

Preparation and structure of bis(μ-acetato)dichlorodicarbonyldiiridium(II) complexes with Group 15 ligands and ESR and density functional theory studies of electronic structure of their cationic radicals

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Abstract

bis(μ -Acetato)dichlorodicarbonyldiiridium(II) complexes with Group 15 compounds as axial ligands, $[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2L_2]$ (L = PPh₃: 1, PCy₃: 2, P(OPh)₃: 3, AsPh₃: 4, SbPh₃: 5) were synthesized. The Ir–Ir distances of complexes 2–5 (2.6200(9)–2.6936(7) Å) were longer than those of the complexes with MeCN, py or dmso ligands at the axial sites. Cyclic voltammograms of 1–5 show a chemically reversible one-electron oxidation wave of which $E_{1/2}$ (vs. Fc⁺–Fc) values were between 0.22 for 2 and 0.75 V for 3 depending on the axial ligands. Oxidation by electrolysis and/or radiolysis of 1, 2 and 4 gave their cationic radicals. The ESR spectra of 1^{+•}, 2^{+•} and 4^{+•} at 77 K were pseudo-axially symmetric with g tensors of $g_{\perp} = 2.15$ and $g_{\parallel} = 1.96$, 2.18 and 1.95, and 2.20 and 1.96, respectively. Their hyperfine coupling indicates that their odd electron is delocalized equivalently onto the two axial phosphorous or arsenic atoms. The odd electron densities were estimated from the hyperfine coupling tensors as $\rho \approx 0.1$ on the P atoms of 1^{+•} and 2^{+•} and $\rho \approx 0.15$ on the As atoms of 4^{+•}. These results indicate that their singly occupied molecular orbital (SOMO) is the σ_{IrIr} orbital with σ_{IrP}^{*} or σ_{IrAs}^{*} character. DFT calculations for model complexes, $[Ir_2(\mu-O_2CH)_2Cl_2(CO)_2(PH_3)_2]^{+•}$ (6^{+•}) and $[Ir_2(\mu-O_2CH)_2Cl_2(CO)_2(AsH_3)_2]^{+•}$ (7^{+•}), gave electronic structures consistent with the ESR results. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Iridium complexes; Metal-metal bonds; Group 15 ligands; Electronic structures; Electron spin resonance; Density functional theory calculations

1. Introduction

Dimetal complexes with metal-metal bond have been a subject of wide interest in these three decades [1]. Enhanced metal-metal and metal-ligand interactions are expected for 5d metal cluster compounds. However, rather limited examples of diiridium(II) complexes have been explored [2]. We reported a one-step preparation of an Ir_2^{4+} complex, $[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2]$ (8), in a previous paper [3]. Axial adducts of 8 with solvent molecules $[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2L_2]$ (L = MeCN: 9, dmso: 10, py: 11, 4-isopropylpyridine: 12) have been also prepared and characterized. We have also reported that cationic radicals derived from 11 and 12 are moderately stable and that their odd electron is accommodated in the δ_{IrIr}^* orbital. The electron configuration for the Rh–Rh bond in paddlewheel-type Rh_2^{5+} complexes depends on both their bridging and axial ligands. Strong σ -donor ligands such as phosphines at the axial sites make the σ_{RhRh} orbital the SOMO with its enhanced delocalization onto the lone-pair orbitals of the axial ligands [4-7]. To examine whether the electron configuration of the Ir–Ir bond in Ir_2^{5+} complexes also depends on the ligands, we synthesize Ir_2^{4+} complexes with ligands with group 15 elements at the axial sites, 1-5 (Scheme 1), and examine their redox behavior by CV. The electronic structures of these complexes are explored by ESR of cationic radicals of 1, 2 and 4 and by density functional theory (DFT) calculations.

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Scheme 1.

2. Experimental

2.1. Syntheses

2.1.1. $[Ir_2(\mu - O_2CMe)_2Cl_2(CO)_2(PPh_3)_2]$ (1)

Complex **8** (98 mg, 0.16 mmol) and PPh₃ (87 mg, 0.33 mmol) in toluene (10 ml) were refluxed for 2 h under Ar to give a yellow solution. The yellow crude product given by evaporation of the solvent was eluted through a silica gel column with CH₂Cl₂/hexane (1:1 v/v). The yellow eluent was dried to give yellow crystals of **1**. Yield 96 mg (53%). *Anal.* Calc. for C₂₁H₁₈ClIrO₃P: C, 43.71; H, 3.14; P, 5.37. Found: C, 43.73; H, 3.15; P, 5.22%. ¹H NMR (CD₂Cl₂, δ in ppm): 7.60 (m, 12H), 7.48–7.40 (m, 18H), 1.77 (s, 6H, O₂CMe). ³¹P NMR (CDCl₃, δ in ppm): -14.42. IR (KBr disc, in cm⁻¹): 2031s, 2013s, 1560s, 1542m, 1508m, 1458m, 1438m, 1093m, 744m, 693m, 518m. UV–Vis (CH₂Cl₂, λ_{max} in nm, and ε in parentheses in M⁻¹ cm⁻¹): 333 (27900), 354 (33200), 395 sh.

