1288. *New Triphenylphosphine–Iridium Compounds*

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The preparation and properties of the unsaturated hydride $IrH_3(PPh_3)_2$ and of the carbonyl hydrides $IrHCO(PPh_3)_2$ and $IrH_3CO(PPh_3)_2$ are reported. From these, with perchloric acid, $IrH_2CO(PPh_3)_2ClO_4$ has been obtained, which by action of carbon monoxide gives $Ir(CO)_3(PPh_3)_2ClO_4$. This perchlorate with alkaline methanol forms the novel organometallic methoxycarbonyl compound $Ir(CO_2Me)(CO)_2(PPh_3)_2$. Tentative structures, deduced from infrared spectra and electric moments in solutions, are assigned to these compounds and to some of their derivatives.

The complex iridium hydrides so far described are of the types IrH_3L_3 with L = PPh_3 [1] or PEt_2Ph [2] and $IrH(CO)L_3$ with L = PPh_3.[3] Continuing our work on complex iridium compounds with triphenylphosphine as ligand, we now report on an unsaturated hydride IrH_3L_2 and two carbonyl hydrides: $IrHCOL_2$ and IrH_3COL_2; also the perchlorate of two complex cations, which can be considered substitution products of $[Ir(CO)_5]^+$, as well as a novel organometallic derivative $Ir(CO_2Me)(CO)_2L_2$.

The Unsaturated Hydride IrH_3L_2.—By reduction of $IrHI_2L_2$ and $[IrI_2L_2]I_3$ with sodium hydroborate or lithium tetrahydroaluminate, we obtained a stable compound (I), almost

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[1] M. Angoletta, *Gazzetta*, 1962, **92**, 811.
[2] J. Chatt, unpublished work.
[3] C. S. Bath and L. Vaska, *J. Amer. Chem. Soc.*, 1963, **85**, 3500.

insoluble in all solvents, which had a ratio Ir : L of 1 : 2. It did not contain either iodine or oxygen and, from the infrared (i.r.) spectrum, appeared to be a hydride. In fact it showed a very strong and wide band at 1945 cm.$^{-1}$, assigned to the Ir–H stretching and a strong band at 884 cm.$^{-1}$ assigned to the bending of the same bond. These assignments were proved by preparing the corresponding deuteride with lithium deuteroaluminate: the stretching band shifted to 1360 cm.$^{-1}$ and the bending band beyond 600 cm.$^{-1}$.

The elemental analysis of these types of compound indicates their stoicheiometry except for the number of hydrogen atoms: the direct oxygen determination is essential in order to exclude the presence of any carbon monoxide ligand, as the latter, though not being present as such in the starting materials, can sometimes be found in the products.[4] The analytical data for compound (I) corresponded to IrH_xL_2: the value of x was taken as 3 from the following reactions:

$$IrH_3L_2\ (I) + HClO_4 = [IrH_2L_2]ClO_4\ (II) + H_2$$
$$[IrH_2L_2]ClO_4 + NaI = IrH_2IL_2 + NaClO_4$$
$$IrH_2IL_2 + L = IrH_2IL_3$$
$$[IrH_2L_2]ClO_4 + 2L = [IrH_2L_4]ClO_4$$
$$IrH_3L_2 + L = IrH_3L_3$$

In the first of these reactions the hydride (I) evolved exactly 1 mol. hydrogen forming the salt-like perchlorate (II), which showed in its infrared spectrum two bands assigned to the symmetric and asymmetric stretching of two hydrogen atoms. The perchlorate (II) reacted very easily with all nucleophilic ligands; with iodide ions it gave the iodohydridebis(triphenylphosphine)iridium and with excess of L the known saturated $[IrH_2L_4]^+$ cation.[5] Besides, compound (I) reacted in cold benzene solution with L, giving the well-known IrH_3L_3,[1] and with an excess of pyridine (Py) giving IrH_3L_2Py, m. p. 134°, which showed two very strong Ir–H stretching band at 1700 and 2120 cm.$^{-1}$. These bands are very similar to the bands of the *trans*-form of IrH_3L_3;[1] the shift to lower wavenumbers being caused by the increase of negative charge on the metal, owing to the replacement of a phosphine by a pyridine. We suggest therefore for this compound an octahedral structure with two hydride ligands in the *trans*-position. Since this compound is dissociated in benzene solution unless an excess of pyridine is present, this structure must be considered the most stable in the solid state. The i.r. spectrum of the hydride (I) itself is consistent with a D_{3h} point group symmetry, which indicates a trigonal bipyramidal structure with the three hydrogen atoms on the equatorial plane and the phosphines at the apices. Unfortunately, we could not confirm this structure by the dipole moment on account of the very low solubility of this compound.

The Carbonyl Hydrides $IrHCOL_2$ *and* IrH_3COL_2.—The hydride (I) reacted with carbon monoxide in benzene suspension at 40—50°, giving a soluble compound, m. p. 132°, which corresponded analytically to a carbonyl hydride of the stoicheiometry IrH_xCOL_2 (III). When we tried to prepare the same compound by reduction of Vaska and Di Luzio's $IrClCOL_2$[6] with sodium borohydride, we obtained a carbonyl hydride (IV), m. p. 145°, not distinguishable analytically from (III), but physically very different, particularly in the infrared spectrum. Moreover, in the reduction of $IrHI_2COL_2$, obtained by reaction of triphenylphosphine with K_2IrCOI_5,[7] we prepared a third carbonyl hydride (IVa), m. p. 135°, still with the same apparent stoicheiometry of (III), but again with a different i.r. spectrum. This compound (IVa) however changed very rapidly in (IV) in benzene solution and we considered it an unstable isomer of (IV).

The carbonyl hydrides (III) and (IV), on the contrary, differed from one another in their hydrogen content, and corresponded to $IrHCOL_2$ (III) and IrH_3COL_2 (IV), respectively.

