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THE PREPARATION AND REACTIONS OF BIS[TRICARBONYL(TRIPHENYLPHOSPHINE)IRIDIUM]

L. MALATESTA and M. ANGOLETTA

Istituto di Chimica Generale e Inorganica, Via Venezian 21, 20133 Milano (Italy)

G. CAGLIO

Centro di studio per la sintesi e la struttura dei composti dei metalli di transizione nei bassi stati di ossidazione del C.N.R., Istituto Chimica Generale, Via Venezian 21, 20133 Milano (Italy)

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Summary

The preparation of $Ir_2(CO)_6(PPh_3)_2$ by a new route is described, as are the reactions of this compound with hydrogen, mercury, tin(II) chloride, hydrogen halides and halogens, leading to new monophosphine carbonyl iridium compounds.

The $[Ir(CO)_3PPh_3]^-$ anion has been isolated as the tris(phenanthroline)-nickel salt.

Introduction

It is well known that octacarbonyldiiridium is not stable even under a very high pressure of carbon monoxide [1], though its substitution products with triphenylphosphine, (L), viz. $Ir_2(CO)_7L$ [2] and $Ir_2(CO)_6L_2$ [3], have been obtained by reaction of carbon monoxide at high temperature and pressure with various triphenylphosphine—iridium derivatives. Having now found a more convenient way to prepare $Ir_2(CO)_6L_2$ (I) from the readily-available $Ir(CO)_2L_2I$ [4], we have been prompted to study the reactivity of I towards many reagents.

Results and discussion

The preparation involves refluxing $Ir(CO)_2L_2I$ with sodium ethoxide in benzene in a CO atmosphere. Since the alkoxycarbonyl compounds $Ir(CO)_2(COOC_2H_5)L_2$ [5] (II) can be isolated as an intermediate we propose the following course:

$$Ir(CO)_2L_2I \xrightarrow{CO} Ir(CO)_3L_2I \xrightarrow{C_2H_5ONa} II$$

The isolated II on refluxing with sodium ethoxide undergoes disproportionation:

$$II \rightarrow I + 2\, Ir(CO)L_3H \quad [6]$$

Unpublished results [7] show that compound I promotes the hydroformylation of propene and one might suppose that by dissociation, it could form a derivative liable to undergo the oxidative addition reactions characteristic of species containing a coordinatively-unsaturated high *d* transition metal in a low oxidation state. In fact the reactions of I are rather different to those expected, as we note below.

The dissociation of CO and phosphine from I is best observed by refluxing it under N_2 in benzene or tetrahydrofuran, in which I is somewhat soluble. As a consequence of this irreversible dissociation, $Ir_4 L_3 (CO)_9$ [8] (V), a cluster compound with bridging CO, is obtained. The addition of excess phosphine does not stabilize I, but transforms it into the more soluble iridium carbonyl $Ir_2(CO)_5L_3$ [9], whose molecular weight could be determined, thus indirectly confirming the dimeric nature of I.

The reduction of I with sodium amalgam in tetrahydrofuran gives a solution containing as the only species the sodium salt of $[Ir(CO)_3L]^-$ anion (VII), which has been postulated by Collman [10] to be the product of the reduction of $Ir(CO)L_2Cl$ [11] under CO pressure with sodium amalgam. The anion, which is a very strong base, stable under CO, is easily protonated by alcohols to give I, probably through the hydride $Ir(CO)_3LH$, which is in reversible equilibrium with I [12]:

$$[Ir(CO)_3L]^- + C_2H_5OH \rightleftharpoons Ir(CO)_3LH + C_2H_5O^-$$

$$2\, Ir(CO)_3LH \rightarrow Ir_2(CO)_6L_2 + H_2$$

The anion $[Ir(CO)_3L]^-$ could be isolated as the tris(phenanthroline)nickel salt (VIII). With mercury(II) cyanide it gives $[Ir(CO)_3L]_2Hg$ (IX) and with chloro(triphenylphosphine)gold, it gives $[Ir(CO)_3L]AuL$ (X), both previously prepared by Collman [10] from the reduction product of $Ir(CO)L_2Cl$. The IR spectrum of the solution of $Na[Ir(CO)_3L]$ in tetrahydrofuran shows three bands ascribable to ν(CO), as expected for a compound of apparent C_{3v} symmetry. Collman reports [10] for this anion the two most intense bands shown by our compound, probably as his spectra were taken with a much more dilute solution.

