VII-B Electronic Structure and Reactivity of Metal Cluster Complexes

Dimetal complexes with metal-metal bond have been a subject of wide interest in these three decades. Meta-metal single- or mulltiple bonds show different reactivitties and properties from those in organic compounds. The reported dimetal complexes were mainly 4d metal complexes. Enhanced metal-metal and metal-ligand interactions are expected for 5d metal cluster compounds. However, rather fewer examples of 5d metal complexes, especially dimetal complexes of iridium(II), have been explored. We have been interested in development of chemistry of Ir_2^{4+} and Ir_2^{5+} complexes.

VII-B-1 A One-Step Synthesis of an Ir(II) Dinuclear Complex. Preparation, Structures and Properties of Bis(μ-acetato)dichlorodicarbonyldiiridium(II) Complexes

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A bis(μ-acetato)dicarbonyldichlorodiiridium(II) complex, $[Ir_2(\mu\text{-}O_2CMe)_2Cl_2(CO)_2]$ **1**, was prepared by the one-step reaction of H_2IrCl_6 with $MeCO_2Li$ under O_2 in a mixture of acetic acid and acetic anhydride. Dissolution of **1** into various ligating solvents gave $[Ir_2(\mu\text{-}O_2CMe)_2Cl_2(CO)_2L_2]$ (L = MeCN: **2**, dmso: **3**, py: **4**, 4-isopropylpyridine: **5**). X-ray structure determinations of **2**, **3** and **4** gave the Ir–Ir distances of 2.569(1), 2.5980(5) and 2.5918(5) Å, respectively, which are in the range of the reported Ir(II)–Ir(II) single-bond distances. CV of **2**, **4** and **5** exhibited a one-electron quasi-reversible oxidation wave at $E_{1/2}$ of 1.30, 0.97 and 0.94 V vs Fc^+/Fc, respectively. Complex **3** gave no CV response in the potential window of dmso.

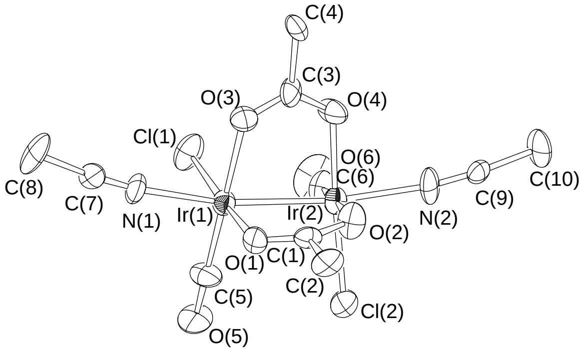

Figure 1. Structure of $[Ir_2(\mu\text{-}O_2CMe)_2Cl_2(CO)_2(CH_3CN)_2]$.

VII-B-2 Preparation and Structure of Bis(μ-acetato)dichlorodicarbonyldiiridium(II) Complexes with group 15 ligands, $[Ir_2(\mu\text{-}O_2CMe)_2Cl_2(CO)_2L_2]$ (L = PPh_3, PCy_3, $P(OPh)_3$, $AsPh_3$, $SbPh_3$), and ESR and DFT Studies of Electronic Structure of Their Cationic Radicals

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Bis(μ-acetato)dichlorodicarbonyldiiridium(II) complex with group 15 compounds as the axial ligands, $[Ir_2(\mu\text{-}O_2CMe)_2Cl_2(CO)_2L_2]$ (L = PPh_3 **6**, PCy_3 **7**, $P(OPh)_3$ **8**, $AsPh_3$ **9**, $SbPh_3$ **10**) were synthesized. The Ir–Ir distances (2.6936(7) Å of **7**, 2.6458(8) Å of **8**, 2.6207(9) Å of **9** and 2.6200(9) Å of **10**) were longer than those of the complexes with axial MeCN, py or dmso. The complexes had a chemically reversible one-electron oxidation wave of which $E_{1/2}$ (*vs.* Fc^+–Fc) values were between 0.22 of **7** and 0.75 V of **8** depending on their axial ligands. Electrolytic or radiolytic oxidation of **6, 7** and **9** gave their cationic radicals. The ESR spectra of $\mathbf{6}^{+\bullet}$, $\mathbf{7}^{+\bullet}$ and $\mathbf{9}^{+\bullet}$ 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 splitting indicates that their odd electron is delocalized equivalently onto the two axial phosphorous or arsenic atoms. The odd electron densities were estimated form the hyperfine coupling tensors as $\rho \approx 0.1$ on the P atom of $\mathbf{6}^{+\bullet}$ and $\mathbf{7}^{+\bullet}$ and $\rho \approx 0.15$ on the As atom of $\mathbf{9}^{+\bullet}$. These ESR results indicate that their SOMO is the σ_{IrIr} orbital with the $\sigma_{IrP}^*/\sigma_{IrAs}^*$ character. DFT calculations for the model complexes, $[Ir_2(\mu\text{-}O_2CH)_2Cl_2(CO)_2(PH_3)_2]^{+\bullet}$ and $[Ir_2(\mu\text{-}O_2CH)_2Cl_2(CO)_2(AsH_3)_2]^{+\bullet}$, gave an electronic structure consistent with the ESR results. A similar DFT calculation of $[Ir_2(\mu\text{-}O_2CH)_2Cl_2(CO)_2(py)_2]^{+\bullet}$ gave a result that its odd electron is accommodated in the orbital with σ_{IrIr}, σ^*_{IrN} and π_{IrCr}^* character. This calculated result, however, is not consistent with the previously reported results of the ESR study of $[Ir_2(\mu\text{-}O_2CMe)_2Cl_2(CO)_2(py)_2]^{+\bullet}$ showing that the odd electron occupies the δ_{IrIr}^* orbital.

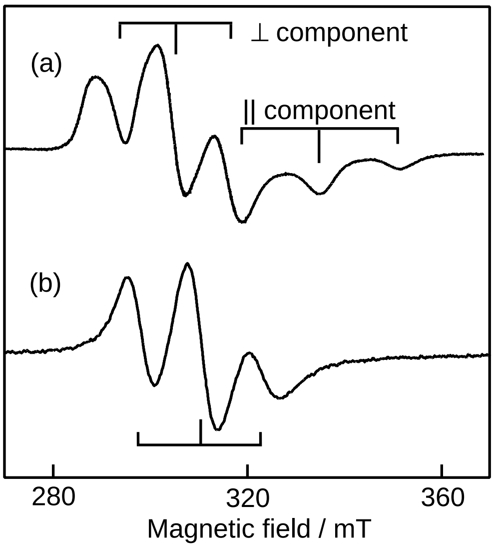

Figure 1. X-Band ESR spectrum of complex $\mathbf{6}^{+\bullet}$ (a) in frozen solution at 77 K and (b) in fluid solution at 273 K.