[4] L. Vaska, *J. Amer. Chem. Soc.*, 1964, **86**, 1943.
[5] M. Angoletta and A. Araneo, *Gazzetta*, 1963, **93**, 1343.
[6] L. Vaska and G. W. Di Luzio, *J. Amer. Chem. Soc.*, 1962, **84**, 679.
[7] L. Malatesta, L. Naldini, and F. Cariati, *J.*, 1964, 961.

This could be proved by the following reactions, which also confirmed the suggested formulae:

$$\mathrm{IrHCOL_2 + L = IrHCOL_3}$$
$$\mathrm{IrH_3COL_2 + L = IrHCOL_3 + H_2}$$
$$\mathrm{IrHCOL_2 + HClO_4 = [IrH_2COL_2]ClO_4}$$
$$\mathrm{IrH_3COL_2 + HClO_4 = [IrH_2COL_2]ClO_4 + H_2}$$

The carbonyl hydride $\mathrm{IrHCOL_3}$, which was obtained in the first and second reaction, had been described by Bath and Vaska, who had observed it in the reaction of $\mathrm{IrClCOL_2}$ with hydrazine.[3] A more evident series of reactions by which we could obtain the same carbonyl hydride was the following:

$$\mathrm{IrH_3L_3 + HClO_4 = [IrH_2L_3]ClO_4 + H_2}$$
$$\mathrm{[IrH_2L_3]ClO_4 + CO = [IrH_2COL_3]ClO_4}$$
$$\mathrm{[IrH_2COL_3]ClO_4 + KOH = IrHCOL_3 + KClO_4 + H_2O}$$

More practicably, both $\mathrm{IrHCOL_2}$ and $\mathrm{IrHCOL_3}$ could be prepared in high yield by bubbling carbon monoxide in the alkaline ethanolic suspension of 1 mol. iridium tetraiodide and of 2 or 3 mol. of triphenylphosphine, respectively.

We obtained the carbonyl hydride $\mathrm{IrHCOL_3}$ in two crystalline forms having different melting points and i.r. spectra. We do not know whether the two forms are polymorphic or isomeric; though the rather large difference in the position of the infrared band seems to favour the latter hypothesis. We determined the electric moment of $\mathrm{IrHCOL_3}$, which is known to have a trigonal bipyramidal structure with the three phosphines on the equatorial plane,[3] to check the value of the partial Ir–H moment, taken as 2D in our calculation on the other carbonyl hydrides. The found figure, 2·4D, was in accordance with this value, the distortion of the bipyramid (angles of 94° 8′ instead of 90°) being taken into account.

The transformation of (IV) into (III) could be brought about indirectly by action of alkali on the perchlorate (V), obtained from the carbonyl trihydride (IV):

$$\mathrm{[IrH_2COL_2]^{+}ClO_4 + KOH = IrHCOL_2 + KClO_4 + H_2O}$$

The direct transformation of (III) into (IV) could also be carried out and proved to be reversible: in fact the carbonyl monohydride (III) gave the carbonyl trihydride (IV) on bubbling hydrogen at ordinary pressure through its benzene solution, while the reverse reaction took place on bubbling nitrogen through the benzene solution of (IV):

$$\mathrm{IrHCOL_2} \underset{-\mathrm{H_2}}{\overset{+\mathrm{H_2}}{\rightleftharpoons}} \mathrm{IrH_3COL_2}$$

The behaviour of $\mathrm{IrHCOL_2}$ is therefore the same as that of Vaska's $\mathrm{IrClCOL_2}$; this is a further argument for the anionoid character of the hydride anion in these compounds.

The features of the infrared spectrum of compounds (III), (IV), and (IVa), and the value of the electric moment of compounds (III) and (IV), let us draw some conclusions on their structure. The monohydride carbonyl (III), which had two bands at 2000 and 1950 cm.$^{-1}$ and an electric moment of 4·5D, appeared to be *cis*-square planar. The trihydride carbonyl (IV) having an electric moment of 4·3D, very close to that of (III), was also considered as having the two phosphines in *cis*-positions. The i.r. spectrum of (IV) showed three strong bands at 2080 (IrH), 1965 (CO), 1785 (IrH), which were assigned by comparison with the corresponding deuteride (IrD: 1510 and 1278 cm.$^{-1}$; CO: 1960 cm.$^{-1}$). For reasons discussed elsewhere,[1] we consider the IrH band at low wavenumber (1700—1800 cm.$^{-1}$) characteristic for the polyhydride complexes having two hydrogen atoms in the *trans*-position, so that we propose for the hydride (IV) the H-*trans*, L-*cis*-structure.

We consider therefore that the *trans*-form of the trihydrotris(triphenylphosphine)-iridium previously reported,[1] the trihydrobis(triphenylphosphine)pyridineiridium described above, and the trihydride carbonyl (IV) have structures with the hydrogen atoms in the same positions. The IrH stretching of the three compounds varies from one to another, in correspondence to the different charge on the metal brought about by the replacement of the phosphine by ligands with less or more π acceptor nature (pyridine and carbon monoxide, respectively).

The electric moment of the trihydride (IVa) could not be measured exactly, because of its instability in benzene solution. An approximate measure showed that (IVa) must have about the same moment as (IV). The i.r. spectrum (2118, 2080, and 1960 cm.$^{-1}$) excluded the *trans*-position for the hydride groups and therefore indicated a structure with the three hydride groups at the corners of the same face of the octahedron. If so, the other groups must lie on the corners of the opposite face, in agreement with the electric moment.

