DINUCLEAR BRIDGED d^8 METAL COMPLEXES

IX *. PREPARATION AND STRUCTURE OF THE COMPLEXES [Ir2(μ-SBu-t)2(CO)2(PR3)2] AND [Ir2(μ-SBu-t)2(CO)3(PR3)]

DOMINIQUE DE MONTAUZON, PHILIPPE KALCK and RENÉ POILBLANC *

Laboratoire de Chimie de Coordination du CNRS, associé à l'Université Paul Sabatier, 205 route de Narbonne, 31030 Toulouse Cedex (France)

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Summary

The addition of two moles of a tertiary phosphine ligand PR_3 to [Ir2(μ-SBu-t)2(CO)4] affords the dinuclear disubstituted iridium(I) complexes [Ir2(μ-SBu-t)2(CO)2(PR3)2]. ^1H, ^{13}C and ^{31}P and infrared data are consistent with a bent geometry, the CO groups being in *cis* dispositions and the t-butyl groups in *anti* dispositions. When R = OMe exchange between this isomer and the *trans-anti* isomer occurs in solution. For R = Ph one isomer, possibly a *trans* isomer, which is transformed irreversibly into the *cis* isomer, is detected. An intermediate complex is observed during substitution, and its spectroscopic data are consistent with the formula [Ir2(μ-SBu-t)2(CO)3(PR3)]. This complex is in equilibrium with the parent complex and [Ir2(μ-SBu-t)2(CO)2(PR3)2], and NMR data suggest that it is an *anti* isomer.

Introduction

Continuing our investigations on the synthesis and reactions of dinuclear rhodium(I) complexes bridged by anionic ligands, we have recently shown, by comparing, for example, [Rh2(μ-SPh)2(CO)2(PMe3)2] [2] with [Rh2(μ-Cl)2-(CO)2(PMe2Ph)]2 [3]. that thiolato groups lead to a more compact core.

Recently, the synthesis in our laboratory of the dinuclear carbonyl complexes of iridium(I), [Ir2(μ-SR)2(CO)4] [4] prompted us to undertake a study of the reactions of the t-butyl complex with phosphine ligands. The addition of PR_3 ligands to rhodium carbonyl [Rh2(μ-Cl)2(CO)4] was previously shown to

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* Some of these results appeared in a preliminary communication [1a]. For part XVIII see ref. 1b.

give a mixture of mononuclear [RhCl(CO)$_{3-n}$(PR$_3$)$_n$] and dinuclear [Rh$_2$(μ-Cl)$_2$(CO)$_{4-n}$(PR$_3$)$_n$] species in equilibrium [5,6]. However, for the complex [Rh$_2$(μ-SR)$_2$(CO)$_4$], at (PR$_3$)/Rh ratio of $\leqslant 1$, only dinuclear species were observed [7]; the infrared and NMR data favoured the existence of the (non-isolated) intermediate [Rh$_2$(μ-SR)$_2$(CO)$_4$(PR$_3$)$_2$], which underwent decarbonylation to the disubstituted complexes [Rh$_2$(μ-SR)$_2$(CO)$_2$(PR$_3$)$_2$] [2,7].

This paper describes the synthesis and structure in solution of the complexes [Ir$_2$(μ-SBu-t)$_2$(CO)$_2$(PR$_3$)$_2$]. Spectroscopic evidence is given for the formation in the solution of the stable intermediate species [Ir$_2$(μ-SBu-t)$_2$(CO)$_3$(PR$_3$)], when phosphine ligands are added to the carbonyl [Ir$_2$(μ-SBu-t)$_2$(CO)$_4$].

Experimental

The complex [Ir$_2$(μ-SBu-t)$_2$(CO)$_4$] (I) was prepared as elsewhere described [4] by reaction of [Ir$_2$(μ-Cl)$_2$(η-C$_8$H$_{12}$)$_2$] [8] with LiSBu-t to give [Ir$_2$(μ-SBu-t)$_2$(η-C$_8$H$_{12}$)$_2$] and by further carbonylation at one atmosphere pressure.

