The Chemistry of Carbonyl(phenylethynyl)bis(triphenylphosphine)iridium(I)

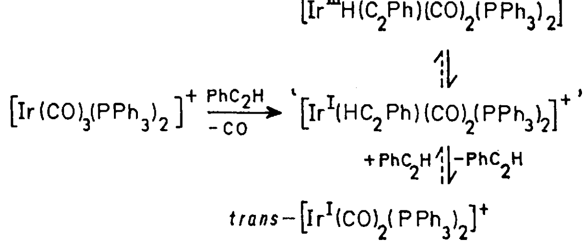
By **Robert H. Walter** and **Brian F. G. Johnson**,* University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The title complex has been prepared by a slightly modified route *via* its carbonyl adduct, and the formation of an intermediate species ' $[Ir(HC_2Ph)(CO)_2(PPh_3)_2]^+$ ' is suggested. The complex $[Ir(C_2Ph)(CO)(PPh_3)_2]$ readily undergoes addition reactions in solution with a wide variety of reagents; in some cases attack is observed only at the metal atom [SO_2, $HgCl_2$, H_2, O_2, CF_3CO_2H, $MeCO_2H$, $C_2(CO_2Me)_2$, MeI, or $C_2(CN)_4$] and in others both at the metal and at the acetylene linkage (HCl, HBr, HI, Cl_2, Br_2, or I_2).

THE white crystalline complex $[Ir(CO)_3(PPh_3)_2][PF_6]$ was prepared by the method described[1] for the preparation of $[Ir(CO)_3(PPh_3)_2][BPh_4]$, using $[NH_4][PF_6]$ in place of $Na[BPh_4]$. Church *et al.*[1] also reported that the complexes $[Ir(CO)_3L_2][BPh_4]$ were stable to loss of carbon monoxide except where $L = P(C_6H_{11})_3$ or PPr^i_3. In these two cases, passage of nitrogen causes the initially colourless chloroform solutions to become orange, and then a deep red on refluxing. The products were characterised as *trans*-$[Ir(CO)_2L_2][BPh_4]$ by analysis and the existence of only one carbonyl band in the i.r. spectrum at *ca.* 2 000 cm^{-1}. In contrast to the corresponding tetraphenylborate salt, $[Ir(CO)_3(PPh_3)_2][PF_6]$ has been observed by us to be moderately unstable to CO loss; its solution becomes yellow on removal of solvent *in vacuo* at room temperature to leave a yellow-orange solid. The i.r. absorption of this solid was found at 1 993 cm^{-1} and is assigned to *trans*-$[Ir(CO)_2(PPh_3)_2][PF_6]$. The mixture could readily be reconverted into pure $[Ir(CO)_3(PPh_3)_2][PF_6]$ by passage of carbon monoxide at room temperature, but, since it was intended to substitute a carbonyl group in an ensuing reaction with phenylacetylene, this step was not necessary.

The reaction of phenylacetylene with $[Ir(CO)_3(PEt_3)_2][BPh_4]$ has been shown[2] to give $[IrH(C_2Ph)(CO)_2(PEt_3)_2][BPh_4]$. However, in the case of $[Ir(CO)_3(PPh_3)_2][PF_6]$, an equilibrium is set up between $[IrH(C_2Ph)(CO)_2(PPh_3)_2][PF_6]$ and *trans*-$[Ir(CO)_2(PPh_3)_2][PF_6]$ as shown by i.r. spectroscopy. The set of bands assigned to the former hydride (comparable to those of Stefanini's complex, see Table 1) decrease in intensity with time after PhC_2H has been added to a solution of $[Ir(CO)_3(PPh_3)_2][PF_6]$ in dichloromethane. Simultaneously, the band at 1 993 cm^{-1}, belonging to *trans*-$[Ir(CO)_2(PPh_3)_2][PF_6]$, increases in intensity with time and the change is accompanied by a gradual darkening of the solution from yellow to orange and eventually (on warming) to red. It is possible to shift this equilibrium partially to the left by the addition of excess of phenylacetylene. Although no i.r. evidence exists for a transition state, it is proposed that the reaction might pass through a short-lived π-bonded iridium(I) intermediate as shown in Scheme 1.

The i.r. bands at 2 164 and 2 146 cm^{-1} for $[IrH(C_2Ph)(CO)_2(PEt_3)_2][BPh_4]$ were attributed[2] to ν(Ir–H) and ν(C≡C) but no specific assignment was made. The corresponding bands for $[IrH(C_2Ph)(CO)_2(PPh_3)_2][PF_6]$ at 2 175 and 2 152 cm^{-1} were assigned to ν(Ir–H) and ν(C≡C) respectively from a deuteriation experiment with CF_3CO_2D in which the band at 2 175 cm^{-1} disappeared, although the Ir–D stretch, expected in the 1 550 cm^{-1} region, was not unambiguously detected. A similar assignment is suggested for $[IrH(C_2Ph)(CO)_2(PEt_3)_2][BPh_4]$. It should be noted that the observation of higher ν(CO) bands in the PPh_3 complex (compared with the PEt_3 analogue) is in accordance with expectation, PPh_3 being the less basic of the two tertiary phosphine ligands.



SCHEME 1

If a mixture of phenylacetylene and triethylamine (both in excess) is added to a solution of $[Ir(CO)_3(PPh_3)_2][PF_6]$ in the minimum volume of acetone the hydrido-species is deprotonated and the equilibrium is thus shifted completely to the right (see Scheme 1). A very pale yellow complex rapidly precipitates and can be separated by filtration and purified by washing with a small volume of cold hexane. Infrared and microanalytical data (Tables 1 and 2 respectively) characterise the material as dicarbonyl(phenylethynyl)bis(triphenylphosphine)iridium, $[Ir(C_2Ph)(CO)_2(PPh_3)_2]$, which is obtained in 100% yield.

