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ADDITION AND MIGRATION OF LIGANDS ON A METAL ATOM PAIR: THE OXIDATIVE ADDITION OF HEXAFLUORO-2-BUTYNE TO DINUCLEAR DIHYDRIDOIRIDIUM(II) COMPLEXES $[Ir(H)(\mu\text{-SBu-t})(CO)(PR_3)]_2(Ir—Ir)$ (R = OMe or Me), AND ITS DEHYDROGENATION REACTION WHEN R = OMe *

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Summary

Dissymmetric dinuclear complexes $(PR_3)(CO)(H)_2Ir(\mu\text{-SBu-t})_2Ir(C_4F_6)(CO)(PR_3)$ (III, R = OMe or Me), which can be described as the juxtaposition of dihydrido and alkyne adducts of Vaska's complex associated through thiolato bridges, were obtained by the reaction of hexafluoro-2-butyne with symmetric dinuclear dihydridoiridium(II) complexes, $[Ir(H)(\mu\text{-SBu-t})(CO)(PR_3)]_2(Ir—Ir)$ (II). When R = OMe, after the loss of H_2, a molecular rearrangement leads to the symmetric dinuclear iridium(II) complex $[Ir(\mu\text{-SBu-t})(CO)(P(OMe)_3)]_2(C_4F_6)$ (IV). A correlation between the presence of an intense absorption near 230 nm in the UV-visible spectra and the existence of a metal—metal bond is established. A sequence of formation, splitting and re-formation of the metal—metal bond is observed along the series of derivatives obtained from $[Ir(\mu\text{-SBu-t})(CO)P(OMe)_3]_2$ (I) to IV, via II and III.

Introduction

We have recently reported the reaction between molecular hydrogen and dinuclear iridium(I) complexes, $[Ir(\mu\text{-SBu-t})(CO)(PR_3)]_2$ (I) to give dihydrido dinuclear iridium(II) complexes $[Ir(H)(\mu\text{-SBu-t})(CO)(PR_3)]_2(Ir—Ir)$ (II) [1]. The similarity between the behaviour of complexes II and other dinuclear complexes containing metal—metal bonds was emphasized in the case of the protonation reaction [2]. It has also been shown that alkynes such as $CF_3C\equiv CCF_3$ undergo insertion into the metal—metal bond of formally isolectronic dinuclear

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* Dedicated to Professor Ernst Otto Fischer on the occasion of his 60th birthday on November 10, 1978.

iron(I) complexes $[FeX(CO)_{3-n}L_n]_2$ [3—5]. The presence of hydride ligands on each metal center of the starting material II a priori brought a supplementary interest. We present here some studies on the reactions of hexafluoro-2-butyne with complexes II.

Results and discussion

$[Ir(H)(\mu\text{-SBu-t})(CO)(PR_3)]_2$ (II, R = Me, OMe) react with hexafluoro-2-butyne at room temperature to give white crystals identified as $[Ir(\mu\text{-SBu-t})(CO)(PR_3)]_2(H)_2(C_4F_6)$ (III).

Assignment of the configuration of complexes III. The ^1H NMR spectrum of III, R = OMe in C_6D_6, shows two sets of high-field signals of equal intensities separated by ca. 9 ppm (Fig. 1a). The first set appears as a doublet of triplets centered at τ 16.09 with a doublet splitting of 20.6 Hz and a triplet splitting of 3.7 Hz, (at 90 as well as at 60 MHz). The second set appears as a doublet of doublets centered at τ 24.99 with doublet splittings of 20.2 and 3.7 Hz.

