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Oxidatively induced metal–carbon bond cleavage reactions in iridium dimethyl complexes: formation of cationic pyridine and nitrosyl iridium(III) alkyl derivatives

Pietro Diversi [a,]*, Valentina Ermini [a], Giovanni Ingrosso [a], Antonio Lucherini [a], Calogero Pinzino [b], Franco Simoncini [a]

[a] *Dipartimento di Chimica e Chimica Industriale dell'Università di Pisa, Via Risorgimento 35, 56126, Pisa, Italy*
[b] *Istituto di Chimica Quantistica ed Energetica Molecolare del CNR, Via Risorgimento 35, 56126, Pisa, Italy*

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Abstract

Reaction of $[Ir(Me)_2Cp^*(L)]$ complexes ($Cp^* = \eta^5$-C_5Me_5; L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3) with equimolar amounts of $[FeCp_2]^+$ in pyridine gives methane and the corresponding cationic derivatives $[Ir(Me)Cp^*(L)(pyridine)]^+$. Reaction with an excess of $NOBF_4$ yields methane and $[Ir(Me)Cp^*(L)(NO)]^{2+}$ (L = PMe_3, PMe_2Ph, $PMePh_2$) or $[Ir(Me)_2Cp^*(NO)]^+$ and $[Ir(Me)Cp^*(L)_2]^+$ (L = PPh_3) via the formation of the primary oxidation products $[Ir(Me)_2Cp^*(L)]^+$, which have been detected by EPR spectroscopy. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Iridium–carbon bond cleavage; Electron transfer behaviour; EPR spectroscopy

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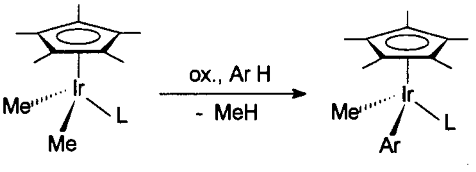
We have recently reported [1] that the complexes $[Ir(Me)_2Cp^*(L)]$ ($Cp^* = \eta^5$-C_5Me_5; L = PPh_3 (**1a**), $PMePh_2$ (**1b**), PMe_2Ph (**1c**), PMe_3 (**1d**)) react with a variety of substituted arenes (including the phenyl substituents of the phosphine ligands) in the presence of catalytic amounts of one-electron oxidants (ETC catalysis) to give methane and the corresponding methyl aryl complexes $[Ir(Me)(Ar)Cp^*(L)]$ (Scheme 1).

In all cases methane is formed by C–H bond activation of the Cp* methyl group with subsequent H abstraction from the solvent.

These 'σ-metathesis reactions' [2] of Ir–Me and C–H aromatic bonds are entirely unexpected since when **1a**–**1d** are oxidized under different conditions no C–H activation products are observed. For instance, the electrochemical one-electron oxidation of **1a** in CH_2Cl_2 gives the unstable species $\mathbf{1a}^+$ [1](b), whereas the chemical oxidation of **1a** in a polar solvent (acetonitrile) yields $[Ir(Me)Cp^*(PPh_3)(MeCN)]^+$ [3]. Such a different



1a - 1d

L = PPh_3 **1a**, $PMePh_2$ **1b**, PMe_2Ph **1c**, PMe_3 **1d**

ox. = $FeCp_2^+$, Ag^+

Scheme 1.

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* Corresponding author. Tel.: +39 50 918225; fax: +39 50 918260; e-mail: div@dcci.unipi.it

