Reactivity of μ-η-Alkyne-Bridged Dinuclear Iridium(II) Complexes $[Ir(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2RCCR$ (A = CH_3, C_6H_5; R = CF_3, $CH_3OC(O)$) toward Hydrogen. An Insight into the Mechanism of These Reactions by a Study of Their Reaction with Formic Acid. A Competitive Elimination of *t*-BuSH and of Alkene

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The $[Ir(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2RCCR$ complexes (A = CH_3, C_6H_5; R = $CH_3OC(O)$, CF_3) react with hydrogen at atmosphere pressure, the reaction path depending on the nature of A. In the case of A = CH_3, the complexes $H_2Ir_2(\mu\text{-H})(\mu\text{-S-}t\text{-Bu})(CO)_2[P(CH_3)_3]_2RCCR$ have been isolated and 1 mol of *t*-BuSH has been eliminated. In the case of A = C_6H_5, the compound $[HIr(\mu\text{-S-}t\text{-Bu})(CO)P(C_6H_5)_3]_2$ is formed with elimination of the cis alkene RCH=CHR. With the $[Ir(\mu\text{-S-}t\text{-Bu})(CO)[P(C_6H_5)_2CH_3]]_2[CH_3OC(O)C]_2$ complex, both paths have been observed. By the action of formic acid on $[Ir(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2RCCR$ complexes (A = CH_3, C_6H_5; R = CF_3, $CH_3OC(O)$) in the acid/complex ratios of 1/1 and 2/1, the complexes $[IrH(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2RCCR$ (**8**, A = C_6H_5, R = $CH_3OC(O)$; **10**, A = CH_3, R = CF_3), $[Ir_2H(\mu\text{-S-}t\text{-Bu})(CO)_2][P(C_6H_5)_3]_2[CH_3OC(O)C]_2$ (**9**), $[Ir_2H(\mu\text{-S-}t\text{-Bu})(\mu\text{-H})(S\text{-}t\text{-Bu})(CO)_2[P(CH_3)_3]_2][CH_3OC(O)C]_2$ (**11**), and $Ir_2H_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-H})(CO)_2[P(C_6H_5)_3]_2[CH_3OC(O)C]_2$ (**12**) have been isolated. The inertness of complexes **8** and **10** toward further action of hydrogen and the isolation of **11** in which one of the S-*t*-Bu bridges is in a terminal position clearly show that the first step in the action of molecular hydrogen is the opening of one of the S-*t*-Bu bridges which creates a vacant site on one iridium. Furthermore, it is shown that elimination of alkene results from the action of *t*-BuSH on **12**. The factors that prevent this elimination of alkene in the $P(CH_3)_3$ complexes are discussed.

Introduction

The chemistry of organic molecules bridging two metal centers is a growing field of interest, and in this context the chemistry of bridged alkyne (μ-η^1 bonded) complexes takes an important place.[1-6]

We have recently shown that in dinuclear iridium(II) complexes $[Ir(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2RCCR$, the μ-η^1-bonded alkyne is inert toward protonation.[6] We have now extended the study of the reactivity of this type of complex to the action of hydrogen. Indeed, if the reactivity of hydrogen toward complexes containing bridging μ-η^2-bonded alkyne ligands has been studied,[7] the case of complexes containing μ-η^1-bridged alkynes has not yet been considered.

Two types of problems are underlying this study: (i) it could be a priori imagined that, as the iridium centers are formally in the oxidation state II, the initial addition of hydrogen occurs either on one iridium center leading to an iridium(IV) center or on two iridium centers leading to two iridium(III) centers; (ii) if hydrogenation of the alkyne is observed, is some degree of stereospecificity of the hydrogenation promoted by a dimetal center?

We have found that the products of the reaction of hydrogen with $[Ir(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2RCCR$ compounds are dependent on the nature of the phosphine ligand. Furthermore, attempts to isolate intermediates during the action of hydrogen have failed as the heterogeneous nature of the reaction (liquid, gas reaction) prevents the use of exact stoichiometric conditions.

To overcome this difficulty, we thought of using the ability of iridium complexes to oxidatively add formic acid, leading to hydride complexes after decarboxylation.[8]

In this case, formic acid could thus be considered as a "soluble form" of hydrogen, but the mechanisms of the reactions of molecular hydrogen and formic acid could be a priori very different. Nevertheless, observation of the hydride part of the reaction mixture during the action of hydrogen and formic acid shows signals common to both systems. Furthermore, it has to be pointed out that in no case can intermediate formato complexes be detected. Consequently, the study of the action of formic acid on our complexes could be expected to lead to the isolation of some intermediates of the reaction of molecular hydrogen.

Results

Action of Hydrogen. The compounds $[Ir(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2RCCR$ (**1**)[9] react with hydrogen under atmospheric pressure and at room temperature if A = CH_3 and R = CF_3 or $CH_3OC(O)$, but if A = C_6H_5, heating to 40 °C (R = $CH_3OC(O)$) or 60 °C (R = CF_3) is necessary. As the path of the reaction is phosphine dependent, we will consider our results for each phosphine, including the case with the ligand $P(C_6H_5)_2CH_3$. In this study, we have further included a complex with two different bridges, $[Ir_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-}CF_3COO)(CO)_2[P(C_6H_5)_3]_2]RCCR$, which results from the action of trifluoroacetic acid on **1**.[6]

Action of Hydrogen on $[Ir(\mu\text{-S-}t\text{-Bu})(CO)P(CH_3)_3]_2RCCR$ Compounds (R = CF_3, $CH_3OC(O)$). At the end of the reaction, the reaction solution smells of *tert*-butanethiol. In both cases, the same type of complex is isolated from the solution (**2a** (R = $CH_3OC(O)$, **2b** (R

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(6) El Amane, M.; Mathieu, R.; Poilblanc, R. *Nouv. J. Chim.* **1982**, *6*, 191.
(7) Muetterties, E. L. *Inorg. Chim. Acta* **1981**, *50*, 1 and references therein.
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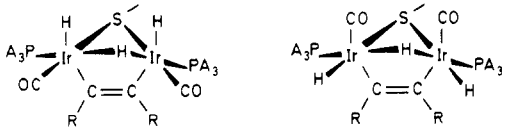

Figure 1. Proposed structures for complexes **2a** and **2b**.

