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[{Ir(η^5-C$_5$Me$_5$)(CO)}$_6$Hg$_8$][CF$_3$CO$_2$]$_6$, a Mixed-Metal Cluster with an Ir$_6$Hg$_6$ Twelve-Membered Ring and Additional Hg Centers and Metal–Metal Bonds**

Giuseppina Chiaradonna, Giovanni Ingrosso,* and Fabio Marchetti*

In 1995 one of us reported that benzene can be directly aminated by diethylamine in the presence of [Ir(η^5-C$_5$Me$_5$)(CO)$_2$] (**1**) and a mercury(II) salt, typically HgSO$_4$; one of the roles played by the latter is most probably that of making the carbonyl ligands more susceptible to nucleophilic attack.[1] Accordingly, the literature[2] documents that the interaction of the metal–base[3] **1** with HgCl$_2$ results in a marked shift of the CO stretching frequencies to higher wavenumbers as a consequence of the formation of the adduct [(η^5-C$_5$Me$_5$)(CO)$_2$IrHgCl][HgCl$_3$] (**2**). These preliminary remarks prompted us to start an extensive investigation of the reaction of **1** with various mercury(II) salts with the aim of exploring further the chemistry of such a reaction. Hereby, we have discovered a quite complex reactivity which varies markedly on varying the nature of the salt. Herein, we report on the reaction of **1** with Hg(CF$_3$CO$_2$)$_2$ in CH$_2$Cl$_2$ which yields the unexpected compound [{Ir(η^5-C$_5$Me$_5$)(CO)}$_6$Hg$_8$][CF$_3$CO$_2$]$_6$ (**3**) as a red crystalline diamagnetic solid. The course of the reaction is still unclear; however, the definite nature of **3** clearly indicates an oxidative role played by the Hg^{2+} ion. Although transition metal compounds containing bonds with mercury have been known for a long time, mercury clusters are relatively rare[4] and the structure of **3** is unique in this field.

The ^{1}H NMR spectrum of compound **3** exhibits two sharp singlets at $\delta = 2.28$ and 2.53 ([D]chloroform) in a 2:1 ratio for two sets of magnetically equivalent η^5-C$_5$Me$_5$ methyl groups, both being downfield from the value for **1** ($\delta = 2.18$, [D]chloroform).[5] The IR spectrum of **3** shows four CO stretching frequencies at 1972, 1957, 1948, and 1935 cm^{-1} (nujol) that are lower than those for **1** (2000 and 1925 cm^{-1}).[5] Thus, a comparison of the ^{1}H NMR and IR data for **3** with those reported for **2** (i.e. $\delta = 2.31$, and ν(CO) = 2085 and 2045 cm^{-1}[2]) provides evidence in favor of increased electron density at the iridium centers in **3**. Thus, the nature of the Ir–Hg bonds in **3** is significantly different from that in **2**. In fact in **2**, the metal–metal bond causes a withdrawal of electron density from the iridium center.[2]

The molecular geometry of **3** was determined by single-crystal X-ray analysis at 293 K (Figure 1). The cationic component of **3**, that is [{Ir(η^5-C$_5$Me$_5$)(CO)}$_6$Hg$_8$]$^{6+}$, contains a novel ring system with an Ir$_6$Hg$_6$ twelve-membered ring with additional Hg centers; Hg–Hg and Hg–Ir bonds give rise to a network within the Ir$_6$Hg$_6$ ring. The whole metal network appears roughly disposed on three different planes bent in a way which is reminiscent of the chair conformation of cyclohexane. The core moiety of [{Ir(η^5-C$_5$Me$_5$)(CO)}$_6$Hg$_8$]$^{6+}$ (Figure 2), formed by the Hg(1), Hg(2), Ir(1), Ir(3), Hg(1′), Hg(2′), Ir(1′), and Ir(3′) metal centers, is almost exactly planar with a maximum deviation of 0.04 Å. Interestingly, the same fascinating arrangement[6] has al-

