Synthesis and Chemical Characterization of the Hexanuclear Anions $[Ir_6(CO)_{14}X]^-$ (X = Cl, Br, I, or SCN). Crystal and Molecular Structures of $[PPh_4][Ir_6(\mu\text{-}CO)_2(CO)_{12}(\mu\text{-}Br)]$ and $[N(PPh_3)_2][Ir_6(\mu\text{-}CO)_2(CO)_{12}(\mu\text{-}X)]$ (X = I or SCN) *

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The salts of the monosubstituted hexanuclear anions $[Ir_6(CO)_{14}X]^-$ [X = Cl (**1**), Br (**2**), I (**3**), or SCN (**4**)] have been prepared by treating $[Ir_6(CO)_{16}]$ with halides or pseudohalides at room temperature in tetrahydrofuran solution. Complex (**2**) crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with $a = 12.653(4)$, $b = 25.566(10)$, $c = 13.351(2)$ Å, $\beta = 91.04(2)°$, and $Z = 4$, (**3**) crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with $a = 17.444(3)$, $b = 14.791(3)$, $c = 23.332(5)$ Å, $\beta = 113.32(2)°$, and $Z = 4$, and (**4**) crystallizes in the monoclinic space group $P2_1$ (no. 4) with $a = 9.441(3)$, $b = 36.952(9)$, $c = 15.663(4)$ Å, $\beta = 91.44(2)°$, and $Z = 4$. The three structures have been solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares to final conventional R values of 0.029 (**2**), 0.036 (**3**) and 0.045 (**4**) on the basis of 4 223, 5 427, and 7 181 independent counter data having $I > 3\sigma(I)$. The three anions consist of slightly distorted octahedra of iridium atoms bearing twelve terminal and two edge-bridging carbon monoxide groups. In all cases the halogen atoms or the pseudohalogen group adopt a bridging co-ordination on an Ir–Ir edge.

We are currently studying the cluster chemistry of the cobalt sub-group and particularly of rhodium and iridium compounds. One field of this chemistry concerns the substitution reactions of the neutral carbonyls with anionic ligands. Some families of compounds have already been characterized, *e.g.* $[Co_4(CO)_{11}X]^-$ (X = Br, I, or SCN),[1] $[Rh_6(CO)_{15}X]^-$ (X = Cl, Br, I, CN, or SCN),[2] and $[Ir_4(CO)_{11}X]^-$ (X = Cl, Br, I, CN, or SCN).[3]

In particular the chemistry of rhodium carbonyl clusters with halides is quite complicated because starting from $[Rh_6(CO)_{16}]$ it is possible to obtain the hexanuclear monosubstituted derivatives $[Rh_6(CO)_{15}X]^-$ (X = Cl, Br, I, CN, or SCN),[2] the disubstituted $[Rh_6(CO)_{14}X_2]^{2-}$ (X = CN),[2] or the heptanuclear dianions $[Rh_7(CO)_{16}X]^{2-}$ (X = Br or I),[4] depending on the metal carbonyl to halide or pseudohalide molar ratio. Also, the reactions of $[Rh_4(CO)_{12}]$ with halides give rise to different products according to the experimental conditions, *e.g.* under nitrogen the $[Rh_6(CO)_{15}X]^-$ (X = Cl, Br, I, or SCN) anions are obtained[2] while under carbon monoxide it is possible to isolate the complex $[Rh_5(CO)_{14}I]^{2-}$.[5]

In all the above families the entering ligand is terminally bonded to the metal atom, except in the case of $[Rh_7(CO)_{16}I]^{2-}$ where the halogen atom bridges the edge between the capping rhodium and one of the rhodium atoms of the octahedral moiety.[6]

Structurally assessed examples of halogen atoms adopting a bridging bonding mode are scarce in cluster chemistry, the few reported being: $[Os_4(CO)_{12}(\mu\text{-}I)(\mu\text{-}H)]$,[7] $[N(PPh_3)_2][Os_{10}C(CO)_{24}(\mu\text{-}I)]$,[8] $[Os_{10}C(CO)_{24}(\mu\text{-}I)_2]$,[8] $[Os_{10}C(CO)_{23}\{P(OMe)_3\}(\mu\text{-}I)_2]$,[8] where the iodine atoms link two non-bonded metal atoms; $[NEt_4][Re_3(CO)_{10}H_3(\mu\text{-}Cl)]$,[9] $[NEt_4][Re_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}I)_2]$,[10] $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}X)]$ (X = Cl[11] or Br[12]) and their substituted derivatives,[13] and the analogue $[Ru_3(CO)_{10}(\mu\text{-}Br)(\mu\text{-}H)]$[14] where the halogen atom spans a metal–metal bond.

Here we report the preparation of the monosubstituted anions $[Ir_6(CO)_{14}X]^-$ (X = Cl, Br, I, or SCN) and the *X*-ray structures of $[PPh_4][Ir_6(CO)_{14}Br]$ and $[N(PPh_3)_2][Ir_6(CO)_{14}X]$ (X = I or SCN) where the entering ligand displaces two carbon monoxide groups of $[Ir_6(CO)_{16}]$ assuming a bridging co-ordination on an Ir–Ir edge. This finding reveals another difference between rhodium and iridium cluster chemistry.

Results and Discussion

Synthesis and Characterization of $[Ir_6(CO)_{14}X]^-$ (X = Cl, Br, I, *or* SCN).—Although the red isomer[15] of $[Ir_6(CO)_{16}]$ has low solubility in organic solvents, it reacts slowly with an excess of halide or pseudohalide salt in dry tetrahydrofuran (thf) at room temperature to produce first an orange species, which shows i.r. absorption bands at 2 037 (sh), 2 017vs, 1 978w, 1 818m, and 1 787m,br cm^{-1}. On the basis of its chemical behaviour this compound has been formulated as $[Ir_6(CO)_{15}X]^-$; however, owing to the long course of the reaction, when all the neutral carbonyl had reacted, only the green anions $[Ir_6(CO)_{14}X]^-$ [X = Cl (**1**), Br (**2**), I (**3**), or SCN (**4**)] were present in solution [equation (1)]. The resulting products can be isolated as green-black solids by addition of solutions of bulky cations salts in Pr^{i}OH. Reaction (1) must be performed in dry media, because the presence in solution of

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* Tetraphenylphosphonium 4,5-μ-bromo-1,2;3,6-di-μ-carbonyl-dodecacarbonyl-*octahedro*-hexairidate, bis(triphenylphosphine)iminium 1,2;3,6-di-μ-carbonyl-dodecacarbonyl-4,5-μ-iodo- and -4,5-μ-thiocyanato-*octahedro*-hexairidate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Infrared spectra data (ν_{CO}/cm^{-1}) for thf solutions

Compound	
(**1**) $[N(PPh_3)_2][Ir_6(CO)_{14}Cl]$	2 050w, 2 020vs, 1 975mw, 1 820m
(**2**) $[N(PPh_3)_2][Ir_6(CO)_{14}Br]$	2 067w, 2 020vs, 1 970mw, 1 815m
(**3**) $[N(PPh_3)_2][Ir_6(CO)_{14}I]$	2 070w, 2 020vs, 1 975mw, 1 820m
(**4**) $[N(PPh_3)_2][Ir_6(CO)_{14}(SCN)]$	2 139vw, 2 069w, 2 024s, 1 973w, 1 822m

v = Very, s = strong, m = medium, and w = weak.

