A Novel d^0–d^8 Heterobimetallic Complex obtained by Co-ordination of a Zirconium(IV) Diphosphine to a Dinuclear Rhodium(I) Moiety leading to a Hydroformylation-active Species

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Addition of the zirconium(IV) diphosphine complex $[(\eta^5\text{-}C_5H_5)_2Zr(CH_2PPh_2)_2]$, to the μ-thiolato dirhodium(I) complex, $[Rh_2(\mu\text{-}SBu^t)_2(CO)_4]$ results in the novel bimetallic species $[Rh_2(\mu\text{-}SBu^t)_2\{\mu^2\text{-}[Ph_2PCH_2]_2Zr(\eta^5\text{-}C_5H_5)_2\}(CO)_2]$ which is a better catalyst for low pressure hydroformylation of hex-1-ene than the analogous compound $[Rh_2(\mu\text{-}SBu^t)_2\{\mu^2\text{-}Ph_2P[CH_2]_4PPh_2\}(CO)_2]$; the special role of the electronic properties induced by zirconium is discussed

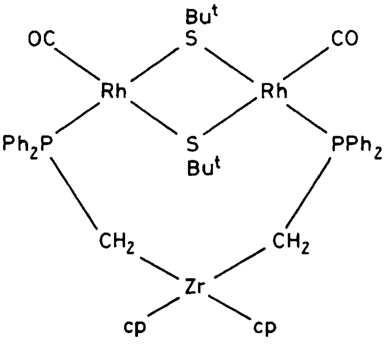
During the past decade, the synthesis of heterobimetallic complexes has received much attention because of the possibility of enhanced catalytic activity when associating electronically different metallic centres.[1] A few examples of extreme d^0–d^8 association are found in the literature.[2–4] Since hydroformylation of hex-1-ene was recently found to be efficiently catalysed at low pressure and low temperature (5 bar,† 80 °C) by the complex $[Rh_2(\mu\text{-}SBu^t)_2\{P(OMe)_3\}_2(CO)_2]$,[5] we have explored the catalytic properties of an analogous complex containing zirconium and rhodium atoms.

Addition of the dinuclear rhodium complex $[Rh_2(\mu\text{-}SBu^t)_2(CO)_4]$ (**2**) (1 equiv.) to the zirconium diphosphine ligand $[cp_2Zr(CH_2PPh_2)_2]$ (**1**) (cp = cyclopentadienyl) in toluene at room temperature gave immediate formation of the complex $[Rh_2(\mu\text{-}SBu^t)_2\{\mu^2\text{-}(Ph_2PCH_2)_2Zrcp_2\}(CO)_2]$, (**3**), which was isolated as a yellow powder by addition of pentane.‡ A splitting of 15 cm^{-1} between the two ν_{CO} bands at 1930 and 1945 cm^{-1} in the solid state is indicative of one CO ligand per rhodium atom. Similarly, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum shows a doublet, δ 53.1 p.p.m., *J* 140 Hz, indicative of two equivalent phosphorus nuclei, each bonded to one rhodium atom. ^1H and ^{13}C n.m.r. spectra§ confirm these results and show that the two Bu^t and the two cp groups are both magnetically inequivalent. Consequently structure (**3**) is proposed with the CO and the phosphorus atoms in a *cis*-arrangement.

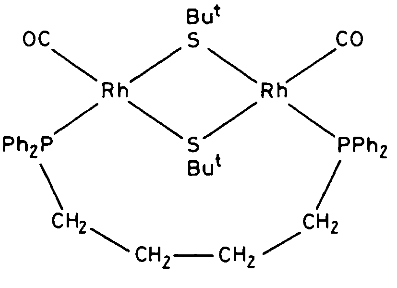
$(\eta^5\text{-}C_5H_5)_2Zr(CH_2PPh_2)_2$
(**1**)

$Rh_2(\mu\text{-}SBu^t)_2(CO)_4$
(**2**)

The catalytic activity of (**3**) as a hydroformylation catalyst was evaluated using hex-1-ene at a constant pressure of 5 bar and temperature of 80 °C. Stoicheiometric amounts of complexes (**1**) and (**2**) were added to hex-1-ene (400 equiv.) in toluene as solvent under argon in a Schlenk tube and the mixture was immediately introduced into the autoclave. The reaction rate was followed by measuring the pressure in the tank containing the 1 : 1 H_2/CO gas mixture. Figure 1 shows the reaction progress as a function of time. The induction period was very short (*ca.* 10 min) and the reaction rate was fast; the initial rate was calculated to be 1.44 mmol dm^{-3} min^{-1}.



