Oligomerisation of Butadiene by Use of Nickel– or Palladium–Hydride Complexes as Catalyst Precursors, and Related Studies

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It is shown that the ability of some hydrides, *trans*-$\mathrm{MHX(PR_3)_2}$, where M = Ni or Pd, to act as catalysts for butadiene oligomerisation depends markedly both on the nature of the substituent X and on the solvent. The cationic hydrides $\mathrm{[PdH(PR_3)(dppe)]^+PF_6^-}$, where R = cyclohexyl or $\mathrm{Pr^i}$ have been prepared and their reactions with butadiene explored.

THERMALLY stable hydrides of nickel and palladium of the type *trans*-$\mathrm{(R_3P)_2MHX}$ are formed when R is a bulky group such as isopropyl ($\mathrm{Pr^i}$) or cyclohexyl (cy).[1] A series of these compounds can be made where X = Cl, Br, or $\mathrm{BH_4}$. It is clear that nickel– and palladium–hydride species occur as members of catalytic cycles which cause the oligomerisation of butadiene, especially when the products involve hydrogen transfers.[2] Therefore it seemed of interest to study the relative effectiveness of a series of the above hydrides as catalysts. It was hoped that some of the factors important in the choice of a good catalyst precursor might become apparent. The oligomerisation of butadiene was chosen as the basic reaction since much is already known about this reaction.[3,4]

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[1] M. L. H. Green, H. Munakata, and T. Saito, *J. Chem. Soc.* (*A*), 1971, 469.

[2] G. Wilke, B. Bogdanovic, P. Heimbach, M. Kroner, and E. W. Muller, *Adv. Chem. Ser.*, 1962, **34**, 137; W. Brenner, P. Heimbach, and G. Wilke, *Annalen*, 1969, **727**, 194.

[3] T. Kashiwagi, N. Yasuda, T. Ucki, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *Bull. Chem. Soc. Japan*, 1968, **41**, 296.

[4] G. Wilke, *Angew. Chem.*, 1966, **78**, 157.

Chemical Studies.—Treatment of the hydrides *trans*-PdHCl(PR$_3$)$_2$, where R = Pr^i or cy, with 1,2-bis-(diphenylphosphino)ethane (dppe) gives the cationic hydrides [PdH(PR$_3$)(dppe)]$^+$ in good yields.[5] They were isolated as the hexafluorophosphate salts and the evidence for their formulation is given in Table 1 and is not further discussed.

TABLE 1

Compound	Colour	Analytical data (%) Found (Calc.) C	H	ν(M–H)[a] cm^{-1}	^{1}H N.m.r.[b]
[PdH(cy$_3$P)(dppe)]$^+$PF$^-_6$	White	56·6 (56·7)	6·9 (6·3)	1895m	2·0—2·8, *20*, *c*, Ph$_4$; 7·2—7·9, *4*, *c*, (CH$_2$)$_2$; 7·8—9·1, *ca. 33*, *c*, cy$_3$; 15·52, *1*, *8*($J_{P,H}$ 196) (*trans*), $J_{P,H}$ 14·8 or 5·6 (*cis*), Pd–H,[c] CH$_2$Cl$_2$
[PdH(PPr$^i_3$)(dppe)]$^+$PF$_6^-$	Pale yellow	51·6 (52·2)	5·7 (5·0)[d]	1959m	1·9—2·8, *20*, *c*, Ph$_4$; 6·8—7·4, *4*, *c*, (CH$_2$)$_2$; 7·4—8·0, *3*, *c*, (CH)$_3$; 8·65—9·0, *18*, *c*, Me$_6$; 15·31, *1*, *4*, $J_{P,H}$ 196 (*trans*), $J_{P,H}$ 19·8 (*cis*), Pd–H. [^{2}H$_6$]Me$_2$CO
[NiH(dppe)$_2$]$^+$PF$_6^-$	Orange			1930w(br)	2·2—3·4, *40*, *c*, Ph$_8$; 7·3—7·9, *8*, *c*, (CH$_2$)$_4$; 23·0, *1*, *5* ($J_{P,H}$ 5·0) Ni–*H*. [^{2}H$_6$]Me$_2$CO
C$_8$H$_{12}$[NiBr(PPr$^i_3$)$_2$]$_2$	Yellow-brown	44·0 (44·4)	7·6 (7·7)		
C$_8$H$_{12}$[NiBr(dppe)]$_2$,C$_6$H$_6$	Bright red	65·2 (64·5)	5·6 (5·4)		
[C$_8$H$_{12}$\{Ni(dppe)\}$_2$]$^{2+}$[PF$_6^-$]$_2$	Yellow, m.p. 148—151 °C	54·1 (54·8)	4·3 (4·6)[e]		
C$_8$H$_{12}$[NiBr(dppe)]$_2$,CHCl$_3$	Orange-red	51·7 (52·4)	4·5 (4·4)		