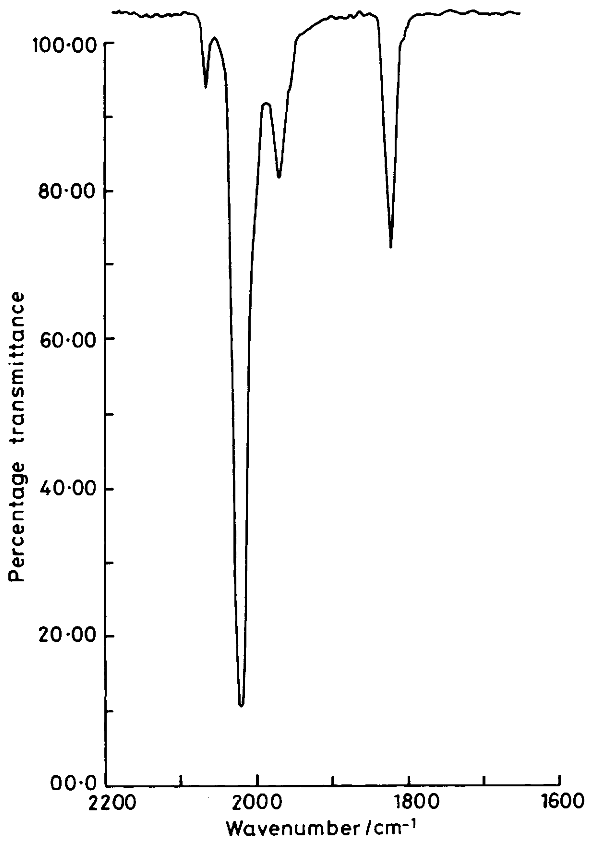

Figure 1. I.r. spectrum of $[N(PPh_3)_2][Ir_6(CO)_{14}Br]$

traces of water results in the concurrent formation of the unreactive $[Ir_6(CO)_{15}]^{2-}$. With halide salts, the reaction course is not appreciably affected by an increase in the temperature and or in the halide to metal carbonyl molar ratio, while in the case of SCN$^-$ a marked dependence is observed; thus increasing the temperature and the SCN$^-$ to metal carbonyl ratio result in fragmentation of the cluster to give $[Ir_3(CO)_6(\mu_3\text{-}S)_2]^-$.[16]

$$[Ir_6(CO)_{16}] + X^- \longrightarrow [Ir_6(CO)_{15}X]^- + CO \longrightarrow [Ir_6(CO)_{14}X]^- + CO \quad (1)$$

The bromo and iodo derivatives can also be obtained by treating $[Ir_6(CO)_{15}]^{2-}$ with 1 mol of Br_2 or I_2 in thf solution [equation (2)]. Also in this case the intermediate formation of $[Ir_6(CO)_{15}X]^-$ can be detected; unfortunately such species could never be isolated because during the work-up of the solution they were always transformed into deep green $[Ir_6(CO)_{14}X]^-$. This reaction can be considered as an electrophilic addition of an X^+ group to the complex with formal oxidation of the cluster and subsequent elimination of a bridging carbon monoxide group which is replaced by the X ligand.

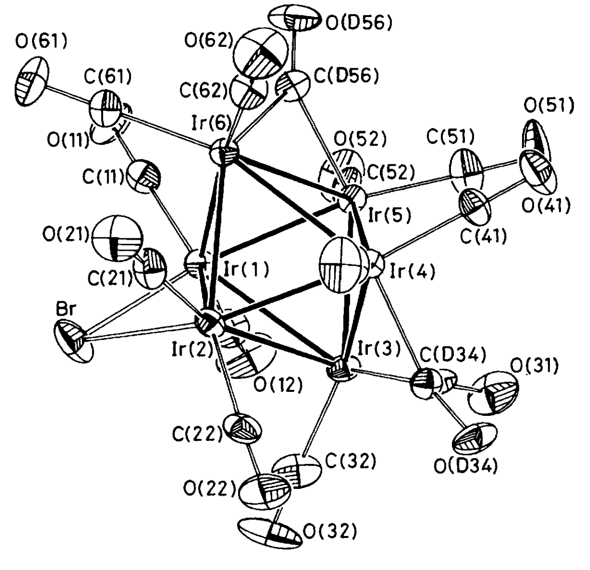

Figure 2. ORTEP drawing of $[Ir_6(CO)_{14}(\mu\text{-}Br)]^-$ (**2**); thermal ellipsoids are drawn at 30% probability

$$[Ir_6(CO)_{15}]^{2-} + X_2 \longrightarrow [Ir_6(CO)_{14}X]^- + X^- + CO \quad (2)$$

The stability of the anions $[Ir_6(CO)_{14}X]^-$ depends on the nature of the X substituent. The chloro derivative is least stable and slowly decomposes in solution in the presence of traces of water to give a mixture of $[Ir_6(CO)_{15}]^{2-}$ with other unidentified products, while the bromo, the iodo, and the thiocyanato complexes are moderately stable under the same experimental conditions. The chloro derivative readily undergoes exchange reactions with thiocyanate, but only partial exchange is observed when it is treated with bromides or iodides even in a ten-fold excess (about 55 and 70% exchange, respectively, based on elemental analysis). This chemical behaviour is in agreement with that found in the case of $[Rh_6(CO)_{15}X]^-$ (X = Cl, Br, I, CN, or SCN).[2] Anions (**2**) and (**3**) do not react with carbon monoxide at 25 °C and 1 atm (101 325 Pa) in thf solution and are also stable in a 0.01 mol dm^{-3} thf solution of HX (X = Br or I).

Figure 1 shows the i.r. spectrum (thf) of $[N(PPh_3)_2][Ir_6(CO)_{14}Br]$. The i.r. spectra of the different derivatives (Table 1) show carbonyl stretching bands attributable, according to the solid-state structure (see later), to terminal and bridging CO groups. For the thiocyanate derivative it is difficult to distinguish the absorption bands of the SCN group owing to partial superimposition with the stretchings of the carbonyl ligands. The i.r. spectra of compounds (**1**)—(**4**) are very similar and suggest for anion (**1**), in solution, the same structure as found for (**2**)—(**4**).

Crystal and Molecular Structures of $[PPh_4][Ir_6(\mu\text{-}CO)_2(CO)_{12}(\mu\text{-}Br)]$ (**2**) and $[N(PPh_3)_2][Ir_6(\mu\text{-}CO)_2(CO)_{12}(\mu\text{-}X)]$ [X = I (**3**) *or* SCN (**4**)].—The crystal structures of compounds (**2**)—(**4**) consist of discrete anions and cations. No unusual bond lengths and angles were found in the counter ions and no short contacts between atoms of different ionic fragments. Selected bond distances and angles are reported in Table 2.

