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Preliminary communication

A ZIRCONIUM-RHODIUM HYDRIDO COMPLEX, $Cp_2Zr(CH_2PPh_2)_2RhH(PPh_3)$, AS CATALYST FOR THE HYDROFORMYLATION OF 1-HEXENE

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Summary

The early-late transition metal complex $Cp_2Zr(CH_2PPh_2)_2RhH(PPh_3)$ has been prepared by the reaction of the zirconium diphosphine $Cp_2Zr(CH_2PPh_2)_2$ with the hydride $RhH(PPh_3)_4$. Its behaviour as a catalyst for the hydroformylation of 1-hexene under mild conditions is compared with that of related species.

The catalytic properties of metal complexes with chelating diphosphine is currently under investigation [1]. Our recent work on bimetallic d^0–d^8 systems such as Zr,Rh, Ti,Rh [2] and their applications in catalysis [3] can lead to a new class of catalytic species with properties derived from a cooperative electronic and/or steric effect with $Cp_2Zr(CH_2PPh_2)_2$ (I) acting as a bridging or chelating ligand. This finding prompted us to investigate the activity of a system resulting from the reaction of I with $RhH(PPh_3)_4$ (II) as a precursor for hydroformylation [4].

Treatment of I with II at room temperature in a THF solution (see eq. 1) and addition of heptane gave a high yield (90%) of crystals of $Cp_2Zr(CH_2PPh_2)_2RhH(PPh_3)$ (III) which gave satisfactory analytical data.

$$\underset{\text{(I)}}{Cp_2Zr(CH_2PPh_2)_2} + \underset{\text{(II)}}{RhH(PPh_3)_4} \rightarrow \underset{\text{(III)}}{Cp_2Zr(CH_2PPh_2)_2RhH(PPh_3)} + 3PPh_3 \qquad (1)$$

At room temperature, the $^{31}P\{^1H\}$ NMR spectrum of III shows an AB_2X pattern with a double triplet and a double doublet ($\delta(P^A)$ 24 ppm; $\delta(P^B)$ 40.4 ppm; $J(Rh–P^A)$ 116.2 Hz; $J(Rh–P^B)$ 151.5 Hz; $J(P^A–P^B)$ 28 Hz). This is indicative of three phosphorus atoms around the rhodium metal, favouring a square planar structure with two *trans* equivalent phosphorus atoms, related to the structure of $RhCl(PPh_3)_3$ [5] or $RhH(PPh_3)_3$ [6]. Such a conformation involving $Cp_2Zr(CH_2PPh_2)_2$ acting as a *trans* chelate on rhodium has previously been observed for $[Cp_2Zr(CH_2PPh_2)_2Rh(CO)Cl]$ [7].

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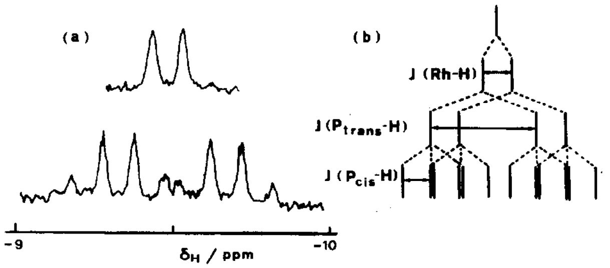
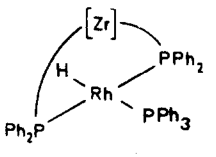


Fig. 1. Hydride region of the 250 MHz ^1H and $^1H\{^{31}P\}$ NMR spectra of $Cp_2Zr(CH_2PPh_2)_2RhH(PPh_3)$ (III): (a) experimental spectra in CD_2Cl_2; (b) splitting pattern for the hydride based on the proposed structure of III.

The ^1H NMR spectrum of III in CD_2Cl_2 shows the expected cyclopentadienyl resonance as a singlet at 5.42 ppm and, in the hydride region (Fig. 1), a doublet of pseudo-quadruplets at −9.49 ppm, which is simplified to a doublet by ^{31}P decoupling (J(Rh–H) 24.6 Hz; $J(P_{cis}$–H) 24.6 Hz; $J(P_{trans}$–H) 85.5 Hz), in agreement with the proposed structure·


(III)

In order to see whether the presence of I enhances the catalytic activity of II, some preliminary studies were carried out on the hydroformylation of 1-hexene under mild conditions of pressure and temperature. As shown in Table 1, we performed experiments with II or III alone (Experiments a and b, respectively) or in mixtures [I + II], [II + $2PPh_3$] and [III + $3PPh_3$] (Experiments c, d, and e, respec-

TABLE 1

HYDROFORMYLATION OF 1-HEXENE [a] IN THE PRESENCE OF $RhH(PPh_3)_4$ (II) AND $Cp_2Zr(CH_2PPh_2)_2(Rh(H)PPh_3)$ (III) AND RELATED SYSTEMS

Experiment	Catalyst	Time required (min)	Conversion (%)	n-Heptanal produced (%)	[Heptanal]/ [methylhexanal]
a	II	40	64	34	1.64
		150	90	38	1.13
b	III	35	81	56	2.32
		85	88	60	2.13
		135	97	65	2.04
		180	100	65	1.90
c	I+II	35	89	66	2.91
		140	100	73	2.76
d	II+$2PPh_3$	35	66	45	2.63
		160	100	56	1.83
e	III+$3PPh_3$	40	61	44	2.61
		90	86	62	2.58
		160	100	72	2.55

[a] Reaction conditions: H_2/CO: 1/1; 20 bar; 80°C; [1-hexene]/[catalyst] 400/1; solvent: THF.

tively), in order to explore the relationship between II and III in the same phosphorus environment, i.e. a phosphorus/rhodium ratio, P/Rh, 6/1, according to the stoichiometry of eq. 1. The reaction was monitored by GPC as well as the fall of pressure in a gas tank connected to the autoclave.

The catalytic activity of II was very poor (Experiment a), but it was enhanced by introduction of $2PPh_3$ (Experiment d). In both cases, the reaction was accompanied by some isomerization of the alkene, although to a smaller extent in Experiment d. Complex III alone is an active hydroformylation catalyst with no induction period and a high rate of conversion (Experiment b) but the normal/branched selectivity decreases during the course of the reaction to reach a ratio of ca. 2. There was a significant improvement in performance when an excess of phosphine was added to III (Experiment e), or when the mixture I + II was used (Experiment c), higher conversion rates and increased ratios of normal to branched aldehydes being observed. This implies that once the active species is formed it does not dissociate back to the initial precursor II. It is noteworthy that in experiments c and e, the composition of the mixture as defined in eq. 1 is the same, and the selectivity remains unchanged throughout the reaction time whereas in other cases the selectivity slowly decreased probably owing to progressive formation of a non selective species.

Although further work is needed to elucidate the catalytic mechanism, an important feature is the increasing polarity of the Rh–H bond in the presence of the zirconium moiety, which is evident by comparing the chemical shift of the hydride region of III with $RhH(PPh_3)_3$ (δ(H) -7.8 ppm; J(Rh–H) 14 Hz) [6]. This feature is probably related to the enhanced catalytic activity of III (increased rate and selectivity).

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