Redox-active Organometallic Ir Complexes containing Biphenyl-2,2′-diyl

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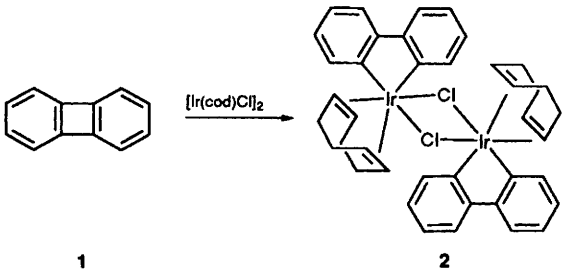
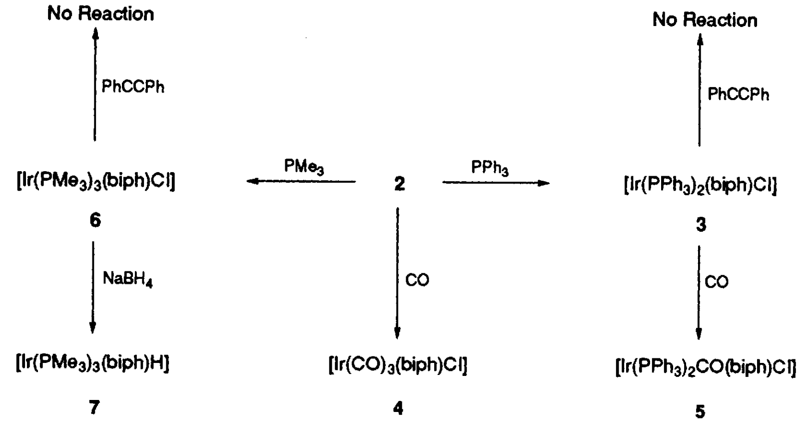
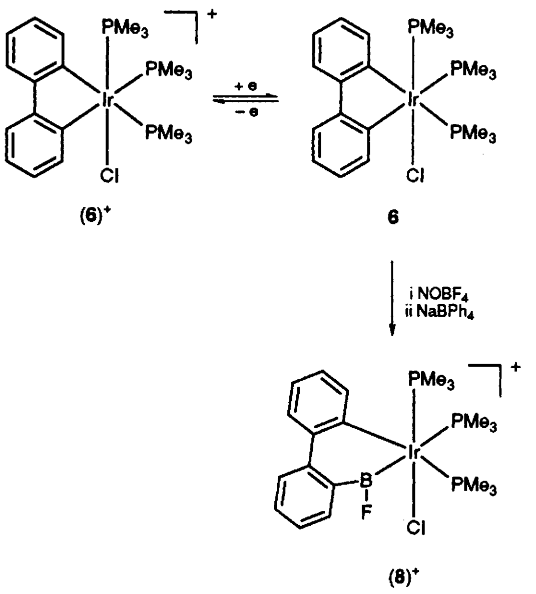
The redox-active complexes [Ir(PPh$_3$)$_2$(biph)Cl] **3** and [Ir(PMe$_3$)$_3$(biph)Cl] **6** contain biphenyl-2,2-diyl (biph), the organometallic analogue of bipy; **3** shows an unexpected five-coordinate structure lying between T and Y geometry and oxidation of **6** by NOBF$_4$ gives [Ir(PMe$_3$)$_3$(biphBF)Cl]$^+$ (**8**)$^+$, an unprecedented Ir^{IV} boryl complex.

Organotransition metal chemistry has been developed largely with cyclopentadienyl or carbonyl groups as the stabilizing C-based ligands.[1] Complexes of 2,2′-dipyridyl (bipy) are often redox active,[2] but the redox chemistry of the C-analogue, biphenyl-2,2′-diyl, or biph, has not been studied in detail, although the ligand itself has been known for many years.[3–5]

Biphenylene **1** reacts with [Ir(cod)Cl]$_2$ (90 °C, 2 h, CH$_2$Cl$_2$, sealed tube) to give [Ir(cod)(biph)Cl]$_2$ (**2**, 89%, Scheme 1) as a yellow powder in a known[4] type of C–C cleavage reaction. Addition of PPh$_3$ (2.0 mol., 20 °C, 5 h, CH$_2$Cl$_2$) produces