An ORTEP view of the $[Ir_6(CO)_{14}Br]^-$ anion is reported in Figure 2 together with the numbering scheme, which is the same as that adopted for $[Ir_6(CO)_{14}I]^-$. Compound (**4**) crystallizes in space group $P2_1$ with two independent molecules per asym-

Table 2. Selected distances (Å) and angles (°) in the anions (**2**)—(**4**) with estimated standard deviations (e.s.d.s) on the last figure in parentheses (t = terminal, br = bridging)

			$[Ir_6(CO)_{14}(SCN)]^-$	
	$[Ir_6(CO)_{14}Br]^-$	$[Ir_6(CO)_{14}I]^-$	Molecule A	Molecule B
Ir(1)–Ir(2)	2.699(1)	2.711(1)	2.682(2)	2.683(2)
Ir(1)–Ir(3)	2.902(1)	2.769(1)	2.773(2)	2.784(2)
Ir(1)–Ir(5)	2.621(1)	2.671(1)	2.687(3)	2.694(2)
Ir(1)–Ir(6)	2.655(1)	2.771(1)	2.777(2)	2.778(2)
Ir(2)–Ir(3)	2.848(1)	2.760(1)	2.785(2)	2.783(2)
Ir(2)–Ir(4)	2.624(1)	2.668(1)	2.684(3)	2.689(2)
Ir(2)–Ir(6)	2.727(1)	2.781(1)	2.784(2)	2.767(2)
Ir(3)–Ir(4)	2.632(1)	2.708(1)	2.757(2)	2.761(2)
Ir(3)–Ir(5)	2.772(1)	2.844(1)	2.779(2)	2.788(2)
Ir(4)–Ir(5)	2.859(1)	2.885(1)	2.841(2)	2.835(2)
Ir(4)–Ir(6)	2.938(1)	2.837(1)	2.794(2)	2.791(2)
Ir(5)–Ir(6)	2.842(1)	2.710(1)	2.755(2)	2.756(2)
Ir–Ir *	2.760	2.760	2.758	2.756
Ir(1)–X	2.568(2)	2.727(1)	2.422(13)	2.375(11)
Ir(2)–X	2.572(2)	2.734(1)	2.402(12)	2.357(10)
Ir–X *	2.570	2.730	2.412	2.366
S–C			1.735(55)	1.696(35)
C–N			1.127(54)	1.174(40)
$Ir–CO_t$ *	1.874	1.874	1.831	1.859
$Ir–CO_{br}$ *	2.068	2.076	2.039	2.108
$C_t–O_t$ *	1.139	1.147	1.172	1.155
$C_{br}–O_{br}$ *	1.179	1.147	1.185	1.185
Ir(1)–X–Ir(2)	63.34(4)	59.53(3)	67.6(3)	69.1(3)
X–Ir(1)–Ir(2)	58.40(4)	60.37(3)	55.9(3)	55.1(2)
X–Ir(2)–Ir(1)	58.25(5)	60.10(3)	56.6(3)	55.8(2)
Ir(1)–S–C			106(2)	106(1)
Ir(2)–S–C			109(2)	109(1)
S–C–N			170(5)	170(4)

* Average value.

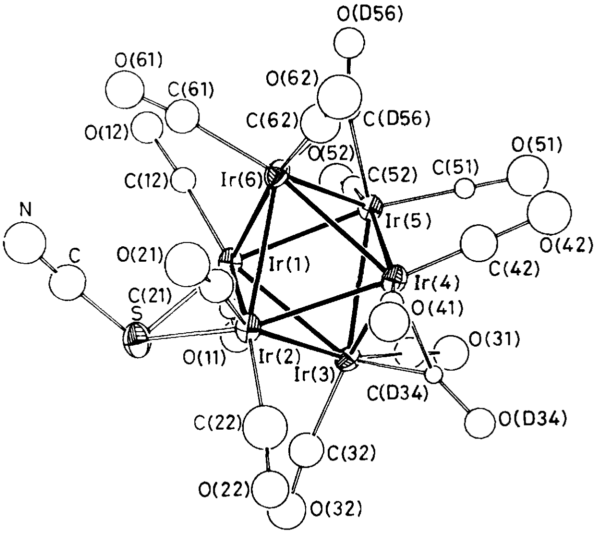

Figure 3. ORTEP drawing of $[Ir_6(CO)_{14}(\mu\text{-}SCN)]^-$ (**4**); thermal ellipsoids are drawn at 30% probability

metric unit, almost related by a pseudo-inversion centre of symmetry, non-compatible however with the 2_1 screw-axis. Figure 3 shows one of the independent anions of compound (**4**) and the numbering scheme used. The two independent anions (**4a**) and (**4b**) show practically the same pattern of bond distances and angles and therefore, if not explicitly stated, we will report the arithmetic average of the two values found in the anions.

The metal skeletons of the three anionic moieties, $[Ir_6(CO)_{14}(\mu\text{-}Br)]^-$ (**2**), $[Ir_6(CO)_{14}(\mu\text{-}I)]^-$ (**3**), and $[Ir_6(CO)_{14}(\mu\text{-}SCN)]^-$ (**4**) consist of an octahedral arrangement of iridium atoms, surrounded by 14 carbonyl ligands and one halogen atom or pseudohalogen group. The stereochemistry of the three $[Ir_6(CO)_{14}X]^-$ anions is strictly related to that of $[Ir_6(CO)_{15}]^{2-}$,[17] from which they can formally be derived by substituting an edge-bridging carbonyl group and one negative charge with a three-electron donor μ-halogen atom or -pseudohalogen group. The idealized symmetry of the whole anion is C_2 owing to the presence of 12 terminal carbonyl ligands (two on each iridium atom), two edge-bridging CO groups, and one μ-X ligand. However, considering only the stereochemistry of the ligands and not their chemical nature, the idealized symmetry is the same as that of $[Ir_6(CO)_{15}]^{2-}$, *i.e.* D_3.[17]

The electron counting of all these anionic compounds results in 86 cluster valence electrons, as always found in all saturated octahedral clusters and predicted by Wade's rules.[18]

The average metal–metal distances observed in (**2**), (**3**), (**4a**), and (**4b**), are almost identical (2.760, 2.760, 2.758, and 2.756 Å respectively), indicating that in all the four cases the amount of Ir–Ir bond electron density, averaged over the twelve edges of the metal octahedron, is almost the same. As a comparison, the average Ir–Ir bond distance found in $[Ir_6(CO)_{15}]^{2-}$ is 2.773 Å.[17]

The metal–carbon distances are also similar [average 1.874, 1.874, and 1.845 Å for terminal ligands and 2.068, 2.076, and 2.074 Å for bridging CO groups in (**2**), (**3**), and (**4**), respectively]; they fall in the normal range found in other octahedral iridium carbonyl compounds; for example the average values found for $Ir–C_{terminal}$ and $Ir–C_{bridging}$ in $[Ir_6(CO)_{15}]^{2-}$ are 1.860 and 2.038 Å, respectively.[17] As in the parent compound $[Ir_6(CO)_{15}]^{2-}$,[17] where the μ-carbonyl ligands are almost symmetrical, the bridging heteroatoms in (**2**), (**3**), and (**4**) define Ir–X–Ir isosceles triangles, with Ir–X–Ir angles of 63.34(4), 59.53(3), and 68.4(3)°, respectively. The Ir–X bond distances are 2.568(2) and 2.572(2) Å for (**2**), 2.727(1) and 2.734(1) Å for (**3**), 2.422(12) and 2.402(12) Å for (**4a**), and 2.375(10) and 2.357(10) Å for (**4b**). The separations found in (**2**) compare well with the value of 2.574(4) Å found in $[Ir_4(CO)_{11}Br]^-$.[3]