As might be anticipated from the behaviour of the analogous carbonyl adduct[3] $[IrCl(CO)_2(PPh_3)_2]$ of Vaska's compound, the complex $[Ir(C_2Ph)(CO)_2(PPh_3)_2]$ loses carbon monoxide very readily. It is stable if stored under an atmosphere of carbon monoxide, but prolonged storage (*ca.* 4 weeks) *in vacuo* leads to a darkening in colour and the production of the known parent four-co-ordinate complex $[Ir(C_2Ph)(CO)(PPh_3)_2]$[4,5] which

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[1] M. J. Church, M. J. Mays, R. N. F. Simpson, and F. P. Stefanini, *J. Chem. Soc.* (*A*), 1970, 2909.

[2] F. P. Stefanini, Ph.D. Thesis, University of Cambridge, 1971.

[3] L. Vaska and S. S. Bath, *J. Amer. Chem. Soc.*, 1966, **88**, 1333.

[4] C. A. Reed and W. R. Roper, *J.C.S. Dalton*, 1973, 1370.

[5] C. K. Brown, D. Georgiou, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 3120.

TABLE 1

Infrared data (cm^{-1})

Complex	$\nu(C\equiv C)$	$\nu(CO)$	ν(other)	Medium	Colour
$[Ir(CO)_3(PPh_3)_2][PF_6]$		2 081w, 2 018s, 2 010s		$CHCl_3$	White
$[Ir(CO)_3(PPh_3)_2][BPh_4]$ [1]		2 074w, 2 018s, 2 010s		$CHCl_3$	White
trans-$[Ir(CO)_2\{P(C_6H_{11})_3\}_2][BPh_4]$ [1]		1 990s		$CHCl_3$	Red
trans-$[Ir(CO)_2(PPh_3)_2][PF_6]$ [a]		1 993s		Nujol	
$[IrH(C_2Ph)(CO)_2(PEt_3)_2][BPh_4]$ [2]	2 146m(sh)	2 093s, 2 061s	2 164m (Ir–H)	$CHCl_3$	White
$[IrH(C_2Ph)(CO)_2(PPh_3)_2][PF_6]$ [a]	2 152m(sh)	2 118s, 2 082s	2 175m (Ir–H)	Nujol	
$[Ir(CO)_2(PPh_3)_2\{C_2(CO_2Me)_2\}][BPh_4]$ [1]	1 814m	2 091s, 2 049s	1 708m (C=O)	Nujol	White
$[Ir(CO)_2(PPh_3)_2\{C_2(CO_2Me)_2\}][PF_6]$	1 823m	2 099s, 2 050s	1 707m (C=O)	Nujol	White
$[Ir(C_2Ph)(CO)_2(PPh_3)_2]$	2 127m	2 030s, 1 961s		Nujol	Pale yellow
$[Ir(C_2Ph)(CO)(PPh_3)_2]$ [4]	2 115m	1 955vs		Nujol	Orange
$[Ir(C_2Ph)(O_2)(CO)(PPh_3)_2]$ [4]	2 125m	1 990vs	835s (O=O)	Nujol	Yellow
$[Ir(C_2Ph)(CO)(PPh_3)_2(SO_2)]$	2 151vw,br. [b]	2 023s [b]	$\left.\begin{matrix}1\,196s\\1\,181s\end{matrix}\right\}\nu_3(SO_2)$ 1 050s $\nu_1(SO_2)$ 569m $\nu_2(SO_2)$	KBr	Lime green
$[Ir(C_2Ph)(SO_4)(CO)(PPh_3)_2]$	2 147m	2 045s	$\left.\begin{matrix}1\,305s\\1\,180\text{—}1\,170s\end{matrix}\right\}\nu_3(SO_4)$ $\left.\begin{matrix}895s\\880s\end{matrix}\right\}\nu_1(SO_4)$ 675s $\nu_4(SO_4)$	KBr	Cream
$[IrCl(HgCl)(C_2Ph)(CO)(PPh_3)_2]$	2 123w,br.	2 045s		CH_2Cl_2	Yellow
$[Ir(C_2Ph)(O_2CCF_3)_2(CO)(PPh_3)_2]$	2 133w,br.	2 054s	1 690s,br. (C=O)	KBr	Pale yellow
$[Ir(O_2CMe)_2(C_2Ph)(CO)(PPh_3)_2]$	2 138w	2 050s	1 710s,br. (C=O)	Nujol	Pale yellow
$[Ir(C_2Ph)(CO)(PPh_3)_2\{C_2(CO_2Me)_2\}]$	2 113m (C_2Ph) 1 745m (ester)	1 988s	1 680m (C=O)	Nujol	Pale yellow
$[IrCl(Me)(C_2Ph)(CO)(PPh_3)_2]$	2 132m	2 010s		$CHCl_3$	Pale yellow
$[IrBr(Me)(C_2Ph)(CO)(PPh_3)_2]$	[c]	2 046s		Nujol	Pale yellow
$[IrI(Me)(C_2Ph)(CO)(PPh_3)_2]$	2 120vw	2 041s		Nujol	Pale yellow
$[Ir(C_2Ph)(CO)(PPh_3)_2\{C_2(CN)_4\}]$	[c]	2 060s	2 225m ($C\equiv N$)	Nujol	White
$[IrH(Cl)(C_2Ph)(CO)(PPh_3)_2]$ [a]	2 130vw,br. [d]	2 030w(sh)	2 226w,vbr. (Ir–H) [d]	Nujol	White
$[IrH(Cl)(CH_2CCl_2Ph)(CO)(PPh_3)_2]$ [a]		2 044s	2 226w,vbr. (Ir–H) [d]	Nujol	White
$[IrH(Cl)(CCl_2CH_2Ph)(CO)(PPh_3)_2]$ [a]		2 050s	2 226w,vbr (Ir–H) [d]	Nujol	White
$[IrH(Br)(CH{=}CBrPh)(CO)(PPh_3)_2]$ [a]		2 046s	2 223vw,br. (Ir–H) [d] 1 665w,br. (C=C) [e]	Nujol	
$[IrH(Br)(CBr{=}CHPh)(CO)(PPh_3)_2]$ [a]		2 071s	2 223vw,br. (Ir–H) [d] 1 665w,br. (C=C) [e]	Nujol	
$[IrCl_2(CCl{=}CClPh)(CO)(PPh_3)_2]$		2 051s	1 680vw (C=C)	KBr	Pale yellow
$[IrBr_2(C_2Ph)(CO)(PPh_3)_2]$ [a]	2 137w	2 080m(sh)		Nujol	
$[IrBr_2(CBr{=}CBrPh)(CO)(PPh_3)_2]$ [a]		2 071s		Nujol	
$[IrBr_2(CBr_2CBr_2Ph)(CO)(PPh_3)_2]$ [a]		2 047s		Nujol	
$[IrI_2(C_2Ph)(CO)(PPh_3)_2]$	2 125w	2 060s		KBr	Dark orange
$[Ir(C_2Ph)(CO)(PPh_3)_2]$ [f,g]	2 108m	1 969s		CH_2Cl_2	Yellow
$[Ir(C_2Ph)(NO)(PPh_3)_2][PF_6]$ [f]	2 120m		1 865s (NO)	MeCN	Maroon

