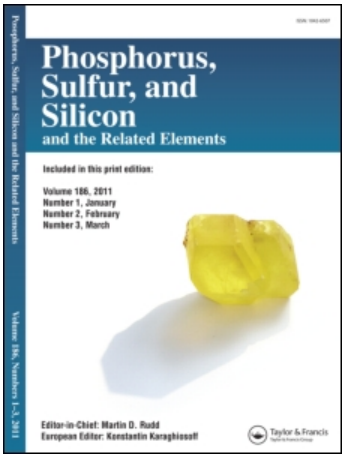

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Steric Effects on the Synthesis, Structure, Reactivity and Selectivity of t-Phosphine Rhodium Complex Hydroformylation Catalysts

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Bulky trivalent phosphorus ligands of transition metal complexes were often observed to affect catalyst activity and selectivity. In the area of the low pressure hydroformylation of α-olefins in the presence of rhodium complexes, Pruett and Smith observed early (1) that the use of bulky ortho-substituted phosphite ester ligands leads to a decrease of the ratio of straight chain versus branched aldehyde products (n/i ratio).

$$RCH{=}CH_2 + CO + H_2 \longrightarrow RCH_2CH_2CHO + RCH(CH_3)CHO$$

More recently van Leeuwen and Roobek have shown (2) that rhodium complexes of such bulky ligands are much more active catalysts than the much studied triphenylphosphine-rhodium catalyst system, in the hydroformylation of linear internal and branched terminal olefins. They suggested that for steric reasons only two bulky ligands could be coordinated to the same rhodium in such complexes and that such ligands could increase the coordinative unsaturation of rhodium, thus leading to a higher reactivity. Indeed a number of coordinatively unsaturated rhodium carbonyl complexes of bulky trialkylphosphine ligands were described by Otsuka and coworkers (3) and by Freeman and Young (4).

In spite of the numerous studies with bulky phosphorus ligands in rhodium complex catalyzed hydroformylation regarding their effect on reactivity and selectivity, there is no known systematic study correlating catalyst structure and properties under H_2/CO pressure, i.e. simulated reaction conditions. In the present work such a study of steric effects was carried out with variously branched alkyldiphenylphosphine ligands. Numerous alkyldiarylphosphine rhodium carbonyl hydride based hydroformylation catalyst systems were investigated at Exxon (5,6). In the following, complexes of structurally simple ligands will be discussed where steric effects could be clearly distinguished. Overall the present study established that branching on the α- or β- carbon of the alkyl groups has a major effect on the structure and equilibria of the rhodium complexes formed under H_2/CO pressure. The hydroformylation activity and selectivity in turn were found to depend on the catalyst complex structure and equilibria. For the generation of active catalyst species, the rate of the reversible dissociation of phosphine or CO ligands to generate coordinatively unsaturated complexes is particularly important.

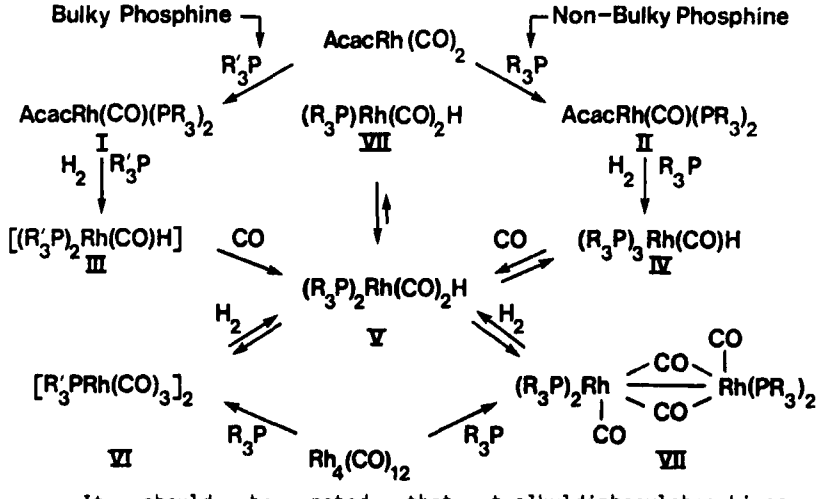
A major part of the present work was carried out with n-, s-, i- and t-butyldiphenylphosphine ligands. Neopentyl- and neophyl- (2,2-methylphenylpropyl-) diphenylphosphines were of another ligand type investigated in detail. As rhodium complex catalyst presursors rhodium

dicarbonyl acetylacetonate and tetrarhodium dodecacarbonyl were used. Reactions of these precursors with triphenylphosphine and H_2/CO were described in the literature (7).

Triphenylphosphine rhodium carbonyl acetylacetonate, derived from triphenylphosphine and rhodium dicarbonyl acetylacetonate, was reported as a hydroformylation catalyst by Janecko, Trzeciak and Ziolkowski (8). In our work we found that, in the presence of excess phosphine, alkyldiarylphosphine rhodium carbonyl acetylacetonates form bis-phosphine complexes which then react with H_2 and H_2/CO to produce acetylacetonate free catalyst complexes. Booth, Else, Fields and Haszeldine discovered that, when tetrarhodium dodecacarbonyl is reacted with equivalent and excess triphenylphosphine under CO, triphenylphosphine rhodium carbonyl dimers are formed (9). These dimers were successfully used as 1-alkene hydroformylation catalysts at 70°C under 120 atm H_2/CO pressure. Also, the bis(triphenylphosphine) rhodium dicarbonyl dimer was converted to the corresponding hydride hydroformylation catalyst by atmospheric hydrogen. Depending on the steric hindrance similar reactions of alkyldiarylphosphines were found in the present study.