In spite of all the similarities found in (**2**)—(**4**) and other iridium clusters, the most striking feature of anion (**2**) is the large scattering of the Ir–Ir distances. The metal skeleton of the bromine derivative is highly distorted from the ideal one, showing minimum and maximum Ir–Ir distances of 2.621 Å [Ir(1)–Ir(5)] and 2.938 Å [Ir(4)–Ir(6)], respectively. The distribution of Ir–Ir bond distances in the actual geometry, however, shows a non-random pattern, with long edges (>2.90 Å) opposite to corresponding long Ir–Ir bonds and, conversely, short distances (<2.70 Å) opposite to each other in the Ir_6 metal skeleton, thus decreasing the idealized symmetry to ($\bar{1}$). Furthermore, one of the Ir–Ir edges spanned by bridging carbonyl ligands [Ir(5)–Ir(6)] shows an unusually long distance of 2.842(1) Å, while the usual effect of a μ-CO is that of shortening the bridged metal–metal bond to a value lower than 2.76 Å [compare with the other μ-CO groups in (**2**)—(**4**)]. No clear explanation of this effect is currently available; however the increasing deformation found in (**2**) can probably be related to the high electronegativity of bromine (3.0 according to Pauling scale), compared to that of Ir (2.2) which is similar to that of I (2.5) and S (2.5).

Steric effects are unlikely to be important in anions (**2**) and (**3**) although they cannot be excluded for (**4**). The average Ir–S bond distance (2.389 Å) in the thiocyanato derivative is slightly shorter than that reported for the terminally bonded thiocyanate group in $[Ir_4(CO)_{11}(SCN)]^-$ [2.455(4) Å];[19] the former value is however affected by the high standard deviations observed in the present compound.

The geometry found in the two pseudohalogen SCN fragments in (**4a**) and (**4b**) shows S–C and C–N distances [S_a–C_a 1.74(5), S_b–C_b 1.70(4), C_a–N_a 1.13(5), and C_b–N_b 1.17(4) Å] comparable with those found in $[Ir_4(CO)_{11}(SCN)]^-$.[19]

Several hexanuclear metal carbonyl clusters of rhodium and iridium containing the same type of substituents have been structurally investigated, and in all cases the geometries of analogous complexes have been found to be different with respect to the bridging carbon monoxide distribution.[20–24] In particular, the structures of the hexanuclear rhodium derivatives $[Rh_6(CO)_{12}\{P(OPh)_3\}_4]$[20] and $[Rh_6(CO)_{15}X]^-$ (X = CO_2Me or COEt)[21] can be obtained from that of the parent carbonyl cluster by replacement of one or more terminal carbonyl groups by the entering substituent. In the case of the hexanuclear iridium carbonyl clusters the stereochemistry of the bridging carbonyls in the substituted derivatives of $[Ir_6(CO)_{16}]$ is always different from that of the red isomer of $[Ir_6(CO)_{16}]$,[15] which is isostructural with $[Rh_6(CO)_{16}]$,[25] and from that of the black isomer of $[Ir_6(CO)_{16}]$ which contains only four edge-bridging carbonyls. Examples of such a behaviour are $[Ir_6(CO)_{12}\{P(OPh)_3\}_4]$,[22] $[Ir_6(CO)_{15}(COEt)]^-$,[23] and

Table 3. Summary of crystal data and intensity collection parameters[a]

Compound	$[PPh_4][Ir_6(CO)_{14}Br]$	$[N(PPh_3)_2][Ir_6(CO)_{14}I]$	$[N(PPh_3)_2][Ir_6(CO)_{14}(SCN)]$
Formula	$C_{38}H_{20}BrIr_6O_{14}P$	$C_{50}H_{30}IIr_6NO_{14}P_2$	$C_{51}H_{30}Ir_6N_2O_{14}P_2S$
M	1 964.66	2 210.85	2 142.02
Space group	$P2_1/c$	$P2_1/c$	$P2_1$
a/Å	12.653(4)	17.444(3)	9.441(3)
b/Å	25.566(10)	14.791(3)	36.952(9)
c/Å	13.351(2)	23.332(5)	15.663(4)
β/°	91.04(2)	113.32(3)	91.44(2)
U/Å^3	4 318(4)	5 528(4)	5 462(5)
D_c/g cm^{-3}	3.022	2.656	2.604
μ(Mo-K_α)/cm^{-1}	193.69	150.07	146.66
θ range/°	3—25	3—23	3—21.5
ω-scan width/°	1.20 + 0.35 tan θ	1.10 + 0.35 tan θ	1.10 + 0.35 tan θ
Octants in the reciprocal space explored	$\pm h, +k, +l$	$\pm h, +k, +l$	$+h, \pm k, \pm l$
Measured reflections	8 063	9 337	14 838
Unique observed reflections [$I > 3\sigma(I)$]	4 223	5 427	7 181
R, R'[b]	0.029, 0.032	0.036, 0.042	0.045, 0.051
No. of variables	421	482	699
Min. transmission factors	0.48	0.76	0.49
E.s.d.[c]	1.078	1.291	1.327

[a] Details common to all three structures: crystal system, monoclinic; $Z = 4$; scan mode, ω. [b] $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$; $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}$. [c] $[\Sigma w(F_o - k|F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$ where N_o = number of observations and N_v = number of variables.

Table 4. Fractional atomic co-ordinates for the complex $[PPh_4][Ir_6(CO)_{14}(\mu\text{-}Br)]$ (**2**) with e.s.d.s in parentheses

