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## 7. Conclusion and Future Prospects

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curs relative to the metallic framework. The possible relationship of the migration of small molecules over clusters to those occurring during the chemisorption of small molecules to a metal surface is an additional incentive for such dynamic studies.

The bulk of the studies on the fluxional behaviour of cluster compounds have dealt with the migration of carbon monoxide

over tri- and tetrametallic CO clusters. The first proposal for a pathway of CO scrambling was made by Cotton in 1966 [1], and involves bridge opening and closing of the CO ligands to move them around the cluster in concerted steps. This pathway is the so-called merry-go-round process.

The present report presents a detailed picture of the merry-go-round, as well as of other scrambling pathways found to take place in homo- and heterometallic dodecacarbonyls of Ir and Rh and their derivatives.

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### 1.1. Clusters of $C_{3v}$ Symmetry

The ground-state geometry of  $\text{Rh}_4(\text{CO})_{12}$  in solution has  $C_{3v}$  symmetry [2]. A simulation of its variable-temperature and -pressure  $^{13}\text{C}$ -NMR spectra [3] (Fig. 1, a) has shown that the fluxional process leading to complete CO scram-

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over tri- and tetrametallic CO clusters. The first proposal for a pathway of CO scrambling was made by Cotton in 1966 [1], and involves bridge opening and closing of the CO ligands to move them around the cluster in concerted steps. This pathway is the so-called merry-go-round process.

The present report presents a detailed picture of the merry-go-round, as well as of other scrambling pathways found to take place in homo- and heterometallic dodecacarbonyls of Ir and Rh and their derivatives.

## 1. The Merry-go-round

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bling is the merry-go-round of six CO's about any one of the triangular faces of an unbridged transition state (the *Cotton* mechanism).

The dependence of the rate constant on pressure gave a negative value for the activation volume (Fig. 1, b), indicating that the transition state has a smaller molar volume than that of the bridged ground state. Since the opening of bridges should lead to an increase in volume, the negative value of  $\Delta V^\ddagger$  suggests a substantial shortening of the unbridged M–M bonds relative to the bridged ones. A statistical study of X-ray diffraction data has indeed shown that the differences between the mean bond lengths for unbridged and CO-bridged M–M bonds have values of  $-0.027$  and  $-0.019$  Å for Rh and Ir, respectively [4]. A recent DFT calculation [5] on both the bridged ( $C_{3v}$ ) and unbridged ( $T_d$ ) forms of  $Rh_4(CO)_{12}$  confirms that the former has a smaller total bonding energy than the latter and their difference in molar volume, as measured with *Connolly* surfaces, agrees surprisingly well with the experimental value of  $\Delta V^\ddagger$  ( $-7$  vs.  $-6 \pm 1$   $\text{cm}^3 \text{mol}^{-1}$ ).

The ground-state geometry of  $IrRh_3(CO)_{12}$  in solution has  $C_{3v}$  symmetry like  $Rh_4(CO)_{12}$  with an Ir-atom replacing the apical Rh-atom [3]. The exchange matrix based on 2D-EXSY spectra and used to simulate correctly the VT- and VP- $^{13}\text{C}$ -NMR spectra implies that CO scrambling is intramolecular (Rh,C couplings are conserved), that the merry-go-round on the basal  $Rh_3$  face has a higher free enthalpy of activation than that on the  $IrRh_2$  faces, and that  $IrRh_3(CO)_{12}$  is less fluxional than  $Rh_4(CO)_{12}$  ( $\Delta G^\ddagger_{298} = 57.9 \pm 0.4$  and  $43.8 \pm 0.4$   $\text{kJ mol}^{-1}$ , respectively [3]). These results suggest that replacing the apical Rh-atom by Ir induces a relative shift of electron density towards the basal  $Rh_3$  face of the cluster. Since bridging CO's are better  $\pi$ -acceptors than terminal CO's, this shift stabilizes the ground state of  $IrRh_3(CO)_{12}$  relative to  $Rh_4(CO)_{12}$  and slows down the merry-go-round, that is the  $3 \mu_2\text{-CO} \rightarrow 3 \eta^1\text{-CO}$  exchange.