= CF_3)). The two compounds show two infrared-active bands in the ν(CO) stretching region shifted toward higher frequencies (about 35 cm^{-1}) compared to those of the starting material (Table I). A band of medium intensity at 1535 (R = $CH_3OC(O)$) or 1578 cm^{-1} (R = CF_3) attributed to the ν(C=C) stretching mode of the alkyne group[6] shows the alkyne to be retained in the reaction.

The proton NMR spectrum of **2a** (Table I) presents one singlet for the OCH_3 group of the alkyne, one triplet ($X_9AA'X'_9$ spin system) for the $P(CH_3)_3$ resonance, and one singlet for the S-*t*-Bu group. The intensity ratio of these three signals is 6:18:9, showing clearly that one S-*t*-Bu group has been lost during the reaction.

In the hydride resonance region, two signals appear in a 2:1 intensity ratio. The first signal is an AAXX′ spin system (J_{AX} = 64 Hz) while the higher field signal is an AX_2 spin system (J_{AX} = 64 Hz). The same type of spectrum is observed for **2b** (Table I).

From these results, we can conclude that molecules **2a** and **2b** both possess two kinds of hydrides: two terminal hydrides and one bridging hydride. The latter is trans to the phosphine ligands as shown by the value of the coupling constant (64 Hz).[10,11] This bridging hydride has replaced one of the S-*t*-Bu bridges. Two structures are consistent with the spectroscopic results (Figure 1): one in which the terminal hydrides are in axial position, the other in which these hydrides are in equatorial position. Finally, the reaction may be summarized by eq 1.

$$[Ir(\mu\text{-S-}t\text{-Bu})COP(CH_3)_3]_2RCCR + 2H_2 \rightarrow t\text{-BuSH} + [H_2Ir_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-H})(CO)_2[P(CH_3)_3]_2]RCCR \quad (1)$$

The products **2a** and **2b** appear as the result of the addition of 2 mol of hydrogen and of the elimination of 1 mol of *tert*-butanethiol.

Action of Hydrogen on the Compounds [Ir(μ-S-*t*-Bu)COP(C_6H_5)$_3$]$_2$RCCR (R = CF_3, C(O)OCH_3). In the case of R = $C(O)OCH_3$, hydrogenation occurs at 40 °C and the complex isolated at the end of the reaction has the same characteristics (Table I) as the product of hydrogenation of [Ir(μ-S-*t*-Bu)(CO)P(C_6H_5)$_3$]$_2$, i.e., [Ir(H)(μ-S-*t*-Bu)(CO)P(C_6H_5)$_3$]$_2$ (**3**).[12]

A proton NMR investigation of the remaining solution gives evidence of the formation of dimethyl maleate (δ(H) 6.80, δ(OCH_3) 3.78) and of traces of dimethyl fumarate (δ(H) 6.35, δ(OCH_3) 3.80), by comparison with authentic samples. We have checked that the amount of dimethyl fumarate increases with time at room temperature in the presence of the hydride **3**, which suggests that **3** catalyzes the isomerization of dimethyl maleate to dimethyl fumarate. The reaction may be summarized by eq 2, i.e., hydrogenation of the alkyne to the cis alkene and formation

$$[Ir(\mu\text{-S-}t\text{-Bu})(CO)P(C_6H_5)_3]_2[CH_3OC(O)CCC(O)OCH_3] + 2H_2 \longrightarrow \underset{CH_3OC(O)}{\overset{H}{}}\!\!>C=C<\!\!\underset{C(O)OCH_3}{\overset{H}{}} + [IrH(\mu\text{-S-}t\text{-Bu})(CO)P(C_6H_5)_3]_2 \quad (2)$$

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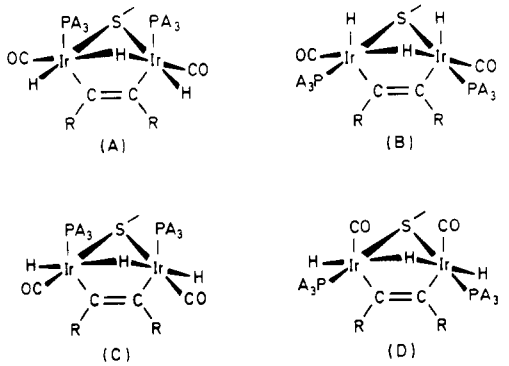


Figure 2. Proposed structures for complexes **4** and **6**.

of an Ir(II) complex, **3**. In the case of R = CF_3, it is necessary to run the reaction at 60 °C under atmospheric pressure of hydrogen to achieve hydrogenation.

Compound **3** can be isolated from the solution, and the proton NMR spectrum of the mother solution shows the existence of another complex, **4**, for which we propose, from the hydride resonance signal and by comparison with the case of $PCH_3(C_6H_5)_2$ complexes (Table I; vide infra), the formula $[Ir_2(H)_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-H})(CO)_2P(C_6H_5)_3]C_4F_6$. Its structure will be discussed later.

Considering the great dependence of the chemical reactivity of the compounds **1** on the nature of groups A, we have considered an intermediate case where the phosphine bonded to the iridium is $P(C_6H_5)_2CH_3$.

Action of Hydrogen on [Ir(μ-S-*t*-Bu)(CO)P(C_6H_5)$_2$$CH_3$]$_2$[$CH_3OC(O)C$]$_2$. Hydrogenation occurs at room temperature. Two complexes have been isolated from the solution by fractional crystallization. The first compound, **5**, has spectroscopic characteristics similar to those of **3** (Table I) and analyzed as [IrH(μ-S-*t*-Bu)(CO)[P(C_6H_5)$_2$$CH_3$]]$_2$. The second compound, **6**, has spectroscopic characteristics similar to those of **4**. Its infrared spectrum shows two bands in the ν(CO) stretching region. A weak band at 1560 cm^{-1} is assigned to the ν(C=C) stretching mode of the coordinated alkyne group indicates the alkyne ligand to be retained in the reaction.

