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Synthesis and reactivity of binuclear 7-azaindolate* complexes of iridium

II**. Oxidative-addition reactions of halogens and halocarbons to $[\{Ir(\mu\text{-aza})(CO)_2\}_2]$

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Abstract

The compound $[\{Ir(\mu\text{-aza})(CO)_2\}_2]$ (**1**) (aza = 7-azaindolate) is oxidized by silver tetrafluoroborate in a donor solvent to $[\{Ir(\mu\text{-aza})(CO)_2(S)\}_2]^{2+}$ (S = acetone or acetonitrile) and to the neutral complex $[\{Ir(\mu\text{-aza})(CO)_2(O_2CMe)\}_2]$ (**2**) by silver acetate. The head-to-tail (HT) and the head-to-head (HH) isomers of complex **1** undergo *trans*-annular oxidative-addition reactions with a variety of substrates. Halogens (X_2) add to **1** giving the diiridium(II) complexes $[\{Ir(\mu\text{-aza})X(CO)_2\}_2]$ (X = Cl (**3**), Br, or I). In addition, bromine selectively attacks position 3 of the five-membered ring in the aza bridges, affording $[\{Ir(\mu\text{-azaBr})Br(CO)_2\}_2]$ as a single isomer. Methyl iodide and polyiodomethanes react with both isomers of **1** to give the iodomethyl complexes $[\{Ir(\mu\text{-aza})(CO)_2\}_2(I)(R)]$ (R = Me, CH_2I, CHI_2, or $(CH_2)_3I$) as a mixture of isomers. The relative disposition, HH and HT, of the bridging ligands is maintained in these reactions. Complex **1** is a powerful photoreductor that reacts with chloroform and carbon tetrachloride giving $[\{Ir(\mu\text{-aza})(CO)_2\}_2(Cl)(R)]$ (R=$CHCl_2$ or CCl_3), respectively, whereas compound **3** results from reaction with 1,2-dichloroethane. Reactions of complex **1** with diethylacetylenedicarboxylate and dimethylacetylenedicarboxylate (A) afford the tetranuclear complexes of the type $[\{Ir(\mu\text{-aza})(CO)_2\}_4(A)_2]$.

Introduction

trans-Annular oxidative-addition is characteristic of bridged binuclear complexes [1]. This reaction results in a formal one-electron oxidation of each metal centre and in the creation of a metal–metal bond.

This type of reaction has been observed in complexes of rhodium, iridium, palladium, platinum, and gold and competes with other oxidative-addition reactions of binuclear complexes [2]. We have reported that tetranuclear species may be involved in this type of reaction [3] and a recent kinetic study reveals that they occur in two distinguishable but poorly understood steps [4].

A certain flexibility in the core of the metals and bridging ligands is required in order for the structure to adapt to the presence and absence of a metal–metal bond. A considerable compression occurs when there is one atom in the bridge as in the complexes $[\{Ir(\mu\text{-SR})L_2\}_2]$ [5,6] in comparison with the complexes with two atoms in the bridges as in $[\{Ir(\mu\text{-pz})L_2\}_2]$ (pz = pyrazolate) [7] upon formation of an M–M bond. The hinge angle in these structures diminishes as the number of atoms in the bridge increases (Fig. 1) and the two sqaure-planar environments of the metal atoms are more face-to-face oriented in complexes where there are three atoms in the bridge, so that the formation of the metal–metal bond should produce some strain. In addition, photochemical properties have been observed for complexes with d^8-d^8 metal centres having two and three atoms in the bridge as in $[\{Ir(\mu\text{-pz})(cod)\}_2]$ (cod = 1,5-cyclooctadiene) [8] and $[\{Ir(Opy)(cod)\}_2]$ (Opy =

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* 1*H*-pyrrolo[2,3-*b*]pyridinate.

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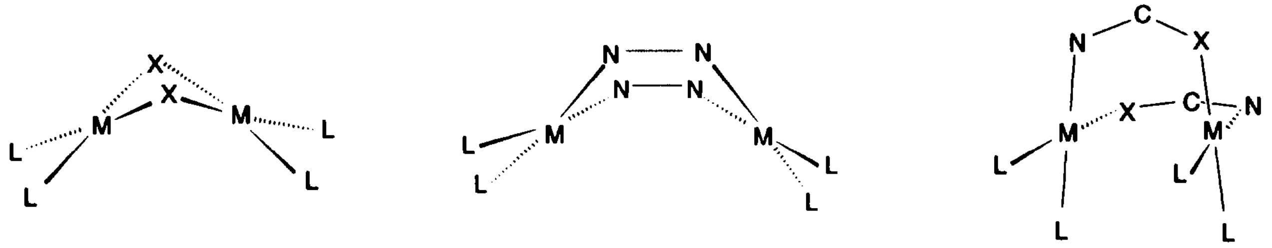

Fig. 1. Structures of binuclear complexes showing the hinge angle formed by the square-planar environments.

2-pyridonate) [9]. This effect is attributed to an interaction between the d_z2 and p_z orbitals of each metal atom and it should be dependent upon the structure of the complexes. We describe here some reactions of the binuclear complex $[\{Ir(\mu\text{-aza})(CO)_2\}_2]$ with three atoms in the bridges, to test how the strain and orbital interactions, as well as the nature of the metal centres, influence the reactivity and the nature of the products.

