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Chlorocarbonyl-1,2-bisdiphenylphosphino-1,2-dicarbadodecaboranerhodium(I) and Chloro-1,2-bisdiphenylphosphino-1,2-dicarbadodecaboranetriphenylphosphinerhodium(I): Preparation and Catalytic Properties

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Although a number of transition metal complexes of 1,2-diphosphino-1,2-dicarbadodecaboranes and analogous diarsino compounds have been reported [1, 2], there are apparently no known rhodium complexes of these ligands. It appeared to be of interest to prepare and study rhodium complexes because of the effectiveness of such compounds as $(Ph_3P)_3$-RhCl or $(Ph_3P)_2Rh(CO)Cl$ as hydrogenation [3] or hydroformylation [4] catalysts. It appeared quite possible that a borane ligand might confer unusual catalytic properties consequent on its individual steric and electronic nature. We now report the results of such an investigation.

Experimental

1,2-Bisdiphenylphosphino-1,2-dicarbadodecaborane (dppb)

This compound was prepared as described [5] but recrystallized from butanone. *Anal.*: C, 61.0; H, 5.9; P, 12.2. Theory requires: C, 60.9; H, 5.9; P, 12.1%. M.p. 212.5–214.5 °C (lit. 219 °C [5] and 208–210 °C [6]).

Preparation of RhCl(CO)(dppb)

The diphosphine (0.395 g) in benzene (50 cm^3) was added dropwise over 30 min to a solution of $Rh_2Cl_2(CO)_4$ (0.15 g, 0.5 mol) in benzene (50 cm^3) at 55 °C, and the solution was then refluxed for 1 h, the colour changing from an original pale yellow to orange red. Filtration and removal of solvent left an orange solid which was well washed with n-pentane and dried *in vacuo* (yield, 0.504 g). Attempted simple recrystallisation from benzene resulted in loss of CO and yielded only a sticky orange powder. However, this loss of CO while in solution was reversible, and recrystallisation from benzene saturated with CO gave a yellow pure crystalline product, m.p. 290–300 °C (decomp.), with a rapid change to an orange colour at 235 °C. Found: C, 48.0; H, 4.3; O, 1.7; Cl, 4.8%. $C_{27}H_{30}OB_{10}ClP_2Rh$ requires: C, 47.8; H, 4.5; O, 2.4; Cl, 5.2%. There was no observable (IR) loss of CO from the solid *in vacuo* over several days. Some CO must have been lost while the solution was under reflux, but this reaction is very readily reversible, treatment of the orange red solution with CO gas producing an immediate change to pale yellow.

Preparation of RhCl(PPh₃)(dppb)

$[RhCl(PPh_3)_3]$ (0.50 g) was stirred in refluxing benzene (25 cm^3) under nitrogen while the diphosphine (0.277 g, 1 mol) was added dropwise in benzene (40 cm^3) during 30 min. The mixture was refluxed for 14 h, giving a clear orange-yellow solution. Removal of the solvent under reduced pressure followed by repeated washing of the residue with boiling n-hexane and drying *in vacuo* gave 0.42 g (85%) yellow powder. Recrystallisation from much benzene gave the pure product, decomp. 235 °C. Found: C, 57.9; H, 4.9; Cl, 3.8%. $C_{44}H_{45}B_{10}ClP_3Rh$ requires: C, 57.9; H, 4.9; Cl, 3.9%. PPh_3 (0.26 g, 92%) was recovered from the hexane washings. $[RhCl(PPh_3)(dppb)]$ was also prepared similarly from $[RhCl(CO)(PPh_3)_2]$ and dppb but this method gave less pure products after recrystallisation than the foregoing method.

Catalytic Hydrogenation

Hydrogenation was carried out at 110 °C for 12 h at 60 atm initial pressure of hydrogen, in 20 cm^3 benzene with 30 mg $[RhCl(PPh_3)(dppb)]$ catalyst and 1 cm^3 alkene. Yields were as follows: (i) hexane gave 100% n-hexane, (ii) cyclo-octa-1,5-diene gave 70% cyclo-octane, and (iii) cyclo-octa-1,3-diene gave 88% cyclo-octane. Yield and identity of product was established by GLC (Hewlett Packard 5830A) employing authentic samples of product for comparison. This method was also used for the products of the hydroformylation reactions.

A comparative run using benzene (15 cm^3) and ethanol (5 cm^3) as a mixed solvent, 1-hexene being the substrate, yielded 98% n-hexane.