The proton NMR spectrum shows, except for the phenyl resonance, a triplet ($X_3AA'X_3$ spin system) for the CH_3 resonance and a singlet for the S-*t*-Bu resonance. The intensity ratio of these three signals is 20:6:9 showing one S-*t*-Bu group is lost.

In the hydride region, two signals appear with the 2:1 intensity ratio. The first signal is an AA′XX′ spin system (J_{AX} = 13.5 Hz) while the higher field signal is an AX_2 spin system (J_{AX} = 12.1 Hz). Therefore, there are some similarities between **6** and **2a** or **2b**, except for the values of the coupling constants of the bridging hydride, which is consistent with the phosphine ligands in a cis position to this hydride. Four structures are compatible with these spectroscopic data. They are shown in Figure 2.

In summary, the behavior of the $P(C_6H_5)_2CH_3$ complex toward hydrogen is intermediate between those of the $P(CH_3)_3$ and $P(C_6H_5)_3$ complexes. Both paths are found, i.e., elimination of *t*-BuSH leading to compound **6** or elimination of dimethyl maleate leading to complex **5**.

Action of Hydrogen on [Ir$_2$(μ-S-*t*-Bu)(μ-CF_3COO)(CO)$_2$[P(C_6H_5)$_3$]$_2$]RCCR. It is necessary to carry out the reaction at 60 °C under atmospheric pressure of hydrogen. At the end of the reaction, the complex isolated, **7**, presents two infrared active bands in the ν(CO) stretching region (Table I) and no vibration is detected in the ν(C=C) stretching region.

The proton NMR spectrum shows the presence of one S-*t*-Bu group for two $P(C_6H_5)_3$ ligands. At very high field

Table I. Spectroscopic Data for the Isolated Complexes

	IR, cm^{-1}					^1H NMR,[c] δ							
compds	CO[a]	M—H	CO[b]	C=C	CO_2CH_3[b]	SC_4H_9	PA_3	J_{PH}, Hz	CO_2CH_3	M-H-M	J_{PH}, Hz	M-H	J_{PH}, Hz
2a	2030 vs[d]	e	2032 vs	1535 m	1682 vs	1.38	1.85 (t)	10.7	3.42	16.27 (t)	64.1	12.21 (t)	19.5
	2018 w												
2b	2035 vs	e											
	2025 w			1578 m		1.61	1.15 (t)	11.2		16.53 (t)	64.5	12.75 (t)	15
3	1990 vs[d]						7.45 (C_6H_5)					14.14 (t)	13.19
	1972 w	2132				0.50						14.99 (t)	14.30
	1965 w												
4	2032 vs	e		1588 m						16.57 (t)	8.8	11.66 (t)	11.8
5	1978 vs	2125[b]	1980 vs			1.07						13.76 (t)	13.2
	1955 w		1955 w			1.04	1.77 (t)	8.1				14.90 (t)	14.4
6	2028 vs[d]	e	2010 vs	1560 m	1690 vs	1.72	1.25 (t)	9.4	3.41	16.40 (t)	12.1	12.35 (t)	13.5
	2005 w		2000 w										
7	2002 vs		1998 vs				7.42 (C_6H_5)						
	1970 w	2068[b]	1965 w		1634 m[b]	0.58						24.53 (t)	14.7
8	2012 vs	2150 s	2000 vs	1590 m	1690 vs	0.80	7.44		3.88			14.43 (d)	13.3
	2015 sh		2015 vs										
9	2000 vs	2240 s	1993 vs		1698 vs	0.32	7.38		2.60	24.27 (dd)	2.9		
	1980 vs		1972 s		1650 vs				2.58		9.6		
10	2012 vs	2142 s	1998 s	1530 m		1.14	1.61 (d)	13.2				14.82 (d)	13.1
	2017 sh		2012 sh										
11	2044 vs[d]	e	2022 vs	1540 m	1672 vs	1.36	1.92 (d)	14.9	3.56	15.22 (dd)	54.4	11.48 (d)	17.5
	2022 vs		2088 vs			1.52		14.4	3.52		62.5		
12	2030 vs	2118	2032 vs	1580 m	1690 vs	1.16	7.22		3.37	6.28 (t)	11.1	12.02 (t)	13.1
	2020 w												

[a] In dichloromethane solution. [b] In CsBr dispersion. [c] In $CDCl_3$ but for 9 (CD_2Cl_2 solution) and 6 (C_6D_6 solution). [d] Hexadecane solution. [e] Not observed. [f] CO_2CF_3.

Table II. Physical and Analytical Data of the Complexes Isolated

					anal. data[a]			
compounds		color	mp, °C	yield, %	C, %	H, %	F, %	S, %
$Ir_2(H)_3(SC_4H_9)(CO)_2[P(CH_3)_3]_2[CH_3OC(O)C]_2$	2a	orange yellow	120	50	26.24 (26.15)	4.38 (4.35)		3.73 (3.87)
$Ir_2(H)_3(SC_4H_9)(CO)_2[P(CH_3)_3]_2C_4F_6$	2b	orange yellow	118	54	22.71 (22.67)	3.57 (3.54)		13.51 (13.45)
$[Ir(H)(SC_4H_9)(CO)P(C_6H_5)_3]_2$	3	yellow		85	52.19 (51.43)	4.92 (4.73)		
$[Ir(H)(SC_4H_9)(CO)PCH_3(C_6H_5)_2]_2$	5	yellow	140	40	42.05 (42.3)	4.53 (4.51)		
$Ir_2(H)_2(SC_4H_9)(\mu\text{-}H)(CO)_2[PCH_3(C_6H_5)_2]_2$	6	brown	138	35	43.91 (43.97)	4.71 (4.71)		
$Ir_2(H)_2(SC_4H_9)(CF_3COO)(CO)_2[P(C_6H_5)_3]_2$	7	yellow	158	80	44.48 (44.59)	3.65 (3.55)	4.72 (4.70)	
$[Ir(H)(SC_4H_9)(CO)P(C_6H_5)_3]_2(CH_3CO_2C)_2$	8	white	178	36	48.38 (48.48)	4.40 (4.35)		
$Ir_2(H)(SC_4H_9)(CO)_2[P(C_6H_5)_3]_2(CH_3CO_2C)_2CH_2Cl_2$	9	yellow		20	45.62 (45.21)	3.78 (3.69)	5.58 (Cl) (5.35)	
$[Ir(H)(SC_4H_9)(CO)P(CH_3)_3]_2(C_4F_6)$	10	white	>300	45	25.75 (25.66)	4.08 (4.06)	12.21 (12.19)	
$Ir_2(SC_4H_9)_2(H)_2(CO)_2[P(CH_3)_3]_2(CH_3CO_2C)_2$	11	yellow	140	10	28.85 (28.85)	4.97 (4.81)		
$Ir_2H_3(SC_4H_9)(CO)_2[P(C_6H_5)_3]_2(CH_3CO_2C)_2$	12	yellow	110	80	48.05 (48.04)	4.03 (4.12)		