The problem of the multiplicity of these hydride signals was partially resolved by the double resonance technique. Irradiation at τ 24.99, centre of the second multiplet, causes the first multiplet to be transformed into a simple doublet with a splitting of 20.6 Hz, as shown in Fig. 1b and irradiation at 16.09, centre of the first multiplet, causes the second multiplet to be transformed into a doublet of doublets, with splittings of 20.2 and 3.7 Hz, as shown in Fig. 1c. Thus it is clear that the two types of non-equivalent protons H^1 (τ 16.09) and

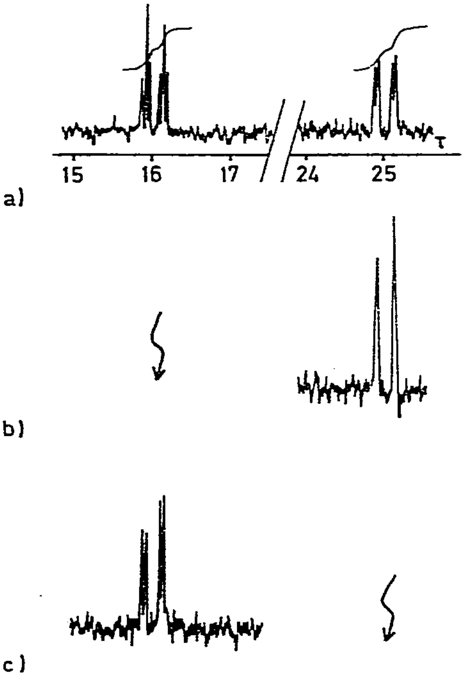


Fig. 1. Highfield 90 MHz ^1H NMR spectra of: (a) III, R = OMe in C_6D_6. (b) after irradiation at τ 16.09, (c) after irradiation at τ 24.99.

H^2 (τ 24.99) are coupled together with a coupling constant $J(H^1H^2)$ of 3.7 Hz. The magnitude of this coupling is very close to the $^2J(HH)$ found for mononuclear hydridoiridium(III) complexes [6—8] and this implies that the hydride ligands H^1 and H^2 are bound to the same iridium atom. In addition, a mutual *cis* position of H^1 and H^2 is strongly suggested by the two strong Ir—H stretching frequencies (2125 and 2095 cm^{-1}). In their deuterium analogues, ν(Ir—D) appear in the region 1520—1550 cm^{-1}, as expected (Table 1).

Two doublets (τ 6.69, $J(PH)$ 12.5 Hz and τ 6.78, $J(PH)$ 11.0 Hz) of equal intensities for the methyl protons of the phosphite ligands are observed whereas the fully proton-decoupled ^{31}P NMR spectrum shows two doublets of equal intensities, each doublet being separated by ca. 40 ppm (Table 2). We therefore propose the presence of two non-equivalent phosphite ligands and the multiplicity of the ^{31}P NMR signals indicates a weak coupling between the phosphorus nuclei P^1 and P^2, ($J(P^1P^2)$ 9.2 Hz).

On the Fig. 1b and 1c, the splittings of respectively 20.6 and 20.2 Hz are clearly attributed to $^2J(P^1H^1)$ and $^2J(P^1H^2)$ couplings and so suggest the presence on the same metal atom of mutually *cis* hydride (H^1, H^2), and phosphite (P^1) ligands. The second phosphite, P^2, necessarily lies on the other metal atom. A long-range coupling $^4J(P^2H^1)$ of 3.7 Hz between the proton at τ 16.09 and the second phosphorus nucleus P^2 then explains the multiplicity of the signal remaining under irradiation (Fig. 1c). The apparent doublet of triplets is in fact a doublet of doublets of doublets due to $^2J(H^1H^2)$ and $^4J(P^2H^1)$ being accidentaly of the same magnitude.

In the complex III, R = Me, the long range coupling $^4J(PH)$ was not detected as only two doublets of doublets are seen in the high field region. This results from the replacement of a tertiary phosphite by a tertiary phosphine as expected [9].

The compounds III, R = OMe and Me exhibit IR bands in the 1600—1800 cm^{-1} region attributable to the ν(C=C) stretching of an alkyne doubly σ-bonded to a single metal atom [10,11]. The ^{19}F NMR spectra indicate the presence of two chemically different CF_3 groups. Similar results were found for the hexafluoro-2-butyne adduct of the *cis*-$IrCl(CO)(PPh_3)_2$ complexes [10].

