Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part 34.[1] Preparation and *X*-Ray Structure of the Polyiodo-compound $[\{Ir(C_5Me_5)\}_2I_6]$ and Related Species

By **Andrés Millan, Pamela M. Bailey,** and **Peter M. Maitlis,*** Department of Chemistry, The University, Sheffield S3 7HF

Reaction of $[\{M(C_5Me_5)\}_2I_4]$ (M = Rh or Ir) with iodine gives first $[\{M(C_5Me_5)\}_2I_6]$ and then $[\{M(C_5Me_5)\}_2I_8]$. The structure of $[\{Ir(C_5Me_5)\}_2I_6]$ has been shown by *X*-ray studies to be composed of two centrosymmetric $[\{Ir(C_5Me_5)\}_2I_4]$ molecules, (A) and (B), with I_2 molecules linking weakly to the terminal iodines of one (B) and more strongly to the terminal iodines of (A). Analytical and spectroscopic measurements indicate similar structures for the other complexes in the series.

IN the course of our studies of the chemistry of pentamethylcyclopentadienyl-rhodium and -iridium complexes[2] we have often considered the possibility that oxidation states higher than +3 may play an important role. For example, the heterolytic activation of H_2 as in equation (i) could well proceed by oxidative addition to

$$[\{M(C_5Me_5)\}_2Cl_4] + H_2 \rightleftharpoons [\{M(C_5Me_5)\}_2HCl_3] + HCl \quad \text{(i)}$$

give an unstable M^{IV} or M^{V} species which immediately undergoes a fast reductive elimination to the M^{III} hydride complex. A somewhat related reaction sequence has been shown to occur in the heterolytic activation of hydrogen by the ruthenium(II) complexes $[RuH(PR_3)_4(MeOH)]^+$.[3] Further, we have had to postulate the intermediacy of Ir^{V}–hydride complexes, *e.g.* $[Ir(C_5Me_5)H(indenyl)]^{2+}$, to explain some exchange processes.[4]

Since the halogens are both strong oxidising agents and good ligands towards rhodium and iridium in these complexes, our first attempts to make higher oxidation-state complexes were to oxidatively add halogens (X_2) to the metal(III) complexes $[\{M(C_5Me_5)\}_2X_4]$.†

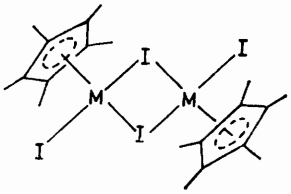
Reactions of $[\{M(C_5Me_5)\}_2X_4]$ with chlorine or bromine gave at best only unstable materials and indeed $[\{Rh(C_5Me_5)\}_2Cl_4]$ did not react at all with chlorine. However, complexes could be isolated when iodine was employed.

RESULTS AND DISCUSSION

The iodo-complexes $[\{M(C_5Me_5)\}_2I_4]$ (1a, M = Rh; 1b, M = Ir)[5,6] reacted with one equivalent of iodine in dry dichloromethane to give $[\{M(C_5Me_5)\}_2I_6]$ (2) and with an excess of iodine to give $[\{M(C_5Me_5)\}_2I_8]$ (3). Complexes (2) were also converted into (3) with excess iodine. All the complexes could be crystallised, with care, from dichloromethane without decomposition. However, they slowly lost iodine *in vacuo*.

The very dark, almost black, complexes were initially characterised by microanalyses and spectroscopy, in particular the far-i.r. In the ^1H n.m.r. spectrum they all showed singlets in the C_5Me_5 region showing that attack had not occurred on the ring.

The far-i.r. spectra showed medium intensity bands in the region 420—450 cm^{-1} in each case which we suggest to arise from metal–ring vibrations[7] since they also occurred in the complexes $[\{M(C_5Me_5)\}_2X_4]$. Bands which can be assigned to rhodium–halogen vibrations (Table 1) are observed at decreasing frequencies as expected: 198m, 243s, 286s for $[\{Rh(C_5Me_5)\}_2Cl_4]$, 162s, 185m for $[\{Rh(C_5Me_5)\}_2Br_4]$, and 100m, 155s cm^{-1} for $[\{Rh(C_5Me_5)\}_2I_4]$. The spectra of the complexes (2a) and (3a) were very similar to those of (1a), with bands at 102w, 145s for $[\{Rh(C_5Me_5)\}_2I_6]$ and 105m, 148s for $[\{Rh(C_5Me_5)\}_2I_8]$. The similarity between the Rh_2I_4, the Rh_2I_6, and the Rh_2I_8 species, both in the number, the relative intensities and the positions of the bands strongly suggested that the basic structure present in (1a) was also present in (2a) and (3a).