2. Results and discussion

The carbonyl complex $[\{Ir(\mu\text{-aza})(CO)_2\}_2]$ (**1**) (aza = 7-azaindolate) * is more reactive and more easily oxidized than its olefin counterpart $[\{Ir(\mu\text{-aza})(cod)\}_2]$ (cod = 1,5-cyclooctadiene). Oxidation of **1** by silver tetrafluoroborate in a solvent such as acetone and acetonitrile is facile giving metallic silver and a yellow solution. Two equivalents of silver per equivalent of **1** are required for the reaction; otherwise mixtures of the starting material and the iridium(II) product are obtained. The produt of this two-electron oxidation could be formulated as $[Ir(\mu\text{-aza})(CO)_2(S)]_2^{2+}$ (S = donor solvent) but our attempts to isolate this solvated species were not successful. Nevertheless, oxidation of complex **1** with silver salts of a coordinating anion such as acetate (Scheme 1) leads to the neutral complex $[\{Ir(\mu\text{-aza})(O_2CMe)(CO)_2\}_2]$ (**2**), isolated as a white solid. Characterization of **2** as the diacetatocomplex is based on its elemental analysis (Table 1) and spectroscopic data (Table 2). Its diamagnetism suggests a single Ir–Ir bond. In addition, the similarity of the framework of complexes **1** and **2** is indicated by their identical pattern of ν(CO) bands*, and the monodentate coordination of the acetate is consistent with the separation (340 cm^{-1}) between the antisymmetric and symmetric ν(O–C=O) bands. These ligands should be *trans* to the metal–metal bond. Furthermore, the ^1H NMR spectrum of **1** shows the presence of the head-to-head (HH) and head-to-tail (HT) isomers, which have equivalent bridging and acetate ligands consistent with the proposed structure in Scheme 1. The structure of the solvated species should be identical to that of **2** but with solvent molecules in place of the acetate.

Clearly, formation of the iridium–iridium bond is a key in the chemical behaviour of **1**, that leads to facile *trans*-annular oxidative-addition reactions. For these reactions we have used a solution of **1** prepared *in situ* from $[\{Ir(\mu\text{-aza})(cod)\}_2]$ by replacement of cod by carbon monoxide. This solution contains a mixture of the HH and HT isomers of complex **1** in a 1:3 ratio. The presence of cod in the reaction medium does not interfere with most of the reactions reported here.

2.1. Reaction of 1 with halogens

Addition of freshly prepared solutions of X_2 (X = Cl, Br or I) to a purple solution of **1** in toluene in the molar ratio 1:1 immediately gives yellow-orange solutions of the complexes $[\{Ir(\mu\text{-aza})X(CO)_2\}_2]$ [X = Cl (**3**), Br (**4**), I (**5**)]. They are isolated as yellow solids, in moderate yield due to their high solubility in most solvents. Their analytical data (Table 1) are in accordance with the proposed formulation but compound **4** was not isolated pure; the nature of the second product in this reaction is discussed below.

Oxidation of **1** and the retention of its framework is deduced from the typical pattern of ν(CO) bands shown by **3**, **4** and **5**, shifted to higher energies relative to **1**. In addition, the ^1H NMR spectra of **3–5** are similar (see Table 2) clearly showing the presence of the HH and HT isomers in the proportion 1:3, the same as in the parent compound. The stoichiometry of the reaction and the structure and diamagnetism of the products suggests that halogens add to **1** in a typical two-electron two-fragment *trans*-annular oxidative-addition reaction in which each isomer gives its corresponding oxidation product (Scheme 2, R = X and B = C).

The result of the reactions of **1** with halogens in an excess depends on the oxidation power and reactivity of the halogen. For iodine, the simplest case, the reaction ends up with the diiridium(II) complex **5**. Bromine in an excess reacts with **1** to give a compound analyzed as the binuclear complex $[\{Ir(\mu\text{-aza})Br_2$-

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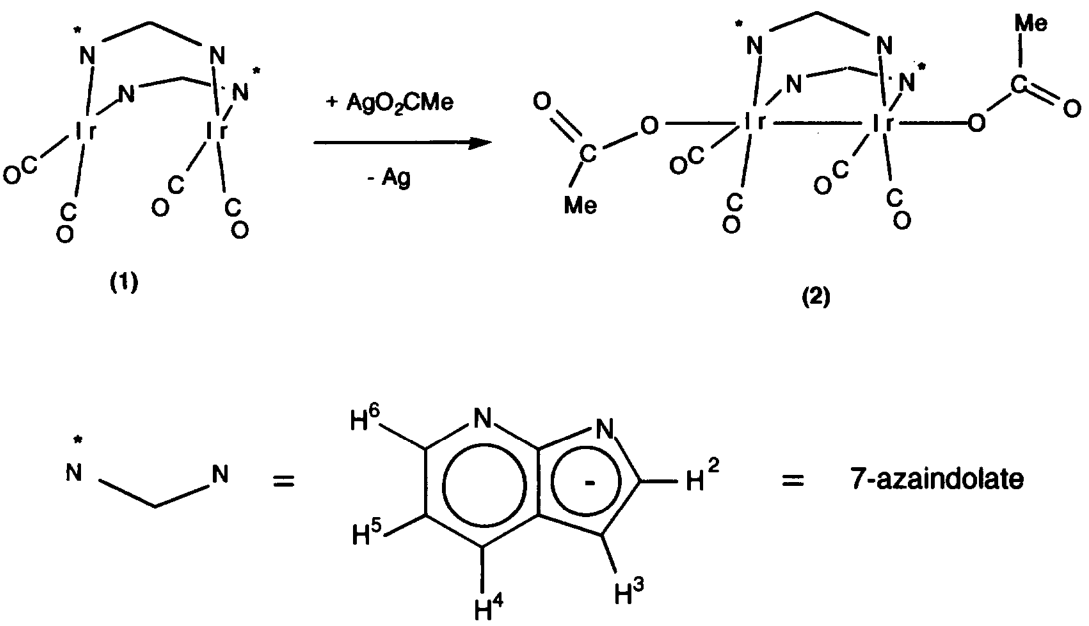
* See preceding paper.