The perchlorate (IV), obtained from both carbonyl hydrides (III) and (IV), behaved in acetone as an uni-univalent electrolyte and showed in the i.r. spectrum three strong stretching bands at 2165, 2085, 2050 cm.$^{-1}$. It is noteworthy that on passing from the carbonyl hydrides (III) and (IV) to the perchlorate (V), the IrH and CO stretching bands shifted to the higher wavenumbers. This means an increase for the Ir–H bond strength, but a decrease for the Ir–C bond strength, since the order of the latter is considered complementary to the order of the C–O bond. The decrease of the order of the carbon-to-metal bond with increasing positive charge on the metal is well known in carbonyl compounds: the strengthening of the Ir–H bond with increasing charge wholly justifies the assumption that in this type of compounds the hydrogen atoms are anionic.

The Perchlorates $[Ir(CO)_3L_2]ClO_4$ *and* $[Ir(CO)_2L_3]ClO_4$.—The perchlorate (V) underwent a very interesting reaction when carbon monoxide was bubbled through its benzene solution under ordinary conditions, giving the perchlorate $[Ir(CO)_3L_2]ClO_4$ (VI), the cation of which can be considered the substitution product of the hypothetical $[Ir(CO)_5]^+$:

$$[IrH_2COL_2]ClO_4 + 2CO = [Ir(CO)_3L_2]ClO_4 \text{ (VI)} + H_2$$

The formula of (VI) was deduced from the elemental analysis and the following gas-volumetric reactions:

$$[Ir(CO)_3L_2]^+ + LiCl = IrCl(CO)L_2 + 2CO + Li^+$$
$$[Ir(CO)_3L_2]^+ + NaI = IrI(CO)_2L_2 + CO + Na^+$$
$$[Ir(CO)_3L_2]^+ + L = [Ir(CO)_2L_3]^+ \text{ (VII)} + CO$$

The absence from (VI) of any hydridic hydrogen, the i.r. spectral stretching band of which could have been covered by the very wide CO band, has been proved by the fact that the evolved carbon monoxide does not contain hydrogen (gas chromatography) and that the products of these reactions are not hydrides.

The perchlorates (VI) and (VII) have a very similar i.r. spectrum, with a very strong unique band at 2020 and 2030 cm.$^{-1}$, respectively. This spectrum is consistent with a D_{3h} point group symmetry, and seems to indicate a trigonal bipyramidal structure, having, in the equatorial plane, the three carbon monoxide molecules in (VI), and the three phosphines in (VII). Analogous symmetric structures were suggested by us for the trihydride (I), and by others for the disubstitution products of $Fe(CO)_5$ with substituted phosphines and isocyanides,[8] for the cation $[Co(CO)_3L_2]^+$,[9] which is isosteric with the cation of (V), and for the monomeric paramagnetic form of $Re(CO)_3L_2$.[10] Since the trigonal structure cannot easily form position isomers, on account of the so-called pseudorotation of the ligands,[11] the isolated forms should represent the most stable structure. It is worth observing that on purely electrostatic grounds, these symmetric structures appear to be the most stable. In fact, since the phosphine and isocyanide ligands carry a larger charge than the carbon monoxide and hydride ligands, they should occupy the farthest

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[8] F. A. Cotton and R. V. Parish, *J.*, 1960, 1440.
[9] O. Vohler, *Chem. Ber.*, 1958, **91**, 1235.
[10] M. Freni, *J. Inorg. Nuclear Chem.*, 1965, **27**, 755.
[11] M. Berry, *J. Chem. Phys.*, 1960, **32**, 933.

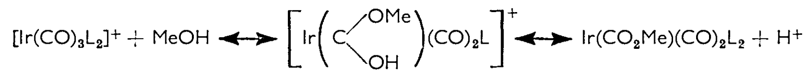
positions, that is the apical positions (angle 180°) when there are two of them, and lie in the equatorial plane (angle 120°) when there are three.

The CO stretching band of the perchlorate (VI) is at lower wavenumber than that of (VII), while the replacement of a carbon monoxide with a phosphine ligand usually brings about a shift in the opposite direction. This behaviour can however be explained, if the structures of these compounds are considered. In the trigonal bipyramidal structures derived from transition metals, having bonds with some π character, the apical bonds are usually longer than the equatorial,[12] and consequently weaker. Besides, the hypothesis can be suggested that the two apical bonds are under the influence of some type of *trans*-effect.

The Alkoxycarbonyl Compound $Ir(CO_2Me)(CO)_2L_2$.—The reaction of the perchlorate (V) with alkaline methanol solution was wholly unexpected, giving a stable soluble crystalline substance (VIII), m. p. 124°, the analytical composition and molecular weight of which corresponded to $Ir(CO)_3L_2(OMe)$. The nuclear magnetic resonance (n.m.r.) spectrum of this substance did not show any band which could be assigned to hydridic hydrogen, and clearly showed the protons of an O–Me group. This compound, however, is not considered by us to be the methoxy-derivative of the original cation, but the dicarbonylmethoxycarbonylbis(triphenylphosphine)iridium, $Ir(CO_2Me)(CO)_2L_2$, that is, a true organometallic compound with an iridium-to-carbon σ-bond.

The reasons for this choice were: (1) The compound is monomeric and cannot have bridging CO; (2) In the i.r. spectrum there are two bands at 1980—1940 cm.$^{-1}$, assigned to the stretching of terminal CO, a band at 1050 cm.$^{-1}$ assigned to –OMe, and a band at 1655 cm.$^{-1}$, which, in the absence of any CO bridge, can only be assigned to a carboxylic carbonyl group; (3) In the suggested structure the metal presents the same effective atomic number as radon; the methoxy-derivative should have two more electrons; (4) The reaction of the perchlorate (V) with methanol (also with ethanol or propanol) takes place at a very low alkalinity, for instance in the presence of very dilute ammonia, when the $[MeO]^-$ concentration can only be exceedingly low.