[a] Theoretical values in parentheses.

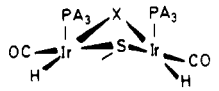


Figure 3. Proposed structures for complex **7** (X = CF_3COO).

(−24.53 ppm), an AA′XX′-type triplet is observed (J_{AX} = 14.7 Hz). This very high-field resonance could suggest the hydride to be in a bridging position,[13] but in iridium hydride complexes, bridging hydrides do not always resonate at a higher field than terminal hydrides.[14] Furthermore, a weak and broad band at 2068 cm^{-1} is detected in the infrared spectrum that is attributed to a terminal IrH stretching frequency.[12]

As the compound analyzes as $Ir_2(H)_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-}CF_3COO)(CO)_2[(P(C_6H_5)_3]_2$, we suggest a structure similar to **3** or **5**[12] in which the terminal hydrides are trans to the trifluoroacetato bridge (Figure 3). This trans position could explain the very high field observed for the resonance of the hydride.

Attempted Catalytic Hydrogenation of $CH_3OC(O)C{\equiv}CC(O)OCH_3$. We have seen the action of hydrogen on $[Ir(\mu\text{-S-}t\text{-Bu})(CO)P(C_6H_5)_3]_2[CH_3OC(O)C]_2$ to yield dimethyl maleate and the complex $[IrH(\mu\text{-S-}t\text{-Bu})COP(C_6H_5)_3]_2$ (**3**). In a recent study, Maisonnat and Poilblanc have shown the analogue of **3** with the $P(OCH_3)_3$ ligand to react with RC≡CR alkynes (R = CF_3, $CH_3OC(O)$) to generate a type 1 complex with hydrogen elimination.[15]

$$[IrH(\mu\text{-S-}t\text{-Bu})(CO)P(OCH_3)_3]_2 + RC{\equiv}CR \rightarrow [Ir(\mu\text{-S-}t\text{-Bu})(CO)P(OCH_3)_3]_2RCCR + H_2 \quad (3)$$

Thus, reaction 2 (phosphine ligand) together with reaction 3 (phosphite ligand) is a model for the steps of a possible catalytic hydrogenation cycle for the alkyne. In fact, at 40 °C under 1 atm of hydrogen, no catalytic hydrogenation of the alkyne occurs in the presence of complex **1** (A = C_6H_5). In the ν(CO) stretching region, complex infrared spectra of the solution give evidence that, with an excess of alkyne, **3** does not react as its trimethyl phosphite analogue with stoichiometric amounts of alkyne.

Action of Formic Acid. As in the case of the action of trifluoroacetic acid,[6] we have studied the action of stoichiometric amounts of formic acid with complex/acid ratios of 1/1 and 1/2.

Case of the Addition of 1 Equiv of Formic Acid to $[Ir(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2RCCR$ Complexes. In the case where A = C_6H_5 and R = CF_3, no reaction occurs.

Case Where A = C_6H_5 and R = $CH_3OC(O)$. The reaction is slow, and after 4 days a complex, **8**, is isolated. Monitoring the reaction by infrared spectroscopy allows the observation of one intermediate, **9**, which may be isolated if the reaction is stopped after four hours.

The spectroscopic properties of both compounds are gathered in Table I. The infrared spectrum of complex **8** presents two bands in the CO stretching region, one broad band at 2150 cm^{-1} attributed to a terminal Ir–H stretching frequency and a weak band at 1590 cm^{-1} which shows the μ-η^1-bonded alkyne to be retained in **8**.

Proton NMR resonances for the phenyl, methoxy, and *tert*-butylthio groups are observed in a 30/6/18 ratio. In the hydride region, one doublet with a coupling constant of 13 Hz and an intensity ratio of 2 is detected. The value of the coupling constant is characteristic of a cis position for the phosphine and hydride ligands.[13] The chemical

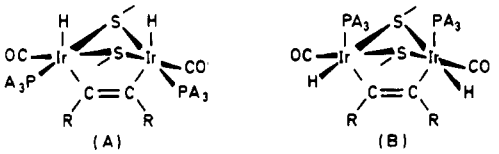


Figure 4. Proposed structures for complexes **8** and **10**.

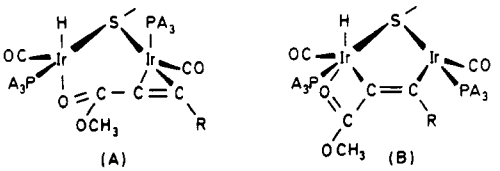


Figure 5. Proposed structures for complex **9**.

analysis is consistent with the formula $[IrH(\mu\text{-S-}t\text{-Bu})(CO)P(C_6H_5)_3]_2[CH_3OC(O)C]_2$ (Table II). The two structures in Figure 4 are consistent with the spectroscopic data.