[a] Not isolated in a pure state. [b] In CH_2Cl_2 solution. [c] Not discernible. [d] In $CHCl_3$ solution. [e] In KBr disc. [f] Not isolated as a solid. [g] In the presence of excess of PPh_3.

TABLE 2

Microanalytical data (%)

	Found				Calc.			
Complex	C	H	P	Other	C	H	P	Other
$[Ir(CO)_3(PPh_3)_2][PF_6]$	49.5	3.3	10.0		49.5	3.2	9.8	
$[Ir(CO)_2(PPh_3)_2\{C_2(CO_2Me)_2\}][PF_6]$	49.7	3.3	8.8		49.9	3.4	8.8	
$[Ir(C_2Ph)(CO)_2(PPh_3)_2]$	63.2	4.1	7.3		63.2	4.0	7.1	
$[Ir(C_2Ph)(CO)(PPh_3)_2(SO_2)]$	59.6	3.8	6.7	[a]	59.4	3.9	6.8	3.5 (S)
$[Ir(C_2Ph)(SO_4)(CO)(PPh_3)_2]$	57.2	3.7	6.9	3.7 (S)	57.4	3.7	6.6	3.4 (S)
$[IrCl(HgCl)(C_2Ph)(CO)(PPh_3)_2]$ [b]			4.7	5.9 (Cl)	48.4	3.2	5.5	6.3 (Cl)
$[IrH_2(C_2Ph)(CO)(PPh_3)_2]$	63.4	4.2	7.6		63.7	4.4	7.3	
$[IrD_2(C_2Ph)(CO)(PPh_3)_2]$	63.7	4.4	7.3		63.6	4.6 (H + D)	7.3	
$[Ir(C_2Ph)(O_2CCF_3)_2(CO)(PPh_3)_2]$	54.7	3.5	5.8		54.9	3.3	5.8	
$[Ir(O_2CMe)_2(C_2Ph)(CO)(PPh_3)_2]$	61.3	4.5	6.2		61.1	4.3	6.4	
$[Ir(C_2Ph)(CO)(PPh_3)_2\{C_2(CO_2Me)_2\}]$	62.1	4.3	6.8		62.0	4.2	6.3	
$[IrCl(Me)(C_2Ph)(CO)(PPh_3)_2]$	61.8	4.4	6.7	3.7 (Cl)	61.6	4.3	6.9	3.9 (Cl)
$[IrBr(Me)(C_2Ph)(CO)(PPh_3)_2]$	58.4	4.0	6.1	9.0 (Br)	58.7	4.1	6.6	8.5 (Br)
$[IrI(Me)(C_2Ph)(CO)(PPh_3)_2]$	55.8	4.0	5.8	13.2 (I)	55.9	3.9	6.3	12.8 (I)
$[Ir(C_2Ph)(CO)(PPh_3)_2\{C_2(CN)_4\}]$	62.6	3.7	6.6	5.8 (N)	62.9	3.6	6.4	5.8 (N)
$[Ir(C_2Ph)(CO)(PPh_3)_2]\cdot 3HCl$ [c]	56.3	4.2	6.3	10.8 (Cl)	56.6	4.0	6.5	11.1 (Cl)
$[Ir(C_2Ph)(CO)(PPh_3)_2]\cdot 2HBr$ [c]	53.9	3.8	6.2	15.4 (Br)	53.6	3.7	6.2	15.9 (Br)
$[IrCl_2(CCl{=}CClPh)(CO)(PPh_3)_2]$	54.5	3.5	6.3	14.1 (Cl)	54.7	3.6	6.3	14.3 (Cl)
$[IrI_2(C_2Ph)(CO)(PPh_3)_2]$	48.8	3.2	5.9	23.2 (I)	49.1	3.2	5.6	23.1 (I)

[a] Analytical technique unsuitable (see text). [b] Carbon and hydrogen analyses are not possible and P is unreliable in the presence of Hg (see text). [c] Mixture of isomers (see text).

is orange. When $[Ir(C_2Ph)(CO)_2(PPh_3)_2]$ is dissolved in solvents such as $CHCl_3$ or CH_2Cl_2 carbon monoxide is rapidly lost (the process can be accelerated by passage of nitrogen) to produce the deep orange colour characteristic of the monocarbonyl complex. Passage of CO restores the pale yellow colour of the dicarbonyl complex, but this reverts to orange on standing under nitrogen. In solution, however, as the monocarbonyl species, it reacts rapidly with oxygen but, in contrast to the behaviour of $[IrCl(O_2)(CO)(PPh_3)_2]$, the adduct does not lose oxygen reversibly on passage of nitrogen.