(**3**)



(**4**)

After 4 h, 90% conversion was achieved. These results are comparable to those of the complex $[Rh_2(\mu\text{-}SBu^t)_2(POMe_3)_2(CO)_2]$[5] and thus superior to those of the reference complex $[RhH(CO)(PPh_3)_3]$. Aldehydes were exclusively produced. However, the linear:branched ratio was *ca.* 1.9:1 whereas this ratio was found to be 4 : 1 in the previous system.[5] I.r. spectra show that some deactivation occurs after catalysis since small amounts of the carbonyl (**2**) were recovered together with the complex (**3**).

In order to determine the role of the zirconium atom, we prepared the complex (**4**), $[Rh_2(\mu\text{-}SBu^t)_2\{\mu_2\text{-}Ph_2P[CH_2]_4PPh_2\}(CO)_2]$, resulting from the addition of one equivalent of bis(diphenylphosphino)butane (dppb) to (**2**). I.r. and ^{31}P n.m.r. spectra are consistent with a structure similar to that of (**3**). Catalytic tests were performed under the same conditions as above, *i.e.* mixing the ligand and the

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† 1bar = 10^5 Pa.

‡ Microanalyses (C, H, P, Rh, and Zr) were in agreement with the proposed formula.

§ Selected n.m.r. data (in CD_2Cl_2) ^1H: δ 6.04 and 5.99 (cp), 1.76 and 1.17 (Bu^t), 1.97 and 1.04 (CH_2). $^{13}C\text{-}\{^1H\}$: δ 193.0 [dd, *J*(Rh–C) 83, *J*(P–C) 12 Hz, CO].

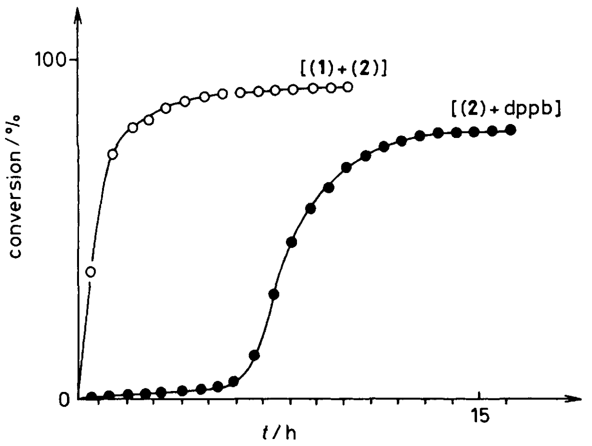

Figure 1. Conversion of hex-1-ene using 1 : 1 CO/H_2 mixture , $P = 5$ bar; $T = 80$ °C.

rhodium complex in the autoclave just before starting the reaction. The results are in Figure 1. In this case, we observed a long induction period of *ca.* 6 h, an initial rate calculated to be 0.42 mmol dm^{-3} min^{-1}, a 80% conversion after 15 h, and a linear : branched ratio of 2.4 : 1.

There are two salient features of this study. Firstly, the superiority of the bridging diphosphine ligand when compared to monophosphine ligands arises from the fact that systems such as $[Rh_2(\mu\text{-}SBu^t)_2(PR_3)_2(CO)_2]$ exhibit low catalytic activity followed by rapid deactivation, leading to (**2**).[6] Secondly, the electronic influence of the zirconium centre is demonstrated by the enhanced activity of the system [(**1**)+(**2**)] when compared to [(**2**)+dppb]. Since complexes (**3**) and (**4**) are recovered after the above catalytic reactions, we assume that, as for $[Rh_2(\mu\text{-}SBu^t)_2\{P(OMe)_3\}_2(CO)_2]$, the catalytic cycle involves a dirhodium intermediate species. Zirconium probably plays an important role by inducing more electron density on one rhodium atom for the oxidative addition of H_2 and by facilitating back-donation for the approach of the olefin.

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