Compound I does not undergo oxidative addition with reagents such as CH_3I, CH_3COCl, but on the other hand reacts very readily with hydrogen, with mercury and with molecules such as $SnCl_2$ and SO_2, having lone pairs and unoccupied orbitals, to give $IrL(CO)_3H$ [12], $[IrL(CO)_3]_2Hg$ [10] (IX), $[IrL(CO)_3]_2SnCl_2$ (XI), $Ir_2(CO)_4L_2(SO_2)_2$ [13], respectively. The fact that hydrogen addition gives rise to an increase of the oxidation number of the metal from zero to one, while the reaction with tin(II) chloride and with mercury reduces the metal to the oxidation number −1 (which is in accordance with the formation of the same mercury compound from $[Ir(CO)_3L]^-$ and $Hg(CN)_2$) is unimportant in that it depends only on our definition of oxidation number. The reaction with hydrogen (which has previously been reported [12]), gives $Ir(CO)_3LH$, which was identified by its IR and NMR spectrum but could not be isolated, along with *fac*-$Ir(CO)_2LH_3$ (XII). The reaction with sodium hydridoborate involves extensive disproportionation with the formation of the well-known $Ir(CO)_2L_2H$ [14] and a mixture of anionic cluster compounds, which was obtained as the tetraethylammonium salts but could not be separated. The analysis and the IR spectrum of this mixture, showing bridging and terminal CO groups and hydridic hydrogen, indicate the probable presence of the anions $[Ir_4(CO)_8L_3H]^-$, $[Ir_4(CO)_9L_2H]^-$ and $[Ir_4(CO)_{10}LH]^-$.

Compound I in benzene suspension reacts with hydrogen chloride giving the hydride $[Ir(CO)LCl_2H]_2$ (XIV) quantitatively. Many paths can be postulated for this reaction, the most obvious being:

$$Ir_2(CO)_6L_2 + 2\ HCl \rightleftharpoons 2\ Ir(CO)_2LCl + H_2 + 2\ CO$$

followed by the oxidative addition of HCl:

$$2\ Ir(CO)_2LCl + 2\ HCl \rightleftharpoons [Ir(CO)LCl_2H]_2 + CO$$

The intermediate compound $Ir(CO)_2LCl$, which was not isolated, may be monomeric or dimeric; the final monohydride is to be considered dimerised through chlorine bridges, on the basis of its IR spectrum, which shows bands in the range of both terminal and bridging chlorine.

The reaction of I in benzene with hydrogen bromide initially follows the same course, giving $[Ir(CO)LHBr_2]_2$ (XV), but any excess of dissolved CO must be rapidly swept out with nitrogen in order to avoid the disproportionation*:

$$[Ir(CO)LHBr_2]_2 + 2\ HBr + CO \rightleftharpoons Ir(CO)L_2HBr_2 + H[Ir(CO)_2Br_4] + H_2$$

(XVII)

The dicarbonyltetrabromoiridate(III) could be isolated as the tetraalkylammonium salt (XIX).

Finally, with hydrogen iodide in benzene we obtained from I a white crystalline precipitate which, from its IR spectrum and analysis, appears to be a mixture, probably of $Ir(CO)LHI_2$ (not yet isolated), $Ir(CO)LI_3$ (XXXIV), and $Ir(CO)L_2HI_2$ [17] (XVIII).

The reaction of I with hydrogen halides in basic solvents such as tetrahydrofuran takes a quite different course, resulting in all cases in disproportionation as follows:

$$Ir_2(CO)_6L_2 + 6\ HX \rightleftharpoons Ir(CO)L_2HX_2 + H[Ir(CO)_2X_4] + 2\ H_2 + 3\ CO$$

With X = Br (XIX) and I (XX) the anions $[Ir(CO)_2X_4]^-$ [16, 18] were isolated as quaternary ammonium salts. We consider that the compounds $[Ir(CO)LHX_2]_2$ are intermediates in the reaction: in fact, dissolution of $IrH(CO)LCl_2$ (XIV) in cold dimethyl sulfoxide immediately causes disproportionation to give $Ir(CO)L_2HCl_2$ [15] (XVI) and an iridium carbonyl compound, not containing any phosphine, which, after addition of some HCl, can be precipitated by tetraphenylarsonium chloride as a mixture of the salts of $[Ir(CO)Cl_4]^-$ [19] and $[Ir(CO)Cl_5]^{2-}$ [18]. The dissolution of $[Ir(CO)LHCl_2]_2$ (XIV) and $[Ir(CO)LHBr_2]_2$ (XV) in tetrahydrofuran containing the corresponding hydrogen halide gives the anions $[Ir(CO)LCl_4]^-$ and $[Ir(CO)LBr_4]^-$ which were isolated in a pure state as tetraalkylammonium salts (XXII) and (XXIII), respectively. It appears, therefore, that

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*$Ir(CO)L_2HBr_2$ see ref. 15; $H[Ir(CO)_2Br_4]$ see ref. 16.

in neutral solution the action of a basic solvent or of CO favours the disproportionation, while in acid solution, in the presence of nucleophilic anions, the new anionic species $[Ir(CO)LX_4]^-$ is obtained.

