Journal of Organometallic Chemistry, 228 (1982) C15—C18
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

A RHODIUM(I)—IRIDIUM(III) HYDRIDO-BRIDGED PHOSPHINE COMPLEX

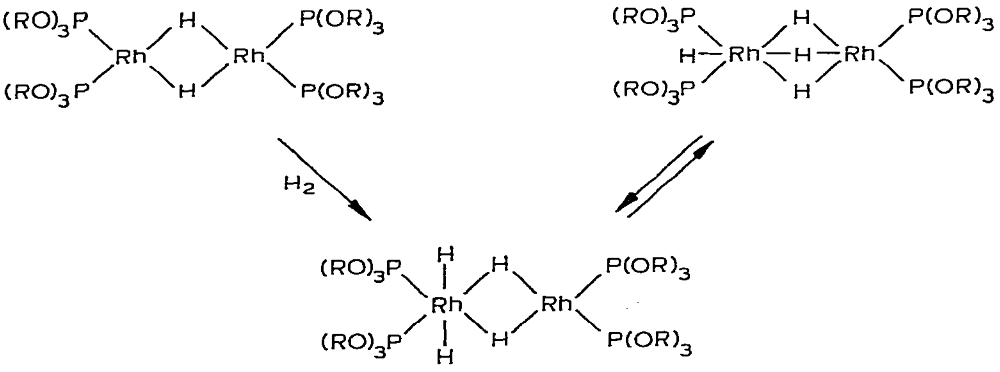
ALFREDO MUSCO, RALPH NAEGELI, LUIGI M. VENANZI,
Laboratorium für Anorganische Chemie, ETH-Zentrum, CH-8092 Zürich (Switzerland)
and ALBERTO ALBINATI
Istituto di Chimica Farmaceutica dell'Università, Milano, and Istituto di Chimica, Politecnico di Milano, Piazza Leonardo Da Vinci 32, I-20133 Milano (Italy)

(Received December 4th, 1981)

Summary

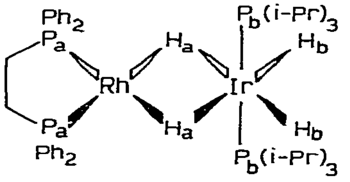
The new compound $[(\text{diphos})\text{Rh}(\mu_2\text{-H})_2\text{IrH}_2(\text{P}\{\text{i-Pr}\}_3)_2]$ (II) (diphos = $Ph_2PCH_2CH_2PPh_2$) was prepared from $[\text{Rh}(\text{diphos})(\text{MeOH})_2]^+$ and $[\text{IrH}_5(\text{P}\{\text{i-Pr}\}_3)_2]$ and characterized by NMR and X-ray methods.

Bimetallic hydrogenation catalysts have received considerable attention in recent years [1,2]. Thus $[Rh_2H_2(P\{OR\}_3)_4]$ species are very active alkene hydrogenation catalysts [1] and it has also been postulated that hydrogenation involves the species shown in the following equilibria:



^{1}H NMR evidence for the presence of a complex of type I has been reported [3].

During the course of our studies on bimetallic hydrido-bridged complexes we have obtained a stable rhodium—iridium complex related to I. Compound II is precipitated as a red crystalline powder (40% yield) by treatment of a methanol solution of $[Rh(diphos)(MeOH)_2]^+$ (obtained by hydrogenation of $[Rh(diphos)(NBD)]BF_4$ [4], NBD = norbornadiene) with an equimolar quantity of $[IrH_5(P\{i\text{-}Pr\}_3)_2]$ [5] suspended in methanol. The yield can be raised to 80% by adding one equivalent of $NEt(i\text{-}Pr)_2$ to the suspension.



(II)

