perature. During this time considerable decomposition occurred, precipitating metallic cobalt. The volatiles were not analyzed.

C. Reaction with Propyne. (η^6-Toluene)bis(pentafluorophenyl)cobalt(II) (0.05 g, 0.1 mmol) was dissolved with methylene chloride (1.5 mL) and then filtered into a Schlenk tube in an inert atmosphere. The Schlenk tube was attached to a vacuum line and the solution freeze-thaw degassed. A 625-torr sample of degassed propyne was introduced over the solution. The color changed from red-brown to dark red. After the mixture was stirred for 90 min, volatiles were removed and analyzed by GLC with methylcyclohexane as an internal standard. Toluene (90%) and pentafluorobenzene (22%) were present. On the basis of the amount of starting arene complex, mesitylene (4.5%) and 1,2,4-trimethylbenzene (12.8%) also were present (identified by GC–MS and retention time). The polymeric residue was not analyzed.

IV. Pyrolysis of Bis(pentafluorophenyl)(η^6-toluene)cobalt(II). Bis(pentafluorophenyl)(η^6-toluene)cobalt(II) (0.099 g, 0.2 mmol) was transferred into a Schlenk tube under an inert atmosphere. The Schlenk tube was evacuated and then placed into an oil bath preheated to 150 °C. The red-brown solid melted and turned black. Clear liquid began refluxing on the walls of the tube. After 15 min of heating, the Schlenk tube was removed from the bath and allowed to cool to room temperature. The vessel was then pressurized with dry nitrogen and opened. The residue was extracted with methylene chloride several times, and the washes were combined. Methylcyclohexane was added as an internal standard, and the mixture was analyzed by GLC. Toluene (100%) and decafluorobiphenyl (93%) were present.

V. Solution Decomposition of Bis(pentafluorophenyl)(η^6-toluene)cobalt(II). Bis(pentafluorophenyl)(η^6-toluene)cobalt(II) (0.108 g, 0.22 mmol) was dissolved with toluene and then filtered under an inert atmosphere. The filtrate was syringed into a one-neck, 50-mL round-bottom flask equipped with a reflux condenser. The condenser was topped with a stopcock for connection to a nitrogen line. The apparatus was then connected to a nitrogen supply. Constant pressure was maintained with a mineral oil bubbler and continuous nitrogen purge. The solution was refluxed for 72 h until colorless. Methylcyclohexane was added as an internal standard and the solution analyzed by GLC. Pentafluorobenzene (135%, 0.3 mmol) and decafluorobiphenyl (29.6%, 0.06 mmol) were present.

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Registry No. **1**, 71589-04-3; **2**, 86197-37-7; **3**, 86197-38-8; **4**, 86197-39-9; $(C_6F_5)_2Ni(THF)_2$, 74153-74-5; $(C_6F_5)_2Ni(THT)_2$, 86197-40-2; $(C_6F_5)_2Ni(py)_2$, 86258-55-3; $(C_6F_5)_2Ni(bpy)$, 38192-72-2; $BNi(C_6F_5)_2$ (B = benzene), 86217-13-2; $BNi(C_6F_5)_2$ (B = benzene-d_6), 74167-02-5; $BNi(C_6F_5)_2$ (B = toluene-d_8), 74167-00-3; $BNi(C_6F_5)_2$ (B = anisole), 74167-01-4; $BCo(C_6F_5)_2$ (B = benzene), 86197-41-3; $BCo(C_6F_5)_2$ (B = benzene-d_6), 86197-42-4; $BCo(C_6F_5)_2$ (B = toluene-d_8), 86197-43-5; $BCo(C_6F_5)_2$ (B = anisole), 86197-44-6; $BCo(C_6F_5)_2$ (B = toluene), 60528-58-7; $BNi(C_6F_5)_2$ (B = toluene), 66197-14-6; NBD, 121-46-0; COD, 111-78-4; pentafluorobenzene, 363-72-4; propyne, 74-99-7; mesitylene, 108-67-8; 1,2,4-trimethylbenzene, 95-63-6; decafluorobiphenyl, 434-90-2.

Further Studies on the Metal to Metal Migration Processes. The Steric Influence of the Phosphorus Ligands on the Oxidative Addition of Dihydrogen and of Hexafluoro-2-butyne to $[Ir(\mu\text{-S-}t\text{-Bu})(CO)(P(O\text{-}t\text{-Bu})_3)]_2$

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The sterically hindered $[Ir(\mu\text{-S-}t\text{-Bu})(CO)(P(O\text{-}t\text{-Bu})_3)]_2$ diiridium(I) complex reacts reversibly with molecular hydrogen to yield 1:1 and 2:1 adducts, identified as $[(H_2(P(O\text{-}t\text{-Bu})_3)(CO)Ir^{III}(\mu\text{-S-}t\text{-Bu})_2Ir^{I}(CO)(P(O\text{-}t\text{-Bu})_3)]$ and $[Ir^{III}(H_2)(\mu\text{-S-}t\text{-Bu})(CO)(P(O\text{-}t\text{-Bu})_3)]_2$, by chemical and spectroscopic evidence. With hexafluoro-2-butyne, an unsymmetrical and a symmetrical 1:1 adduct, $[(CO)(P(O\text{-}t\text{-Bu})_3)Ir^{I}(\mu\text{-S-}t\text{-Bu})_2Ir^{III}(CO)(P(O\text{-}t\text{-Bu})_3)(\eta^2\text{-}C_4F_6)]$ and $\{[Ir^{II}(\mu\text{-S-}t\text{-Bu})(CO)(P(O\text{-}t\text{-Bu})_3)]_2(\mu\text{-}\eta^1\text{-}C_4F_6)\}$(Ir–Ir) were obtained. $[(H)_2(P(O\text{-}t\text{-Bu})_3)(CO)Ir^{III}(\mu\text{-S-}t\text{-Bu})_2Ir^{I}(CO)(P(O\text{-}t\text{-Bu})_3)]$ reacts with C_4F_6 and $[(CO)(P(O\text{-}t\text{-Bu})_3)Ir^{I}(\mu\text{-S-}t\text{-Bu})_2I^{III}(CO)(P(O\text{-}t\text{-Bu})_3)(\eta^2\text{-}C_4F_6)]$ reacts with H_2 to yield quantitatively in both cases $[(H)_2(CO)(P(O\text{-}t\text{-Bu})_3)Ir^{III}(\mu\text{-S-}t\text{-Bu})_2Ir^{III}(P(O\text{-}t\text{-Bu})_3)(CO)(\eta^2\text{-}C_4F_6)]$. In the context of bimetallic activation processes, the bulkiness of the ligand $P(O\text{-}t\text{-Bu})_3$ appears as an effective reactivity modulator, probably through its influence on the flexibility of the bimetallic Ir_2S_2 core.