Scheme 1.

TABLE 1. Analytical and physical data for the new complexes

Compound	Colour	Yield (%)	Analysis (%) [a] C	H	N	Mol. weight [b]	ν(CO) (cm^{-1})
$[\{Ir(\mu\text{-aza})(MeCO_2)(CO)_2\}_2]$ **(2)**	White	59	31.03 (31.13)	1.77 (1.89)	6.63 (6.60)	789 (848)	2128s, 2112sh, 2094m, 2074s, 2054sh, 2025w [e]
$[\{Ir(\mu\text{-aza})(Cl)(CO)_2\}_2]$ **(3)**	Pale-yellow	60	27.31 (26.97)	1.63 (1.25)	6.95 (6.98)	770 (801)	2128s, 2105w, 2078s, 2070sh [d]
$[\{Ir(\mu\text{-aza})(I)(CO)_2\}_2]$ **(5)**	Orange	70	22.55 (21.95)	1.16 (1.02)	5.55 (5.69)	1044 (984)	2119s, 2110sh, 2090w, 2070s, 2065sh [e]
$[\{Ir(\mu\text{-aza-Br})(Br)(CO)_2\}_2]$ **(6)**	Yellow	75	20.97 (20.62)	0.98 (0.76)	5.21 (5.34)	1119 (1048)	2132s, 2104m, 2082s, 2070sh [d]
$[Ir_2(\mu\text{-aza})_2(CH_3)(I)(CO)_4]$ (7)	Orange	74	25.67 (26.15)	1.31 (1.50)	6.18 (6.42)	828 (872)	2110sh, 2105s, 2090w, 2075m, 2050s, 2030w [e]
$[Ir_2(\mu\text{-aza})_2(CH_2I)(I)(CO)_4]$ **(8)**	Yellow	83	22.15 (22.85)	1.65 (1.21)	5.48 (5.61)	1064 (998)	2113s, 2079m, 2061s, 2040sh [e]
$[Ir_2(\mu\text{-aza})_2(CHI_2)(I)(CO)_4]$ **(9)**	Red	80	19.86 (20.29)	0.89 (0.98)	4.92 (4.98)	1197 (1124)	2120s, 2084m, 2070s, 2047sh [d]
$[Ir_2(\mu\text{-aza})_2(\{CH_2\}_3I)(I)(CO)_4]$ **(10)**	Yellow	70	24.88 (24.56)	1.58 (1.57)	5.32 (5.45)	1037 (1026)	2110s, 2075m, 2055s [d]
$Ir_2(\mu\text{-aza})_2(C_3H_5)(Br)(CO)_4]$ **(11)**	Yellow	65	29.83 (29.61)	1.95 (1.77)	6.58 (6.57)	[c]	2128sh, 2112s, 2078m, 2056s, 2032sh [e]
$[Ir_2(\mu\text{-aza})_2(CHCl_2)(Cl)(CO)_4]$ **(12)**	Orange	70	27.29 (26.84)	1.42 (1.30)	6.73 (6.59)	877 (850)	2125s, 2090m, 2074s, 2047m [d]
$[Ir_2(\mu\text{-aza})_2(CCl_3)(Cl)(CO)_4]$ **(13)**	Orange	75	26.30 (25.80)	1.39 (1.13)	6.20 (6.33)	– –	2130s, 2117m, 2070s, 2060sh [d]
$Ir_2(\mu\text{-aza})_2(C_6H_5COO)(CO)_4]$ **(14)**	White	70	40.05 (39.50)	2.55 (2.07)	5.89 (5.75)	890 (973)	2129s, 2096m, 2066s [d]
$[Ir_4(\mu\text{-aza})_4\{(C_2(COOEt)_2\}_2(CO)_8]$ **(15)**	Brown	70	34.90 (34.66)	2.37 (2.23)	6.18 (6.21)	1840 (1801)	2093s, 2069s, 2038m, 2018m [e]
$[Ir_4(\mu\text{-aza})_4\{(C_2(COOMe)_2\}_2(CO)_8]$ **(16)**	Orange	60	32.68 (33.02)	1.76 (1.84)	5.92 (6.42)	1813 (1744)	2092s, 2068s 2039m, 2020m [e]

[a] Calculated values are given in parentheses. [b] In $CHCl_3$. [c] Decomposes in solution. [d] In CH_2Cl_2. [e] In cyclohexane.

(CO)$_2$}$_2$]. Its ^{1}H NMR spectrum shows that this compound is the byproduct that contaminates complex **4** when the reaction is carried out with a molar ratio 1 : 1. Moreover, as the resonance due to H^3 is missing and that due to H^2 becomes a singlet, it is evident that both 7-azaindolate bridges have been brominated in position 3 of the five-membered ring. On this basis, this compound should be reformulated as the diiridium(II) complex [{Ir(μ-azaBr)Br(CO)$_2$}$_2$] (**6**). Furthermore, a single isomer with 3-bromo-7-azaindolate bridges (either the HH or the HT) is isolated in this reaction although the starting material is a mixture of isomers.