The complex $[Ir(C_2Ph)(CO)(PPh_3)_2]$ undergoes addition reactions extremely readily with a wide variety of reagents, and in this respect parallels the well documented chemistry of Vaska's compound.[6,7] However, in some cases, reagents were found to attack not only at the metal centre (by ' oxidative addition ') but also at the triple bond of the acetylene linkage. The following reactions are thus grouped in two categories. Infrared, microanalytical, and ^1H n.m.r. data for the products are given in Tables 1—3 respectively.

TABLE 3

Hydrogen-1 n.m.r. data

Complex	τ	J(PH)/Hz	Solvent
$[IrH(C_2Ph)(CO)_2(PPh_3)_2][PF_6]$	18.8(t)	12 ± 2	CH_2Cl_2
$[Ir(C_2Ph)(CO)(PPh_3)_2\{C_2(CO_2Me)_2\}]$	6.70(s), 6.8(s)		$CDCl_3$
$[Ir(C_2Me)(CO)(PPh_3)_2\{C_2(CO_2Me)_2\}]$ [5]	7.97(s)		$CDCl_3$
$[Ir(O_2CMe)_2(C_2Ph)(CO)(PPh_3)_2]$	8.50(s)		$CDCl_3$
$[IrH(Cl)(CH_2CCl_2Ph)(CO)(PPh_3)_2]$	3.17(t),* 26.69(t)	12.4	$CDCl_3$
$[IrH(Cl)(CCl_2CH_2Ph)(CO)(PPh_3)_2]$	4.35(s), 24.85(t)	11.6	$CDCl_3$
$[IrH(Br)(CH{=}CBrPh)(CO)(PPh_3)_2]$	3.22(t),* 26.03(t)	12.8	$CDCl_3$
$[IrH(Br)(CBr{=}CHPh)(CO)(PPh_3)_2]$	4.52(s), 24.48(t)	12.0	$CDCl_3$

* Triplet poorly resolved. s = Singlet and t = triplet.

General Experimental Details.—All the reactions were performed at room temperature with $[Ir(C_2Ph)(CO)_2(PPh_3)_2]$ (*ca.* 50 mg) in dichloromethane (*ca.* 5 cm^3) using an excess of reagent, unless otherwise stated. The orange colour of the monocarbonyl solution always changed very rapidly (often instantaneously) on treatment with the reagent. In general, the products were recovered by reduction of volume and addition of ethanol (absolute), and were washed with ethanol and hexane (or pentane) before drying *in vacuo* to produce the analytically pure complex in essentially quantitative yield (*i.e.* always >90%). Recrystallisation was necessary in a few cases and could be effected using dichloromethane–hexane mixtures. Only significant deviations from the practical details outlined above will be mentioned in the following section.

Reactions involving only the Metal Centre.—(i) *Sulphur dioxide.* The passage of oxygen-free sulphur dioxide gas gave a lime-green solution, which in turn yielded similarly coloured crystals of carbonyl(phenylethynyl)(sulphur dioxide)bis(triphenylphosphine)iridium, $[Ir(C_2Ph)(CO)(PPh_3)_2(SO_2)]$. A sulphur analysis on this complex was not obtainable since the technique involved burning the sample in oxygen before estimating the sulphur content as sulphate. Under these conditions, sulphur dioxide is lost (see below). However, the i.r. spectrum and other properties closely resemble those of $[IrCl(CO)(PPh_3)_2(SO_2)]$.[3] The complex, as a solid, is very slowly converted in air (or by bubbling oxygen through its solution) into the corresponding sulphato-complex, $[Ir(C_2Ph)(SO_4)(CO)(PPh_3)_2]$. Heating the complex in air causes loss of sulphur dioxide up to 145 °C, producing the yellow oxygen adduct $[Ir(C_2Ph)(O_2)(CO)(PPh_3)_2]$ {or orange $[Ir(C_2Ph)(CO)(PPh_3)_2]$ *in vacuo*}; above this temperature decomposition takes place. The complex $[IrCl(CO)(PPh_3)_2(SO_2)]$ is reported [3] as green stable crystals, produced by passing oxygen-free SO_2 through a solution of $[IrCl(CO)(PPh_3)_2]$, which lose SO_2 on heating above 150 °C. The crystal structure [8] is a tetragonal pyramid with an *S*-bonded sulphur dioxide at the apex and *trans*-phosphine ligands in the basal plane. The structure of $[Ir(C_2Ph)(CO)(PPh_3)_2(SO_2)]$ is assumed to be analogous.

As indicated above, $[Ir(C_2Ph)(SO_4)(CO)(PPh_3)_2]$ is not conveniently prepared by reaction of the sulphur dioxide adduct with oxygen. It has been pointed out by Reed *et al.*[9] that attention to the catalysed oxidation of SO_2 to $[SO_4]^{2-}$ using transition-metal complexes (with a view, for example, to controlling SO_2 in exhaust gases) has been focused on Group 8 metals containing oxygen ligands, *i.e.* on the general reaction (1). The corresponding reaction (2) proceeds, however, only in a limited

$$M{-}O_2 + SO_2 \longrightarrow M{-}SO_4 \qquad (1)$$

$$M{-}SO_2 + O_2 \longrightarrow M{-}SO_4 \qquad (2)$$

number of instances. Accordingly, we have found that if a solution of $[Ir(C_2Ph)(CO)(PPh_3)_2]$ is treated first with oxygen (to give the yellow dioxygen adduct) and then sulphur dioxide a greenish yellow colouration is instantly produced, which yields cream crystals of $[Ir(C_2Ph)(SO_4)(CO)(PPh_3)_2]$ (decomposition point in air, 250 °C). The i.r. spectrum of this complex is very similar to that of $[IrCl(SO_4)(CO)(PPh_3)_2]$,[10] which is a buff complex decomposing at 300 °C.[11]

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[6] L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, 1961, **83**, 2784.

[7] L. Vaska, *Science*, 1963, **140**, 809.

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[10] J. J. Levison and S. D. Robinson, *J. Chem. Soc.* (*A*), 1971, 762.