With perchloric acid in ethanol a disproportionation takes place, which in a CO atmosphere takes the following course:

$$3\,Ir_2(CO)_6L_2 + 2\,HClO_4 \rightarrow \underset{(XXV)}{2[Ir(CO)_3L_2]ClO_4} + Ir_4(CO)_{10}L_2 + H_2 + 2\,CO$$

Under nitrogen the result is different, as follows:

$$3\,Ir_2(CO)_6L_2 + 2\,HClO_4 \rightarrow \underset{(XXVI)}{2[Ir(CO)_2L_2H_2]ClO_4} + Ir_4(CO)_{10}L_2 + 4\,CO$$

Both these perchlorates have been previously prepared by us [20], while the cluster was described by Caglio [8]. The reaction of I with halogens (X_2) at low temperature, followed by addition of alkaline ethanol has been previously described by us [21], and gives the dimeric alkoxycarbonyl derivatives:

$$Ir_2(CO)_6L_2 + X_2 + 2\,C_2H_5O^- \rightarrow [Ir_2(CO)_4L_2(COOC_2H_5)_2]^{2+} + 2\,X^-$$

This reaction shows that the first product must still be dimeric, probably $Ir_2(CO)_6L_2X_2$. With an excess of halogen, the compounds of the type $Ir(CO)LX_3$ are obtained as benzene adducts, namely XXVIII, XXX and XXXIII which, at 100° under vacuum lose the benzene molecules to give the unsolvated species XXIX, XXXI and XXXIV. These compounds are formulated as dimeric, with halogen bridges, in view of their low solubility and their coordinative unsaturation as monomers. This, in the case of the chloro-derivative, seems confirmed by the IR spectrum, which shows absorptions ascribable to terminal (324-347 cm^{-1}) and bridging chlorine (250 cm^{-1}). Furthermore, the bromo- and iodo-derivatives are soluble in DMF, giving adducts $Ir(CO)LX_3 \cdot DMF$ (XXXII, XXXV), which can be recrystallized from other solvents without losing the DMF. When the three $Ir(CO)LX_3$ compounds react with the corresponding hydrogen halides in THF, they give the acids $H[Ir(CO)LX_4]$, which are obtained in a pure state as the quaternary ammonium salts XXI, XXII, XXIII and XXIV. By the action of chlorine on I, at 0°, in a CO atmosphere, a mixture of $Ir(CO)_2LCl_3$, $Ir(CO)LCl_3$ [ν(CO) 2070 cm^{-1}] and $Ir(CO)LCl_4$ [ν(CO) 2140 cm^{-1}] was obtained, but could not be separated. This mixture on crystallization from ethanol gave the pure monocarbonyliridium(III) derivative XXIX. By carrying out the reaction between iodine and (I) at 0° under CO, $Ir(CO)_2LI_3$ (XXXVII) was obtained. The reaction under the same conditions with chlorine and bromine gave only unstable dicarbonyl compounds, in accordance with the greater stability of iodopolycarbonyl-compounds compared with that of the analogous bromo and chloro compounds.

Results are summarized in Table 1.

Experimental

I and II. Bis[tricarbonyl(triphenylphosphine)iridium] $[Ir(CO)_3PPh_3]_2$ *(I)*

$IrI(CO)_2(PPh_3)_2$ [4] (2 g) in benzene (35 ml) was stirred with 2 *N* NaOEt in EtOH (60 ml), under CO at room temperature for 5 h. The yellowish crystalline powder obtained (I) was washed with warm EtOH, H_2O, cold EtOH, and hexane, and then dried in vacuo. (0.55 g; 92%) m.p. 167-170° (uncorr.). From the mother liquor an equivalent amount of the known $IrH(CO)(PPh_3)_3$ [6] (II) was obtained.

III and IV. Bis[tricarbonyl(diphenyl-p-tolylphosphine)iridium], $[Ir(CO)_3PPh_2\text{-}CH_3C_6H_4]_2$ *(III)*

Prepared as I, from the appropriate phosphine, together with $IrH(CO)[PPh_2\text{-}(CH_3C_6H_4)]_3$ (IV).