All reaction were carried out under dry, oxygen-free nitrogen. All solvents were distilled and saturated with nitrogen prior to use. Hexachloroiridic acid, t-butylmercaptan, butyllithium, trimethylphosphite, triphenyl- and tris(dimethylamino)phosphine were of commercial origin. Trimethylphosphine [9] and dimethylphenylphosphine [10] were prepared according to published methods.

Infrared spectra were recorded on a Perkin—Elmer 225 grating spectrometer equipped with a scale expander working in optical density. Hexadecane solutions or caesium bromide pellets were used. In the carbonyl stretching region, the spectra were calibrated by water vapor lines.

Proton NMR spectra were obtained on Varian Associates A-60 A or Brüker WH 90 spectrometers. Some spectra were recorded with a Cameca apparatus at 62.86 MHz for ^{13}C, and 250 MHz for the proton. Dichloromethane, deuteriodichloromethane, deuteriochloroform, benzene and deuteriotoluene were used as solvents, and tetramethylsilane as internal standard.

Molecular weights were determined by tonometry in benzene solutions using a Mechrolab apparatus.

Elemental microanalyses were carried out by the "Service Central de Microanalyse du CNRS".

[Ir$_2$(μ-SBu-t)$_2$(CO)$_2$(PMe$_3$)$_2$] (II)

I (0.736 g, 1.09 mmol) was dissolved in 10 ml of toluene, and trimethyl phosphine (0.222 ml, 2.18 mmol) was added dropwise at room temperature with vigorous stirring. The red solution was slightly concentrated under reduced pressure during 1 h, then the volume was reduced to about 5 ml. Hexane, in which the product is only slightly soluble, was added without mixing the solvents. Slow mutual diffusion of the two solvents at —20°C gave somewhat air sensitive red crystals of II (0.71 g, yield 85%). M.p. 198°C dec. Found: C, 24.83; H, 4.79; S, 7.93. C$_{16}$H$_{36}$O$_2$P$_2$S$_2$Ir$_2$ calcd.: C, 24.94; H, 4.67; S, 8.32%. Molecular weight found 775, calcd. 771.

[Ir$_2$(μ-SBu-t)$_2$(CO)$_2$(PMe$_2$Ph)$_2$] (III)

The same procedure was used to prepare III, but all attempts to obtain the complex in crystalline form failed.

TABLE 1

^{1}H NMR AND IR DATA FOR THE $[Ir_2(\mu\text{-}SBu\text{-}t)_2(CO)_2(PR_3)_2]$ COMPLEXES AND $[Ir_2(\mu\text{-}SBu\text{-}t)_2(CO)_4]$

	$\nu(CO)$ (cm^{-1})		$\delta(SBu\text{-}t_{endo})$ (ppm)		$\delta(SBu\text{-}t_{exo})$ (ppm)		$\delta(P\text{—}CH_3)$ (ppm)		$J(P\text{—}H)$ (Hz)
	hexadecane	C_3Br	C_6H_6	CH_2Cl_2	C_6H_6	CH_2Cl_2	C_6H_6	CH_2Cl_2	
$[Ir_2(\mu\text{-}SBu\text{-}t)_2(CO)_4]$ (I)	2061s, 2040vs, 1986vs		1.41	1.60					
$[Ir_2(\mu\text{-}SBu\text{-}t)_2(CO)_2(PMe_3)_2]$ (II)	1956vs, 1942vs	1941vs, 1927vs	1.58	1.57	1.92	1.44	1.30d	1.65d	9.7, 9.7
$[Ir_2(\mu\text{-}SBu\text{-}t)_2(CO)_2(PMe_2Ph)_2]$ (III)	1957vs, 1943vs			1.68		1.08		1.69d	9.3 (in CD_2Cl_2)
$[Ir_2(\mu\text{-}SBu\text{-}t)_2(CO)_2(P(NMe_2)_3)_2]$ (IV)	1959vs, 1943vs			1.64		1.49		2.79d	10.0
$[Ir_2(\mu\text{-}SBu\text{-}t)_2(CO)_2(PPh_3)_2]$ (Va)	1966vs, 1951s	1956vs, 1936s	1.08	1.74	1.98				
(Vb)	1955vs, 1936vs			1.60 (C_6H_6) or 2.36 ($CDCl_3$)		0.75			
$[Ir_2(\mu\text{-}SBu\text{-}t)_2(CO)_2(P(OMe)_3)_2]$ (VIa)	1976vs, 1956vs	1976vs, 1956vs	1.63		1.87(t) J 0.6 Hz		3.47d		12.0
(VIa + VIb)	1985vs, 1975vs, 1964vs								

