Rhodium Complexes with the Tripodal Triphosphine MeC(CH_2PPh_2)$_3$ as Highly Reactive Systems for Hydrogenation and Hydroformylation of Alkenes

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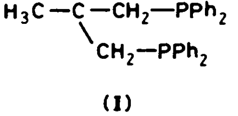
The (triphos)Rh fragment [triphos = MeC(CH_2PPh_2)$_3$] is able to form strong bonds with several reactive species (hydride, alkyl, carbon monoxide, alkenes), some reactions of which are highly specific; preliminary results on the hydrogenation and hydroformylation of hex-1-ene using (triphos)RhH(C_2H_4) as catalyst precursor are discussed.

The geometry of the tripodal polyphosphine MeC(CH_2PPh_2)$_3$, triphos (**I**) is such that it can occupy three facial sites on a co-ordination polyhedron. In this way the ligand provides rigorous control on both the stereochemistry and reactivity of the resulting complexes,† which, consequently offer a wider range of catalyst selectivity and stereospecificity than can be obtained with comparable complexes of monophosphines.[1]

The rhodium hydride (triphos)RhH(C_2H_4)[2] (**1**) exhibits a surprisingly rich chemistry.‡ Stirring a tetrahydrofuran (THF) solution of (**1**) under a C_2H_4 atmosphere at room temperature causes migration of the hydride ligand to a carbon atom of η^2-ethylene. As a result, the (ethyl)ethylene complex (triphos)Rh(C_2H_5)(C_2H_4) (**2**) is obtained as pale yellow crystals. The reaction is reversible, *i.e.* (**1**) is quantitatively reformed on stirring a THF solution of (**2**) under nitrogen (β-elimination). Alternatively, (**2**) can be synthesized by the reaction of the chloride derivative (triphos)RhCl(C_2H_4)[2] (**3**) in THF with EtMgBr under C_2H_4 (Scheme 1). Hydride migration on η^2-C_2H_4 in (**1**) is promoted by CO (1 atm, room temperature) to give yellow crystals of the (acyl)carbonyl complex (triphos)Rh(CO)(COC_2H_5) (**4**) (route **a**). Compound (**4**) can be prepared by treatment of the (ethyl)(ethylene) complex (**2**) in THF with an excess of CO (route **b**). Although the two reactions proceed by different initial steps (hydride migration to η^2-C_2H_4 or ethylene displacement by CO), it is reasonable



(**I**)

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† All the remaining sites are *trans* to a phosphorus atom. Therefore, as phosphorus donors lie high in the *trans* influence series, triphos complexes should be highly reactive.

‡ All compounds were isolated as crystalline solids which gave satisfactory elemental analyses. *Selected spectroscopic data:* (**2**) $^{31}P\{^1H\}$ n.m.r. (121.4 MHz, positive shifts in p.p.m. to high frequency of external H_3PO_4 85%) AB_2X system [THF–C_6D_6 (2 : 1), 294 K], δ 8.45 [P_A, $J(P_AP_B)$ 32.0, $J(P_ARh)$ 74.2 Hz], 8.90 [P_B, $J(P_B$-$Rh)$ 131.2 Hz]; ^1H n.m.r. (300 MHz, [$^2H_8$]THF, 294 K) δ 3.29 (C_2H_4, m, 2H), 2.77 (C_2H_4, m, 2H), 1.17 (CH_2Me, m, 2H), 0.40 (CH_2Me, m, 3H). (**4**) I.r. (Nujol mull), ν(CO) 1895 cm^{-1} (s), ν(COC_2H_5) 1630 cm^{-1} (s); $^{31}P\{^1H\}$ n.m.r., A_3X system [THF–C_6D_6 (2 : 1), 294 K], δ 4.51 [$J(PRh)$ 113.3 Hz]; ^1H n.m.r. ([$^2H_8$]THF, 294 K), δ 2.56 [$COCH_2Me$, q, 2H, $J(HH)$ 7.4 Hz), 0.46 ($COCH_2Me$, t, 3H].

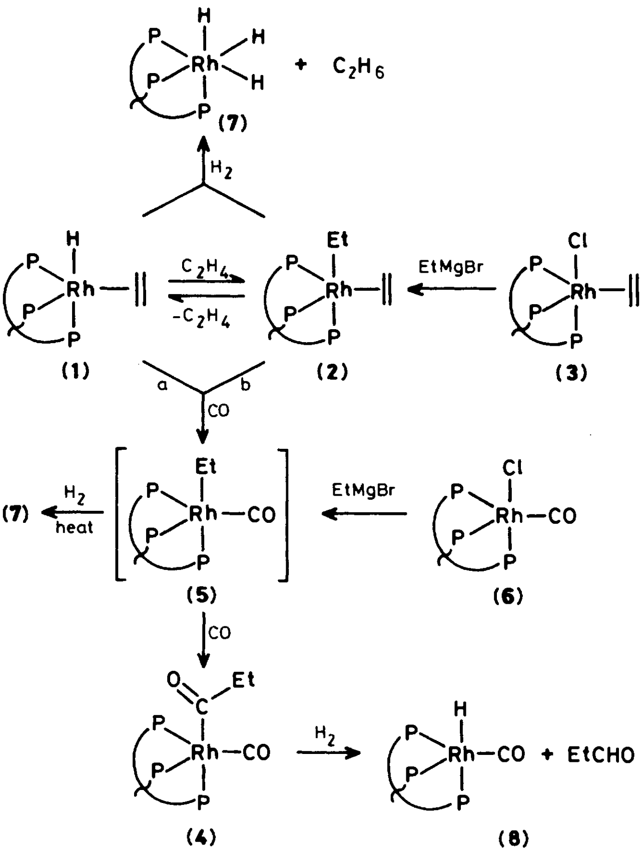
Table 1. Hydrogenation of hex-1-ene.[a]

