Novel Dinuclear Iridium(I) and Mixed Iridium(I)-Rhodium(I) Complexes. *X*-Ray Crystal Structure of Di-μ-benzenethiolato-bis[dicarbonyliridium(I)]

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Summary The thiolato-bridged iridium(I) carbonyl complexes [{Ir(SR)(CO)$_2$}$_2$] (R = Bu^t or Ph) have been prepared by the reaction of [{Ir(SR)(C$_8$H$_{12}$)}$_2$] in pentane with CO, and the crystal structure of [{Ir(SPh)(CO)$_2$}$_2$] suggests the existence of intra- and inter-molecular metal–metal interactions; similar mixed iridium(I)–rhodium(I) chloro-bridged complexes have also been prepared.

As part of a study of bridged d^8 complexes[1] a series of thiolato-bridged rhodium(I) dinuclear complexes[2] has been reported: [Rh(SR)(C$_8$H$_{12}$)]$_2$ (C$_8$H$_{12}$ = cyclo-octa-1,5-diene), [Rh(SR)(CO)$_2$]$_2$, [Rh(SR)(CO)$_2$L]$_2$, and [Rh(SR)(CO)L]$_2$. We now report the synthesis, i.r. data, reactivity towards nucleophiles, and preliminary *X*-ray results of an analogous series of iridium(I) complexes.

The dimeric chloro-bridged complex [{IrCl(C$_8$H$_{12}$)}$_2$] reacts with LiSR (R = Bu^t or Ph), leading quantitatively to the dimeric thiolato-bridged complexes [{Ir(SR)(C$_8$H$_{12}$)}$_2$]. When CO is bubbled through a pentane solution of [{Ir(SR)(C$_8$H$_{12}$}$_2$] the di-iridium(I) carbonyl compounds [{Ir(SR)(CO)$_2$}$_2$] (I) are obtained in quantitative yield. These compounds are stable to air and moisture and crystallize as bronze (R = Bu^t) or black (R = Ph) prisms. Their i.r. spectra in hexadecane solution exhibit three CO stretching bands analogous to those of the previously reported[2] rhodium complexes (Table).

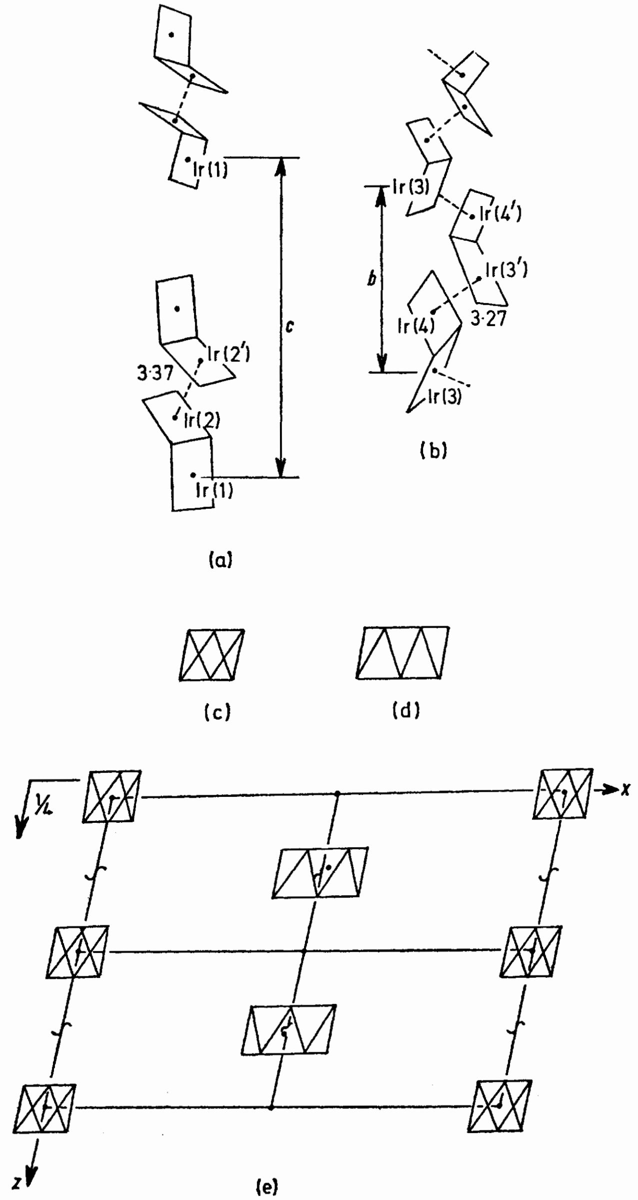
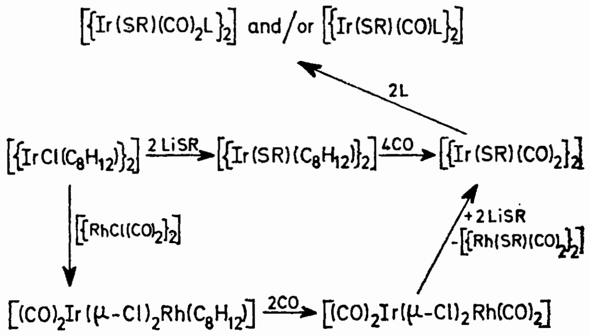


Figure. Association modes of the 'butterfly' units in $[\{Ir(SPh)(CO)_2\}_2]$. (a) Intermolecular Ir–Ir interactions forming associations of two dinuclear units; (b) intermolecular Ir–Ir interactions forming an infinite chain parallel to the *b* axis; (c) symbol representing (a) units; (d) symbol representing (b) units; (e) packing arrangement of (a) units and (b) infinite chains in the unit cell projected on to the 010 plane.

