16. Intramolecular Dynamics of Tetranuclear Iridium Carbonyl Cluster Compounds

Part III[1])

Crystallographic and Dynamic Evidence for the Intermediate of the 'Merry-go-round' Process in Nonacarbonyl-μ_3-(1,3,5-trithiane)-tetrairidium

by **Gianfranco Suardi**[2]), **Andres Strawczynski**, **Renzo Ros**[3])*, and **Raymond Roulet***

Institut de Chimie Minérale et Analytique de l'Université de Lausanne, 3, place du Château, CH–1005 Lausanne

and **Fabrizia Grepioni** and **Dario Braga***

Dipartimento di Chimica 'G. Ciamician', Università di Bologna, Via Selmi 2, I–40126 Bologna

(16.X.89)

The title complex crystallises in two C_{3v} isomeric forms differing in carbonyl-ligand arrangement. In solution, the isomer **1b** with three edge-bridging carbonyls on a common face of the metal tetrahedron converts *via* an endothermic equilibrium into the isomer **1u** with no bridging carbonyls. The latter was shown by ^{13}C-NMR to be the intermediate of the 'merry-go-round' process which exchanges the sites of the basal CO's.

Introduction. – Two structural forms prevail for the solid and solution ground states of tetranuclear dodecacarbonyl clusters: the T_d form with no bridging carbonyls and the C_{3v} form with three edge-bridging carbonyls on a common face [1]. For most of the tetrahedral clusters, these structures are configurationally non-rigid, and a fluxional $C_{3v} \rightleftarrows T_d$ process was first outlined by *Cotton* for $[Co_4(CO)_{12}]$ [2]. The local bridge-radial exchange in the 'C_{3v} form', known as the 'merry-go-round' of basal CO's is commonly observed in derivatives of these carbonyl clusters [3–6]. In analogy with bimetallic complexes such as $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ [7], the 'merry-go-round' process is thought to proceed *via* an unbridged intermediate, and we report here the first experimental evidence for this.

Synthesis and Crystallographic Studies of Nonacarbonyl-μ_3-(1,3,5-trithiane)-tetrairidium (1). – In the course of a systematic study of the fluxional behaviour of clusters derived from $[Ir_4(CO)_{12}]$ [8], the title compound was obtained on reaction of equimolar equivalents of $NEt_4[Ir_4(CO)_{11}I]$, 1,3,5-trithiane, and $Ag[BF_4]$ in THF at 258 K, followed by filtration and solution reflux. Chromatography of the products on silica-gel TLC plates with CH_2Cl_2/hexane 2:3 gave yellow decacarbonyl-μ_2-(1,3,5-trithiane)-tetrairidium ($[Ir_4(CO)_{10}(SCH_2)_3]$; 12%) and yellow-orange $[Ir_4(CO)_9(SCH_2)_3]$ (**1**; 71%). Crystallisation of **1** from CH_2Cl_2 at low temperature or from CH_2Cl_2/heptane at room temperature gave some yellow crystals of isomers **1b** and **1u**, respectively.

The molecular structures of both isomers were determined by single-crystal X-ray diffractometry at room temperature and are shown in *Fig. 1*. Relevant bond distances and angles for **1b** and for both independent molecules of **1u** are listed in the *Table*.

---

[1]) Part I and II: see [8].

[2]) In part from the doctoral dissertation of *G.S.*, University of Lausanne, 1989.

[3]) Permanent address: Istituto di Chimica Industriale dell'Università, Via Marzolo 9, I–35131 Padova.