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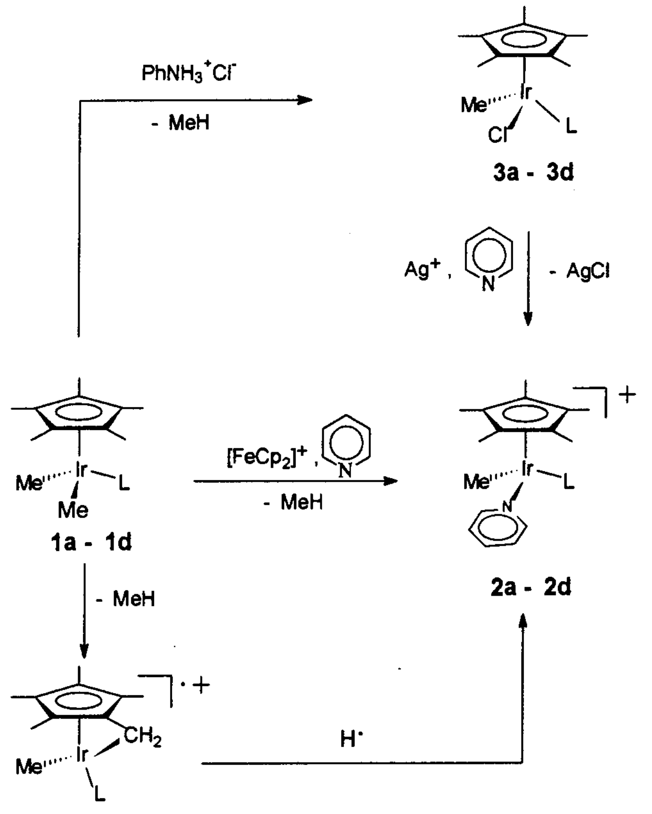


Scheme 2.

reactivity illustrates quite well the unusual sensitivity of the oxidation reactions of **1a**–**1d** to the experimental conditions [1](b); [4], and has stimulated further research.

In the course of this study we met with some oxidatively induced stoichiometric iridium–carbon cleavage reactions, which allow further insight in the above C–H activation reactions, and provide a route to new pyridine and nitrosyl cationic derivatives of iridium(III).

On reacting **1a**–**1d** with pyridine in the presence of $[FeCp_2]PF_6$, no catalytic activation of pyridine C–H bonds is observed, instead the cationic methyl derivatives $[Ir(Me)Cp^*(L)(pyridine)]^+$ (L = PPh_3 **2a**, $PMePh_2$ **2b**, PMe_2Ph **2c**, PMe_3 **2d**) [5] are produced together with methane (Scheme 2).

By using equimolar amounts of oxidant **2c** and **2d** are formed in almost quantitative yields and have been isolated, while **2a** and **2b** have been only detected by ^{1}H-NMR spectroscopy as the pyridine-d_5 derivatives. The reaction has been found to require 1–75 h by ^{1}H-NMR monitoring, depending on the nature of the phosphine ligand (see ref. [5]). Structural assignment was done on the basis of elemental analysis (**2c** and **2d**), ^{1}H-NMR spectroscopy, and confirmed by the synthesis of the hexafluorophosphate salts by treatment of **1a**–**1d** with equimolar amounts of anilinium chloride to give the corresponding complexes $[Ir(Me)(Cl)Cp^*(L)]$ **3a**–**3d** [6], and by subsequent reaction with $AgPF_6$ in pyridine (Scheme 2).

It is interesting to note that, when the oxidation of **1a**–**1d** is carried out in deuteriated pyridine, only CH_4 (δ 0.10) is evolved as monitored by ^{1}H-NMR spectroscopy. Therefore, hydrogen is abstracted from one of the ligands in the coordination sphere of iridium, most probably from the Cp* to give the same 'tucked-in' intermediate [2](c) (Scheme 2) already proposed for explaining the formation of CH_4 in addition to CH_3D in the activation of aromatic C–D bonds by **1a**–**1d** under ETC catalysis. Then this intermediate may abstract D from the solvent to restore the η^5-C_5Me_5 ligand.

1a–**1d** have been also reacted with $NOBF_4$. The reaction can be conveniently studied by EPR spectroscopy, carrying out the reaction in the cavity of the spectrometer [7]. The resulting one-electron oxidation products **1a**$^+$–**1d**$^+$ have been detected at low temperature (183 K) where single line spectra at $g = 1.931$ (**1a**$^+$), 1.939 (**1b**$^+$), 1.942 (**1c**$^+$) and 1.943 (**1d**$^+$) are observed. Lowering the temperature to 113–123 K, the spectra appear as structured signals, as shown in Fig. 1, where the spectrum of **1d**$^+$ is reported as an example.

