

Preliminary communication

A NON-CLOSED TETRANUCLEAR METAL CLUSTER DERIVATIVE OF RHODIUM AND IRON: SYNTHESIS AND MOLECULAR STRUCTURE

RAYMOND J. HAINES*, NICK D.C.T. STEEN,

Department of Chemistry, University of Natal, Pietermaritzburg (Republic of South Africa)

MICHAEL LAING* and POLLY SOMMERVILLE

Department of Chemistry, University of Natal, Durban (Republic of South Africa)

(Received July 16th, 1980)

Summary

The structure of one isomer of $[\text{Rh}_3\text{Fe}\{\text{P}(\text{C}_6\text{H}_5)_2\}_3(\text{CO})_8]$, synthesised by treatment of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ with $[\text{Fe}(\text{CO})_4\{\text{P}(\text{C}_6\text{H}_5)_2\text{H}\}]$ in the presence of a base, has been determined by single crystal X-ray diffraction. This species rearranges in solution to a second isomer whose structure has been elucidated by ^{31}P NMR spectral measurements. The reactions of these compounds with carbon monoxide are described.

The reaction of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ with $[\text{Fe}(\text{CO})_4\{\text{P}(\text{C}_6\text{H}_5)_2\text{H}\}]$ in the presence of a base has been found to lead to the formation of a wide range of products, the nature of which is dependent on the reaction conditions, the molar ratio of the reactants, the solvent employed and whether the reaction is performed in the absence or presence of carbon monoxide. One of the products isolated from these reactions has been characterised as $[\text{Rh}_3\text{Fe}\{\text{P}(\text{C}_6\text{H}_5)_2\}_3(\text{CO})_8]$ (I). The solid state IR spectrum of this species contained peaks corresponding to both bridging and terminal carbonyl groups with the frequency difference between the two bridging carbonyl stretching bands (66 cm^{-1}) being sufficiently large to suggest that they result from non-equivalent carbonyls. It was apparent that the compound had an unusual structure and thus the latter was determined by X-ray diffraction.

Crystals of I are black, monoclinic with space group $P2_1/c$, $a = 19.52(2)$, $b = 10.75(1)$, $c = 21.23(2)$ Å, $\beta = 94.7(1)^\circ$, $U = 4440$ Å³, $Z = 4$. Data were collected on a Philips PW1100 diffractometer (N.P.R.L., Pretoria) with graphite-monochromated Mo- K_α radiation to $\theta = 20^\circ$. The structure was solved by standard Patterson and Fourier methods and refined by block-diagonal least squares to $R = 0.087$ for the 1994 observed data ($I > 3.0\sigma(I)$; Rh and P atoms anisotropic).

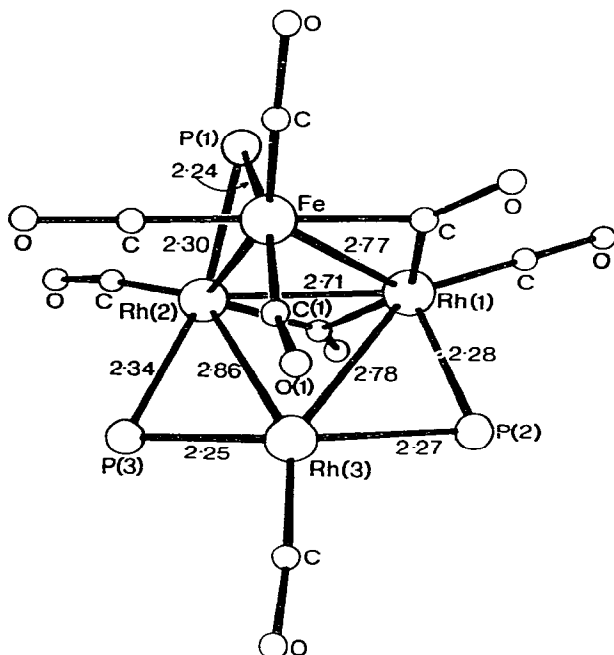


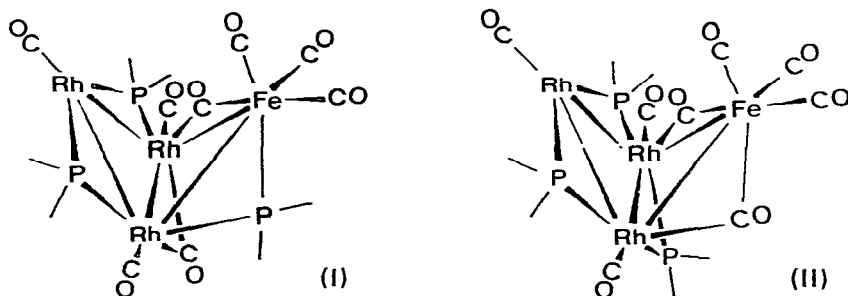
Fig. 1. Molecular stereochemistry of I (phenyl groups omitted). Bond lengths shown are ± 0.01 Å.

