Journal of Organometallic Chemistry, 266 (1984) C37—C40
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

A HETEROBIMETALLIC COMPLEX OF ZIRCONIUM(IV) WITH RHODIUM(I): UNEXPECTED FORMATION OF THE MONOMERIC *trans*-[$(\eta^5$-$C_5H_5)_2Zr(CH_2PPh_2)_2Rh(CO)Cl$]

ROBERT CHOUKROUN and DANIELE GERVAIS*

Laboratoire de Chimie de Coordination du CNRS associé à l'Université Paul Sabatier, 205, route de Narbonne, 31400 Toulouse (France)

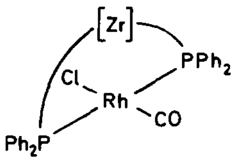
(Received February 13th, 1984)

Summary

Unexpectedly the compound *trans*-[$(\eta^5$-$C_5H_5)_2Zr(CH_2PPh_2)_2Rh(CO)Cl$] was found to be monomeric and the $^{31}P\{^1H\}$NMR spectra demonstrated that two non-equivalent phosphorus atoms are *trans*-bonded to the rhodium giving the six-membered ring $\overline{CH_2PRhPCH_2Zr}$. A carbonyl band at 1650 cm^{-1} in the IR spectrum of the solid state, is attributable to a strong interaction between the oxophilic zirconium atom and the carbonyl oxygen of the rhodium fragment in one of the rotamers.

There is considerable interest in complexes in which diphosphine ligands bridging two metals give heterometallic species [1]. When the two metals are very different in oxophilicity, novel types of ligand bonding can be obtained; for instance, novel types of bridged CO [2]. The extreme case of association of an early transition metal d^0 with a late d^8 one is much less well documented, although very promising observations have been made [3].

We found that the previously reported diphosphinomethylzirconium $Cp_2Zr(CH_2PPh_2)_2$ can act as a diphosphine ligand towards d^8 metals and thus promote the formation of binuclear d^0—d^8 species arising from the presence of the zirconium atom in the phosphine chain [4]. We now describe a heterobimetallic complex, *trans*-[$Cp_2Zr(CH_2PPh_2)_2Rh(CO)Cl$] (1), obtained by treating $Cp_2Zr(CH_2PPh_2)_2$ with $(Rh(CO)_2Cl)_2$ (2/1).



(1)

The synthesis of 1 was tried using different mixtures of solvents, but only the addition of a pentane solution of the rhodium complex on a toluene/THF (9/1) solution of $Cp_2Zr(CH_2PPh_2)_2$ led conveniently to 1 (45% yield) with satisfactory analytical data (C, H, P, Zr, Rh) and unambiguous ^1H NMR spectra. (δ ppm) in C_6D_6 : 2.16 (dt, 4H, ^2J(P—H) + ^4J(P—H) 3.37 Hz, ^3J(Rh—H) 0.9 Hz, CH_2), 6.10 (s, 10H, η^5-C_5H_5), 7.10—7.80 (m, C_6H_5). The complex, which is poorly soluble in benzene, was found by cryoscopy to be monomeric in dioxane (M = 750, calcd. 785.7) and non-conducting in tetrahydrofuran (THF) solution. The $^{31}P\{^1H\}$NMR spectra (in THF or dioxane) show essentially an ABX pattern at room temperature and at —70°C, (Fig. 1), indicating the non-equivalence of the P nuclei in a sterically rigid arrangement, and may be compared with spectra for similar non fluxional Zr-Rh complexes previously obtained from the monophosphine $Cp_2ZrCl(CH_2PPh_2)$ [3] (ppm average H_3PO_4: 37.4 and 24.0, ^1J(Rh—P) 136, ^2J(P—P) 316 Hz). The ^2J(P—P) constant (316 Hz), taken together with the doublet of triplets observed for the methylene group in the ^1H NMR spectrum, is characteristic of a *trans*-arrangement of the two phosphorus atoms bonded to the rhodium, giving a six atoms nucleus $\overline{CH_2PRhPCH_2Zr}$, in this novel monomeric complex 1. This is, to our knowledge, the first example of a monomeric species containing a five-membered chain diphosphine spanning *trans*-coordination sites. It is also the first example of a Zr-Rh complex in which the chelation of the $\overline{CH_2PRhPCH_2Zr}$ moiety maintains the two metals in close proximity, making novel bimetallic activation possible, specially for CO.

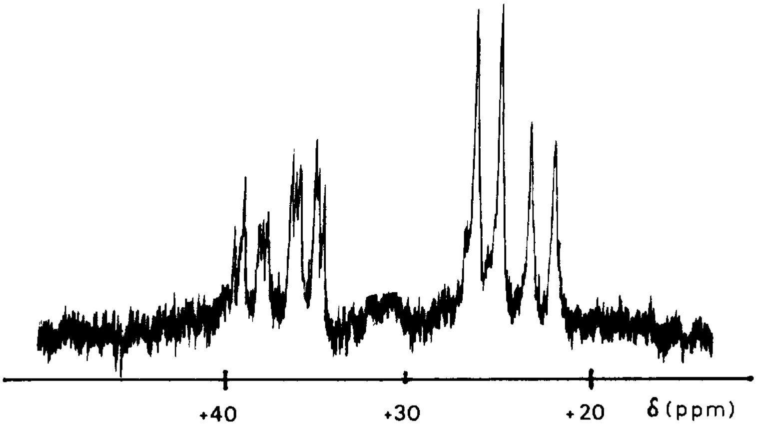


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum (101.27 MHz) of 1 in THF/toluene-d_8 at ca. —70° C.