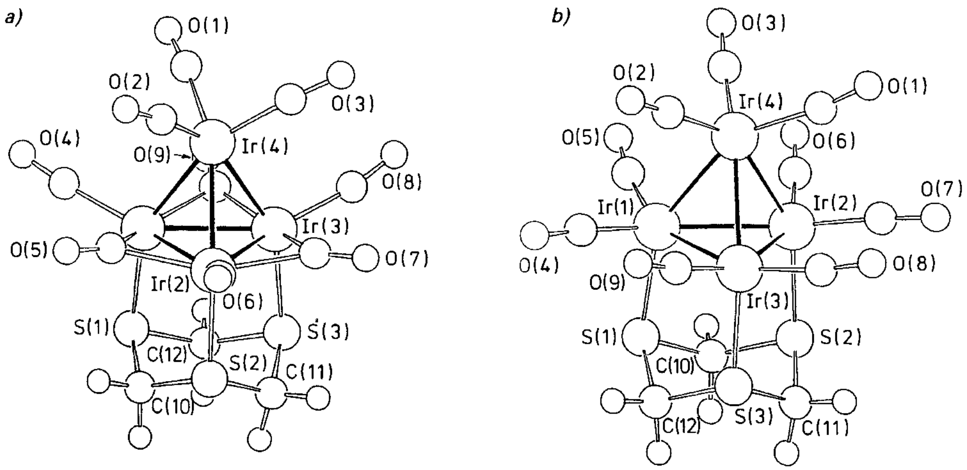


Fig. 1. *Molecular structures of* a) *tri-μ-carbonyl-hexacarbonyl-μ_3-(1,3,5-trithiane)-*tetrahedro-*tetrairidium* (**1b**) *and* b) *nonacarbonyl-μ_3-(1,3,5-trithiane)-*tetrahedro-*tetrairidium* (**1u**). The numbering of the Ir-atoms is arbitrary.

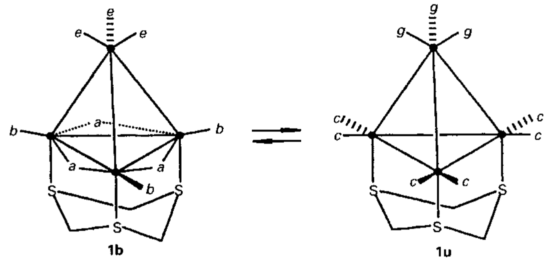
Table. *Selected Bond Distances* [Å] *and Angles* [°] *for the Two Isomers of* $[Ir_4(CO)_9(SCH_2)_3]$ (standard deviation in parentheses)

Bond	**1b**	**1u**		Angle	**1b**	**1u**	
Ir(1)–C(4)	1.93(3)	1.80(2)	1.88(3)	Ir(1)–C(4)–O(4)	177(3)	175(2)	175(3)
Ir(1)–C(5)	2.02(3)	1.89(2)	1.87(2)	Ir(1)–C(5)–O(5)	143(2)	172(2)	175(2)
Ir(1)–C(9)	2.18(3)			Ir(1)–C(9)–O(9)	143(3)		
Ir(2)–C(5)	2.14(3)			Ir(2)–C(5)–O(5)	137(2)		
Ir(2)–C(6)	1.84(4)	1.86(2)	1.88(2)	Ir(2)–C(6)–O(6)	174(4)	173(2)	175(2)
Ir(2)–C(7)	2.11(3)	1.87(2)	1.92(3)	Ir(2)–C(7)–O(7)	140(3)	175(29)	176(3)
Ir(3)–C(7)	2.08(3)			Ir(3)–C(7)–O(7)	140(3)		
Ir(3)–C(8)	1.91(3)	1.88(3)	1.87(3)	Ir(3)–C(8)–O(8)	171(3)	173(2)	175(2)
Ir(3)–C(9)	2.13(3)	1.89(3)	1.90(3)	Ir(3)–C(9)–O(9)	140(3)	176(2)	174(2)
Ir(4)–C(1)	1.99(3)	1.95(4)	1.90(4)	Ir(4)–C(1)–O(1)	173(3)	173(2)	170(2)
Ir(4)–C(2)	1.90(3)	1.91(2)	1.85(3)	Ir(4)–C(2)–O(2)	174(3)	176(3)	172(3)
Ir(4)–C(3)	1.93(3)	1.85(3)	1.89(2)	Ir(4)–C(3)–O(3)	176(3)	176(3)	168(3)
Ir–Ir[a])	2.683(2)	2.655(2)	2.655(2)	S(1)–C(10)–S(2)	120(2)	113(1)	117(2)
Ir–S[a])	2.297(7)	2.364(5)	2.344(5)	S(2)–C(11)–S(3)	117(2)	114(1)	113(2)
S–C[a])	1.81(4)	1.82(3)	1.82(4)	S(1)–C(12)–S(3)	119(2)	113(2)	114(2)
C–O[a])	1.15(3)	1.15(3)	1.15(3)	C–S–C[a])	100(2)	100(1)	101(2)