[Ir$_2$(μ-SBu-t)$_2$(CO)$_2$(P(NMe$_2$)$_3$)$_2$ (IV)

I (0.451 g, 0.66 mmol) was dissolved in 10 ml of toluene, and tris(dimethyl-amino)phosphine (0.242 ml, 1.33 mmol) was added at room temperature. The solution was stirred for 5 min. The addition of hexane and crystallization at −20°C gave 0.535 g of red crystals (yield 75%). M.p. 150°C dec. Found: C, 28.20; H, 5.78; N, 8.76; S, 6.75. C$_{22}$H$_{54}$N$_6$O$_2$P$_2$S$_2$Ir$_2$ calcd.: C, 27.97; H, 5.72; N, 8.89; S, 6.78%. Molecular weight found 960, calcd. 945.

[Ir$_2$(μ-SBu-t)$_2$(CO)$_2$(PPh$_3$)$_2$] (V)

20 ml of a pentane solution of triphenylphosphine (0.530 g, 2 mmol) were added to 0.675 g of I (1 mmol) in 10 ml of toluene. After a few minutes crystals appeared and crystallization was completed at −20°C; 1.01 g of red-orange microcrystals were obtained (yield 90%). M.p. 220°C dec. Found: C, 49.11; H, 4.35; S, 5.30. C$_{46}$H$_{48}$O$_2$P$_2$S$_2$Ir$_2$ calcd.: C, 48.35; H, 4.20; S, 5.60%. Molecular weight found 1120, calcd. 1143.

[Ir$_2$(μ-SBu-t)$_2$(CO)$_2$(P(OMe)$_3$)$_2$] (VI)

Complex VI was similarly prepared from an hexane solution of I. Crystallization at −20°C gave orange crystals (yield ∼90%). M.p. 110°C. Found: C, 22.38; H, 4.23; S, 7.14. C$_{16}$H$_{36}$O$_8$P$_2$S$_2$Ir$_2$ calcd.: C, 22.17; H, 4.15; S, 7.40%. Molecular weight found 886, calcd. 867.

[Ir$_2$(S-Bu-t)$_2$(CO)$_3$(PR$_3$)]

These compounds were not obtained in the solid state, and all attempts to crystallize them failed. The IR and NMR spectra of the mixture from equimolar quantities of I and [Ir$_2$(μ-SBu-t)$_2$(CO)$_2$(PR$_3$)$_2$] were recorded, and the bands of the signals due to all the three compounds were observed together during the exchange and finally in the equilibrium conditions.

Results and discussion

1. [Ir$_2$(μ-SBu-t)$_2$(CO)$_2$(PR$_3$)$_2$]

Addition of 2 mol of a tertiary phosphine or phosphite ligand to the carbonyl complex [Ir$_2$(μ-SBu-t)$_2$(CO)$_4$] (I) [4], followed for the more basic ligand by decarbonylation under a slightly reduced pressure, leads to the complexes [Ir$_2$(μ-SBu-t)$_2$(CO)$_2$(PR$_3$)$_2$]. This reaction is quite general, and the basicity of the ligands can vary considerably. The complexes were prepared for R$_3$ = Me$_3$, Me$_2$Ph, (NMe$_2$)$_3$, Ph$_3$, (OMe)$_3$. The elemental analysis and the molecular weight measurements, except for the complexe R$_3$ = Me$_2$Ph, are consistent with this formula.