From these observations, it is clear that the reaction takes place in two consecutive steps. First, a further oxidation of **4** to an iridium(III) compound does not

TABLE 2. ^{1}H NMR spectra of the new complexes [a]

Complex	Isomer	Abundance (%)	aza ligands [b] H^2	H^3	H^4	H^5	H^6	Others
2	HT		7.69 (d)	6.42 (d)	7.84 (d)	6.90 (dd)	8.49 (d)	2.53 (s, O$_2$C*Me*)
	HH		7.70	6.47	7.88	6.89	8.53	2.57 (s,O$_2$C*Me*)
3	HT	70	8.23 (d)	6.42 (d)	7.84 (dd) [c]	6.90 (dd)	9.21 (dd)	
	HH	30	8.30 (d)	6.43 (d)		6.80 (dd)	9.13 (dd)	
4	HT	75	8.13 (d)	6.46 (d) [c]	7.85 (d) [c]	6.94 (dd) [c]	9.08 (d)	
	HH	25	8.18 (d)				9.01 (d)	
5	HT	65	8.35 (d)	(d) [c]	7.79 (d)	6.81 (dd)	9.36 (dd)	
	HH	35	8.43 (d)	6.33 (d)	7.80 (d)	6.80 (dd)	9.28 (dd)	
6		100	8.21 (s)	–	7.82 (dd)	7.03 (dd)	9.30 (dd)	
7	A	80	7.44 (d)	6.39 (d)	7.82 (d)	6.87–6.73 (m) [c]	9.60 (d)	1.87 (s, CH$_3$)
			8.45 (d)	6.27 (d)	7.52 (d)		8.14 (d)	
	B	15	7.58 (d)	6.41 (d)	7.74 (d)		9.47 (d)	1.24 (s, CH$_3$)
	C	5	8.53 (d)	–	–		–	1.99 (s, CH$_3$)
8	A	65	7.35 (d)	6.44 (d)	7.89 (d)	6.97 (dd)	9.60 (d)	δ_A = 3.69 δ_B = 3.48
			8.39 (d)	6.30 (d)	7.79 (d)	6.85 (dd)	8.21 (dd)	J_{AB} = 7 (AB system, –CH$_2$I)
	B	20	7.54 (d)	6.48 (d)	7.78 (d)	6.80 (dd)	9.46 (dd)	3.75 (s, –CH$_2$I)
	C	15	8.51 (d)	6.31 (d)	7.87 (dd)	6.90 (dd)	7.98 (dd)	3.40 (s, –CH$_2$I)
9	A	70	7.50 (d)	6.48 (d)	7.89 (dd)	6.97 (dd)	9.36 (dd)	4.55 (s, –CHI$_2$)
			8.34 (d)	6.30 (d)	7.77 (dd)	6.79 (dd)	8.07 (dd)	
	B	15	7.65 (d)	6.49 (d)	7.78 (d)	6.78 (dd)	9.30 (dd)	4.63 (s, –CHI$_2$)
	C	15	8.37 (d)	6.35 (d)	7.81 (d)	6.85 (dd)	7.88 (d)	4.44 (s, –CHI$_2$)
10	HT		7.48 (d)	6.52 (d)	7.94 (dd)	6.98 (dd)	9.72 (d)	3.56 (s, –CH$_2$I); 2.78 (m, –CH$_2$–)
			8.52 (d)	6.34 (d)	7.86 (d)	6.90 (dd)	8.18 (d)	
11	A	75	7.44 (d)	6.41 (d)			9.47 (d)	6.8–6.6 (m, C$_3$H$_5$)[c]; 5.34 (d, H$_a$,$^3J_{ac}$ = 16.7, C$_3$H$_5$) [b,c]
			8.35 (d)	6.35 (d)	7.83 (m) [c]	6.92–6.82 (m) [c]	8.19 (d)	4.90 (d, H$_b$,$^3J_{bc}$ = 10, C$_3$H$_5$)[c]; 3.70 (m, –CH$_2$–C$_3$H$_5$)[b,c]
	B	25	7.55 (d)	6.44 (d)			9.37 (d)	
12	A	75	7.45 (d)	6.42 (d)	7.90 (d)	6.95 (m) [c]	9.23 (d)	6.61 (s, –CHCl$_2$)
			8.19 (d)	6.45 (d)	7.86 (dd)		8.25 (d)	
	B	25	7.64 (d)	6.48 (d)	8.01 (d)		9.16 (d)	6.71 (s, –CHCl$_2$)
14			7.86 (d)	6.50 (d)	8.34 (m)	6.95 (dd)	8.65 (d)	8.34 (m, H^o benzoate); 7.61 (m, H^m and H^p benzoate)
15		100	7.49 (d)	6.41 (d)	7.82 (d)	6.77 (dd)	8.40 (d)	4.17 (q, –CH$_2$–)
			7.40 (d)	6.17 (d)	7.62 (d)	6.65 (dd)	8.28 (d)	1.25 (t, –CH$_3$)
16		100	7.51 (d)	6.42 (d)	7.83 (d)	6.77 (dd)	8.28 (d)	
			7.48 (d)	6.41 (d)	7.82 (d)	6.75 (dd)	8.37 (d)	3.74 (s, –CH$_3$)
			7.41 (d)	6.18 (d)	7.64 (d)	6.64 (dd)	8.29 (d)	3.73 (s, –CH$_3$)
			7.40 (d)	6.17 (d)	7.63 (d)	6.63 (dd)	8.29 (d)	3.72 (s, –CH$_3$)
								3.70 (s, –CH$_3$)

[a] In CDCl$_3$ at 20°C. Chemical shifts (δ) in ppm, coupling constants in Hz, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

[b] For the proton numbering scheme see the preceding paper. [c] Signal that includes the resonances of all the isomers.