2.1.2. $[Ir_2(\mu - O_2CMe)_2Cl_2(CO)_2(PCy_3)_2] \cdot CH_2Cl_2$ (2· CH_2Cl_2)

To a toluene (20 ml) suspension of complex 8 (92 mg, 0.15 mmol), PCy₃ (1 ml of 25% solution in toluene, 0.76 mmol) was added under Ar. The solution was refluxed for 2 h to give a vellow solution and evaporated to dryness. The yellow crude product was purified by silica gel column chromatography eluting with CH₂Cl₂/hexane (1:1 v/v). Slow evaporation of solvent from a CH₂Cl₂ solution of the purified product gave yellow crystals of 2·CH₂Cl₂. Yield 32 mg (19%). Anal. Calc. for C₄₃H₇₄Cl₄Ir₂O₆P₂: C, 40.05;H, 5.85; P, 4.86. Found: C, 39.79; H, 5.75; P, 4.62%. ¹H NMR (CD₂Cl₂, δ in ppm): 2.40 (br, m, 6H), 2.03 (s, 6H, O₂CMe), 2.05-1.98 (m, 12H), 1.85–1.62 (m, 30H), 1.29 (br, 18H). ³¹P NMR (CDCl₃, δ in ppm): -1.93. IR (KBr disc, in cm⁻¹): 2928s, 2850s, 2025s, 2006s, 1560s, 1542m, 1508m, 1458m, 1439s, 1268w, 1006w, 848w, 708w, 538w. UV–Vis (CH₂Cl₂, λ_{max} in nm, and ε in parentheses in M⁻¹ cm⁻¹): 267 (16100), 322 (29000), 337 (28200), 401 sh.

2.1.3. $[Ir_2(\mu - O_2CMe)_2Cl_2(CO)_2\{P(OPh)_3\}_2]$ (3)

Complex 8 (89 mg, 0.14 mmol) and P(OPh)₃ (118 mg, 0.71 mmol) in toluene (25 ml) were refluxed for 2 h under Ar to give a yellow solution. The oily yellow

residue obtained by evaporation of the solvent was dissolved into CH₂Cl₂ (10 ml). Pale yellow crystals were grown by slow diffusion of hexane (10 ml) to the solution. Yield 98 mg (72%). *Anal.* Calc. for C₂₁H₁₈ClIrO₆P: C, 40.36; H, 2.90; P, 4.96; Cl, 5.67. Found: C, 40.39; H, 2.86; P, 4.70; Cl, 5.75%. ¹H NMR (CD₂Cl₂, δ in ppm): 7.29–7.21 (m, 24H), 7.22 (d, 6H), 1.51 (s, 6H, O₂CMe). ³¹P NMR (CDCl₃, δ in ppm): 57.90. IR (KBr disc, in cm⁻¹): 2056s, 2039s, 1590m, 1560m, 1490s, 1450m, 1448m, 1212m, 1186s, 1072w, 1025m, 1007w, 920s, 759s, 719w, 688m, 617w, 593w. UV–VIS (CH₂Cl₂, λ_{max} in nm, and ε in parentheses in M⁻¹ cm⁻¹): 301(20800), 340 sh, 378 sh.

2.1.4. $[Ir_2(\mu - O_2CMe)_2Cl_2(CO)_2(AsPh_3)_2]$ (4)

This complex was prepared by a similar method to that for complex **2** from complex **8** (86 mg, 0.14 mmol) and AsPh₃ (86 mg, 0.28 mmol) in toluene (10 ml) to give **4** as yellow crystals. Yield 72 mg (42%). *Anal.* Calc. for C₂₁H₁₈AsClIrO₃: C, 40.62; H, 2.92; Cl, 5.71. Found: C, 40.35; H, 2.81; Cl, 5.93%. ¹H NMR (CD₂Cl₂, δ in ppm): 7.60–7.57 (m, 12H), 7.51–7.40 (m, 18H), 1.89 (s, 6H, O₂CMe). IR (KBr disc, in cm⁻¹): 2032s, 2015s, 1560s, 1543m, 1508m, 1438m, 1186w, 1077w, 1023w, 995w, 736m, 693m. UV–VIS (CH₂Cl₂, λ_{max} in nm, and ε in parentheses in M⁻¹ cm⁻¹): 328 (39300), 346 sh, 416 (10900).

2.1.5. $[Ir_2(\mu - O_2CMe)_2Cl_2(CO)_2(SbPh_3)_2]$ (5)

This complex was synthesized by a similar method to that for complex **2** from complex **8** (57 mg, 0.091 mmol) and SbPh₃ (70 mg, 0.19 mmol) in toluene (10 ml) to give **5** as orange-yellow crystals. Yield 12 mg (10%). *Anal.* Calc. for C₂₁H₁₈ClIrO₃Sb: C, 37.77; H, 2.72; Cl, 5.31. Found: C, 37.49; H, 2.76; Cl, 5.42%. ¹H NMR (CD₂Cl₂, δ in ppm): 7.65 (d, 12H), 7.51–7.42 (m, 18H), 2.03 (s, 6H, O₂CMe). IR (KBr disc, in cm⁻¹): 2031s, 2012s, 1560s, 1543m, 1508m, 1432m, 1068w, 730w, 694w. UV–Vis (CH₂Cl₂, λ_{max} in nm, and ε in parentheses in M⁻¹ cm⁻¹): 296 (13700), 346 (35600), 363 (37500), 433 (16400).

