

(Alkoxycarbonyl)iridium Compounds with *N*-Donor Bases and with Triphenylphosphine

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(Alkoxycarbonyl)iridium compounds of type $[\text{IrI}_2(\text{CO}_2\text{R})(\text{CO})\text{L}_2]$ have been prepared by the reaction of $\text{K}[\text{Ir}(\text{CO})_2\text{I}_4]$ with nitrogen bases L and alcohols ROH. The reaction takes place through nucleophilic attack of the alcohols on the intermediate cations $[\text{IrI}_2(\text{CO})_2\text{L}_2]^+$, some of which have been isolated. Other (alkoxycarbonyl)iridium compounds containing triphenylphosphine (Y), $[\text{IrI}_2(\text{CO}_2\text{R})(\text{CO})\text{Y}_2]$ and $[\text{IrI}(\text{CO}_2\text{R})(\text{CO})_2\text{Y}]_2$ were obtained by the reaction of $[\text{IrI}(\text{CO})_2(\text{Y}_2)]$ and $[\text{Ir}(\text{CO})_3\text{Y}]_2$ respectively with iodine and alcohols.

THE formation of many transition-metal (alkoxycarbonyl)-compounds has been reported.¹⁻⁸ These are generally prepared by the reaction of a carbonylmetallate

anion and a chloroformic ester, but some are also obtained by attack with alkoxide ion or even alcohol on cationic carbonyl compounds, by alcoholysis of carbamoyl deriva-

¹ T. Kruck, M. Hoffer, and M. Noak, *Chem. Ber.*, 1966, **99**, 1153.

² R. B. King, M. B. Bisnette, and A. Fronzaglia, *J. Organometallic Chem.*, 1966, **5**, 341; L. Busetto and R. I. Angelici, *Inorg. Chim. Acta*, 1968, **2**, 391.

³ W. Hieber and H. Duchatsch, *Chem. Ber.*, 1965, **98**, 1744.

⁴ W. Hieber and V. Frey, *Chem. Ber.*, 1966, **99**, 2614.

⁵ W. Hieber, V. Frey, and P. Joan, *Chem. Ber.*, 1967, **100**, 1961.

⁶ L. Malatesta, G. Caglio, and M. Angoletta, *J. Chem. Soc.*, 1965, 6974.

⁷ A. J. Demming and B. L. Shaw, *J. Chem. Soc. (A)*, 1969, 443.

⁸ H. C. Clark, K. R. Dixon, and W. J. Jacobs, *Chem. Comm.*, 1968, 548.

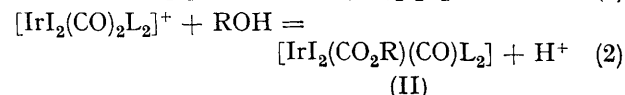
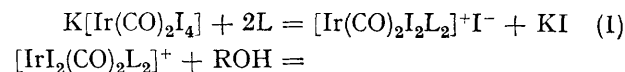
tives and, in the case of iridium,⁶ by the oxidative addition of chloroformic esters on the chlorocarbonylbis-(triphenylphosphine) compound.

Here we report new readily formed (alkoxycarbonyl)-iridium derivatives.

RESULTS AND DISCUSSION

Compounds with *N*-Donor Ligands.—The reaction of $K[Ir(CO)_2I_4]$ ⁹ in a primary or secondary alcohol with pyridine (L), 2,2'-bipyridyl (L_2) or 1,10-phenanthroline (L_2) gives the monomeric nonelectrolyte $[IrI_2(CO_2R)(CO)L_2]^+$.^{*} The i.r. spectra show two bands, one at *ca.* 2050 cm^{-1} (co-ordinated 'inorganic' carbonyl), another at 1650 cm^{-1} ('organic' carbonyl). The ¹H n.m.r. spectrum of the compound with $R = Me$ and $L_2 = 2,2'$ -bipyridyl shows the methyl absorbance at τ 6.2. An X-ray structural determination of this compound¹¹ has shown that the unidentate ligands CO and CO_2Me and the bidentate bipyridyl are on the equatorial plane of a distorted octahedron having the two iodine atoms at the apices, slightly inclined in opposite direction with respect to the vertical axis. The peculiarity of this structure, that the methoxycarbonyl group is coplanar with the equatorial plane, may be attributed either to some π -interaction between the metal and the methoxycarbonyl carbon atom or to the interaction between the carboxy-oxygen atom and an α -hydrogen of the bipyridyl.