1a$^+$–**1d**$^+$ exhibit anisotropic behaviour, with well separated components of a recognizably axial spectrum implying metal-centred character. Hyperfine splitting of the perpendicular absorption into a quartet is attributable to spin-coupling to the iridium nucleus (^{191}Ir, 37%; ^{193}Ir, 63%: both $I = 3/2$). However, computer simulations by spectral optimization software [8] show that the spectra are better interpreted as corresponding to rhombic EPR symmetry ($g_1 \neq g_2 \neq g_3$; $A_1 \neq A_2 \neq A_3$; all tensor axes coincident) where g_1 and g_2, because of the linewidths of the resonances, are overlapping (see Table 1 and Fig. 1). Although in principle the associated geometry is in contrast with that one could have

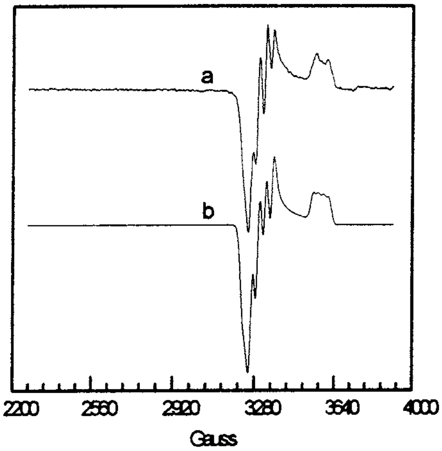


Fig. 1. EPR spectrum of the species deriving from the reaction of $Ir(Me)_2Cp^*(PMe_3)$ (**1d**) with $NOBF_4$ in CH_2Cl_2. (a) Observed spectrum; (b) simulated spectrum.

Table 1
X-band EPR parameters of the **1a**$^+$–**1d**$^+$ species generated by oxidation of **1a**–**1d** with NOBF$_4^a$

Species	g_1	g_2	g_3	$\langle g \rangle$	A_1(G)	A_2(G)	A_3(G)
1a$^+$	2.067	2.033	1.879	1.993	23.46	30.77	26.07
1b$^+$	2.011	1.975	1.830	1.939	19.09	30.71	24.01
1c$^+$	2.009	1.977	1.830	1.939	20.10	29.60	24.75
1d$^+$	2.013	1.979	1.831	1.941	18.08	30.42	22.42

[a] Spectra recorded at 113 K in the case of **1a**$^+$ e **1d**$^+$; at 123 K in the case of **1b**$^+$ e **1c**$^+$.

expected, small distortions could be sufficient to make all of the axes of g and A coincident.