[a]) Mean values.

The four Ir-atoms define an almost regular tetrahedron in both isomers, with relatively longer Ir–Ir distances in **1b** (ranging from 2.675(1) to 2.690(1) Å) than in **1u** (2.633(1) to 2,672(1) Å). The heterocyclic ligand adopts a chair conformation underneath a face of the metal tetrahedron with each S-atom σ-bonded to a basal Ir-atom. The nine CO ligands adopt an all-terminal bonding mode in **1u**, whereas in **1b** three CO's are edge-bridging around the basal face, and six are terminal. This is the first time that both CO ligand distributions have been observed in the solid state for the same neutral Ir_4 compound [9]. The bridging CO's in **1b** show a large degree of asymmetry (Ir–C(bridge) range from 2.02(3) to 2.18(3) Å), even though the 'short-long' bond sequence does not

Scheme



conform to the idealised threefold symmetry of the molecule. The apical Ir(CO)$_3$ group in **1b** is tilted by *ca.* 16° from the 'pseudo-*trans*' position with respect to the basal-apical Ir—Ir bond, while such a deformation is not observed in **1u** nor in most other Ir$_4$ species. This deformation seems to be related to a tighter crystal packing in **1b** relative to **1u**. This is illustrated by a difference in densities (3.98 and 3.72 g·cm^{-3}, resp.) and by shorter values for the minimum intermolecular O···O and O···H distances (2.87 and 2.22 Å, resp., in **1b**; 3.22 and 2.34 Å, resp., in **1u**). The molecular units in **1b** have also less rigidbody vibrational freedom than in **1u** (U_{eq} mean values: Ir 0.0081 and 0.0196, S 0.017 and 0.040, C 0.020 and 0.038, and O 0.041 and 0.073 Å^2 in **1b** and **1u**, resp.).