This reaction, on the other hand, can be understood as a shift towards the right of an equilibrium of the type:



$$[Ir(CO)_3L_2]^+ + MeOH \rightleftarrows \left[Ir\left(C{\begin{smallmatrix}OMe\\OH\end{smallmatrix}}\right)(CO)_2L\right]^+ \rightleftarrows Ir(CO_2Me)(CO)_2L_2 + H^+$$

The main objection could be that a carboxylic ester is not expected to form and be stable in alkaline solution, but one must consider that the electronic density on the carboxyl group of (VIII) must be higher than in usual organic substances, and that consequently the chemical behaviour must be different.

The reaction of (VIII) with dilute acids is also peculiar in that, if no co-ordinating anions are present, the cation of (VI) is immediately re-obtained:

$$Ir^{I}CO_2Me(CO)_2L_2 + H^+ = [Ir(CO)_3L_2]^+ + MeOH$$

In the presence of nucleophilic anions the cation reacts further, as expected:

$$Ir(CO_2Me)(CO)_2L_2 + HCl = IrClCOL_2 + 2CO + MeOH$$
$$Ir(CO_2Me)(CO)_2L_2 + HI = IrI(CO)_2L_2 + CO + MeOH$$

The electric moment of the ester (VIII) is 6·4D. If we admit the trigonal bipyramidal structure, this moment indicates that the two phosphines cannot be at the apices, while the presence of two strong CO stretching bands in the i.r. spectrum seem to eliminate the structure with the CO groups at the apices. The moments of the remaining structures, *a*, *b*, *c* can be calculated as (*a*) 4·1D, (*b*) 6·0D, (*c*) 6·7D, the partial moments being taken as

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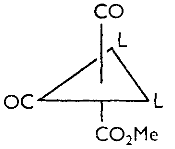
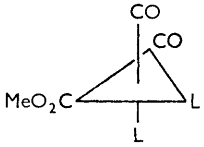
[12] R. G. Gillespie, *J.*, 1963, 4679.

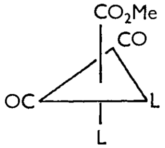
L, 4·2D;[13] CO_2R, 1·1D;[14] CO, 0·5D; the angles are assumed to have theoretical values. The third of these structures seems therefore the most probable.



(a)



(b)



(c)

An alkoxycarbonyl compound of manganese(I) has recently been described[15] and though its reaction with acid does not proceed in such a reversible way, it is strictly analogous to our iridium compound (VII) and confirms the general stability of this type of organometallic derivatives.

EXPERIMENTAL

Formulae, microanalyses, and melting points of new compounds are in Table 1. The significant infrared absorption bands, taken on the Perkin-Elmer spectrometer model 237, are in Table 2. The electric moments, calculated from the dielectric constants of the dilute benzene solution, determined on the W.T.W. dipolmeter model D.M. 01, by the formula of Halverstaht and Kumler,[16] are in Table 3. Molecular weights were determined on the Mechrolab vapour pressure osmometer model 301A.

TABLE 1

		Found (%)					Required (%)				
	Compound	C	H			Formula	C	H			M. p.
(1)	$IrHI_2L_2$	44·2	3·3	I	26·1	$C_{36}H_{31}IrI_2P_2$	44·44	3·19	I	25·97	220°
(2)	$[IrI_2L_2]I_3$	31·9	2·2	I	46·9	$C_{36}H_{30}IrI_5P_2$	31·95	2·23	I	46·96	168
(3)	IrH_3L_2	59·2	4·8	Ir	26·5	$C_{36}H_{33}IrP_2$	59·91	4·62	Ir	26·69	127
(4)	IrD_3L_2	59·3	4·5			$C_{36}H_{30}D_3IrP_2$	59·67	4·97			127
(5)	IrH_3L_2Py	61·4	4·9	N	1·8	$C_{41}H_{38}IrNP_2$	61·50	4·78	N	1·75	134
(6)	$[IrH_2L_2]ClO_4$	52·8	3·9	Cl	4·3	$C_{36}H_{32}ClIrO_4P_2$	52·75	3·93	Cl	4·32	152
(7)	IrH_2IL_2	50·7	4·0	I	15·0	$C_{36}H_{32}IrIP_2$	51·06	3·81	I	15·00	167
(8)	$IrHCOL_2$	59·1	4·2	O	2·1	$C_{37}H_{31}IrOP_2$	59·44	4·18	O	2·14	132
(9)	$[IrH_2COL_2]ClO_4$	52·4	3·7	Cl	4·2	$C_{37}H_{32}ClIrO_5P_2$	52·42	3·80	Cl	4·18	103
(10)	$IrHI_2COL_2$	44·6	3·1	I	24·2	$C_{37}H_{31}IrIOP_2$	44·44	3·10	I	25·38	155
(11)	IrH_3COL_2 *	59·00	4·5	O	4·0	$C_{37}H_{33}IrOP_2$	59·30	4·41	O	4·27	135
	IrH_3COL_2 †	58·9	4·6	O	4·1	$C_{37}H_{33}IrOP_2$	59·30	4·41	O	4·27	145
	IrD_3COL_2	59·2	4·5			$C_{37}H_{30}D_3IrOP_2$	59·00	4·82			
(12)	$IrHCOL_3$ *	65·3	4·7	O	3·0	$C_{55}H_{46}IrOP_3$	65·47	4·59	O	3·17	145
	$IrHCOL_3$ †	65·7	4·9	O	2·9	$C_{55}H_{46}IrOP_3$	65·47	4·59	O	3·17	161
	$IrDCOL_3$	65·8	4·8			$C_{55}H_{45}DIrOP_3$	65·40	4·69			
(13)	$[IrH_2COL_3]ClO_4$	59·3	4·2	Cl	3·2	$C_{55}H_{37}ClIrO_5P_3$	59·56	3·36	Cl	3·19	137
	$[IrH_2COL_3]ClO_4$	59·5	4·1	Cl	3·2	$C_{55}H_{37}ClIrO_5P_3$	59·56	3·36	Cl	3·19	210
(14)	$[Ir(CO)_3L_2]ClO_4$	52·0	3·5	Cl	3·8	$C_{39}H_{30}ClIrO_7P_2$	51·98	3·35	Cl	3·93	203
(15)	$[Ir(CO)_2L_3]ClO_4$	59·4	3·9	Cl	3·3	$C_{56}H_{45}ClIrO_6P_3$	59·26	3·99	Cl	3·99	183
(16)	$IrI(CO)_2L_2$	52·0	3·8	I	14·6	$C_{38}H_{30}IrIO_2P_2$	50·71	3·36	I	14·10	155
(17)	$Ir(CO)_2L_2CO_2Me$	57·2	4·2	O	7·1	$C_{40}H_{33}IrO_4P_2$	57·67	3·99	O	7·68	124

* Low m. p. † High m. p.