TABLE 1

INFRARED DATA (cm^{-1}) FOR $[Ir(\mu\text{-SBu-t})(CO)(PR_3)]_2(X)_2(C_4F_6)$ (III) AND $[Ir(\mu\text{-SBu-t})(CO)(PR_3)]_2(C_4F_6)$ (IV)

	R	X	ν(CO) ^{a}	ν(IrX)	ν(C=C)
III	OMe	H	2011vs 1998m	2125(br) ^{a} 2095(br)	1780 ^{a}
III	OMe	D	2010vs 1982m	1526 ^{b}	1780 ^{a}
III	Me	H	2011s 2002vs 1973m	2120(br) ^{a} 2080(br)	1775 ^{a}
IV	OMe		2027vs 2010s		1597 ^{b}

[a] Measured in hexadecane. [b] Measured in KBr pellets.

TABLE 2

^{1}H (90 MHz), $\{^1H\}^{31}P$ (36.43 MHz) AND ^{19}F (56.46 MHz) NMR DATA FOR III AND IV. Measured in $CDCl_3$. τ values ±0.02, J values ±0.2 Hz. ^{31}P shifts are relative to external H_3PO_4 and ^{19}F shifts are relative to external CF_3COOH

	R		^{1}H NMR							$\{^1H\}^{31}P$ NMR		^{19}F NMR δ (ppm)
			τ(t-Bu)	τ(R)	J(PH)	τ(H)	^2J(PH)	^2J(HH)	^4J(PH)	δ (ppm)	^4J(PP)	
III	OMe		8.80(s)	6.38(d)	12.3	16.44(ddd)	19.8	3.7	3.7	99.57(d)	9.2	27.3(s)
			8.55(s)	6.35(d)	11.4	25.34(dd)	20.5	3.7		60.33(d)	9.2	26.4(s)
			8.53(s) [a]	6.78(d) [a]	11.0	16.09(ddd) [a]	20.6	3.7	3.7			
			8.25(s)	6.69(d)	12.5	24.99(dd)	20.2	3.7				
III	Me	isomer a	8.81(s)	8.55(d)	10.6	15.38(dd)	22.8	2.9				
			8.52(s)	8.28(d)	10.6	25.73(dd)	17.6	2.9				
		isomer b	8.73(s)	8.20(d)	11.1	27.10(dd)	25.0	5.1				
			8.69(s)	8.03(d)	10.6	29.76(dd)	27.2	5.1				
IV	OMe		8.71(s)	6.23(vt)	12.5					87.5(s)		27.1(s)
			8.58(s)									

[a] Measured in C_6D_6.

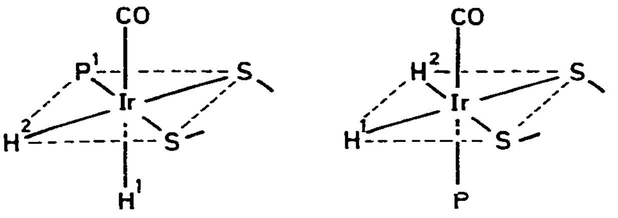
These results, and elemental analysis and molecular weight data strongly suggest a dissymmetric thiolato bridged dinuclear configuration in which one iridium atom is surrounded by one carbonyl, one phosphine and two hydride ligands, whereas the other is surrounded by one carbonyl, one phosphine and the alkyne ligands.

There are two possibilities (a and b) for the hydride-containing moiety to accomodate the ligands so that both hydrogen and phosphorus are mutually *cis* (Fig. 2). In case b, the non-equivalence of the two hydride ligands could be due to the dissymmetry of the part of the molecule which is not shown in Fig. 2. The differences between (i) the high field NMR signals, ca. 9 ppm, and (ii) the Ir—H stretching frequencies, ca. 40 cm^{-1}, demonstrate a situation comparable to the hydrogenated adduct of the Vaska's complex [12] and we retain the configuration a where the hydride H^1 having the lower τ value is *trans* to the carbonyl group and the other, H^2, is *trans* to a thiolato group.