2.2. Measurements

¹H and ³¹P NMR spectra were recorded on a JEOL α 400 or a Varian UNITY INOVA 400 spectrometer, UV–Vis absorption spectra on a Shimadzu UV-3100PC spectrophotometer and IR spectra by using a Perkin–Elmer FT IR-1640 spectrophotometer. CV studies were performed with a BAS 50W electrochemical analyzer employing a conventional three-electrode cell with a platinum disk working electrode, a platinum wire counter electrode, and a BAS RE-5 Ag⁺ | Ag reference electrode. Electrolytic solutions were CH₂Cl₂ or MeCN containing 0.1 M ⁿBu₄NPF₆. After each CV measurement, the oxidation potential of ferrocene in

Table 1

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	$2 \cdot CH_2Cl_2$	3	4	5
Empirical formula	C ₄₃ H ₇₄ Cl ₄ Ir ₂ O ₆ P ₂	C ₄₂ H ₃₆ Cl ₂ Ir ₂ O ₁₂ P ₂	C42H36As2Cl2Ir2O6	C42H36Cl2Ir2O6Sb2
Formula weight	1275.25	1250.03	1241.93	1335.59
Crystal system	tetragonal	monoclinic	monoclinic	triclinic
Space group	$P\overline{4}2_1c$ (no. 114)	$P2_1/c$ (no. 14)	$P2_1/a$ (no. 14)	$P\overline{1}$ (no. 2)
a (Å)	14.797(1)	13.626(3)	16.103(2)	13.6363(9)
b (Å)	14.797(1)	21.015(4)	16.879(2)	15.301(1)
c (Å)	23.881(2)	15.328(2)	16.890(2)	11.506(1)
α (°)				97.136(8)
β (°)		94.46(1)	115.621(9)	92.839(8)
γ (°)				67.163(5)
$V(Å^3)$	5228.5(6)	4376(1)	4139.4(9)	2195.3(3)
Z	4	4	4	2
<i>T</i> (°C)	23	-40	-80	23
μ (Mo K α) (cm ⁻¹)	54.05	63.49	82.03	74.40
Data, measured	6622	14265	14984	14355
Data, used ^a	2580	5439	4026	5340
R _{int}	0.029	0.047	0.032	0.031
R, R'	0.035, 0.034	0.069, 0.060	0.057, 0.054	0.045, 0.042

^a $I > 2.0\sigma(I)$ for 2·CH₂Cl₂, 4 and 5, and $I > 1.3\sigma(I)$ for 3.

the same electrolytic solution was measured and the electrode potential was converted into that relative to the Fc⁺-Fc couple. For coulometry, the working electrode was a platinum coil and the counter a gold coil in a two-compartment cell connected by a sintered glass disk. Cationic radicals for ESR study were generated by electrochemical oxidation in the coulometry cell. Radiolysis was also adopted for their generation: a degassed Freon mixture (CH₂Cl₂-CFCl₃-CF₂BrCF₂Br: 1:5:5 by vol) saturated with a complex was sealed in an ESR sample tube [5,8,9]. The frozen solution was exposed to X-ray (Mo Ka, 14.5 kW) at 77 K for 4 h to generate the cationic radical of the solute. The frozen solution was annealed carefully to decay radicals derived from the solvent. ESR spectra were measured on a JEOL JES-TE200 spectrometer. Field sweep was monitored with an Echo Electronics EFM-200 ¹H NMR gaussmeter. The gaussmeter probe was attached beside the ESR cavity; the field difference between ESR and NMR sample positions was calibrated by measuring the field intensity at the resonance of perylene cationic radical in concentrated H_2SO_4 (*g* = 2.002583).

2.3. Crystallographic study

Slow evaporation of $CH_2Cl_2^{-n}PrCN$ (10:1 v/v) solution of **2**·CH₂Cl₂ gave its yellow single crystals. Prismatic yellow crystals of **3**, **4** and **5** were prepared by slow diffusion of *n*-hexane into their CH₂Cl₂ solutions. All measurements were carried out on a Rigaku AFC7R diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å). The data were collected using the $\omega - 2\theta$ scan technique to a maximum 2θ

value of 55°. All calculations were performed by using the TEXSAN program package [10]. Scattering factors for neutral atoms were from Cromer and Waber [11] and anomalous dispersion [12] was included. Crystallographic data and structure refinement parameters are listed in Table 1. The structures of 2·CH₂Cl₂, 4 and 5 were solved by direct methods, SHELXS-86 [13] and that of 1 by SIR 92 [14]. An analytical absorption correction [15] was applied for $2 \cdot CH_2Cl_2$, 4 and 5 and DIFABS for 3 [16]. In the crystal of 4 four of the six phenyl groups (C(13)-C(18), C(25)-C(30), C(31)-C(36) and C(37)-C(42)) on the As atoms were disordered. The phenyl groups were refined in two different conformations (A and B) by using a rigid model. The C(13) and C(31) atoms were shared by both of the disordered conformations. In all the analyses, all non-hydrogen atoms that are not involved in the disorder were refined with anisotropic thermal parameters and all hydrogen atoms at calculated positions using idealized geometries of 0.95 Å of C-H distance with isotropic thermal parameters which were 1.2 times those of the connected atoms.

