

## Catalytic Properties of a Heteronuclear Palladium–Cobalt Complex Anchored on Phosphinated Silica: Synergetic Effects in Propylene Hydroformylation

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The catalytic activity of a heteronuclear palladium–cobalt complex, anchored on phosphinated silica, in the gas-phase hydroformylation of propylene under mild conditions (40–100 °C, 1 atm of CO) greatly exceeds the overall catalytic activity of homonuclear Co and Pd complexes under the same conditions.

Heteronuclear complexes of transition metals provide a promising area in catalysis and their catalytic properties may differ markedly from those of homonuclear ones.<sup>1</sup> For example, in olefin hydroformylation activation of the hydrogen molecule may be facilitated by introducing a palladium atom into the catalyst composition (in the presence of carbonylcobalt complexes the rate-determining step is the acylcarbonylcobalt hydrogenation).

We have synthesized heteronuclear palladium–cobalt complexes, anchored on phosphinated silica, and compared their catalytic properties in the gas-phase hydroformylation of propylene with those of homonuclear anchored complexes of Co and Pd.

For the catalyst preparation, silica, with a specific surface area of 110 m<sup>2</sup> g<sup>-1</sup>, heated at 600 °C at 0.01 Torr, was used. Phosphine ligands were anchored by the reaction of surface hydroxyl groups of silica with (EtO)Si(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Pcy<sub>2</sub>)<sub>3</sub> (cy = cyclohexyl) as described in ref. 2, to form {Si}–(CH<sub>2</sub>CH<sub>2</sub>–CH<sub>2</sub>Pcy<sub>2</sub>)<sub>3</sub> which we denote by P<sub>3</sub>.

Homonuclear anchored complexes of P<sub>3</sub>Pd<sup>0</sup> and P<sub>3</sub>Co<sub>2</sub>(CO)<sub>8</sub> were prepared by interaction of phosphinated silica with Pd<sub>2</sub>L<sub>4</sub> [L = (PhCH=CH)<sub>2</sub>C=O] and Co<sub>2</sub>(CO)<sub>8</sub>, respectively. The anchored complexes prepared were characterized by comparison of their i.r. and electronic transmission spectra with the corresponding spectra of the homogeneous ana-

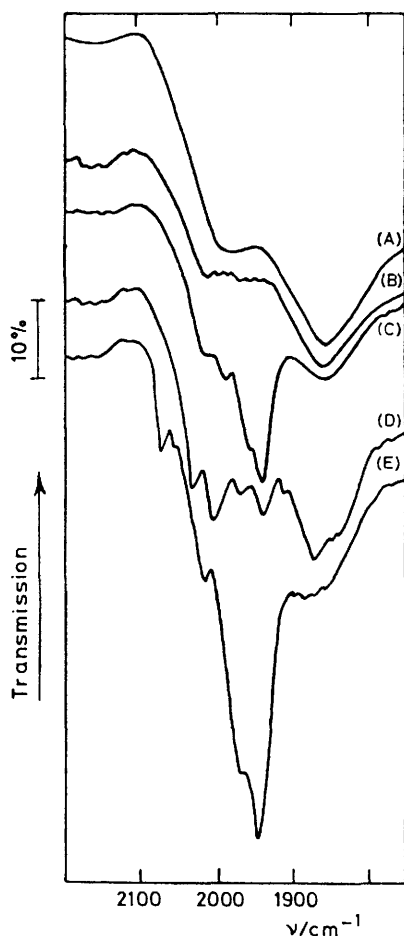
**Table 1.** Elemental analysis data for anchored palladium and cobalt complexes.

Complex	Content <sup>a</sup>		
	P	Pd	Co
P <sub>3</sub> + Pd <sub>2</sub> L <sub>4</sub>	1.9	0.5	—
P <sub>3</sub> + Co <sub>2</sub> (CO) <sub>8</sub>	1.9	—	1.1
P <sub>3</sub> + Co <sub>2</sub> (CO) <sub>8</sub> + Pd <sub>2</sub> L <sub>4</sub>	1.9	0.7	1.1

<sup>a</sup> Elemental content/10<sup>-4</sup> g-atom of element per g of SiO<sub>2</sub>.

logues. The synthesis and identification of similar phosphine complexes of Pd and Co have been previously described.<sup>2,3</sup> Note that the formula P<sub>3</sub>Co<sub>2</sub>(CO)<sub>6</sub> does not correspond to any particular stoichiometry of the supported complex since only two phosphine groups of the surface ligand appear to be bonded to the cobalt.

