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A rare unsupported iridium(II) dimer, [IrCl$_2$(CO)$_2$]$_2$

FEATURE ARTICLE
Stephen J. Connon
Asymmetric catalysis with bifunctional cinchona alkaloid-based urea and thiourea organocatalysts

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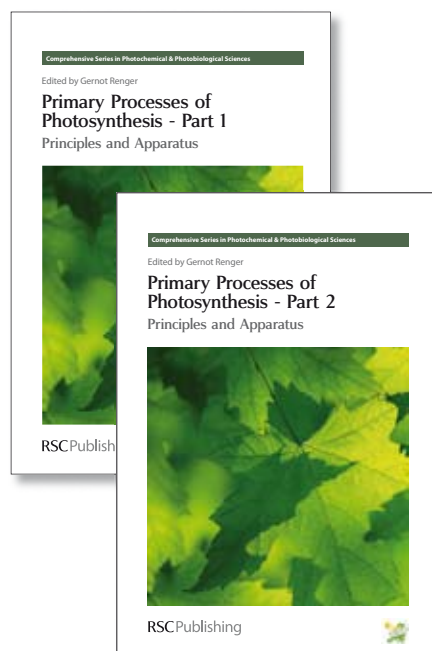# A rare unsupported iridium(II) dimer, [IrCl$_2$(CO)$_2$]$_2$†

**Sanjib K. Patra, S. M. Wahidur Rahaman, Moumita Majumdar, Arup Sinha and
Jitendra K. Bera***

**Oxidative additions of dichloromethanes to a diiridium(I) core,
bridged by 2-ferrocenyl-1,8-naphthyridines (NP-Fc), provide an
iridium(II) dimer, [IrCl$_2$(CO)$_2$(η^1-NP-Fc)]$_2$, featuring an unsupported Ir–Ir single bond (2.7121(8) Å).**

Unsupported diiridium(II) compounds are distinguished by
their rarity. Only three examples of an Ir^{II} dimer possessing
an unsupported Ir–Ir single bond are known.[1] This extraordinary set of compounds involves octaethylporphyrin (oep),[2]
phthalocyanine (pc)[3] or dianion of tetracyanobisimidazole
(tcbim),[4] hinting at the prerequisite of ligand-elaboration in
stabilizing an unbridged Ir^{II}–Ir^{II} bond. The wide ranging
applications of dirhodium(II) compounds in organic transformations[5] and the recent utilization of diruthenium(I) compounds in C–H bond activation and C–C bond formation
reactions[6] prompted our interest in isoelectronic diiridium(II)
chemistry. An intriguing result of our exploration, the chemical synthesis of a novel diiridium(II) compound featuring an
unsupported Ir–Ir bond, is reported herein.

Reaction of [Ir(COD)(MeCN)$_2$][BF$_4$] with 2-R-1,8-
naphthyridine (NP-R) affords [Ir(COD)(η^1-NP-R)$_2$][BF$_4$]
(Scheme 1). X-ray structures of compounds for R = phenyl
(**1**) and ferrocenyl (**2**) reveal 8-N coordination of two NP
ligands (see Fig. S1 and S2†). When carbon monoxide is
bubbled through a dichloromethane solution of **1**, [Ir$_2$(CO)$_4$-
(μ-NP-Ph)$_2$][BF$_4$]$_2$ (**3**) precipitates out which is isolated and
characterized by IR, mass and elemental analysis. Utilization of
NP-Me provides an analogous compound [Ir$_2$(CO)$_4$(μ-NP-Me)$_2$]-
[BF$_4$]$_2$ (**4**), the structure of which has been established by an X-
ray technique.‡ The molecular structure of **4** consists of a
diiridium core with two *cis* NP-Me ligands, arranged in a
head-to-tail fashion, bridging metal centres (Fig. 1). Each
iridium is additionally bonded to two carbonyls. The Ir···Ir
non-bonding distances 2.8151(7) and 2.8051(7) Å, noted for
two independent molecules in the asymmetric unit, are similar
to those found in weakly interacting d^8–d^8 systems.[7,8] The
Ir–N distances are in the range 2.116(7)–2.133(7) Å. The
N11–Ir1–N12 and C1–Ir1–C2 angles are 86.1(2)° and
90.5(4)°, respectively, manifesting a square planar environment around each metal centre. Two Ir^I ions held in close