Atom	x	y	z
Ir(1)	0.723 42(4)	0.132 05(2)	0.794 38(4)
Ir(2)	0.758 20(4)	0.030 19(2)	0.753 38(4)
Ir(3)	0.736 58(4)	0.099 27(2)	0.586 87(4)
Ir(4)	0.916 84(4)	0.054 46(2)	0.638 31(4)
Ir(5)	0.883 13(4)	0.162 09(2)	0.686 12(4)
Ir(6)	0.908 20(4)	0.090 18(2)	0.847 18(4)
Br	0.610 0(1)	0.059 35(8)	0.870 3(2)
C(11)	0.742(1)	0.178 8(6)	0.907(1)
O(11)	0.755 9(9)	0.206 7(4)	0.973 8(7)
C(12)	0.630(1)	0.173 1(7)	0.718(1)
O(12)	0.580 4(9)	0.204 0(5)	0.678(1)
C(21)	0.821(1)	−0.016 2(6)	0.849(1)
O(21)	0.860 5(9)	−0.046 3(4)	0.899 7(9)
C(22)	0.710(1)	−0.021 6(6)	0.659(1)
O(22)	0.685 6(9)	−0.053 0(4)	0.601 2(9)
C(31)	0.739(1)	0.149 3(6)	0.480(1)
O(31)	0.744(1)	0.178 3(5)	0.410 1(9)
C(32)	0.605(1)	0.074 9(7)	0.565(1)
O(32)	0.527 2(8)	0.059 4(5)	0.551(1)
C(41)	1.037(1)	0.074 2(6)	0.575(1)
O(41)	1.108 4(8)	0.087 2(5)	0.536 9(9)
C(42)	0.964(1)	−0.014 2(6)	0.663(1)
O(42)	0.992 2(8)	−0.055 3(4)	0.678 7(8)
C(51)	0.979(1)	0.182 5(6)	0.590(1)
O(51)	1.036(1)	0.197 9(5)	0.531(1)
C(52)	0.836(1)	0.229 9(6)	0.693(1)
O(52)	0.808(1)	0.272 2(5)	0.701 0(9)
C(61)	0.873(1)	0.090 2(6)	0.990(1)
O(61)	0.852(1)	0.089 8(6)	1.077 6(8)
C(62)	1.027(1)	0.052 9(6)	0.866(1)
O(62)	1.096 3(9)	0.028 3(6)	0.879(1)
C(D34)	0.826(1)	0.047 9(6)	0.506(1)
O(D34)	0.819 2(8)	0.024 7(4)	0.427 7(7)
C(D56)	0.971 (1)	0.161 8(5)	0.820(1)
O(D56)	1.027 7(8)	0.190 2(5)	0.862 1(9)
P	0.356 1(3)	0.166 9(2)	1.045 2(3)
C(111)	0.456(1)	0.136 8(6)	1.117(1)
C(112)	0.551(1)	0.159 8(6)	1.125(1)
C(113)	0.628(1)	0.134 5(6)	1.178(1)
C(114)	0.610(1)	0.088 9(7)	1.233(1)
C(115)	0.513(1)	0.066 6(7)	1.231(1)
C(116)	0.439(1)	0.090 5(7)	1.172(1)
C(211)	0.397(1)	0.230 6(6)	1.002(1)
C(212)	0.466(1)	0.233 5(7)	0.923(1)
C(213)	0.501(1)	0.280 8(7)	0.891(1)
C(214)	0.460(1)	0.325 2(7)	0.934(1)
C(215)	0.388(1)	0.324 7(7)	1.008(1)
C(216)	0.355(1)	0.275 2(6)	1.046(1)
C(311)	0.329(1)	0.129 4(6)	0.929(1)
C(312)	0.351(1)	0.077 3(8)	0.922(1)
C(313)	0.325(2)	0.051 5(9)	0.829(2)
C(314)	0.283(2)	0.074 5(9)	0.750(2)
C(315)	0.255(2)	0.125 8(9)	0.752(2)
C(316)	0.278(1)	0.155 0(7)	0.846(1)
C(411)	0.248(1)	0.171 4(6)	1.126(1)
C(412)	0.154(1)	0.171 8(7)	1.083(1)
C(413)	0.073(1)	0.177 6(7)	1.144(1)
C(414)	0.080(1)	0.184 7(7)	1.251(1)
C(415)	0.172(1)	0.184 5(8)	1.295(1)
C(416)	0.260(1)	0.180 1(7)	1.235(1)

$[Ir_6(CO)_{15}(CO_2Me)]^-$.[24] These structures are always in keeping with the tendency of the 5*d* elements to avoid face-bridging carbonyls.

Experimental

All reactions were carried out in an atmosphere of nitrogen with Schlenk-tube and vacuum line techniques.[26] Solvents were purified and dried by distillation under a nitrogen atmosphere from the following solvent/drier combinations: thf–sodium diphenylketyl, acetone–P_2O_5, Pr^iOH–$Al(OPr^i)_3$. Infrared spectra were recorded on a Perkin-Elmer 781 spectrophotometer using calcium fluoride cells previously purged with nitrogen; the spectra were calibrated with polystyrene. The compound $[Ir_6(CO)_{16}]$, red isomer, was prepared as described.[15] Microanalyses were carried out by the Laboratorio Analisi Universitá di Milano and by Pascher Mikroanalytisches Laboratorium of Bonn.

Syntheses.—$[N(PPh_3)_2][Ir_6(CO)_{14}Cl]$ (**1**). A stirred suspension of $[Ir_6(CO)_{16}]$ (0.583 g, 0.36 mmol) in thf (50 cm^3) was treated with $[N(PPh_3)_2]Cl$ (0.82 g, 1.44 mmol). The reaction was monitored by i.r. spectroscopy until all the $[Ir_6(CO)_{16}]$ had reacted and the i.r. spectrum clearly showed the formation of $[Ir_6(CO)_{14}Cl]^-$ (*ca.* 24 h). The product was recovered by addition of Pr^iOH and concentration *in vacuo*. The resulting precipitate was filtered off, washed first with Pr^iOH then with hexane, and vacuum dried. The crude product was recrystallized from thf–2-propanol (0.6 g, 78%) (Found: C, 28.8; H, 1.3; Cl, 1.5; Ir, 54.0; N, 0.5. Calc. for $C_{50}H_{30}ClIr_6NO_{14}P_2$: C, 28.3; H, 1.4; Cl, 1.5; Ir, 54.4; N, 0.7%). Compound (**1**) is soluble and stable, under a nitrogen atmosphere, for a few days in anhydrous CH_2Cl_2, $CHCl_3$, thf, or CH_3CN, insoluble in Pr^iOH, aliphatic and aromatic hydrocarbons. The $[NMe_3(CH_2Ph)]^+$, $[NEt_4]^+$, $[NMe_4]^+$, and $[PPh_3(CH_2Ph)]^+$ salts were obtained similarly.

$[PPh_4][Ir_6(CO)_{14}Br]$ (**2**). This derivative was prepared as described for (**1**) starting from $[Ir_6(CO)_{16}]$ (0.654 g, 0.41 mmol) and $[PPh_4]Br$ (0.68 g, 1.64 mmol) (Found: C, 23.9; H, 1.1; Br, 4.2; Ir, 59.5. Calc. for $C_{38}H_{20}BrIr_6O_{14}P$: C, 23.2; H, 1.0; Br, 4.0; Ir, 58.7%).

$[N(PPh_3)_2][Ir_6(CO)_{14}Br]$. This compound was prepared by stirring $[Ir_6(CO)_{16}]$ (0.95 g, 0.59 mmol) and KBr (0.42 g, 3.51 mmol) in thf (50 cm^3). The reaction was complete after *ca.* 48 h. The $[N(PPh_3)_2]^+$ salt was isolated by addition of $[N(PPh_3)_2]Br$ (1.5 g) in Pr^iOH (50 cm^3). The crude product was recovered by concentration *in vacuo* and recrystallized from thf–2-propanol (1.02 g, 80%) (Found: C, 28.6; H, 1.2; Br, 3.6; Ir, 53.1; N, 0.5. Calc. for $C_{50}H_{30}BrIr_6NO_{14}P_2$: C, 27.8; H, 1.4; Br, 3.7; Ir, 53.3; N, 0.6%).

$[N(PPh_3)_2][Ir_6(CO)_{14}I]$ (**3**). This compound was prepared as described for $[N(PPh_3)_2][Ir_6(CO)_{14}Br]$ by using $[Ir_6(CO)_{16}]$ (0.6 g, 0.37 mmol) and KI (0.12 g, 0.73 mmol). The reaction was complete after *ca.* 4 h (0.58 g, 71%) (Found: C, 27.5; H, 1.7; I, 5.9; Ir, 53.0; N, 0.7. Calc. for $C_{50}H_{30}IIr_6NO_{14}P_2$: C, 27.2; H, 1.4; I, 5.8; Ir, 52.2; N, 0.6%).

