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Preliminary communication

SOME NEW RHODIUM(I)-IRIDIUM(III) COMPLEXES WITH BRIDGING HYDRIDE AND CHLORIDE LIGANDS

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Summary

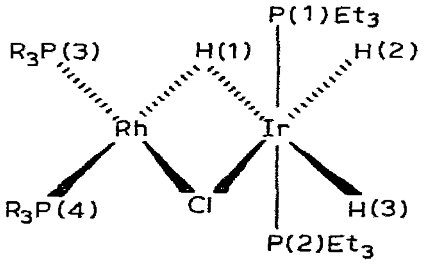
$[IrH_5(PEt_3)_2]$ reacts with $[(PR_3)_2Rh(\mu_2\text{-}Cl)_2(PR_3)_2]$ ($PR_3 = PEt_3$ or $2\ PR_3 = Ph_2PCH_2CH_2PPh_2$) to give the hydrido-bridged binuclear species $[(PR_3)_2Rh(\mu_2\text{-}H)(\mu_2\text{-}Cl)IrH_2(PR_3)_2]$ which show catalytic activity in alkene hydrogenation.

Binuclear complexes containing bridging hydrides together with halide ligands have not been extensively studied [1—3] although some compounds of this type, i.e., $[M_2H_nX_{3-n}(C_5Me_5)_2]^+$ (M = Rh and Ir; X = Cl, Br and I; n = 1 and 2), I, are active catalysts for alkene hydrogenation [2].

During the course of a study of binuclear complexes with bridging hydride ligands it was observed that mononuclear dihydrido complexes formed more stable hydrido-bridged binuclear species with the $\{cis\text{-}Rh(PR_3)_2\}^+$ moiety than with the $\{trans\text{-}PtPh(PR_3)_2\}^+$ fragment [4]. As Van Dongen et al. [1] report the formation of unstable species of the type $[(PR_3)ClM(\mu_2\text{-}H)(\mu_2\text{-}Cl)IrH_2(PR_3)_2]$ (M = Pt and Pd), II, from $[(PR_3)_2ClM(\mu_2\text{-}Cl)_2MCl(PR_3)]$, III, and $[IrH_5(PR_3)_2]$, IV, we studied the reaction of this pentahydride with $[(PR_3)_2Rh(\mu_2\text{-}Cl)_2Rh(PR_3)_2]$, V, or its precursor $[RhCl(C_2H_4)(PR_3)_2]$, VI, [5], to prepare stable rhodium-iridium species containing both hydride and chloride bridging ligands which might show catalytic activity.

Compounds of the types V or VI ($PR_3 = PEt_3$, Va or VIa; $2\ PR_3 \equiv Ph_2PCH_2CH_2PPh_2 \equiv$ diphos, Vb or VIb), in toluene, react with the iridium pentahydride $[IrH_5(PEt_3)_2]$, IVa, giving orange-brown complexes of the type $[(PR_3)_2Rh(\mu_2\text{-}H)(\mu_2\text{-}Cl)IrH_2(PR_3)_2]$, VII.

The molecular geometry of complex VIIa was established by X-ray diffrac-



(VIIa, PR$_3$ = PEt$_3$;
VIIb, 2 PR$_3$ = *diphos*)