V. Enneacarbonyltris(triphenylphosphine)tetrairidium—benzene [8], $Ir_4(CO)_9\text{-}(PPh_3)_3\cdot C_6H_6$

Compound I (0.2 g) in benzene (50 ml) was refluxed until the solution was clear (10—15 min); then most of the solvent was distilled off and V was precipitated by hexane. Yellow crystals, m.p. 170° (uncorr.; under vacuum). Mol. wt. (in benzene) 1950 (calcd. 1884).

VI. Enneacarbonyltris(diphenyl-p-tolylphosphine)tetrairidium, $Ir_4(CO)_9[PPh_2\text{-}(CH_3C_6H_4)]_3$.

Prepared as V from the appropriate phosphine. Mol. wt. (in benzene) 1880 (calcd. 1848).

VII. Sodium tricarbonyl(triphenylphosphine)iridate $Na[Ir(CO)_3PPh_3]$

Compound I (0.2 g) suspended in THF (12 ml) was treated with sodium amalgam (0.2% Na) under CO until the solution was clear. (The CO was prepared from formic acid and Ac_2O, to avoid the presence of hydrogen.) The yellowish-green solution of VII is rapidly hydrolysed by H_2O or EtOH, giving I.

VIII. Tris(1,8-phenanthroline)nickel(II) bis(tricarbonyl)(triphenylphosphine)-iridate $[Ni(phen)_3][Ir(CO)_3PPh_3]_2$

The solution of VII (0.2 g in 12 ml THF) was evaporated to 2 ml under vacuum, cooled to —10° and rapidly stirred under nitrogen with a solution of tris(1,8-phenanthroline)nickel dichloride (0.14 g) in 5 ml H_2O. The red crystalline powder was filtered and rapidly washed with chilled EtOH, THF, and hexane.

IX. Bis[tricarbonyl(triphenylphosphine)iridium] mercury, $Hg[Ir(CO)_3PPh_3]_2$

To the solution of VII (0.2 g in 12 ml), $Hg(CN)_2$ (0.05 g) was added with stirring under N_2. The white precipitate was washed with H_2O, EtOH, THF and hexane. The same compound was obtained from I (0.2 g) in THF (15 ml) with Hg at 40—50° under stirring for 3 days.

X. Tricarbonyl(triphenylphosphine)[(triphenylphosphine)aurio] iridium, $Ir(CO)_3\text{-}(PPh_3)AuPPh_3$

A solution of $AuPPh_3Cl$ in THF (1 ml) was added with stirring under N_2, to a solution of VII (0.2 g) in THF (12 ml). After 3 h, MeOH (25 ml) was added to precipitate X, as a white crystalline powder (0.222 g; 60%). Mol. wt. 980 (calcd. 998).