Introduction

Continuing studies in this laboratory have focused on the interaction of $[Ir(\mu\text{-S-}t\text{-Bu})(CO)(PR_3)]_2$ (R = OMe, Ph, NMe_2, Me) with small molecules. These dimeric Ir(I) complexes undergo facile and irreversible oxidative addition of a variety of substances including molecular hydrogen,[1] iodine,[2] and hexafluoro-2-butyne.[3] The products are symmetrical 1:1 adducts with Ir–Ir single bonds as shown in Scheme I.

From our point of view, these reactions exemplify some specific types of behavior of polymetallic entities[4] including

(1) Bonnet, J.-J.; Thorez, A.; Maisonnat, A.; Galy, J.; Poilblanc, R. *J. Am. Chem. Soc.* **1979**, *101*, 5940–5948.

(2) Bonnet, J.-J.; Kalck, P.; Poilblanc, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 551–552.

(3) Devillers, J.; Bonnet, J.-J.; de Montauzon, D.; Galy, J.; Poilblanc, R. *Inorg. Chem.* **1980**, *19*, 154–159.

(4) (a) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Moore, E. J.; Rose-Munch, F. *Inorg. Chem.* **1982**, *21*, 146–156. (b) Poilblanc, R. *Inorg. Chim. Acta* **1982**, *62*, 75–86 and references.

(5) Our hypothesis was partially supported by the fact that the symmetrical dihydridodiiridium(II) complexes react irreversibly in solution with hexafluoro-2-butyne to yield a diiridium(III) species in which both hydrides are found on the same iridium atom while the alkyne is bound to the other iridium atom.[6] Moreover, this result strongly suggested the existence of an equilibrium between the symmetrical (H)Ir–Ir(H) and the unsymmetrical $(H)_2Ir$...Ir dihydrido complexes.

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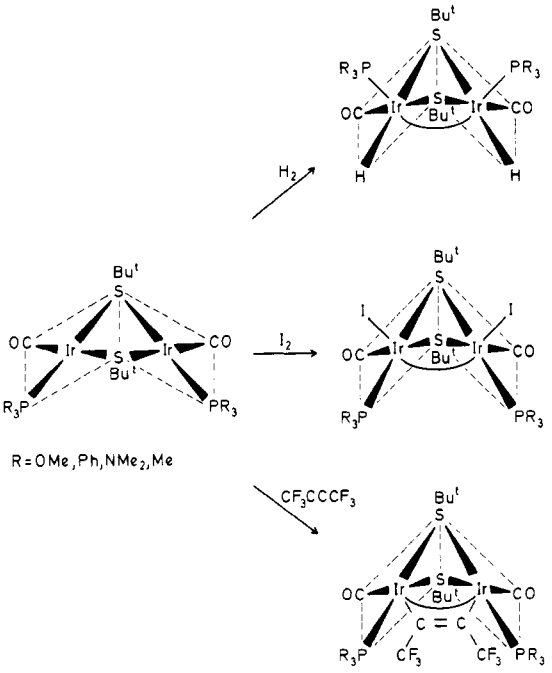
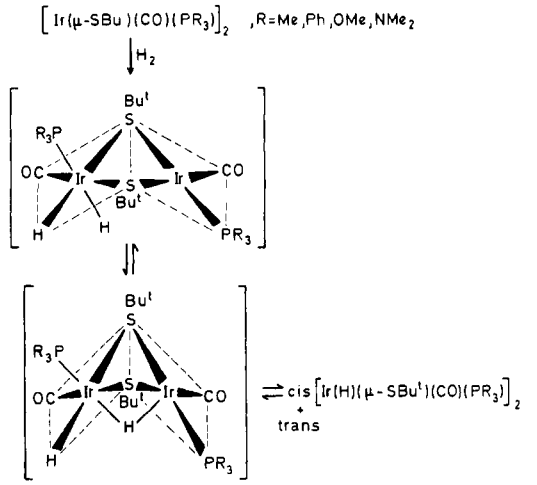
Scheme I



Scheme II



the binding of a substrate to two metal atoms and the migration of ligands from one metal to another.

Thus, concerning the mechanism of the formation of the dihydridodiiridium adducts, we previously suggested a process involving a cis addition of H_2 at one metal atom center followed by the migration of one hydride from one iridium atom to the other;[1] this migration would be associated with the formation of an iridium–iridium bond. Thus a species containing one terminal and one bridging hydride was postulated as a possible intermediate (Scheme II), the folding around the S–S axis being an essential step.

Keeping in mind this mechanistic aspect, the study of the factors which are able to affect the deformations of the Ir_2S_2 core around the S–S axis are of obvious interest in the context of bimetallic activation processes. For this reason, we initiated an investigation of the steric influence of the phosphorus ligand on the course of the addition of small molecules, including H_2 and C_4F_6, to iridium(I) complexes.

We report here the reactivity of a diiridium(I) complex containing the bulky *tert*-butyl phosphite ligand toward H_2 and C_4F_6 along with the reactivity of the products obtained.