[a] In mulls. [b] Given as: chemical shift (τ), *relative intensity*, *multiplicity* (*J* in Hz), assignment; *etc.* [c] One P of the dppe group occupies the *trans*-position, the two *cis*-phosphorus atoms are non-equivalent. [d] Λ in CH$_2$Cl$_2$ (10^{-3}M) = 60 Ω^{-1} cm^2. [e] Λ in MeNO$_2$ (10^{-3}M) = 92 Ω^{-1} cm^2.

TABLE 2

Comparison of catalytic reactivities of nickel and palladium hydride complexes in butadiene oligomerisation

Hydride complex (*trans*)/g (mmol)	Butadiene/g	Other reactants	Reaction *t*/°C	Time/h	Total product/g	Conversion (%)	Reaction products[a]	Selectivity (%)
NiHCl(PPr$^i_3$)$_2$ 0·234 (0·563)	5·9		100	6		0		
NiHCl(PPr$^i_3$)$_2$ 0·141 (0·339)	6·0	MeOH 1 ml	100	6		0		
NiH(BH$_4$)(Pcy$_3$)$_2$ 0·228 (0·360)	5·34		60	6	0·71	13	*cis*-1,2-Divinylcyclobutane[b,c,d]	30
							4-Vinylcyclohex-1-ene[c,d]	20
							cis,*cis*-Cyclo-octa-1,5-diene[c,d]	29
							trans,*trans*,*trans*-Cyclododeca-1,5,9-triene[c,b]	18
NiH(BH$_4$)(Pcy$_3$)$_2$ 0·201 (0·317)	5·96	MeOH 1 ml	60	6	4·43	67	Octa-1,3,7-triene[c,d]	89
PdHCl(PPr$^i_3$)$_2$ 0·143 (0·309)	5·58		100	6·20	0·13	2·3	4-Vinylcyclohex-1-ene[b]	
PdHCl(PPr$^i_3$)$_2$ 0·141 (0·305)	6·53	MeOH 1 ml	60	6	4·4	51	Octa-1,3,7-triene[c,d]	37
							3-Methoxyocta-1,7-diene[c,d]	18
							1-Methoxyocta-2,7-diene[c,d]	46
PdH(BH$_4$)(Pcy$_3$)$_2$ 0·197 (0·288)	5·28		100	6·20	0·63	12	4-Vinylcyclohex-1-ene Butadiene dimers	
PdH(BH$_4$)(Pcy$_3$)$_2$ 0·202 (0·296)	6·22	MeOH 1 ml	60	1	6·7	97	Octa-1,3,7-triene	67
							3-Methoxyocta-1,7-diene[c,d]	4
							1-Methoxyocta-2,7-diene[c,d]	27
[PdH(Pcy$_3$)(dppe)]$^+$PF$_6^-$ 0·100 (0·107)	6·48		60	6				
[PdH(Pcy$_3$)(dppe)]$^+$PF$_6^-$ 0·100 (0·107)	6·25	MeOH 1 ml	60	6	6·26	72	Octa-1,3,7-triene[c,d]	50
							3-Methoxyocta-1,7-diene[c,d]	7
							1-Methoxyocta-2,7-diene[c,d]	38

[a] G.l.c. analysis. [b] Comparison of the retention time with an authentic sample. [c] I.r. spectrum of the isolated sample was examined. [d] ^{1}H N.m.r. spectrum of the isolated sample was examined.