TABLE 1

No.	Compound	Empirical formula	Color	Analyses found (calcd.) (%)			ν(CO) (cm^{-1})	Other absorbtions (cm^{-1})
				C	H	Other		
I	$[Ir(CO)_3PPh_3]_2$	$[C_{21}H_{15}IrO_3P]_2$	Pale yellow	46.43 (46.80)	2.94 (2.78)	9.3 (O) (8.9)	1960vs	
II	$IrH(CO)(PPh_3)_3{}^a$	$C_{55}H_{46}ItOP_3$	Pale yellow	65.4 (65.6)	4.82 (4.57)		1920s	ν(IrH) 2120ms
III	$[Ir(CO)_3(PPh_2CH_3C_6H_4)]_2$	$[C_{22}H_{17}IrO_3P]_2$	Pale yellow	47.75 (47.8)	3.03 (3.08)		1970(sh) 1945s 1895(sh)	
IV	$IrH(CO)(PPh_2C_7H_7)_3$	$C_{58}H_{52}IrOP_3$	Yellow-green	65.9 (66.5)	4.90 (4.95)		1910s	ν(IrH) 2050(ms)
V	$Ir_4(CO)_9(PPh_3)_3\cdot C_6H_6{}^b$	$C_{69}H_{51}Ir_4O_9P_3$	Pale yellow	44.0 (43.6)	2.9 (2.71)		2042m 1985ms(sh) 1964s 1780ms	
VI	$Ir_4(CO)_9(PPh_2CH_3C_6H_4)_3\cdot C_6H_6$	$C_{72}H_{57}Ir_4O_9P_3$	Pale yellow	45.0 (44.5)	3.2 (2.98)		2020m 1970s 1945(sh) 1770ms	
VII	$[Ir(CO)_3PPh_3]^-Na^+$	$C_{21}H_{15}IrNaO_3P$	Pale green				1860s 1895s 1925vs	
VIII	$[Ni(phen)_3][Ir(CO)_3PPh_3]_2$	$C_{78}H_{54}Ir_2NiN_6O_6P_2$	Deep red	53.8 (55.8)	3.25 (3.22)	4.28 (N) (5.0)	1835s 1840s 1900m 1940mw 1960(sh)	
IX	$Hg[Ir(CO)_3PPh_3]_2{}^c$	$C_{42}H_{30}HgIr_2O_6P_2$	White	39.20 (39.4)	2.39 (2.35)		1915w 1945vs 1985m	
X	$[Ir(CO)_3PPh_3][AuPPh_3]^c$	$C_{39}H_{30}AuIrO_3P_2$	White	46.44 (46.88)	3.20 (3.01)		1930vs 1990w	
XI	$SnCl_2[Ir(CO)_3PPh_3]$	$C_{42}H_{30}Ir_2P_2SnCl_2$	Yellow	39.46 (39.8)	2.50 (2.38)	6.1(Cl) (5.65)	1970vs 2000w	
XII	$Ir(CO)_2H_3(PPh_3)^d$	$C_{20}H_{18}IrO_2P$	White cream	46.41 (46.7)	3.35 3.5	7.21(P) (6.24)	1970s 1980s	ν(IrH) 2080s 2100s
XIII	$Ir(CO)_2H(PPh_3)_2{}^e$	$C_{38}H_{31}IrO_2P_2$	White	58.70 (58.80)	3.97 (4.10)	4.0 (4.2)	1970s 1915s	ν(IrH) 2030s δ(IrH) 845ms
XIV	$[Ir(CO)Cl_2HPPh_3]_2$	$[C_{19}H_{16}IrOPCl_2]_2$	White	40.8 (41.0)	2.95 (2.8)	12.90(Cl) (12.75)	2060vs	ν(IrH) 2250w ν(IrClIr) 255—265m ν(IrCl) 350m
XV	$[IrBr_2(CO)HPPh_3]_2$	$[C_{19}H_{16}IrOPBr_2]_2$	White	35.2 (35.5)	2.54 (2.50)	24.5 (Br) (24.9)	2040s	ν(IrH) 2215w
XVI	$Ir(CO)Cl_2H(PPh_3)_2{}^f$	$C_{37}H_{31}IrOP_2Cl_2$	White	54.42 (54.3)	3.80 (3.80)		2020s	ν(IrH) 2230mw
XVII	$[IrBr_2(CO)HPPh_3]_2{}^f$	$C_{37}H_{31}IrOP_2Br_2$	White	49.3 (49.0)	3.52 (3.32)	17.2(Br) (17.7)	2000s	ν(IrH) 2200mw