(1)

These results also ruled out structures in which further metal–iodine bonds had been formed, and therefore oxidative addition had not occurred; ionic structures such as a tri-μ-iodo tri-iodide, $[(C_5Me_5)Rh(\mu\text{-}I)_3Rh(C_5Me_5)][I\text{–}I\text{–}I]$, were also unlikely for the same reason.

Although the far-i.r. spectra of the iridium complexes were more complicated to interpret (Table 1), the same conclusions could be drawn.

In order to determine the exact nature of the bonding of the extra one or two I_2 units to the complex (1), a single-crystal *X*-ray structure determination was carried out on $[\{Ir(C_5Me_5)\}_2I_6]$. This showed it to contain two different molecules (Figure 1). One is a centrosymmetric $[\{Ir(C_5Me_5)\}_2I_4]$ dimer (A) which has both of its terminal iodines loosely linked ($I \cdots I_2$ 3.241 Å) to an I_2 unit

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† *Note added at Proof.* Genuine Rh^{IV} and Ir^{IV} complexes have now been isolated (K. Isobe, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1981, 808; K. Isobe, D. G. Andrews, B. E. Mann, and P. M. Maitlis, *ibid.*, 1981, 809).

TABLE 1

Spectroscopic and microanalytical data

Complex	Far-i.r. ν/cm^{-1}	Microanalyses [a] (%)			^{1}H N.m.r.[b] δ/p.p.m.
		C	H	I	
$[\{Rh(C_5Me_5)\}_2Cl_4]$	286s, 243s, 198m				
$[\{Rh(C_5Me_5)\}_2Br_4]$	185m, 162s				
$[\{Rh(C_5Me_5)\}_2I_4]$ (1a)	155s, 100m, 80w				
$[\{Rh(C_5Me_5)\}_2I_6]$ (2a)	145s, 102w	19.1 (19.4)	2.5 (2.4)	61.5 (61.6)	1.95
$[\{Rh(C_5Me_5)\}_2I_8]$ (3a)	148s, 105m, 76w	16.4 (16.1)	2.1 (2.0)	68.2 (68.1)	1.80
$[\{Ir(C_5Me_5)\}_2Cl_4]$	292s, 248s, 200w, 185s				
$[\{Ir(C_5Me_5)\}_2I_4]$ (1b)	200s, 160—140s, 102—80s				
$[\{Ir(C_5Me_5)\}_2I_6]$ (2b)	155s, 140s, 105s, 95w	16.8 (17.0)	2.3 (2.1)	53.8 (53.8)	1.80
$[\{Ir(C_5Me_5)\}_2I_8]$ (3b)	140vs, 100m, 80	14.7 (14.4)	2.0 (1.8)	60.6 (60.8)	1.80

[a] Calculated values in parentheses. [b] In $CDCl_3$.

(I–I 2.787 Å). The second molecule is another centrosymmetric $[\{Ir(C_5Me_5)\}_2I_4]$ dimer (B) which has rather weaker interactions to the extra iodine groups ($I \cdots I_2$ 3.557 Å).

TABLE 2

Important bond angles (°) and bond lengths (Å) in $[\{Ir(C_5Me_5)\}_2I_6]$ and a comparison with $[\{Ir(C_5Me_5)\}_2I_4]$ [a]

	$[\{Ir(C_5Me_5)\}_2I_6]$		
	Molecule (A)	Molecule (B)	$[\{Ir(C_5Me_5)\}_2I_4]$ [b]
$<Ir-I_b-Ir$	95.62(3)	97.15(3)	97.42(2)
$<Ir-I_t \cdots I_2$	112.20(5)	126.14(4)	
$<I_t \cdots I-I$	167.8(1)	173.8(1)	
$Ir-I_b$	2.701(1) 2.713(1)	2.712(1) 2.713(1)	2.707(1) 2.712(1)
$Ir-I_t$	2.690(1)	2.687(1)	2.694(1)
$Ir \cdots\cdots Ir$	4.011(1)	4.068(1)	4.072(1)
$I_t \cdots I_2$	3.241(2)	3.557(2)	
I–I	2.787(2)		
Ir–C(1)	2.159(16)	2.155(14)	2.178(9)
Ir–C(2)	2.125(14)	2.153(15)	2.179(8)
Ir–C(3)	2.149(15)	2.197(15)	2.182(9)
Ir–C(4)	2.161(16)	2.146(15)	2.174(9)
Ir–C(5)	2.156(16)	2.160(14)	2.149(9)
mean	2.150	2.162	2.172