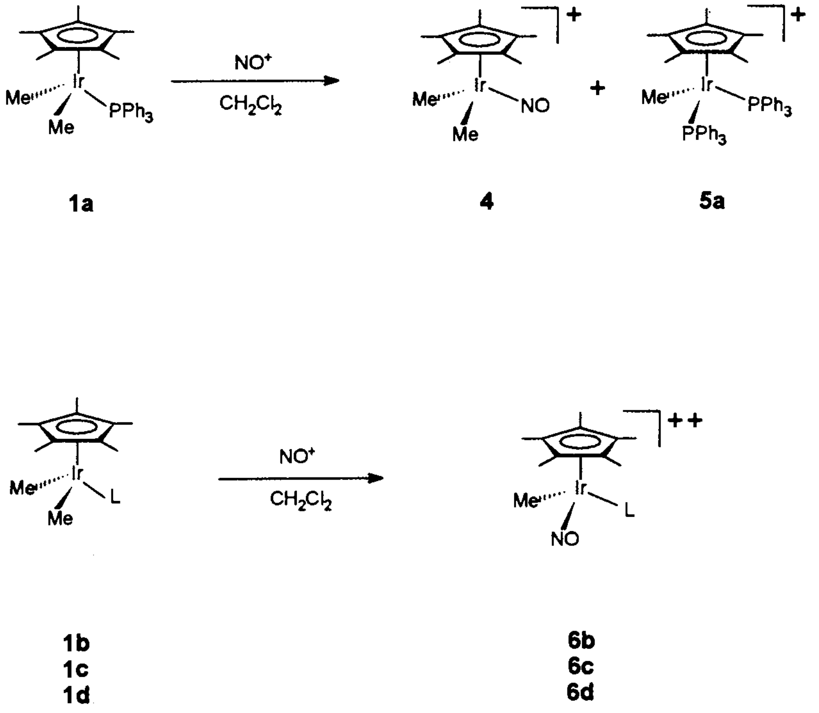
On raising the temperature, the EPR signals decrease in intensity disappearing in the −30–0°C range (depending on the nature of the phosphine). By carrying out the reaction on a preparative scale at room temperature, by using a NO$^+$/Ir ratio = 2, methane is evolved, and a mixture of the cationic nitrosyl derivative [Ir(Me)$_2$Cp*(NO)]$^+$ (**4**) and [Ir(Me)Cp*(PPh$_3$)$_2$]$^+$ (**5a**) is formed from **1a**, while the dicationic nitrosyl derivatives [Ir(Me)Cp*(L)(NO)]$^{2+}$ (L = PMePh$_2$ (**6b**), PMe$_2$Ph (**6c**), PMe$_3$ (**6d**)) are formed from **1b, 1c** and **1d** respectively (Scheme 3) [9]

The IR spectra show for all the nitrosyl complexes strong NO absorptions at very high frequencies (1909–1843 cm^{-1}), pointing to a linear Ir–NO$^+$ arrangement.

In the case of **1b**–**1d** the reaction is quite sensitive to the NO$^+$/Ir ratio: actually when a 1/1 ratio is used, the dications are not obtained, instead complex reaction mixtures are obtained which contain **4** (by ^{1}H-NMR).

By reaction of **1a**–**1d** in deuteriated solvents, CH$_4$ is formed exclusively (δ 0.20 in dichloromethane-d_2, δ 0.14 in benzene-d_6, δ 0.16 in nitromethane-d_3) as in the case of the oxidation reactions with [FeCp$_2$]$^+$ in pyridine. Moreover, the ^{2}H-NMR spectrum of **6d** shows the presence of deuterium on the Cp* ligand (nitromethane-d_3, δ 2.08). This clearly shows that the loss of methane occurs intramolecularly and that the resulting intermediate [2](c) on its turn abstracts D from the solvent.

As for the origin of the nitrosyl derivatives, EPR spectroscopic evidences are consistent in all cases with the hypothesis of the formation of the primary oxidation products **1a**$^+$–**1d**$^+$ as the first step. Then there are two possible reaction patterns, depending on the nature of the phosphine: the loss of triphenylphosphine (in the case of **1a**$^+$) or the loss of methane followed by coordination of NO. According to this picture, the **1a**→**4** reaction should involve the phosphine substitution by NO in the transient oxidation product **1a**$^+$, rather than



Scheme 3.

the more common phosphine substitution by NO^+ in **1a** (as suggested in the literature [10] for similar cases).

The above oxidatively induced cleavage reactions of the Ir–Me bonds of **1a**–**1d** result in the formation of methane via the C–H activation of the Cp* group with subsequent H abstraction from the solvent, the organometallic fragment being trapped by the nitrogen ligand (pyridine or NO^+). Then such reactions appear to mimic the early mechanistic steps which are at the basis of the activation of arenes by **1a**–**1d** under electron transfer catalysis, where, in the absence of strong coordinating agents as pyridine or NO, the aryl radicals deriving from the aromatic solvent enter the coordination sphere of the metal [1].

Finally the reaction of **1a**–**1d** with $NOBF_4$ opens the route to a new class of alkyl nitrosyl complexes, a topic which has recently received much attention in the literature in the last 10 years [11].