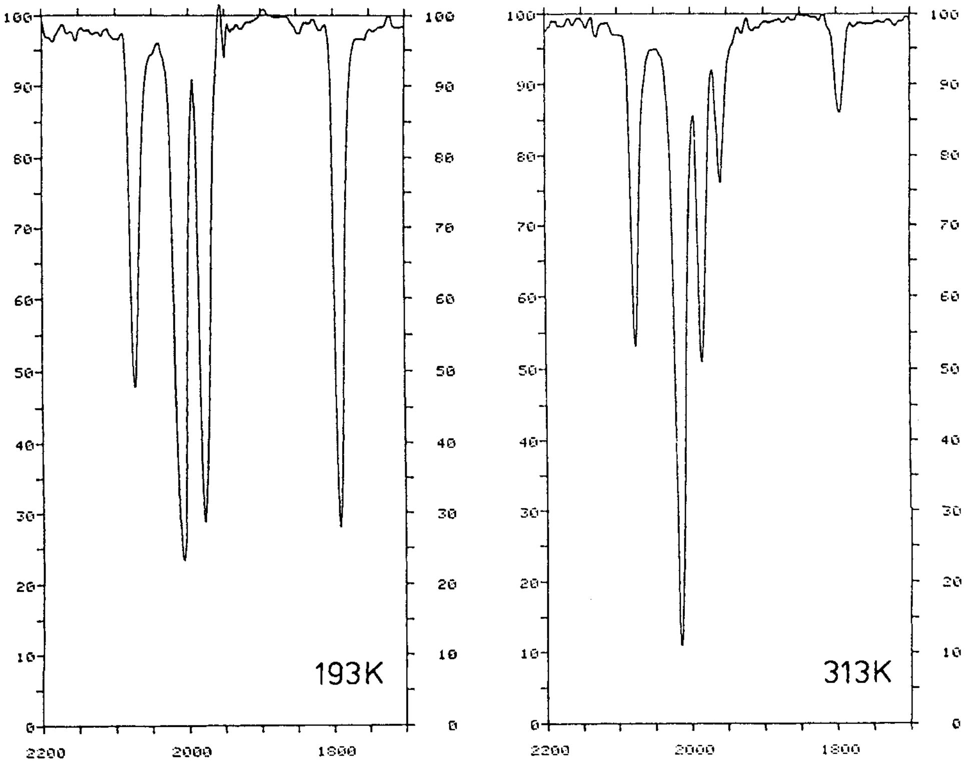


Fig. 2. *Variable-temperature IR spectra of* **1** *in THF solution*

IR and NMR Study of 1 in Solution. – The variable-temperature IR spectra of **1** in THF show that an isomerisation equilibrium takes place between **1b** ($\nu(\mu_2\text{-CO})$ at 1795 cm^{-1}) and **1u** (this characteristic band is absent from the nujol spectrum of **1u** at r. t.), since a reversible variation of absorbance for the band at 1795 cm^{-1} is observed upon changing the temperature *(Fig. 2)*. From the absorbance measurements at 313 K, a ratio [**1u**]/[**1b**] of 10.6 is obtained, which agrees within 4% with the value obtained by ^{13}C-NMR spectroscopy.

The ^{13}C-NMR spectrum of **1** in (D_8)THF at 168 K (see *Exper. Part*) presents five CO resonances (see *a–c, e,* and *g* in the *Scheme*). Three equal-intensity resonances are due to the presence of **1b** (233.3 *(a)*, 183.5 *(b)*, and 160.2 *(e)* ppm) and two (relative intensity 2:1) to the presence of **1u** (169.8 *(c)* and 160.8 *(g)* ppm). In the region of slow exchange, the relative population of signal *c* increases with respect to that of *a* (or *b*) upon warming from 168 to 215 K. These spectral results imply that the isomerisation **1b**$\rightleftarrows$**1u** is endothermic, and a quantitative calculation gave the following thermodynamic parameters: $\Delta H_{298} = 15.15 \pm 0.09$ kJ·mol^{-1} and $\Delta S_{298} = 67.7 \pm 0.4$ J·mol^{-1}·K^{-1} ($K_{298} = 7.5$).