Hydrodi-iodobis(triphenylphosphine)iridium $IrHI_2L_2$.—A benzene solution of iodine (0·518 g.; 4 equiv.) was added to a benzene solution (60 ml.) of IrH_3L_3 (1 g.). The yellow compound which separated was recrystallised from chloroform by careful addition of ethanol. The same compound could also be obtained from $IrHCl_2L_3$ [3] dissolved in acetone, with an excess of sodium iodide.

Di-iodobis(triphenylphosphine)iridium Tri-iodide $[IrI_2L_2]I_3$.—A benzene solution (50 ml.) of iodine (0·905 g.; 7 equiv.) was added to an ethanol suspension (50 ml.) of IrH_3L_3 (1 g.).

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[13] W. Strohmeier, *Angew. Chem. Internat. Edn.*, 1964, **11**, 730.

[14] T. Truck and M. Naack, *Chem. Ber.*, 1964, **97**, 1693.

[15] W. Strohmeier and H. Hellmann, *Ber.*, 1964, **68**, 481.

[16] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.

After a few minutes' boiling and dilution with ethanol, brown crystals were obtained, the molar conductance of which, in $1{\cdot}2 \times 10^{-3}$M-nitrobenzene at 20°, was $\Lambda = 16$ ohm^{-1} cm.$^{-1}$.

TABLE 2

Compound	ν(Ir–H) and ν(CO)	δ(Ir–H)
(1) $IrHI_2L_2$	2270	—
(2) $[IrI_2L_2]I_3$	—	—
(3) IrH_3L_2	1945	878
(4) IrD_3L_2	1360	<600
(5) IrH_3L_2Py	2120—1700	834—820
(6) $[IrH_2L_2]ClO_4$	2315—2280	878—855
(7) IrH_2IL_2	2220	
(8) $IrHCOL_2$	2040—1980—1920	842
	2000—1950 *	830
(9) $[IrH_2COL_2]ClO_4$	2165—2085—2050	885—820
(10) $IrHI_2COL_2$	2180—2040	842
(11) IrH_3COL_2	2118—2080—1960 †	850—840—820—800
	2080—1955—1780 *	830
	2080—1965—1785 †	845—802
IrD_3COL_2	1960—1510—1278	
(12) $IrHCOL_3$	2120—1920 †	840
	2070—1930 *	785
	2090—1935 ‡	780
$IrDCOL_3$	1943	<600
(13) $[IrH_2COL_3]ClO_4$	2155—2118—2011 †	850—838—823
	2185—2118—2011 ‡	845—820
(14) $[Ir(CO)_3L_2]ClO_4$	2020 (1978 sh)	
(15) $[Ir(CO)_2L_3]ClO_4$	2030 (1975 sh)	
(16) $IrI(CO)_2L_2$	1990—1930	
(17) $Ir(CO)_2L_2CO_2Me$	1980—1940—(1965—1050)	

* Benzene solution. † Low m. p. ‡ High m. p.

TABLE 3

Compound	$10^3\omega$	$\Delta\varepsilon/\omega$	$-\Delta\nu/\omega$	
$IrHCOL_2$	10·8	3·61	—	$_{T}P = 607$
	11·8	3·22	—	$_{E}P = 175$ †
	—	—	0·56 *	$_{O}P = 432$
				$\mu = 4{\cdot}5$D
IrH_3COL_2	7·2	3·19	—	$_{T}P = 551$
	8·9	2·8	—	$_{E}P = 177$ †
	8·9	3·03	—	$_{O}P = 374$
	—	—	0·56 *	$\mu = 4{\cdot}3$D
$IrHCOL_3$	9·3	0·967	—	$_{T}P = 386$
	17·11	0·935	—	$_{E}P = 261$ †
	32·8	0·914	—	$_{O}P = 125$
	48	0·979	—	$\mu = 2{\cdot}4$D
	20·9	—	0·4406	
	28·54	—	0·4522	
	57·2	—	0·4527	
$IrI(CO)_2L_2$	10·18	1·866	—	$_{T}P = 483$
	19·5	2	—	$_{E}P = 179$ †
	24·2	2·04	—	$_{O}P = 304$
	11·1	—	0·5765	$\mu = 3{\cdot}8$D
	11·5	—	0·5565	
	17·3	—	0·5722	
$IrCO_2Me(CO)_2L_2$	4·59	5·43	—	$_{T}P = 1039$
	12·3	5·93	—	$_{E}P = 191$ †
	9·8	—	0·6020	$_{O}P = 848$
	18·5	—	0·524	$\mu = 6{\cdot}4$D

* Calculated from M.R. † Estimated value.