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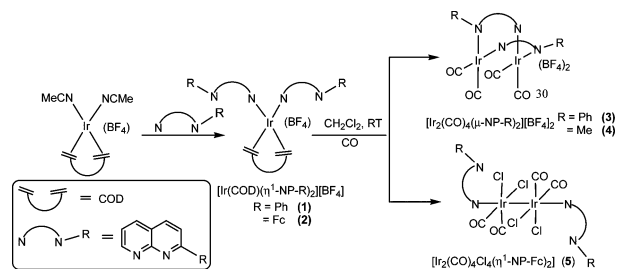
Scheme 1 Synthesis of NP-R bridged diiridium(I) and unsupported
diiridium(II) compounds.

proximity by neutral N-donor ligands, as in **4**, is an exceptional example although diiridium(I) compounds incorporating anionic ligands are abundant.

Substitution of COD from [Ir(COD)(η^1-NP-Fc)$_2$][BF$_4$] (**2**)
by CO in dichloromethane affords a purple solid, characterized as [Ir$_2$Cl$_4$(CO)$_4$(η^1-NP-Fc)$_2$] (**5**).‡ The X-ray structure of **5**
reveals a dimer of '[IrCl$_2$(CO)$_2$]' (Fig. 2). The molecule has an
imposed $C2$ axis across the unsupported Ir–Ir bond. The
geometry about the iridium centres is near-octahedral with
two *cis* CO and two *cis* chlorides bonded to each iridium atom.
The remaining sites are satisfied by axial NP-Fc and the
second iridium. The Ir1–Cl1 and Ir1–Cl2 distances are
2.378(2) and 2.386(3) Å; Ir1–C1 and Ir1–C2 distances are
1.871(11) and 1.892(10) Å respectively. The axial NP-Fc forms
a linear N1–Ir1–Ir1–N1 axis as reflected in the N1–Ir1–Ir1
bond angle 178.8(2)°. The Ir1–N1 distance is 2.183(7) Å. The
iridium and the coordinating atoms at equatorial sites around
it are arranged in a plane; the largest deviation from the best
plane is less than 0.01 Å. The staggered geometry of the dimer
is shown in the Cl1–Ir1–Ir1–Cl1 twist angle of 48.54(13)°
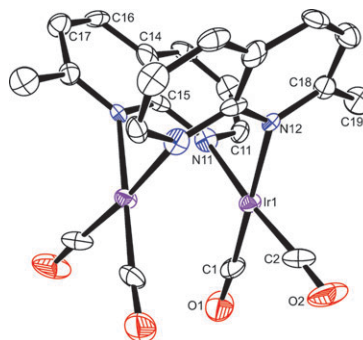(Table 1). An assortment of diiridium compounds pioneered

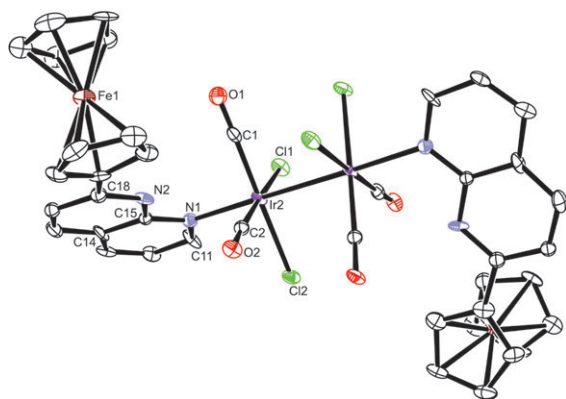**Fig. 1** ORTEP view of dicationic [Ir$_2$(CO)$_4$(μ-NP-Me)$_2$] unit in
compound **4**.