We discuss the contribution of this study to the concerted mechanism for the iridium to iridium migration of the hydrogen ligand previously suggested. We present evidence for the mechanism of the addition of hexafluoro-2-butyne to diiridium(I) complexes.

Experimental Section

General Remarks. All reactions and manipulations were routinely performed under a nitrogen atmosphere in Schlenk-type glassware. All solvents were appropriately dried and freed of molecular oxygen prior to use. Microanalyses were performed by the Service de Microanalyses du Laboratoire de Chimie de Coordination du CNRS. Molecular weights were measured in benzene by using a Mechrolab osmometer. Infrared spectra were recorded in hexadecane or cyclohexane solutions, using a Perkin-Elmer Model 225 grating spectrometer; in the carbonyl stretching region, the spectra were calibrated with water vapor lines.[8] ^1H NMR spectra were obtained at 90 and 250 MHz on a Bruker WH 90 FT and on a Bruker WM 250 FT spectrometer, respectively; chemical shifts were measured with respect to internal tetramethylsilane (Me_4Si) and are given in parts per million, downfield positive. ^{31}P NMR spectra were performed at 36.4 MHz on a Bruker WH 90 FT spectrometer and at 101.1 MHz on a Bruker WM 250 FT spectrometer. Chemical shifts were measured with respect to external H_3PO_4 and are given in parts per million, downfield positive.[8] ^{19}F NMR spectra were performed at 84.7 MHz on a Bruker WH 90 FT spectrometer. Chemical shifts were measured with respect to external CF_3COOH and are given in parts per million, downfield positive.

The starting material $Ir(\mu\text{-}S\text{-}t\text{-}Bu)(CO)_2]_2$ was prepared according to a published procedure.[7] Hexachloroiridic acid, *tert*-butylmercaptan, butyllithium, and hexafluoro-2-butyne were of commercial origin. Tri-*tert*-butyl phosphite was prepared according to a published method.[9]

Preparation of $[Ir(\mu\text{-}S\text{-}t\text{-}Bu)(CO)(P(O\text{-}t\text{-}Bu)_3)]_2$ (1). $[Ir(\mu\text{-}S\text{-}t\text{-}Bu)(CO)_2]_2$ (0.579 g, 0.858 mmol) was dissolved in 20 mL of hexane, and an excess of tri-*tert*-butyl phosphite (0.617 mL, 2.25 mmol) was added dropwise at room temperature with vigorous stirring. The resulting red solution was concentrated under reduced pressure; slow addition of 20 mL of methanol with stirring afforded orange-yellow crystals. After the mother liquor was decanted, the crystals were washed with methanol and dried under vacuum (0.742 g, 77%): IR ν(CO) 1958 (vs), 1945 (s) cm^{-1} (hexadecane); ^1H NMR (intensity in parentheses) $\delta(CH_3)$ 1.80 (s, 2.6) and 1.74 (s, 2.7) (SC_4H_9), 1.64 (s, 16.1 $P(OC_4H_9)_3$); $^{31}P\{^1H\}$ NMR δ 78.5 (s) (benzene-d_6). Anal. Calcd for $C_{34}H_{72}S_2P_2O_8Ir_2$: C, 36.47; H, 6.49; mol wt, 1119. Found: C, 36.90; H, 6.58; mol wt., 1070.

Reaction of $[Ir(\mu\text{-}S\text{-}t\text{-}Bu)(CO)(P(O\text{-}t\text{-}Bu)_3)]_2$ (1) with H_2. Preparation $[Ir(H)_2(\mu\text{-}S\text{-}t\text{-}Bu)(CO)(P(O\text{-}t\text{-}Bu)_3)]_2$ (3) and Spectroscopic Characterization of $[(CO)(P(O\text{-}t\text{-}Bu)_3)(H)_2Ir(\mu\text{-}S\text{-}t\text{-}Bu)_2Ir(P(O\text{-}t\text{-}Bu)_3)(CO)]$ (2). A solution of $[Ir^I(\mu\text{-}S\text{-}t\text{-}Bu)(CO)(P(O\text{-}t\text{-}Bu)_3)]_2$ (1) (0.260 g, 0.23 mmol) in degassed hexane (15 mL) was allowed to absorb hydrogen in a hydrogenation apparatus, at room temperature and atmospheric pressure. The solution changed from orange to pale yellow. The absorption was found to correspond to 2 mol of hydrogen/mol of the starting material. The reaction time was 4 h. Pale yellow crystals of 3 (0.194 g, 75%) were obtained upon cooling the hexane solution at −20 °C: IR ν(CO) 1990 (vs), 1982 (s), cm^{-1}, ν(IrH) 2165 (s), 2103 (br) cm^{-1} (hexadecane); $^{31}P\{^1H\}$ NMR 56.7 ppm (s); ^{31}P NMR 56.7 ppm (br t, J_{PH} = 20 Hz) (benzene-d_6); ^1H NMR $\delta(CH_3)$ 1.76 and 1.66 (SC_4H_9), 1.55 ($P(O\text{-}t\text{-}Bu)_3$); high-field ^1H NMR, two doublet of doublets of equal intensities at δ(H) −5.71 (J_{HH} = 3.7 Hz, J_{PH} = 21.3 Hz) and −15.35 (J_{HH} = 3.7 Hz, J_{PH} = 20.6 Hz). Anal. Calcd for $C_{34}H_{76}S_2P_2O_8Ir_2$: C, 36.34; H, 6.83; mol wt, 1124.

(6) Maisonnat, A.; Poilblanc, R. *J. Organomet. Chem.* **1978**, *160*, 307–317.

(7) de Montauzon, D.; Poilblanc, R. *Inorg. Synth.* **1980**, *20*, 237–240.

(8) For IR data: vs = very strong; s = strong; m = medium; w = weak; br = broad. For NMR data: s = singlet; d = doublet; t = triplet; dd = doublet of doublet; dt = doublet of triplet; br = broad.