$[N(PPh_3)_2][Ir_6(CO)_{14}(SCN)]$ (**4**). This compound was prepared as described for $[N(PPh_3)_2][Ir_6(CO)_{14}Br]$ by using $[Ir_6(CO)_{16}]$ (0.31 g, 0.20 mmol) and K[SCN] (0.039 g, 0.4

Table 5. Fractional atomic co-ordinates for the complex $[N(PPh_3)_2][Ir_6(CO)_{14}(\mu\text{-}I)]$ (**3**) with e.s.d.s in parentheses

Atom	x	y	z
Ir(1)	0.215 75(4)	0.324 51(4)	0.066 44(2)
Ir(2)	0.101 99(4)	0.189 98(4)	0.021 55(2)
Ir(3)	0.177 14(4)	0.259 55(4)	−0.053 09(2)
Ir(4)	0.208 62(4)	0.089 20(4)	−0.007 14(2)
Ir(5)	0.332 94(4)	0.227 45(4)	0.047 77(2)
Ir(6)	0.255 90(4)	0.152 71(4)	0.116 90(2)
I	0.060 37(7)	0.344 92(8)	0.066 40(5)
C(11)	0.220 4(9)	0.427(1)	0.021 1(6)
O(11)	0.228 8(8)	0.492 6(7)	−0.001 7(5)
C(12)	0.281(1)	0.369(1)	0.145 9(6)
O(12)	0.317 2(8)	0.402(1)	0.192 5(5)
C(21)	0.009 1(8)	0.173(1)	−0.053 1(6)
O(21)	−0.049 8(7)	0.164 8(8)	−0.098 8(5)
C(22)	0.078(1)	0.100(1)	0.071 5(6)
O(22)	0.054 9(7)	0.046 5(8)	0.094 3(4)
C(31)	0.090 2(9)	0.338(1)	−0.090 2(6)
O(31)	0.030 0(7)	0.385 2(8)	−0.112 2(5)
C(32)	0.242(1)	0.301(1)	−0.096 7(6)
O(32)	0.282 8(7)	0.324 2(8)	−0.122 7(4)
C(41)	0.286 9(8)	0.022(1)	−0.024 3(6)
O(41)	0.331 7(8)	−0.025 2(8)	−0.034 7(6)
C(42)	0.155(1)	−0.017(1)	0.001 0(6)
O(42)	0.122 3(8)	−0.082 1(7)	0.005 7(5)
C(51)	0.411(1)	0.153(1)	0.032 2(7)
O(51)	0.460 1(8)	0.112(1)	0.023 7(6)
C(52)	0.389(1)	0.332(1)	0.041 7(7)
O(52)	0.422 8(8)	0.395 9(8)	0.037 2(6)
C(61)	0.229(1)	0.180(1)	0.185 6(6)
O(61)	0.213 8(9)	0.196(1)	0.227 5(5)
C(62)	0.287(1)	0.033(1)	0.140 6(6)
O(62)	0.306(1)	−0.041 7(8)	0.153 1(6)
C(D34)	0.143(1)	0.133 9(9)	−0.098 6(7)
O(D34)	0.108 2(7)	0.107 8(7)	−0.147 8(4)
C(D56)	0.377(1)	0.198(1)	0.140 8(7)
O(D56)	0.437 8(8)	0.201 4(8)	0.185 7(5)
P(1)	0.683 5(3)	0.338 2(3)	0.156 4(2)
P(2)	0.748 7(3)	0.167 1(3)	0.224 0(2)
N	0.684 9(8)	0.244 1(8)	0.189 1(5)
C(111)	0.620(1)	0.414(1)	0.178 7(6)
C(112)	0.560(1)	0.379(1)	0.196 3(7)
C(113)	0.509(1)	0.437(1)	0.215 2(8)
C(114)	0.522(1)	0.530(1)	0.212 8(8)
C(115)	0.581(1)	0.565(1)	0.195 3(8)
C(116)	0.628(1)	0.509(1)	0.176 4(7)
C(121)	0.636 3(9)	0.324 0(9)	0.073 0(6)
C(122)	0.613(1)	0.397(1)	0.033 6(7)
C(123)	0.579(1)	0.386(1)	−0.029 6(7)
C(124)	0.572(1)	0.302(1)	−0.054 6(8)
C(125)	0.592(1)	0.228(1)	−0.016 3(7)
C(126)	0.625(1)	0.241(1)	0.047 2(7)
C(131)	0.782 1(9)	0.391 6(9)	0.177 1(6)
C(132)	0.823(1)	0.394(1)	0.136 6(6)
C(133)	0.902(1)	0.433(1)	0.155 7(7)
C(134)	0.941(1)	0.467(1)	0.215 4(7)
C(135)	0.901(1)	0.464(1)	0.256 4(7)
C(136)	0.825(1)	0.425(1)	0.237 1(6)
C(211)	0.844 0(9)	0.172 2(9)	0.214 1(6)
C(212)	0.915 3(9)	0.217 1(9)	0.258 5(6)
C(213)	0.987(1)	0.227(1)	0.246 4(7)
C(214)	0.988(1)	0.195(1)	0.191 0(7)
C(215)	0.922(1)	0.152(1)	0.149 7(8)
C(216)	0.848(1)	0.143(1)	0.158 8(7)
C(221)	0.699 1(9)	0.059 0(9)	0.194 5(6)
C(222)	0.745(1)	−0.015(1)	0.200 2(7)
C(223)	0.708(1)	−0.100(1)	0.178 3(7)
C(224)	0.623(1)	−0.101(1)	0.153 2(8)
C(225)	0.575(1)	−0.028(1)	0.147 9(8)
C(226)	0.613(1)	0.054(1)	0.169 0(7)
C(231)	0.772 4(9)	0.170 1(9)	0.307 1(5)
C(232)	0.826(1)	0.106(1)	0.346 4(6)
C(233)	0.845(1)	0.112(1)	0.410 0(7)
C(234)	0.808(1)	0.176(1)	0.432 3(8)
C(235)	0.758(1)	0.241(1)	0.393 2(7)
C(236)	0.739(1)	0.238(1)	0.331 4(7)