The cationic hydrides, and some neutral hydrides *trans*-MHX(PR$_3$)$_2$, were treated with butadiene. The reactions and experimental conditions are given in Table 2. In order to facilitate comparison of any catalytic activity, closely similar conditions were used for each reaction. Some of the hydrides caused extensive oligomerisation of butadiene and this was first apparent from the decrease in the volume of the reaction mixture. The reaction products were distilled and the distillate was analysed by g.l.c. The separated products were identified by comparison of their retention times with those of authentic samples. Also, most of the major products were isolated and their ^{1}H n.m.r. and i.r. spectra were determined. Examination of the involatile reaction products yielded in most cases intractable materials. However, white crystals of the compound cy$_3$PBH$_3$ were

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[5] M. L. H. Green and H. Munakata, *Chem. Comm.*, 1971, 549.

isolated from the reaction between *trans*-$NiHBH_4(Pcy_3)_2$ and butadiene. The dichloride *trans*-$PdCl_2(PPr^i_3)_2$ was isolated from the reaction between *trans*-$PdHCl(PPr^i_3)_3$ and butadiene in methanol.

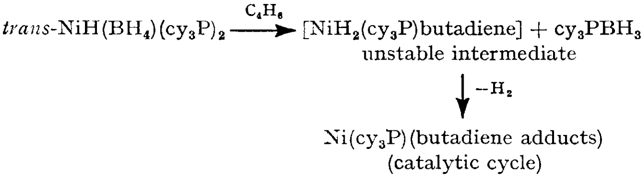
The nature and yields of the volatile products are given in Table 2.

Treatment of the methylnickel derivative *trans*-$NiMeBr(PPr^i_3)_2$ with liquid butadiene in a sealed tube at room temperature caused a rapid reaction. The volatile products showed no evidence for butadiene oligomers; however, from the involatile residue were isolated yellow-brown crystals. Crystal-structure determination and the data in Table 1 shows them to be the dinuclear compound μ-(octa-1,7-di-π-enyl)$[NiBr(PPr^i_3)_2]_2$. Treatment of this compound with 1,2-bis(diphenylphosphino)ethane gave brick-red crystals which the crystal-structure determination and data in Table 1 show to be the dimer μ-(octa-1,7-di-π-enyl)$[NiBr(dppe)]_2$, which crystallises from chloroform with one molecule of crystallisation. The crystal structures are described elsewhere[6] and the preparative details and other data are given here in the Experimental section and in Table 1.

DISCUSSION

Table 2 shows that the different hydrides vary markedly in their ability to act as catalyst precursors for butadiene oligomerisation. However, where activity was observed then the identity and relative yields of the oligomers correspond closely to those found with many other nickel or palladium systems. It seems reasonable to assume that where oligomerisations with a given metal form similar products there is present in the reaction mixture a similar series of compounds and intermediates which comprise the catalytic cycle. We therefore assume that, for example, butadiene oligomerisation catalysed by *trans*-$NiH(BH_4)(Pcy_3)_2$ proceeds *via* compounds of the type $Nicy_3P$ (butadiene adducts), as suggested by Wilke.[4]

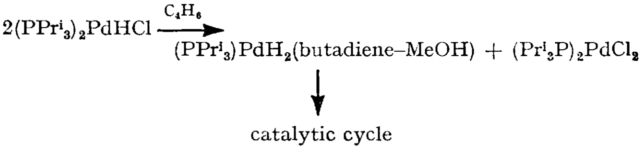
It is observed that the compounds *trans*-$NiHX(cy_3)P_2$ where X = BH_4 or Cl, differ markedly in their ability to oligomerise butadiene, the chloro-derivative being inactive. The very active borohydrido-analogue presumably gains entry to the catalytic system, represented as $Nicy_3P$(butadiene adducts), by elimination of cy_3PBH_3, as indicated in Scheme 1. This shows that one mole of tricyclohexylphosphine is effectively removed from competition on the nickel site by formation of the stable cy_3PBH_3 complex and also that a dihydrido-nickel species is formed. Clearly such possibilities are not available for *trans*-$NiHCl(cy_3P)_2$ and the chloride therefore effectively blocks entry to the catalytic cycle.



$$\begin{tikzcd} trans\text{-}NiH(BH_4)(cy_3P)_2 \arrow[r, "C_4H_6"] & {[NiH_2(cy_3P)\text{butadiene}] + cy_3PBH_3} \\ & \text{unstable intermediate} \arrow[d, "-H_2"] \\ & Ni(cy_3P)(\text{butadiene adducts}) \\ & (\text{catalytic cycle}) \end{tikzcd}$$