Fig. 2 ORTEP view of the molecular structure of $[IrCl_2(CO)_2-(\eta^1\text{-NP-Fc})]_2$ (**5**).

largely by Oro and Stobart allows scrutiny of the metal–metal distances.[7,9] The unsupported Ir–Ir distance of 2.7121(8) Å in **5** is shorter than that found in association dimers of Ir^I and longer than the corresponding distances in bridged diiridium(II) compounds.[9] Notably, the NP-bridged $Ir^I\cdots Ir^I$ distance in **4** is 0.1 Å longer than the unsupported Ir^{II}–Ir^{II} distance in **5**, strongly suggesting a single bond between metals in the latter compound.
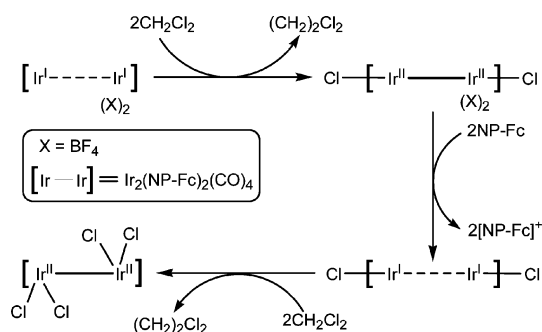
Tedious and unconventional methods have been adopted in the synthesis of unsupported diiridium(II) compounds: $[Ir(oep)]_2$ is obtained through the photolysis of $[Ir(oep)(CH_3)]$ in C_6D_6; $[Ir_2(pc)_2(pyridine)_2]$ is synthesized via controlled thermal decomposition of di(acido)phthalocyaninatoiridates; and $[Ir_2(tcbim)_2(CO)_4(CH_3CN)_2]$ is prepared from electrolysis of salts of $[Ir^I(CO)_2(tcbim)]^-$ in acetonitrile.[2–4] Compound $[Ir_2Cl_4(CO)_4(\eta^1\text{-NP-Fc})_2]$ (**5**) is a unique addition to this list which has been synthesized via chemical oxidation under mild conditions with reasonably good yield (68%). The Ir–Ir distance in **5** (2.7121(8) Å) is similar to that observed for $[Ir_2(pc)_2(py)_2]$ (2.7071(1) Å) but significantly smaller than the 2.826(2) Å reported for $[Ir_2(tcbim)_2(CO)_2\{P(OEt)_3\}_2$ $(CH_3CN)_2]$.

The source of the chlorides in **5** is the solvent, dichloromethane. In 1,2-dichlorobenzene, carbon monoxide treatment of $[Ir(COD)(\eta^1\text{-NP-Fc})_2][BF_4]$ (**2**) provides the substituted product $[Ir(CO)_2(\eta^1\text{-NP-Fc})_2][BF_4]$. We propose a mechanism detailing the formation of **5**, depicted in Scheme 2. Two-fragment, two-centre oxidative addition of haloalkane to the diiridium(I) core, spanned by two anionic bridges, afforded a class of neutral Ir^{II}–Ir^{II} compounds.[9] The NP-Fc offers unusual reactivity, introducing four chlorides to the diiridium(II) core. Initially, incorporation of two chlorides occurs via activation of dichloromethanes across a diiridium(I) com-

Table 1 Comparison of selected bond lengths (Å) and angles (°) of $[Ir_2Cl_4(CO)_4]$ derived from X-ray crystallography (compound **5**) and DFT calculation

	Ir–Ir	Ir–Cl	Ir–C	φ^a
X-Ray	2.7121(8)	2.378(2)	1.892(10)	48.54(13)
		2.386(3)	1.871(11)	44.1(6)
DFT	2.683	2.329	1.904	53.21
		2.352	1.912	48.50

^{a} Torsional angles Cl1–Ir1–Ir1–Cl1 and C2–Ir1–Ir1–C2, respectively.