### 1.2. Clusters of Symmetry Lower Than $C_{3v}$

About 17 clusters of the type  $Ir_4(CO)_{11}L$  of  $C_s$  symmetry have been examined to

date. For  $L = \text{PPh}_2, \text{PH}_2\text{Ph}$  [6],  $\text{P(OPh)}_3, \text{P(OMe)}_3$ , and  $\text{P(OCH}_2)_3\text{CEt}$  [7], three interconverting isomers are observed in solution (Fig. 2).

The observed isomers merely correspond to three minima on the kinetic pathways of CO scrambling, whose free enthalpies differ at most by *ca.* 9  $\text{kJ mol}^{-1}$  at 298 K. For  $L = \text{P(OPh)}_3$ , only the equilibrium between B and A is observed ( $\Delta G^0 = 1.8 \pm 0.1$   $\text{kJ mol}^{-1}$  at 298 K [6]). The dependence of the population ratio of the two isomers and of the rate constant  $k_1(\text{B} \rightarrow \text{A})$  on pressure gave values of  $-8.3 \pm 0.2$  and  $-9.4 \pm 1.1$   $\text{cm}^3 \text{mol}^{-1}$  for  $\Delta V_0$  and  $\Delta V^\ddagger$ , respectively [3]. The negative value of  $\Delta V_0$  indicates that the unbridged isomer A has a smaller volume than the bridged one (B), and, therefore, that unbridged Ir–Ir bonds are shorter than bridged Ir–Ir bonds (as observed in the solid state [4]). Since  $\Delta V^\ddagger \cong \Delta V_0$ , the transition state should have a bridged-like geometry when the ground state has  $C_s$  symmetry. This finding supports an earlier proposal that the unbridged species A is a poor representation of the transition state of a merry-go-round in clusters of  $C_s$  symmetry with