[11] J. J. Levison and S. D. Robinson, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 407.

The sulphato-complex reported by Reed *et al.*,[9] $[RuCl(SO_4)(NO)(PPh_3)_2]$, was found to be accessible both by reaction of the oxygen adduct with SO_2 and by reaction of the sulphur dioxide adduct with O_2. The bidentate nature of sulphato-ligands in Group 8 complexes, previously implied only from i.r. studies,[12] has been confirmed by an *X*-ray structural analysis of $[RuCl(SO_4)(NO)(PPh_3)_2]$.[9]

(ii) *Mercury*(II) *chloride.* The addition of solid $HgCl_2$ produced a rapid sequence of colour changes from orange through dark green, red, and pale green to yellow. The suspended excess of $HgCl_2$ was removed by filtration through Kieselguhr before recovery of the solid product. It was washed initially with water to remove trace amounts of $HgCl_2$. The new complex was deduced to be carbonylchloro(chloromercurio)(phenylethynyl)bis(triphenylphosphine)iridium, $[IrCl(HgCl)(C_2Ph)(CO)(PPh_3)_2]$, by analogy with $[IrCl_2(HgCl)(CO)(PPh_3)_2]$.[13] The decomposition points are respectively 290 and 270 °C. Carbon and hydrogen analyses could not be performed in the presence of mercury, but reasonable data for chlorine and phosphorus were obtained, although phosphorus data can also be unreliable under these circumstances. The presence of mercury was verified qualitatively by a mercury(II) iodide test.

(iii) *Deuterium and hydrogen.* Reaction with deuterium gas produced a pale yellow solution which yielded carbonyldideuterio(phenylethynyl)bis(triphenylphosphine)iridium, $[IrD_2(C_2Ph)(CO)(PPh_3)_2]$, as a very pale yellow solid. As with the corresponding reaction of D_2 with Vaska's compound,[14] this addition was found to be easily reversible by bubbling nitrogen and gave the original orange colour of $[Ir(C_2Ph)(CO)(PPh_3)_2]$. Grinding the solid in air for the preparation of a Nujol mull gave some $[Ir(C_2Ph)(O_2)(CO)(PPh_3)_2]$ by loss of deuterium and subsequent atmospheric oxidation. A KBr disc was therefore prepared, without grinding the sample.

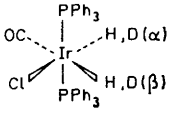
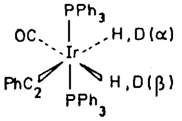
The corresponding reaction of $[Ir(C_2Ph)(CO)(PPh_3)_2]$ with hydrogen similarly yielded a very pale yellow hydride product. As with the deuterio-complex, grinding caused decomposition; the i.r. spectrum was thus determined on a powdered sample with previously ground KBr as above. The solid complex darkens *in vacuo* and should be stored under an atmosphere of hydrogen. Satisfactory analytical data were obtained for the formulation of the complex as carbonyldihydrido(phenylethynyl)bis(triphenylphosphine)iridium, $[IrH_2(C_2Ph)(CO)(PPh_3)_2]$. Preliminary investigations of the solution i.r. and ^1H n.m.r. spectra showed changes with time after the passage of hydrogen was stopped, revealing a kind of dynamic behaviour in solution which may involve the acetylide ligand. This phenomenon will be the subject of further studies.

A comparison of the solid-state i.r. spectra of these dideuterio- and dihydrido-complexes with the analogous chloro-complexes derived from Vaska's compound[15,16] is made in Scheme 2. The following points should be noted.

(*a*) The dihydrido- and dideuterio-adducts of Vaska's compound are isostructural as shown by *X*-ray diffraction patterns of the crystalline complexes.[16] The configuration is deduced to be *cis* from the i.r. data and this is assumed also for the phenylethynyl complexes by analogy.

(*b*) ν(M–H) (α) in complex (1) is much higher than that recorded for (2). This is expected since the i.r. stretches of hydrides *trans* to halogen are among the highest known.[17] The value for complex (2) falls in a region more commonly associated with metal–hydride absorptions. The values of ν(M–H) (β) are comparable since the hydride ligand is in both cases *trans* to carbonyl.

(*c*) The phenomenon of resonance interaction between *trans* hydride and carbonyl ligands produces a lower ν(CO) than for the corresponding deuterio-complex. Coupled with this shift is an anomalous ν(M–H)/ν(M–D) value for the position *trans* to carbonyl.[16] ν(M–H)/ν(M–D) (α) for complex (1) is in the same region as for other related complexes, but ν(M–H)/ν(M–D) (β) is higher. This trend is also reported for the iodo- and

	I.r. spectrum (cm^{-1})					
	Hydride		Deuteride			
Complex	ν(MH)	ν(CO)	ν(CO)	ν(MD)	ν(MH)/ν(MD)	Medium
(1) 	2 196 (α)	1 982	2 003	1 575 (α)	1.394 (α)	Nujol mull
	2 100 (β)			1 497 (β)	1.403 (β)	
(2) 	2 117 (α)	1 968	1 992	1 512 (α)	1.400 (α)	KBr disc
	2 102 (β)			1 497 (β)	1.404 (β)	

SCHEME 2

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[12] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Wiley–Interscience, New York, 1970, pp. 173—175.

[13] R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 1965, 5337.

[14] L. Vaska, *Accounts. Chem. Res.*, 1968, **1**, 335.

[15] L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, 1962, **84**, 679.

[16] L. Vaska, *J. Amer. Chem. Soc.*, 1966, **88**, 4100.

[17] J. P. Jesson, 'Transition Metal Hydrides,' ed. E. L. Muetterties, Marcel Dekker, New York, 1971, ch. 4, p. 89.

bromo-analogues [16] and is observed here for the phenylethynyl complex (2). In addition, complex (2) shows a somewhat high value for ν(M–H)/ν(M–D) (α); this could also be explained as due to a resonance interaction with the acetylide.