SCHEME 1

The observation that the chloride *trans*-$PdHCl(PPr^i_3)_2$ in methanol catalyses butadiene oligomerisation simultaneously giving crystals of the dichloride *trans*-$PdCl_2(PPr^i_3)_2$ suggests the mechanism for removal of a chloride and formation of an active palladium system may occur as a result of the overall reaction shown in Scheme 2.



$$\begin{tikzcd} 2(PPr^i_3)_2PdHCl \arrow[r, "C_4H_6"] & (PPr^i_3)PdH_2(\text{butadiene–MeOH}) + (Pr^i_3P)_2PdCl_2 \\ & \text{catalytic cycle} \arrow[from=1-2, d] \end{tikzcd}$$

SCHEME 2

EXPERIMENTAL

All preparation involving metals were carried out in the absence of oxygen. Crude commercial butadiene was purified by distillation over potassium hydroxide pellets and then molecular sieves (4A-XW). G.l.c. was carried out on a Pye–Unicam programmed chromatograph, model 14, with a flame ionisation detector and splitter assembly for sample collection. Columns were made of 10% Apiezon on Embacel. ^1H N.m.r. spectra were determined on a JEOL-CO 60 MHz instrument and were calibrated with tetramethylsilane as internal standard.

Hydridotricyclohexylphosphine-1,2-*bis*(*diphenylphosphino*)-*ethanepalladium Hexafluorophosphate*.—The hydride *trans*-$PdHCl(Pcy_3)_2$[1] in benzene (5 ml) and methanol (5 ml) was treated with 1,2-bis(diphenylphosphino)ethane (0·21 g) and, subsequently, with a saturated aqueous solution of ammonium hexafluorophosphate (2 ml). After 1 h the solvent was removed under reduced pressure and the residue was washed with water (10 ml × 3) and the solution was filtered. The filtrate was concentrated under reduced pressure (50%) and left at 0 °C for 12 h. Colourless crystals separated which were washed with aqueous acetone and dried under vacuum (yield *ca.* 8%).

The complex $[PdH(PPr^i_3)(dppe)]^+PF_6^-$ was prepared analogously starting from the hydride *trans*-$PdHCl(PPr^i_3)_2$. It was recrystallised from acetone–ether. The compound $[NiH(dppe)_2]^+PF_6^-$ was similarly prepared from *trans*-$NiCl(PPr^i_3)_2$[1] (0·62 g) and dppe (0·59 g).

Preparation of μ-*Octa*-1,7-*dienyl-bis*{*bromobis*(*tri-isopropylphosphine*)*nickel*}.—The complex *trans*-$NiMeBr(PPr^i_3)_2$[7] (0·53 g) was treated with purified butadiene and the mixture was warmed to room temperature in a sealed tube. The solution became yellow-brown, then dark green and, finally, after 1 h, orange. The butadiene was removed and the residue was recrystallised from benzene–light petroleum giving yellow-brown crystals (*ca.* 40%).

μ-*Octa*-1,7-*dienyl-bis*[*bromo*{1,2-*bis*(*diphenylphosphino*)-*ethane*}*nickel*]-*Benzene*.—The complex $C_8H_{12}[NiBr(PPr^i_3)_2]_2$ (0·2 g) in benzene (10 ml) was treated with 1,2-bis(diphenylphosphino)ethane (0·26 g). After 10 min brick-red crystals were deposited. The solution was reduced in volume under reduced pressure (50%) and light petroleum added giving further crystals. These were collected and washed with light petroleum and dried *in vacuo*

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[6] T. S. Cameron, M. L. H. Green, H. Munakata, C. K. Prout, and M. J. Smith, *J. Co-ordination Chem.*, 1972, **2**, 43.

[7] M. L. H. Green and M. J. Smith, *J. Chem. Soc.* (*A*), 1971, 639.

(*ca.* 90%). The compound was recrystallised from chloroform–light petroleum which gave the chloroform adduct, $C_8H_{12}[NiBr(dppe)]_2,CCl_3H$. The hexafluorophosphate salt $\{C_8H_{12}[Ni(dppe)]_2\}^{2+}[PF_6^-]_2$ was prepared by addition of a saturated aqueous solution of ammonium hexafluorophosphate to a solution of the compound $C_8H_{12}[NiBr(dppe)]_2$ (0·152 g) in ethanol (10 ml) and water (1 ml). The yellow precipitate was collected, washed with ethanol–water, recrystallised from methanol–acetone, and dried *in vacuo* (*ca.* 20%).

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