2.4. DFT calculations

Geometry optimization was performed with the DFT method with the B3LYP functional [17–19] by using the Gaussian 98 program [20]. The ECPs (effective core potentials) and the basis functions for the Ir, P, Cl and As atoms were those of LANL2DZ (split valence type) [21] supplemented with a single-primitive polarization function for Cl, P and As atoms [22]. The 6-31G set [23] was used for the H, C, N and O atoms. The d functions were of the manually orthogonal five-function type.

Geometries of model complexes, $6^{0/+}$ and $7^{0/+}$, were optimized in C_2 geometries to the default criteria of GAUSSIAN-98 [20]. ESR hyperfine coupling tensors of the nuclei at the axial sites (P, As) were performed also by the GAUSSIAN-98 program package based on the DFT-B3LYP method at the above-mentioned optimized geometries but the basis functions of the P and As atoms were replaced by the 6-31G* set.



Fig. 1. ORTEP diagram of $[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2(PCy_3)_2]$ (2) in 2·CH₂Cl₂ with the 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. A crystallographic C_2 axis bisects the Ir–Ir bond and the line between C(1) and C(C1').



Fig. 2. ORTEP diagram of $[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2\{P(OPh)_3\}_2]$ (3) with the 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.



Fig. 3. ORTEP diagram of $[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2(AsPh_3)_2]$ (4) with the 30% probability ellipsoids. Only one (designated by adding A to the atom numbers) of each pair of the disordered phenyl groups are displayed. Hydrogen atoms are omitted for clarity.



Fig. 4. ORTEP diagram of $[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2(SbPh_3)_2]$ (5) with the 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2

Selected bond distances (Å), bond angles (°) and torsion angles (°) for $[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2(PCy_3)_2]$ ·CH₂Cl₂ (2·CH₂Cl₂)^a

Bond lengths			
Ir(1)-Ir(1')	2.6936(7)	Ir(1)-Cl(1)	2.344(3)
Ir(1)–P(1)	2.466(3)	Ir(1)–O(1)	2.098(7)
Ir(1)–O(2')	2.062(7)	Ir(1)–C(3)	1.86(1)
Bond angles			
Ir(1')-Ir(1)-P(1)	170.55(6)	Cl(1)–Ir(1)–O(2')	173.6(2)
O(1)-Ir(1)-C(3)	175.1(4)		
Torsion angles			
O(1)–Ir(1)–Ir(1')–O(2)	9.9(3)		

^a ': 1 - x, -y, z.

3. Results and discussion

3.1. Structure

Figs. 1-4 show ORTEP [24] drawings of complexes 2-5, respectively. Selected bond distances and angles of 2 are summarized in Table 2, and those of 3-5 in Table 3. The geometries of the core unit, $Ir_2(\mu-O_2CMe)_2$ - $Cl_2(CO)_2$, in these complexes resemble each other. The difference in Ir-Cl, Ir-O and Ir-CO distances are within experimental errors (Ir-Cl: 2.337(3)-2.350(6), Ir-O: 2.06(1)-2.098(7) and Ir-C: 1.82(2)-1.89(2) Å). The Ir-P distance in 3 (2.356(4) and 2.376 (4) Å) is shorter than that in 2 (2.466(3) Å). Similar difference in M-P_{axial} distances are observed between [Rh₂(µ- $O_2CR_4(PPh_3)_2$ and $[Rh_2(\mu - O_2CR)_4\{P(OPh)_3\}_2]$ (R = Me [25], CF_3 [26]). The Ir–Ir distance depends on the axial ligands (Table 4). The Ir-Ir distance of 2 (2.6939(7) Å) is the longest in the current $[Ir_2(\mu O_2CMe_2Cl_2(CO)_2L_2$ complexes and 0.12 Å longer than that of complex 9. The other three current complexes also have longer Ir-Ir distances than those of the solvent adducts, 9-11 [3]. This trend indicates that the enhanced σ donation from the axial ligands into the Ir-Ir bond elongates the metal-metal bond.

3.2. Electrochemistry

Fig. 5 shows the CVs of a triad, 1, 4 and 5. Their first oxidation responses are chemically reversible. The scans to more positive potentials gave second responses, which are irreversible. Table 5 summarizes the redox potentials of $[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2L_2]$ complexes. All the complexes in this table did not show a reduction response down to -1.5 V. Table 5 shows that the stronger σ donor ligands such as a phosphine makes the oxidation potential lower. On the other hand, complex 9 which has a weak donor ligand, MeCN, has the highest oxidation potential. The dmso adduct, 10, did not show any redox response in the potential window of the dmso electrolytic solution [3].