(*d*) ν(M–H) and ν(M–D) are of medium intensity; ν(M–D) occur as shoulders to a triphenylphosphine absorption in complex (2). ν(CO) are strong. Complex (2) also exhibits a band at *ca.* 2 128w(sh) cm^{-1} in both the hydrido- and deuterio-complexes, assigned to ν(C≡C).

(*e*) For the complexes reported by Brown *et al.*,[5] reaction with hydrogen occurred only in the presence of excess of triphenylphosphine and resulted in elimination of the acetylene to give [MH(CO)$(PPh_3)_3$] (M = Rh or Ir).

(iv) *Trifluoroacetic acid and acetic acid.* In the reaction with trifluoroacetic acid a very pale yellow solution yielded a similarly coloured solid, which was washed initially with water to remove trace amounts of acid. The product was formulated as carbonyl(phenylethynyl)bis(trifluoroacetato)bis(triphenylphosphine)iridium, [Ir(C_2Ph)$(O_2CCF_3)_2$(CO)$(PPh_3)_2$], in comparison with [Ru$(O_2CCF_3)_2(CO)_2(PPh_3)_2$] reported by Collman and Roper.[18] The corresponding reaction with glacial acetic acid proceeded similarly to yield a pale yellow product which, being appreciably soluble in ethanol, was washed initially with a mixture of equal volumes of ethanol and water. The complex was deduced to be diacetatocarbonyl(phenylethynyl)bis(triphenylphosphine)iridium.

(v) *Dimethyl acetylenedicarboxylate.* This ligand forms a very pale yellow 1 : 1 adduct with [Ir(C_2Ph)(CO)$(PPh_3)_2$], *i.e.* carbonyl(dimethyl acetylenedicarboxylate)(phenylethynyl)bis(triphenylphosphine)iridium, [Ir(C_2Ph)(CO)$(PPh_3)_2${$C_2(CO_2Me)_2$}]. The ^{1}H n.m.r. spectrum (Table 3) shows two separate methyl resonances indicating that the methyl groups are inequivalent. Assuming an essentially trigonal-bipyramidal structure with *trans*-phosphine ligands, this means that the ester C≡C axis cannot lie parallel to the P–Ir–P axis. It is interesting to compare this complex with the methylethynyl analogue [5] which shows only a single methyl resonance for the ester at room temperature. This implies that the orientation of the ester (C≡C axis) is perpendicular to the trigonal plane or perhaps that it is rotating rapidly on the n.m.r. time scale. Attempts to induce such rotation in the phenylethynyl molecule by increasing the temperature (and also investigations into protonation of the complex) are incomplete. It has been found [5] that [Ir(C_2Ph)(CO)$(PPh_3)_2$] will also react with a large excess of phenylacetylene itself, yielding not a π-co-ordinated adduct as above but the six-co-ordinate oxidative-addition product [IrH$(C_2Ph)_2$(CO)$(PPh_3)_2$]. A similar reaction is reported for [Ir(C_2Et)(CO)$(PPh_3)_2$] giving [IrH(C_2Et)(C_2Ph)(CO)$(PPh_3)_2$], the ethylethynyl group subsequently being ejected with the hydride as the free acetylene to leave [Ir(C_2Ph)(CO)$(PPh_3)_2$].

(vi) *Methyl halides.* Methyl halides MeX (X = Cl, Br, or I) react very readily with [Ir(C_2Ph)(CO)$(PPh_3)_2$] to yield pale yellow oxidative-addition products of the type [IrX(Me)(C_2Ph)(CO)$(PPh_3)_2$]. The solubility of these complexes is too low to permit the measurement of n.m.r. spectra, even using Fourier-transform techniques.

(vii) *Tetracyanoethylene* (*tcne*). Analysis of the white reaction product indicates a 1 : 1 adduct of [Ir(C_2Ph)(CO)$(PPh_3)_2$] and tcne. The absence of an i.r. band at *ca.* 2 100 cm^{-1} for ν(C≡C) led initially to the assumption that the ethylene might attack at the triple bond of the acetylide; however, no sensible product formulation could be derived from this. Brown *et al.*[5] encountered a similar problem with complexes of the type [M(C_2R)(CO)$(PPh_3)_2${$C_2(CN)_4$}]. With M = Ir, a value of ν(C≡C) is given for R = Me but not for R = Bu^n; with M = Rh, ν(C≡C) is unreported for R = Me and not discernible for R = Et. A simple π-co-ordinated adduct is therefore proposed for [Ir(C_2Ph)(CO)$(PPh_3)_2${$C_2(CN)_4$}]. The mass spectrum showed the correct molecular ion but did not provide any unambiguous structural information.

Reactions involving both the Metal Centre and the Acetylide Linkage.—(i) *Hydrogen halides.* These reagents can be used in the gaseous form, but it was more convenient to use a few drops of the aqueous acids. The solid products were washed initially with water. Hydrogen chloride gave a cream microcrystalline powder shown by analysis to contain three atoms of chlorine per molecule. The i.r. spectrum showed an Ir–H absorption at 2 226w, vbr. cm^{-1}, a C≡C absorption at 2 130 vw,br. cm^{-1}, and three carbonyl stretches at 2 050s, 2 044s, and 2 030w(sh) cm^{-1}. The acetylide band is assigned to a very small amount of the simple oxidative-addition product [IrH(Cl)(C_2Ph)(CO)$(PPh_3)_2$], the corresponding carbonyl band appearing at *ca.* 2 030 cm^{-1} as a weak shoulder to the band at 2 044 cm^{-1} {[IrHCl_2(CO)$(PPh_3)_2$] shows a carbonyl absorption at 2 046 cm^{-1} in chloroform solution [14]}. The hydride absorption is assumed to be part of the very broad band at *ca.* 2 226 cm^{-1}. The major products of this reaction are taken to be two isomers corresponding to the formulation IrH(Cl)(C_2Ph·2HCl)(CO)$(PPh_3)_2$ for which analyses for C, H, P, and Cl are consistent when performed on the whole product mixture. (Attempts to separate the various components by fractional crystallisation were unsuccessful and t.l.c. on silica plates led to decomposition.) These isomers have hydride stretches at *ca.* 2 226 cm^{-1} in the i.r. which are not identified separately as the absorption is too broad in solution ($CHCl_3$). The carbonyl bands are both observed in the solid state, at 2 050 and 2 044 cm^{-1}; since the triple bond of the acetylide linkage is saturated, no C≡C band is observed.