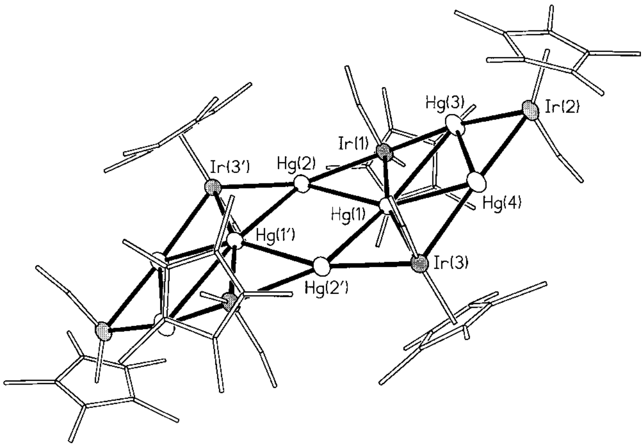

Figure 1. The molecular structure of the cation in **3**. The CF$_3$CO$_2^-$ ions and H atoms are omitted for clarity. The metals are represented by thermal ellipsoids at 30% probability. The superscript ′ denotes the atoms generated by the symmetry operation $1-x, 1-y, -z$. Metal–metal bond lengths [Å] (standard deviations are given in parentheses): Hg(1)-Ir(1) 2.739(2), Hg(1)-Ir(3) 2.749(2), Hg(1)-Hg(2′) 2.982(2), Hg(1)-Hg(2) 3.0278(18), Hg(1)-Hg(3) 3.070(2), Hg(1)-Hg(4) 3.078(2), Hg(2)-Ir(1) 2.675(2), Hg(2)-Ir(3′) 2.679(2), Hg(2)-Hg(1′) 2.982(2), Hg(3)-Ir(2) 2.599(2), Hg(3)-Ir(1) 2.685(2), Hg(3)-Hg(4) 2.962(2), Hg(4)-Ir(2) 2.604(2), Hg(4)-Ir(3) 2.701(2).

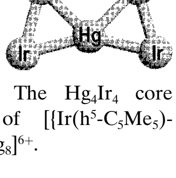

Figure 2. The Hg$_4$Ir$_4$ core moiety of [{Ir(h^5-C$_5$Me$_5$)(CO)}$_6$Hg$_8$]$^{6+}$.

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[*] Prof. Dr. G. Ingrosso, Dr. G. Chiaradonna
Dipartimento di Chimica e Chimica Industriale
Università di Pisa
Via Risorgimento 35, 56126 Pisa (Italy)
Fax: (+39) 050-918410
E-mail: vanni@dcci.unipi.it
Prof. Dr. F. Marchetti
Dipartimento di Ingegneria Chimica, dei Materiali, delle Materie Prime e Metallurgia
Università La Sapienza
Via del Castro Laurenziano 7, 00161 Roma (Italy)
Fax: (+39) 050-918260
E-mail: fama@dst.unipi.it

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ready been found in two structurally characterized compounds, namely $[\{Mn(\eta^5\text{-}C_5H_4Me)(CO)_2Hg\}_4]$[7] and $[\{Re(\eta^5\text{-}C_5H_5)(CO)_2Hg\}_4]$.[8]

$[\{Ir(\eta^5\text{-}C_5Me_5)(CO)\}_6Hg_8]^{6+}$ allows a crystallographic inversion operation; its local symmetry is higher and may approximately be considered as $2/m$ (C_{2h}), with the twofold axis passing through the Hg(2) and Hg(2′) atoms. According to the ^{1}H NMR spectrum, this is probably the symmetry that **3** has in solution.

Interestingly, either the Hg–Ir or the Hg–Hg bond lengths show a significant increase on increasing the coordination number of the metal centers (see caption to Figure 1).

Two of the six trifluoroacetate anions in **3** (not shown in Figure 1) point their oxygen atoms towards Hg(1) and towards Hg(1′), respectively, both at a Hg$\cdots$O distance of 2.95 Å on opposite sides of the cluster; each is located where the corresponding mercury centers are less sterically shielded by the bulky η^5-C_5Me_5 ligands. The other four anions are distributed around the cation with different orientations.