Acknowledgements

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[5] General procedure for the preparation of **2a**–**2d**: To a solution of **1** in pyridine an equimolar amount of $[FeCp_2]PF_6$ was added to give a red/brown solution. After the reaction was over (**2a**, 75 h; **2b**, 70 h; **2c**, 24 h; **2d**, 1 h) the solvent was removed under reduced pressure, and the residue was purified by precipitation from dichloromethane/diethyl ether to give **2** as a beige solid. **2a**: ^{1}H-NMR (C_5D_5N): δ 0.89 (3 H, d, $J_{HP} = 6.4$ Hz, IrMe), 1.23 (15 H, d, $J_{HP} = 1.8$ Hz, C_5Me_5), 7.00–7.50 (15 H, m, PPh_3). **2b**: ^{1}H-NMR (C_5D_5N): δ 0.73 (3 H, d, $J_{HP} = 6.3$ Hz, IrMe), 1.33 (15 H, d, $J_{HP} = 1.8$ Hz, C_5Me_5), 1.94 (3 H, d, $J_{HP} = 9.3$ Hz, $PMePh_2$), 7.15–7.50 (15 H, m, $PMePh_2$). **2c**: Analysis Found: C, 51.25; H, 6.02; N, 2.35. $C_{24}H_{34}IrNP$ Calc.: C, 51.41; H, 6.12; N, 2.50%. ^{1}H-NMR (C_5D_5N): δ 0.65 (3 H, d, $J_{HP} = 6.9$ Hz, IrMe), 1.29 (15 H, d, $J_{HP} = 1.9$ Hz, C_5Me_5), 1.49 (3 H, d, $J_{HP} = 9.9$ Hz, PMe_2Ph), 1.62 (3 H, d, $J_{HP} = 9.9$ Hz, PMe_2Ph). ^{1}H-NMR (CD_2Cl_2): δ 0.70 (3 H, d, IrMe), 1.43 (15 H, d, C_5Me_5), 1.54 (3 H, d, PMe_2Ph), 1.72 (3 H, d, PMe_2Ph), 7.30–7.60 (7 H, m, $H_m + PMe_2Ph$), 7.88 (1 H, ddt, $J_{HH} = 7.6$ Hz, H_p), 8.40 (2 H, dd, $J_{HH} = 6.2$ Hz, H_o). **2d**: Analysis Found: C, 45.62; H, 6.21; N, 2.41. $C_{19}H_{32}IrNP$ Calc.: C, 45.77; H, 6.47; N, 2.81%. ^{1}H-NMR (C_5D_5N): δ 0.51 (3 H, d, $J_{HP} = 7.3$ Hz, IrMe), 1.26 (9 H, d, $J_{HP} = 10.0$ Hz, PMe_3), 1.39 (15 H, d, $J_{HP} = 1.8$ Hz, C_5Me_5). ^{1}H-NMR (CD_2Cl_2): δ 0.60 (3 H, d, IrMe), 1.40 (9 H, d, PMe_3), 1.58 (15 H, d, C_5Me_5), 7.41 (2 H, ddd, H_m), 7.90 (1 H, ddt, H_p), 8.35 (2 H, dd, H_o). ^{1}H-NMR (CD_3COCD_3): δ 0.67 (3 H, d, IrMe), 1.52 (9 H, d, PMe_3), 1.66 (15 H, d, C_5Me_5), 7.55 (2 H, ddd, H_m), 8.08 (1 H, ddt, H_p), 8.65 (2 H, dd, H_o). ^{31}P-NMR (CD_2Cl_2): δ -32.12.