The infrared spectrum of complex **9** (Table I) shows two bands separated by 20 cm^{-1} in the ν(CO) stretching region and a weak band at 2240 cm^{-1} that could be attributed to an Ir–H stretching frequency. In addition, two strong bands at 1698 and 1560 cm^{-1} are detected. The band at 1698 cm^{-1} is attributed to the CO ester group of the alkyne, but the 1560-cm^{-1} band is too strong to be attributed to the ν(C=C) mode of the coordinated alkyne. It seems more reasonable to attribute it to a stretching frequency of an ester group bonded by the oxygen to the iridium, a situation which has been observed for the $[[Fe(\mu\text{-}SCH_3)(CO)[P(CH_3)_3]_2]_2CH_3OC(O){=}C(H)C(O)OCH_3]^+$ complex.[2]

The proton NMR spectrum shows a complex signal for the phenyl resonance, two singlets for the OCH_3 resonance, and one singlet for the S-*t*-Bu group in the ratio of 30/3/3/9. In the hydride region, a doublet of doublets (J_1 = 2.9 and J_2 = 9.6 Hz) is detected at −24.27 ppm with the intensity ratio of 1. This very high-field resonance value has to be compared with the value found for the complex $[Ir_2(H)_2(\mu\text{-}CF_3COO)(\mu\text{-S-}t\text{-Bu})(CO)_2[P(C_6H_5)_3]_2]$ complex (−24.53 ppm) for which we suggest that the hydride is trans to the oxygen of the trifluoroacetate bridge.

The chemical analysis (Table II) agrees with NMR results and is consistent with the formula $Ir_2(H)(S\text{-}t\text{-Bu})(CO)_2[P(C_6H_5)_3]_2[CH_3OC(O)C]_2$. All the spectroscopic data indicate an unsymetrical structure: one of the CO ester groups is bonded to one iridium atom and the hydride is coupled to two different phosphorus atoms. Furthermore, the very high-field resonance observed for the hydride suggests this ligand to be trans to the oxygen of the bonded ester group.

From these results, we can suggest two structures for complex **9** (Figure 5), the infrared spectrum giving no information about the mode of bonding of the alkyne since the ν(C=C) stretching frequency region is obscured by the ester group absorption. Nevertheless, structure B seems less realistic from the point of view of steric constraints.

The conditions of isolation of complexes **8** and **9** suggest that they are interrelated. Indeed, **9** reacts with *t*-BuSH to generate **8** and **8** can be considered as the result of the oxidative addition of the thiol to **9**.

Case Where A = $P(CH_3)_3$ and R = CF_3. After 3 days of a slow reaction, the final product, complex **10**, is isolated from the solution. **10** has spectroscopic characteristics similar to those of **8** (Table I). Especially, the infrared spectra show the presence of a terminal hydride and the presence of a coordinated alkyne which is μ-η^1 bonded. The chemical analysis (Table II) is in agreement with

(13) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231.
(14) Crabtree, R. *Acc. Chem. Res.* **1979**, *12*, 331.
(15) Maisonnat, A.; Poilblanc, R. *J. Organomet. Chem.* **1978**, *160*, 307.

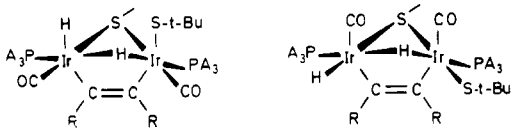


Figure 6. Proposed structures for complex **11**.

$[IrH(\mu\text{-S-}t\text{-Bu})(CO)P(CH_3)_3]_2C_4F_6$, and we propose the same structure as for **8** (Figure 4).

Case Where A = CH_3 and R = $CH_3OC(O)$. At room temperature, the addition of 1 equiv of formic acid leads to a complex mixture from which $Ir_2H_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-H})(CO)_2[P(CH_3)_3]_2RCCR$ (**2a**) can be identified by its hydride resonances in the proton NMR spectrum.

To achieve some selectivity in the reaction, it was carried out at −30 °C and the proton NMR spectrum at this temperature gives evidence of a major product that is present during the action of hydrogen. Keeping the reaction temperature in the range −20 to −30 °C, it has been possible to isolate complex **11** by crystallization.

The infrared spectrum of **11** presents two bands of the same intensity in the ν(CO) stretching region separated by 20 cm^{-1}, a strong band at 1672 cm^{-1} for the CO ester group, and a weak band at 1540 cm^{-1} for the ν(C=C) of the μ-η^1-bonded alkyne. The proton NMR spectrum run at −20 °C shows two singlets for the S-*t*-Bu resonance. In the hydride part, two sets of signals are observed: one doublet at −11.48 ppm (J = 17.5 Hz) and a double doublet at −15.22 ppm (J_1 = 54.4 and J_2 = 62.5 Hz). These signals are in the ratio 3/3/9/9/9/9/1/1.

The chemical analysis is consistent with the formula $[IrH(S\text{-}t\text{-Bu})(CO)P(CH_3)_3]_2[CH_3OC(O)C]_2$. Stereochemical examination of the hydride resonances indicates one hydride to be terminal (−11.48 ppm) while the other (−15.22 ppm), bridging two iridium atoms, is trans to two slightly different phosphine ligands. All this spectroscopic information is consistent with the two structures presented in Figure 6. In these structures, one of the initially bridging S-*t*-Bu ligands is now in a terminal position and has been replaced by an hydride ligand. Complex **11** in solution is not very stable and quickly evolves *t*-BuSH to generate $Ir_2H_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-H})(CO)_2[P(CH_3)_3]_2[CH_3OC(O)C]_2$, **2a**, and $[Ir(\mu\text{-S-}t\text{-Bu})(CO)P(CH_3)_3]_2[CH_3OC(O)C]_2$.

The overall stoichiometry of this reaction seems to be

$$2\,\mathbf{11} \rightarrow Ir_2H_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-H})(CO)_2[P(CH_3)_3]_2[CH_3OC(O)C]_2 + [Ir(\mu\text{-S-}t\text{-Bu})COP(CH_3)_3]_2[CH_3OC(O)C]_2 + t\text{-BuSH} \quad (4)$$

Case of the Addition of 2 Equiv of Formic Acid to $[Ir(\mu\text{-S-}t\text{-Bu})COPA_3]_2RCCR$ Complexes. Case Where A = C_6H_5 and R = $CH_3OC(O)$. Depending on the reaction conditions, two complexes have been isolated. (i) If the reaction is left to stand in a closed vessel for 36 h, the same result as in the hydrogen reaction is observed: the compound $[IrH(\mu\text{-S-}t\text{-Bu})COP(C_6H_5)_3]_2$ is isolated and dimethyl maleate is formed. (ii) If the reaction is stopped after 4 h, we observe a mixture of the starting material and a new complex, **12**, which may be separated. Infrared spectra of **12** present two ν(CO) stretching frequences (Table I) and a broad band at 2118 cm^{-1} that is attributed to a M–H stretching vibration. A medium intensity band at 1580 cm^{-1} shows that the μ-η^1-bonded alkyne is present in **12**.