The addition of two molecules of HCl across the triple bond gives three possible isomers: Ir–CH_2–CCl_2Ph (a), Ir–CCl_2–CH_2Ph (b), and Ir–C*HCl–C*HClPh, the last possessing four optical isomers by virtue of the presence of the two chiral carbon atoms. The observed ^{1}H

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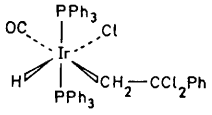
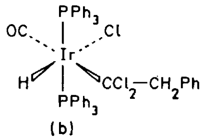
[18] J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, 1965, **87**, 4008.

n.m.r. spectrum is consistent with a mixture of (a) and (b). Two sets of absorptions were recorded: (a)



(a)



(b)

τ 3.17(poorly resolved t) and 26.69[t, J(PH) 12.4 Hz] in the ratio 2 : 1, ν(CO) at 2 044 cm^{-1}; (b) τ 4.35(s) and 24.85[t, J(PH) 11.6 Hz] in the ratio 2 : 1, ν(CO) at 2 050 cm^{-1}. The approximate relative total intensities of these two sets of signals are 65 [isomer (*a*)], and 35% [(*b*)]. The ν(CO) assignments are based on the expected relative electron-withdrawing powers of the ligands *trans* to CO.

The high-field hydride signals are clearly defined triplets due to coupling with two equivalent phosphorus atoms (through iridium). The low-field signal in isomer (b) is too remote from phosphorus (and the hydride) to experience a large coupling and its low position compared with ordinary benzyl methylene protons (*ca.* τ 7.5) is attributed to the deshielding effect of the adjacent chlorine atoms. The low-field signal in isomer (a) shows signs of coupling with phosphorus, but through both the iridium and the carbon atoms this is only poorly resolved. The presence of adjacent chlorine atoms and the iridium atom accounts for the large downfield shift experienced by this methylene group. Similar chemical shifts have been reported by Johnson *et al.*[19] for some related complexes of Pt^{II} and Pd^{II}. For the analogous alkynyl complexes,[5] it is interesting to note that hydrogen chloride liberates the free acetylene and yields the simple dichlorohydrido-product as shown in Scheme 3. This difference in behaviour between the phenylethynyl and the other alkynyl complexes presumably lies in an unusually strong iridium–carbon bond in the former case. This bond was not cleaved in any of the reactions performed on $[Ir(C_2Ph)(CO)(PPh_3)_2]$.

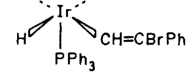
$$[Ir(C_2R)(CO)(PPh_3)_2] \xrightarrow{HCl} [IrH(Cl)(C_2R)(CO)(PPh_3)_2] \xrightarrow{-RC_2H}$$

$$[IrCl(CO)(PPh_3)_2] \xrightarrow{HCl} [IrHCl_2(CO)(PPh_3)_2]$$

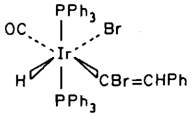
R = Me, Et, Bu^n, Bu^t, C_6H_{11}, *etc.*

SCHEME 3

The corresponding reaction of $[Ir(C_2Ph)(CO)(PPh_3)_2]$ with aqueous hydrobromic acid proceeded similarly to give a pale yellow product, for which analytical data revealed that only two atoms of bromine had been added per molecule of substrate. The i.r. spectrum did not show the presence of the simple oxidative-addition product $[IrH(Br)(C_2Ph)(CO)(PPh_3)_2]$ under these conditions, no acetylide stretching frequency being detectable. ν(Ir–H) was observed at 2 223w,vbr. cm^{-1} and ν(CO) at 2 071s and 2 046s cm^{-1}. A weak broad absorption at *ca.* 1 665 cm^{-1} was tentatively assigned to ν(C=C). The addition of only one molecule of hydrogen bromide across the triple bond gives rise to two possible isomers: Ir–CH=CBrPh (c) and Ir–CBr=CHPh (d), and the ^{1}H n.m.r. spectrum is consistent with a mixture of these. (Each of these species could exist as both *cis* and *trans* isomers, but the i.r. and n.m.r. spectra show evidence of only *one* isomer in each case. It is not clear, however, which geometrical isomer this might be.) The two sets of bands and their assignments are as follows: (c) τ 3.22(poorly resolved t) and 26.03[t, J(PH) 12.8 Hz] in the ratio of 1 : 1, ν(CO) at 2 046 cm^{-1}; (d) τ 4.52(s) and 24.48[t, J(PH) 12.0 Hz] in the ratio of 1 : 1, ν(CO) at 2 071 cm^{-1}. The approximate relative total intensities of these sets of signals are 80 [isomer (c)] and 20% [(d)]. The interpretation of these spectra is as for the chlorinated products.



(c)



(d)

If there is any trend in the behaviour of hydrogen halides with $[Ir(C_2Ph)(CO)(PPh_3)_2]$ one would expect hydrogen iodide to attack only by oxidative addition across the metal, leaving the triple bond intact. A preliminary experiment suggests this to be the case.

(ii) *Halogens.* The reaction of chlorine yields a very pale yellow complex containing four chlorine atoms per molecule. The mass spectrum showed the correct molecular ion and isotope pattern (although no useful structural information) for the formulation $[IrCl_2(CCl{=}CClPh)(CO)(PPh_3)_2]$, which was further suggested by a weak i.r. absorption at 1 680 cm^{-1} assignable to ν(C=C), ν(C≡C) being totally absent. (The possible presence of *cis* and *trans* isomers here was not revealed in the i.r. spectrum.)