XVIII	$Ir(CO)HI_2(PPh_3)_2$[g]	$C_{37}H_{31}IrOP_2I_2$	White	44.51 (44.44)	3.11 (3.10)	24.9(I) (25.4)	2040s	ν(IrH) 2180m
XIX	$[NEt_4][IrBr_4(CO)_2]$[h]	$C_{10}H_{20}IrO_2Br_4$	Orange	17.13 (17.20)	3.0 (2.9)	1.96(N) (2.0)	2060s 2110s	
XX	$[(PhCH_2)Me_3N][Ir(CO)_2I_4]$[i]	$C_{12}H_{16}IrO_2I_4$	Red	15.28 (15.9)	1.92 (1.76)	1.58(N) (1.55)	2050s 2100s	
XXI	$[(PhCH_2)Me_3N][Ir(CO)Cl_4PPh_3]$	$C_{29}H_{31}IrNOPCl_4$	Yellow	45.58 (45.0)	3.98 (4.0)	1.80(N) 18.4(Cl) (1.80) (18.4)	2010s	
XXII	$[NEt_4][Ir(CO)Cl_4PPh_3]$	$C_{27}H_{35}IrNOPCl_4$	Yellow	41.28 (41.5)	4.49 (4.65)	1.75(N) (1.85)	2050s	
XXIII	$[NEt_4][IrBr_4(CO)PPh_3]$	$C_{27}H_{35}IrNOPBr_4$	Yellow	34.84 (34.94)	3.74 (3.71)	1.51(N) (1.50)	2040s	
XXIV	$[NEt_4][Ir(CO)I_4PPh_3]$	$C_{27}H_{35}IrNOPI_4$	Red	28.8 (29.2)	3.7 (3.6)	1.10(N) 45.4(I) (1.26) (45.0)	2030s	
XXV	$[Ir(CO)_3(PPh_3)_2]ClO_4$[l]	$C_{39}H_{30}IrO_7P_2Cl$	White	52.1 (51.98)	3.31 (3.35)		2020s 1978(sh)	
XXVI	$[IrH_2(CO)_2(PPh_3)_2]ClO_4$[l]	$C_{38}H_{32}IrO_6P_2Cl$	White	52.5 (52.42)	3.85 (3.80)		2085s 2050s	ν(IrH) 2165m δ(IrH) 885m 820m
XXVII	$Ir_4(CO)_{10}(PPh_3)_2$[b]	$C_{46}H_{30}Ir_4O_{10}P_2$	Yellow	35.9 (35.1)	2.2 (1.91)		2060s 2030s 2000s 1830s 1790ms	
XXVIII	$[IrCl_3(CO)PPh_3]_2 \cdot 2\ C_6H_6$	$[C_{25}H_{21}IrOPCl_3]_2$	Pale yellow	44.2 (45.0)	2.92 (3.15)	16.2(Cl) (15.9)	2070s	ν(IrClIr) 250w ν(IrCl) 325–347m
XXIX	$[IrCl_3(CO)PPh_3]_2$	$[C_{19}H_{15}IrOPCl_3]_2$	Pale yellow	39.2 (38.8)	2.44 (2.54)	17.8(Cl) (18.0)	2070s	ν(IrClIr) 250m ν(IrCl) 324–347m
XXX	$[IrBr_3(CO)PPh_3]_2 \cdot 2\ C_6H_6$	$[C_{25}H_{21}IrOPBr_3]_2$	Pale yellow	36.93 (37.4)	2.53 (2.68)		2050s	
XXXI	$[IrBr_3(CO)PPh_3]_2$	$[C_{19}H_{15}IrOPBr_3]_2$	Pale yellow	31.8 (31.5)	1.94 (2.08)	2.68(O) 33.10(Br) (2.21) (33.2)	2050s	
XXXII	$IrBr_3(CO)PPh_3 \cdot HCONMe_2$	$C_{22}H_{22}IrNO_2PBr_3$	Yellow	32.85 (32.4)	2.79 (2.75)	4.21(O) 1.68(N) (4.02) 1.76	2040s 1645s	
XXXIII	$[Ir(CO)I_3PPh_3]_2 \cdot 2\ C_6H_6$	$[C_{25}H_{21}IrOPI_3]_2$	Red	32.23 (31.9)	2.31 (2.25)		2040s	
XXXIV	$[Ir(CO)I_3PPh_3]_2$	$C_{19}H_{15}IrOPI_3$	Red	26.83 (26.4)	1.79 (1.74)	2.26(O) 44.0(I) (1.85) (44.1)	2040s	
XXXV	$IrCOI_3PPh_3 \cdot HCONMe_2$	$C_{22}H_{22}IrNO_2PI_3$	Red	28.16 (28.1)	2.35 (2.35)	1.51(N) 1.50	2040s 1640s	
XXXVI	$[Ir(CO)I_3(PPh_2CH_3C_6H_4)]_2$	$[C_{20}H_{17}IrOPI_3]_2$	Red	27.26 (27.8)	2.08 (1.98)		2050s	
XXXVII	$Ir(CO)_2I_3PPh_3$	$C_{20}H_{15}IrO_2PI_3$	Garnet red	27.16 (27.0)	1.63 (1.68)	3.59(O) 42.6(I) (3.59) (42.6)	2130s 2085s	

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[a] Ref. 6. [b] Ref. 8. [c] Ref. 10. [d] Ref. 12. [e] Ref. 14. [f] Ref. 15. [g] Ref. 17. [h] Ref. 16. [i] Ref. 18. [l] Ref. 20.

XI. Dichlorobis[tricarbonyl(triphenylphosphine)iridio] tin, $SnCl_2\ [Ir(CO)_3(PPh_3)]_2$

A solution of $SnCl_2$ (0.05 g) in THF (5 ml) was added to a suspension of (I) (0.25 g) in THF (12 ml) under CO. After stirring for 20 min, the yellow clear solution was treated with hexane (30 ml) to give XI as a yellow crystalline powder (0.163 g; 85%) m.p. (dec.) 283—286°. Mol. wt. (in $CHCl_3$) 1240 (calcd. 1265).