(9) Elegant, L.; Gal, J. F.; Jouany, C.; Jugie, G. *Can. J. Chem.* **1978**, *56*, 857–860.

Found: C, 36.84; H, 6.92; mol wt, 1110.

The reaction above was repeated with deuterium gas. Similarly, a pale yellow tetradeuteride derivative (3) was obtained: IR ν(CO) 2025 (vs), 2018 (s) cm^{-1} (hexadecane); $^{31}P\{^1H\}$ NMR 50.5 ppm (s) (benzene-d_6).

The IR spectrum of $[Ir(\mu\text{-S-}t\text{-Bu})(CO)(P(O\text{-}t\text{-Bu})_3)]_2$ (1) (0.072 g) in cyclohexane (15 mL) under a hydrogen atmosphere was monitored over a period of 4 h. In the ν(CO) region, the absorptions of the starting material, at 1958 and 1945 cm^{-1}, progressively decrease and two sets of new absorptions appear. A first set of absorptions at 1990 and 1982 cm^{-1}, attributable to the tetrahydrido derivative 3, progressively grows but two absorption bands of a second set at 2003 and 1950 cm^{-1}, attributable to an intermediate species (2), remain weak and approximately constant until the complete disappearance of the starting material and then slowly decrease. We did not observe the complete disappearance of these two weak bands. After 4 h, ν(CO) equals 2003 (vw), 1990 (vs), 1982 (vs), and 1950 (w) cm^{-1}, and later on, no significant changes of the spectrum were observed. In the terminal ν(IrH) region, two sets of absorptions appear: a first set at 2165 and 2103 cm^{-1}, for the tetrahydrido derivative 3, which gradually grows, and a second set at 2135 and 2085 cm^{-1}, detectable after 30 min and, then, progressively hidden by the first two bands.

After removal of H_2 under vacuum, the light yellow solution slowly loses hydrogen leading to quantitative recovery of the orange starting material 1. The intermediate species 2 observed during the hydrogenation reaction (ν(CO) 2003 and 1950 cm^{-1}) was also observed during the dehydrogenation reaction.

The above procedure was repeated with deuterium gas, verifying the ν(IrH) assignements. In the ν(CO) region, the formation of the tetradeuterio derivative 3 was observed at 2025 and 2018 cm^{-1} while an intermediate species (2) was observed at 2014 and 1950 cm^{-1}.

The $^{31}P\{^1H\}$ NMR spectra of the species in solution were obtained by repeating the procedure above in benzene-d_6 solution. The formation of the tetrahydrido derivative 3 was observed at δ 56.7, together with the presence of the intermediate 2 which exhibits two signals of equal intensities at 52.3 and 77.8 ppm. Similarly, with deuterium gas, the tetradeuterio derivative appears at δ 50.5 ppm and the intermediate species exhibits two signals of equal intensities at 50.3 and 76.4 ppm.

Reaction of $[Ir(\mu\text{-S-}t\text{-Bu})(CO)(P(O\text{-}t\text{-Bu})_3)]_2$ with C_4F_6. Preparation and Characterization of Two 1:1 Adducts $[(\eta^2\text{-}C_4F_6)(CO)(P(O\text{-}t\text{-Bu})_3)Ir(\mu\text{-S-}t\text{-Bu})_2Ir(P(O\text{-}t\text{-Bu})_3)(CO)]$ (4) and $\{[Ir(\mu\text{-S-}t\text{-Bu})(CO)(P(O\text{-}t\text{-Bu})_3)]_2(\mu\text{-}\eta^2\text{-}C_4F_6)\}$ (5). A solution of $[Ir(\mu\text{-S-}t\text{-Bu})(CO)(P(O\text{-}t\text{-Bu})_3)]_2$ (0.140 g) in hexane (15 mL) was saturated with hexafluoro-2-butyne and stored under 1 atm of hexafluoro-2-butyne for 48 h. The change in the IR spectrum indicated the formation of a complex (4) having two ν(CO) at 2008 and 1959 cm^{-1} and a ν(C≡C) at 1765 cm^{-1} and much more slowly of another complex (5) having two ν(CO) at 2015 and 2005 cm^{-1} and a ν(C≡C) at 1592 cm^{-1}.

Yellow crystals of 4 were obtained by fractional crystallization on cooling the hexane solution at −20 °C after a reaction time of 12 h. The elemental analysis indicated a 1:1 adduct formulation: IR ν(CO) 2008 (vs), 1959 (vs) cm^{-1}, ν(C≡C) 1765 cm^{-1} (hexadecane); $^{31}P\{^1H\}$ NMR, two doublets of equal intensities at 76.69 and 23.60 ppm ($^4J_{PP}$ = 10.3 Hz) (benzene-d_6); ^{19}F NMR, two singlets of equal intensities at 27.1 and 26.2 ppm (benzene-d_6). Anal. Calcd for $C_{38}H_{72}F_6S_2P_2O_8Ir_2$: C, 35.61; H, 5.67. Found: C, 35.57; H, 5.66.

Compound 4 slowly transforms into another complex (5) in hexane solution, at room temperature, as shown by the changes in the IR spectrum in the ν(CO) and ν(C≡C) regions. After 5 days, this new complex was quantitatively obtained. Orange crystals of 5 were obtained on cooling the hexane solution at −20 °C. The elemental analysis was also consistent with a 1:1 adduct formulation: IR ν(CO) 2015 (vs), 2006 (vs) cm^{-1}, ν(C≡C) 1592 cm^{-1} (hexadecane); $^{31}P\{^1H\}$ NMR 34.18 (s) (benzene-d_6). ^{19}F NMR 26.9 (s) ppm (benzene-d_6). Anal. Calcd for $C_{38}H_{72}F_6S_2P_2O_8Ir_2$: C, 35.61; H, 5.67. Found: C, 36.21; H, 5.65.