[a] Estimated standard deviations are in parentheses in Tables 2—4. Subscripts b = bridging, t = terminal. [b] Data from ref. 6.

The bond distances and angles in the dimers (A) and (B) were very similar to each other and not significantly different to those found for $[\{Ir(C_5Me_5)\}_2I_4]$ itself[6] (Table 2). The only noticeable difference (and this may arise from packing effects) is in the Ir–I(bridging) distances in dimer (A) where one set is very significantly (0.012 Å, 12σ) shorter than the other. This leads to a more acute angle $Ir-I_b-Ir$ in dimer (A) (95.6°) than in (B) (97.2°).

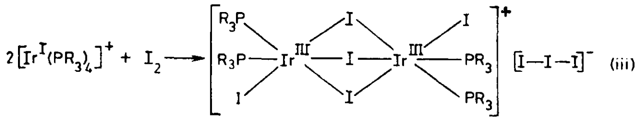
Three types of product, exemplified by (4),[8] (5),[9] and (6) or (7),[10] have been characterised from reactions (ii)—(iv) of I_2 with appropriate metal complexes (phen = 1,10-phenanthroline). They can be described as simple oxidative addition, formation of the tri-iodide salt, and formation of molecular iodine adducts; an oxidative addition has also taken place incidentally in the two latter cases.

The compound $[\{Ir(C_5Me_5)\}_2I_6]$ is very closely related to (6) and (7) and all three have the common feature of a non-linear M–I–I–I–I–M array with I–I contacts of alternating lengths *b*, *c*, and *d*, as shown in Table 3.

Although tri-iodide can be symmetric (*e.g.* in Ph_4AsI_3, where both I–I bonds are 2.919 Å),[11] in asymmetric surroundings it is itself asymmetric. For example, in CsI_3 the I–I bond lengths are 2.842 and 3.038 Å,[11] and in NH_4I_3 they are 2.791 and 3.113 Å.[12] This compares with the distance in solid molecular iodine itself which is 2.715 Å, and where the interatomic contacts are as short as 3.496 Å.[15] There is clearly a continuum of bonding types all the way from the symmetrical $[I-I-I]^-$ to the totally asymmetric $I^- \cdots I-I$.

$$[Pt^{II}(AsR_3)_2I_2] + I_2 \longrightarrow [Pt^{IV}(AsR_3)_2I_4] \qquad \text{(ii)}$$

(4)



(5)

$$[Pt^{II}(phen)Cl_2] + I_2 \longrightarrow [Pt^{IV}(phen)I_5] \xrightarrow{I_2} [Pt^{IV}(phen)I_6] \qquad \text{(iv)}$$

(6) (7)

These two possible limiting structures can also be considered for dimer (A) [and for complexes (6) and (7)]. In fact the bond lengths *b*, *c*, and *d* (Table 3) suggest that the bonding is better described in all the cases as a molecular iodine adduct, *e.g.* $Ir-I \cdots I-I$, rather than as a tri-iodide complex, Ir–I–I–I. The degree to which bond *c* differs from the value in iodine itself (2.715 Å) is probably a useful measure of the tendency to a tri-iodide ligand. On this basis $[\{Ir(C_5Me_5)\}_2I_6]$ might be anticipated to have about 30% tri-iodide character, with comparable amounts for (6) and (7).

Although no *X*-ray structural studies were carried out on the rhodium analogue (2a), this may be expected to have the same structure as $[\{Ir(C_5Me_5)\}_2I_6]$; further, it may also be anticipated that the $[\{M(C_5Me_5)\}_2I_8]$ complexes (3a) and (3b) have the same structures as dimer (B) and its associated I_2 molecules.

