Synthesis of stable monomeric iridium(0) and iridium($-$1) complexes

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Using the tropp^{Ph} ligand 1, stable monomeric d^8-Ir^{+I}, d^9-Ir^0 and d^{10}-Ir^{-I} complexes could be isolated and structurally characterized; in all complexes, the metal centre lies within a coordination sphere intermediate between a square plane and a tetrahedron.

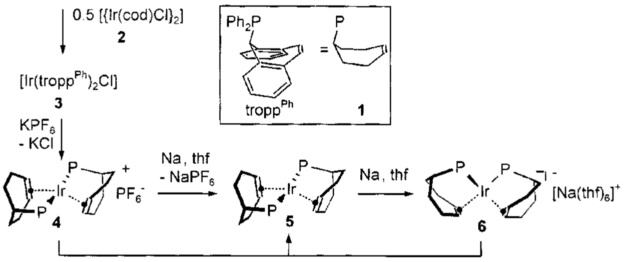
Upon stepwise reduction of a square planar d^8-metal complex, electrons are filled into metal–ligand antibonding orbitals, which eventually will lead to structural distortion towards a tetrahedron.[1] Qualitative MO-arguments indicate, that strong σ-donors will induce a preference for a tetrahedral structure while π-acceptor ligands may give rise to a more square planar structure. In line with these predictions pioneering electrochemical and EPR studies by Pilloni *et al.*[2] and Orsini and Geiger[3] showed that while d^9-[Rh(cod)$_2$] and d^9-[Rh{P(OR)$_3$}$_4$] probably have almost planar structures, [Rh(PPh$_3$)$_4$] is likely to have a tetrahedral co-ordination.

Using the new ligand (dibenzo[*a*,*d*]cycloheptene-5-yl)diphenylphosphine **1** (dibenzo*trop*ylidenyl *p*hosphine = tropp^{Ph}, the superscript indicates substituents bonded to phosphorus),[4,5] we were able to isolate a series of stable mononuclear [Ir(tropp^{Ph})$_2$] complexes were the metal centre formally adopts a d^8, d^9, and d^{10} valence electron configuration.

Thus, we prepared the lemon yellow pentacoordinated chloro iridium complex [Ir(tropp^{Ph})$_2$Cl] **3** and the orange–red tetracoordinated complex [Ir(tropp^{Ph})$_2$]$^+$ PF$_6^-$ **4** using standard synthetic methods as shown in Scheme 1. Both the neutral complex **3** and the cationic species **4** are easily reduced by lithium or sodium metal in thf to give the deep green paramagnetic iridium(0) complex **5** (μ_{eff} = 1.7 μ_B). Further reduction with sodium metal leads to the diamagnetic burgundy red iridate complex [Na(thf)$_6$]$^+$ [Ir(tropp^{Ph})$_2$]$^-$ **6**. A comproportionation reaction between **6** and **4** is the preferred synthetic method for radical **5**, which is isolated in almost quantitative yield because of its low solubility.†

X-Ray structural studies‡ for **4**, **5** and **6** show structural changes caused by the stepwise addition of two electrons without changing either the number or the coordination mode of the metal bound ligands.[6]

The structures of the d^8-Ir cation **4** and that of d^9-**5** are remarkably similar and are superimposed in Fig. 1. In both compounds two phosphorus centres of each tropp^{Ph} ligand are coordinated in *trans*-positions at the iridium centre. The Ir–P and Ir–C distances (see Table 1) lie within the expected range.



Scheme 1

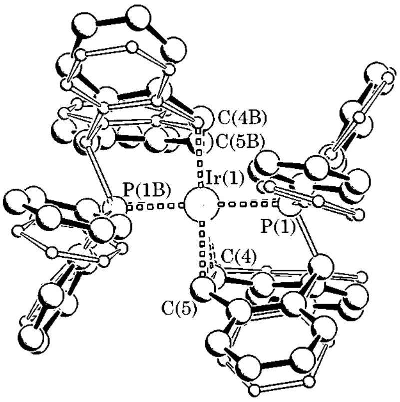


Fig. 1 Overlaid molecular structures of cation **4** (filled lines) and radical **5** (unfilled lines). Selected bond lengths and angles are given in Table 1.