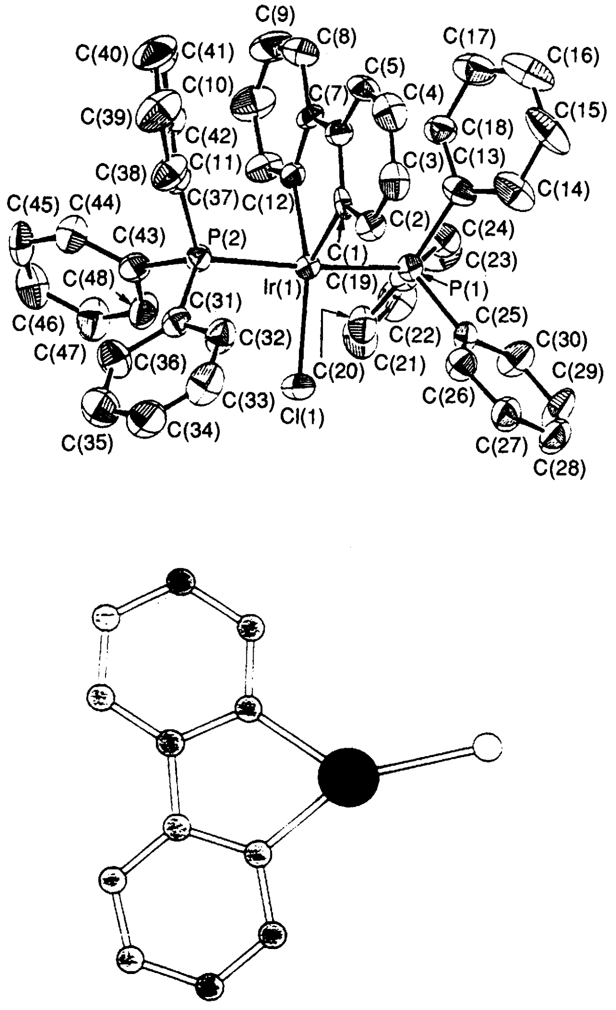


Fig. 1 ORTEP drawing of [Ir(PPh_3)$_2$(biph)Cl] **3** with the (biph)IrCl fragment in insert. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Ir–Cl 2.384(4), Ir–P(1) 2.342(4), IrP(2) 2.334(4), Ir–C(1) 2.01(1), Ir–C(12) 1.99(2). Selected bond angles (°): Cl–Ir–P(1) 93.1(1), Cl–Ir–P(2) 90.2(1), Cl–Ir–C(1) 132.4(5), Cl–Ir–C(12) 150.9(5), P(1)–Ir–P(2) 173.6(2). Selected bond distances and bond angles are for one of two independent molecules in the same unit cell.

[Ir(PPh_3)$_2$(biph)Cl] (**3**, 90%, Scheme 2) as red crystals. The ring-opened structure was confirmed by X-ray crystallography† (Fig. 1). The structure is distorted because the two C–Ir–Cl angles differ significantly (132.4 and 150.9°).

Biph is stable to a variety of common reagents and the {Ir(biph)} group remains unchanged even on treatment with CO, PhCCPh, PR_3 or $NaBH_4$ (Scheme 2). Reaction of **2** with CO gives [Ir(CO)$_3$(biph)Cl] [**4**, ν(CO) = 2155, 2116, and 2092 cm^{-1}] but the CO insertion product fluorenone is not formed, even on heating (CH_2Cl_2, 90 °C). **3** does not react with H_2 or PPh_3, but rapidly reacts with CO (Scheme 2) at 20–60 °C to form [Ir(PPh_3)$_2$(biph)(CO)Cl] **5** [ν(CO) = 2001 cm^{-1}]. PMe_3 does not displace biph from **2**, but forms [Ir(PMe_3)$_3$(biph)Cl] (**6**, 78%) as a white powder (CH_2Cl_2, room temp., 2 h). ^{31}P NMR (δ −42.29, *d*, 2P; −54.70, *t*, 1P) suggests a *fac* arrangement of the three PMe_3 ligands in **6**. When **6** is treated with $NaBH_4$ (CH_2Cl_2–EtOH, 90 °C, 5 h), [Ir(PMe_3)$_3$(biph)H] (**7**, 68%) is obtained in which the hydride is *cis* to both biph Ir–C bonds as shown by ^1H NMR (Ir–H, δ −11.05, *J*(H,P *trans*) 133 Hz, *J*(H,P *cis*) 22.7 Hz). Reductive elimination of Ir–C with the *cis*-hydride is not observed. Unlike most other unsaturated metallacyclic complexes, cyclo-trimerization does not take place when **3** and **6** were treated with PhCCPh (CH_2Cl_2, 85 °C).