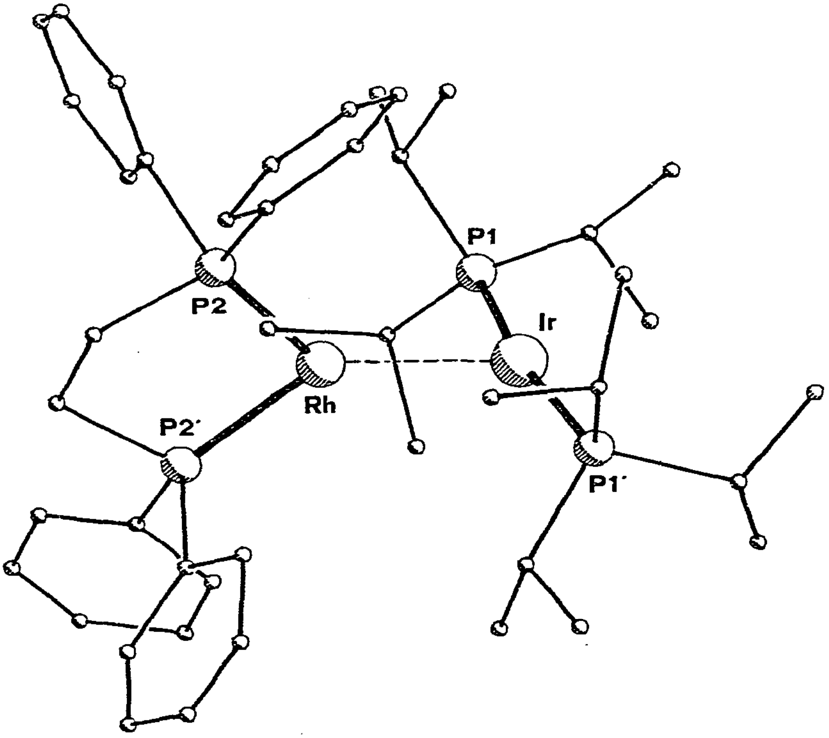
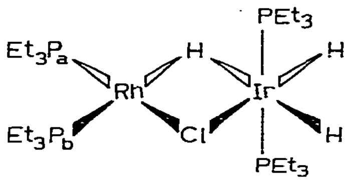


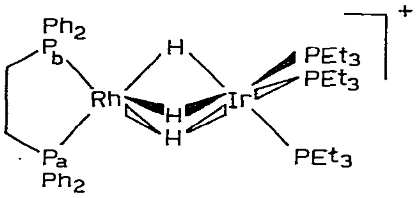
Fig. 1. Molecular structure of $[(diphos)Rh(\mu_2\text{-}H)_2IrH_2(P\{i\text{-}Pr\}_3)_2]$ (II). Bond lengths (Å): Ir—Rh 2.662(1); Ir—P(1) 2.293(2); Rh—P(2) 2.197(2); <P(1)—C> average value 1.877(4)±0.008; <P(2)—C> average value 1.844(4)±0.007. Bond angles (°): Ir—Rh—P(2) 137.98(2); Rh—Ir—P(1) 95.35(4); P(1)—Ir—P(1') 169.30(10); P(2)—Rh—P(2') 84.02(10). Torsion angles (°), average error ~0.6; P(1)—Ir—Rh—P(2) — 96.1; Ir—Rh—P(2)—C(diphos) 167.1.

The molecular geometry of II has been established by X-ray diffraction [6]; a perspective view of the complex is given in Fig. 1. The molecule lies on a crystallographic binary axis passing through the rhodium and iridium atoms.

The rhodium center has the expected distorted square planar geometry (the P(2)—Rh—P(2′) angle is 84.0(1)°), while the iridium atom shows a distorted octahedral coordination with two phosphorus ligands *trans* to each other; this coordination geometry is consistent with the presence of two bridging and two terminal hydride ligands in a planar arrangement. The P(1)—Ir—P(1′) angle of 169.3(1)° is comparable to the value of 166.4(2)° found for the corresponding angle in $[(PEt_3)_2Rh(\mu_2\text{-}H)(\mu_2\text{-}Cl)IrH_2(PEt_3)_2]$ (III) [7]. The rhodium—iridium distance (2.662(1) Å) is shorter than that in III (2.899(1) Å) but longer than in $[(diphos)Rh(\mu_2\text{-}H)_3Ir(PEt_3)_3]^+$ (IV) (2.636(1) Å) [8] where the metal atoms are bridged by three hydrogen atoms.