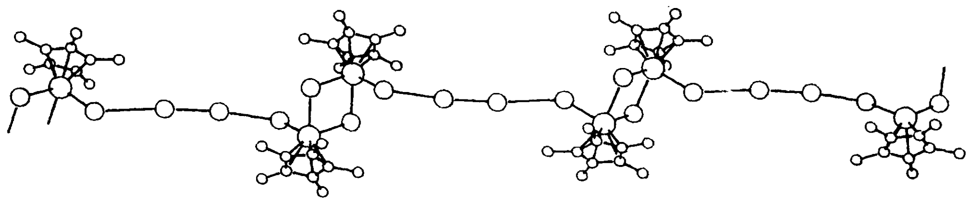


Figure 1 Overall geometry and arrangement of $[\{Ir(C_5Me_5)\}_2I_6]$ molecules

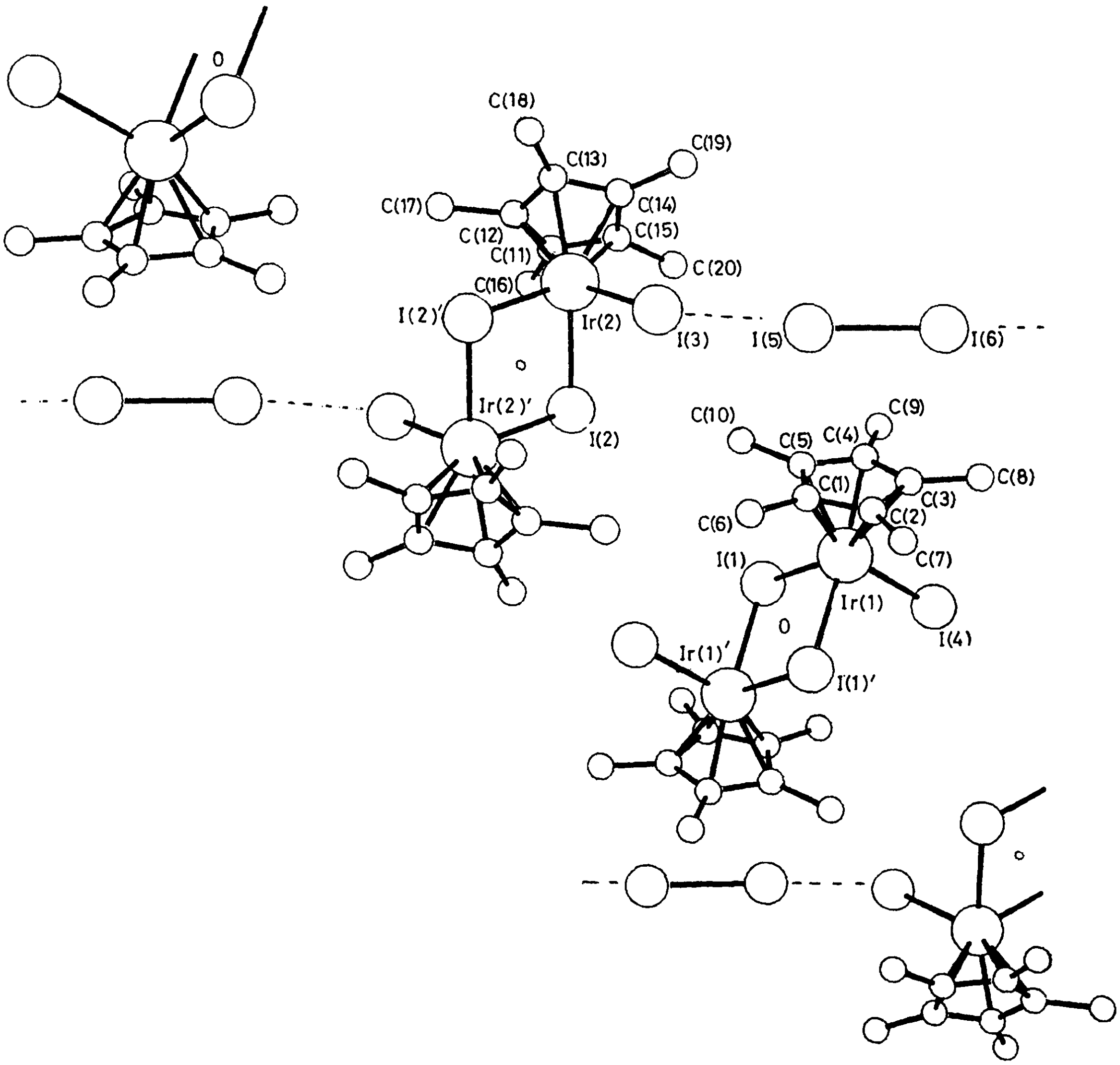


Figure 2 Atom labelling scheme for $[\{Ir(C_5Me_5)\}_2I_6]$

EXPERIMENTAL

Microanalyses were carried out by the University of Sheffield Microanalytical Service, far-i.r. spectra were measured on a PE-180 i.r. spectrophotometer with far-i.r. attachment, and ^1H n.m.r. spectra on a Perkin-Elmer R-12B spectrometer. Analytical and spectroscopic data are presented in Table 1. Typical procedures are illustrated for (2b) and (3b); the rhodium complexes were prepared in the same way.

$[\{Ir(C_5Me_5)\}_2I_4]$ (1b).—A suspension of $[\{Ir(C_5Me_5)\}_2Cl_4]$ (254.9 mg, 0.32 mmol) and sodium iodide (500 mg, 3.3 mmol) in acetone (30 cm^3) was refluxed with stirring under nitrogen for 5 h. The solution was allowed to cool overnight, the red brownish crystals were collected on a filter, washed with water, a small amount of acetone and ether, and dried in air to yield 250 mg (84%) of the iodo-complex (1b). Recrystallisation of the complex from dichloromethane–methanol afforded 210 mg of pure product.

$[\{Ir(C_5Me_5)\}_2I_6]$ (2b).—Iodine (0.0253 g, 0.1 mmol) was added to a solution of $[\{Ir(C_5Me_5)\}_2I_4]$ (116.2 mg, 0.1 mmol) in dichloromethane (50 cm^3) and the mixture stirred overnight at room temperature. The solvent was removed *in vacuo* and the residue crystallised from dichloromethane–

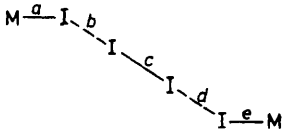
diethyl ether to give dark purple crystals of the pure complex (2b).