Table 1 Selected bond lengths (Å), bond angles (°) and interplane angles φ (°) of **4**, **5** and **6**

	Ir–P	Ir–C4/C4A	Ir–C5/C5A	C4/C4A–C5/5A	α/°	β/°	φ
4	2.308(3)	2.18(1)	2.19(1)	1.42(2)	169.7(1)	143.5(5)	38.0
5	2.272(3)	2.21(1)	2.15(1)	1.46(2)	165.5(1)	149.4(5)	33.8
6	2.241(1)	2.171(6)	2.127(6)	1.472(9)	98.5(7)	101.0(4)	50.6

The iridium centres deviate significantly from square planar arrangements even in the cation for which planar coordination is expected.[7] Also, the P–Ir–P angles α [**4**: 169.7(1)°; **5**: 165.5(1)°] and (•)–Ir–P angles β [**4**: 143.5(5)°; **5**: 149.5(5)°; (•) = midpoint of the coordinated C=C unit] deviate significantly from 180°. Furthermore, the interplane angles φ (**4**: 38°; **5**: 34°) between the intersections of the P–M–(•) planes show this distortion. A plot of the structure of the iridate anion of [Na(thf)$_6$]$^+$ [Ir(tropp^{Ph})$_2$]$^-$ **6** is shown in Fig. 2.

Both phosphorus centres now occupy mutually *cis*-positions in the distorted coordination sphere which remains intermediate

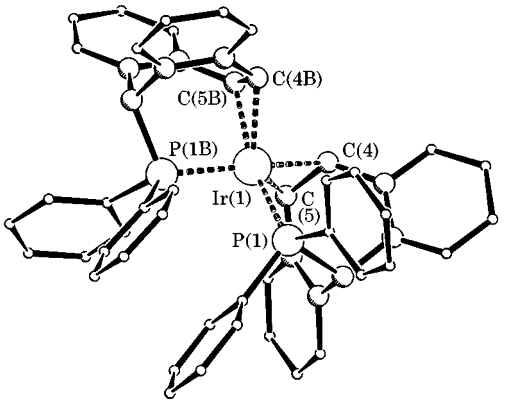


Fig. 2 Molecular structure of the anion of **6.** Selected bond lengths and angles are given in Table 1.

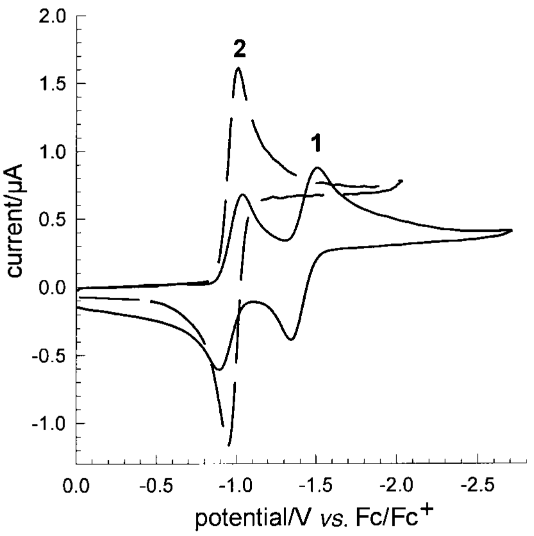


Fig. 3 Cyclic voltammogram of **4** in th–$Bu^n_4NPF_6$ electrolyte (trace 1) or MeCN–$Bu^n_4NPF_6$ electrolyte (trace 2); 298 K, 100 mV s^{-1}; Pt working electrode (0.785 mm^2/ Pt counter electrode/ Ag reference electrode, ferrocene as internal standard for calibration (+0.352 V *vs.* Ag/AgCl).