(III)



(IV)

It is interesting to note that the rhodium—phosphorus distances (2.197(2) Å) in II are within two e.s.d.'s of the value of Rh—P_a, (the larger rhodium—phosphorus distance) in IV which is 2.194(5) Å. The hydride ligands were not located but evidence for their presence and positions is provided by the ^1H NMR spectrum. In the high field region there are two sets of signals centered at −8.5 and −19.0 ppm (benzene-d_6, 90 MHz, 28°C), of relative intensities 1/1, assigned to $H_{a,a'}$ and $H_{b,b'}$ respectively [9]. The $^{31}P\{^1H\}$ NMR spectrum (benzene-d_6, 36.43 MHz, 29°) of compound II shows two types of magnetically inequivalent phosphorus atoms; i.e. a doublet assignable to P_a at 69 ppm (^1J(Rh—P_a) 160 Hz) and a singlet assigned to P_b at 64 ppm. The infrared spectrum (Nujol) shows one intense band at 2100 cm^{-1} assignable to a stretching vibration of the hydride ligands. No other absorptions between 1600 and 2600 cm^{-1} were observed. A benzene solution of compound II does not react with ethylene at room temperature and one atmosphere pressure within weeks as indicated by the unchanged NMR spectra. However, when carbon monoxide is bubbled through a benzene solution of II, an immediate colour change to yellow is observed. One of the reaction products was identified as $[IrH_3(CO)(P\{i\text{-}Pr\}_3)_2]$ [10]. Attempts to prepare analogous compounds $[Rh(diphos)(\mu_2\text{-}H)_2IrH_2(PR_3)_2]$ ($R = C_2H_5$, cyclo-C_6H_{11}) by the same method gave products which are still under investigation.

References

1 E. Muetterties, J. Organometal. Chem., 200 (1980) 177.
2 P.M. Maitlis, Accounts Chem. Res., 11 (1978) 301 and ref. quoted therein.
3 A.J. Sivak and E.L. Muetterties, J. Amer. Chem. Soc., 101 (1979) 4878.
4 J. Halpern, D.P. Riley, A.S.C. Chan and J.J. Pluth, J. Amer. Chem. Soc., 99 (1977) 8055.
5 M.G. Clerici, S.D. Gioacchino, F. Maspero, E. Perotti and A. Zanobi, J. Organometal. Chem., 84 (1975) 379.

6 Compound II is monoclinic; space group *C2/c*:, *a* 20.601(6); *b* 11.582(4); *c* 21.058(6) Å; *β* 67.8(2)° (from the least squares refined values of the 2θ angles of 20 high order reflections); $Z = 4$. 4089 independent reflections were collected using an automated Philip PW 1100 four circle diffractometer using Mo-K_α graphite-monochromated radiation up to 2θ 50.0°. 3623 reflections were considered as observed having $I_{\mathrm{net}} \geqslant 3\,\sigma\,(I)$ and used in the structure determination. The structure was solved by Patterson and Fourier methods and refined by block diagonal least squares to the present agreement index of 3.9%.

7 H. Lehner, A. Musco, L.M. Venanzi and A. Albinati, J. Organometal. Chem., 213 (1981) C46.

8 A. Albinati, A. Musco, R. Naegeli and L.M. Venanzi, Angew. Chem., 93 (1981) 1018.

9 Spin system: $AA'MXX'B_2YY'$ $^1J(\mathrm{Rh,H_a})$ 30 Hz (from $^1\mathrm{H}\{^{31}\mathrm{P}\}$NMR). The 59 Hz coupling is assigned to $^2J(\mathrm{P_a,H_a'})$ on the assumption that $^2J(\mathrm{P,H}_{trans}) > {}^2J(\mathrm{P,H}_{cis})$. $^2J(\mathrm{P_a,H_a})$ is presumed to be < 1 Hz. $^2J(\mathrm{P_b,H_a})$ 7 Hz; $^2J(\mathrm{P_b,H_b})$ 16 Hz; $^4J(\mathrm{P_a,H_b})$ 16 Hz; $^2J(\mathrm{H,H})$, $^3J(\mathrm{Rh,H_b})$, $^4J(\mathrm{P_a,H_b'}) < 1$ Hz.

10 IR (Nujol): 2080(m), 2050(m), 1950(d), 1930(m), 1795(s), 1780(s) ^{1}H NMR (90 MHz, benzene-d_6, 28°C): —11.2 ppm, doublet of triplets, 2H, $^2J(\mathrm{H,P})$ 15 Hz, $^2J(\mathrm{H,H})$ 5 Hz; —12.6 ppm, triplet of triplets, 1H, $^2J(\mathrm{H,P})$ 19 Hz. ^{31}P NMR (36.43 MHz, benzene-d_6, 30°C): 45 ppm, singlet. The compound was also prepared by lithium aluminium hydride reduction of a mixture of $[\mathrm{IrHCl_2(CO)}$-$(\mathrm{P}\{\text{i-Pr}\}_3)_2]$ and $[\mathrm{IrCl(CO)(P}\{\text{i-Pr}\}_3)_2]$.