Recently the crystal structure of [Ir$_2$(μ-SBu-t)$_2$(CO)$_2$(P(OMe)$_3$)$_2$] (VI) was determined [11]. In the solid state the geometry of VI consists of two square planes making a dihedral angle of 132.2°. The distance between the two metal atoms is 3.216(2) Å, the phosphite ligands and carbonyl ligands are in a *cis*-arrangement, the t-butyl groups are mutually *anti*, and the endo group lies between the two CO ligands. (Fig. 1).

Complex VI presents two ν(CO) bands in the solid state, at 1976 and 1956 cm^{-1}, of about equal intensity (Table 1). Such splitting had been previously dis-

TABLE 2

31P AND 13C NMR DATA (TMS AND H₃PO₄ AS STANDARDS)

Numbering scheme
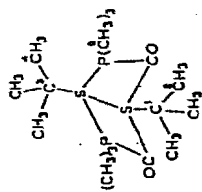
	t-Bu in endo position			t-Bu in exo position		Phosphine ligand			Carbonyl ligand	
	$\delta(C(1))$	$\delta(C(2))$	$J(PC)$	$\delta(C(3))$	$\delta(C(4))$	$\delta(C(6))$	$J(PC)$	$\delta(^{31}P)$	$\delta(CO)$	$J(PC)$
[Ir₂(μ-SBu-t)₂(CO)₄]	49.87 [a]	33.94							174.25	
[Ir₂(μ-SBu-t)₂(CO)₂(PMe₃)₂]	46.37 [b]	33.48		53.29	39.66	18.40d	38.8	−29.4	179.67	9.3
[Ir₂(μ-SBu-t)₂(CO)₂(P(OMe)₃)₂]	47.70 [b]	33.87t	2.9	52.76	38.19	52.17	—	110.7 [c]	177.84d {177.96d, 177.75d}	12.9, 7.4, 7.4
[Ir₂(μ-SBu-t)₂(CO)₃(PMe₃)]	48.13 [b]	33.57		54.08	38.16	18.29	38.8		178.61d, 178.33, 174.45	12.9

[a] In CDCl₃. [b] In CD₂Cl₂. [c] In C₆D₆. d, doublet; t, triplet.

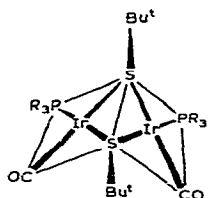Fig. 1. *cis-anti*-Isomeric structure for the complexes [Ir$_2$(μ-SBu-t)$_2$(CO)$_2$(PR$_3$)$_2$].

cussed [3,7] and is consistent with one CO ligand per metal. For the complex [Ir$_2$(μ-SBu-t)$_2$(CO)$_2$(PMe$_3$)$_2$] the *cis*-geometry is retained in the solid state, since there are two ν(CO) bands of the same intensity with a splitting of 14 cm^{-1}. This value is very close to that found for the complex [Rh$_2$(μ-SPh)$_2$(CO)$_2$-(PMe$_3$)$_2$] [2] for which the crystal and molecular structure show a dihedral angle of 113°.

When considering the structure of the complexes in solution, it is necessary to deal with each complex individually.

(a) [Ir$_2$(μ-SBu-t)$_2$(CO)$_2$(PMe$_3$)$_2$] (II). The infrared spectra of hexadecane solutions show two ν(CO) bands, at 1956 (47.5% of the total intensity) and 1942 cm^{-1} (52.5%). In the approximation in which the CO oscillator is considered as a dipole vector, the angle ω between the two CO vectors is calculated from the ratio between the intensities of the symmetric and antisymmetric bands as $I_{sym}/I_{asym} = \cot^2(\omega/2) = 0.475/0.525$. The calculated angle ω 93° corresponds with a *cis*-isomer [3].

