Rhodium Complexes with the Tripodal Triphosphine MeC(CH₂PPh₂)₃ as Highly Reactive Systems for Hydrogenation and Hydroformylation of Alkenes

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The (triphos)Rh fragment [triphos = MeC(CH₂PPh₂)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(C₂H₄) 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 C₂H₄ (Scheme 1). Hydride migration on η^2 -C₂H₄ in (1) is promoted by CO (1 atm, room temperature) to give yellow crystals of the (acyl)carbonyl complex (triphos)Rh(CO)(COC₂H₅) (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 -C₂H₄ or ethylene displacement by CO), it is reasonable

$$H_{3}C - C - CH_{2} - PPh_{2}$$

$$H_{3}C - C - CH_{2} - PPh_{2}$$

$$CH_{2} - PPh_{2}$$

$$(1)$$

[†] 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) ³¹P{¹H} n.m.r. (121.4 MHz, positive shifts in p.p.m. to high frequency of external H₃PO₄ 85%) AB₂X system [THF-C₆D₆ (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, [²H₈]THF, 294 K) δ 3.29 (C₂H₄, m, 2H), 2.77 (C₂H₄, m, 2H), 1.17 (CH₂Me, m, 2H), 0.40 (CH₂Me, m, 3H). (4) I.r. (Nujol mull), v(CO) 1895 cm⁻¹ (s), v(COC₂H₅) 1630 cm⁻¹ (s); ³¹P{¹H</sup> n.m.r., A₃X system [THF-C₆D₆ (2:1), 294 K], δ 2.56 [COCH₂Me, q, 2H, J(HH) 7.4 Hz], 0.46 (COCH₂Me, t, 3H].

	H ₂ pressure/ atm	Temp./ °C	Conversion ^{b/} %	Product distribution/%			
Catalyst				n-Hexane	Hex-2-ene	Remarks	
(triphos)RhH(C ₂ H ₄)	1	20	100	55	45	Ethane and ethylene evolved	
(triphos)RhH(C ₂ H 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 ₂ H ₄)	1	20	0	—		Propionaldehyde and ethylene evolved	
(triphos)RhH(C ₂ H ₄)	30	100	66	20/80		Propionaldehyde and ethylene evolved	
(PPh ₃) ₃ RhH(CO) (PPh ₃) ₃ RhH(CO)	1 30	20 100	28 95	23 32	3/77 2/68		

Table 1. Hydrogenation of hex-1-ene.^a

^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, \rightarrow conversion of hex-1-ene, products n-hexane and hex-2-ene. Gas phase: Poropack Q, 1.5 m, \rightarrow ethane and ethylene. ^c CO:H₂ 1:1 (mole ratio). ^d G.c. analysis. Liquid phase: OV-17, 1.5 m, \rightarrow iso/n of aldehyde. Gas phase: Poropack Q, 1.5 m, \rightarrow ethylene.



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)RhH₃⁵ (7) and the (hydride)carbonyl (triphos)RhH(CO)⁵ (8) together with C₂H₆ and C₂H₅CHO, 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 H₂. 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 H₂ the isomerization activity of (1) is completely depressed and hydrogenation proceeds quantitatively. Interestingly, the conversion of hex-1-ene into the C₇ aldehyde occurs with twice the normal : iso ratio of the widely used catalyst (PPh₃)₃RhH(CO).^{6,7} The increase in selectivity, accompanied by a decrease in activity, is certainly a consequence of the large steric bulk of triphos⁷ 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 C₂H₄ 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

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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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