between a square plane and a tetrahedron (φ = 50.6°). Selected structural data are also listed in Table 1. The Ir–P and Ir–C bond distances do not show significant changes with the formal metal oxidation state in $[Ir(tropp^{Ph})_2]^{+1/0/-1}$ complexes. A slight lengthening of the co-ordinated C=C bond [C4–C5 1.42(2) Å in **4** *vs.* 1.472(9) Å in **6**] indicates increasing metal to ligand d–p(π)-back-donation. Hence, the only significant change is found in the interplane angle φ which changes by about 15° towards a more tetrahedral structure when d^8-**4** and d^9-**5** ($\varphi \approx$ 36°) are transformed into d^{10}-**6** ($\varphi \approx$ 51°). Note that both centrosymmetric planar structures (φ = 0°) or tetrahedral structures (φ = 84°) are found in $[M(tropp^{Ph})_2]^n$ complexes for M = Rh, n = +1, or Co, n = 0, respectively.[5,8] Hence, the structural features of the iridium complexes described in this work are not merely caused by steric requirements of the ligand. The Ir^{+1}/Ir^0 and Ir^0/Ir^{-1} redox couples are shifted to remarkably low potentials. The cyclic voltammogram of **4** in a $Bu^n_4NPF_6$–THF (trace 1) and $Bu^n_4NPF_6$–MeCN electrolyte (trace 2) is shown in Fig. 3.

While in thf the Ir^{+I}/Ir^0 and Ir^0/Ir^{-I} redox couples ($E^1_{\frac{1}{2}}$ = −0.97 V, ΔE = 149 mV; $E^2_{\frac{1}{2}}$ = −1.426 V; ΔE = 165 mV) appear separately, proving an overall stepwise EE mechanism, a further cathodic shift of the second wave is observed in MeCN leading to only one two-electron wave at $E^{1,2}_{\frac{1}{2}}$ = −0.982 V (ΔE = 91.4 mV).[9] It will be now interesting to study the application of tropp type complexes in electrocatalytic cycles running over four formal oxidation states at the metal centre (*i.e.* Ir^{+III}–Ir^{-I}).

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Notes and references

† $[Ir(tropp^{Ph})_2Cl]$ **3**: $tropp^{Ph}$ **1** (2.29 g, 6.074 mmol) and $[Ir(cod)Cl]_2$ **2** (1.02 g, 1,52 mmol) were dissolved in toluene (50 ml). The resulting yellow solution was stirred for 2 h at *ca.* 70 °C. Compound **3** crystallised overnight at room temp. to give a lemon yellow powder, 2.8 g (94.0%). ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS) δ 5.03 (t, J_{PH} 3.5 Hz, 2H, CHP), 4.10 (m, 2H, CH=CH), 3.45 (q, $^3J_{HH+PH}$ 3.4 Hz, 2H, CH=CH); ^{31}P NMR ($CDCl_3$, 81 MHz) δ 48.15 (s); ^{13}C NMR ($CDCl_3$, 75.43 MHz, 25 °C): δ 49.9 (m, CHP), 48.7 (s, CH=CH), 43.9 (s, CH=CH). $[Ir(tropp^{Ph})_2]^+PF_6^-$**4**: KPF_6 (130 mg, 0.706 mmol) was added to a solution of **3** (700 mg, 0.714 mmol) in 10 ml thf. The reaction mixture was stirred for 4 h at room temp. forming an orange–red suspension. Precipitates were filtered off and washed with thf until only colourless KCl remained. The filtrate was concentrated to *ca.* 5 ml and was layered with toluene. Compound **5** crystallized as orange–red crystals (760 mg, 97.7%). ^1H NMR (CD_2Cl_2, 300 MHz, 25 °C, TMS) δ 5.89 (t, J_{PH} 3.7Hz, 2H, CHP), 5.37 (t, 2H, $^3J_{HH+PH}$ 3.3 Hz, 4H, CH=CH); ^{31}P NMR (CD_2Cl_2, 81 MHz, 25 °C) δ 71.44 (s); ^{13}C NMR (CD_2Cl_2, 75.43 MHz, 25 °C) δ 68.9 (s, CH=CH), 49.5 (t, J_{CP} = 13.4 Hz CHP). UV–VIS: λ_{max} = 444 nm. $[Na(thf)_6][Ir(tropp^{Ph})_2]$ **6**: sodium (30.0 mg, 1.3 mmol) was added to a solution of **2** (500 mg, 0.51 mmol) in 10 ml thf and the reaction mixture was stirred for 48 h at room temp. The resulting deep red solution was filtered from the precipitate which was washed several times with thf until only colourless NaCl remained. The combined thf extracts were concentrated to 3 ml and were layered with *n*-hexane (5 ml). Compound **6** crystallized as deep red crystals (690 mg, 96.6%). ^1H NMR (thf-d$_8$, 300 MHz, 25 °C, TMS) δ 4.56 (d, J_{HP} 9.5 Hz, 2H, CHP), 4.03 (m, 2H, CH=CH), 2.14 (m, 2H, CH=CH); ^{31}P NMR (thf-d$_8$, 81 MHz) δ 82.7 (s); ^{13}C NMR (thf d$_8$, 75.43 MHz, 25 °C) δ 54.3 (m, CHP), 44.7 (m, CH=CH), 44.2 (m, CH=CH). UV–VIS: λ_{max} = 450 nm. $[Ir(tropp^{Ph})_2]$ **5**: **3** (500 mg, 0.51 mmol) and **6** (714 mg, 0.51 mmol) were dissolved in thf (15 ml) and stirred for 2 h at room temp. The resulting deep green solution was separated from the precipitate. The latter was treated as before and the combined thf extracts were reduced to 10 ml and layered with *n*-hexane (5 ml). Compound **5** crystallized as black crystals (750 mg, 77.8%). UV–VIS: λ_{max} = 592 nm.