Table 3

Selected bond distances (Å), bond angles (°) and torsion angles (°) for $[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2\{P(OPh)_3\}_2]$ (3), $[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2-(AsPh_3)_2]$ (4) and $[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2(SbPh_3)_2]$ (5)

	3	4	5
Bond lengths			
Ir(1)-Ir(2)	2.6458(8)	2.6207(9)	2.6200(9)
Ir(1)–Ax(1) ^a	2.356(4)	2.532(2)	2.678(1)
Ir(1)–Cl(1)	2.344(4)	2.350(6)	2.345(3)
Ir(1)–O(1)	2.062(9)	2.06(1)	2.064(8)
Ir(1)–O(3)	2.071(10)	2.09(1)	2.096(8)
Ir(1)-C(5)	1.82(2)	1.89(2)	1.82(1)
Ir(2)–Ax(2) ^a	2.376(4)	2.550(2)	2.680(1)
Ir(2)–Cl(2)	2.340(4)	2.349(6)	2.337(3)
Ir(2)–O(2)	2.062(10)	2.09(1)	2.091(8)
Ir(2)–O(4)	2.067(9)	2.07(1)	2.065(8)
Ir(2)–C(6)	1.82(2)	1.86(2)	1.82(1)
Bond angles			
Ir(2)–Ir(1)–Ax(1) ^a	169.2(1)	169.74(5)	168.03(3)
Ir(1)–Ir(2)–Ax(2) ^a	168.07(10)	169.10(5)	168.29(3)
Cl(1)–Ir(1)–O(1)	174.5(3)	173.6(4)	175.1(2)
O(3)–Ir(1)–C(5)	175.6(6)	178.8(8)	177.3(5)
Cl(2)–Ir(2)–O(4)	174.4(3)	173.0(4)	173.1(2)
O(2)–Ir(2)–C(6)	174.9(5)	177.2(8)	178.4(5)
Torsion angles			
O(1)-Ir(1)-Ir(2)-O(2)	12.3(4)	17.8(5)	17.3(3)
O(3)–Ir(1)–Ir(2)–O(4)	12.4(4)	18.0(5)	17.9(3)

^a Ax denotes the atom at the axial site: P for **3**, As for **4**, and Sb for **5**.

Table 4

Ir-Ir distances (Å)	in $[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2L_2]$
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Complex	Distance
$[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2(MeCN)_2]$ (9) ^a	2.569(1)
$[Ir_{2}(\mu-O_{2}CMe)_{2}Cl_{2}(CO)_{2}(py)_{2}]$ (11) ^a	2.5918(5)
$[Ir_{2}(\mu-O_{2}CMe)_{2}CI_{2}(CO)_{2}(dmso)_{2}]$ (10) ^a	2.5980(5)
$[Ir_{2}(\mu-O_{2}CMe)_{2}CI_{2}(CO)_{2}(SbPh_{3})_{2}]$ (5)	2.6200(9)
$[Ir_{2}(\mu-O_{2}CMe)_{2}CI_{2}(CO)_{2}(AsPh_{3})_{2}]$ (4)	2.6207(9)
$[Ir_{2}(\mu-O_{2}CMe)_{2}CI_{2}(CO)_{2}{P(OPh)_{3}}]$ (3)	2.6458(8)
$[Ir_{2}(\mu-O_{2}CMe)_{2}Cl_{2}(CO)_{2}(PCy_{3})_{2}]$ (2)	2.6936(7)



Fig. 5. Cyclic voltammograms of complexes (a) 1, (b) 4 and (c) 5 in CH₂Cl₂. The dotted lines represent the CV responses scanned beyond the first oxidation response.

Table 5

Oxidation potentials (V vs. Fc^+ –Fc) of $[Ir_2(\mu$ -O₂CMe)₂Cl₂(CO)₂L₂] in CH₂Cl₂ containing 0.1 M ⁿBu₄NPF₆

Complex	$E_{1/2}^{\mathrm{ox1}}$	$E_{\mathrm{pa}}^{\mathrm{ox2}\ \mathrm{a}}$
$\frac{1}{[Ir_{2}(\mu-O_{2}CMe)_{2}Cl_{2}(CO)_{2}(MeCN)_{2}]^{b,c}(9)}$	1.30	
$[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2(py)_2]^{b}$ (11)	0.97	
$[Ir_{2}(\mu-O_{2}CMe)_{2}Cl_{2}(CO)_{2}(Pr^{i}py)_{2}]]^{b}$ (12)	0.94	
$[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2\{P(OPh)_3\}_2]$ (3)	0.75	
$[Ir_2(\mu - O_2CMe)_2Cl_2(CO)_2(AsPh_3)_2]$ (4)	0.66	1.13
$[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2(SbPh_3)_2]$ (5)	0.62	1.21
$[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2(PPh_3)_2]$ (1)	0.47	0.85
$[Ir_{2}(\mu - O_{2}CMe)_{2}Cl_{2}(CO)_{2}(PCy_{3})_{2}] (2)$	0.21	1.11

^a Irreversible, anodic peak potential.

^b Ref. [3].

° In MeCN.