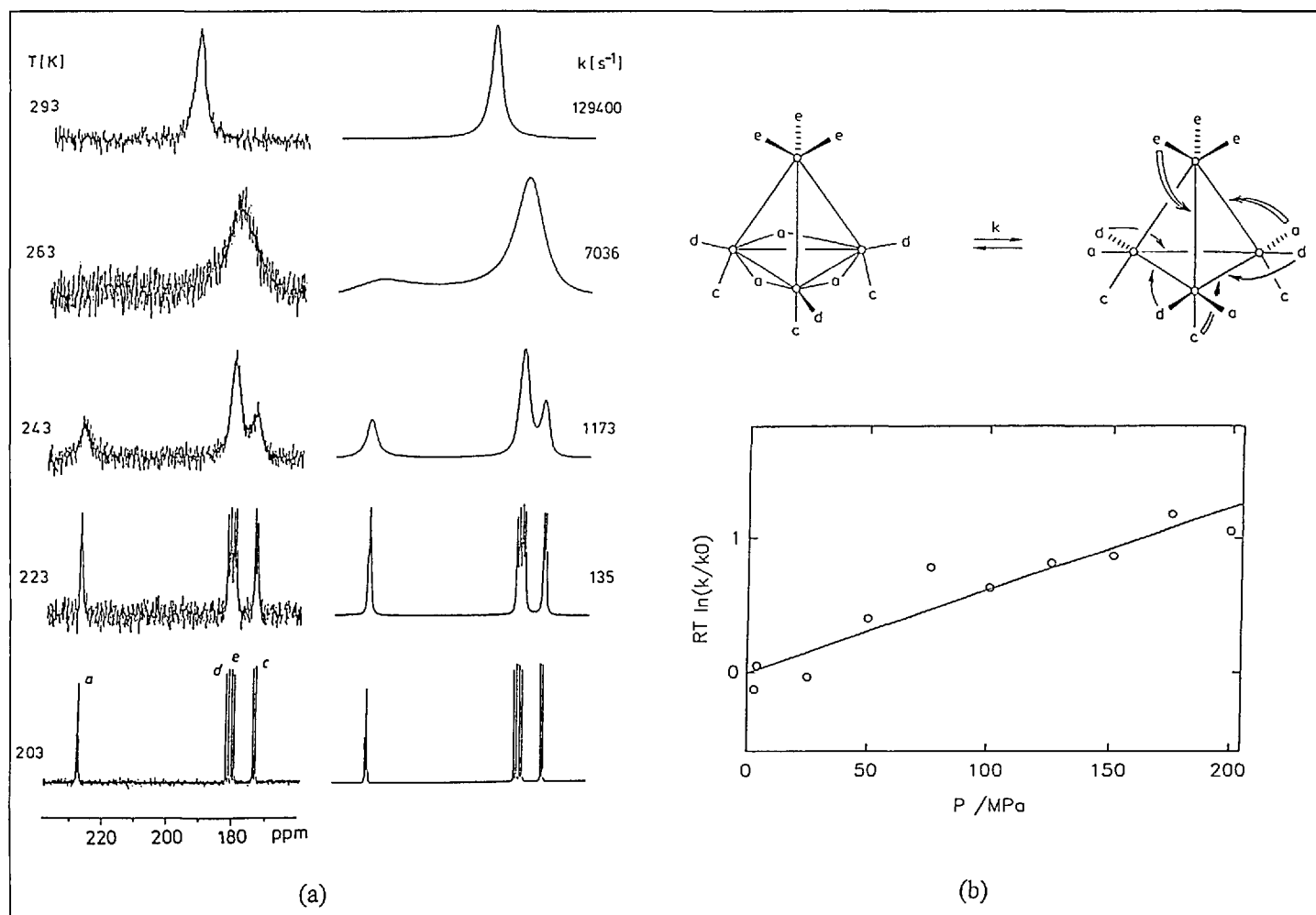


Fig. 1. a) Experimental and calculated  $^{13}\text{C}$ -NMR spectra of  $Rh_4(CO)_{12}$  in  $CD_2Cl_2$  ( $\Delta G^\ddagger = 43.8 \pm 0.4$   $\text{kJ mol}^{-1}$  at 298 K); b) Rate dependence on pressure ( $\Delta V^\ddagger = -6 \pm 1$   $\text{cm}^3 \text{mol}^{-1}$ )

basic ligands such as  $L = \text{Br}^-$  [8] or  $\text{PEt}_3$  [9].

As proposed in *Sect. 1.1*, the effect of substituting Ir by Rh in the metal framework should slow down the merry-go-round. The results collected in *Table 1* confirm this proposal.

Last, a merry-go-round seems to be characterized by a negative volume of activation when the ground state has 3 bridging CO's irrespective of its actual symmetry (in addition to the values reported for  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Ir}_4(\text{CO})_{11}\text{P}(\text{OMe})_3$ , a value of  $-7.7 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$  has been measured for the  $\Delta V^\ddagger$  of  $\text{IrRh}_3(\text{CO})_{12}$  [3]).

## 2. The Change of Basal Face

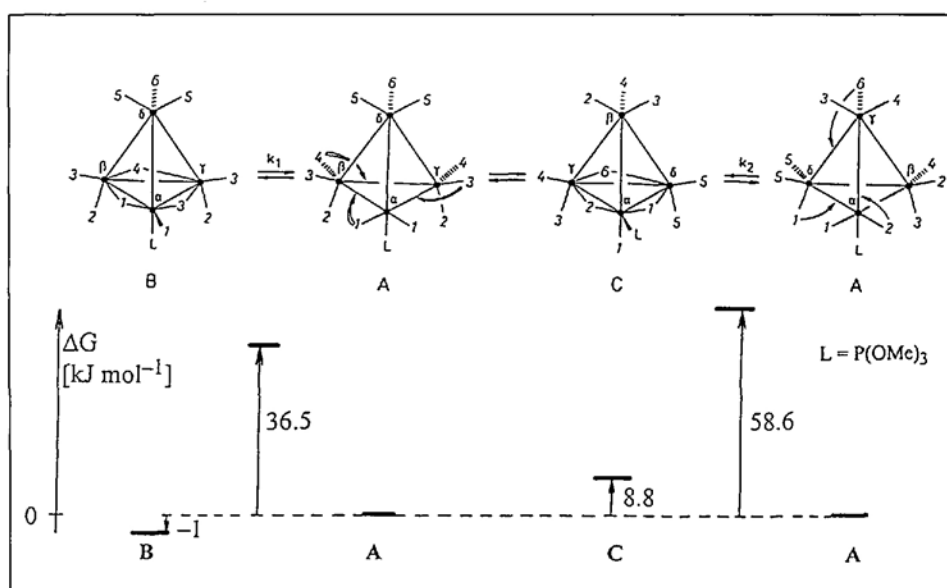
The ground-state geometry of  $\text{Ir}_2\text{Rh}_2(\text{CO})_{12}$  in solution has  $C_s$  symmetry with three CO's edge-bridging one  $\text{IrRh}_2$  face [11]. It is fluxional above 230 K with the dynamic connectivities  $b \leftrightarrow f \leftrightarrow g$ ,  $d \leftrightarrow c$  and  $e \leftrightarrow h$  (*Fig. 3*).