Reaction of $[(\eta^2\text{-}C_4F_6)(CO)(P(O\text{-}t\text{-Bu})_3)Ir(\mu\text{-S-}t\text{-Bu})_2Ir(CO)(P(O\text{-}t\text{-Bu})_3)]$ (4) with H_2. Preparation of $[(\eta^2\text{-}C_4F_6)(CO)(P(O\text{-}t\text{-Bu})_3)Ir(\mu\text{-S-}t\text{-Bu})_2Ir(CO)(P(O\text{-}t\text{-Bu})_3)(H)_2]$ (6). A solution of $[(\eta^2\text{-}C_4F_6)(CO)(P(O\text{-}t\text{-Bu})_3)Ir(\mu\text{-S-}t\text{-Bu})_2Ir(CO)(P(O\text{-}t\text{-Bu})_3)]$ (4) in hexane was saturated with hydrogen and stored under 1 atm of hydrogen at room temperature. After 6 h, the initial compound 4 was consumed as indicated by the IR spectrum, and pale yellow crystals of a mixed dihydrido(hexafluoro-2-butyne)diiridium(III) adduct (6) were obtained on cooling the hexane solution at −20 °C: IR ν(CO) 2005 (vs), 1995 (vs) cm^{-1}, ν(C≡C) 1763 (m) cm^{-1}, ν(IrH) 2153 (br), 2115 (br) cm^{-1} (hexane); $^{31}P\{^1H\}$ NMR, two doublet of doublets of equal intensities at 47.93 and 22.62 ppm ($^4J_{PP}$ = 8.8 Hz) (benzene-d_6); high-field ^1H NMR, two multiplets of equal intensities at δ 5.53 (dt, $^2J_{HH}$ = 3.2, $^4J_{PH}$ = 3.2, $^2J_{PH}$ = 22.8 Hz) and 15.56 (dd, $^2J_{HH}$ = 3.2, $^2J_{PH}$ = 25.3 Hz); ^{19}F NMR, two singlets of equal intensities at 27.5 and 26.6 ppm (benzene-d_6). Removal of H_2 under vacuum followed by heating at 60 °C leads to quantitative recovery of the starting compound 4.

A deuterium analogue, $[(\eta^2\text{-}C_4F_6)(CO)(P(O\text{-}t\text{-Bu})_3)Ir(\mu\text{-S-}t\text{-Bu})_2(CO)(P(O\text{-}t\text{-Bu})_3)(D)_2]$ was similarly obtained with D_2: IR ν(CO) 2017 (vs), 2005 (vs) cm^{-1}, ν(C≡C) 1763 (m) cm^{-1} (hexane). $[(\eta^2\text{-}C_4F_6)(CO)(P(O\text{-}t\text{-Bu})_3Ir(\mu\text{-S-}t\text{-Bu})_2Ir(CO)(P(O\text{-}t\text{-Bu})_3)(H)_2]_2$ was also quantitatively obtained when a mixture of the dihydrido intermediate $[(CO)(P(O\text{-}t\text{-Bu})_3)(H)_2Ir(\mu\text{-S-}t\text{-Bu})_2Ir(CO)(P(O\text{-}t\text{-Bu})_3)]$ (2) and of the tetrahydrido adduct $[Ir(H)_2(\mu\text{-S-}t\text{-Bu})(CO)(P(O\text{-}t\text{-Bu})_3)]_2$ (3) was treated by hexafluoro-2-butyne.

Table I. CO Stretching Frequencies of $[Ir(\mu\text{-S-}t\text{-Bu})(CO)(PR_3)]_2$ Complexes and Cone Angles of PR_3 Ligands

R	ν(CO),[a] cm^{-1} (hexadecane)	cone angle,[b] deg
Me	1955 (vs), 1941 (vs)	118
NMe_2	1959 (vs), 1943 (vs)	160
O-t-Bu	1958 (vs), 1945 (vs)	182

[a] From ref 1. [b] From ref 10.

Results and Discussion

As shown by CO stretching frequencies of $[Ir(\mu\text{-S-}t\text{-Bu})(CO)(PR_3)]$ (Table I), the tri-*tert*-butyl phosphite, tris(dimethylamino)phosphine, and trimethylphosphine ligands exert quite analogous electronic influence to the metal basicity, but with a cone angle of about 182°,[10] $P(O\text{-}t\text{-Bu})_3$ appears as one of the bulkiest phosphorus ligands. Therefore, $[Ir(\mu\text{-S-}t\text{-Bu})(CO)(P(O\text{-}t\text{-Bu})_3)]_2$ is an appropriate candidate to study the steric influence of the terminal ligands toward the addition of small molecules to dinuclear complexes.

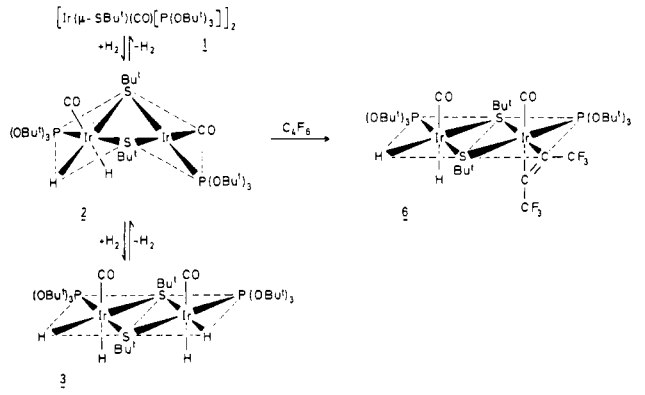
Addition of H_2 to $[Ir(\mu\text{-S-}t\text{-Bu})(CO)(P(O\text{-}t\text{-Bu})_3)]_2$ (1). The complex $[Ir(\mu\text{-S-}t\text{-Bu})(CO)(P(O\text{-}t\text{-Bu})_3)]_2$ (1) adds molecular hydrogen reversibly in hexane, toluene, or dichloromethane solution, at room temperature and at 1 atm. Elemental analysis, molecular weight data, volumetic measurements of H_2 uptake, and intensity ratios in NMR spectra show that the final product is correctly formulated as a 2:1 adduct $[Ir(H)_2(\mu\text{-S-}t\text{-Bu})(CO)(P(O\text{-}t\text{-Bu})_3)]_2$ (3). In the IR spectrum, the ν(IrH) vibrations appear in the terminal Ir–H region. In the deuterium analogue, ν(IrD) appear in the region expected in consideration of the isotopic effect.