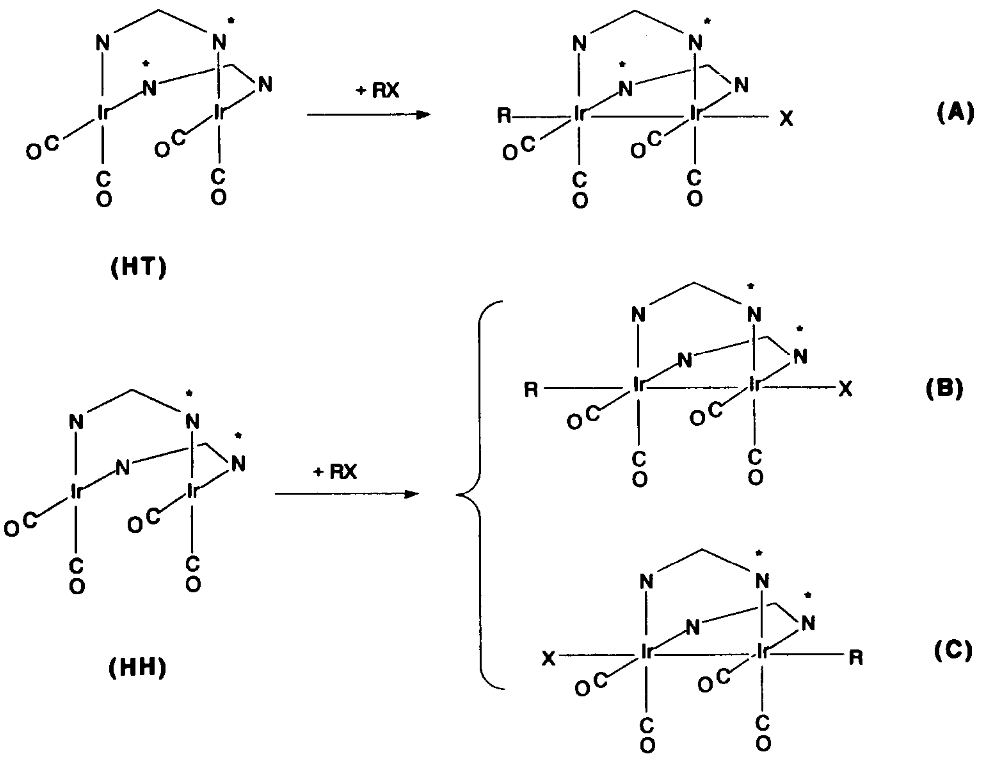
occur but, once complex **4** is formed, bromination of the aromatic rings in **4** to give **6** takes place at such a rate that it competes with the first reaction. This bromination of the bridging ligands is accompanied by an isomerization yielding a single isomer of **6** since **4** is still a mixture of isomers. Bromination at C3 in the free pyrrolopyridines is an electrophilic substitution at the most activated site and it takes place smoothly in the absence of catalyst. Upon protonation of the nitrogen of the pyridine ring, and probably upon coordination, the nucleophility at C^3 is markedly lowered [10]. This electrophilic attack of bromine on the bridging ligands could then occur in the starting complex **1**, but oxidation of the metals is preferred.

With the diiridium(II) complex **4** the situation is reversed. Once the metal–metal bond is formed, electrophilic substitution takes place instead of oxidation of the metals, and specifically at C^3, the most preferred site in the free 7-azaindole. As this site is also far away from the metals, bromine probably attacks C^3 directly. Consistent with this is the lack of substitution in the reaction with iodine in an excess, since iodine does not readily undergo electrophilic substitutions. In any case, the isomerization should occur either on formation of the non-aromatic intermediate, where the electronic distribution of the bridging ligands is strongly modified, or on protonation of the bridging ligands with the hydrogen bromide formed in this electrophilic substitution.

In contrast with the selectivity shown in the reaction with bromine, compound **1** reacts with chlorine in an excess to give a complex mixture of products, which could not be resolved. Probably chlorination of the bridging ligands and oxidation to iridium(III) complexes take place, confirming the observations.

2.2. Reactions of 1 with halocarbons

The ease of oxidation of **1** prompted us to study its reaction with other electrophiles, some of which have been scarcely used in such reactions and others of which are widely employed as solvents: iodomethane, diiodomethane, iodoform, 1,3-diiodopropane, allylbromide, 1,2-dichloroethane, chloroform and carbon tetrachloride. All these halocarbons (RX), except 1,2-dichloroethane, react with compound **1** by two-electron two-fragment transannular oxidative-addition shown in Scheme 2 to give the compounds of the general formula $[Ir_2(\mu\text{-aza})_2X(R)(CO)_4]$ ($X = I$, $R = Me$ (**7**), CH_2I (**8**), CHI_2 (**9**), $(CH_2)_3I$ (**10**); $X = Br$; $R = C_3H_5$ (**11**); $X = Cl$, $R = CHCl_2$ (**12**); CCl_3 (**13**)). Complex **1** abstracts chlorine from 1,2-dichloroethane to give $[\{Ir(\mu\text{-aza})Cl(CO)_2\}_2]$ (**3**) and probably ethylene.



Scheme 2. New isomers resuting from *trans*-annular oxidative-addition reactions to the HH and HT isomers.