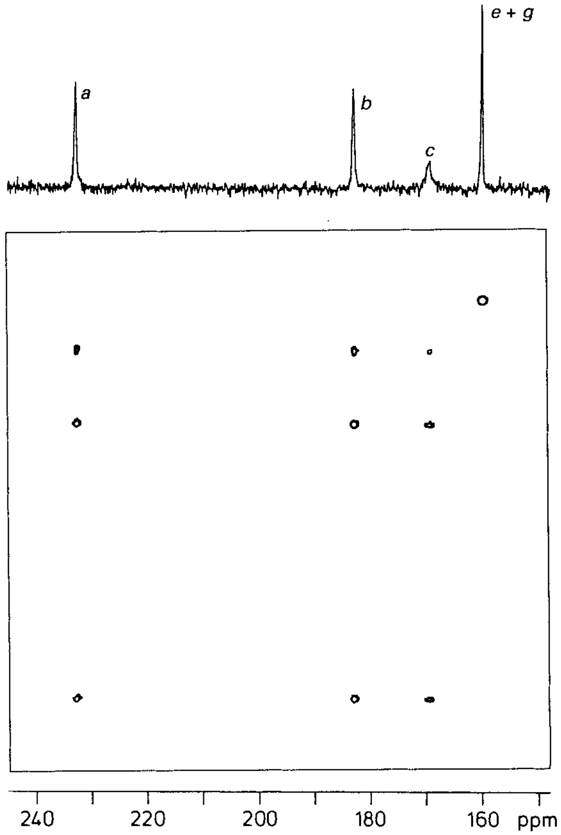


Fig. 3. *2D-Exchange ^{13}C-NMR spectrum of ^{13}C-enriched* **1** *in (D_8)THF at 195 K.* Mixing time: 100 ms. For the attribution of the CO groups, see *Scheme*; signals of *e* and *g* superimposed.

The 2D ^{13}C-NOESY NMR spectrum of **1** in (D_8)THF at 195 K *(Fig. 3)* shows the dynamic connectivities $a \leftrightarrow b$, $a \leftrightarrow c$, $b \leftrightarrow c$, and $e \leftrightarrow g$, but no exchanges between *e* and *a, b, c*. This rules out edge-bridging of CO's to an alternative face of the metal core. Therefore, the fluxional process up to 323 K corresponds to the 'merry-go-round' of the bridged and unbridged CO's of the basal face.

The last step was to show that isomer **1u** is the intermediate of the fluxional process. This was confirmed by simulation of the variable-temperature ^{13}C-NMR spectra *(Fig. 4)*.

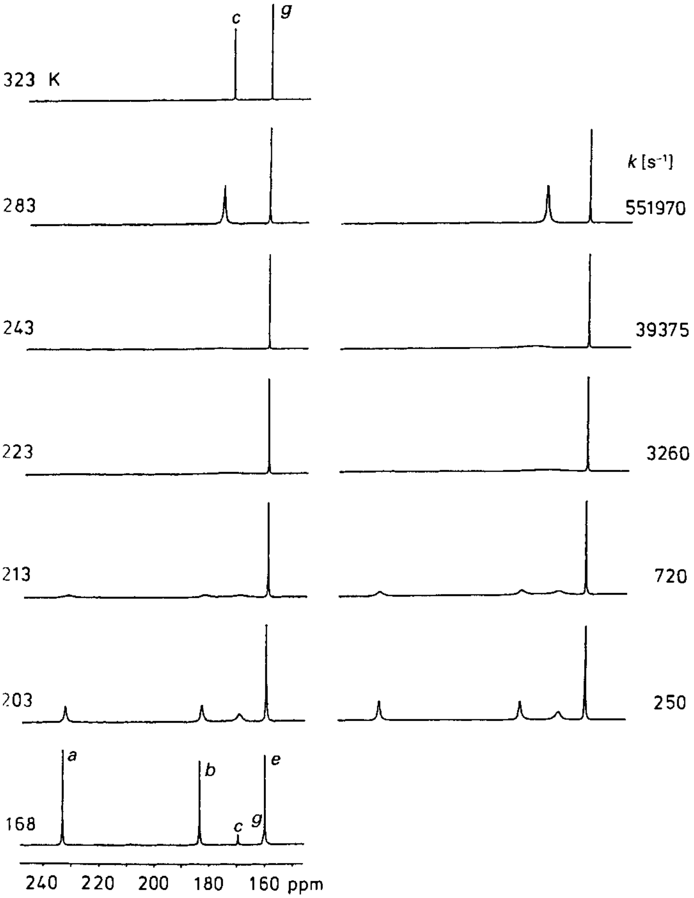


Fig. 4. *Variable-temperature ^{13}C-NMR spectra of ^{13}C-enriched* **1** *in (D_8)THF.* At 323 K, the ratio **1u**/**1b** is 9:1.