XII. Dicarbonyltrihydrido(triphenylphosphine)iridium, $Ir(CO)_2H_3(PPh_3)$

As previously reported [12], on bubbling H_2 through a suspension of I (0.1 g) in THF (10 ml), the solution of the monohydride $IrH(CO)_3PPh_3$, which almost immediately forms, is converted in 4 h into a solution which, on IR and NMR evidence, was considered a mixture of the two isomeric forms of XII. From this solution with hexane (20 ml) a compound was obtained analyzing as XII, but with a IR spectrum different from that of the solution.

XIII. Dicarbonylhydridobis(triphenylphosphine)iridium, $Ir(CO)_2H(PPh_3)_2$ [14]

From I (0.1 g) in EtOH suspension (40 ml), by refluxing with $NaBH_4$ (0.035 g) under CO and evaporating the solution to 10 ml, the known hydride XIII was obtained, m.p. 136°. On addition of Et_4NCl the mother liquor gave a salt of a cluster anion which could not be characterized.

XIV. Bis[carbonyldichlorohydrido(triphenylphosphine)iridium] $[Ir(CO)Cl_2(H)(PPh_3)]_2$

Bubbling HCl through a suspension of I (0.25 g) in benzene (25 ml) at room temperature for a few minutes gave a white crystalline precipitate of XIV, which was insoluble in all solvents (0.168 g; 65%), m.p. 224—230°.

XV. Bis[dibromocarbonylhydrido(triphenylphosphine)iridium] $[IrBr_2(CO)H(PPh_3)]_2$

Bubbling through a suspension of I (0.200 g) in benzene (15 ml), initially HBr for a few minutes and then N_2 (to remove the excess of HBr) gave a white crystalline precipitate of XV, insoluble in all solvents (0.143 g; 60%).

XVI. Carbonyldichlorohydridobis(triphenylphosphine)iridium, $Ir(CO)Cl_2H(PPh_3)_2$

This was obtained from I (0.2 g) in THF (10 ml), by action of HCl. From the yellow solution, after some minutes, was formed a white crystalline precipitate, almost insoluble in all solvents (0.120 g; 80%), m.p. (in vacuo) 249—252°.

XVII. Dibromocarbonylhydridobis(triphenylphosphine)iridium, $IrBr_2(CO)H(PPh_3)_2$

As XVI, from I (0.250 g) but with HBr. The compound (0.176 g; 80%), m.p. 247—249°, was recrystallized from CH_2Cl_2 by addition of EtOH.

XVIII. Carbonylhydridodiiodobis(triphenylphosphine)iridium, $Ir(CO)HI_2(PPh_3)_2$

From a suspension of I (0.300 g) in EtOH (60 ml) and 55% hydroiodic acid (1 ml), by refluxing under CO. White crystals (0.220 g; 76%), m.p. 155°.

XIX. Tetraethylammonium tetrabromodicarbonyliridate [NEt$_4$] [IrBr$_4$(CO)$_2$]

The mother liquor of XVII was evaporated to dryness, dissolved in EtOH (5 ml), treated with NEt$_4$Br and left overnight. Well-formed shiny crystals were obtained (0.117 g; 72%).

XX. Benzyltrimethylammonium dicarbonyltetraiodoiridate [Me$_3$(PhCH$_2$)N]-[Ir(CO)$_2$I$_4$]

The mother liquor of XVIII was evaporated to dryness, the residue dissolved in EtOH and precipitated with [Me$_3$(PhCH$_2$)N]I. Red crystals (0.150 g; 60%).

XXI. Benzyltrimethylammonium carbonyltetrachloro(triphenylphosphine)iridate [Me$_3$(PhCH$_2$)N] [Ir(CO)Cl$_4$(PPh$_3$)]

(a). From XIV (0.100 g) in THF (10 ml) and an excess of HCl at room temperature followed by addition of [Me$_3$(PhCH$_2$)N]Cl. Yellow crystals (0.188 g; 85%), m.p. 267—270°.

(b). From XXIX (0.150 g) in THF (15 ml) saturated with HCl at room temperature by addition of [Me$_3$(PhCH$_2$)N]Cl and dilution with MeOH (0.163 g; 82%).

XXII. Tetraethylammonium carbonyltetrachloro(triphenylphosphine)iridate [NEt$_4$][Ir(CO)Cl$_4$(PPh$_3$)]

As for XXI but using NEt$_4$Cl.