Crystal data. $C_{40}H_{60}I_{12}Ir_4$; $M = 2832.57$, Monoclinic, $a = 15.49(2)$, $b = 8.373(6)$, $c = 23.607(13)$ Å, $\beta = 100.8(1)°$, $U = 3\,007(5)$ Å^3 (unit-cell parameters were obtained from a least-squares fit to the setting angles of 72 reflections centred manually), $Z = 2$ (double dimer units), $D_c = 3.13$ g cm^{-3}, $F(000) = 2\,488$. Systematic absences indicate the space group to be $P2_1/c$ (C^5_{2h}, no. 14), Mo-K_α radiation (graphite monochromator) $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 149.13 cm^{-1}.

A crystal of approximate dimensions 0.03 × 0.004 × 0.02 cm, mounted along a non-standard axis, was used for data collection, with a Stoe STADI-2 diffractometer in the stationary-counter–moving-crystal mode ($6.5 < 2\theta < 50°$). Variable-width peak scans were measured at 0.01 degree intervals in omega, with background measured at each end of the scan. 3 928 Independent reflections were obtained with $I_{obs.} > 3\sigma(I_{obs.})$ and background difference $\Delta < 4\sigma(B)$; the data were corrected for Lorentz, polarisation and absorption (integration by Gaussian quadrature).

TABLE 3

Comparison of structures of molecular iodine complexes *



	Bond lengths (Å)				
	a	*b*	*c*	*d*	*e*
$[\{Ir(C_5Me_5)\}_2I_6]$	2.690(1)	3.241(2)	2.787(2)	3.557(2)	2.687(1)
$[Pt(phen)I_5]$	2.669(2)	3.289(3)	2.739(3)	3.457(3)	2.669(2)
$[Pt(phen)I_6]$	2.677(2)	3.481(3)	2.750(3)	3.452(3)	2.662(2)
I_2		3.496(6)	2.715(6)	3.496(6)	

	Bond angles (°)			
	ab	*bc*	*cd*	*de*
$[\{Ir(C_5Me_5)\}_2I_6]$	112.2	167.8	173.8	126.2
$[Pt(phen)I_5]$	108.9	177.5	168.7	98.7
$[Pt(phen)I_6]$	101.9	164.2	177.3	106.1

* Data for $[Pt(phen)I_5]$, $[Pt(phen)I_6]$ and I_2 taken from refs. 10 and 13 respectively.