[6] (a) **3a** [6c] **3b** [6c] and **3d** [6b] were already reported in the literature, **3c** is a new compound which has been prepared by a similar procedure. **3c**: Analysis found: C, 44.02; H, 5.21. $C_{19}H_{29}IrClP$ Calc.: C, 44.17; H, 5.66%; ^{1}H-NMR (C_6D_6): δ 1.21 (3 H, d, $J_{HP} = 6.4$ Hz, IrMe), 1.29 (15 H, d, $J_{HP} = 1.9$ Hz, C_5Me_5), 1.32 (3 H, partially obscured d, PMe_2Ph), 1.64 (3 H, d, $J_{HP} = 10.5$ Hz, PMe_2Ph), 7.00–7.12 (3 H, bm, Ph), 7.52–7.64 (2 H, bm, Ph). ^{1}H-NMR (CD_3COCD_3): δ 0.75 (3 H, d, IrMe), 1.43 (15 H, d, C_5Me_5), 1.66 (3 H, d, $J_{HP} = 10.6$ Hz, PMe_2Ph), 1.70 (3 H, d, PMe_2Ph), 7.40–7.50 (3 H, bm, Ph), 7.72–7.84 (2 H, bm, Ph). (b) J.M. Buchanan, J.M. Stryker, R.G. Bergman, J. Am. Chem. Soc. 108 (1986) 1537. (c) D.S. Glueck, R.G. Bergman, Organometallics 10 (1991) 1479.

[7] EPR spectra were obtained by using an EPR Varian E 112 instrument equipped with an Oxford EPR 900 for temperature control. The spectrometer was interfaced to a PC 486/100 MHz by means of an acquisition board.

[8] (a) The software was provided by the Illinois EPR Research Center, NIH Division of research, Resonances Grant. No RR01811. (b) K.J. Mattson, R.B. Clarkson, R.L. Belford, 11th International EPR Symposium, 30th Rocky Mountains Conference, Denver, Colorado, August 1988.

[9] **1a** (0.05 g, 0.081 mmol) was dissolved in CH_2Cl_2 (5 ml) and added with $NOBF_4$ (0.010 g, 0.081 mmol). Methane (δ 0.20, dichloromethane-d_2) evolved and the colour changed from light yellow to golden yellow. After stirring for 3 h, the solvent was evaporated to dryness; the residue was repeteadly washed with benzene and dried under vacuum to give a mixture (0.029 g) of **4** (64%) and **5a** (36%). By fractional crystallization from acetone, pure **4** and **5a** were obtained. **4**: Analysis found: C, 30.05; H, 4.40. $C_{12}H_{21}BF_4IrNO$ Calc.: C, 30.31; H, 4.45%; IR (Nujol, cm^{-1}) 1843 (s, NO), 1054 (s, BF); ^{1}H-NMR (CD_3COCD_3): δ 1.81 (6 H, s, IrMe), 2.25 (15 H, s, C_5Me_5). ^{1}H-NMR (CD_2Cl_2): δ 1.71 (6 H, s, IrMe), 2.14 (15 H, s, C_5Me_5); IS-MS (MeOH), *m/e*: 386 $[M]^+$, 370 $[M-MeH]^+$, 340 $[M-MeH-NO]^+$, 326 $[IrC_5Me_5]^+$, 87 $[BF_4]^-$. **5a**: Analysis found: C, 58.91; H; 4.91. $C_{47}H_{48}BF_4IrP_2$ Calc.: C, 59.10; H, 5.07%; IR (Nujol, cm^{-1}) 1062 (BF_4); ^{1}H-NMR (CD_3COCD_3): δ 1.26 (15 H, t, $J_{HP} = 2.2$ Hz, C_5Me_5), 1.56 (3 H, t, $J_{HP} = 4.9$ Hz, IrMe). ^{1}H-NMR (CD_2Cl_2): 1.19 (15 H, t, C_5Me_5), 1.50 (3 H, t, IrMe); IS-MS (MeOH), *m/e*: 866 $[M]^+$, 603 $[M-PPh_3]^+$, 587 $[M-PPh_3-CH_4]^+$. **5a** was also prepared by reaction in a NMR tube of $[Ir(Me)(Cl)Cp^*(PPh_3)]$ with $AgBF_4$ in the presence of PPh_3 in CD_2Cl_2, its ^{1}H-NMR spectrum being identical to that of **5a** prepared as above. **6b**: **1b** (0.1 g, 0.18 mmol) in CH_2Cl_2 (5 ml) was added with $NOBF_4$ (0.042 g, 0.36 mmol). The reaction mixture was stirred at room temperature for 3 h. Methane was evolved and a deep orange solid was formed, which was washed repeteadly with CH_2Cl_2 and C_6H_6, and then dried under vacuum. **6b** was obtained as a maroon hygroscopic solid (0.071 g, 53%). Analysis found: C, 36.98; H, 1.71; N, 3.83. $C_{24}H_{31}B_2F_8IrNOP$ Calc.: C, 38.54; H, 1.87; N, 4.18%; IR (Nujol, cm^{-1}) 1900 (s, NO), 1059 (BF); ^{1}H-NMR (CD_3COCD_3): δ 2.25 (3 H, d, $J_{HP} = 4.8$ Hz, IrMe), 2.30 (15 H, d, $J_{HP} = 1.9$ Hz, C_5Me_5), 2.96 (3H, d, $J_{HP} = 11.6$ Hz, PMe), 7.7–8.2 (10 H, bm, Ph); ^{1}H-NMR (CD_3CN): δ 2.02 (3 H, d, IrMe), 2.09 (15 H, d,