XXIII. Tetraethylammonium tetrabromocarbonyl(triphenylphosphine)iridate [NEt$_4$] [IrBr$_4$(CO)(PPh$_3$)]

(a). From XV (0.1 g) in boiling THF with HBr for a few minutes and subsequent addition of Et$_4$NBr. Recrystallized from CH$_2$Cl$_2$ and hexane (0.114 g; 78%) m.p. 259—261°.

(b). From XXXI (0.1 g) in THF (10 ml) with HBr and Et$_4$NBr as above (0.103 g; 80%).

XXIV. Tetraethylammonium carbonyltetraiodo(triphenylphosphine)iridate, [NEt$_4$] [Ir(CO)I$_4$(PPh$_3$)]

From XXXIV (0.15 g) in THF (10 ml) with 55% HI (0.4 g) in EtOH (5 ml) after refluxing for 1 h, on addition of Et$_4$NI (0.2 g). Red crystals (0.127 g; 50%).

XXV. Tricarbonylbis(triphenylphosphine)iridium perchlorate, [Ir(CO)$_3$(PPh$_3$)$_2$]-[ClO$_4$]

By refluxing I (0.1 g) in EtOH (35 ml) with HClO$_4$ 70% (0.5 g) under CO for 2 h. The white crystals which separated on cooling were washed with benzene (0.05 g; 60%).

XXVI. Dicarbonyldihydridobis(triphenylphosphine)iridium perchlorate [IrH$_2$(CO)$_2$(PPh$_3$)$_2$] [ClO$_4$]

As for the above compound but under N$_2$.

XXVII. Decacarbonylbis(triphenylphosphine)tetrairidium Ir$_4$(CO)$_{10}$(PPh$_3$)$_2$

From the mother liquor of XXV and XXVI, after evaporation to 5 ml. Recrystallized from MeOH. Yellow crystals.

XXVIII. Bis[carbonyltrichloro(triphenylphosphine)iridium] bisbenzene, $[IrCl_3(CO)(PPh_3)]_2 \cdot 2\ C_6H_6$

By refluxing I (0.2 g) in benzene (20 ml) with a solution of Cl_2 (40 mg) in CCl_4 (10 ml). The yellow crystals which separated (0.18 g; 73%) lost the molecul of C_6H_6 on recrystallization from EtOH, to give XXIX. m.p. 320°.

XXX. Bis(tribromocarbonyl(triphenylphosphine)iridium] bis(benzene), $[IrBr_3(CO)(PPh_3)]_2 \cdot 2\ C_6H_6$

By refluxing I (0.2 g) in benzene (20 ml) with Br_2 (0.045 g) in CCl_4 (10 ml). The yellowish solvated compound which precipitated looses the benzene molecule on heating at 100° in vacuo for 3 h to give the non solvated compound XXXI, m.p. $> 320°$ (0.19 g; 73%).

XXXII. Tribromocarbonyl(triphenylphosphine)iridium dimethylformamide, $IrBr_3(CO)PPh_3 \cdot HCONMe_2$

From XXXI (0.25 g) dissolved in DMF (10 ml) by addition of EtOH (30 ml). Red crystals, m.p. 280—285° (0.225 g; 81%).

XXXIII. Bis[carbonyltriiodo(triphenylphosphine)iridium] bisbenzene, $[Ir(CO)I_3PPh_3]_2 \cdot 2\ C_6H_6$

On refluxing for 3 h I (0.2 g) in benzene (35 ml) with I_2 (0.2 g). The red solvate which separated (0.128 g; 40%) was recrystallized from CH_2Cl_2 or $CHCl_3$ to give the non solvated compound XXXIV. M.p. 277° (dec.) (0.128 g; yield 40%)

XXXV. Carbonyltriiodo(triphenylphosphine)iridium dimethylformamide, $Ir(CO)I_3PPh_3 \cdot HCONMe_2$

From XXXIII by recrystallization from DMF and EtOH.

XXXVI. Bis[carbonyl(diphenyl-p-tolylphosphine)triiodoiridium] $[Ir(CO)I_3PPh_2(CH_3C_6H_4)]_2$

As for the preparation of XXXIII, but from III. Soluble in $CHCl_3$ and CH_2Cl_2 Mol. wt. (in $CHCl_3$) 1730 (calcd. 1754).

XXXVII. Dicarbonyltriiodo(triphenylphosphine)iridium, $Ir(CO)_2I_3(PPh_3)$

Iodine (0.28 g) was added with stirring under CO at room temperature to a suspension of I (0.3 g) in benzene (30 ml). After 1 h the clear solution was treated with hexane to precipitate garnet red crystals (0.3 g; 60%), m.p. 285° (dec.); soluble in CH_2Cl_2 and C_6H_6.

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