In all known examples, nucleophilic attack on a metal carbonyl to give the (alkoxycarbonyl)-derivative occurs on a cationic carbonyl compound, and it is considered that the positive charge probably enhances the electrophilic character of the carbonyl group. In none of the cases so far reported had the metal of the carbonyl-containing cation an oxidation number >1 , a large polarizability of the metal apparently being a necessary condition for the stability of the carbonyl cations. However, the consideration that iridium is the only metal to give stable tricarbonyl-⁹ and (alkoxycarbonyl)-compounds⁷ in the oxidation state three, led us to suppose that a cation $[IrI_2(CO)_2L_2]^+$ (I) could exist and, behaving analogously to $[Ir(CO)_3L_2]^+$,⁶ be the first product in the reaction of the tetracarbonyliridate with *N*-bases [reaction (1)]. The cation (I) would be immediately attacked by alcohols to give the (alkoxycarbonyl)-derivatives (II) [reaction (2)]:



By carrying out the reaction in an alcohol-free solvent, at low temperature and in carbon monoxide,

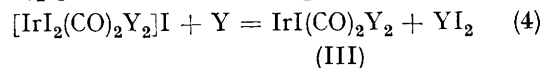
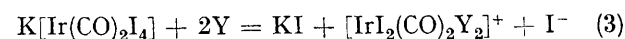
^{*} This compound has been previously considered to be $[IrI_2(CO)_2L_2]$ (ref. 10).

⁹ L. Malatesta, L. Naldini, and F. Cariati, *J. Chem. Soc.*, 1964, 961.

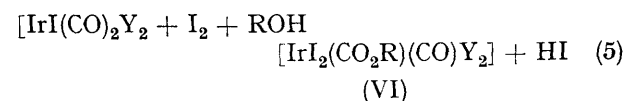
¹⁰ M. Angoletta, *Gazzetta*, 1960, **90**, 1021.

we could in fact isolate the iodides of (I) ($L_2 =$ bipyridyl) as red crystalline compounds, which behave as univalent electrolytes in nitrobenzene and have an i.r. spectrum with two terminal bands due to carbonyl at *ca.* 2040 cm^{-1} , as expected. These compounds react immediately with alcohols, giving the (alkoxycarbonyl)-derivatives (II). This behaviour shows that the presence of iridium(III) in the cations (I) has much enhanced the electrophilic character of the co-ordinated carbon monoxide, without completely destabilizing the iridium-carbon bonds. Thus, these cations undergo nucleophilic attack even in neutral solution, whereas the cation $[Ir(CO)_3L_2]^+$ ⁶ requires an alkaline medium.

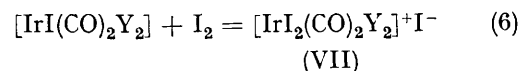
Compounds with Triphenylphosphine.—The reaction of $K[Ir(CO)_2I_4]$ with triphenylphosphine (Y) in alcohols, in contrast to that with nitrogen bases, gives a mixture of the iododicarbonyl compound $[IrI(CO)_2Y_2]$ (III) and the hydridodi-iodocarbonyl compound $[IrHI_2(CO)Y_2]$ (IV).¹² Either of these compounds can be prepared almost quantitatively: the monoiodide at low temperature under carbon monoxide with an excess of the phosphine, and the hydride (IV) when heated under reflux in ethanol with two moles of the phosphine. We considered that the (alkoxycarbonyl)-derivative of type (II) is not formed in the reaction between tetraiododicarbonyliridate(III) and triphenylphosphine in alcohols, because of the reduction of the hypothetical intermediate cation $[Ir(CO)_2Y_2I_2]^+$ (V) to (III) by the phosphine [reactions (3) and (4)]:



We then investigated whether the isolated species (III) could be reoxidized by iodine to give the cationic species (V), which would immediately react with alcohol to give the (alkoxycarbonyl)-compound. By the addition of iodine to (III) in alcohol, we did obtain quantitatively the (alkoxycarbonyl)triphenylphosphine derivatives (VI) analogous to the derivative (II) [reaction (5)].



We also isolated a compound (VII), which we consider as the iodide of the intermediate cation (V), by carrying out the reaction in the absence of alcohols at low temperature and under carbon monoxide [reaction (6)].



Compound (VII) was impure, probably owing to the presence both of the periodide $[IrI_2(CO)_2Y_2]I_3$ and the tri-iodide $IrI_3(CO)Y_2$ (VIII); it changes to the latter by

¹¹ V. G. Albano, P. L. Bellon, and M. Sansoni, *Inorg. Chem.*, 1969, **8**, 298.

¹² M. Angoletta and G. Caglio, *Rend. Ist. Lombardo Sci. Lett. (Italy)*, 1963, **97**, 823.

loss of carbon monoxide and could not therefore be purified. However, its i.r. spectrum which shows the two expected CO stretching bands in the high-frequency region at 2120–2080 and its immediate reaction with alcohols, giving the (alkoxycarbonyl)-compounds (VI), strongly favours the formula (VII).

Since the oxidation of the partially substituted iridium

and obtained an (alkoxycarbonyl)iridium(II) derivative [reactions (7) and (8)].

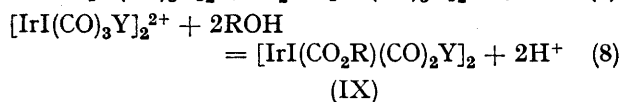


TABLE 1
I.r. spectra and other physical data

Compound *	Colour	M.p. (°)	$\nu(\text{CO})$ (cm. ⁻¹)	Solubility
$[\text{IrI}_2(\text{CO}_2\text{Me})(\text{CO})(\text{bipy})]$	Yellow	260	2060, 1670	DMSO, nitrobenzene, DMF
$[\text{IrI}_2(\text{CO})_2(\text{bipy})]\text{I}$	Red		2080, 2040	
$[\text{IrI}_2(\text{CO}_2\text{Et})(\text{CO})(\text{bipy})]$	Yellow	225	2040, 1645	DMSO, DMF
$[\text{IrI}_2(\text{CO}_2\text{Pr}^i)(\text{CO})(\text{bipy})]$	Yellow	224	2060, 1640	Isopropanol
$[\text{IrI}_2(\text{CO}_2\text{allyl})(\text{CO})(\text{bipy})]$	Yellow	178–180	2060, 1660	Allyl alcohol
$[\text{IrI}_2(\text{CO}_2\text{Me})(\text{CO})(p\text{-tol})_2]$	Yellow	177	2080, 1650	Benzene-acetone
$[\text{IrI}_2(\text{CO}_2\text{Me})(\text{CO})(\text{phen})]$	Yellow	> 300	2068, 1654	DMF
$[\text{IrI}_2(\text{CO}_2\text{Me})(\text{CO})(\text{py})_2]$	Yellow	180 †	2050, 1660	Chloroform, dichloromethane
$[\text{IrI}_3\text{CO}(\text{bipy})]$	Orange-yellow	> 300	2060	
$[\text{IrI}(\text{CO})_2(\text{PPh}_3)_2]^a$	Yellow	225	1990, 1930	Benzene, dichloromethane
$[\text{IrI}(\text{CO})(\text{PPh}_3)_2]^b$	Yellow	> 300	1975	Benzene
$[\text{IrHI}_2(\text{CO})(\text{PPh}_3)_2]^c$	White	160	2040, 2180 (IrH)	Benzene, chloroform, THF
$[\text{IrI}_3\text{CO}(\text{PPh}_3)_2]$	Orange	263	2080	Dichloromethane, benzene
$[\text{IrI}_2(\text{CO}_2\text{Me})(\text{CO})(\text{PPh}_3)_2]$	Yellow	160	2050, 1650	Dichloromethane, benzene
$[\text{IrI}_2(\text{CO})_2(\text{PPh}_3)_2]\text{I}$	Red-brown		2120, 2080	
$[\text{IrI}_2(\text{CO}_2\text{Et})(\text{CO})(\text{PPh}_3)_2]$	Yellow	174	2060, 1700	Benzene, ethanol
$[\text{IrI}(\text{CO}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2]$	Yellow	166	2070, 2040, 1650	Dichloromethane
$[\text{IrI}(\text{CO}_2\text{Et})(\text{CO})_2(\text{PPh}_3)_2]$	Yellow	146	2040, 2070, 1660, 1640	Benzene, dichloromethane
$[\text{IrBr}(\text{CO}_2\text{Et})(\text{CO})_2(\text{PPh}_3)_2]$	Yellow	128–130	2100, 2050, 1670	Benzene
$[\text{IrCl}(\text{CO}_2\text{Et})(\text{CO})_2(\text{PPh}_3)_2]$	Green	110–115 †	2090, 2040, 1650	Benzene
$[\text{Ir}(\text{CO}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2]$			1980, 1940, 1615	
$[\text{IrCl}_2(\text{CO}_2\text{Me})(\text{CO})(\text{PMe}_2\text{Ph})_2]$			2053, 1677	
$[\text{IrCl}_2(\text{CO}_2\text{Et})(\text{CO})(\text{PMe}_2\text{Ph})_2]$			2049, 1663	