In the case R = Me, the problem is slightly complicated by the presence of two isomers. One of these isomers (a) is quite analogous to the complex III, R = OMe; it exhibits two doublets of equal intensities in the methyl protons of the phosphine (τ 8.55, ^2J(PH) 10.6 Hz and τ 8.28, ^2J(PH) 10.6 Hz), two singlets of equal intensities in the t-butyl protons region (τ 8.81 and 8.52) and two doublets of doublets of equal intensities, separated by ca. 10 ppm (τ 15.38, ^2J(PH) 22.8, ^2J(HH) 2.9 Hz and τ 25.73, ^2J(PH) 17.6, ^2J(HH) 2.9 Hz). The second isomer (b) presents the same ^{1}H NMR patterns and differs essentially by a smaller separation between the two high field doublets of doublets, ca. 2.5 ppm (Me τ 8.03 (d), ^2J(PH) 10.6 Hz, τ 8.20 (d), ^2J(PH) 11.1 Hz; t-Bu τ 8.69 (s), 8.73 (s); H τ 27.10 (dd), ^2J(PH) 25.0, ^2J(HH) 5.1 Hz and τ 29.76 (dd), ^2J(PH) 27.2, ^2J(HH) 5.1 Hz). The shift of ca. 2.5 ppm between the two high-field signals is rather consistent with the configuration b where the hydride ligands are mutually *trans* to each thiolato group.

For the alkyne containing moiety, three possibilities (a′, b′ and c′) are a priori to be considered (Fig. 3). The existence of a long-range $^4J(P^1P^2)$ in the case R = OMe, suggests that the phosphorus P^1 of the first moiety and the phosphorus P^2 of the second moiety are "coplanar" with iridium and sulphur atoms. We retain therefore the configuration a′ which allows such a situation.
hydride H^1 and the phosphorus P^2. We retain therefore the configuration a′ which allows such a situation.

Four possibilities remain for the two mononuclear moieties a and a′ to bind together through the thiolato bridges (Fig. 4). The compound III, R = OMe



(a) (b)

Fig. 2. Possible configurations for the hydride containing moiety of complexes III.

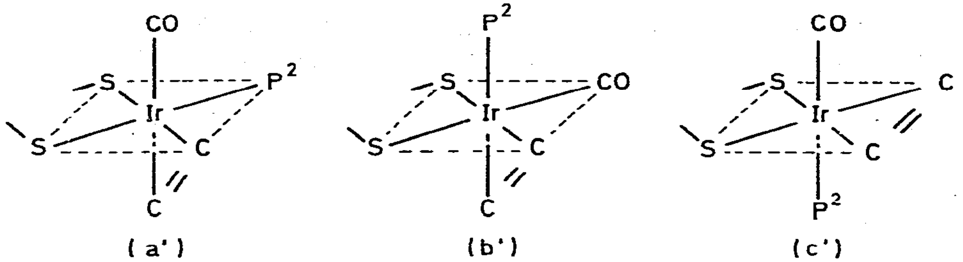


Fig. 3. Possible configurations for the alkyne containing moiety of complexes III.

exhibits two ν(CO) bands. The highest frequency can be reasonably assigned to the in phase mode; it appears as the most intense and this is consistent with the configurations $(aa')_1$ or $(aa')_2$ where carbonyl groups are mutually *cis*. The ^1H NMR spectrum exhibits two singlets of equal areas in the t-butyl region. A weak coupling $^5J(PH)$ between the t-Bu protons at τ 8.53 (in C_6D_6) and the phosphorus nuclei is suggested by the broadness of this signal compared with the one at τ 8.25. It has been already observed that only the SR protons *trans* to phosphine showed coupling to ^{31}P [13]. So these t-butyl protons are necessarily coupled with the two phosphorus nuclei P^1 and P^2; on the contrary, the other t-butyl protons being therefore in *cis* position relative to P^1 and P^2 are not coupled and appear as a narrow singlet. Thus we prefer the configuration $(aa')_1$ in which the phosphite ligands are mutually *cis*. For R = Me, the coupling constant $^5J(PH)$ is not detected since the two t-Bu signals appear as two identical singlets.