In the proton NMR spectrum, one complex signal is observed in the phenyl region, one singlet for the OCH_3 resonance, and one singlet for the S-*t*-Bu group. These signals are in the ratio of 30/6/9. In the hydride region, two signals are observed in the ratio 2/1: one AAXX′ spin system at −12.02 ppm (J_{AX} = 13 Hz) and one AX_2 spin system at −16.28 ppm (J_{AX} = 11 Hz). These data are very similar to those of the complex $Ir_2H_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-H})(CO)_2[P(C_6H_5)_2CH_3]_2[CH_3OC(O)C]_2$, **6**, and the same structure is proposed.

We have seen that the reaction time is very important for the isolation of **12** which seems to be the kinetic product of the reaction with formic acid. Furthermore, it has not been possible to detect its presence in the reaction with hydrogen at 50 °C. All these observations suggest a possible action of *t*-BuSH in the elimination of alkene starting from **12**. Actually, we have observed reaction 5 at room temperature.

$$\mathbf{12} + t\text{-BuSH} \rightarrow [Ir(H)(\mu\text{-S-}t\text{-Bu})(CO)O(C_6H_5)_3]_2 + CH_3OC(O)HC{=}CHC(O)OCH_3 \quad (5)$$

Case Where A = CH_3 and R = CF_3 or $CH_3OC(O)$. The same results as in the reaction with hydrogen have been observed.

Discussion

A rough analysis of the results shows that, whatever the true chemical path followed may be, the reaction of molecular hydrogen can be described as the succession of an oxidative addition of one hydrogen molecule and of a reductive elimination of *t*-BuSH or alkene, followed by an oxidative addition of a second molecule of hydrogen. Furthermore, the cis alkene is obtained.

To obtain an insight into the mechanism of these reactions, we have to answer to the following questions. (i) What is the first step of the action of hydrogen: does the attack occur on one iridium center or on the two centers? (ii) Why do the $P(CH_3)_3$ and $P(C_6H_5)_3$ complexes show such different behavior?

Hoping to trap some intermediate, we have run the reaction with 1 equiv of molecular hydrogen/mol of complex **1**. Unfortunately, the reaction is not selective and leads to a complex mixture from which pure compounds cannot be isolated. Thus, it seems difficult to obtain any answer to the above questions through the study of direct hydrogenation.

Therefore, we thought of taking advantage of the properties of iridium complexes toward formic acid. Indeed, the results of this investigation offer a satisfying answer to our aim: a better approach to the mechanism of the action of hydrogen on $[Ir(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2RCCR$ complexes.

First, in the case where A = CH_3, the action of formic acid allowed us to isolate an intermediate, **11**, found in the reaction with hydrogen. This intermediate, $Ir_2H(\mu\text{-S-}t\text{-Bu})(\mu\text{-H})(S\text{-}t\text{-Bu})(CO)_2[P(CH_3)_3]_2[CH_3OC(O)C]_2$, gives an insight into the preliminary step of the hydrogen action: *the attack of hydrogen seems to result from the opening of a t-BuS bridge.*

Second, in the case where A = C_6H_5, the action of formic acid allowed the isolation of complex **12**, $Ir_2H_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-H})(CO)_2[P(C_6H_5)_3]_2[CH_3OC(O)C]_2$. Furthermore, **12** *reacts with t-BuSH to generate* $[IrH(\mu\text{-S-}t\text{-Bu})(CO)P(C_6H_5)_3]_2$ *with liberation of the alkene.* This seems to be the key to the difference of reactivity between the complexes with A = CH_3 or A = C_6H_5.

Third, in some cases, the action of formic acid allowed the isolation of $[IrH(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2RCCR$ complexes **8** and **10** in which one hydrogen atom is bonded to each iridium atom. This situation corresponds to a possible path of the initial attack of the hydrogen molecule. For this reason, we have checked the reactivity of **8** and **10** toward hydrogen: no reaction occurs. Consequently, the attack of hydrogen on $[Ir(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2RCCR$

Figure 7. Limiting structures for the intermediate resulting from the opening of the S-*t*-Bu bridge.

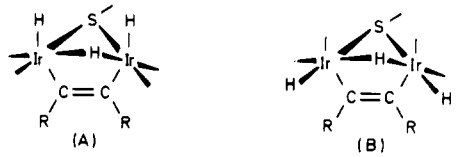


Figure 8. Possible relative positions of the hydrides and alkyne ligands in complexes $[Ir_2H_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-H})(CO)_2(PA_3)_2]RCCR$

molecules does not proceed through this intermediate and is not a concerted attack on the two iridium centers. This also seems to be the case for the attack of hydrogen on $[Ir(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2$ complexes.[12] From all these observations, let us now consider the problem of the mechanism of hydrogenation of $[Ir(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2RCCR$ complexes.

Mechanism of Hydrogenation of $[Ir(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2RCCR$ Complexes. We have seen that two types of problems have to be considered: (i) the first step of the hydrogen attack and (ii) the difference of behavior of complexes **1** with A = CH_3 and A = C_6H_5.

Discussion of the First Step of the Hydrogen Attack. The isolation of complexes **8** and **10** in which one atom of hydrogen is bonded to each iridium and their inertness toward further hydrogenation have proved that the initial attack is not a concerted attack on the two iridium centers. Moreover, the isolation of complex **11** is very useful in order to get an insight into this first stage. This complex appears during the first step of the action of hydrogen, and its structure, presented in Figure 6, shows that one S-*t*-Bu bridge is now in a terminal position. This suggests that a vacant site for the attack of the hydrogen molecule results from the opening of one of the bridges.