The proton-decoupled ^{31}P NMR spectrum, in benzene-d_6, shows one singlet at 54.18 ppm whereas the nondecoupled ^{31}P NMR spectrum appears as a triplet with broad components and with triplet spacings of about 20 Hz.

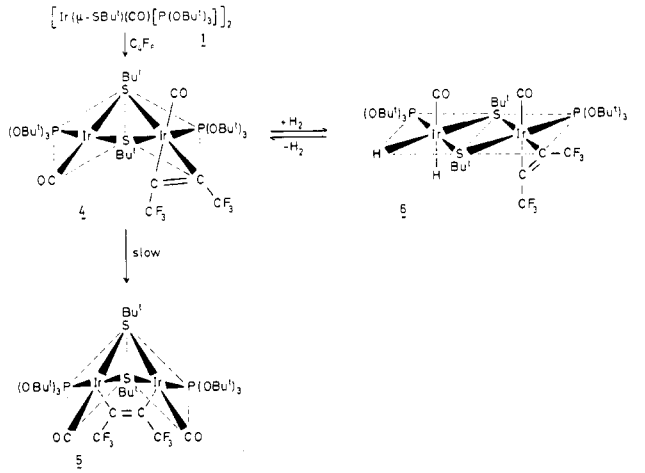
The proton spectrum exhibits one singlet for the phosphite protons (δ 1.55), two singlets of equal intensities for the S-*t*-Bu protons(δ 1.76, 1.66), and two doublet of doublets of equal intensities in the high-field region for the hydride protons (δ −5.98 ($^2J_{HH}$ = 3.7 Hz, $^2J_{PH}$ = 21.3 Hz), −16.62 ($^2J_{HH}$ = 3.7 Hz, $^2J_{PH}$ = 20.6 Hz)). Integration of these three types of proton signals gives approximately

(10) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

Scheme III



Scheme IV



total areas in the expected ratios 27:9:2. The problem of the multiplicity of the high-field signals and the coupling attributions was unambiguously resolved by homonuclear (^1H) and heteronuclear ($^1H\{^{31}P\}$) double-resonance techniques.

These data clearly indicate a symmetric thiolato-bridged diiridium (III) species containing two equivalent phosphites, two groups of two equivalent hydrides, and two nonequivalent S-*t*-Bu groups. Each metal atom is then surrounded by two hydrides, one phosphite, one terminal carbonyl ligand, and two *tert*-butylthiolato-bridging ligands. On each iridium, both hydrides and the phosphite ligand are mutually cis as indicated by the $^2J_{PH}$ and $^2J_{HH}$ values.[11] The comparison of the vibrational spectra of the tetrahydrido and of the tetradeuterio analogues reveals a strong resonance interaction between ν(IrH) and ν(CO) modes and, consequently, indicates a mutual trans disposition between one H and the CO ligands.[12] The other hydride is then necessarily trans to one *tert*-butylthiolato ligand, and the phosphite is trans to the other *tert*-butylthiolato ligand. The presence of two CO bands is not consistent with a centrosymmetric configuration, and the most probable structure for **3** is shown in Scheme III.

The only intermediate **2** observed during either the hydrogenation of **1** or the dehydrogenation of **3** processes exhibits in $^{31}P\{^1H\}$ NMR two poorly resolved signals of equal intensities centered at 52.3 and 77.8 ppm and, in the IR spectrum, two ν(IrH) bands at 2135 and 2085 cm^{-1} and two ν(CO) bands at 2003 and 1950 cm^{-1}. The higher frequency absorption alone is affected by the resonance interaction between the ν(IrH) and ν(CO) modes as revealed by the comparison of the spectra of the hydrido and deuterio intermediates **2**. (The deuterio intermediate **2** exhibits two ν(CO) at 2014 and 1950 cm^{-1}). These observations, compared to the spectroscopic data of compounds **1** and **3**, strongly suggest a unsymmetrical diiridium species in which one of its iridium atoms, namely, Ir(III), has the same coordination as both metal atoms in the tetrahydrido compound **3** while the other one, namely, Ir(I), has the same coordination as both metal atoms in the starting compound **1**.

These results are of special interest since, in contrast with the previously studied homologous compounds, it appears that $[Ir(\mu\text{-S-}t\text{-Bu})(CO)(P(O\text{-}t\text{-Bu})_3)]_2$, adds successively and reversibly 2 mol of dihydrogen leading, therefore, to a 2:1 adduct by the intermediacy of a 1:1 adduct[13] (Scheme III).

The initial attack of molecular hydrogen occurs at one of the metal centers, as previously suggested,[1] and it is of interest that whereas Ir(I) is allowed to add further hydrogen, the formation of a symmetrical dihydride seems to be forbidden. According to our previous observations and proposal, the result is consistent with a determining influence of the bulkiness of the terminal ligands on the iridium to iridium migration of hydride ligand. More precisely, one can imagine that the folding up of the Ir_2S_2 core around the SS axis is considerably hindered by the presence of the bulky *tert*-butyl phosphite ligand, preventing the migration process and leaving the second Ir(I) atom free for addition of a second H_2 molecule.