Dehydrogenation of the complex III, R = OMe. A solution of the white complex III, R = OMe (and only in this case) in dichloromethane, toluene or cyclo-

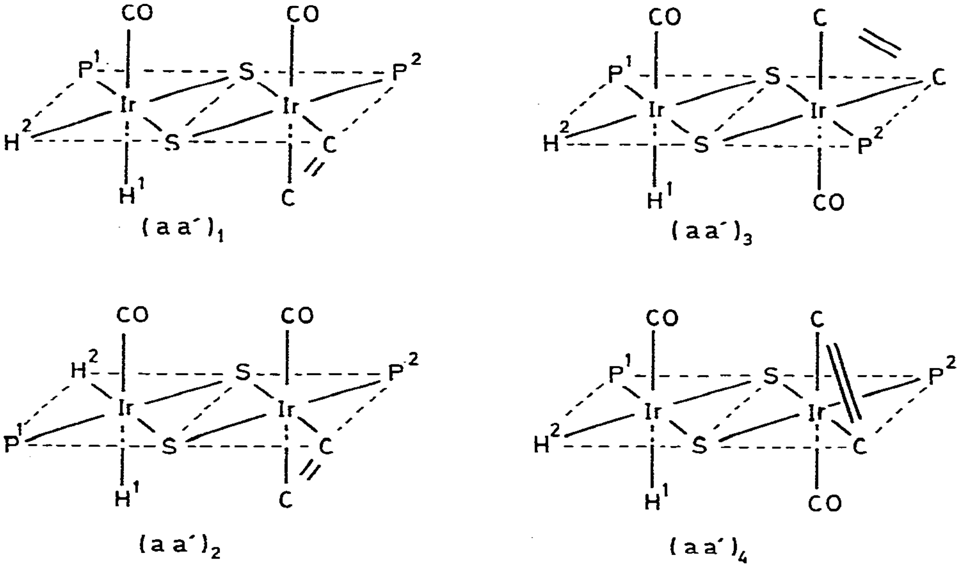


Fig. 4. The different possibilities for the moieties a and a' to bind together through the thiolato bridges.

hexane, slowly loses hydrogen as shown by the disappearance of both the Ir—H stretchings and the high field NMR signals, to give quantitatively a yellow compound identified as $[Ir(\mu\text{-SBu-t})(CO)(P(OMe)_3)]_2(C_4F_6)$ (IV). Although it has not been directly identified, we can reasonably postulate that molecular hydrogen is evolved.

The changes in the methyl proton resonances which accompanied the loss of hydrogen are shown in Fig. 5. The two phosphite doublets of equal intensities at τ 6.35 and 6.38 and the two t-butyl singlets at τ 8.55 and 8.80 are successively replaced respectively by one triplet at τ 6.23 (J(PH) 12.5 Hz) and two singlets at τ 8.58 and 8.71. The infrared spectra show two new carbonyl bands appearing at 2027 and 2010 cm^{-1} whereas the disappearance of the ν(C=C) band at