‡ *Crystal data:* **4**·1.5thf: monoclinic, space group $P2_1/n$; a = 13.382(2), b = 30.666(5), c = 15.611(2) Å, β = 108.913(1)°, V = 6060.5(16) Å^3; Z = 4, Mo Kα radiation, $2\theta_{max}$ = 46.5°. 29467 reflections, 8718 independent (R_{int} = 0.0981); direct methods; full-matrix least-squares refinement (based on F^2) with SHELXTL (Version 5.0); R_1 = 0.0639, wR_2 = 0.1471 (based on F^2) for 715 parameters and 5487 reflections with $I > 2\sigma(I)$. **5**: twinned black needles. By cutting larger crystals into smaller pieces, we obtained a crystal, where one twin individium was dominant. The diffraction pattern of this crystal could be indexed by neglecting weak reflections of the smaller twin component and the structure could be solved successfully. Nevertheless, occasional overlapping of reflections of the twin components affects the accuracy of the structure refinement as well as the resulting R-values. Monoclinic, space group $P2_1/n$, a = 20.544(3), b = 9.359(1), c = 22.179(3) Å, β = 101.44(1)°; V = 4179.7(11) Å^3; Z = 4, Mo Kα radiation, $2\theta_{max}$ = 49.4°. 19535 reflections, 7092 independent (R_{int} = 0.0543); direct methods; full-matrix least-squares refinement (based on F^2) with SHELXTL (Version 5.0); R_1 = 0.0683, wR_2 = 0.1614 (based on F^2) for 514 parameters and 5328 reflections with $I > 2\sigma(I)$. **6**: orthorhombic, space group *Pcca*; a = 23.777(4), b = 12.679(2), c = 23.819(4) Å; V = 7199.1(6) Å^3; Z = 4, Mo Kα radiation, $2\theta_{max}$ = 55°. 37241 reflections, 7626 independent ($R_{int.}$ = 0.0939); direct methods; full-matrix least-squares refinement (based on F^2) with SHELXTL (Version 5.0); R_1 = 0.0467, wR_2 = 0.0969 (based on F^2) for 422 parameters and 3927 reflections with $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were refined on calculated positions using the riding model. In **4**, PF_6 and thf were refined as rigid bodies. In **5**, anisotropic displacement factors were restrained using SIMU and ISOR (see SHELX-97 manual, W.S. Sheldrick, Göttingen University). CCDC 182/1078. See http://www.rsc.org/suppdata/cc/1998/2623/for crystallographic files in .cif format.

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