* bipy = 2,2'-Bipyridyl, *p*-tol = *p*-toluidine, phen = 1,10-phenanthroline, py = pyridine. † Decomp.

^a Ref. 10. ^b Ref. 14. ^c Ref. 12.

TABLE 2
Analytical data

Compound	Found (%)							Calc. (%)						
	C	H	Cl, Br, I	Ir	N	O	—OR	C	H	Cl, Br, I	Ir	N	O	—OR
$[\text{IrI}_2(\text{CO}_2\text{Me})(\text{CO})(\text{bipy})]$	23.0	1.3	36.5	26.5	3.85	6.90	OMe 4.4	22.6	1.6	36.8	27.8	4.05	6.95	OMe 4.5
$[\text{IrI}_2(\text{CO})_2(\text{bipy})]\text{I}$	19.0	1.25			3.7			18.3	1.0			3.45		
$[\text{IrI}_2(\text{CO}_2\text{Et})(\text{CO})(\text{bipy})]$	23.0	1.75	35.9	27.2	4.15	6.74		23.9	1.85	36.2	27.4	4.0	6.8	
$[\text{IrI}_2(\text{CO}_2\text{Pr}^i)(\text{CO})(\text{bipy})]$	25.5	2.25	35.4	26.5	3.9	7.59		25.2	2.2	35.4	26.9	3.9	6.7	
$[\text{IrI}_2(\text{CO}_2\text{allyl})(\text{CO})(\text{bipy})]$	25.0	1.9	34.3	26.2	4.05	6.68		25.0	1.8	35.5	26.8	3.9	6.7	
$[\text{IrI}_2(\text{CO}_2\text{Me})(\text{CO})(p\text{-tol})_2]$	27.85	2.65	33.5	25.0	3.75	6.76	OMe 4.15	27.3	2.8	34.0	25.8	3.75	6.5	OMe 4.15
$[\text{IrI}_2(\text{CO}_2\text{Me})(\text{CO})(\text{phen})]$	25.7	1.9	34.5	27.0	4.1	6.83	OMe 4.1	25.2	1.55	35.5	27.0	3.95	6.7	OMe 4.35
$[\text{IrI}_2(\text{CO}_2\text{Me})(\text{CO})(\text{py})_2]$	22.35	1.85	36.3	27.5	4.25	7.07	OMe 5.0	22.6	1.9	36.7	27.9	4.05	6.9	OMe 4.5
$[\text{IrI}_3\text{CO}(\text{bipy})]$	17.45	1.05	50.2		3.75	2.46		17.4	1.05	50.1		3.7	2.1	
$[\text{IrI}(\text{CO})_2(\text{PPh}_3)_2]$	51.15	3.55	14.2			3.50		50.8	3.3	14.1			3.55	
$[\text{IrICO}(\text{PPh}_3)_2]^a$	50.25	3.4	14.2					51.0	3.45	14.5				
$[\text{IrHI}_2\text{CO}(\text{PPh}_3)_2]$	44.8	3.25	25.1					44.45	3.1	25.4				
$[\text{IrI}_3\text{CO}(\text{PPh}_3)_2]$	39.6	2.7	33.8			1.41		39.4	2.7	33.8			1.45	
$[\text{IrI}_2(\text{CO}_2\text{Me})(\text{CO})(\text{PPh}_3)_2]$	44.5	3.1	24.5			4.83	OMe 2.85	44.4	3.1	24.0			4.55	OMe 2.95
$[\text{IrI}_2(\text{CO})_2(\text{PPh}_3)_2]\text{I}$	36.5	2.65	35.0					39.5	2.6	33.0				
$[\text{IrI}_2(\text{CO}_2\text{Et})(\text{CO})(\text{PPh}_3)_2]$	46.2	3.35	23.1			5.61	OEt 3.2	44.8	3.1	23.1			4.45	OEt 4.2