Trihydrobis(triphenylphosphine)iridium IrH_3L_2.—This compound was first obtained from the reduction of both compounds described above, in ethanol suspension with an excess of sodium hydroborate. More convenient preparation methods were the following:

(*a*) An aqueous solution (30 ml.) of sodium hexachloroiridate(IV), obtained by dissolving the reaction product of iridium powder (3 g.) sodium chloride, and chlorine at 500°, was slowly dropped into an ethanol solution (800 ml.) containing triphenylphosphine (8·15 g.; 2 mol.) and an excess

(10 g.) of sodium iodide at 70°. The yellow precipitate, a mixture of $IrHI_2L_2$ and IrH_2IL_2 with very little IrH_2IL_3, became crystalline in about 1 hr. It was washed with hot water, with ethanol and dried (10·2 g.): then it was reduced in ethanol (250 ml.) with sodium hydroborate (1·1 g.) until the suspension was cream-white. The crude product was washed with hot methanol, then with water and again with methanol. The whitish residue (6·8 g.), a mixture of insoluble IrH_3L_2 with some soluble IrH_3L_3, was purified by suspending it in hot benzene (300 ml.) and filtering off the solution. The final yield was 5·91 g. corresponding to 53% on Ir.

(*b*) An aqueous solution containing iridium(III) in soluble form was obtained by reduction of potassium hexabromoiridate(IV) (5 g.), suspended in hydrobromic acid (2%; 200 ml.), with formaldehyde at 80°. This solution, concentrated to about 50 ml., was dropped into a warm (80°) solution of triphenylphosphine (7 g., 4 mol.) in ethoxyethanol and kept on the water-bath for about 2 hr. The brown precipitate which formed was dissolved in dichloromethane and crystallised (6·7 g.) on addition of ethanol; it was identical with $IrHBr_2L_3$.[5] A solution of bromine (0·128 g.; 3·2 equiv.) in carbon tetrachloride (100 ml.) was added to the solution of this compound (5·7 g.), in dichloromethane (200 ml.). The solvent was then evaporated *in vacuo* almost to dryness and ethanol (200 ml.) was added. The yellow crystalline compound which precipitated (4·2 g.), corresponding roughly to $IrBr_{3.2}L_2$ was reduced as such in ethanol suspension (200 ml.) by slow addition of sodium hydroborate (*ca.* 0·7 g.) at ordinary temperature.

Trideuterobis(triphenylphosphine)iridium IrD_3L_2.—$[IrI_2L_2)I_3$ (0·5 g.) in tetrahydrofuran (20 ml.) was treated with lithium tetradeuteroaluminate (0·1 g.) and refluxed for *ca.* 10 min. A few drops of deuterium oxide were introduced in the cold solution, which was then poured into 50 ml. aqueous 15% potassium hydroxide. The precipitate was filtered off, washed with potassium hydroxide solution, then with ethanol, benzene, and hexane.

Trihydrobis(triphenylphosphine)pyridineiridium $IrH_3L_2(C_5H_5N)$.—IrH_3L_2 (0·5 g.) was dissolved in pyridine (5 ml.) at 60° (*ca.* 10 min.). The excess of pyridine was partially removed *in vacuo* and the product precipitated by careful addition of methanol (20 ml.). On dissolving in benzene it partially dissociated, giving some insoluble IrH_3L_2.

Dihydrobis(triphenylphosphine)iridium Perchlorate $[IrH_2L_2]ClO_4$.—IrH_3L_2 (0·5 g.) was stirred with a solution of perchloric acid (1 g.) in 70 ml. of ethanol. The reaction was complete when all the hydride had dissolved (*ca.* 1 hr.). On evaporating *in vacuo* a white crystalline solid was obtained (0·4 g.). Its molar conductance Λ ($1·5 \times 10^{-3}$M in nitrobenzene) at 25° was 23·2 ohm^{-1} $cm.^{-1}$. The same reaction, carried out gas-volumetrically, on 0·061 g. IrH_3L_2, gave 1·87 ml. of hydrogen (S.T.P.) (Calc. 1·9 ml.). The benzene solution of the perchlorate (0·3 g. in 20 ml.) on addition of triphenylphosphine (0·2 g.) gave the known $[IrH_2L_4]ClO_4$,[5] insoluble in benzene (0·35 g.).

Dihydrioiodobis(triphenylphosphine)iridium IrH_2IL_2.—An ethanol solution of the above perchlorate on addition of sodium iodide gave quantitatively the product, which was recrystallised from benzene–hexane. On addition of triphenylphosphine (0·2 g.) to a solution of IrH_2IL_2 (0·2 g.) in dichloromethane (10 ml.), the known IrH_2IL_3 [5] formed, which was precipitated from the solution with hexane.

Hydrocarbonylbis(triphenylphosphine)iridium $IrHCOL_2$.—(*a*) *From* IrH_3L_2. Carbon monoxide was bubbled through a suspension of IrH_3L_2 (1 g.) in benzene (40 ml.) at 40—50° for 1 hr. The almost clear solution was filtered, evaporated to 5 ml., and precipitated by ethanol. The product, redissolved in benzene, was obtained on addition of hexane as pale yellow needles (0·7 g.).

(*b*) *From* $[IrH_2COL_2]ClO_4$ *and alkali.* The perchlorate, described below (0·3 g.), was dissolved in warm ethanol (30 ml.) and treated with ethanolic 0·1N-potassium hydroxide (3·6 ml.). On cooling, yellow needles (0·1 g.) separated, which from the analyses, i.r. spectrum, and mixed m. p. appeared to be identical to the compound prepared as in (*a*).

(*c*) *From* $IrHCOL_3$ *with carbon monoxide at high pressure.* $IrHCOL_3$ (1·9 g.), prepared as indicated below, were suspended in a few ml. of ethanol and treated for 15 hr. at 70° with carbon monoxide at 200 atm. The solid product (1·2 g.) was filtered off and washed with hexane; it crystallised from benzene on addition of hexane.

(*d*) *From* IrH_3COL_2. The carbonyl trihydride (0·2 g.) (see below) was dissolved in benzene (50 ml.) and a slow current of pure nitrogen was bubbled though the cold solution for 4 hr. On evaporation and addition of ethanol the compound separated.

