3 h gave, after removal of the volatiles and washing with hexane, 0.19 g (82% yield) of the dinitrogen adduct **2**. A solution of **2** in NCMe (0.25 g, 0.32 mmol, 2 mL) was heated at 60 ºC overnight. The volatiles were removed under vacuum, and the residue washed with hexane affording 0.21 g of the desired compound **3** (94% yield). Crystallization from a mixture of Et_2O:pentane:CH_2Cl_2 afforded crystals suitable for X-ray studies. Selected spectroscopic data: IR(nujol): ν(B-H) 2465; ν(C≡N) 2290 cm^{-1}. ^1H NMR ($CDCl_3$, 25 ºC): δ 3.71, 2.10 (d, 1 H each, $^2J_{HH}$ = 11.1 Hz, $IrCH_2$), 2.73, 1.95 (d, 1 H each, $^2J_{HH}$ = 10.8 Hz, $IrCH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ 3.4 (NC*Me*), -0.3, -1.1 (Ir-CH_2). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ -3.1.

$Tp^{Ms'}IrCl(=C(H)pz^{Ms})$ (5).

The chlorocarbene compound **4** was generated from **3** (0.050 g, 0.065 mmol) dissolved in 3 mL of CH_2Cl_2 by heating at 80 ºC for 0.5 h. The resulting solution was reacted with 1 equiv of 3-mesitylpyrazol to give compound **5** as an orange microcrystalline solid, which can be chromatographied on SiO_2. Crystallization from Et_2O:pentane:CH_2Cl_2 gave crystals suitable for X-ray studies. Selected spectroscopic data: IR(nujol): ν(B-H) 2485 cm^{-1}. ^1H NMR ($CDCl_3$, 25 ºC): δ 15.34 (s, 1 H, Ir=C*H*pz^{Ms}), 4.43, 2.25 (d, 1 H each, , $^2J_{HH}$ = 11.7 Hz, $IrCH_2$. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ 231.5 (Ir=*C*Hpz^{Ms}), 2.5 (Ir-CH_2). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ -3.0.