$[\text{IrI}(\text{CO}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2]$	37.25	2.6	17.6			9.31	OMe 4.25	37.9	2.6	18.2			9.15	OMe 4.45
$[\text{IrI}(\text{CO}_2\text{Et})(\text{CO})_2(\text{PPh}_3)_2]$	39.6	2.95	17.9			8.94	OEt 6.4	39.1	2.8	17.9			8.95	OEt 6.35
$[\text{IrBr}(\text{CO}_2\text{Et})(\text{CO})_2(\text{PPh}_3)_2]$	40.9	3.0	12.7					41.7	3.0	12.1				
$[\text{IrCl}(\text{CO}_2\text{Et})(\text{CO})_2(\text{PPh}_3)_2]$	44.35	3.1	5.7					44.6	3.25	5.75				

^a Ref. 14.

carbonyl compounds with iodine in alcohols appeared to be a convenient route to the (alkoxycarbonyl)-derivatives, we extended this reaction to $[\text{Ir}(\text{CO})_3\text{Y}]_2^{13}$

¹³ L. Malatesta, M. Angoletta, and G. Caglio, *Proc. VIII Internat. Conference Co-ordination Chem.*, 1964, 210.

Compound (IX) is dimeric and diamagnetic and can probably be formulated with a metal-metal bond and no iodine bridges, so that the iridium atom acquires the effective atom number of radon. The analogous compounds with bromine and chlorine were also obtained.

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These compounds are one of the few examples of dimeric derivatives of iridium containing a metal-metal bond and the first example of such a compound with the metal in the oxidation number two.

Table 1 reports the i.r. spectra of these compounds, and for comparison, the spectra of the (alkoxycarbonyl)-iridium(I)⁶ and -iridium(III) derivatives.⁷ It can be observed that no general correlation may be found between the stretching frequencies of the carbonyl and the carboxy-groups either with the oxidation number of the metal or with the electronegativity of the other ligands. In fact, the fluctuations which appear in the carbonyl group stretching frequency of compounds of the same type, with different alkoxy-groups or *N*-donor bases are of the same order of magnitude as the fluctuations in compounds with the metal in different oxidation states or having a different halogen. The intermediate cationic species, on the contrary, have higher carbonyl stretching frequencies as expected.