Table 6. Fractional atomic co-ordinates for the complex $[N(PPh_3)_2][Ir_6(CO)_{14}(\mu\text{-SCN})]$, molecules (**4a**) and (**4b**), with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ir(1A)	−0.110 3(1)	0.616	0.718 18(8)	Ir(1B)	−0.003 1(1)	0.801 36(4)	0.068 88(9)
Ir(2A)	0.168 3(2)	0.611 94(5)	0.689 92(9)	Ir(2B)	0.276 3(1)	0.798 62(4)	0.042 17(9)
Ir(3A)	0.073 6(2)	0.602 67(5)	0.855 49(9)	Ir(3B)	0.168 6(2)	0.856 90(5)	0.132 41(8)
Ir(4A)	0.186 1(2)	0.546 43(5)	0.763 50(9)	Ir(4B)	0.273 9(2)	0.864 78(5)	−0.029 42(8)
Ir(5A)	−0.109 9(2)	0.550 03(5)	0.790 87(9)	Ir(5B)	−0.022 2(2)	0.867 22(5)	−0.004 18(9)
Ir(6A)	−0.008 4(2)	0.557 00(5)	0.628 37(9)	Ir(6B)	0.093 7(2)	0.811 28(4)	−0.095 55(9)
S(A)	0.028(1)	0.664 9(3)	0.660 0(7)	S(B)	0.144 3(9)	0.750 6(3)	0.099 3(6)
C(A)	−0.015(5)	0.666(1)	0.552(3)	C(B)	0.170(4)	0.750(1)	0.207(2)
N(A)	−0.030(4)	0.664(1)	0.480(3)	N(B)	0.205(4)	0.747(1)	0.279(2)
C(11A)	−0.197(3)	0.643 2(9)	0.805(2)	C(11B)	−0.165(4)	0.783(1)	0.020(2)
O(11A)	−0.246(3)	0.657 8(8)	0.861(2)	O(11B)	−0.268(4)	0.771(1)	−0.008(2)
C(12A)	−0.271(3)	0.613(1)	0.653(2)	C(12B)	−0.085(5)	0.811(1)	0.181(3)
O(12A)	−0.377(3)	0.610 5(8)	0.608(2)	O(12B)	−0.133(3)	0.818 3(9)	0.241(2)
C(21A)	0.246(4)	0.599(1)	0.587(3)	C(21B)	0.365(5)	0.772(1)	−0.052(3)
O(21A)	0.297(4)	0.593(1)	0.519(2)	O(21B)	0.409(3)	0.755 5(9)	−0.101(2)
C(22A)	0.331(5)	0.632(2)	0.738(3)	C(22B)	0.441(4)	0.804(1)	0.111(2)
O(22A)	0.436(3)	0.645 4(8)	0.766(2)	O(22B)	0.551(3)	0.808(1)	0.143(2)
C(31A)	−0.037(4)	0.590(1)	0.952(2)	C(31B)	0.076(4)	0.893(1)	0.181(2)
O(31A)	−0.078(3)	0.581 6(9)	1.013(2)	O(31B)	0.008(3)	0.915 3(8)	0.216(2)
C(32A)	0.129(5)	0.649(1)	0.892(3)	C(32B)	0.258(5)	0.839(1)	0.237(3)
O(32A)	0.173(3)	0.675 9(9)	0.920(2)	O(32B)	0.306(3)	0.832 9(8)	0.301(2)
C(41A)	0.354(3)	0.542 3(9)	0.714(2)	C(41B)	0.446(4)	0.854(1)	−0.055(2)
O(41A)	0.467(3)	0.540 6(9)	0.682(2)	O(41B)	0.563(3)	0.845 2(8)	−0.087(2)
C(42A)	0.187(5)	0.505(1)	0.805(3)	C(42B)	0.279(5)	0.909(1)	−0.093(3)
O(42A)	0.204(4)	0.471(1)	0.827(2)	O(42B)	0.258(3)	0.928 1(9)	−0.150(2)
C(51A)	−0.104(3)	0.511 4(9)	0.856(2)	C(51B)	−0.029(4)	0.911(1)	−0.031(2)
O(51A)	−0.099(3)	0.486(1)	0.898(2)	O(51B)	−0.031(3)	0.942 5(9)	−0.060(2)
C(52A)	−0.292(4)	0.562(1)	0.830(2)	C(52B)	−0.196(5)	0.870(2)	0.053(3)
O(52A)	−0.397(3)	0.574 1(8)	0.849(2)	O(52B)	−0.300(3)	0.877 6(9)	0.081(2)
C(61A)	0.072(5)	0.519(1)	0.583(3)	C(61B)	0.035(5)	0.766(1)	−0.133(3)
O(61A)	−0.137(3)	0.582 0(8)	0.459(2)	O(61B)	0.004(4)	0.739(1)	−0.159(2)
C(62A)	−0.093(4)	0.571(1)	0.522(2)	C(62B)	0.191(5)	0.824(1)	−0.194(3)
O(62A)	0.143(4)	0.497(1)	0.546(2)	O(62B)	0.247(3)	0.832 2(9)	−0.260(2)
C(D34A)	0.235(3)	0.568 8(8)	0.879(2)	C(D34B)	0.332(4)	0.890(1)	0.088(2)
O(D34A)	0.320(3)	0.566 0(7)	0.937(2)	O(D34B)	0.397(3)	0.914 6(7)	0.110(2)
C(D56A)	−0.153(4)	0.521(1)	0.683(2)	C(D56B)	−0.087(6)	0.836(2)	−0.123(3)
O(D56A)	−0.236(3)	0.501 8(7)	0.651(2)	O(D56B)	−0.165(3)	0.848 1(8)	−0.179(2)
P(1)	0.809 0(9)	0.870 9(3)	0.518 7(5)	C(234)	0.621(4)	0.733(1)	0.748(2)
P(2)	0.843 8(9)	0.788 7(3)	0.522 3(5)	C(235)	0.649(4)	0.713(1)	0.677(2)
P(3)	0.318(1)	0.625 0(3)	0.226 3(6)	C(236)	0.718(4)	0.729(1)	0.608(2)
P(4)	0.357(1)	0.542 9(3)	0.228 6(5)	C(311)	0.403(3)	0.650 4(8)	0.145(2)
N(1)	0.790(3)	0.830 5(8)	0.510(2)	C(312)	0.436(3)	0.684(1)	0.150(2)
N(2)	0.371(3)	0.584 6(8)	0.226(2)	C(313)	0.507(4)	0.701(1)	0.079(2)
C(111)	0.742(3)	0.886 4(9)	0.615(2)	C(314)	0.539(4)	0.685(1)	0.011(2)
C(112)	0.611(3)	0.874 9(9)	0.642(2)	C(315)	0.515(5)	0.645(1)	0.001(3)
C(113)	0.566(4)	0.887(1)	0.727(2)	C(316)	0.428(4)	0.627(1)	0.063(2)
C(114)	0.638(4)	0.912(1)	0.773(2)	C(321)	0.377(3)	0.647 6(8)	0.325(2)
C(115)	0.765(4)	0.926(1)	0.743(3)	C(322)	0.509(4)	0.640(1)	0.356(3)
C(116)	0.836(4)	0.915(1)	0.666(2)	C(323)	0.566(5)	0.662(1)	0.434(3)
C(121)	0.990(4)	0.882(1)	0.509(2)	C(324)	0.459(5)	0.684(1)	0.474(3)
C(122)	1.028(4)	0.904(1)	0.430(2)	C(325)	0.318(3)	0.686 8(9)	0.443(2)
C(123)	1.173(5)	0.912(1)	0.418(3)	C(326)	0.274(4)	0.671(1)	0.363(2)
C(124)	1.267(5)	0.897(1)	0.493(3)	C(331)	0.131(4)	0.628(1)	0.213(2)
C(125)	1.235(4)	0.881(1)	0.563(2)	C(332)	0.034(3)	0.614 8(9)	0.269(2)
C(126)	1.085(3)	0.874 3(9)	0.576(2)	C(333)	−0.104(4)	0.617(1)	0.266(2)
C(131)	0.707(4)	0.892(1)	0.434(2)	C(334)	−0.158(4)	0.637(1)	0.196(2)
C(132)	0.680(4)	0.871(1)	0.360(2)	C(335)	−0.075(4)	0.651(1)	0.129(2)
C(133)	0.604(4)	0.889(1)	0.293(2)	C(336)	0.083(4)	0.647(1)	0.140(2)
C(134)	0.556(4)	0.924(1)	0.305(2)	C(411)	0.457(4)	0.525(1)	0.318(2)
C(135)	0.581(4)	0.943(1)	0.378(3)	C(412)	0.476(4)	0.545(1)	0.392(2)
C(136)	0.658(4)	0.927(1)	0.450(2)	C(413)	0.571(6)	0.534(2)	0.464(3)
C(211)	1.030(3)	0.783 0(9)	0.538(2)	C(414)	0.607(5)	0.498(1)	0.456(2)
C(212)	1.089(4)	0.764(1)	0.609(2)	C(415)	0.592(4)	0.473(1)	0.377(2)
C(213)	1.231(5)	0.759(1)	0.621(3)	C(416)	0.508(4)	0.490(1)	0.309(2)
C(214)	1.321(4)	0.774(1)	0.567(3)	C(421)	0.422(3)	0.522 0(9)	0.132(2)
C(215)	1.274(4)	0.790(1)	0.491(2)	C(422)	0.366(4)	0.494(1)	0.092(2)
C(216)	1.124(4)	0.796(1)	0.477(2)	C(423)	0.433(4)	0.477(1)	0.021(2)
C(221)	0.800(4)	0.763(1)	0.425(2)	C(424)	0.560(5)	0.492(1)	−0.009(3)
C(222)	0.888(4)	0.741(1)	0.386(2)	C(425)	0.620(4)	0.521(1)	0.033(3)
C(223)	0.859(4)	0.718(1)	0.314(3)	C(426)	0.552(4)	0.536(1)	0.100(2)
C(224)	0.713(5)	0.729(1)	0.283(3)	C(431)	0.178(3)	0.528 8(9)	0.245(2)