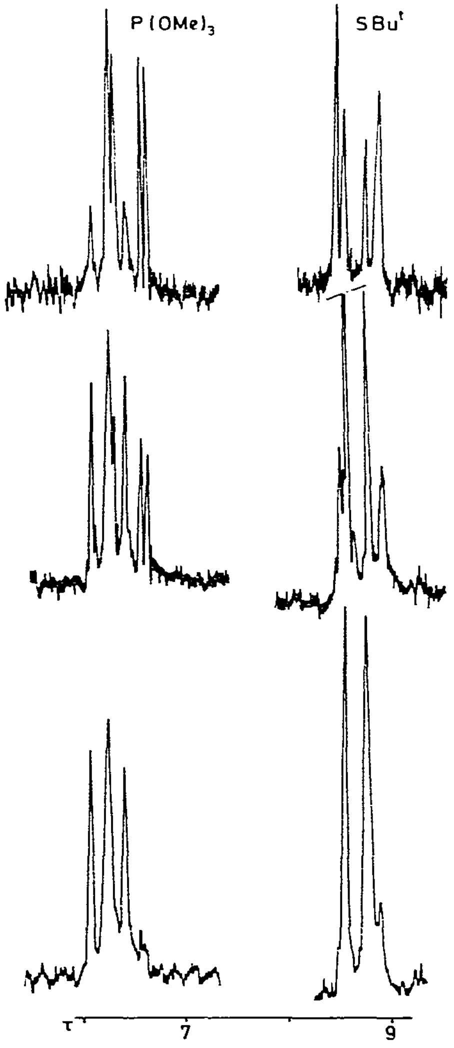
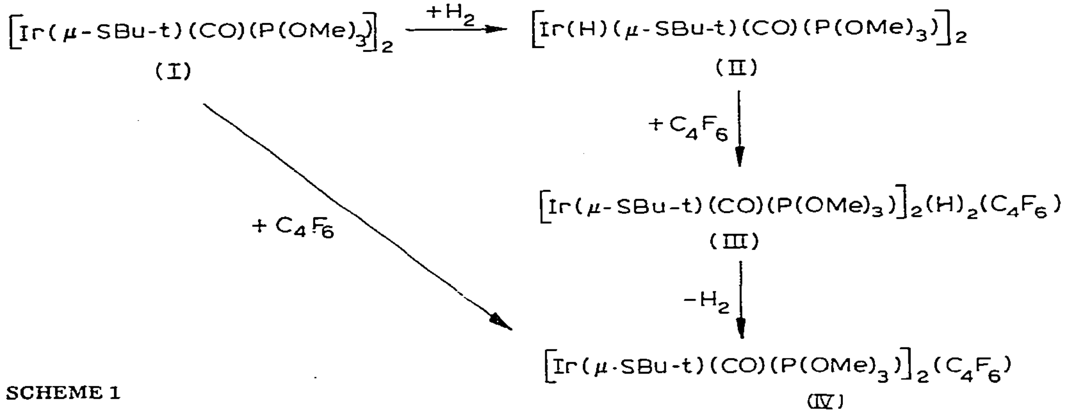


Fig. 5. The changes in the methyl proton resonances (60 MHz) which accompanied the loss of hydrogen from III, R = OMe in CDCl$_3$.

1780 cm^{-1} is observed together with a new absorption at 1597 cm^{-1}.

The ^{19}F NMR spectrum of complex IV which exhibits one singlet at δ 27.1 ppm indicates the chemical equivalence of the CF_3 groups whereas the ^1H and the $\{^1H\}^{31}P$ NMR spectra indicate the chemical equivalence of the $P(OMe)_3$ groups. Some of these data have been already discussed recently [14] for the same complex IV which was prepared directly by the oxidative addition of hexafluoro-2-butyne to complex I, and it has been suggested that a bridging fluoroalkyne group is σ-bonded to both iridium atoms according to a symmetrical configuration comparable with those obtained in the hexafluoro-2-butyne adduct of the $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ complex [15].

Chemical filiations between the compounds I—IV, R = OMe are summarized in Scheme 1.



SCHEME 1

Modifications in the UV-visible spectra when going from complex I, R = OMe, to II, III and IV (according to Scheme 1). The spectra of complexes I are quite similar to those of mononuclear square planar iridium I complexes containing π-acceptor ligands [16—20]. For example, the absorption spectrum of I, R = OMe exhibits four bands at 445 nm (ϵ 4190 l mol^{-1} cm^{-1}), 385 nm (ϵ 4410 l mol^{-1} cm^{-1}), 360 nm (ϵ 4010 l mol^{-1} cm^{-1}) and 312 nm (ϵ 4700 l mol^{-1} cm^{-1}) as shown in Fig. 6.

The four absorption bands progressively disappeared by addition of one mole of H_2 to one mole of the complex I, R = OMe to give complex II and are replaced by a strong absorption at 322 nm (ϵ 10070 l mol^{-1} cm^{-1}). This strong absorption then disappeared on addition of the fluoroalkyne to complex II to form the Ir^{III}—Ir^{III} species III and a similar result was already observed in the case of the oxidative addition of H_2 or O_2 on mononuclear complexes of iridium(I), to form six-coordinate complexes of iridium(III) [16,18]. The loss of hydrogen to give complex IV is accompanied by the appearance of a new strong absorption at 317 nm (ϵ 7480 l mol^{-1} cm^{-1}).