EXPERIMENTAL

Di-iodobipyridylcarbonyl(methoxycarbonyl)iridium, $[\text{IrI}_2(\text{CO}_2\text{Me})(\text{CO})(\text{bipy})]_2$.—This was prepared from $\text{K}[\text{Ir}(\text{CO})_2\text{I}_4]$ (0.5 g.) in methanol (30 ml.) and 2,2'-bipyridyl (0.1 g.) at 40° as yellow needles, and was recrystallized from *NN*-dimethylformamide and cold methanol (75%); n.m.r. spectrum ($[\text{H}_6]$ dimethyl sulphoxide) τ 6.2 (CH_3).

Di-iododicarbonyl(bipyridyl)iridium Iodide $[\text{IrI}_2(\text{CO})_2(\text{bipy})]\text{I}$.—This was prepared from $\text{K}[\text{Ir}(\text{CO})_2\text{I}_4]$ (0.3 g.) in diethyl ether (10 ml.) at -15° and bipyridyl (0.118 g.) in diethyl ether (10 ml.) with stirring under carbon monoxide. The red compound could not be recrystallized without loss of carbon monoxide; Λ 18.5 ohm⁻¹ cm.² mol.⁻¹ (0.01M in nitrobenzene).

Di-iodobipyridylcarbonyl(methoxycarbonyl)iridium, $[\text{IrI}_2(\text{CO}_2\text{Et})(\text{CO})(\text{bipy})]_2$.—This was prepared from $\text{K}[\text{Ir}(\text{CO})_2\text{I}_4]$ (0.5 g.) in ethanol (40 ml.) and bipyridyl (0.1 g.) in ethanol (15 ml.) at 40° and was recrystallized from ethanol (70%); *M* (CHCl_3) 781, *M* (calc.) 704.

Di-iodobipyridylcarbonyl(isopropoxycarbonyl)iridium, $[\text{IrI}_2(\text{CO}_2\text{Pr})(\text{CO})(\text{bipy})]_2$.—This was prepared from $\text{K}[\text{Ir}(\text{CO})_2\text{I}_4]$ (0.5 g.) in isopropanol (15 ml.) and bipyridyl (0.1 g.) at 40°, and was recrystallized from isopropanol (75%).

Di-iodo(allyloxycarbonyl)bipyridylcarbonyliridium, $[\text{IrI}_2(\text{CO}_2\text{allyl})(\text{CO})(\text{bipy})]_2$.—This was prepared from $\text{K}[\text{Ir}(\text{CO})_2\text{I}_4]$ (0.5 g.) in allyl alcohol (30 ml.) and 2,2'-bipyridyl (0.1 g.) at 40°, as yellow crystals which were recrystallized from allyl alcohol (50%); *M* (CHCl_3) 712, *M* (calc.) 716.

*Di-iodocarbonyl(methoxycarbonyl)di-*p*-toluidineiridium*, $[\text{IrI}_2(\text{CO}_2\text{Me})(\text{CO})(p\text{-tol})]_2$.—This was prepared from $\text{K}[\text{Ir}(\text{CO})_2\text{I}_4]$ (1.1 g.) in methanol (20 ml.) and *p*-toluidine (0.3 g.) at 40° and recrystallized from benzene (64%). *M* (CHCl_3) 778, *M* (calc.) 748; n.m.r. spectrum ($[\text{H}_6]$ dimethyl sulphoxide) τ 6.4 (CH_3).

Di-iodocarbonyl(methoxycarbonyl)-1,10-phenanthrolineiridium, $[\text{IrI}_2(\text{CO}_2\text{Me})(\text{CO})(\text{phen})]_2$.—This was prepared from $\text{K}[\text{Ir}(\text{CO})_2\text{I}_4]$ (0.618 g.) in methanol (20 ml.) and 1,10-phenanthroline (0.14 g.), at 40°, and recrystallized by dissolving in cold dimethylformamide and precipitating with methanol (79%).