The ^{1}H, ^{13}C and ^{31}P NMR data (Tables 1 and 2) are also consistent with the existence of a single *cis*-isomer, and a single signal is detected at -29.4 ppm in ^{31}P NMR, as expected for two equivalent phosphorus atoms. In the ^{1}H NMR these two equivalent ligands give a doublet due to ^2J(PH) coupling. Two t-butyl signals are detected since one group is located between the two CO ligands, and two different magnetic environments are expected. The same type of informa-

TABLE 3

NMR AND IR DATA FOR THE COMPLEXES Ir$_2$(μ-SBu-t)$_2$(CO)$_3$L (s, singlet; d, doublet; br, broad)

L	ν(CO) (cm^{-1}) in hexadecane solution	δ(SBu-t) (ppm)	δ(Me) (ppm)	J(P—H) (Hz)
PMe$_3$	2046vs 1979vs 1957vs	+1.47 [a] +1.66 [a]	+1.25d	9.6
P(NMe$_2$)$_3$	2044vs 1977vs 1960vs	+1.55 [b] s(br)	+2.81 [b] d	9.8
P(OMe)$_3$	2049vs 1988vs 1982vs	+1.52 [a] s +1.65 [a] s	+3.38 [a] d	12.2
PFh$_3$	2045vs 1978vs 1966vs	+1.21 [a] s +1.70 [a] s		

[a] Benzene solutions. [b] CH$_2$Cl$_2$ solutions.

tion is given by the ^{13}C NMR spectra (Table 2). The carbonyl signal is a doublet indicating a *cis*-coupling with the phosphorus atom. In addition, it is possible to assign the various ^1H and ^{13}C t-butyl signals. The structure of the carbonyl analogue $[Ir_2(\mu\text{-}SPh)_2(CO)_4]$ has the phenyl groups in *endo* positions [12]. The parent complex I, which should certainly have the same *syn-endo* isomerism, presents a t-Bu signal at 1.41 ppm in benzene or 1.60 ppm in CH_2Cl_2 solutions. In complex II the signal from the *endo* t-Bu group is almost unchanged on going from benzene to dichloromethane, the signal from the *exo*-t-Bu group, which is much influenced by the solvents, is assigned to 1.92 in C_6H_6 and 1.44 in CH_2Cl_2.

For the complex $[Ir_2(\mu\text{-}SBu\text{-}t)_2(CO)_4]$ the *endo* quaternary carbon signal is detected at 49.87 ppm and the methyl groups at 33.94 ppm in $CDCl_3$. In the case of the complex $[Ir_2(\mu\text{-}SBu\text{-}t)_2(CO)_2(PMe_3)_2]$ our assignment for the *endo* t-Bu group is δ 46.37 and 33.48 ppm and for the *exo*-t-Bu group δ 53.29 and 39.66 ppm. As observed in the ^1H NMR spectrum, the magnetic environment for *endo*-CH_3 groups is almost unaffected in complexes I and II.

(b) [Ir₂(μ-SBu-t)₂(CO)₂(PMe₂Ph)₂] (III). The infrared $\nu(CO)$ bands observed in solution are indicative of a *cis*-isomer. Since no symmetry plane contains the Ir—P bonds, diastereotopic methyl groups are thus expected for the phosphine ligands. The ^1H NMR spectra at 303 K present a single doublet inconsistent with this expectation. A variable temperature study was undertaken, and at 183 K a broad singlet was observed for the PMe_2Ph-methyl groups. An intramolecular rearrangement leading to the equivalence of phosphine ligands would explain this observation. The slow exchange limit at low temperature was not reached even at 250 Hz, at which a higher coalescence temperature is expected. Dynamic behaviour of some thiolato-bridged rhodium(I) dinuclear complexes has been described [13]. As in that case, the fast exchange phenomenon we have observed does not require Ir_2S_2 ring-opening. However, since the complex has a *cis* geometry, the rotation of Ir—S bonds to give inversion of configuration (and therefore to place the t-Bu group in *endo* position between the two phosphine ligands) is certainly unfavourable because of steric hindrane. The ring-inversion may imply a CO and PMe_2Ph exchange through a tetrahedral intermediate [13] to give again a structure with the two phosphine ligands in *cis* positions and the t-butyl group between them in an *exo* position.