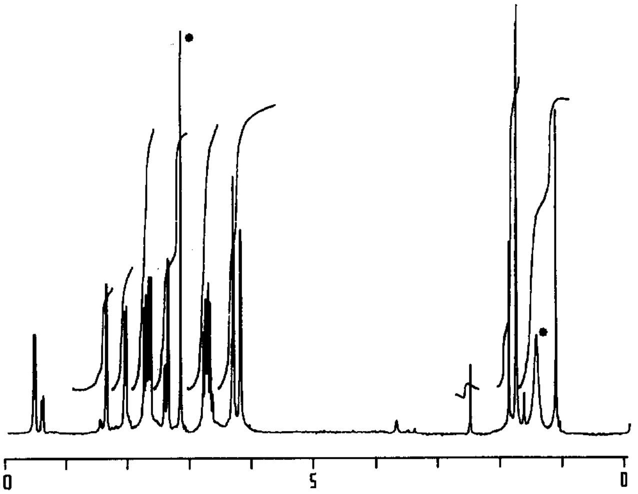


Fig. 2. ^1H NMR spectrum of complex **7**. The asterisks denote solvent signals.

In general, three isomers should result from these reactions because the parent HT isomer gives a single product (A, Scheme 2) whereas the HH generates two new isomers (B and C, Scheme 2). The difference between B and C is the position of the group R relative to the pyridine nitrogen of the bridging ligands. For the iodo-derivatives, the two fragments (R and I) add to the HT isomer independently of the HH since the relative proportion A:B + C is *ca.* 75:25, identical to the HT:HH ratio for **1** (see Table 2). In other words, the relative disposition of the bridging ligands is maintained in these reactions.

However, the relative proportions of B:C are not 1:1. B is always more abundant than C, perhaps due to kinetic effects. For example, the ^1H NMR spectrum of the solid isolated from the reaction of **1** with methyl iodide (Fig. 2) shows four compounds, since there are four resonances between δ 2.6 and 1.2 for methyl groups. Comparison of the relative intensities of these resonances and those in the aromatic region shows that the main component of the mixture is isomer A, with inequivalent aza bridges. Furthermore, there is a noticeable shift between the resonances of the H^6 and H^2 protons of both bridging ligands (see Table 2). Those more deshielded are in the neighbourhood of the halogeno-ligand, as is particularly clear for complexes **3**–**5**. This allows the identification of the isomers B and C in general. As the bridging ligands are equivalent in both B and C, isomer B is that in which the pyridine H^6 is the more deshielded, whereas the more deshielded proton is the pyrrole H^2 in C.

The fourth product in this mixture results from a side reaction which involves the insertion of one carbonyl group into the Ir–Me bond. The acyl group is easily identified from the chemical shift of the resonance of the methyl carbon (δ = 2.60 ppm) and a weak band in the IR of the solid at 1720 cm^{-1}. The proportion of this compound in the mixture is very low and does not increase with time even under an atmosphere of carbon monoxide, which proves that it does not arise from the isomers **7**. Then the insertion reaction occurs before the *trans*-annular oxidative addition is completed and before the halogen migrates to the second metal centre. Presumably, this compound is the mononuclear acyl complex with a chelating aza ligand $[Ir(aza)(\eta^1\text{-}COMe)I(CO)]$.

Iodoform and diiodomethane react with complex **1** affording the compounds formulated as **8** and **9**, respectively, on the basis of their microanalyses and molecular weights. Both reactions are complete within a few minutes but exposure of the mixtures to sunlight accelerates noticeably the process. ^1H NMR spectroscopy reveals three isomers in each reaction since, apart from the aromatic region, three close resonances around δ 3.6 and 4.5 are observed in the spectra (Table 2). As both iodo-derivatives are able, in principle, to produce a *trans*-annular oxidative-addition reaction (to give isomers A, B and C) and a double oxidative-addition reaction to give methylene-bridged compounds (isomers D and E, Fig. 3), we first address the nature of the products.

The main component of the isomers **8** has diasterotopic methylene protons giving rise to an AB system and inequivalent bridging ligands, compatible only with isomer A, where R is the iodomethyl (CH_2I) group. In addition the two minor components of isomers **9** have equivalent bridges which is incompatible with the iodomethylene-bridged structues D and E (where X=I). They are isomers of types B and C where R is the diiodomethyl (CHI_2) ligand. Evidence that the remaining three compounds are the isomers **8B**, **8C** and **9A** is the characteristic deshieldings of the protons H^2 and H^6 close to the iodo-ligand, and the constant differ-

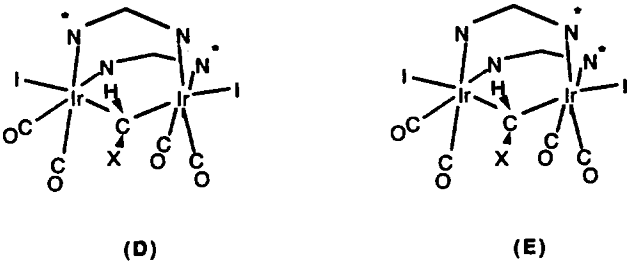


Fig. 3. Structures for the possible iodomethylene complexes.

ence (0.96 ± 0.07 ppm) between the chemical shifts for the R groups in both series of compounds **8** and **9** [11]. Thus, the reactions of complex **1** with diiodomethane and iodoform stop at the diiridium(II) complexes. Attempts to produce an intramolecular oxidative-addition reaction by heating **8** and **9** in toluene at reflux lead to their decomposition to uncharacterizable solids.