The Patterson function showed two possible solutions: either the two independent iridium atoms formed a dimer, or each iridium atom formed a dimer with its own centrosymmetrically related partner. The overall geometry of the molecule seen in the Fourier syntheses calculated on each of these interpretations was very similar, but successful refinement only occurred in the model containing two centrosymmetric dimers. Block diagonal-matrix least-squares refinement reduced R to 0.033, at which stage all thermal parameters were anisotropic, with unit weights for each reflection. A difference-Fourier synthesis at this stage showed the only significant peaks to be in positions expected for methyl hydrogen atoms. Analysis of the structure factors did not show significant variations of the residual in terms of $(\sin\theta)/\lambda$, Miller index, or $|F_{obs.}|$.

The overall geometry of the molecules is shown in Figure 1; Figure 2 shows the atom labelling scheme relating to the atomic co-ordinates in Table 4, and distance-angle values are in Table 2. Tables of structure factors, and the anisotropic and isotropic thermal parameters are deposited in Supplementary Publication SUP 23179 (67 pp.).*

TABLE 4

Fractional atomic co-ordinates (× 10^4 for C, × 10^5 for Ir and I) for $[\{Ir(C_5Me_5)\}_2I_6]$

Atom	*x/a*	*y/b*	*z/c*
Ir(01)	3 560(3)	7 100(6)	8 351(2)
Ir(02)	55 355(3)	45 776(6)	8 276(2)
I(01)	6 439(6)	−17 813(11)	1 596(4)
I(02)	41 699(6)	34 901(11)	391(4)
I(03)	44 847(8)	68 781(13)	11 149(5)
I(04)	−10 221(7)	−8 894(13)	10 955(4)
I(05)	31 865(8)	55 498(15)	19 362(5)
I(06)	78 507(8)	229(15)	22 365(6)
C(01)	1 339(9)	2 560(17)	931(5)
C(02)	675(9)	2 990(17)	1 242(7)
C(03)	697(9)	1 786(18)	1 697(6)
C(04)	1 314(9)	568(18)	1 618(6)
C(05)	1 738(8)	1 127(17)	1 151(6)
C(06)	1 617(12)	3 598(21)	460(7)
C(07)	146(12)	4 489(20)	1 193(8)
C(08)	174(13)	1 817(23)	2 169(7)
C(09)	1 544(12)	−1 922(25)	1 971(8)
C(10)	2 514(11)	328(26)	953(9)
C(11)	6 159(11)	2 272(17)	983(6)
C(12)	6 773(9)	3 405(18)	950(5)
C(13)	6 802(9)	4 582(18)	1 386(6)
C(14)	6 147(10)	4 097(20)	1 711(6)
C(15)	5 747(10)	2 669(19)	1 452(7)
C(16)	6 023(18)	770(24)	641(9)
C(17)	7 453(13)	3 343(30)	546(9)
C(18)	7 397(14)	5 999(24)	1 495(10)
C(19)	5 937(14)	4 845(28)	2 246(7)
C(20)	5 038(12)	1 691(29)	1 654(9)

Atomic scattering factors for neutral Ir, I, C, H were used with corrections for real and imaginary components of anomalous dispersion.[14] Calculations were computed on the University of Sheffield ICL 1906S computer, using programs from the Sheffield X-Ray System.

$[\{Ir(C_5Me_5)\}_2I_8]$ (3b).—Iodine (0.254 g, 1 mmol) was added to a solution of $[\{Ir(C_5Me_5)\}_2I_4]$ (116.2 mg, 0.1 mmol) in dichloromethane (50 cm^3) and the reaction mixture stirred overnight. The solvent was removed *in vacuo* and the residue crystallised from dichloromethane–diethyl ether to give (after 3 days) dark crystals of the pure complex (3b). Iodine was liberated when the crystals were kept under vacuum (10^{-1} mmHg) † and heated for a short period (4—6 h).

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

† Throughout this paper: 1 mmHg = (101 325/760) Pa.

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