A bulk electrolysis of 1 at 0.60 V in CH_2Cl_2 containing 0.1 M ⁿBu₄NPF₆ at -15 °C gave a dark-red solution. Similar electrochemical oxidation of 2 at 0.35 V and 4 at 0.80 V gave dark-brown solutions. These colors of the cationic radicals faded out in several minutes when the solutions were warmed to room temperature and finally changed to yellow. This behavior is similar to that of 11 [3] and shows limited stability of the cationic species derived from 1, 2 and 4. Cationic radicals of 3 and 5 were unstable even at -15 °C.

3.3. ESR

Solutions of cationic radicals of 1, 2 and 4 formed by electrolysis were quickly frozen at 77 K and their ESR spectra were measured. The spectrum of $1^{+\bullet}$ at 77 K is shown in Fig. 6(a). This is a pseudo-axially symmetric one with $g_{\perp} = 2.15$ and $g_{\parallel} = 1.96$ with hyperfine splitting of a 1:2:1 triplet. The triplet splitting is due to a pair of equivalent ³¹P nuclei. The principal values of the hyperfine tensor are $A_{\perp} = 11.9 \times 10^{-3}$ and $A_{\parallel} = 15.4 \times 10^{-3}$ cm⁻¹ (Table 6). The same spectrum was observed for a frozen Freon mixture solution of 1 at 77 K which



Fig. 6. X-Band ESR spectra of complex $1^{+\bullet}$ (a) in frozen solution at 77 K and (b) in fluid solution at 273 K.

had been irradiated with X-ray and annealed appropriately to decay the solvent radicals. This confirms that the spectrum in Fig. 6(a) arises from $1^{+\bullet}$, because the frozen Freon mixture is known to be an appropriate matrix for trapping cationic species formed from a solute upon radiolysis [8,9]. A fluid solution spectrum of $1^{+\bullet}$ at 273 K is shown in Fig. 6(b). This isotropic spectrum is a broad 1:2:1 triplet with $g_{\text{sltn}} = 2.11$ and $A_{\rm sltn} = 12.4 \times 10^{-3}$ cm⁻¹. The large shifts of the principal values of the g tensor from the free spin value $(g_e = 2.00)$ show that the odd electron of this cationic radical is distributed predominantly on the iridium atoms. The $A_{\rm sltn}$ value is consistent only with the assignment of the same sign to both of A_{\parallel} and A_{\perp} values. The physically meaningful choice of the signs for these principal values is positive. The isotropic and anisotropic parts of the ³¹P hyperfine coupling tensor are $A_{\rm iso} = (2A_{\perp} + A_{\parallel})/3 = 13.1 \times 10^{-3}$ and $2b = A_{\parallel} - 10^{-3}$ $A_{\rm iso} = 2.3 \times 10^{-13}$ cm⁻¹, respectively. Odd electron densities on the 3s and 3p orbitals on each P atom can be estimated by dividing the A_{iso} and 2b values by the corresponding atomic values as ρ (P 3s) = 13.1 × 10⁻³/ and $\rho(P = 3p) = 2.3 \times 10^{-3}/$ $(443.8 \times 10^{-3}) = 0.03$

Table 6 ESR spin Hamiltonian parameters of $[Ir_2(\mu\text{-}O_2CMe)_2Cl_2(CO)_2(L)_2]^{+\bullet}$



 $(24.4 \times 10^{-3}) = 0.10$, respectively [5,27]. In this estimation, the spin polarization of inner-shell s and p electrons on the P atoms has been neglected. The large odd electron density on the two P atoms (total 26%) leads to a conclusion that the odd electron is delocalized into the phosphine lone-pair orbitals. Consequently, the SOMO has the σ symmetry with respect to the P–Ir–Ir–P axis. The lone-pair orbitals on the P atoms can interact with the local σ_{IrIr} and σ_{TrIr}^* orbitals as shown in Scheme 2. The SOMO can be assigned to the $\sigma_{IrIr}/\sigma_{IrP}^*$ orbital.

Cationic radicals of 2 and 4 were generated also by electrolysis. The ESR spectra of $2^{+\bullet}$ in frozen and fluid solutions were similar to those of $1^{+\bullet}$ and were analyzed as listed in Table 6. The frozen (77 K) and fluid solution (223 K) spectra of $4^{+\bullet}$ are shown in Fig. 7(a) and (b), respectively. This frozen solution spectrum was analyzed also as pseudo-axially symmetric one. The 1:2:3:4:3:2:1 septet splitting patterns in both of the parallel and perpendicular components show that there are two magnetically equivalent ⁷⁵As nuclei (I = 3/2,100% natural abundance). The principal values of the g tensor and of the As hyperfine coupling tensor of 4^{+} are summarized also in Table 6. Odd electron densities on the P or As atoms are estimated as $\rho(P \ 3s) = 0.02$ and $\rho(P \ 3p) = 0.11$ for $2^{+\bullet}$ and $\rho(As \ 4s) = 0.03$ and ρ (As 4p) = 0.15 for 4^{+•}. Complexes 2^{+•} and 4^{+•} have also large odd electron densities on the two P atoms

Complex	$g_{ m sltn}$ ^a	g_{\perp}	g_{\parallel}	$g_{ m iso}{}^{ m b}$	$\left A_{\rm sltn}\right ^{ m a,c}$	$\left A_{\perp}\right $ °	$ A_{ } ^{ m c}$	$\left A_{\mathrm{iso}}\right ^{\mathrm{b,c}}$
1+•	2.11	2.15	1.96	2.09	12.4	11.9	15.4	13.1
2+ •	2.10	2.18	1.95	2.10	10.8	9.3	13.2	10.6
4 +•	2.18	2.20	1.96	2.12	12.7	11.9	16.0	13.3

^a From fluid solution spectrum.