Carbonyl *a* remains unaffected, excluding site exchanges by a merry-go-round of six CO's, as proposed for  $\text{Rh}_4(\text{CO})_{12}$ . Since restricted axial-basal site exchanges are observed, this fluxional process may be called a 'change of basal face' ( $\text{Rh}(1)\text{-Rh}(2)\text{-Ir}(1)$  to  $\text{Rh}(1)\text{-Rh}(2)\text{-Ir}(2)$ ). Its activation volume is positive ( $+7.9 \pm 0.9 \text{ cm}^3 \text{ mol}^{-1}$ ).  $\text{Ir}_4(\text{CO})_9(\mu_2\text{-CO})_2(\mu_2\text{-SO}_2)(C_s, \Delta V^\ddagger = +15 \pm 1 \text{ cm}^3 \text{ mol}^{-1}$  [3]) and  $\text{Ir}_4(\text{CO})_8(\mu_2\text{-EtO})_2\text{POP}(\text{OEt})_2$  ( $C_s, \Delta V^\ddagger = +6.0 \pm 0.1 \text{ cm}^3 \text{ mol}^{-1}$  [3]) display the same fluxional behaviour as  $\text{Ir}_2\text{Rh}_2(\text{CO})_{12}$ . In contrast with the merry-go-round, the change of basal face is characterized by the global exchange  $1 \mu_2\text{-CO} \leftrightarrow 1 \eta^1\text{-CO}$  and by a positive activation volume. Its transition state is clearly not an unbridged species. The carbonyl exchange could take place *via* a face-bridged mechanism (*Fig. 4*), as proposed by *Shapley et al.* [16] for  $\text{Ir}_4(\text{CO})_{10}(\eta^2\text{-diarsine})$ .

The effect of substituting Ir by Rh in the basal face of the metal framework also slows down the change of basal face (*Table 2*).

## 3. The Rotation of Apical Carbonyl Ligands

A third site exchange process is observed in these cluster compounds which involves only one metal centre. It is the rotation of three terminal CO's about a local  $C_3$  axis passing through the apical metal atom (always an Ir-atom). The effect of substituting Ir by Rh in the basal

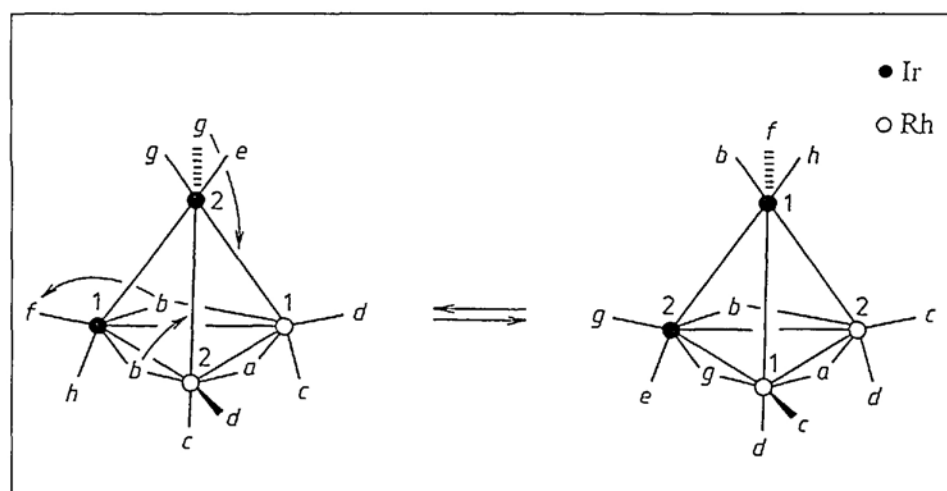


*Fig. 2. Relative stabilities of the isomers of  $\text{Ir}_4(\text{CO})_{11}\text{P}(\text{OMe})_3$  in  $\text{CH}_2\text{Cl}_2$  and free enthalpies of activation of the two CO site exchange processes*