Scheme 2 Proposed pathways leading to unsupported $Ir_2Cl_4(CO)_4$ core.

pound,[10] presumably $[Ir_2(CO)_4(\mu\text{-NP-Fc})_2][BF_4]_2$, generated *in situ* via displacement of COD in **2** by carbon monoxides. Isolation of $[Ir_2(CO)_4(\mu\text{-NP-Me})_2][BF_4]_2$ (**4**) supports the premise of a dimetal intermediate. Although a mononuclear product, $[Ir(CO)_2(\eta^1\text{-NP-Fc})_2][BF_4]$, is crystallized in 1,2-dichlorobenzene (see Fig. S3†), spectroscopic data reveal dinuclear species in solution.[11] Furthermore, the NP-Fc is shown to bridge a dimetal unit in $[cis\text{-}Rh_2(OAc)_2(\mu\text{-NP-Fc})_2(OH_2)](BF_4)_2$, synthesized and structurally characterized in our laboratory (see Fig. S4†). Reduction of dichloromethanes and subsequent addition of chlorides result in dicationic $[Cl\text{–}Ir^{II}\text{–}Ir^{II}\text{–}Cl]$. The by-product of this reaction, 1,2-dichloroethane, has been identified by a GC technique.

It is our assertion that the $[Cl\text{–}Ir^{II}\text{–}Ir^{II}\text{–}Cl]^{2+}$ species undergoes reduction, generating the $[Cl\text{–}Ir^I\cdots Ir^I\text{–}Cl]$ core (Scheme 2). The NP-Fc, present in excess of two equivalents per diiridium, is most likely the reducing agent. The cyclic voltammogram of NP-Fc in dichloromethane exhibits an irreversible oxidation at $E_{p,a} = +0.85$ V (*vs*. Ag/AgCl) with a return reduction wave at $E_{p,c} = +0.50$ V. The dicationic $[Cl\text{–}Ir^{II}\text{–}Ir^{II}\text{–}Cl]$ core, likely to be a stronger oxidant compared to its neutral diiridium(II) analogues involving anionic bridges,[9] is reduced, yielding neutral $[Cl\text{–}Ir^I\cdots Ir^I\text{–}Cl]$. The oxidized product $[NP\text{-}Fc]^+$ proved to be elusive for identification. Our attempts to identify the oxidized species invariably led to the isolation of protonated salt $[H\cdot NP\text{-}Fc]^+[BF_4]^-$ (see Fig. S5†). Subsequent activation of dichloromethanes results in oxidative additions of two more chlorides across the diiridium(I) core that proceeds with concomitant growth of an Ir^{II}–Ir^{II} single bond. Incorporation of four chlorides, in addition to the four carbonyls present at the diiridium core, leads to migration of NP-Fc to an axial position, resulting in unsupported iridium(II) dimer **5**.

DFT calculations on $[Ir_2Cl_4(CO)_4]$ provide insight into the electronic structure of the diiridium(II) core. The X-ray structure of **5** was used as an initial geometry for optimization in $C2$ symmetry and was characterized fully via analytical frequency calculation as the minima on the potential energy surface. The metrical parameters obtained from the X-ray structure and DFT calculation are in good agreement (Table 1). The calculated Ir–Ir distance (2.683 Å) is marginally shorter than that measured experimentally. Truncation of two axially coordinated NP-Fc in the calculated structure possibly contributes to a shorter metal–metal distance. The staggered disposition of ligands about the metals suggests the absence of any δ
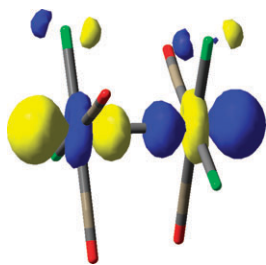
Fig. 3 Contour surface of the LUMO (σ) in [Ir₂Cl₄(CO)₄].

bonding. Calculated orbital occupancies support the electronic configuration of the $[Ir_2]^{4+}$ unit as $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}\sigma^{*0}$, the LUMO being a σ orbital resulting virtually from the anti-bonding interaction of Ir d_{z^2} orbitals (Fig. 3), corresponding to a formal Ir–Ir bond order of 1. Careful analyses of occupied MOs illustrate two-orbital, four-electron interactions between chloride and Ir orbitals. This situation is stabilized by the admixture of CO π* into the anti-bonding Ir–Cl combination. Thus, there is a transfer of electron density from chloride to carbonyl through Ir centres. This charge delocalization can be traced as the origin of the stable unsupported iridium(II) dimer **5**.