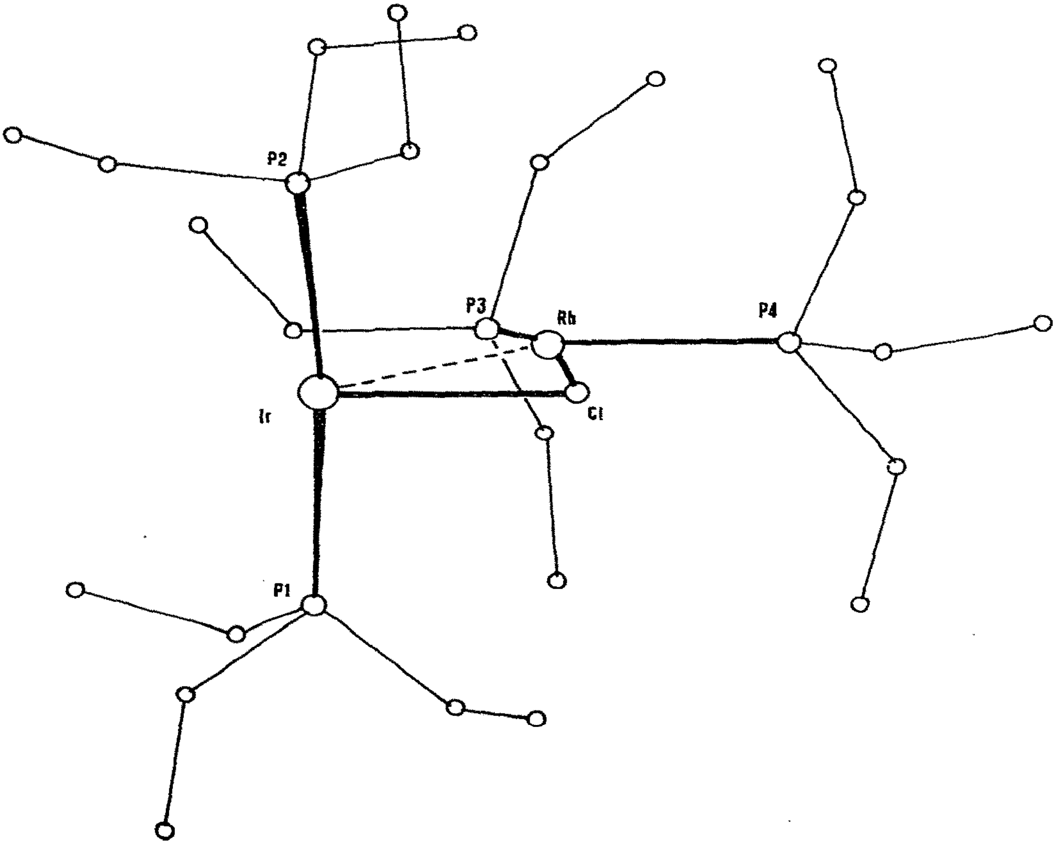


Fig. 1. Molecular structure of [(Et$_3$P)$_2$Rh(μ_2-H)(μ_2-Cl)IrH$_2$(PEt$_3$)$_2$]. VIIa. Bond lengths (Å): Rh—Ir 2.899(1); Ir—Cl 2.494(3); Rh—Cl 2.427(3); Ir—P(1) 2.263(4); Ir—P(2) 2.272(4); Rh—P(3) 2.199(3); Rh—P(4) 2.245(3); ⟨P—C⟩ av. value 1.85(2). Bond angles (°) Ir—Cl—Rh 72.2(1); Rh—Ir—P(1) 91.7(1); Rh—Ir—P(2) 101.8(1); P(1)—Ir—P(2) 166.4(2); Ir—Rh—P(3) 117.0(1); Ir—Rh—P(4) 145.1(1); P(3)—Rh—P(4) 97.9(1). Torsion angles (°, av. error ~0.5) P(1)—Ir—Rh—P(4) 96.4; P(2)—Ir—Rh—P(4) −85.3; Cl—Ir—Rh—P(3) 178.9; Cl—Ir—Rh—P(4) 1.0. Average displacement of Cl and Ir from LSQ plane defined by Rh, P(3) and P(4) < 0.04 Å.

tion [6] and the main features of the structure are shown in Fig. 1. The hydride ligands were not located. From the positions of the heavy atoms one can postulate a distorted square planar coordination around rhodium and a distorted octahedral coordination around iridium. The bridging Rh(μ_2-H)(μ_2-Cl)-Ir region is strongly asymmetric as shown by the different metal—chlorine bond distances (see Fig. 1) and the long Ir—Cl bond can be accounted for by the *trans* influence of H [2]. Noteworthy are also the Rh—P(3) and Rh—P(4) bond distances, the latter being considerably longer than the former, presumably because of the presence of a hydride ligand in the *trans* position.

The presence of the hydride ligands in compounds VIIa and VIIb is indicated by their ^{1}H NMR spectra. Thus, compound VIIb shows three sets of signals centered at −12.2, −12.7 and −24.2 ppm (toluene-d_8, 250 MHz), of relative intensities 1:1:1, assigned to H(1), H(3) and H(2) respectively [7].

The ^{31}P{^{1}H} NMR spectrum of compound VIIb (toluene-d_8, 101.27 MHz) shows three sets of signals: (1) a doublet of doublets, δ = 80.0 ppm, assigned to P(3); a set of four triplets; δ = 58.8 ppm, assigned to P(4); and a doublet δ = 4.2 ppm, assigned to P(1) and P(2) [8].

The ^{1}H and ^{31}P NMR spectra of compound VIIa are analogous to those of compound VIIb.

The infrared spectrum of compound VIIb shows medium intensity bands at 2060 and 2210 cm^{-1} assignable to the stretching vibrations of the terminal hydride ligands, H(2) and H(3). The absorption due to the bridging hydride ligand, H(1), in this type of complex is expected to occur below 1300 cm^{-1} [9].

Preliminary tests show that compound VIIb catalyses the hydrogenation of 1-hexene at room temperature and 5 atm. H_2. Thus, in this respect, compounds of type VII behave similarly to those of type I.

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6 Compound VIIb is monoclinic; space group $P2_1/c$; a = 11.507(7); b = 15.974(6); c = 19.198(7) Å; β = 103.2(4)° (least squares refined values); Z = 4. 4846 independent reflections were collected using an automated Philips PW 1100 four-circle diffractometer using Mo-K_α graphite-monochromated radiation up to $2\theta \leqslant 45°$. 4277 observed reflections (having $I_{net} \geqslant 3\sigma(I)$) were 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 6.0% using anisotropic temperature factors for Ir, Rh, Cl and P atoms, isotropic for the others.

7 The assignment of the signals due to H(1) is based on the magnitude of ^2J(P(4),H) [J.P. Jesson, Stereochemistry and Stereochemical Nonrigidity in Transition Metal Hydrides in E.L. Muetterties (Ed.), Transition Metal Hydrides, M. Dekker, New York, 1971, p. 75] and the assignment of the signals due to H(2) and H(3) is based on the empirical observation [A. Immirizu, A. Musco, P.S. Pregosin and M. Venanzi, Angew. Chem., 92 (1980) 744; idem, Angew. Chem. Int. Ed. Engl., 19 (1980) 721] that in related binuclear hydrido-bridged complexes ^2J(H,H-*cis*) > ^2J(H,H-*trans*). ^2J(H(1),P(4)) = 61.2 Hz; ^2J(H(1),H(3)) = 2.4 Hz; ^2J(H(2),H(3)) = 9.5 Hz; ^2J(H(3),P(1) and P(2)) = 16.3 Hz.

8 The assignment of the low-field signals to P(3) and P(4) was made on the basis of an off-resonance spectrum which showed only a broadening of the lines centered at 58.8 ppm and the assumption that ^2J(P,H-*trans*) > ^2J(P,H-*cis*). ^1J(Rh,P(3)) = 202.5 Hz; ^1J(Rh,P(4)) = 172.8 Hz; ^2J(P(3),P(4)) = 35.3 Hz; ^4J(P(4),P(1) and P(2)) = 3.3 Hz.

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