A comparison of the results of the reactions of **1** and those carried out on the related binuclear complexes $[\{Ir(\mu\text{-pz})(CO)(PPh_3)\}_2]$, $[Ir_2(\mu\text{-pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ and $[\{Ir(\mu\text{-SR})(CO)(PR_3)\}_2]$ with halogens [12–14] and diiodomethane [7,15,16] suggests why they differ. The four show a sequential opening of the hinge angle and undergo a *trans*-annular oxidative-addition reaction with halogens but only the last two are able to add a second molecule of halogen and break the metal–metal bond. This shows the high flexibility of the double thiolate and the mixed thiolate pyrazolate bridge, which can support a wide range of hinge angle. This flexibility is shared to some degree by the double pyrazolate bridge, since both types of system are able to give methylene-bridged compounds on reaction with diiodomethane. In contrast, the double azaindolate bridged complex is more rigid in several aspects. Although it adapts to a short metal–metal distance, it is unable to accommodate a single halide ligand under the bridge to form a triple bridge. It is not fluxional, whereas the thiolate complexes are [17]. Moreover, while the face-to-face structures having the two bridging ligands in a *trans* disposition found in complexes with bis(diphenylphosphino)methane bridges [18] change easily to A frame structures by sharing a third bridging ligand, the *cis* disposition of the bridging ligands in complex **1** and its derivatives hinders such flexibility of the double azaindolate bridge.

To test the possibility of migration of a carbonyl group to a bridging position, complex **1** was allowed to react with allyl bromide, since the allyl group usually can occupy two coordination positions. Nevertheless, the diiridium(II) compound **11** is the product of this reaction, with bridging carbonyl groups, and the allyl is η^1-bonded to one iridium atom as deduced from its ^{1}H NMR parameters. Complex **1** always forms a metal–metal bond upon reaction. When it reacts with an excess of 1,3-diiodopropane, it gives **10**, as isomers of types A and B (Table 2). As this complex still has an unchanged I–C bond, the reaction was carried out with less than an equivalent of the diiodopropane in order to form a polymethylene-bridged complex, but a mixture of **10** and unreacted **1** is isolated at room temperature.

The rigidity imposed by the double bridge and the face-to-face orientation has two effects. First, it prevents migration of fragments from one metal centre to the other and, second, the proximity forces the orbitals perpendicular to the molecular plane, d_z2 and p_z, to interact strongly. This interaction is associated with a strong band in the visible region of the mixture of isomers **1** ($\lambda_{max} = 530$ nm), attributed to $p\sigma \leftarrow d\sigma^*$ transitions in d^8-d^8 systems. The interaction is stronger the lower the energy of this band, and, in this sense, the metals interact better in **1** than in the pyrazolate [8] and 2-pyridonate [9] systems. Previous studies on photochemistry of binuclear d^8 complexes have shown that this interaction is responsible for the photoreduction of alkyl halides [9,19].

Abstraction of chlorine from 1,2-dichloroethane by **1** in sunlight is comparable to the reaction reported by Gray [8] for $[\{Ir(\mu\text{-pz})(cod)\}_2]$ for which a S_{NR} radical mechanism has been proposed. Moreover, complex **1** reacts cleanly with chloroform and carbon tetrachloride giving complexes **12** and **13**, respectively, through an oxidative-addition reaction, which does not occur with its thiolate counterparts, and the related complex $[\{Ir(\mu\text{-OPy})(cod)\}_2]$ gives the mononuclear chloro-complex $[Ir(OPy)Cl_2(cod)]$ [20]. The speed of the reactions described here is noticeably increased by the direct sunlight. In particular, the reaction of **1** with chloroform is completed in few minutes in direct sunlight, whilst it takes hours in the dark under otherwise identical conditions. A small amount of complex **3** is also obtained in the reaction of **1** with chloroform, which is indicative of free radical involvement. Complex **1** is thus a powerful photoreducer of chlorocarbons since chloroform is hard to reduce [21] and the product, **12**, is a rare example of a complex containing a dichloromethyl ligand [22]. We have not performed kinetic measurements on these reactions because of their high sensitivity to light and because complex **1** is very sensitive to oxygen. However, complex **1** reacts quantitatively with dibenzoyl peroxide, a well known promoter of free radicals. Characterization of the product of this reaction as the dibenzoatediiridium complex **14** having a structure similar to the acetate complex **2**, was based on its analytical and spectroscopic properties and by comparison with an authentic sample prepared by reaction of complex **5** with silver benzoate.

The reactions of **1** with the activated acetylenes dimethyl- and diethyl-acetylenedicarboxylate occur thermally to give the tetranuclear complexes $[\{Ir(\mu\text{-aza})(CO)_2\}_4\{C_2(CO_2R)_2\}_2]$ [R = Et (**15**), or Me (**16**)], as judged by microanalytical data and molecular weights in solution. A single isomer of complexes **15** and **16** is produced in these reactions (^{1}H NMR spectra) but they differ in symmetry. Complex **16** (R = Me) has no element of symmetry, showing four inequivalent aza ligands and methyl groups whereas **15** (R = Et) has two sets of two equivalent aza ligands and four equivalent ethyl groups. However, **15** and **16** show the same pattern of four terminal ν(CO) bands, different from that of the complexes **1–14**, which indicates a change in the spatial distribution of the carbonyl groups but no bridging carbonyl groups. Assuming that the acetylene behaves as a two-electron ligand, **15** and **16** are 68-valence-electron complexes, which requires two metal–metal bonds. Further details of the structure of these complexes cannot be achieved by spectroscopic methods in view of the complexity.