Addition of C_4F_6 to $[Ir(\mu\text{-S-}t\text{-Bu})(CO)(P(O\text{-}t\text{-Bu})_3)]_2$ (1). The reaction of $[Ir(\mu\text{-S-}t\text{-Bu})(CO)(P(O\text{-}t\text{-Bu})_3)]_2$, in hexane, with an excess of hexafluoro-2-butyne, at room temperature, leads to formation of a complex (**4**) for which chemical and spectroscopic data are consistent with a dimeric 1:1 adduct formulation: $[Ir(\mu\text{-S-}t\text{-Bu})(CO)(P(O\text{-}t\text{-Bu})_3)]_2[CCF_3]_2$.

The infrared spectrum of **4** shows two ν(CO) bands at 2008 and 1959 cm^{-1} and a $\nu(C{\equiv}C)$ band at 1765 cm^{-1} which is attributed to a π-bonded alkyne. The proton-decoupled ^{31}P NMR spectrum shows two doublets of equal intensities at 76.69 and 23.60 ppm, with a doublet spacing of 10.3 Hz. The ^{19}F NMR spectrum, showing two singlets of equal intensities at 27.1 and 26.2 ppm, indicates two nonequivalent CF_3 groups. These data clearly indicate an unsymmetrical 1:1 adduct in which C_4F_6 has added to only one metal atom. The phosphite ligand on that iridium(III) atom gives rise to the higher field doubled in the ^{31}P spectrum, and the CO ligand at that end gives rise to the higher frequency band in the ν(CO) IR spectrum. The other metal atom preserves the same coordination as both iridiums in the starting compound **1**, as reflected by the chemical shift of the lower field doublet in the ^{31}P spectrum and by the position of the lower frequency band in the ν(CO) IR spectrum.

In hexane solution, complex **4** very slowly transforms into a new species (**5**) for which chemical and spectroscopic data again are consistent with a dimeric 1:1 adduct formulation. In contrast with **4**, the $^{31}P\{^1H\}$NMR spectrum

(11) For J_{HH} values in mononuclear and dinuclear hydridoiridium(III) complexes, see, for example: (a) Chatt, J.; Coffey, R. S.; Shaw, B. L. *J. Chem. Soc.* **1965**, 7391–7405. (b) Mann, B. E.; Masters; C.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1970**, 846–847. (c) Mann, B. E.; Masters, C.; Shaw, B. L. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2195–2204. (d) Reference 6.

(12) No resonance interaction between ν(IrH) and ν(CO) modes has been detected between H and CO ligands in a mutual cis disposition. See, for example: (a) Vaska, L.; Diluzio, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 679–680. (b) Vaska, L. *Chem. Commun.* **1966**, 614–616. (c) *J. Am. Chem. Soc.* **1966**, *88*, 4100–4101. (d) Reference 1.

(13) We checked that the formation of the intermediate **2** is not due to a redistribution of the hydride ligands between **1** and **3**.

5 shows a single singlet at 34.18 ppm and the ^{19}F NMR spectrum shows a single singlet at 26.9 ppm. The infrared spectra show two $\nu(CO)$ bands at 2015 and 2006 cm^{-1} and, more significantly, a $\nu(C{\equiv}C)$ band at 1597 cm^{-1} instead of at 1765 cm^{-1} for **4**. These data, compared to those previously published for the $(CCF_3)_2$ adducts of $[Fe(CO)_3(\mu\text{-}SR)]_2$ (R = CF_3,[14a] CH_3, and C_6H_5[14b]), $[IrCOD(\mu\text{-}pz)]_2$,[15] $[Pd(\mu\text{-}dppm)Cl]_2$,[16] $(\eta^5\text{-}C_5H_5)Rh(CO)_2$,[17] $[RhCl(CO)(\mu\text{-}dppm)]_2$[18] and for the $(CCF_3)_2$ and the $[C(COOCH_3)]_2$ adducts of $[Ir(\mu\text{-}S\text{-}t\text{-}Bu)(CO)(P(OMe)_3)]_2$,[3] demonstrate for **5** a symmetrical dimeric configuration, in which the alkyne group, σ bonded to both iridiums, is parallel to the iridium–iridium axis, as shown in Scheme IV. It is, therefore, expected that compound **5** has an iridium–iridium bond.

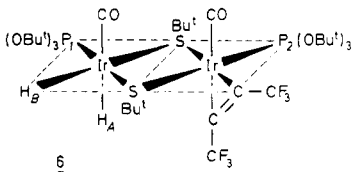
By reference to the previously studied homologous compounds, for which the addition of activated alkynes yields quantitatively and readily symmetrical 1:1 adducts, this result points out a significative feature on the mechanism of the addition of C_4F_6 to $[Ir(\mu\text{-}S\text{-}t\text{-}Bu)(CO)(PR_3)_2]$ complexes. As already observed for the addition of dihydrogen, the initial attack of the substrate occurs at one of the metal centers. The transformation of the resulting unsymmetrical 1:1 adduct into the symmetrical one, containing a dimetallacyclobutene ring, not only suppose an intramolecular electron redistribution but also a significant change in geometry. Namely, this transformation which must be accompanied by a pinching of the Ir_2S_2 core around the SS axis is considerably hindered by the presence of the bulky *tert*-butyl phosphite ligand.

Addition of H_2 to $[(P(O\text{-}t\text{-}Bu)_3)(CO)Ir(\mu\text{-}S\text{-}t\text{-}Bu)_2Ir(CO)(P(O\text{-}t\text{-}Bu)_3)(\eta^2\text{-}C_4F_6)]$ (4). Although the Ir(I) atom in **4** remains open to attack by electrophilic reagents, we did not observe the addition of further C_4F_6 to yield a 2:1 adduct. But the reaction of **4** in hexane with H_2, at room temperature and atmospheric pressure, leads to formation of a complex (**6**) identified as $[Ir(\mu\text{-}S\text{-}t\text{-}Bu)(CO)(P(O\text{-}t\text{-}Bu)_3)]_2(H)_2C_4F_6)]$ (Scheme IV).