Looking at the metal arrangements observed to date in mixed-metal mercury clusters,[4] the Hg centers in **3** show quite surprising structural environments. Indeed, according to their coordination, the eight Hg centers can be subdivided into three categories: the six-coordinate Hg(1) centers, the four-coordinate Hg(3) and Hg(4) centers, and the four-coordinate Hg(2) centers. Moreover, two types of iridium centers may be distinguished: one is represented by Ir(1) and Ir(3) (Figure 1) that are bonded to a η^5-C_5Me_5 ligand, a terminal CO ligand, and three Hg centers, and the other one is represented by Ir(2) centers that are bonded to a η^5-C_5Me_5 ligand, a terminal CO ligand, and two Hg centers. All the iridium atoms are located on the cluster edges. Probably due to steric reasons, the η^5-C_5Me_5 and CO ligands are alternately placed on opposite sides of the metal cluster. Remarkably, while the Ir(2) centers exhibit the well-known "three-legged piano stool geometry", the Ir(1) and Ir(3) centers exhibit unprecedented coordination number and coordination geometry which can be described as a highly distorted square pyramid; the square is defined by three Hg and one C (CO) atoms, and the apex by the centroid of the η^5-C_5Me_5 group.

In conclusion, **3** is a highly unusual mixed-metal cluster whose bonding properties cannot be explained readily by standard electron counting. Therefore, further work is necessary to throw light on the complex metal–metal bonding situation exhibited by this compound.

Experimental Section

A mixture of $Hg(CF_3CO_2)_2$ (61 mg, 0.14 mmol) and $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$ (55 mg, 0.14 mmol) in dichloromethane (10 mL) was stirred for 30 min at room temperature under a pure argon atmosphere. Slow diffusion of diethyl ether (10 mL) into the above solution caused the precipitation of analytically pure **3** (53 mg) as red, well-shaped crystals in the course of ten days. Elemental analysis calcd for $C_{78}H_{90}F_{18}O_{18}Hg_8Ir_6$ (4415.57) (%): C 21.22, H 2.05; found: C 20.82, H 2.11.

X-ray structure analysis for **3**: a deep red prism of approximate dimensions $0.45 \times 0.22 \times 0.014$ mm^3 was glued at the end of a glass fiber, and the intensity data were collected on a Siemens P4 diffractometer using the $Mo_{K\alpha}$ graphite-monochromated radiation ($\lambda = 0.71073$ Å). Cell parameters were calculated on the accurately centered setting angles of 35 strong reflections with $5.2° < q < 11.2°$. Crystal data: $C_{78}H_{90}F_{18}Hg_8Ir_6O_{18}$, $M_r = 4415.57$, $T = 293(2)$ K, space group $P2_1/n$ (no. 14), $a = 12.2292(13)$, $b = 19.681(2)$, $c = 21.304(2)$ Å, $\beta = 101.869(9)°$, $V = 5018(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.922$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 20.194$ mm^{-1}, $F(000) = 3932$. The intensities of 7695 reflections with $2° \leq \theta \leq 22°$ were collected. After merging the equivalent ones and after correction for Lorentz, polarization, and absorption effects with an integration method,[9] an internal R value $[\Sigma\,|F_o^2 - F_o^2(\text{mean})|/\Sigma(F_o^2)]$ of 0.0686 was obtained. The structure was solved by standard direct and Fourier methods and refined by full-matrix least-squares procedures. Rotational disorder was present in the three independent anions and two of them had to be refined as rigid groups. Some degree of disorder also extended to the η^5-Cp* ligands. The disorder could not be accounted for through a simple model characterized by two distinct positions. In the final refinement cycle anisotropic thermal parameters were used for Ir, Hg, and some of the C and O atoms, giving a conventional R factor (F_o) of 0.0767, calculated for 312 parameters on 4096 observed reflections, and a value of 0.1185 for all 6140 data. Thirteen residual peaks of 2–5 e Å^{-3} were present in the final difference Fourier map at distances between 1.0 and 1.6 Å from Hg and Ir atoms. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-145995. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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