3. Experimental details

All reactions were carried out under dinitrogen using Schlenk techniques. Solvents were dried and distilled under dinitrogen immediately prior to use. The reactions of $[\{Ir(\mu\text{-aza})(CO)_2\}_2]$ (**1**) were carried out on solutions of the complex prepared *in situ* by bubbling carbon monoxide through a solution of $[\{Ir(\mu\text{-aza})(cod)\}_2]$ for 10 min and subsequent removal of the dissolved carbon monoxide under vacuum. ^1H NMR spectra were recorded on a Varian XL-200 spectrometer operating at 200.057 MHz; chemical shifts are reported relative to tetramethylsilane. Infrared spectra (range 4000–200 cm^{-1}) were recorded on a Perkin–Elmer 783 spectrometer using Nujol mulls between polyethylene sheets or in solution in NaCl windows. Elemental analyses were carried out with a Perkin–Elmer 240B microanalyzer. Molecular weights were determined with a Knauer osmometer using chloroform solutions.

3.1. $[\{Ir(\mu\text{-aza})(Me\text{-}CO_2)CO)_2\}_2]$ (2)

Solid silver acetate (60 mg, 0.36 mmol) was added to a solution of complex **1** (0.18 mmol) in tetrahydrofuran. The mixture was stirred in the dark for 30 min to give metallic silver and a pale-yellow solution, which was filtered and evaporated to dryness under vacuum. The residue was extracted with a 1 : 1 dichloromethane hexane mixture (15 ml) and then filtered. Concentration of the solution to 1 ml, further addition of hexane, and cooling to − 15°C afforded the complex as a white solid which was filtered, washed with cold hexane and vacuum-dried.

3.2. $[\{Ir(\mu\text{-aza})(X)(CO)_2\}_2]$ [X = Cl (3), X = Br (4) X = I (5)]

Slow addition of a freshly prepared solution of the appropriate halogen (X_2) (0.15 mmol) in dichloromethane to a solution of complex **1** (0.15 mmol) in toluene (10 ml), prepared as described above, resulted in an immediate change from deep purple to orange. The volatiles were pumped off and the residue extracted with dichloromethane (10 ml) and then filtered. Concentration of the filtrate to *ca.* 1 ml and addition of cold hexane gave the complexes as microcrystalline solids wich were filtered, washed with cold hexane and vacuum dried.

3.3. $[\{Ir(\mu\text{-aza-Br})(Br)(CO)_2\}_2]$ (6)

To a solution of complex **1** (0.15 mmol) in dichloromethane (15 ml) at 0°C, was added very slowly a recently prepared solution of bromine in dichloromethane (0.62 mmol in 5 ml). After 2 h, the volatiles were pumped off and the residue extracted with diethyl ether (10 ml). The extract was filtered and then evaporated to *ca.* 1 ml; addition of hexane gave the complex as a solid which was filtered, washed with cold hexane and dried under vacuum.

3.4. $[Ir_2(\mu\text{-aza})_2(R)(I)(CO)_4]$ [R = CH_3 (7), CH_2I (8), CHI_2 (9), $CH_2\text{-}CH_2\text{-}CH_2I$ (10)]

To a solution of complex **1** (0.15 mmol) in toluene (10 ml), a large excess (1 mmol) of the appropiate alkyl iodide (RI) was added. The solution became yellow or orange inmmediately, and then was evaporated to dryness. The residue was extracted with dichloromethane (5 ml) (complexes **7**, **8**, and **10**) or benzene (5 ml) (complex **9**) and then filtered. Concentration of these solutions and addition of hexane afforded the complexes as microcrystalline solids after refrigeration for 2 h. The complexes were filtered, washed with cold hexane and dried under vacuum.

3.5. $[Ir_2(\mu\text{-aza})_2(R)(X)(CO)_4]$ [X = Br, R = allyl (11); X = Cl, R = $CHCl_2$ (12), CCl_3 (13)]

To a solution of complex **1** (0.15 mmol) in toluene (10 ml), a large excess (0.5 ml) of allyl bromide (complex **11**), chloroform (complex **12**), and carbon tetrachloride (complex **13**), was added. The solutions were stirred in direct sunlight for 10 min to give orange solutions. The solvent was removed and the residue extracted with dichloromethane (5 ml) and then filtered. Concentration of these solutions and addition of cold hexane gave the complexes as yellow-orange solids which were filtered, washed with cold hexane and vacuum dried.

3.6. $[\{Ir(\mu\text{-aza})(C_6H_5COO)(CO)_2\}_2]$ (14)

Solid benzoyl peroxide (0.050 g, 0.20 mmol) was added to a solution of complex **1** (0.20 mmol) in dichloromethane (10 ml) to give an orange solution. The solution was stirred in an ice bath in direct sunlight for 30 min. White crystals of the compound were obtained by addition of hexane (10 ml) and cooling to −15°C. The crystals were filtered, washed with cold hexane and dried under vacuum.

3.7. $[\{Ir_2(\mu\text{-}aza)_2\{C_2(COOR)_2\}(CO)_4\}_2]$ [R = Et (15), Me (16)]

A mixture of $[\{Ir(\mu\text{-aza})(cod)\}_2]$ (0.100 g, 0.12 mmol) and the appropriate acetylene $C_2(COOEt)_2$ (20 μl, 0.12 mmol) (complex **15**), or $C_2(COOMe)_2$ (17 μl, 0.12 mmol) (complex **16**) was heated under reflux while carbon monoxide was present for 2 h to give a red-orange solution. Hexane (5 ml) was added and then the solutions were filtered to remove the solid in suspension. Concentration of these solutions and addition of cold hexane gave the complexes as solids which were filtered, washed with cold hexane and vacuum dried.

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