Di-iodocarbonyl(methoxycarbonyl)bis(pyridine)iridium,

$[\text{IrI}_2(\text{CO}_2\text{Me})(\text{CO})(\text{py})]_2$.—This was prepared from $\text{K}[\text{Ir}(\text{CO})_2\text{I}_4]$ (0.5 g.) in ethanol (20 ml.) with pyridine (0.3 g.). *M* (CHCl_3) 684, *M* (calc.) 692.

Tri-iodocarbonylbipyridyliridium, $[\text{IrI}_3\text{CO}(\text{bipy})]$.—This was prepared by three methods: (i) by heating under reflux $[\text{IrI}_2(\text{CO}_2\text{Pr})(\text{CO})(\text{bipy})]$ in isopropanol with hydroiodic acid for 24 hr. (40%), (ii) from $\text{K}[\text{Ir}(\text{CO})_2\text{I}_4]$ (0.5 g.) and bipyridyl (0.1 g.) in *t*-butanol, and (iii) by heating under reflux $\text{IrI}_2(\text{CO}_2\text{Me})(\text{CO})(\text{bipy})$ in dimethylformamide with hydriodic acid.

Iododicarbonylbis(triphenylphosphine)iridium, $[\text{IrI}(\text{CO})_2(\text{PPh}_3)_2]$.—This was prepared by four methods: (i) from $\text{K}[\text{Ir}(\text{CO})_2\text{I}_4]$ (1 g.) in ethanol (30 ml.) at 0° under carbon monoxide and triphenylphosphine (1.32 g.) in benzene (10 ml.) and recrystallized from benzene (88%).

(ii) A solution of $\text{K}_2[\text{IrCOI}_5]$ (1.5 g.) in methanol (60 ml.) was stirred under carbon monoxide for $\frac{1}{2}$ hr. at room temperature. Potassium hydroxide (2 g.) and triphenylphosphine (0.84 g., 2 moles) were then added, the stirring was continued for 24 hr., and the product then recrystallized from benzene-ethanol.

(iii) A solution of $[\text{IrCO}(\text{PPh}_3)_2]$ (1 g.) in benzene (50 ml.) was stirred for 24 hr. under carbon monoxide at room temperature and the product precipitated with ethanol.

(iv) $[\text{IrClCO}(\text{PPh}_3)_2]$ (3 g.) and sodium iodide (3 g.) in methanol-benzene (90 ml., 5:4 v/v) were stirred under carbon monoxide at room temperature in the dark for 5–6 hr.¹⁰ *M* (CHCl_3) 930, *M* (calc.) 899.

Iodocarbonylbis(triphenylphosphine)iridium, $[\text{IrICO}(\text{PPh}_3)_2]$.— $[\text{IrI}(\text{CO})_2(\text{PPh}_3)_2]$ in 2-methoxyethanol were heated under reflux for 2 hr. under nitrogen to give golden yellow crystals (80%).¹⁴

Hydriodi-iodocarbonylbis(triphenylphosphine)iridium, $[\text{IrHI}_2\text{CO}(\text{PPh}_3)_2]$.—This was prepared (i) from $[\text{IrI}(\text{CO})_2(\text{PPh}_3)_2]$ (0.5 g.) in benzene (50 ml.) and an excess of hydroiodic acid (90%) and (ii) from $\text{K}[\text{Ir}(\text{CO})_2\text{I}_4]$ (0.5 g.) and triphenylphosphine (0.33 g., 2 moles) in ethanol (25 ml.) by heating under reflux for 2 hr.¹²

Tri-iodocarbonylbis(triphenylphosphine)iridium, $[\text{IrI}_3\text{CO}(\text{PPh}_3)_2]$.—This was prepared from $[\text{IrI}(\text{CO})_2(\text{PPh}_3)_2]$ (0.5 g.) in benzene (25 ml.) and an excess of iodine in ethanol at room temperature (80%).