Catalyst	H_2 pressure/ atm	Temp./ °C	Conversion[b]/ %	Product distribution/%		Remarks
				n-Hexane	Hex-2-ene	
(triphos)RhH(C_2H_4)	1	20	100	55	45	Ethane and ethylene evolved
(triphos)RhH(C_2H_4)	30	100	100	100	0	Ethane and ethylene evolved
$(PPh_3)_3$RhH(CO)	1	20	100	76	24	

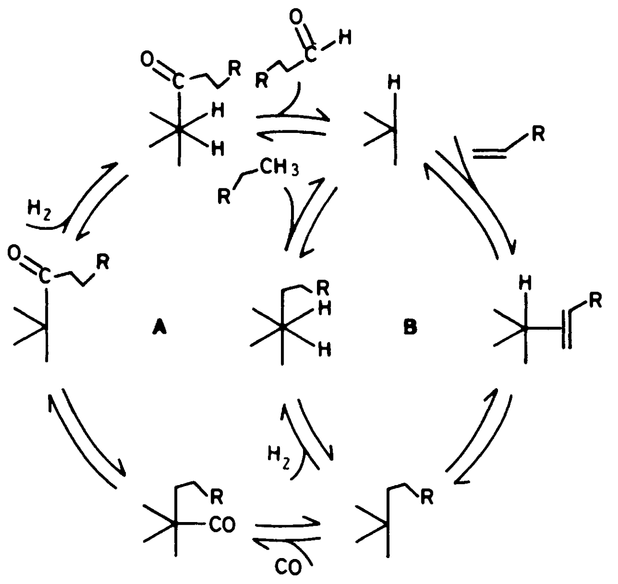
Hydroformylation of hex-1-ene.[a]

Catalyst	CO/H_2 pressure[c]/ atm	Temp./ °C	Conversion[d]/ %	Product C-7 aldehyde iso/n	Remarks
(triphos)RhH(C_2H_4)	1	20	0	—	Propionaldehyde and ethylene evolved
(triphos)RhH(C_2H_4)	30	100	66	20/80	Propionaldehyde and ethylene evolved
$(PPh_3)_3$RhH(CO)	1	20	28	23/77	
$(PPh_3)_3$RhH(CO)	30	100	95	32/68	

[a] *Reaction conditions:* hex-1-ene (2.0 mmol), THF (25 ml), catalyst (0.2 mmol), 3 h. [b] G.c. analysis. Liquid phase: OV-101, 40 m, → conversion of hex-1-ene, products n-hexane and hex-2-ene. Gas phase: Poropack Q, 1.5 m, → ethane and ethylene. [c] CO:H_2 1:1 (mole ratio). [d] G.c. analysis. Liquid phase: OV-17, 1.5 m, → iso/n of aldehyde. Gas phase: Poropack Q, 1.5 m, → ethylene.



Scheme 1



Scheme 2

to conclude that both routes leading to (**4**) share a common intermediate, (triphos)Rh(C_2H_5)(CO) (**5**). This complex appears to be very unstable, especially with respect to ethyl ligand migration to the carbon atom of the co-ordinated carbonyl. It is likely that a transient four-co-ordinate species of formula (triphos)Rh(COC_2H_5) is formed,[3] which is stabilized by the addition of a second CO molecule. The (chloride)carbonyl (triphos)RhCl(CO)[4] (**6**) in THF reacts with EtMgBr. When CO is bubbled into the reaction mixture, (**4**) is formed quantitatively. Both the (ethyl)(ethylene) complex (**2**) and the (acyl)carbonyl (**4**) undergo hydrogenolysis under standard conditions to give the trihydride (triphos)RhH_3[5] (**7**) and the (hydride)carbonyl (triphos)RhH(CO)[5] (**8**) together with C_2H_6 and C_2H_5CHO, respectively.

Having considered the various types of reactions that can occur at the (triphos)Rh fragment, it is evident that the latter has promise in catalytic processes involving CO, alkenes, and H_2. Indeed, we have found that a catalytic system involving (**1**) as precursor is effective in the isomerization, hydrogenation, and hydroformylation of hex-1-ene (Table 1). In good agreement with our experimental findings (see Scheme 1), the termination products of the two catalytic cycles are the trihydride (**7**) (hydrogenation) and the (hydride)carbonyl (**8**) (hydroformylation). At 30 atm of H_2 the isomerization activity of (**1**) is completely depressed and hydrogenation proceeds quantitatively. Interestingly, the conversion of hex-1-ene into the C_7 aldehyde occurs with twice the normal : iso ratio of the widely used catalyst $(PPh_3)_3RhH(CO)$.[6,7] The increase in selectivity, accompanied by a decrease in activity, is certainly a consequence of the large steric bulk of triphos[7] which has a low propensity for bonding modes other than the tridentate one.[8] It is an important point that catalytic cycles involving sequences of 16- and 18-electron species without phosphine dissociation (Scheme 2, **A**, hydroformylation; **B**, hydrogenation) account for the chemistry of the (triphos)RhH fragment (the precycles relating to hydrogenation and hydroformylation of C_2H_4 have been omitted for clarity).

Kinetic studies are presently under way to determine the rate-determining step in the hydroformylation reaction. In the light of previous studies of phosphine-substituted rhodium catalysts,[7] it seems reasonable that the slowest step in the catalytic cycle is the oxidative addition of hydrogen to the 16-electron four-co-ordinate acyl intermediate. In this respect, it is noteworthy that the reaction of (**6**) in THF with EtMgBr, followed by addition of H_2 gives the trihydride (**7**) only, at reflux temperature.

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