(c) [Ir₂(μ-SBu-t)₂(CO)₂(P(NMe₂)₃)₂] (IV). From infrared and ^1H NMR data, quite similar to those of $[Ir_2(\mu\text{-}SBu\text{-}t)_2(CO)_2(PMe_3)_2]$, this complex is shown to present a single *cis* isomer.

(d) [Ir₂(μ-SBu-t)₂(CO)₂(PPh₃)₂] (V). When PPh_3 is allowed to react with the carbonyl complex I, along with the formation of the complex $[Ir_2(SBu\text{-}t)_2(CO)_3(PPh_3)]$ (vide infra), we observe that two $\nu(CO)$ bands of almost the same intensity arise at 1955 and 1936 cm^{-1}. After isolation of V, the infrared spectra show, in addition to these $\nu(CO)$ bands, one band at 1966 cm^{-1} and a shoulder at 1951 cm^{-1}. The ratio between these two systems of bands depends on the experimental conditions. Refluxing the mixture in benzene for 24 h led, after crystallization at $-25°C$, to red crystals which show two $\nu(CO)$ bands at 1966 and 1951 cm^{-1} in hexadecane solution or 1956 and 1936 cm^{-1} in CsBr pellets, and two t-Bu signals in the ^1H NMR spectrum. Calculation of the angle between the two CO oscillators from the band intensities, 1966 (0.57) and 1951 (0.43)

gives 81°. This value and the spectroscopic data are consistent with a *cis* geometry for this isomer Va.

Concerning the isomer Vb, which is formed in a first step, as shown by infrared data, a single t-Bu signal is detected in the ^{1}H NMR at low temperature with freshly prepared solutions. This observation suggests a *syn-trans* geometry in which the t-Bu groups are magnetically equivalent. However a value of about 110° for the angle between the CO vectors is expected, i.e. strong and very strong intensities; in addition, a lower splitting than that observed for the *cis* isomer (15 cm^{-1} in solution) should be observed [3]. Our attempts to obtain this isomer in a pure form failed. Because of the discrepancy between the indications from the infrared and NMR data we cannot assign a geometry to isomer Vb.

(e) [Ir$_2$(μ-SBu-t)$_2$(CO)$_2$(P(OMe)$_3$]$_2$] (VI). Three ν(CO) bands were observed in solution, at 1985 vs, 1975 vs and 1964 vs, either from crystals of VI or after the substitution reaction, whatever the experimental conditions. However, in the solid state the infrared spectra show two ν(CO) bands of almost the same intensity. Since a *cis-anti* structure is known for isomer VIa from the X-ray studies [11], the equilibrium in solution between isomers can be retained to explain the infrared spectra. The ^{31}P and ^{1}H NMR data are apparently consistent with this *cis-anti*-isomer, since a single signal was observed for the ^{31}P spectra and two t-Bu peaks in ^{1}H NMR. Similarly the signal at 1.87 ppm (triplet, J 0.6 Hz) can be assigned to the t-Bu group in *exo* position, the splitting being induced by the two phosphorus atoms in *cis* position. At low temperature and at 250 MHz broader signals were observed, but the slow exchange limit was not reached. For the ^{13}C NMR spectra the shifts for the phosphine ligand tertiary t-butyl groups are in agreement with this isomer, the triplet at 34.07 ppm being assigned to the *endo*-t-Bu group with a coupling of 2.9 Hz with two equivalent phosphorus atoms in a *trans* disposition. However in the CO region three doublets were detected (Table 2). The more intense doublet can tentatively be assigned to the CO ligands of the *cis* isomer with a coupling constant ^2J(PC) of 12.9 Hz. The other two doublets (^2J(PC) 7.4 Hz) could be due to the CO groups of the *anti-trans* isomer, a slight difference in the magnetic environments being induced by the t-Bu groups in the *endo*- and the *exo*-positions.

According to these results an exchange presumably occurs in solution between the *cis* isomer VIa and another isomer, possibly the *trans-anti* isomer VIb. This process is fast on the ^{1}H NMR time scale; it is slow, however, at 62.86 MHz for the ^{13}CO groups for which the relaxation time is short, whereas it is faster for the t-Bu groups which are characterized by longer relaxation times.