The infrared spectra of **6** show two $\nu(IrH)$ bands at 2153 and 2115 cm^{-1} and two $\nu(CO)$ bands, at 2005 and 1995 cm^{-1}. One of the CO frequencies band is affected by the resonance interaction between the $\nu(IrH)$ and the $\nu(CO)$ modes (the deuterio analogue exhibits two $\nu(CO)$ at 2017 and 2005 cm^{-1}). The $\nu(C{\equiv}C)$ absorption, at 1763 cm^{-1}, is attributed to a π-bonded alkyne at one iridium center. The $^{31}P\{^1H\}$ NMR spectrum indicates two nonequivalent and mutually coupled phosphorus nuclei P_1 and P_2 ($\delta(P_1)$ 47.93 and $\delta(P_2)$ 22.62 ($J_{P_1P_2}$ = 8.8 Hz)). The ^{19}F NMR spectrum indicates two nonequivalent CF_3 groups. The high-field ^1H NMR spectrum shows two sets of signals of equal intensities corresponding to two types of nonequivalent protons $\delta(H_A)$ and $\delta(H_B)$. The first set appears as a doublet of triplets centered at $\delta(H_A)$ −5.53 with a doublet splitting of 22.8 Hz and a triplet splitting of 3.2 Hz. The second set appears as a doublet of doublets centered at $\delta(H_B)$ −15.56 with doublet splittings of 25.3 and 3.2 Hz. The problem of the multiplicity of these hydride signals was unambiguously resolved by homonuclear and heteronuclear ($^1H\{^{31}P\}$) double-resonance techniques.[19]. These experiments indicate that H_A and H_B, H_A and P_2, H_A and P_1, and H_B and P_1 are coupled together with coupling constants $J_{H_AH_B}$ = 3.2 Hz, $J_{H_AP_2}$ = 3.2 Hz, $J_{H_AP_1}$ = 22.8 Hz, and $J_{H_BP_1}$ = 25.3 Hz.

These results suggest a unsymmetrical thiolato-bridged dimer in which one iridium atom is surrounded by one carbonyl, one phosphite, and two hydride ligands, whereas the other is surrounded by one carbonyl, one phosphite, and the alkyne ligands.

Moreover, the magnitude of the $J_{H_AH_B}$, $J_{H_AP_1}$ and $J_{H_BP_1}$, together with the existence of two $\nu(IrH)$ bands and of a strong resonance interaction between $\nu(IrH)$ and $\nu(CO)$ modes, indicate that one iridium atom of **6** has the same coordination as both metal atoms in the tetrahydrido complex **3** previously described, namely, two hydride and one phosphite ligands mutually cis and one hydride and one carbonyl ligands mutually trans.



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It is noteworthy that similar compounds were previously obtained by the reaction of hexafluoro-2-butyne with solutions of symmetrical dihydridodiiridium complexes $[Ir(H)(\mu\text{-}S\text{-}t\text{-}Bu)(CO)(PR_3)]_2$ (R = OMe, Me).[6]

More significantly, complex **6** was also obtained by the reaction of hexafluoro-2-butyne with a solution of the tetrahydrido diiridium complex **3** containing the dihydrido unsymmetrical intermediate **2** (Scheme III). In that case, the formation of **6** could then be explained by oxidative addition of the alkyne on the Ir(I) atom of the intermediate **2**.

Finally, the unsymmetrical dihydrido complexes $[(H)_2PR_3(CO)Ir(\mu\text{-}S\text{-}t\text{-}Bu)_2Ir(CO)(PR_3)]$ can be proposed as the common intermediates in the hydrogenation of $[Ir(\mu\text{-}S\text{-}t\text{-}Bu)(CO)(PR_3)]_2$ complexes whatever the size of the phosphorus ligand.

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Registry No. **1**, 86119-65-5; **2**, 86119-66-6; **3**, 86119-67-7; **4**, 86119-68-8; **5**, 86119-69-9; **6**, 86119-70-2; $[Ir(\mu\text{-}S\text{-}t\text{-}Bu)(CO)_2]_2$, 63312-27-6; C_4F_6, 692-50-2; Ir, 7439-88-5; H_2, 1333-74-0; tri-*tert*-butyl phosphite, 15205-62-6.

(14) (a) Davidson, J. L; Harrison, W.; Sharp, D. W. A.; Sim, G. A. *J. Organomet. Chem.* **1972**, *46*, C47–C49. (b) Mathieu, R.; Poilblanc, R. *Ibid.* **1977**, *142*, 351–355.

(15) Coleman, A. W.; Eadie, D. T.; Stobart, S. R.; Zaworotko, M. J.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 922–923.

(16) Balch, A. L.; Lee, C. L.; Lindsay, C. H.; Olmstead, M. M. *J. Organomet. Chem.* **1979**, *177*, C22–C26.

(17) Dickson, R. S.; Kirsch, H. P.; Lloyd, D. J. *J. Organomet. Chem.* *1975*, 101, C48–C50.

(18) Cowie, M.; Southern, T. G. *J. Organomet. Chem.* **1980**, *193*, C46–C50.

(19) In ^1H NMR, irradiation at δ −5.53 causes the doublet of doublets at −15.56 ppm to be changed to a simple doublet with a splitting of 25.3 Hz. Irradiation of δ −15.56 causes the doublet of triplets at −5.53 ppm to be transformed into a doublet of doublets, with splittings of 22.8 and 3.2 Hz. Irradiation at $\delta(P_2)$ 22.62 (H_3PO_4) causes the doublet of triplets at −5.53 ppm to be transformed into a doublet of doublets with splittings of 22.8 and 3.2 Hz, and the poorly resolved doublet of doublets at −15.56 ppm into a well-resolved doublet of doublets. Irradiation at $\delta(P_1)$ 47.92 causes the doublet of triplets at −5.53 ppm to be transformed into a simple triplet with splitting of 3.2 Hz, whereas the doublet of doublets at −15.56 ppm is transformed into a simple doublet with splitting of 3.2 Hz.