In general, the synthesis of alkyldiarylphosphine rhodium complexes started with toluene solutions of $AcacRh(CO)_2$ or $Rh_4(CO)_{12}$ having concentrations equivalent to 0.4% Rh. These solutions were then reacted with varying amounts of the appropriate phosphine ligand typically to provide a 9/1 P/Rh ratio and then ^{13}CO and H_2 in the 2 to 35 atm pressure range. All the experiments were carried out in thick walled NMR tubes of 10 mm outside diameter, equipped with Teflon screw valves. ^{31}P and ^{13}C NMR spectra were obtained mostly at -30°C using a JEOL FX 90Q multinuclear NMR spectrometer. The rhodium complex structures, equilibria, and dissociation rates were primarily characterized in terms of ^{31}P and ^{13}C chemical shifts, Rh-P and P-C coupling constants, and line broadening.

The reactions studied are outlined with both bulky and non-bulky phosphines in the following.



It should be noted that t-alkyldiphenylphosphines and neoalkyldiphenylphosphines are regarded as definitely bulky while n-alkyldiphenylphosphines certainly are not. Iso- and sec. alkyldiphenylphosphines are intermediate and as such exhibit intermediate complexing behavior as explained in the following.

The reactions of $AcacRh(CO)_2$ with excess phosphine resulted in bis-phosphine rhodium carbonyl acetylacetonates (I and II) which were isotopically enriched under 2 atm ^{13}CO. With the exception of the highly bulky phosphine complexes these acetylacetonates were readily reacted with H_2 at ambient conditions or under pressure to selectively form tris-phosphine rhodium carbonyl hydrides (IV). The latter reversibily react with CO to give bis-phosphine rhodium dicarbonyl hydrides (V) which can also be formed with the highly bulky t-butyl- and neoalkyldiphenylphosphines under H_2/CO pressure, apparently via a coordinatively unsaturated carbonyl hydride (III). The equilibria between the mono- and dicarbonyl hydride complexes (IV and V) depend on the bulkiness and the excess concentration of the phosphine ligand and the CO partial pressure.

Under H_2/CO, the dicarbonyl hydrides (III) are also in variable equilibria with rhodium carbonyl dimers (VI and VII). In the presence of excess phosphine, non-bulky phosphines particularly dimethylphenylphosphine form bis-phosphine rhodium dicarbonyl dimers (VII). The highly bulky t-alkyl- and neoalkyldiphenylphosphines give monophosphine rhodium tricarbonyl dimers (VI). Rhodium carbonyl dimer formation is frequently inhibited by the steric bulk of the phosphine ligand. Secondary and isobutyldiphenylphosphines mostly form bis-phosphine rhodium carbonyl hydrides (V) rather than bis-phosphine rhodium dicarbonyl dimers (VII). Similarly t-butyldiphenylphosphine leads to hydride (V) rather than rhodium tricarbonyl dimer (VII) formation.

Starting with tetrarhodium dodecacarbonyl and excess phosphine in toluene solution the dimers are produced at first. However, in case of the α-branched sec-butyldiphenylphosphine and t-butyldiphenylphosphine significant amounts of the dicarbonyl hydrides are also formed on standing probably via hydrogen abstraction from toluene.

The catalytic activity of the alkyldiarylphosphine rhodium carbonyl complexes studied was qualitatively correlated with their steric crowding. Steric crowding results in the rate enhancement of the dissociation of phosphine and/or CO ligands, which could be determined by NMR. Ligand dissociation leads to highly reactive, coordinatively unsaturated species which initiate the catalytic cycle of hydroformylation (6, 10). Thus the concentration of coordinatively unsaturated species can be correlated with catalyst effectiveness. The coordinatively unsaturated species containing a bulky phosphine ligand and only one such ligand per rhodium (VIII) is more reactive toward internal olefins but less selective in α - olefin hydroformylation the trans- bis-phosphine complex species (Type III) from complexes of non-bulky ligands.

With a bulky cis-chelated bis-phosphine ligand $Ph_2PCH_2C(CH_3)_2CH_2PPh_2$, steric crowding and chelate stabilization led to a rapid but selective CO dissociation of the dicarbonyl hydride (V). However, as a result of the cis- rather than trans-stereochemistry of the resulting active species also lead to a low n/i ratio of hydroformylation products.

The catalytic activity of rhodium carbonyl hydride complexes (IV and V) is well known in low pressure hydroformylation(6,10). In the present work, it was found that rhodium dimers, (VI and VII) also possess low pressure hydroformylation activity at ambient temperature, where the maintenance of the dimer structure could be followed by NMR. Since dimer formation highly depends on the structure of the bulky ligand, ligand modification may lead to more active and stable catalysts of this type.

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