2 [Ir$_2$(μ-SBu-t)$_2$(CO)$_3$(PR$_3$)]

The addition of trimethylphosphine ligand to concentrated solutions of I leads to the isolation of the trinuclear compound [Ir$_3$(μ-SBu-t)$_3$(μ-CO)(CO)$_4$-(PMe$_3$)$_2$] [14]. Moreover, following by infrared spectroscopy the progressive addition of two PR$_3$ ligands (R = Me, NMe$_2$, Ph, OMe) to the carbonyl I, we observed that a system of three bands grows as the carbonyl bands decrease. For the ratio PR$_3$/Ir = 1 the infrared spectra show the bands of compounds I, [Ir$_2$(μ-SBu-t)$_2$(CO)$_2$(PR$_3$)$_2$] and the three bands already mentioned. The same

behaviour is observed when trimethylphosphine is added to dilute solutions of I, or when the transformation of the trinuclear complex is followed in the infrared cell. The same infrared spectra are finally observed when equimolar quantities of $[Ir_2(\mu\text{-}SBu\text{-}t)_2(CO)_4]$ and $[Ir_2(\mu\text{-}SBu\text{-}t)_2(CO)_2(PR_3)_2]$ are mixed all at one. Crystallization did not give the intermediate complex. For this reason we followed the change by infrared and NMR spectra after mixing the two complexes. Such studies are examplified by the case R = Me. When the equilibrium is reached (about 6 h), the infrared and ^{1}H NMR data at 250 MHz for CD_2Cl_2 solutions are consistent with the formula $[Ir_2(\mu\text{-}SBu\text{-}t)_2(CO)_3(PMe_3)]$ VII for the intermediate. In addition to the signals of I and II, two t-Bu signals of the same intensity are observed together with a doublet for the PMe_3 resonance (Table 3); in the infrared there are three bands of almost the same intensity at 2046, 1979 and 1957 cm^{-1}. Similarly the ^{13}C NMR spectra were recorded (Table 2): three CO resonances are observed, one being split by coupling with the *cis* phosphorus atom. For one t-Bu group the shifts of the CH_3 and the quaternary carbon are little different from those of the *endo*-t-Bu signals for I and II, and we assign for this group an *endo* position between the CO ligands. Comparison of the shifts of the second t-Bu group for II and VII indicates an *exo* position (Table 2). Consequently complex VII presents the *anti* geometry illustrated in Fig. 2.

It is of interest to consider the left-hand moieties of this complex with the t-Bu in *exo* position as arising from the complex II; similarly the right-hand moiety resembles that of the carbonyl complex with the t-Bu group in *endo* position. The slow exchange observed may involve a splitting of the bridges to give mononuclear fragments. In this case, stochastic recombination of the fragments should give rise to many isomers of complexes I, II and VII according to the various positions of the t-Bu groups. That is not observed. Moreover in ^{1}H NMR the shifts of the phosphine ligands and of the t-Bu groups in I and II are very slightly changed after the mixture of the reagents; for instance, 1.42 instead of 1.41 for the t-Bu peak of I. (In the case of the $P(NMe_2)_3$ analogues a single broad t-Bu signal is detected.) This observation is characteristic of an exchange phenomenon between the various species I, II and VII. This process is slow on the NMR time scale, and the $Ir(SBu\text{-}t)(CO)_2$ and $Ir(SBu\text{-}t)(CO)(PMe_3)$ mononuclear fragments would be detected by infrared spectroscopy if they were present in appreciable amounts. Thus we suggest an intermediate species having four metal centers. Such tetranuclear intermediates have been already proposed in palladium and platinum chemistry [15,16].
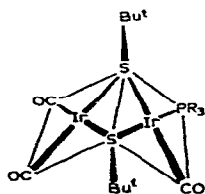

Fig. 2. Geometry of the complex $[Ir_2(\mu\text{-}SBu\text{-}t)_2(CO)_3(PMe_3)]$.

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