Line-shape analysis [10] was effected using the following *Kubo-Sack* matrix elements: $(a,a) = (b,b) = (e,e) = -k, (a,c) = (b,c) = (e,g) = k, (c,a) = (c,b) = k/2K, (g,e) = k/K, (c,c) = (g,g) = -k/K$, with k = rate constant of CO exchange in s^{-1} and K = [**1u**]/[**1b**]. The calculated K and its temperature dependance were in excellent agreement with the values calculated from the thermodynamic parameters. A value of 38.0 ± 0.5 $KJ \cdot mol^{-1}$ was obtained for the free enthalpy of activation of the 'merry-go-round' process at 298 K.

Conclusion. – Complex $[Ir_4(CO)_9(SCH_2)_3]$ (**1**) is the first example where the unbridged intermediate of a 'merry-go-round' process is sufficiently stable to be observed. It seems logical to propose that in this system, the transition state is a C_3 species with three semi-bridging, basal CO's.

No general extrapolation concerning the nature of the intermediate or transition state in other tetranuclear clusters can be made since this seems to depend on the symmetry of the ground-state structure. Indeed, we have already shown that the 'merry-go-round' process in $[Ir_4(CO)_{11}Br]^-$ does not pass through the unbridged intermediate of a non-mutual [12] exchange [8]. This can be related to the ground-state structure of this anion which features two asymmetrically bridging CO's with shorter bonds to the same Ir-atom [11]. Formation of an unbridged intermediate would require the rupture of one of the two shorter bonds, and is, therefore, not the lowest activation energy process.

We have also prepared nonacarbonyl-μ_3-(1,3,5-trithiane)-dirhodiumdiiridium ($[Rh_2Ir_2(CO)_9(SCH_2)_3]$ which has a geometry analogous to that of **1b** with three bridging basal CO's on the Rh_2Ir basal plane [13]. Its lowest activation energy process is a local rotation of the apical CO's, even though the 'merry-go-round' process is not hampered by radial substituents. This last example illustrates that the general assumption that the 'merry-go-round' process is the lowest activation energy process in these systems is not always correct.

We thank the *Swiss National Science Foundation* and the *Ministero della Pubblica Istruzione Italiana* for financial support.

Experimental Part

1. *General.* IR spectra: *Perkin-Elmer-880* spectrophotometer, *P/N 21.000* variable-temperature cell *(Specac Ltd.)* with CaF_2 windows. ^{1}H- and ^{13}C-NMR spectra: *Bruker WH 360* (90.55 MHz); in (D_8) THF at normal atmospheric pressure; δ in ppm, J in Hz. 2D ^{13}C-NMR spectra: in (D_8) THF at 195 K from a NOESY experiment using TPPI [15]; 256 t_1 increments with 2-K transients; spectral width 8928.6 Hz in the F_2 domain and 4464.3 Hz in the F_1 domain; the spectra were zero-filled to 2 K × 2 K and shifted, a squared sine bell was applied in both domains prior to *Fourier* transformation.

2. *Decacarbonyl-μ_2-(1,3,5-trithiane)-tetrairidium* ($[Ir_4(CO)_{10}(SCH_2)_3]$) *and Nonacarbonyl-μ_3-(1,3,5-trithiane)-tetrairidium* ($[Ir_4(CO)_9(SCH_2)_3]$; **1**). A soln. of $NEt_4[Ir_4(CO)_{11}I]$ [14] (500 mg, 0.374 mmol) and 1,3,5-trithiane (78 mg, 0.562 mmol, *Fluka*) in THF (150 ml) was vigorously stirred, after addition of $Ag[BF_4]$ (109 mg, 0.562 mmol), for 1 h at 258 K. The mixture containing solid AgI was filtered through a 15 × 3 cm column packed with silica gel (70–230 mesh) and eluted with cold THF (150 ml). The yellow filtrate was warmed to 338 K for 21 h. Then, THF was evaporated and the residue dissolved in CH_2Cl_2 and chromatographed on silica-gel TLC plates. Elution with CH_2Cl_2/hexane 2:3 gave 2 main fractions, affording yellow $[Ir_4(CO)_{10}(SCH_2)_3]$ (53 mg, 12%) and yellow-orange **1** (308 mg, 71%) after crystallisation from CH_2Cl_2/MeOH and CH_2Cl_2/heptane, resp.