The crystal structure of $[\{Ir(SPh)(CO)_2\}_2]$ was determined on an Enraf Nonius CAD4 computer-controlled four-circle diffractometer. The compound crystallizes in the $P2_1/c$ space group with $a = 24{\cdot}251(7)$, $b = 8{\cdot}934(2)$, $c = 17{\cdot}298(6)$ Å, $\beta = 103{\cdot}95(5)°$, $Z = 8$.

The two independent dinuclear $\{Ir(SPh)(CO)_2\}_2$ units have a comparable geometry. In both cases the iridium atom exhibits a square-planar arrangement of two carbonyl groups and two sulphur atoms, the latter forming the bridge within a given dinuclear unit. The dihedral angle between the two squares is *ca.* 100°. The distance between the two iridium atoms of such a 'butterfly' unit is 3·10 Å suggesting a metal–metal interaction.



Scheme. R = Bu^t or Ph; L = PMe_3, $P(NMe_2)_3$, PPh_3, or $P(OMe)_3$.

The main feature of the structure lies in the association mode of the 'butterfly' units (Figure). These associations are due to intermolecular iridium–iridium interactions, and are of two types. In the first type (a) association of two dinuclear units leads to an inversion centre, in a unit of composition $[\{Ir(SPh)(CO)_2\}_2]_2$. Thus only one of the iridium atoms of each dinuclear unit is involved in a metal–metal 'interbutterfly' interaction: Ir(2)–Ir(2') = 3·37 Å. In the second type (b) interaction involving both iridium atoms of a given unit leads to a continuous chain of 'butterflies' running parallel to the *b* direction, around a two-fold helical axis. The Ir(3)–Ir(4') and Ir(4)–Ir(3') distances are *ca.* 3·27 Å. Full details of the structure will be described elsewhere; a simple visualization of the packing arrangement is given in the Figure (e).

Table. I.r. data for the dinuclear iridium(I) and iridium(I)–rhodium(I) complexes

Compounds	$\nu_{CO}/cm^{-1\,a}$
$[\{Ir(SBu^t)(CO)_2\}_2]$	2061s, 2040vs, 1986vs
$[\{Ir(SPh)(CO)_2\}_2]$	2072m, 2052vs, 2003vs
$[\{Ir(SBu^t)(CO)_2(PMe_3)\}_2]$	2038vs, 1969vs, 1956vs
$[\{Ir(SBu^t)(CO)(PMe_3)\}_2]$	1955vs, 1941vs
$[(CO)_2Ir(\mu\text{-}Cl)_2Rh(C_8H_{12})]$	2077vs, 2005vs
$[(CO)_2Ir(\mu\text{-}Cl)_2Rh(CO)_2]$	2087s, 2068s, 2021vs

[a] s = strong, m = medium, v = very.

Monitoring by i.r. spectroscopy of the addition of 2 mol of a tertiary phosphine ligand L to the complex $[\{Ir(SBu^t)(CO)_2\}_2]$ indicated the existence of two types of complexes. Strong evidence for the formation of five-co-ordinate dinuclear complexes $[\{Ir(SBu^t)(CO)_2L\}_2]$ was obtained, decarbonylation of which gave the dinuclear complexes $[\{Ir(SBu^t)(CO)L\}_2]$ [L = PMe_3, $P(NMe_2)_3$, PPh_3, or $P(OMe)_3$] in good yields.

By mixing equimolecular amounts of $[\{IrCl(C_8H_{12})\}_2]$ and $[\{RhCl(CO)_2\}_2]$ in toluene the chloro-bridged dinuclear iridium(I)–rhodium(I) complex $[(CO)_2IrCl_2Rh(C_8H_{12})]$ (II) was prepared. Addition of 2 equiv. of CO to this compound led to the dinuclear complex $[(CO)_2IrCl_2Rh(CO)_2]$ (III). Compounds (II) and (III) constitute, to our knowledge, the second examples of dinuclear complexes with two different d^8 metals in a square-planar environment.[3]

These results are summarized in the Scheme and Table.

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[1] See R. Poilblanc, *J. Organometallic Chem.*, 1975, **94**, 241 and references therein.

[2] P. Kalck and R. Poilblanc, *Inorg. Chem.*, 1975, **14**, 2779.

[3] C. Masters and J. P. Visser, *J.C.S. Chem. Comm.*, 1974, 932.