*Table 1. Free Enthalpy of Activation for the Merry-go-round in Isostructural Series of Tetrametallic Cluster Compounds*

Cluster	$\Delta G^\ddagger_{298} [\text{kJ mol}^{-1}]$			
	$\text{Ir}_4$	$\text{Ir}_3\text{Rh}$	$\text{Ir}_2\text{Rh}_2$	$\text{IrRh}_3$
$\text{M}_4(\text{CO})_{11}\text{L}$				
$L = \text{Br}^-$	$37.0 \pm 0.6$ [8]	$51.7 \pm 0.5$ [10]	$> 70$ [11]	other structure
$L = \text{I}^-$	$36.8 \pm 0.4$ [12]	$52.4 \pm 0.6$ [10]	$> 70$ [11]	other structure
$\text{M}_4(\text{CO})_{10}(\text{L-L})$				
$L = \eta\text{-NBD}^a$	$36.3 \pm 0.8$ [12]	$52.8 \pm 0.8$ [10]	–	unstable
$L = \eta\text{-COD}^a$	$43.8 \pm 0.4$ [13]	$55 \pm 1$ [10]	–	unstable
$\text{M}_4(\text{CO})_9(\text{L})$				
$L = \mu\text{-trithiane}^b$	$38.0 \pm 0.5$ [14]	$51.8 \pm 0.4$ [10]	$> 70$ [11]	$> 80$ [3]
$L = \mu\text{-tripod}^b$	$43.3 \pm 0.4$ [15]	$48.4 \pm 0.5$ [10]	$> 70$ [11]	$> 80$ [3]

<sup>a)</sup> Chelating diolefins. <sup>b)</sup> Face-capping ligands; trithiane = 1,3,5-trithiacyclohexane.



*Fig. 3. The 'change of basal face' in  $\text{Ir}_2\text{Rh}_2(\text{CO})_{12}$  ( $\Delta G^\ddagger = 51.2 \pm 0.4 \text{ kJ mol}^{-1}$  in  $\text{CD}_2\text{Cl}_2$  at 298 K). Labels *a* or *b* designate bridging CO's, *d* or *f* radial CO's, *c* or *h* axial CO's and *e* or *g* apical CO's.*

face of the cluster is to accelerate the rotation of the apical CO's (Table 3). The energy barrier of rotation is probably due to the electron density in the 5d orbitals of the apical Ir-atom residing in between the Ir-CO bonds. As proposed in Sect. 1.1, substituting Ir by Rh in the basal face should decrease the electron density in the apical 5d orbitals and consequently decrease the energy barrier of rotation of the 3 CO's bonded to the apical Ir-atom.

The results presented in Tables 1-3 show that the effect of substituting Ir by Rh in the basal face is twofold: it slows the

merry-go-round and the change of basal face, *i.e.*, the two processes which require debridging of CO's, and it accelerates the rotation of CO's about the apical Ir-atom. It, therefore, seems that Rh has a greater tendency to maintain M-M bonds with edge-bridging CO's in a cluster than does Ir. This is the same trend as that found in different  $d^8$  metal clusters (*e.g.*  $\text{Fe}_3(\text{CO})_{12}$  has bridged M-M bonds, whereas  $\text{Os}_3(\text{CO})_{12}$  has a structure with all terminal ligands). In other words, Rh is more electronegative than Ir.

The majority of the results described in this report have been obtained by *Katya Besançon, Giacomo Bondietti, Chris Hall, Gábor Laurenczy, Tito Lumini, Andrés Strawczynski* and *Gianfranco Suardi* at the University of Lausanne, with financial support from the *Swiss National Science Foundation*.