^b From frozen solution spectrum as $iso = (||+2\perp)/3$.

^c Hyperfine coupling energy in unit of 10^{-3} cm⁻¹.



Fig. 7. X-Band ESR spectra of complex 4^{+} (a) in frozen solution at 77 K and (b) in fluid solution at 223 K.

(total 26%) and on the two As atoms (total 36%), respectively. The SOMO of $2^{+\bullet}$ and $4^{+\bullet}$ are also the $\sigma_{IrIr}/\sigma_{IrP}^*$ and the $\sigma_{IrIr}/\sigma_{IrAs}^*$ orbital, respectively. As discussed in the analysis of the ESR of $[Rh_2(\mu - O_2CR)_4(PR_3)_2]^{+\bullet}$ complexes [5,6], the observed g tensors of $1^{+\bullet}$, $2^{+\bullet}$ and $4^{+\bullet}$ with $g_{\perp} > g_e$ and $g_{\parallel} \approx g_e$ are

Table 7

Optimized geometries and relative energies of Ir_2^{4+} and Ir_2^{5+} model complexes ^{a,b}

consistent with the present assignment of their SOMO to the $\sigma_{IrIr}/\sigma_{IrP}^*$ or the $\sigma_{IrIr}/\sigma_{IrAs}^*$ orbital. The relatively large deviations of the g_{\parallel} values of $1^{+\bullet}$, $2^{+\bullet}$ and $4^{+\bullet}$ from the g_e value would originate partly from the current approximation to analyze their spectra based on the co-axially symmetric spin Hamiltonians and partly from the ground states of these radicals to be described with multiconfigurational wave-functions [28].

3.4. DFT calculations

The DFT calculations of geometry optimization of the model complexes, $6^{0/+}$ and $7^{0/+}$, and of hyperfine coupling tensors of the axial heavy nuclei of these cationic radicals were performed in the C_2 symmetry where the C_2 axis bisects the Ir–Ir bond. The results of geometry optimization and hyperfine coupling tensors are summarized in Tables 7 and 8, respectively.

The calculated ground state of $6^{+\bullet}$ is ²A with the SOMO of the $\sigma_{IrIr}/\sigma_{IrP}^{*}$ orbital which is also delocalized onto the equatorial Cl atoms with π_{IrCl}^{*} character. The atomic spin populations on each of the Ir, P and Cl

State	SOMO	rel E ^c	Ir–Ir ^d	Ir–Cl ^d	Ir–Ax ^d
$[Ir_{2}(O_{2}CH)_{2}(C$	$[O)_2 Cl_2 (PH_3)_2]^{0/+} (6^{0/+})$				
$Ir_{2}^{5+2}A$	$\sigma_{\rm IrIr}, \sigma_{\rm IrP}^*, \pi_{\rm IrCl}^*$	0	(0.1127)	(-0.0556)	(-0.0861)
$Ir_{2}^{5+2}B$	$n(\mathrm{Ir})^{\mathrm{e}}, \pi_{\mathrm{IrCl}}^{*}$	16.4	(-0.0047)	(-0.0557)	(0.0610)
$Ir_{2}^{4+1}A$		-172.2	2.6753	2.3968	2.4745
$[Ir_{2}(O_{2}CH)_{2}(C$	$(O)_2 Cl_2 (AsH_3)_2]^{0/+} (7^{0/+})$				
$Ir_{2}^{5+2}A$	$\sigma_{\rm IrIr}, \sigma^*_{\rm IrP}, \pi^*_{\rm IrCl}$	0	(0.1018)	(-0.0543)	(-0.0891)
$Ir_{2}^{5+2}B$	$n(\mathrm{Ir})^{\mathrm{e}}, \pi_{\mathrm{IrCl}}^{*}$	15.0	(0.0012)	(-0.0553)	(0.0524)
$Ir_{2}^{4+1}A$		-173.3	2.6670	2.3948	2.5870

^a Geometries of the Ir_2^{5+} complexes were optimized for each of the low-lying doublet states.

^b B3LYP, LANL2DZ for Ir, As, Cl, and P supplemented with d polarization functions for the heavy typical elements, and 6-31G for O, N, C, and H.

^c Energies relative to the lowest doublet state of the Ir_2^{5+} complex in kcal mol⁻¹.

^d Bond lengths (Å) for the Ir_2^{4+} complexes and bond length changes (Å) in parentheses arising from one-electron oxidation for the Ir_2^{5+} complexes.

^e An Ir non-bonding MO.