Bromine gives a less straightforward reaction, also leading to a pale yellow product. Whether performed in dichloromethane in the cold or under reflux, the i.r. spectrum showed a mixture of products, with bands at 2 137w, 2 080m(sh), 2 071s, and 2 047s cm^{-1}. The first two bands are assigned, respectively, to ν(C≡C) and ν(CO) in the simple oxidative-addition product $[IrBr_2(C_2Ph)(CO)(PPh_3)_2]$ {*cf.* $[IrBr_2Cl(CO)(PPh_3)_2]$ has[14] ν(CO) at 2 072 cm^{-1}}. Since attack by bromine should reduce the π-acceptor ability of the organic ligand, this

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[19] B. F. G. Johnson, J. D. Jones, J. Lewis, and K. A. Taylor, *J.C.S. Dalton*, 1974, 34.

in turn causing a lowering of the carbonyl-stretching frequency, the remaining two bands are assigned to ν(CO) in [$IrBr_2(CBr{=}CBrPh)(CO)(PPh_3)_2$] (*cis* and/or *trans* isomers) and [$IrBr_2(CBr_2{-}CBr_2Ph)(CO)(PPh_3)_2$] respectively. Analytical data (C, H, P, and Br) consistently fell in a region associated with a mixture of these three products. ν(C=C) for the proposed ethylene complex was not observed.

Reaction with iodine produced dark orange crystals of [$IrI_2(C_2Ph)(CO)(PPh_3)_2$] and no other products. The carbonyl-stretching frequency at 2 060 cm^{-1} is comparable to that at 2 067 cm^{-1} in [$IrClI_2(CO)(PPh_3)_2$].[14]

In addition to the above, a number of unsuccessful reactions and reactions yielding unstable products were also performed.

(*i*) Unlike Vaska's compound, [$Ir(C_2Ph)(CO)(PPh_3)_2$] does not react with acetylene or ethylene under ordinary conditions.[20]

(*ii*) Addition of a variety of aliphatic and aromatic amines (*e.g.* NMe_3, NEt_3, and C_5H_5N) produced no reaction discernible by i.r. spectroscopy.

(*iii*) Following the report by Flynn and Vaska [21] of the reversible addition of carbon dioxide to *trans*-[$M(OH)(CO)(PPh_3)_2$] (M = Rh or Ir), a reaction was attempted between [$Ir(C_2Ph)(CO)(PPh_3)_2$], both in CH_2Cl_2 solution and as the solid, with carbon dioxide gas. No change was observed over a period of several hours. In the light of Flynn and Vaska's suggestion that the CO_2 was hydrogen bonded to the OH group in the hydroxo-complexes, our negative result with the phenylethynyl complex was not unexpected.

(*iv*) The addition of excess of PPh_3 to a solution of [$Ir(C_2Ph)(CO)(PPh_3)_2$] in dichloromethane produced an immediate colour change from orange to yellow. The carbonyl-stretching frequency in the i.r. spectrum changed from 1 958 (ref. 4) to 1 969 cm^{-1}; ν(C≡C) (not discernible in solution for the starting material [4]) became visible at 2 108 cm^{-1}. This shift corresponds to similar shifts observed [5] on addition of one molecule of PPh_3 to [$M(C_2R)(CO)(PPh_3)_2$] to yield [$M(C_2R)(CO)(PPh_3)_3$] (M = Rh or Ir). By analogy, the present product is taken to be [$Ir(C_2Ph)(CO)(PPh_3)_3$], stable only in solutions containing excess of PPh_3 and not isolable in a pure state as the solid.

(*v*) If nitrosonium hexafluorophosphate is added to a suspension of [$Ir(C_2Ph)(CO)(PPh_3)_2$] in very dry acetonitrile there is an instantaneous colour change from the yellow suspension to a maroon solution, accompanied by vigorous evolution of carbon monoxide. The i.r. spectrum of this solution in MeCN shows a strong broad band at 1 865 cm^{-1} and a band at 2 120 cm^{-1}, assigned to ν(NO) and ν(C≡C) respectively. The absence of ν(CO) suggests the formulation [$Ir(C_2Ph)(NO)(PPh_3)_2$]-[PF_6], but the complex was unstable in solution and not obtainable in the solid state. Attempts to isolate a stable neutral nitrosyl complex by subsequent attack on this intermediate with nucleophiles ([BH_4]$^-$, I^-, Cl^-, [OMe]$^-$, and [OH]$^-$) all resulted in decomposition.

Conclusions.—The following general comments may be made concerning the complexes reported.

(*a*) The position and intensity of the acetylide stretching frequency are variable and do not appear to show any particular trend. The phenyl group may be acting as an electron buffer so that ν(C≡C) does not accurately represent the electron density on the metal. On the other hand, the trend in ν(CO) values is very similar to that observed [22] for the series of Vaska analogues, and one could use ν(CO) as a sensitive indicator of the effective oxidation state of the iridium in these complexes.[14]

(*b*) ν(CO) values are generally higher than for the corresponding chloro-analogues derived from Vaska's compound, indicating the better π-acceptor ability of C_2Ph compared with Cl. If the π acidity of C_2Ph is considered to be greater than for C_2R (R = alkyl),[5] *i.e.* the former has a lower-lying π* orbital, then the Ir–C bond order should be higher in the phenylethynyl complexes with the result that this ligand is harder to displace. While this is certainly borne out in practice, one would also expect to observe higher carbonyl-stretching frequencies in the phenylethynyl complexes. Paradoxically, this is not found to be particularly evident.

[7/759 *Received*, 5*th May*, 1977]

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[20] L. Vaska and R. E. Rhodes, *J. Amer. Chem. Soc.*, 1965, **87**, 4970.

[21] B. R. Flynn and L. Vaska, *J.C.S. Chem. Comm.*, 1974, 703.

[22] W. H. Baddley, *J. Amer. Chem. Soc.*, 1966, **88**, 4545.