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Preliminary communication

THE SYNTHESIS OF TRIS(TRIMETHYLPHOSPHITE)(η^3-ALLYL)RHODIUM AND A STUDY OF ITS REACTIONS WITH HYDROGEN, SILANES AND DONOR LIGANDS

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Summary

Addition of $P(OMe)_3$ to $[Rh(\eta^3\text{-}C_3H_5)(CO)_2]$ gives $[Rh(\eta^3\text{-}C_3H_5)\{P(OMe)_3\}_3]$; this reacts with hydrogen or silanes to form a species which is an effective hydrogenation catalyst for olefins and a hydrosilylation catalyst for terminal olefins, aldehydes and ketones.

Recently [1,2], the complex tris(trimethylphosphite)(η^3-allyl)cobalt has been shown to be a homogeneous catalyst for the hydrogenation of aromatic compounds. We have observed, as part of a general study of the reactions of allyl complexes, that the potentially interesting rhodium analogue can easily be prepared. Addition (room temperature) of an excess of trimethylphosphite to dicarbonyl(η^3-allyl)rhodium [3] in hexane solution leads to the rapid** evolution of carbon monoxide and the formation of the yellow crystalline, air-sensitive, complex tris(trimethylphosphite)(η^3-allyl)rhodium (I). ^{1}H NMR resonances: (20°C, C_6D_6) at τ(ppm)4.95(m, 1H, H_3, $J(H_3H_2)$ 6.0 Hz, $J(H_3H_1)$ 8.0 Hz, $J(^{103}RhH_3)$ 2.0 Hz), 6.55(m, 27H, $POCH_3$), 7.25(d, 2H, H_2) and 8.0(d, 2H, H_1); ^{31}P NMR resonance (20°C, toluene-d_8) at −162 ppm (rel. ext. H_3PO_4)($J(^{103}Rh—^{31}P)$ 230 Hz); at −40°C resonances at −163.4(d, 2P, basal ^{31}P, $J(^{103}Rh—^{31}P)$ 236 Hz) and −161.5(d, 1P, apical ^{31}P, $J(^{103}Rh—^{31}P)$ 305 Hz). The spectra are consistent with the illustrated static structure, and the dynamic behaviour is clearly related to that reported for the analogous cobalt complex. The ^{31}P NMR spectrum of $[Rh(\eta^3\text{-}C_3H_5)\{P(OMe)_3\}_3]$ in the presence of free $P(OMe)_3$ showed the expected two resonances, but at 80°C these merged to give one resonance. Under these conditions the ^{1}H resonances due to H^1 and H^2 broadened, i.e. *syn—anti* exchange. This indicates that phosphite exchange occurs by phosphite dissociation and also by σ-allyl formation.

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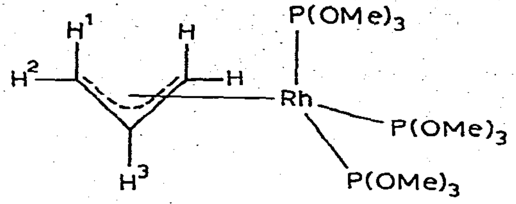
**Reaction of trimethylphosphite with $Co(\eta^3\text{-}C_3H_5)(CO)_3$ gives, in contrast $[Co(\eta^3\text{-}C_3H_5)(CO)_2\{P(OMe)_3\}]$.



(I)

Carbon monoxide reacts reversibly with the complex to give a σ-allyl complex (ν (CO)(hexane) 1973 and 1960 cm^{-1}). The ^{31}P spectrum (−120°C) of the adduct showed only one resonance, there being no evidence for uncoordinated phosphite; an observation which is consistent with the presence of interconverting (Berry pseudorotation process) trigonal bipyramidal species.

In contrast, with the cobalt species the rhodium complex is not a homogeneous hydrogenation catalyst for aromatic compounds the difference arising from the ease of cleavage of the Rh—C bond. A hexane or benzene solution of $[Rh(\eta^3\text{-}C_3H_5)\{P(OMe)_3\}_3]$ absorbs two molar equivalents of molecular hydrogen (1 atm, room temp.) to give a red solution [ν(RhH) 2260, 2269 and 1944 cm^{-1}] containing propane (GC). Addition of an excess of trimethylphosphite to the red solution gave a quantitative yield of $[RhH\{P(OMe)_3\}_4]$ (II) [ν(RhH) 1944 cm^{-1}]. The red solution is an active hydrogenation catalyst (1 atm, room temp.) for olefins, hex-1-ene > cyclohexene. Acetylenes, 1,3-dienes, 1,4-dienes or ketones are not hydrogenated, and there was no evidence for hydrogenation of benzene. Addition of H_2 to a benzene-d_6 solution of I did not lead to deuterium—hydrogen exchange. Attempts to isolate the active species have so far been unsuccessfull. Examination of the ^{31}P and ^{1}H spectra (−120° to +20°C) of the red solution showed only resonances due to II. It is suggested that initially formed $[RhH\{P(OMe)_3\}_3]$ undergoes a disproportionation reaction to form II and the catalyst $[RhH\{P(OMe)_3\}_2]_x$. Separate experiments confirmed that II has no catalytic activity, and it is interesting that solutions containing $[RhCl\{P(OPh)_3\}_3]$ have been reported to show no activity as hydrogenation catalysts.

Addition of silanes (Et_3SiH, Me_3SiH) to I forms an effective (room temp.) hydrosilylation catalyst for terminal olefins, aldehydes and ketones. Reaction of Et_3SiH with hex-1-ene produced exclusively the terminal silane, and the reactivity sequence cyclohexanone > benzaldehyde > acetone > acetophenone was observed. Hydrosilylation of 4-t-butylcyclohexanone followed by hydrolysis of the resulting silyl ether gave (GC) 4-t-butylcyclohexanol *e—e(cis)/e—a(trans)* = 2.9 :1 (with Me_3SiH) and 2.4 :1 (with Et_3SiH). The addition of Et_3SiH to cyclohex-2-enone gave only the *o*-silyated derivative.

As would be expected, addition of free $P(OMe)_3$ to solutions of I completely inhibited the reaction with H_2 and silanes. Further work is in progress on the details of these reactions.

Acknowledgment

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