The quasi-reversible electrochemical reduction of [Pt(biph)(bipy)] has been briefly reported.[5] Many of the complexes in

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† *Crystal data* for **3**: $C_{96}H_{76}Cl_2P_4Ir_2$, M = 108.90 (there are two independent but essentially identical $C_{48}H_{38}ClP_2Ir$ molecules in the unit cell) monoclinic, space group $P2_1/c$, a = 23.259(2), b = 18.955(2), c = 19.096(2) Å, β = 114.143(9)°, V = 7682(3) Å^3, Z = 4, Mo-Kα λ = 0.71069 Å, D_c = 1.56 g cm^{-3}. There were 13948 unique reflections collected with $2\theta \leqslant 50°$; of those reflections, 8026 with $I \geqslant 3\sigma(I)$ were adjudged observed. The final residuals for 937 variables refined with 8026 data points were R = 3.5% and R_w = 3.9%

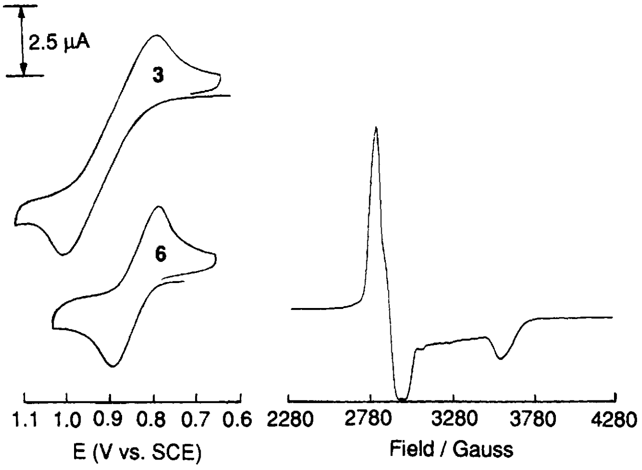

Fig. 2 Comparative cyclic voltammetry of 1.0 × 10^{-3} mol dm^{-3} [Ir(PPh$_3$)$_2$(biph)Cl] **3** and 3.0 × 10^{-4} mol dm^{-3} [Ir(PMe$_3$)$_3$(biph)Cl] **6** and the X-band EPR spectrum of [Ir(PMe$_3$)$_3$(biph)Cl]$^+$ [**6**]$^+$ at 7 K

our study, however, undergo quasi-reverisble oxidation (Fig. 2); for example, the cyclic voltammogram (CV) of **6** showed a quasi-reversible (ΔE = 108 mV) wave at 836 mV *vs.* saturated calomel reference electrode (SCE).‡ The resulting Ir^{IV} species, which can also be generated by bulk electrolysis, has been detected by its strong EPR resonances (g_x = 2.37, g_y = 2.28, g_z = 1.84, Fig. 2). The reversibility of the CV suggests that this Ir^{IV} cation can be formulated as [Ir^{IV}(PMe$_3$)$_3$(biph)Cl]$^+$, (**6**)$^+$ (Scheme 3). **3** and **5** have very similar quasi-reversible one-electron oxidation waves (only **3** is shown in Fig. 2) at 950 and 1120 mV, respectively, but in these cases the Ir^{IV} products were not stable enough for detection by EPR.

Complex (**6**)$^+$ could not be obtained in a crystalline form. A solution containing **6** and NOBF$_4$, after isolation with NaBPh$_4$ (Scheme 3), gave the new complex [Ir(PMe$_3$)$_3$Cl(biphBF)]$^+$ (**8**)$^+$ (46%), having different EPR signals (g_{xy} = 2.15 and g_z = 1.96) from those of **6**$^+$. The X-ray§ crystal structure of (**8**)$^+$ (Fig. 3) shows it to be an Ir^{IV} organometallic boryl compound with a BF unit inserted into one of the Ir–C bonds. This insertion may take place *via* electrophilic attack of BF$_3$ on the Ir–C bond. Organometallic Ir^{IV} complexes are not common,[6] and no Ir^{IV} boryl compounds have been reported.[7] As expected, the boryl group (Ir–BF–C) is planar. The key evidence for the presence of an inserted BF group comes from the high resolution mass spectroscopy. The spectrum confirms the formulation both from the mass of the molecular ion peak of (**8**)$^+$ (638.1344, obs.; 638.1347, calc.) and from its characteristic seven-line isotope pattern (computer matched), which cannot be accommodated by any other group.