(*e*) *From iridium tetraiodide.* Carbon monoxide was bubbled for 2 hr. through a suspension of iridium tetraiodide (4·3 g.) in a solution of triphenylphosphine (1·63 g.) and potassium hydroxide

(4 g.) in ethanol (100 ml.). The mass was then dried *in vacuo* and the residue extracted with benzene (2 × 50 ml.). The filtered extracts, evaporated to 10 ml., on addition of methanol gave the pure compound (1·2 g.; yield, based on phosphine, 50%). The relative amount of triphenylphosphine in this preparation was kept very low to avoid the formation of $IrHCOL_3$ [see below].

Reaction of $IrHCOL_2$ *with triphenylphosphine.* The carbonyl monohydride $IrHCOL_2$ (0·5 g.) was dissolved in warm benzene (10 ml.), some triphenylphosphine (0·2 g.) was added, and the solution refluxed for 5 min. On addition of 30 ml. of hexane the yellow $IrHCOL_3$ (0·3 g.) was obtained. No evolution of any gas was observed in this reaction.

Dihydrocarbonylbis(triphenylphosphine)iridium Perchlorate $[IrH_2COL_2]ClO_4$.—(*a*) *From* $IrHCOL_2$. The carbonyl monohydride (0·5 g.) in ethanol (50 ml.) reacted smoothly at 60° with a 1% ethanolic solution of perchloric acid (20 ml.) without evolution of gas. By careful addition of water, the perchlorate $[IrH_2COL_2]ClO_4$ was obtained; Λ (1·4 × 10^{-3}M in acetone) at 30° = 1·33 ohm^{-1} cm.$^{-1}$. No evolution of gas was observed.

(*b*) *From* IrH_3COL_2 [*see* (10)]. The carbonyl trihydride gave exactly the same reaction as the carbonyl monohydride but with evolution of pure hydrogen: 0·052 g. gave 1·48 ml. of hydrogen (S.T.P.) (Calc., 1·55 ml.).

Hydrodi-iodocarbonylbis(triphenylphosphine)iridium $IrHI_2COL_2$.—Dipotassium pentaiodocarbonyliridate(III) [7] (6·7 g.) in ethanol (120 ml.) were refluxed with triphenylphosphine (4·1 g.) for 20 min. Yellow $IrHI_2COL_2$ (2·8 g.) separated and was crystallised from tetrahydrofuran by careful addition of ethanol. The same compound could be obtained from the reaction of $IrHCOL_3$ (2 g.), in benzene (50 ml.), with iodine (1·36 g.). The precipitate, a by product which did not contain CO, was discarded; from the mother-liquor, on evaporation and addition of ethanol, $IrHI_2COL_2$ (0·8 g.) was obtained.

Trihydrocarbonylbis(triphenylphosphine)iridium IrH_3COL_2 *and the Corresponding Deuteride.*—(*a*) *From* $IrClCOL_2$.[6] $IrClCOL_2$ (0·5 g), in tetrahydrofuran (30 ml.), was refluxed with lithium hydroaluminate until the yellow solution discoloured. The unchanged hydroaluminate was decomposed with a few drops of ethanol: the cold solution was evaporated to dryness under vacuum, then the residue was extracted with cold benzene (25 ml.) and precipitated with hexane (50 ml.) as white needles, very soluble in benzene, dichloromethane, tetrahydrofuran, and very slightly soluble in ethanol: they had m. p. 145° (high-melting form).

By the same method, but using lithium tetradeuteroaluminate as reducing agent and heavy water to decompose the excess of the latter, we prepared the corresponding trideuterocarbonylbis(triphenylphosphine)iridium IrD_3COL_3.

(*b*) *From* $IrHI_2COL_2$. A 2% ethanol solution (25 ml.) of sodium hydroborate was slowly added to a boiling benzene solution (100 ml.) of $IrHI_2COL_2$ (2·5 g.) [see above]. After 1 hr. the low-melting form (m. p. 132°) of the carbonyl trihydride was precipitated (1·12 g.) by addition of ethanol (200 ml.). On crystallisation from benzene–hexane, the high-melting form (m. p. 142°) was obtained.

(*c*) *From* $IrHCOL_2$ *with sodium hydroborate.* A few drops of an ethanol solution of sodium hydroborate were added to the carbonyl monohydride (0·2 g.) in benzene. On evaporating the solution, a white compound was obtained, which, on crystallisation from ethanol, gave the pure high-melting form of the compound.

(*d*) *From* $IrHCOL_2$ *with molecular hydrogen.* The hydrogenation could be brought about by bubbling pure hydrogen at ordinary conditions in the solution of $IrHCOL_2$ (0·11 g.) in ethanol at 50° for *ca.* 2 hr. On cooling the pure carbonyl trihydride separated (0·04 g.; high-melting form).

Reaction of $IrHCOL_2$ *with triphenylphosphine.* The carbonyl trihydride (0·5 g.) reacted smoothly in benzene (30 ml.) with triphenylphosphine (0·3 g.) giving a yellow solution from which, by evaporation and addition of hexane, $IrHCOL_3$ was obtained (0·5 g.). In this reaction 13·4 ml. of pure hydrogen (S.T.P.) were produced (Calc. 15·0 ml.).