It seems now generally accepted that intense bands in the same energy region are characteristic of d^7—d^7 metal—metal bonded complexes and are attributable to σ—σ^* transition [20—24]. In the case of previously characterized d^7—d^7 complexes II [25], the presence of a strong band near 325 nm was related to the Ir^{II}—Ir^{II} bond. The electronic spectrum of complex IV seems then quite consis-

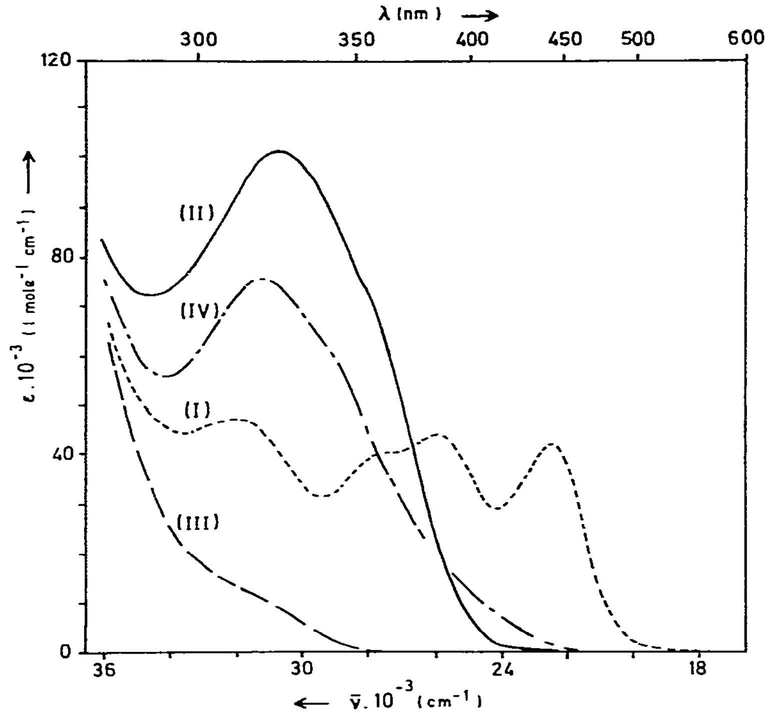


Fig. 6. Electronic absorption spectra of complexes I—IV, R = OMe in CH_2Cl_2 at 298 K.

tent with the presence of a metal—metal bond and, therefore, with the hypothesis of a formally one electron oxidative addition of the fluoroalkyne to each iridium atom via σ bonds.

Conclusion

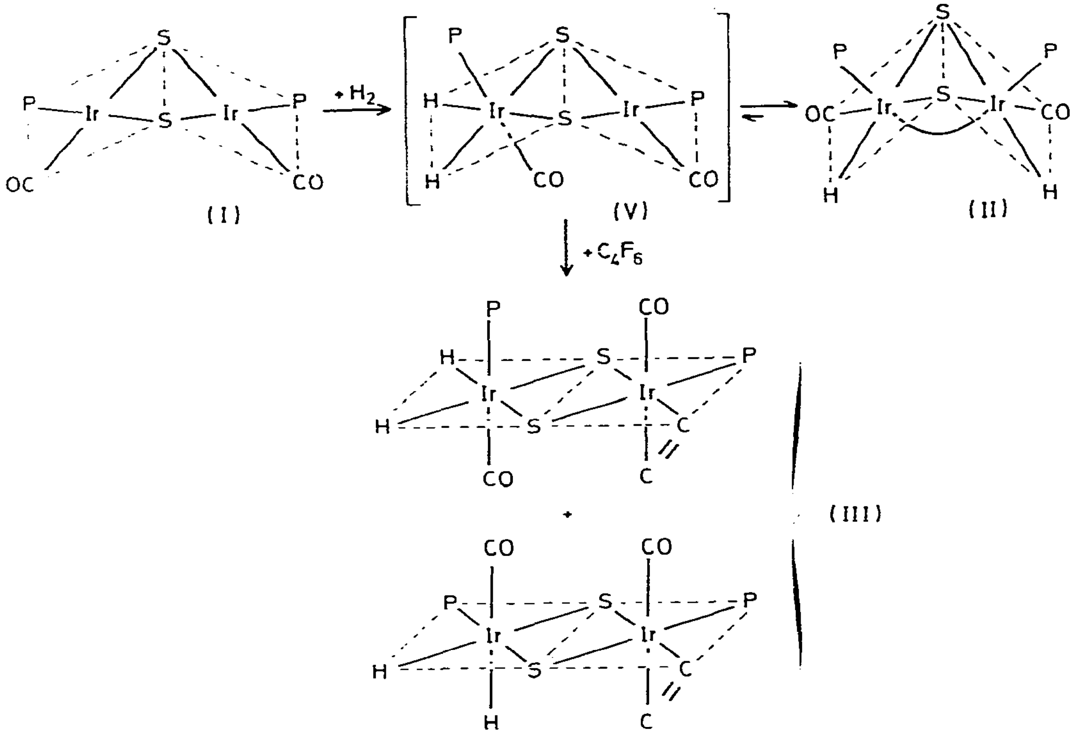
In relation to the insertion reaction of fluoroalkynes in the metal—metal bond of other d^7—d^7 metal complexes, the formation of the dissymmetric species III leads to an unexpected result.