Under mild conditions, namely hydrogen pressure 1 atm, temperature 40 °C, $[RhCl(PPh_3)(dppb)]$ 30 mg, solvent toluene (30 cm^3) and chloroform (10 cm^3), 1-hexene was not hydrogenated.

Catalytic Hydroformylation

Trials were carried out under several different conditions of temperature and pressure using hex-1-ene (0.71 g) as substrate. Highest yields were obtained with CO (45 atm) and H_2 (45 atm) in benzene (20 cm^3) at 55 °C for 12 h, using RhCl-(CO)(dppb) (30 mg). Under these conditions the following products were obtained from different alkenes:

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hex-1-ene $\longrightarrow$

2-methylhexanal (46%) + n-heptanal (53%)

pent-1-ene $\longrightarrow$

2-methylpentanal (43%) + n-hexanal (57%)

trans-pent-2-ene $\longrightarrow$

2-methylpentanal (44%) + 2-ethylbutanal (44%)

The relative proportions of the products from *trans*-pent-2-ene are only approximate, as the two GLC peaks were barely separable. At 100 °C, yields were much lower (30% total) and some formation of condensation products was apparent.

Discussion

The synthesis of the two complexes proceeded without difficulty, except that the ready dissociation of CO from [RhCl(CO)(dppb)] necessitated that purification was carried out in the presence of excess CO. Doubtless the loss of CO led to reversible formation of a dimer [(dppb)Rh(μ-Cl)$_2$Rh-(dppb)]. The readily reversible loss of CO is presumably the consequence of the *trans*-effect of one of the two *cis*-chelate PPh$_2$ groups in [RhCl(CO)(dppb)] and would support a monomeric formulation; unfortunately the solubilities of both complexes were too small for molecular weight measurements. The IR CO stretching frequency of 2020 cm^{-1} observed for [RhCl(CO)(dppb)] is closely similar to that of [RhCl(CO)Ph$_2$PC$_2$H$_4$PPh$_2$] (2010 cm^{-1}) and in full accord with a *trans* OC–Rh–P geometry; contrast [{RhCl(CO)(Ph$_2$PC$_4$H$_8$PPh$_2$)}$_2$] where *trans*-Cl–Rh–CO gives ν_{CO} = 1957 cm^{-1} [7]. The similarity of ν_{CO} for the complexes [RhCl(CO)L] (L = dppb, Ph$_2$PC$_2$H$_4$PPh$_2$) suggests a somewhat similar nature of the Rh–P bond in both compounds. Both dppb complexes of course show in their IR spectra features characteristic of the PPh$_2$ group, and strong ν_{B-H} bands are present at 2540–2620 cm^{-1} for [RhCl-(CO)dppb] and 2540–2660 cm^{-1} for [RhCl(PPh$_3$)-(dppb)].

Regarding their catalytic activity, the ways in which the dppb ligand might influence this are by (a) its electronic properties, (b) its bulk, (c) its *cis*-configuration, and (d) by its presumed non-dissociable character owing to its chelate nature. The CO IR frequency suggests that (a) may show little difference from complexes of more conventional ligands. Our limited catalytic tests indicate that [RhCl(CO)-(dppb)] is an effective hydroformylation catalyst under what are fairly mild conditions for this reaction, but that it is somewhat unselective as regards products, and that [RhCl(PPh$_3$)(dppb)] is an effective hydrogenation catalyst but only at higher temperatures.

The lack of selectivity in the carbonylation reaction is somewhat surprising, although [RhH(CO)-PPh$_3$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)], which also incorporates a chelate diphosphine, shows a similar lack of specifity [8]. Using [RhCl(CO)(dppb)] as catalyst, or strictly as catalyst precursor, the selectivity-determining stage would probably be the alkene addition:

$$\mathrm{RhH(CO)_2(dppb)} \xrightarrow{\mathrm{RCH{=}CH_2}}$$

$$\mathrm{Rh(CH_2CH_2R)(CO)_2(dppb)}$$

or

$$\mathrm{Rh\{CH(CH_3)R\}(CO)_2(dppb)}$$

The very bulky carboranediphosphine would be expected to exert a considerable influence on whether a 1- or a 2-metalloalkane is formed, and might be expected to lead to a considerable preponderance of the 1-formyl product whereas in practice a straight chain: branched chain ratio of only ~5:4 was obtained.

The reduced hydrogenation catalytic activity of [RhCl(PPh$_3$)(dppb)] compared with [RhCl(PPh$_3$)$_3$], in the sense that a higher temperature is needed, could possibly be caused by less ready coordination of the alkene to a sterically demanding intermediate such as RhH$_2$Cl(dppb), where the comparatively large bulk of the dppb ligand is of importance.

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