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Preliminary communication

STERIC CONTROL OF DIENE INSERTION IN A DIENE HYDRIDO COBALT COMPLEX

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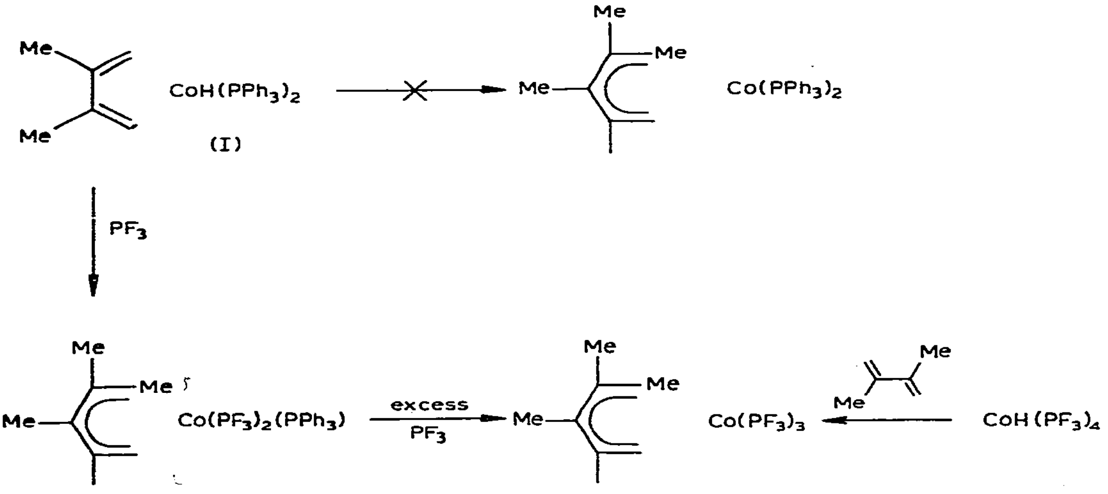
Summary

Substitution of PPh_3 by PF_3 in CoH(2,3-dimethyl-1,3-butadiene)$(PPh_3)_2$ leads to olefin insertion into the cobalt—hydrogen bond to form Co(h^3-1,1-dimethyl-2-methylallyl)$(PF_3)_3$.

Although transition metal hydrido-diene complexes have been postulated as intermediates in hydrogenation [1] and isomerisation [2] reactions relatively few have been characterised [3—8]. Structures of $IrH(C_4H_8)(P\text{-}i\text{-}Pr_3)_2$ [3] and $[RuH(C_4H_6)(PMe_2Ph)][PF_6]$ [4] have been determined by X-ray crystallographic studies, and recently Ir(h^3-C_6H_9)(h^4-C_8H_{12}) and Ir(h^3-C_7H_{11})(h^4-C_8H_{12}) have been shown to be in equilibrium with their respective hydrido-diene isomers at room temperature [6]. The reactivity of Co(h^3-C_8H_{13})(h^4-C_8H_{12}) can also be



(II)

understood in terms of an equilibrium involving the isomeric diene-hydride complex [9] while intermediates of this type were previously invoked by us to explain the thermal isomerisation of M(h^3-1,1-dimethylallyl)$(PF_3)_3$ to M(h^3-1,2-dimethylallyl)$(PF_3)_3$ (M = Co, Rh) [10—12].

The thermal stability of the very air sensitive yellow crystalline complex CoH(2,3-dimethyl-1,3-butadiene)$(PPh_3)_2$ (I) (dec. > 70°C) obtained by Rinze [7] probably reflects both the steric effects of the bulky PPh_3 ligands and the presence of two methyl substituents on the diene which inhibit the usual rapid insertion reaction leading to an h^3-allyl complex.

Previously we have shown how small fluorophosphine ligands can readily induce reactivity between two groups attached to the same transition metal [13—15], e.g.:

$$[Pd(h^3\text{-}C_3H_5)Cl]_2 \xrightarrow{PF_2R} Pd(RPF_2)_4 + C_3H_5Cl$$

$$RuH(CO_2Me)(PPh_3)_3 \xrightarrow{PF_2R} Ru(PF_2R)_5 + MeCO_2H$$

$$RhHCl(h^3\text{-}C_3H_5)(PF_3)_3 \longrightarrow [RhCl(PF_3)_2]_2 + C_3H_6$$

We now report that treatment of I with the small fluorophosphine PF_3 at room temperature leads to PPh_3 displacement and the lowering of steric constraints induces rapid diene insertion into the cobalt—hydrogen bond to form high yields (>90%) of the orange, volatile, solid Co(h^3-1,1-dimethyl-2-methylallyl)$(PF_3)_3$, (II). (Spectroscopic evidence for Co(h^3-C_6H_{11})$(PF_3)_2(PPh_3)$ in the involatile residues was also obtained).

Complex II has previously been reported to be formed in only 10% yield in a mixture with inseparable organic impurities from the reaction between $CoH(PF_3)_4$ and 2,3-dimethyl-1,3-butadiene and was identified solely by its mass spectrum [16].

The ^{19}F NMR spectrum of I shows the complex pattern expected for the X part of an $[X_3A]_3$ spin system (X = F, A = P) and is similar to that observed in related Co(h^3-allylic)$(PF_3)_3$ systems [12] ($\phi_F = 12.8$ ppm (rel. CCl_3F); $[J(PF) + 2J(PF')] = 1269$ Hz).

The use of small ligands like PF_3 or CO has been reported very recently by Tulip and Ibers [17] to liberate β-methylstyrene from the stable h^3-allyl-hydride iridium(III) complex, IrClH(h^3-C_3H_4(1-Ph))$(PPh_3)_2$, whereas no reaction occurred using the larger PPh_3 ligand. These authors favour an explanation involving preferential stabilisation of the resulting Ir^I complex, IrCl(L)$(PPh_3)_2$, (L = CO,PF_3), by the more π-acid ligands but differing steric factors of these ligands might also be responsible for the easier formation of the likely iridium(III) intermediate IrClH(h^1-C_3H_4(1-Ph))(L)$(PPh_3)_2$, (L = CO, PF_3), prior to the reductive-elimination step.

The importance of steric effects is notable in the isolation of stable allylmetal hydrides containing bulky ligands e.g. MoH(h^3-C_3H_5)(dppe)$_2$ [18] and IrClH(h^3-C_3H_4(1-Ph))L_2 (L = PPh_3, $AsPh_3$, $SbPh_3$, P(p-tolyl)$_3$ and As(p-tolyl)$_3$) [17], and that replacement of the phenyl group in the latter series with smaller substituents on the allyl ligand led to much less thermally stable complexes.

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