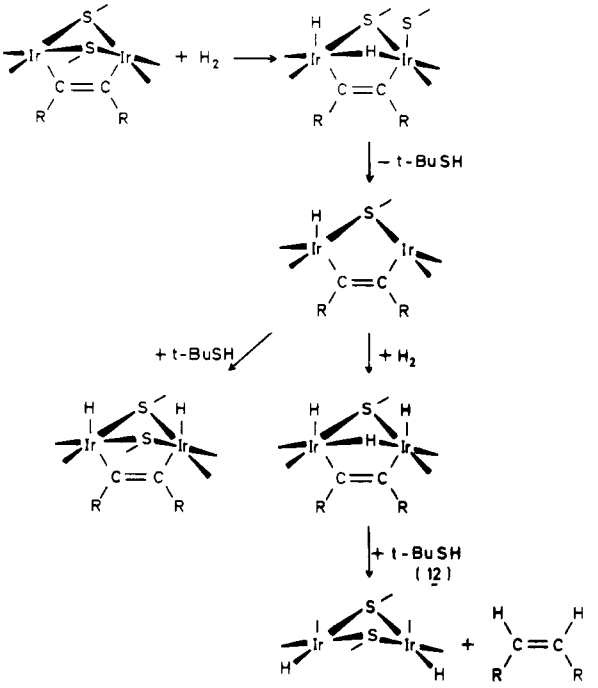
Let us now examine the situation created by this opening from the point of view of valence electron counting. Figure 7 gathers both limiting cases that may be considered.

In (A), there is only an opening of one S-*t*-Bu bridge leaving, if the metal–metal bond is preserved, one iridium atom (Ir(1)) with a formal oxidation state of II with 16 valence electrons. This situation is a priori propitious to oxidative addition of hydrogen even though it should lead to an iridium(IV) center that is not common in the organometallic chemistry of iridium. This difficulty could be overcome if we consider an heterolytic cleavage of hydrogen that could be promoted by the presence of the metal–metal bond. This metal–metal bond could stabilize the proton liberated and could lead directly to the structure found for **11**. An heterolytic activation of hydrogen has been invoked recently in the case of hydrogenation of alkylzirconium(IV) compounds.[16]

In (B), there would be an electronic reorganization by the intermediate of the *t*-BuS bridge leading to one iridium with a formal oxidation state of I (Ir(1)) and the second (Ir(2)) with a formal oxidation state of III. These two iridium atoms are surrounded by 16 valence electrons. In this configuration, oxidative addition of hydrogen on Ir(1) is thus easily conceivable. So, it appears that, whatever the exact electronic structure of the intermediate resulting from the bridge opening in (A) or (B), addition of molecular hydrogen is always possible.

A problem still remains, concerning the mechanism of the attack of the second molecule of hydrogen. The isolation of complex **9** suggests that its first step is reductive elimination of *t*-BuSH. In this case, this intermediate[17]

Scheme I



is stabilized by the coordination of the ester CO group of the alkyne.

Discussion about the Difference of Reactivity toward Hydrogen of the $[Ir(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2RCCR$ Complexes with the Nature of A. As seen in the case of the complex where A = C_6H_5, elimination of alkene results from the action of *t*-BuSH on **12** and we have checked that the complexes $Ir_2H_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-H})(CO)_2[P(CH_3)_3]_2RCCR$ are not reactive toward *t*-BuSH.

If we consider the trihydride complexes (**12** or its analogue with A = CH_3), these molecules have 34 valence electrons. Consequently, nucleophilic attack of *t*-BuSH is easily conceivable. Two factors could explain the difference of reactivity: an electronic effect or a stereochemical effect.

Interference of the electronic factor may occur at two levels: (i) at the level of the nucleophilic attack of *t*-BuSH as the more basic trimethylphosphine may reduce the electrophilic power of iridium; (ii) at the level of the strength of iridium–hydrogen bonds which may be increased by the trimethylphosphine ligand.

(16) Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846.

(17) For the complexes with A = CH_3, no intermediate has been isolated but it appears from the proton NMR spectrum that, except the resonance of the complexes $[Ir_2H(\mu\text{-S-}t\text{-Bu})(\mu\text{-H})(S\text{-}t\text{-Bu})(CO)_2(P(CH_3)_3)_2][CH_3OC(O)C]_2$, (**4**) and $Ir_2(H)_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-H})(CO)_2(P(CH_3)_3)_2[CH_3OC(O)C]_2$, one triplet is detected at −15.22 ppm in the bridging hydride area. This resonance could be attributed to the complex resulting from *t*-BuSH elimination showing a structure where the phosphines are assumed to be cis to the hydride bridge when the value of the coupling constant (10 Hz) is considered. This implies a great reorganization of the molecule **4** that could be considered if the *t*-BuSH eliminated came from the *t*-BuS bridge. This structure shows 32 valence electrons, and oxidative addition of an hydrogen molecule is easily conceivable.

The stereochemical factor is more difficult to ascertain as the exact structure of the two trihydride complexes could not be inferred from the spectroscopic data; the only relative positions to be surely known are those of the bridging hydride and of the phosphine ligands. Thus, both geometries presented in Figure 8 are equally likely for the two complexes. Obviously, elimination of alkene is hardly conceivable in case A, as the terminal hydride is trans to the alkyne.

In conclusion, the study of the action of formic acid on $[Ir(\mu\text{-S-}t\text{-Bu})COPA_3]_2RCCR$ complexes has been of great value for obtaining an understanding of the mechanism of action of hydrogen on the same complexes. It has been clearly shown that the attack of the first molecule of hydrogen is allowed by the opening of one of the S-*t*-Bu bridges. Furthermore, elimination of alkene RCH=CHR results from the action of *t*-BuSH on the compound $[Ir_2H_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-H})(CO)_2[P(C_6H_5)_3]_2]RCCR$. Scheme I summarizes these results.

Experimental Section

All the reactions were performed under an inert atmosphere. The infrared spectra were recorded on a Perkin-Elmer 225 apparatus and proton NMR spectra on a Perkin-Elmer R12 or Bruker WH90 apparatus.