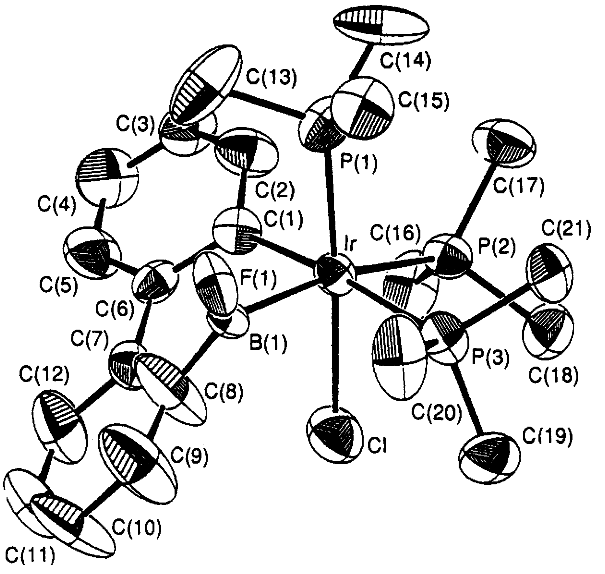

Fig. 3 ORTEP drawing of [Ir(PMe$_3$)$_3$Cl(biphBF)]$^+$ [**8**]$^+$. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Ir–Cl 2.504(4), Ir–P(1) 2.333(4), Ir–P(2) 2.348(3), Ir–P(3) 2.432(3), Ir–C(1) 2.07(1), Ir–B(1) 2.00(1), B(1)–C(8) 1.47(2), F–B(1) 1.09(1). Selected bond angles (°): Cl–Ir–P(1) 176.5(1), Cl–Ir–P(2) 78.9(1), Cl–Ir–P(3) 87.6(1), Cl—Ir–C(1) 88.7(4), Cl–Ir–B(1) 87.3(5), P(1)–Ir–P(2) 102.6(1), P(1)–Ir–P(3) 95.5(1), C(1)–Ir–P(1) 88.2(4), B(1)–Ir–P(1) 90.9(5), Cl–Ir–B(1) 86.7(5), B(1)–Ir–P(2) 165.5(4), Ir–B(1)–F(1) 118(1), Ir–B(1)–C(8) 114(4), F(1)–B(1)–C(8) 127(2).

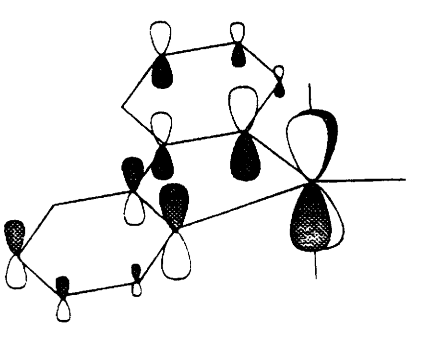

Fig. 4 The key orbital interaction in [Ir(PPh$_3$)$_2$(biph)Cl] **3**, derived from EHT studies

Unlike complexes of most other unsaturated metallacycles,[7] our biph complexes can also be catalytically active because of the stability of the [Ir(biph)] group. As we report in more detail elsewhere,[8] **6** is an active catalyst for the unusual head-to-head dimerization of terminal alkynes.

The equatorial groups in five-coordinate 16e d^6 systems normally take up a Y or T shape.[9] π-donors like Cl favour the Y structure, but in **3** we see a structure intermediate between Y and T. EHT calculations[10] on **3** show that the rigid angular constraint of the biph ligand leads to an unexpected geometrical preference for the Cl lying off the C_2 axis (calc., 23° away from the Y-shape; obs., 10.3°). The calculations also suggest an origin for the easy oxidation of **3**. The highest filled π-level of biph has an antibonding interaction with the M(d_{yz}) which results in a high lying HOMO with predominant metal character (Fig. 4); similar interactions also occur in **6**.

In conclusion, the biph system seems suitable for use as a stabilizing ligand in organometallic chemistry, where it can promote redox and catalytic activities in its metal complexes.

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‡ Cyclic voltammetry on **3** and **6** was carried out in CH$_2$Cl$_2$ solution with 0.1 mol dm^{-3} TBAP as supporting electrolyte and a saturated calomel reference electrode (SCE). We used 3.0 mm glassy carbon disk as the working electrode and a Pt wire as the counter electrode. The scan rate was 100 mV^{-1} s.

§ *Crystal data* for [**8**][BPh$_4$]: $C_{45}H_{55}B_2FP_3ClIr$, M = 957.14, monoclinic, space group $P2_1/n$, a = 9.689(2), b = 35.555(6), c = 12.576(2) Å, β = 94.44(1)°, V = 4320(2) Å^3, Z = 4, Mo-Kα λ = 0.71069 Å, D_c = 1.472 g/cm^3. The final cycle of refinement was based on 4459 observed reflection ($I \geqslant 3\sigma(I)$) and 478 variable parameters and converged with R = 5.1% and R_w = 6.1%. The C$_6$H$_4$B–F group shows unusually large anisotropic thermal ellipsoids probably owing to conformational flexibility of the metallacycle. This leads to an artificially short B–F distance of 1.09 Å, which should not be regarded as well determined. No disorder model we tried was satisfactory. The BPh$_4$ counter ion is not shown. Atomic coordinates, bond lengths and angles, and thermal parameters for both compounds **3** and **8** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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