μ_2-Complex $[Ir_4(CO)_{10}(SCH_2)_3]$: IR (CH_2Cl_2, 298 K): 2097*s* (CO), 2068 (sh), 2057v*s*, 2036v*s*, 2015*s*, 1964*w*, 1844*w* (br.), 1819*w* (br.). Anal. calc. for $C_{13}H_6Ir_4O_{10}S_3$ (1187.24): C 13.15, H 0.51; found: C 13.48, H 0.56.

μ_3-Complex **1**: IR (THF, 298 K): 2080*s*, 2018v*s*, 1983*s*, 1955*m*, 1795*m* (CO). IR (nujol, 298 K): 2084*s*, 2016v*s*, 2004 (sh), 1972v*s*, 1954*s*, 1933*s*, 1922*s*. (These data indicate that for **1**, two isomers **1b** and **1u** are present in soln., since the characteristic band at 1795 cm^{-1} (μ_2-CO) is absent from the nujol spectrum of **1u** at r.t.) ^{1}H-NMR ((D_6)acetone, 303 K): 8.55 (*m*, 3 H); 4.26 (*m*, $J(AB) = 13$, 3 H). ^{13}C-NMR (^{13}C-enriched sample of **1** (*ca.* 25% ^{13}CO); (D_8)THF, 168 K): **1b**: 233.3 (*a*), 183.5 (*b*), 160.2 (*e*); **1u**: 169.8 (*c*), 160.8 (*g*) (for *a–c*, *e* and *g*, see the *Scheme*). Anal. calc. for $C_{12}H_6Ir_4O_9S_3$ (1159.23): C 12.43, H 0.52; found: C 12.68, H 0.52.

Slow recrystallisation of **1** from CH_2Cl_2 at *ca.* 250 K gave some yellow crystals of isomer **1b**; the mother liquor was removed with a syringe and the residue washed with 2-propanol and vacuum dried. Suitable yellow-orange crystals of isomer **1u** were grown by the solvent diffusion technique by layering hexane over a concentrated CH_2Cl_2 soln. of **1**.

3. *Crystral-Structure Determination.* Diffraction intensities were collected at r.t. on an *Enraf-Nonius CAD4* diffractometer using Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å) and $\omega/2\theta$ scans. Isomer **1b**: monoclinic cell (Cc) with $a = 13.100(2)$, $b = 9.708(3)$, $c = 15.222(2)$ Å, $\beta = 92.56(1)°$, $V = 1934(1)$ Å^3, $Z = 4$, $F(000) = 2023$, $\mu = 268.0$ cm^{-1}. An absorption correction was applied by the *Walker* and *Stuart* method [16] once a complete model was obtained, and all atoms were refined isotropically. Refinement of 147 parameters using 3459 independent reflections with $F_0 > 4\sigma(F_0)$ collected in the range $2.5 < \theta < 35°$ gave residual R and $R_w = 0.064$ and 0.068, resp. Isomer **1u**: triclinic cell ($P\bar{1}$) with $a = 16.84(1)$, $b = 16.862(9)$, $c = 8.697(5)$ Å, $\alpha = 104.63(6)$, $\beta = 104.17(6)$, $\gamma = 111.24(5)°$, $V = 2067(2)$ Å^3, $Z = 4$, $F(000) = 2023$, $\mu = 250.8$ cm^{-1}. An absorption correction was applied by azimutal scanning of 10 reflections ($\chi > 80°$) and by subsequent application of the *Walker* and *Stuart* method. Two independent molecules were present in the asymmetric unit. The possible choice of an orthorhombic cell was ruled out on the basis of unmatching reflection equivalences and confirmed by successful treatment of the data in $P\bar{1}$. Refinement of 298 parameters using 5227 observables with $F_0 > 4\sigma(F_0)$ in the range $2.5 < \theta < 25°$ gave R and $R_w = 0.066$ and 0.071, resp. In both **1b** and **1u**, Ir and S-atoms were treated anisotropically, while C- and O-atoms were treated isotropically. H-Atoms of the CH_2 groups were added in calculated positions (C–H, 1.08 Å) and refined 'riding' on their corresponding C-atoms. For all calculations, the SHELX76 package of programs was used [17].