The $[Ir(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2RCCR$ compounds were prepared according to published procedures.[6] All the hydrogenation reactions were run in a constant pressure reactor built at the laboratory.[18]

Physical properties and analyses of isolated complexes are given in Table II.

Reaction of Hydrogen with $[Ir(\mu\text{-S-}t\text{-Bu})(CO)P(C_6H_5)_3]_2RCCR$ Complexes. R = $CH_3OC(O)$. A toluene (20 mL) solution of the complex (0.3 g) was stirred under an hydrogen atmosphere at 40 °C for 12 h. At the end of the reaction toluene was evaporated and complex **3** was isolated by crystallization from a toluene–hexane mixture (yield 70 %). Proton NMR spectra showed the presence of dimethyl maleate and dimethyl fumarate in the mother liquor.

R = CF_3. The experiment was run under the same conditions except for the temperature (60 °C). Compound **3** was isolated from the solution but compound **4** could not be isolated free from **3** and was only identified by spectroscopy.

Reaction of Hydrogen with $[Ir(\mu\text{-S-}t\text{-Bu})(CO)L]_2RCCR$ Complexes. L = $P(C_6H_5)_2CH_3$ and $P(CH_3)_3$. All the reactions were run at room temperature in a toluene solution.

L = $P(C_6H_5)_2CH_3$ (R = $CH_3OC(O)$). After toluene evaporation, crystallization at −20 °C from a CH_2Cl_2/hexane mixture gave **5** in a 40% yield. Evaporation of the mother liquor and crystallization of the residue from a toluene/hexane mixture at −20 °C gave **6** in 35% yield.

L = $P(CH_3)_3$. Crystallization from a toluene/hexane mixture at −20 °C gave **2a** or **2b** in 50% yield.

Reaction of Hydrogen with $Ir_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-}CF_3COO)(CO)_2[P(C_6H_5)_3]_2RCCR$ Complexes. The reaction was run in toluene/hexane solution under atmospheric pressure of hydrogen at 60 °C. Crystallization from a toluene/hexane mixture at −20 °C gave **7** in 80% yield.

Action of 1 Equiv of Formic Acid on $[Ir(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2RCCR$ Complexes. (a) A = C_6H_5 and R = $CH_3OC(O)$. To a solution of 0.3 g of the iridium complex in dichloromethane was added 9 μL of formic acid. When the solution was stirred for 4 days in a closed Schlenk tube, the complex $[IrH(\mu\text{-S-}t\text{-Bu})(CO)P(C_6H_5)_3]_2RCCR$, **8**, was isolated by crystallization from dichloromethane/hexane at 20 °C (40% yield). When the reaction was stopped after 4 h, solvent evaporation, followed by extraction with hexane and crystallization, gave **9** (20% yield).

(b) A = CH_3 and R = CF_3. To a solution of 0.3 g of $[Ir(\mu\text{-S-}t\text{-Bu})(CO)P(CH_3)_3]_2C_4F_6$ in dichloromethane was added 2 μL of formic acid. The solution was stirred for 3 days in a closed vessel system. The resulting solution was concentrated to 50% of its volume, and an equal amount of methanol was added. The product isolated was complex **10**, yield 45%.

(c) A = CH_3 and R = $CH_3OC(O)$. To 0.3 g of the iridium complex in dichloromethane solution maintained at −30 °C was added 12 μL of formic acid. The solution was stirred for 10 min. The resulting solution was concentrated and cold methanol added. Crystallization at −20 °C gave a 40% yield of **11**.

Action of 2 Equiv of Formic Acid on $[Ir(\mu\text{-S-}t\text{-Bu})(CO)PA_3]_2RCCR$ Complexes. (a) A = C_6H_5 and R = $CH_3OC(O)$. To 0.3 g of the iridium complex in dichloromethane was added 18 μL of formic acid. When the solution was left for 12 h in a closed vessel, the complex $[IrH(\mu\text{-S-}t\text{-Bu})(CO)P(C_6H_5)_3]_2$ was crystallized from dichloromethane/hexane, yield 85%. When the solution was run under a slight vacuum for 2 h and the solvent gently evaporated for two additional hours, crystallization from dichloromethane/methanol gave the complex **12**, yield 65%.

(b) A = CH_3 and R = $CH_3OC(O)$ or CF_3. To 0.3 g of a solution of the complex in dichloromethane was added formic acid in the acid/complex ratio of 2/1. The reaction was over after 30 min. The complex $[Ir_2H_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-H})(CO)_2[P(CH_3)_3]_2]RCCR$ was isolated according to the same procedure as described for the reaction with hydrogen.

Registry No. 2a, 87070-72-2; **2b**, 87070-73-3; **3**, 64783-16-0; **4**, 87070-74-4; **5**, 87070-75-5; **6**, 87070-76-6; **7**, 87070-77-7; **8**, 87070-78-8; **9**, 87088-24-2; **10**, 87070-79-9; **11**, 87070-80-2; **12**, 87070-81-3; $[Ir(\mu\text{-S-}t\text{-Bu})(CO)P(C_6H_5)_3]_2CH_3OC(O)CCC(O)OCH_3$, 87070-82-4; $[Ir(\mu\text{-S-}t\text{-Bu})(CO)P(C_6H_5)_3]_2CF_3CCCF_3$, 87144-14-7; $[Ir(\mu\text{-S-}t\text{-Bu})(CO)P(C_6H_5)_2CH_3]_2CH_3OC(O)CCC(O)OCH_3$, 87088-25-3; $[Ir(\mu\text{-S-}t\text{-Bu})(CO)P(CH_3)_3]_2CH_3OC(O)CCC(O)OCH_3$, 87099-43-2; $Ir_2(\mu\text{-S-}t\text{-Bu})(\mu\text{-}CF_3COO)(CO)_2[P(C_6H_5)_3]_2CH_3OC(O)CCC(O)OCH_3$, 87070-83-5; $[Ir(\mu\text{-S-}t\text{-Bu})(CO)P(CH_3)_3]_2CF_3CCCF_3$, 87070-84-6.

(18) Labroue, D. Thèse d'Etat, 1978, Toulouse.