Monohydrocarbonyltris(triphenylphosphine)iridium $IrHCOL_3$.—This could be prepared from $IrHCOL_2$ and IrH_3COL_2 as described above, as well as by bubbling carbon monoxide through a solution of $[IrH_2L_3]ClO_4$ [1] in ethanol for about 1 hr. and then by treating the solution, which contained $[IrH_2COL_3]ClO_4$, with alkali. This compound (0·2 g.) formed also when $[ir(CO)_2L_3]ClO_4$ (0·5 g.) in methanol was refluxed with potassium hydroxide (0·1 g.) or when $[Ir(CO)_2L_3]ClO_4$ (0·5 g.) in tetrahydrofuran was reduced with lithium hydroaluminate. We used this reaction to prepare the corresponding deutero-derivative by using lithium deuteroaluminate. More convenient ways for the preparation were the following:

(*a*) A warm ethanol solution (150 ml.) of triphenylphosphine (7·1 g.) was added to an ethanol solution (300 ml.) of potassium tetraiodocarbonyliridate(III) (5·4 g.) at 70°. A brown suspension formed, which was reduced with a 1% ethanol solution of sodium hydroborate, until it turned yellow and $IrHCOL_3$ was precipitated (5 g.). This, crystallised from benzene–ethanol, gave the high-melting form (m. p. 161°); and from chloroform–hexane, the low-melting form (m. p. 145°).

(*b*) Iridium tetraiodide (2·6 g.) was suspended in an ethanol solution (200 ml.) containing triphenylphosphine (3 g.) and potassium hydroxide (4 g.). Carbon monoxide was bubbled through the solution at 60° for 2 hr. The yellow precipitate was dissolved in hot benzene and re-precipitated with ethanol [2·0 g.; corresponding to a 70% yield on iridium(IV) iodide].

Dihydrocarbonyltris(triphenylphosphine)iridium Perchlorate $[IrH_2COL_3]ClO_4$.—(*a*) *Low melting form.* A 5% ethanol solution of perchloric acid was slowly added to the suspension of $IrHCOL_3$ (2·6 g.) in cold ethanol (40 ml.) until the solution was acid to Congo Red. On careful addition of water the perchlorate, m. p. 137°, crystallised (2 g.); Λ (10^{-3}M in acetone) at 30° = 130 ohm^{-1} cm.$^{-1}$.

(*b*) *High-melting form.* The same reaction carried out at 80° gave the form melting at 210—212°. This could also be obtained both by recrystallisation of the low-melting form from hot dilute ethanol and by warming it above its m. p.; Λ (10^{-3}M in acetone) at 30° = 132 ohm^{-1} cm.$^{-1}$.

Tricarbonylbis(triphenylphosphine)iridium Perchlorate $[Ir(CO)_3L_2]ClO_4$.—Carbon monoxide was bubbled through a solution (50 ml.) of $[IrH_2COL_2]ClO_4$ (1 g.) at 75° for 2 hr. On cooling under carbon monoxide, a white precipitate was obtained, soluble in dichloromethane, ethanol, and acetone. Λ (10^{-3}M in acetone) at 30° = 125 ohm^{-1} cm.$^{-1}$; Λ ($1·35 \times 10^{-3}$M in benzene) at 25° = 29·4 ohm^{-1} cm.$^{-1}$. The same compound (0·8 g.) was obtained when the "ester" $Ir(CO_2Me)(CO)_2L_2$ (1 g.) in methanol (15 ml.) was acidified with dilute perchloric acid.

Dicarbonyltris(triphenylphosphine)iridium Perchlorate $[Ir(CO)_2L_3]ClO_4$.—The above perchlorate (0·6 g.), in cold methanol, reacted with an excess (0·3 g.) of triphenylphosphine giving carbon monoxide (14·85 ml.) (S.T.P.) (Calc. for the displacement of 1 CO, 14·95 ml.). From the solution, $[Ir(CO)_2L_3]ClO_4$ (0·16 g.) was obtained, soluble in ethanol, dichloromethane, and acetone; Λ ($2·6 \times 10^{-3}$M in nitrobenzene) at 25° = 26·8 ohm^{-1} cm.$^{-1}$.

Iodocarbonylbis(triphenylphosphine)iridium $IrI(CO)_2L_2$.—0·8 g. of $[Ir(CO)_3L_2]ClO_4$ suspended in 5 ml. of methanol were treated with an excess (0·2 g.) of sodium iodide in the cold. 19·12 ml. gas at S.T.P. were briskly evolved (Calc. for the displacement of 1 CO, 19·90 ml.) while the product precipitated as orange-brown needles (0·7 g.). $[Ir(CO)_2L_3]ClO_4$ with sodium iodide gave the same product with no evolution of any gas.

Dicarbonylmethoxycarbonylbis(triphenylphosphine)iridium $IrCOMe(CO)_2L_2$.—(*a*) The perchlorate $[Ir(CO)_3L_2]ClO_4$ (1·2 g.) was suspended in cold methanol (30 ml.) and methanolic potassium hydroxide was added until the solution was alkaline to phenolphthalein. A clear yellowish solution was obtained from which white crystals (0·82 g.), soluble in benzene and dichloromethane, separated. The n.m.r. spectrum obtained on a Varian instrument at 60 Mc./sec. in deuteropyridine, showed a band at $-7·34$ p.p.m., assigned to the protons of the phenyl groups, and a band at $-2·93$ p.p.m. assigned to the protons of the methoxy-group (internal reference, tetramethylsilane). The ratio of the areas was $12 \pm 0·5$ (calc. 12). No absorptions appeared which could be assigned to hydridic hydrogen atoms. The same reaction carried out in ethanol and propanol gave the corresponding dicarbonylethoxycarbonylbis(triphenylphosphine)iridium and dicarbonylisopropoxycarbonylbis(triphenylphosphine)iridium. The same results were obtained by using dilute ammonia instead of potassium hydroxide.

(*b*) When carbon monoxide was bubbled for 15 min. through a cold suspension of $IrI(CO)_2L_2$ in (0·6 g.) methanol (20 ml.), containing potassium hydroxide (0·5 g.), a crystalline product (0·63 g.) was obtained. An analogous reaction was observed in the same conditions as above from $IrClCOL_2$ (0·4 g.) which gave, in about 20 min., product (0·3 g.), and from $[Ir(CO)_2L_3]ClO_4$ (0·5 g.) 0·33 g. of product was obtained.

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