C_5Me_5), 2.55 (3H, d, PMe), 7.3–7.65 (10 H, bm, Ph). IS-MS, *m*/*e*: 585 $[M-NO^+ + MeCN]^+$, 543 $[M-NO^+]^+$, 527 $[M-NO^+ -MeH]^+$, 286 $[M]^{2+}$, 263 $[M-MeNO]^{2+}$, 87 $[BF_4]^-$. **6c**: maroon hygroscopic solid prepared as above in 56% yield. Analysis found: C, 32.87; H, 4.56; N, 1.18. $C_{19}H_{29}B_2F_8IrNOP$ Calc.: C, 33.28; H, 4.27; N, 2.04%.; IR (Nujol, cm^{-1}) 1899 (s, NO), 1057 (BF); ^1H-NMR (CD_3COCD_3): 2.28 (15 H, d, $J_{HP} =$ 2.1 Hz, C_5Me_5), 2.36 (3 H, d, $J_{HP} = 5.3$ Hz, IrMe), 2.56 (3H, d, $J_{HP} = 12.5$ Hz, PMe), 2.54 (3 H, d, $J_{HP} = 11.9$ Hz, PMe); IS-MS (MeCN), *m*/*e*: 520 $[M-NO^+ + MeCN]^+$, 479 $[M-NO^+]^+$, 463 $[M-NO^+ -MeH]^+$, 273 $[M-MeNO + 2MeCN]^{2+}$, 254.7 $[M]^{2+}$, 87 $[BF_4]^-$. **6d**: deep orange solid, prepared as above in 60% yield. Analysis found: C, 26.6; H, 4.5; N, 2.2. $C_{14}H_{27}B_2F_8IrNOP$ Calc.: C, 26.0; H, 4.4; N, 2.2%. IR (Nujol, cm^{-1}) 1903 (s, NO), 1056 (s, BF); ^1H-NMR (CD_3COCD_3): δ 2.28 (9 H, d, $J_{HP} = 12.6$ Hz, PMe), 2.31 (3 H, d, $J_{HP} = 6.2$ Hz, IrMe), 2.53 (15 H, d, $J_{HP} = 1.9$ Hz, C_5Me_5); ^1H-NMR (CD_3CN): δ 1.97 (9 H, d, PMe), 2.05 (3 H, d, IrMe), 2.28 (15 H, d, C_5Me_5); IS-MS (MeCN), *m*/*e*: 460 $[M-NO^+ + MeCN]^+$, 446 $[M-H^+]^+$, 417 $[M-NO^+]^+$, 401 $[M-NO^+ -MeH]^+$, 224 $[M]^{2+}$, 87 $[BF_4]^-$.

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