The molecular stereochemistry of I is illustrated in Fig. 1 (phenyl rings have been omitted for clarity). The compound adopts a "butterfly" configuration comprising two triangles of metal atoms sharing a common edge (Rh(1)—Rh(2)), the dihedral angle between the two metal atom planes (defined by Rh(3)Rh(1)—Rh(2) and FeRh(1)Rh(2)) being 77° . Five of the metal—metal distances correspond to formal metal—metal bonds with each being bridged by either a diphenylphosphino or a carbonyl group; each rhodium atom has a single terminal carbonyl group coordinated to it. Three of the metal atoms, Rh(1), Rh(2) and Fe formally obey the "Effective Atomic Number" rule while the fourth, Rh(3), is formally a 16-electron system, and as a consequence is effectively coordinatively unsaturated.

The difference in character between Rh(2) and Rh(3) is clearly reflected by consideration of the Rh—P bond lengths associated with them (Rh(2)—P(1) = 2.30; Rh(2)—P(3) = 2.34; Rh(3)—P(2) = 2.27; Rh(3)—P(3) = 2.25 Å); the distances for the 16-electron system are significantly shorter than those for the 18-electron system. A similar effect has been found in ruthenium phosphine complexes [1].

The two phosphorus atoms, P(2) and P(3), are both displaced down from the trirhodium plane by about 0.3 Å such that Rh(3) is sterically blocked on the underside by their phenyl rings while the carbonyl group attached to the Fe atom, lying above and parallel to the trirhodium plane, effectively shields the top of Rh(3); Rh(3) . . . C(1) = 2.62; Rh(3) . . . O(1) = 3.16 Å. This will account for the apparent inability of Rh(3) to coordinate a further molecule of carbon monoxide.

The structure of I shows a close resemblance with that found for



$[\text{Rh}_4\{\text{P}(\text{C}_6\text{H}_5)_2\}_5(\text{CO})_5]^-$ [2], except that the latter has a more "open" structure; the dihedral angle for this species is 124° compared with 77° for I.

I was found to rearrange in solution to produce a second isomer which exhibited a band pattern in the C—O stretching region of its solid state IR spectrum substantially different from that observed in the solid state spectrum of I, suggesting that the isomerism involved a significant structural change. Although single crystals of this isomer could be isolated they were found to degrade readily on irradiation with X-rays and thus the structure could not be determined by diffraction methods. However, ^{31}P NMR spectral measurements on this species revealed that two of the phosphorus atoms were equivalent with the third unique. It is therefore proposed that this isomer has the structure illustrated, II.

Treatment of isomer II with carbon monoxide in solution produced an orange solution from which a yellow-orange crystalline compound characterised as $[\{\text{Rh}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_2\}_2]$, was isolated by removal of the solvent under a stream of CO. Solutions of $[\{\text{Rh}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_2\}_2]$ rapidly turned green in the absence of excess carbon monoxide and finally to brown on prolonged standing. A black crystalline tetranuclear product, characterised as $[\text{Rh}_4\{\text{P}(\text{C}_6\text{H}_5)_2\}_4(\text{CO})_6]$ was isolated from the final reaction mixture. These di- and tetranuclear derivatives can also be isolated from the reactions of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ with $\text{P}(\text{C}_6\text{H}_5)_2\text{H}$ under appropriate reaction conditions [3]. $[\text{Rh}_4\{\text{P}(\text{C}_6\text{H}_5)_2\}_4(\text{CO})_6]$ is also one of the products isolated from the reactions of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ with $[\text{Fe}(\text{CO})_4\{\text{P}(\text{C}_6\text{H}_5)_2\text{H}\}]$ discussed above.

Acknowledgements

The authors express their sincere thanks to the South African Council for Scientific and Industrial Research and the University of Natal for financial support, Johnson Matthey for the loan of rhodium salts and the National Institute for Metallurgy for a studentship to N.D.C.T. Steen and Dr. G. Gafner (CSIR) for the data collection.

References

- 1 M. Laing, *Acta Cryst. B*, 34 (1978) 2100.
- 2 P.F. Kreter, Jr., D.W. Meek and G.G. Christoph, *J. Organometal. Chem.*, 188 (1980) C27.
- 3 N.D.C.T. Steen, unpublished results.