This result could be rationalized by the existence of a dihydrido intermediate species V with two hydride ligands on the same metal centre (Scheme 2). Such a structure has been previously postulated for the product of hydrogenation of $[RhCl(P(p\text{-tolyl})_3)_2]_2$ [26]. It has been suggested [25] that V could also be an intermediate in the formation of complexes II. Therefore, the formation of III could be explained by reaction of C_4F_6 with one of the compounds (namely V) of the equilibrium $\mathrm{II} \rightleftharpoons \mathrm{V}$. In this case, the isomer b of the complex III, R = Me would appear as the kinetic product of the addition reaction.

Experimental

Physical measurements. Infrared spectra were recorded as hexadecane solutions or as caesium bromide dispersions, using a Perkin—Elmer 225 grating spectrometer: in the carbonyl stretching region, the spectra were calibrated by

SCHEME 2



water vapor lines. ^1H NMR spectra were obtained at 90 MHz on a Bruker WH 90 spectrometer, in the FT mode and at 60 MHz on a Varian A 60 spectrometer. Chemical shifts were measured with respect to internal TMS and are reported on the τ scale. Proton noise-decoupled ^{31}P NMR spectra were performed at 36.4 MHz on a Bruker WH 90 spectrometer. Chemical shifts were measured with respect to external H_3PO_4. ^{19}F NMR spectra were obtained on a Perkin—Elmer R 10. Chemical shifts were measured with respect to external CF_3COOH. Optical spectra were recorded from 600 to 300 nm with a Cary 14 spectrophotometer. Microanalyses were carried out by the Service Central de Microanalyses du C.N.R.S. Molecular weights were determined by tonometry in benzene using a Mechrolab apparatus.

Preparations. II, R = OMe and Me were prepared as previously described [25].

Preparation of III, R = OMe. 0.324 g of the complex II, R = OMe was transferred to a thick glass reaction vessel fitted with a teflon stopcock. It was evacuated, cooled to 77 K and methanol (20 ml) and the alkyne (0.08 g) condensed in. The reaction mixture was then allowed to warm slowly to room temperature and was stirred during 3 h. Progressively a white precipitate appears. The product was filtered off, washed with hexane, and dried in vacuo (0.185 g, yield 48%). The IR spectrum of the filtrate indicates the total consumption of the starting compound II and the presence of the complex IV, together with the title product, which explains the low yield in complex III. Found: C, 23.45; H, 3.80; F, 11.38; Mol. wt., 1030 ± 30. $C_{20}H_{38}F_6Ir_2O_8P_2S_2$ calcd.: C, 23.29; H, 3.72; F, 11.05%; Mol. wt., 1032.

Preparation of III, R = Me. 0.150 g of the complex II, R = Me was treated with hexafluoro-2-butyne (0.05 g) in methanol (10 ml), for 2 h, following an identical procedure. The yellow solution slowly became light yellow. Crystallization from the methanol solution gave white-yellow crystals of the title compound (0.120 g, yield 66%).

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