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Table 2. Free Enthalpy of Activation for the Change of Basal Face in Isostructural Series of Tetrametallic Cluster Compounds

Cluster	$\Delta G^\ddagger_{298}$ [kJ mol <sup>-1</sup> ]			
	Ir <sub>4</sub>	Ir <sub>3</sub> Rh	Ir <sub>2</sub> Rh <sub>2</sub>	IrRh <sub>3</sub>
$\text{M}_4(\text{CO})_{10}(\text{L-L})$ L = $\eta^2$ -diars <sup>a)</sup>	30 ± 1 [13]	52.3 ± 0.6 [10]	> 55 [17]	unstable
$\text{M}_4(\text{CO})_8(\text{L-L})_2$ L-L = $\mu$ -dppm <sup>b)</sup>	47.1 ± 0.5 [15]	-	-	61.9 ± 0.4 [3]
L-L = $\mu$ -dmpm <sup>b)</sup>	43.3 ± 0.6 [3]	-	-	> 50 [3]

<sup>a)</sup> Chelating diarsine. <sup>b)</sup> Edge-bridging diphosphines; dmpm =  $\text{Me}_2\text{PCH}_2\text{PMe}_2$

Table 3. Free Enthalpy of Activation for the Rotation of Terminal CO's in Isostructural Series of Tetrametallic Cluster Compounds

Cluster	$\Delta G^\ddagger_{298}$ [kJ mol <sup>-1</sup> ]			
	Ir <sub>4</sub>	Ir <sub>3</sub> Rh	Ir <sub>2</sub> Rh <sub>2</sub>	IrRh <sub>3</sub>
$\text{M}_4(\text{CO})_{10}(\text{L-L})$ L = $\eta$ -NBD	~ 53 [12]	49.4 ± 0.6 [10]	46.6 ± 0.6 [12]	unstable
L = $\eta$ -COD	> 70 [13]	-	46.9 ± 0.4 [12]	unstable
L = $\mu$ -dppm	60.7 ± 0.4 [18]	-	-	50.1 ± 0.5 [3]
$\text{M}_4(\text{CO})_8(\text{L-L})_2$ L = $\eta$ -NBD	46.7 ± 0.6 [15]	42.9 ± 0.3 [10]	43.9 ± 0.6 [10]	unstable
L = $\eta$ -COD	62.2 ± 0.3 [15]	59.9 ± 0.3 [10]	56.6 ± 0.3 [10]	unstable

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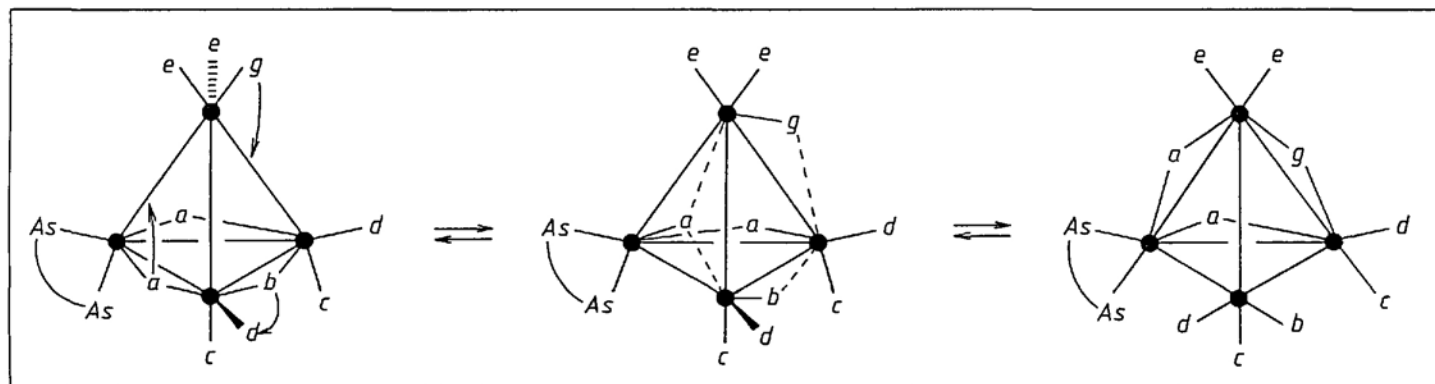


Fig. 4. The 'change of basal face' in  $\text{Ir}_4(\text{CO})_{10}(\eta^2\text{-diarsine})$