Accurate examination of the spectrum, especially in the low field region, shows that each of the broad peaks is separated into three (at least) closely spaced sharp peaks. (δ 37.68, ^1J(Rh—P) 140.4, 133.0, ^2J(P—P) 320 Hz; 37.46, ^1J(Rh—P) 131.7, ^2J(P—P) 316 Hz; 37.20, ^1J(Rh—P) 136.7, 139.2, ^2J(P—P) 317 Hz).

Although diphosphinerhodium complexes are well documented [5], there are very few cases where the rhodium metal is *trans*-chelated by a diphosphine, and long or medium chains are then required [6]. Recently, a platinum-rhodium complex obtained by Shaw [1] and containing the moiety Pt(μ-dppm)$_2$Rh was described as containing an eight-membered ring $PCH_2PPtPCH_2PRh$. In the case of the zirconium-rhodium complex (1), the novel stereochemical feature arises from the constrained structure of the six-membered ring, $CH_2PRhPCH_2Zr$, which affects the eclipsed geometry of such a system (Fig. 2) and twists the rhodium square plane. Different rigid conformations due to the restrictions imposed by the ring system give different rotamers with non-equivalent phosphorus nuclei.

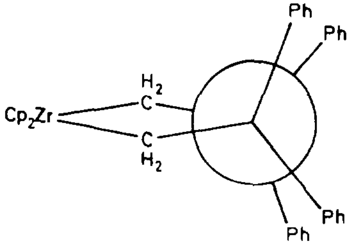
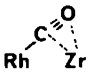


Fig. 2. Newman projection of 1 along the P—Rh—P axes (Cl—Rh—CO axes are omitted for clarity).

Whereas the IR spectrum of 1 in THF showed only one strong broad ν(Rh—CO) band at 1960 cm^{-1}, there were three ν(CO) bands, at 1950, 1900, and 1650 cm^{-1}, in the solid state. In the solid state, the first two bands can be assigned to rotamers with the chlorine atom or the CO group *gauche* to the sets of the phenyl group. The band at 1650 cm^{-1} of the third rotamer probably arises from an interaction between the carbonyl group of the rhodium and the oxophilic zirconium atom to give a η^2-carbonyl complex, (2), as already reported by Bercaw and by Caulton in M—CO—Zr systems (M = Co, Mo) [7,8].



(2)

Studies of the catalysis of hydroformylation by Zr-Rh systems of the type reported are now in progress.

Acknowledgment. We thank the CNRS and GRECO Oxydes de Carbone for financial support and Mr. Gérard Commenges for technical assistance with the NMR spectra.

References

1 C.R. Langrick, D.M. McEwan, P.G. Pringle, and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1983) 2487 and references therein; J.M. Brown and L.R. Canning, J. Chem. Soc., Chem. Commun., (1983) 460; S. Sabo, B. Chaudret, and D. Gervais, J. Organomet. Chem., 258 (1983) C19.
2 J.A. Marsella, K. Folting, J.C. Huffman, and K.G. Caulton, J. Am. Chem. Soc., 103 (1981) 5596; J.A. Marsella and K.G. Caulton, J. Am. Chem. Soc., 102 (1980) 1747; P.T. Wolczanski, R.S. Threlkel, and J.E. Bercaw, J. Am. Chem. Soc., 101 (1979) 218.

3 R. Choukroun and D. Gervais, J. Chem. Soc., Chem. Commun., (1982) 1300.
4 N.E. Schore and H. Hope, J. Am. Chem. Soc., (1980) 4251.
5 C. Crocker, R.J. Errington, R. Markham, J. Moulton, and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1982) 387; C. Crocker, R.J. Errington, R. Markham, C.J. Moulton, K.J. Odell, and B.L. Shaw, J. Am. Chem. Soc., 102 (1980) 4373; M. Cowie and S.K. Dwight, Inorg. Chem., 19 (1980) 2500; A.R. Sanger, J. Chem. Soc., Dalton Trans., (1977) 120; F.C. March, R. Mason, K.M. Thomas, and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1975) 584.
6 R. Mason and G.R. Scollary, Aust. J. Chem., 31 (1978) 781; N.A. Bennett, R.N. Johnson, and I.B. Tomkins, J. Organomet. Chem., 128 (1977) 73.
7 P.T. Barger and J.E. Bercaw, J. Organomet. Chem., 201 (1980) C39.
8 B. Longato, J.R. Norton, J.C. Huffman, J.A. Marsella, and K.G. Caulton, J. Am. Chem. Soc., 103 (1981) 209.