Table 8

Calculated isotropic and anisotropic hyperfine coupling constants ^a (and directions ^b in parentheses) of the ³¹P and ⁷⁵As nuclei in model complexes

State	SOMO	$A_{\rm iso}$	B _{XX} ^c	B _{YY} ^c	B _{ZZ} ^c
[Ir ₂ (μ-0 ₂ CH	$(Cl_{2}(CO)_{2}(PH_{3})_{2})^{+\bullet}$ (6 ^{+•})				
² A	$\sigma_{\rm IrIr}, \sigma_{\rm IrP}^*, \pi_{\rm IrCl}^*$	13.06	-1.31 (84)	-1.24 (92)	2.55 (6)
^{2}B	$n(\mathrm{Ir}), \pi^*_{\mathrm{IrCl}}$	-0.56	-0.05 (27)	0.01 (97)	0.05 (115)
$[Ir_2(\mu - O_2CH)]$	$(2)_{2}Cl_{2}(CO)_{2}(AsH_{3})_{2}]^{+\bullet}$ (7 ^{+•})				
^{2}A	$\sigma_{\rm IrIr}, \sigma^*_{\rm IrAs}, \pi^*_{\rm IrCl}$	23.27	-1.12 (85)	-1.06 (92)	2.19 (6)
² B	$n(\mathrm{Ir}), \pi^*_{\mathrm{IrCl}}$	-1.02	-0.06 (17)	0.02 (92)	0.04 (106)

^a In unit of 10^{-3} cm⁻¹.

^b From the Ir-Ir axis in unit of degree.

^c X, Y and Z are the local principal axes for anisotropic hyperfine coupling tensor, B.

atoms in this state are 0.21, 0.16 and 0.12, respectively. The odd electron is considerably delocalized onto the Cl atoms. The hyperfine anisotropic parameter for the axial P nucleus was calculated to be $B_{ZZ} = 2.6 \times 10^{-3}$ cm^{-1} (Z is the local unique axis of the calculated anisotropic hyperfine tensor of a P nucleus and deviates slightly (6°) from the Ir-P bond axis). This result is consistent with the corresponding experimental values of $(A_{\parallel} - A_{\rm iso}) = 2.3 \times 10^{-3}$ for 1^{+} and 2.6×10^{-3} cm^{-1} for $2^{+\bullet}$. The calculated second-lowest doublet state was ²B, which is located 16.5 kcal mol⁻¹ above the ²A ground state in energy. The SOMO for this state can be best described as the *b*-symmetry combination of the pair of $5d_{xz}$ atomic orbitals on both of the Ir atoms, where the local z and x axes are the Ir–Ir and Ir-Cl bond axes, respectively. This orbital is also extensively delocalized onto the equatorial Cl atoms in π^*_{IrCl} phase. The calculated hyperfine coupling tensor of the axial P nucleus for this excited state listed in Table 8 is inconsistent with the experimental ones for $1^{+\bullet}$ and 2^{+} , supporting that the ²B state does not correspond the experimental ground state.

The calculated ground state of model-complex 7^{+•} is ²A with the $\sigma_{IrIr}/\sigma_{IrAs}^*$ SOMO which is also delocalized extensively onto the equatorial Cl atoms in π_{IrCl}^* phase. The second-lowest doublet-state is ²B where the SOMO is similar to the SOMO of the ²B state for 6^{+•}. The experimental ⁷⁵As hyperfine coupling tensor of 4^{+•} (Table 6) is consistent only with that for the calculated ²A ground-state for the model complex (Table 8).

4. Concluding remarks

The reaction of complex 8 with a ligand with a heavy Group 15 element gives a half-paddlewheel-type complex, $[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2(ER_3)_2]$ (E = P, As, Sb; R = Cy, Ph, OPh), in moderate yield. The Ir-Ir bond lengths of complexes of the $[Ir_2(\mu-O_2CMe)_2Cl_2(CO)_2L_2]$ type range from 2.569(1) for $L = CH_3CN$ [3] to 2.6936(7) Å for L = PCy₃, depending on the σ -donation strength of the axial ligand. They show a chemically reversible one-electron oxidation response in the range of 1.30 for $L = CH_3CN$ [3] and 0.21 V versus $Fc^+ - Fc$ for $L = PCy_3$. Some of the oxidized species are moderately stable. ESR studies revealed that when the axial ligand is pyridine the paramagnetic cation has its oddelectron in the δ_{IrIr}^* orbital [3], whereas the σ_{IrIr} orbital is shifted upward in energy to become the SOMO when the axial sites are substituted by P- or As-ligands. The latter is because the strong σ -donation of the axial ligands induces their lone-pair orbitals to mix into the σ_{IrIr} orbital in σ -antibonding phase. DFT calculations of model cations have reasonably reproduced the ESR hyperfine coupling tensors of the axial P or As nuclei and showed that their SOMO is the $\sigma_{IrIr}/\sigma^*_{IrP(As)}$ orbital

which is also delocalized onto the equatorial Cl atoms with π^*_{IrCl} character.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 167648, 167649, 167650, and 167651 for 2·CH₂Cl₂, 3, 4 and 5, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033; e-mail: deposit@aadc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk].

Acknowledgements

This work was supported by grants-in-aid for Scientific Research (11440194 and 10149105) from the Ministry of Education, Science, Sports and Culture, Japan. The DFT calculations were performed on the IBM SP2 workstation cluster and on the NEC SX5 computer at the computer center of the Institute for Molecular Science (Okazaki).

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