The 1,8-naphthyridine ligand with a redox-active ferrocene appendage provides easy access to an unsupported diiridium(II) compound. The synthesis and structural elucidation of the title compound **5** underscore the stability of unsupported Ir^{II} dimer with a combination of common π-donor/π-acceptor ligands chlorides and carbonyls. Furthermore, the chlorides offer the prospect of derivatization of the diiridium(II) core which is being pursued actively. It is our expectation that compound **5** will emerge as a key precursor in the exploration of diiridium(II) chemistry.

Notes and references

‡ Synthesis of **4**: TlBF₄ (46 mg, 0.15 mmol) was added to an acetonitrile solution (10 mL) of [IrCl(COD)]₂ (51 mg, 0.075 mmol) and the yellow mixture was stirred for 30 min. The TlCl was removed by Schlenk filtration, then NP-Me (45 mg, 0.31 mmol) was added to the filtrate and the mixture was stirred for 8 h at RT. The resulting orange solution was concentrated under vacuum and 15 mL of diethyl ether were added with stirring to induce precipitation. The isolated solid was dissolved in dichloromethane (10 mL) and carbon monoxide was bubbled for 5 min. The purple solid [Ir₂(CO)₄(μ-NP-Me)₂][BF₄]₂ (**4**) precipitated out slowly from the reaction medium. The solution was filtered off through a filter paper-stripped cannula and the solid residue was washed with hexane (3 × 5 mL) and dried in vacuum. Crystals were grown by layering a benzene solution of [Ir(COD)(η¹-NP-Me)₂][BF₄] over dichloromethane saturated with carbon monoxide. Yield: 65 mg (90%, based on iridium). Anal. Calcd for C₂₂H₁₆N₄O₄B₂-F₈Ir₂: C, 27.57; H, 1.68; N, 5.85. Found: C, 27.49; H, 1.74; N, 5.79%. IR (KBr pellet): ν(CO) 2058, 2005; ν(BF₄⁻) 1069 cm⁻¹.
5: Carbon monoxide was bubbled for 5 min through a dichloromethane (10 mL) solution of **2** (30 mg, 0.031 mmol) and the resultant

purple solution was stirred for 6 h at RT. It was then concentrated under vacuum and hexane (15 mL) was added with stirring to induce precipitation. The solid residue obtained was washed with diethyl ether (3 × 5 mL) and dried in vacuum. Crystals suitable for X-ray study were obtained by layering hexane over the dichloromethane solution of the compound. Yield: 12 mg (68%, per iridium). ¹H NMR (CDCl₃, δ, ppm): 9.1–8.5 (br, m, 10H), 4.1 (br, 18H). IR (KBr pellet): ν(CO) 2061,1983 cm⁻¹ Anal. Calcd for C₄₀H₂₈N₄O₄Cl₄Fe₂Ir₂: C, 37.93; H, 2.23; N, 4.42. Found: C, 37.88; H, 2.29; N, 4.51%. UV–Vis spectra [λ_max, nm (ε, dm³ mol⁻¹ cm⁻¹)] (in CH₃CN): 234 (8.21 × 10³), 322 (4.89 × 10³), 472 (3.88 × 10²), 590 (2.42 × 10²).
Crystal data for compound **4**: formula C₂₂H₁₆B₂F₈Ir₂N₄O₄, M = 958.41, orthorhombic, space group $Pbcn$ (No. 60), a = 10.8097(7), b = 32.184(2), c = 19.7274(14) Å, V = 6863.2(8) Å³, Z = 8, ρ_c = 1.855 g cm⁻³, F_{000} = 3552, T = 100(2) K, $2\theta_{max}$ = 49.4°, 5861 unique, $GooF$ = 0.973, $R1$ = 0.0394, $wR2$ = 0.0843.
Crystal data for compound **5**: C₄₂H₂₈Cl₈Fe₂Ir₂N₄O₄, M = 1432.38, monoclinic, space group $C2/c$ (No. 15), a = 16.473(2), b = 14.541(2), c = 20.961(3) Å, β = 97.097(2)°, V = 4982.5(12) Å³, Z = 4, ρ_c = 1.910 g cm⁻³, F_{000} = 2728, T = 100(2) K, $2\theta_{max}$ = 52.7°, 13 966 reflections collected, 5057 unique, $GooF$ = 0.991, $R1$ = 0.0554, $wR2$ = 0.1187.

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