Table 6 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(225)	0.622(4)	0.752(1)	0.320(2)	C(432)	0.082(5)	0.532(1)	0.167(3)
C(226)	0.649(4)	0.770(1)	0.392(2)	C(433)	−0.056(6)	0.525(2)	0.174(3)
C(231)	0.761(4)	0.766(1)	0.611(2)	C(434)	−0.094(5)	0.506(1)	0.255(3)
C(232)	0.725(3)	0.786 5(9)	0.679(2)	C(435)	−0.021(3)	0.507 6(9)	0.326(2)
C(233)	0.667(4)	0.770(1)	0.753(2)	C(436)	0.132(4)	0.516(1)	0.316(3)

mmol). The reaction was complete after *ca.* 3 h (0.20 g, 47%) (Found: C, 27.9; H, 1.5; Ir, 53.1; N, 1.5. Calc. for $C_{51}H_{30}Ir_6N_2O_{14}P_2S$: C, 28.6; H, 1.4; Ir, 53.8; N, 1.3%).

Crystals for X-*Ray Analysis*.—Suitable green-black crystals of $[N(PPh_3)_2][Ir_6(CO)_{14}X]$ (X = I or SCN) and $[PPh_4][Ir_6(CO)_{14}Br]$ were grown by the solvent diffusion technique by layering Pr^iOH over concentrated thf solutions of the salts.

Reactions.—$[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$ *with* I_2 *and* Br_2. A stirred solution of $[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$ (0.83 g, 0.31 mmol) in CH_2Cl_2 (30 cm^3) was treated dropwise with a 0.1 mol dm^{-3} solution of I_2 in CH_2Cl_2 (3.5 cm^3). The colour of the solution immediately changed from brown-yellow to deep green. After 30 min the i.r. spectrum clearly showed the quantitative formation of $[Ir_6(CO)_{14}I]^-$. The salt $[N(PPh_3)_2][Ir_6(CO)_{14}Br]$ was obtained analogously starting from $[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$ (0.36 g, 0.13 mmol) and a Br_2 solution in CH_2Cl_2 (1.5 cm^3, 0.1 mol dm^{-3}).

$[N(PPh_3)_2][Ir_6(CO)_{14}Cl]$ *with* Br^-, I^-, *or* SCN^-. Compound (**1**) (0.712 g, 0.33 mmol) was added with stirring to an anhydrous acetone (30 cm^3) solution of Li[SCN] (0.290 g, 4.5 mmol). The resulting green solution was refluxed for 4 h, cooled, and a solution of $[N(PPh_3)_2]SCN$ (0.298 g, 0.5 mmol) in Pr^iOH (20 cm^3) was added. After reducing the volume of the solution to 10 cm^3 in vacuum a green precipitate was obtained which was washed with 2-propanol and dried. This product (0.57 g, 80%) was identical to compound (**4**) according to its i.r. spectrum and analytical data (Found: C, 27.4; H, 1.6; Ir, 52.1; N, 1.5. Calc. for $C_{51}H_{30}Ir_6N_2O_{14}P_2S$: C, 28.6; H, 1.4; Ir, 53.8: N, 1.3%).

In a similar way, compound (**1**) (0.51 g, 0.24 mmol) was treated with LiBr (0.29 g, 3.4 mmol) (Found: C, 28.9; H, 1.3; Br, 2.1; Cl, 0.75; Ir, 52.0; N, 0.5%, corresponding to 55% exchange) and also (0.89 g, 0.42 mmol) with LiI (0.67 g, 5.0 mmol) (Found: C, 27.1; H, 1.3; Cl, 0.45; I, 4.3; Ir, 51.9; N, 0.6%, corresponding to 70% exchange).

X-*Ray Data Collection and Structure Determination*.—The crystal data for compounds (**2**)—(**4**) are summarized in Table 3 together with some experimental details. Data collections were performed at room temperature on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo-K_α radiation (λ = 0.710 73 Å). The collected intensities were reduced to F_o values and corrected for Lorentz, polarization, decay, and absorption effects; the absorption correction was performed following the empirical method described in ref. 27. The structures were solved by Patterson and Fourier methods, and refined by full-matrix least squares, the function minimized being $\Sigma w(F_o - k|F_c|)^2$. Weights assigned to individual atoms were $w = 1/\sigma^2(F_o)$, where $\sigma(F_o) = [\sigma^2(I) + (iI)^2]^{\frac{1}{2}}/2F_oL_p$, and *i*, the ignorance factor, was 0.03 for (**2**) and 0.04 for (**3**) and (**4**). Anisotropic thermal parameters were refined for all the anion atoms and P atoms for (**2**) and (**3**), but only for Ir, S, and P for compound (**4**). Scattering factors and anomalous dispersion corrections were taken from ref. 28.

All computations were done on a PDP 11/34 computer using the Enraf-Nonius Structure Determination Package (SDP) and the physical constants tabulated therein.[29]

The positional parameters are reported in Tables 4—6 for compounds (**2**)—(**4**). The handedness of the crystal of (**4**) was tested by refining the co-ordinates of the two enantiomorphs.[30] Those listed in Table 6 gave lower *R* factors (*R'* = 0.051 *vs.* 0.053, *R* 0.045 *vs.* 0.048).

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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