The synthesis of the anchored heteronuclear palladium–cobalt complex is based on oxidative addition of Pd<sup>0</sup> complexes to Co<sub>2</sub>(CO)<sub>8</sub> via insertion into the Co–Co bond.<sup>4</sup> The silica sample containing the anchored P<sub>3</sub>Co<sub>2</sub>(CO)<sub>6</sub> complexes was treated with a benzene solution of Pd<sub>2</sub>L<sub>4</sub> at room temperature for 50 h. The sample was then thoroughly washed with benzene and dried at 80 °C for 30 min until a pressure of 0.01



**Figure 1.** I.r. spectra of anchored palladium and cobalt complexes. (A) Silica sample used for preparation of the anchored complexes; (B)  $P_3 + Pd_2L_4$  complex [ $L = (PhCH=CH)_2C=O$ ]; (C)  $P_3 + Co_2(CO)_8$  complex; (D) + (E)  $P_3 + Co_2(CO)_8 + Pd_2L_4$  complex, (D) an initial sample, (E) the same sample after heating for 2 h at 100 °C.

Torr was attained. The elemental analysis data are presented in Table 1. I.r. spectra of the samples prepared (suspension in hexadecane), recorded on a Specord-75-IR, are given in Figure 1.

The i.r. spectrum of  $P_3Co_2(CO)_6 + Pd_2L_4$  differs appreciably from the initial spectrum of  $P_3Co_2(CO)_6$ . It has new bands at 1870, 1975, 2005, and 2035  $cm^{-1}$ . A similar spectrum was observed for the unsupported palladium-cobalt complex  $(Ph_2PCH_2CH_2PPh_2)_2PdCo_2(CO)_7$ ,<sup>6</sup> which shows absorption bands at 1979, 2000, and 2040  $cm^{-1}$  ascribed to terminal CO-groups. The visible and u.v. spectrum of  $P_3Co_2(CO)_6 + Pd_2L_4$  differs also from those of  $P_3Co_2(CO)_6$  and  $P_3Pd^0$  complexes. This spectrum has no bands, typical of anchored homonuclear complexes, at 26 000 and 29 000  $cm^{-1}$ ; instead, there appears a new wide band at 32 000  $cm^{-1}$ .

The above facts suggest that anchored heteronuclear carbonylphosphinecobaltpalladium complexes mainly are formed on the surface.

Propylene hydroformylation in the presence of the synthesized anchored complexes was performed in a flow reactor at 40–100 °C, a total pressure of reaction mixture ( $H_2:CO:C_3H_6 = 1:1:1$ ) of 3 atm and space velocity of 1  $s^{-1}$  ensuring

**Table 2.** Catalytic properties of anchored palladium and cobalt complexes in the gas-phase hydroformylation of propylene.

Catalyst	Reaction temperature/ °C	Catalytic activity <sup>a</sup>	Selectivity for straight-chain products (%)
$P_3 + Pd_2L_4$	60	0.1	—
	80	1	—
	100	10	32
$P_3 + Co_2(CO)_8$	60	0.1	—
	80	6	84
	100	80	84
$P_3 + Co_2(CO)_8 + Pd_2L_4$	40	21	39
	60	110	68
	80	270	84
	100	345	87

<sup>a</sup> ( $\mu mol$  of  $C_4H_8O + C_4H_9OH$ )[g-atom of Pd(or Co)  $s^{-1}$ ] for first two catalysts and ( $\mu mol$   $C_4H_8O + C_4H_9OH$ )[g-atom of (Pd + Co)  $s^{-1}$ ] for third catalyst; after a 1 h catalytic run at the temperature indicated.

a conversion of CO <5%. The data obtained are compiled in Table 2. The main products obtained under these conditions were n- and iso-butyraldehydes, the yield of butyl alcohols being not more than 15–20% of the overall yield of oxo-products. The catalytic activity of  $P_3 + Co_2(CO)_8 + Pd_2L_4$  greatly exceeded the overall activity of  $P_3 + Co_2(CO)_8$  and  $P_3 + Pd_2L_4$ . In the presence of palladium-cobalt catalyst, the products were produced at temperatures as low as 40–60 °C, while homonuclear complexes were practically inactive at these temperatures. The activity of the heteronuclear catalysts gradually decreased in the course of the reaction, the catalyst deactivation being accompanied by an increase in the relative yield of the straight-chain products. At elevated temperatures deactivation became faster. The i.r. analysis [Figure 1, curve (D)] showed that some of the surface heteronuclear complexes were destroyed after the catalytic run at 100 °C which may account for the decrease in catalytic activity and variations in its selectivity to straight-chain products.

The results obtained provide support for the existence of a synergistic effect in propylene hydroformylation when palladium is introduced into the carbonylcobalt catalyst. This effect is especially pronounced at low temperatures (40–60 °C). In the presence of a catalyst prepared by co-impregnation of silica with cobalt and palladium complexes and containing a surface metallic phase, no such specific effect has been observed under otherwise identical conditions.

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