Supplementary Material. – Lists of observed and calculated structure factors, of crystal data, of fractional atomic coordinates and anisotropic thermal parameters, and of interatomic distances and angles are available on request and deposited at the *Cambridge Crystallographic Data Center.*

REFERENCES

[1] E. Band, E. L. Muetterties, *Chem. Rev.* **1978,** *78,* 6.

[2] F. A. Cotton, *Inorg. Chem.* **1966,** *5,* 1083.

[3] G. F. Stuntz, J. R. Shapley, *J. Organomet. Chem.* **1981,** *213,* 389; *J. Chem. Soc.* **1977,** *99,* 607; J. R. Shapley, G. F. Stuntz, M. R. Churchill, J. P. Hutchinson, *J. Am. Chem. Soc.* **1979,** *101,* 7425.

[4] B. E. Mann, C. M. Spencer, A. K. Smith, *J. Organomet. Chem.* **1983,** *244,* C17; B. E. Mann, B. T. Pickup, A. K. Smith, *J. Chem. Soc., Dalton Trans.* **1989,** 899.

[5] D. Braga, R. Ros, R. Roulet, *J. Organomet. Chem.* **1985,** *286,* C8; R. Ros, A. Scrivanti, V. G. Albano, D. Braga, L. Garlaschelli, *J. Chem. Soc., Dalton Trans.* **1986,** 2411; D. Braga, F. Grepioni, G. Guadalupi, A. Scrivanti, R. Ros, R. Roulet, *Organometallics* **1987m,** *6m,* 56.

[6] R. Della Pergola, L. Garlaschelli, S. Martinengo, F. Demartin, M. Manassero, M. Sansoni, *Gazz. Chim. Ital.* **1987,** *117,* 245.

[7] J.G. Bullit, F. A. Cotton, T. J. Marks, *J. Am. Chem. Soc.* **1970,** *92,* 2155.

[8] A. Strawczynski, R. Ros, R. Roulet, *Helv. Chim. Acta* **1988,** *71,* 867; A. Strawczynski, R. Ros, R. Roulet, *Helv. Chim. Acta* **1988,** *71,* 1885.

[9] A. Strawczynski, G Suardi, R. Roulet, R. Ros, 'Abstract of the XIIIth International Conference on Organometallic Chemistry', Torino 4–9. 9. 1988, p. 15.

[10] 'EXCHANGE', program library, Computing Center, University of Lausanne.

[11] G. Ciani, M. Manassero, A. Sironi, *J. Organomet. Chem.* **1980,** *199,* 271.

[12] P. J. Jesson, E. L. Muetterties, 'Dynamic Nuclear Magnetic Resonance', Eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1725, p. 255.

[13] G. Suardi, doctoral dissertation, University of Lausanne, 1989.

[14] P. Chini, G. Ciani, L. Garlaschelli, M. Manassero, S. Martinengo, A. Sironi, F. Canziani, *J. Organomet. Chem.* **1978,** *152,* C35.

[15] G. Bodenhausen, H. Kogler, R. R. Ernst, *J. Magn. Reson.* **1984,** *58,* 370.

[16] N. Walker, D. Stuart, *Acta Crystallogr., Sect. A* **1983,** *39,* 158.

[17] G. M. Sheldrick, 'SHELX76 System of Computer Programs', University of Cambridge, England, 1976.