Di-iodocarbonyl(methoxycarbonyl)bis(triphenylphosphine)iridium, $[\text{IrI}_2(\text{CO}_2\text{Me})(\text{CO})(\text{PPh}_3)_2]$.—A suspension of $[\text{IrI}(\text{CO})_2(\text{PPh}_3)_2]$ (0.5 g.) in benzene-methanol (1/1 v/v) (40 ml.) at -10° under carbon monoxide was treated dropwise with iodine (0.5 g.) in methanol (20 ml.) with stirring. Potassium hydroxide (1 g.) in methanol (20 ml.) was then added and the stirring continued for 5–6 hr. (70%).

Di-iododicarbonylbis(triphenylphosphine)iridium Iodide, $[\text{IrI}_2(\text{CO})_2(\text{PPh}_3)_2]\text{I}$ $[\text{IrI}(\text{CO})_2(\text{PPh}_3)_2]$ (0.5 g.) in toluene (20 ml.) and iodine (0.141 g., 1 mole) were stirred at -15° under carbon monoxide. The red-brown compound could not be purified because in solution it lost carbon monoxide to give $[\text{IrCO}(\text{PPh}_3)_2\text{I}_3]$.

Di-iodocarbonyl(ethoxycarbonyl)bis(triphenylphosphine)iridium, $[\text{IrI}_2(\text{CO}_2\text{Et})(\text{CO})(\text{PPh}_3)_2]$.—This was prepared similarly in 1:1 benzene-ethanol (60%).

Bis[iododicarbonyl(methoxycarbonyl)(triphenylphosphine)iridium] $[\text{IrI}(\text{CO}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2]_2$.—A suspension of $[\text{Ir}(\text{CO})_3(\text{PPh}_3)_2]$ (0.15 g.) in methanol (10 ml.) was stirred

¹⁴ G. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, 1966, **88**, 3511.

with a solution of iodine (2 moles) for 2 hr. at 0° under carbon monoxide and recrystallized from methylene chloride-methanol (50%).

Bis[iododicarbonyl(ethoxycarbonyl)triphenylphosphineiridium], $[\text{IrI}(\text{CO}_2\text{Et})(\text{CO})_2(\text{PPh}_3)]_2$.—This was prepared similarly from ethanol, and recrystallized from benzene-ethanol (50%); *M* (benzene) 1375, *M* (calc.) 1422. The n.m.r. spectrum (deuteriochloroform) showed a quadruplet at τ 6.3 (CH_2) and a triplet at τ 8.8 (Me); *J*, 7 Hz.

Bis[bromodicarbonyl(ethoxycarbonyl)triphenylphosphineiridium], $[\text{IrBr}(\text{CO}_2\text{Et})(\text{CO})_2(\text{PPh}_3)]_2$.—A suspension of $[\text{Ir}(\text{CO})_3(\text{PPh}_3)]_2$ (200 mg.) in ethanol (10 ml.) was stirred with a solution of bromine (0.1M) in carbon tetrachloride (7.4 ml.) for 15 min. at -10° under carbon monoxide. The

solution was then evaporated and the residue recrystallized from benzene-ethanol (50%).

Bis[chlorodicarbonyl(ethoxycarbonyl)triphenylphosphineiridium], $[\text{IrCl}(\text{CO}_2\text{Et})(\text{CO})_2(\text{PPh}_3)]_2$.—A suspension of $[\text{Ir}(\text{CO})_3(\text{PPh}_3)]_2$ (200 mg.) in ethanol (15 ml.) was stirred with a 0.1M-solution of chlorine in carbon tetrachloride (7.4 ml.) under carbon monoxide at -10° for 10 min. The clear green solution was concentrated and the product was precipitated with hexane, and recrystallized from benzene-hexane (70%); *M* (benzene) 1270, *M* (calc.) 1237.

Analytical data are collected in Table 2.

N.m.r. Spectra.—These were recorded at 60 Mc./sec. on a Perkin-Elmer R10 Spectrometer.

[9/2052 Received, November 28th, 1969]