Reactions of Amines and Active Methylene Compounds with Buta-1,3-diene and Isoprene: Catalysis by Nickel, Cobalt, Rhodium, and Iridium Complexes

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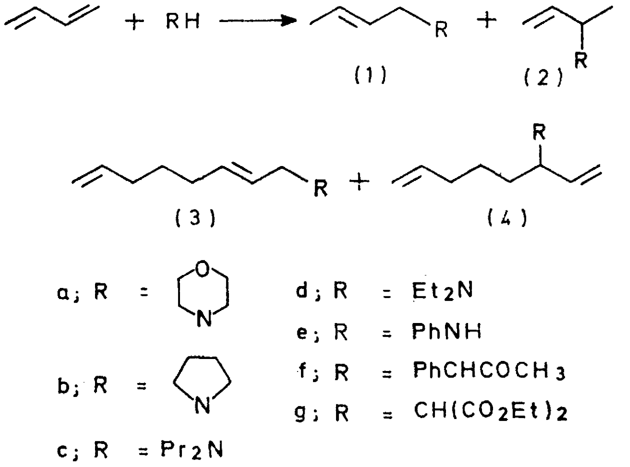
The reaction of buta-1,3-diene with morpholine and di-n-propylamine in the presence of $NiCl_2–Ph_3P–NaBH_4$, $CoCl_2–Ph_3P–NaBH_4–Al(OPr^i)_3$, and $IrCl_3$ has been shown to yield two isomeric 2 : 1 and 1 : 1 adducts with the former predominating. In the presence of $RhCl_3$ and $CoCl_2–Ph_3P–NaBH_4$ mainly 1 : 1 adducts were obtained. Lower conversions were found with morpholine and the nickel-containing system when the ligands di-isopropoxyphenylphosphine, tri-(*o*-tolyl)phosphite, and tri-(*o*-biphenylyl)phosphite were employed although exclusive 2 : 1 adduct formation was found with the last ligand. The addition of triphenyl-phosphine and -arsine to the $RhCl_3$ catalyst also favoured formation of the 2 : 1 adduct and the catalytic activity of $IrCl_3$ was markedly enhanced by small amounts of hydrochloric acid. Some reactions of diethylamine, pyrrolidine, and aniline have been studied. Reaction of benzyl methyl ketone and diethyl malonate with buta-1,3-diene catalysed by $NiCl_2–Ph_3P–NaBH_4$ yields mainly the 2 : 1 adducts. With the system $CoCl_2–Ph_3P–NaBH_4$, prior formation of the sodium salt of diethyl malonate was required for reaction with buta-1,3-diene.

REACTIONS of active hydrogen compounds with buta-1,3-diene have been reported with catalysis by both nickel and palladium complexes. Palladium(0) complexes have been shown to catalyse the reactions of butadiene with alcohols,[1,2] water,[3] amines,[1,2,4] carboxylic acids,[1,2,5] and active methylene and methyne compounds.[4,6] In previous studies we have described the reaction of amines [7] and active methylene compounds [8] with 1,3-dienes catalysed by nickel salts in the presence of di-isopropoxyphenylphosphine. Mixtures of 1 : 1 (butenyl) and 1 : 2 (octadienyl) adducts were obtained and the octadienyl adducts were favoured in reactions of butadiene and active methylene compounds. With amines and butadiene, although morpholine gave up to 65% octadienylamine, with other amines the butenyl adduct was generally favoured.

The present work was undertaken to investigate the effects of a change of metal in the catalyst system. With amines, good yields of 1 : 2 adducts have been found with nickel-, iridium-, and rhodium-containing catalysts and both the methods of reduction of the metal and added ligands have been shown to be important. Reactions of active methylene compounds with isoprene have been studied since good conversions to 1 : 2 adducts could provide intermediates for terpenoid syntheses. A catalyst system consisting of nickel chloride, triphenylphosphine, and sodium borohydride has been shown to yield a product mixture containing 64% 1 : 2 adducts which although comprising three different isomeric products, had a major head-to-tail dimer adduct amounting to 61% of the total.

RESULTS

The results for reactions of amines and active methylene compounds with buta-1,3-diene are summarised in Tables 1 and 2; spectroscopic properties of the products have been published.[7,8] The ratio of formation of 1 : 1 and 1 : 2 adducts is evidently complex but a number of generalisations can be made. Conditions can be obtained in which >80% of either of the two adducts can be formed. In general, this does not appear to be solely a function of the metal, but is also determined by the reagents required for reduction to a lower active valency state and the nature of the added ligands. Thus between 80—90% of the 1 : 2 adducts of secondary amines can be obtained with the $NiCl_2–PPh_3–NaBH_4$ and $IrCl_3$ catalyst systems. 1 : 1 Adducts can be obtained with the $CoCl_2–PPh_3–NaBH_4$ and $RhCl_3$ systems.



In the nickel- and rhodium-containing catalyst systems, changes in the composition of adducts can be made by a change in the added ligands. With $NiCl_2–NaBH_4$–organophosphorus compounds, the amount of C_8 adduct in the product is 92, 9, 70, and 100% when the ligand is Ph_3P, $PhP(Pr^iO)_2$, (O-*o*-tolyl)$_3$P, and (O-*o*-biphenylyl)$_3$P, re-

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spectively. Addition of ligands to $RhCl_3$ in ethanol can also drastically change the adduct composition. Thus 96% 1 : 1 adduct formation with morpholine is found in the absence of ligands which changes to 100, 38, and 48% when $(C_6H_{11})_3P$, PPh_3, and $AsPh_3$ are added (Rh : ligand, 1 : 1), respectively.

Distinct differences are also found with the two types of cobalt system. With $CoCl_2$–PPh_3–$NaBH_4$ (1 : 1.5 : 1) at room temperature, the total product was the 1 : 1 adduct but in these reactions the ratio of metal to amine was 2 : 5. This ratio could be reduced to 3 : 20 without a decrease in activity provided a three molar excess of triphenylphosphine to cobalt chloride was used. The alternative cobalt system $CoCl_2$–PPh_3–$NaBH_4$–$Al(OPr^i)_3$ (1 : 3 : 4 : 16) was used on the assumption that a catalytic species could be produced *in situ*; at 100°, with a cobalt chloride to morpholine ratio of 1 : 40, 59% of the 1 : 2 adduct was formed. In the absence of aluminium alkoxide, no alkylation of morpholine

TABLE 1

Reactions of amines with buta-1,3-diene

Substrate	Conditions	Amine : metal salt	Time (h)	Temp. (°C)	Yield (%)	1 : 1 adduct		1 : 2 adduct	
						(1)	(2)	(3)	(4)
Morpholine	$NiCl_2$–PPh_3–$NaBH_4$ (1 : 2 : 4)	13 : 1	6	20	95	8	8	65	19
	$NiCl_2$–PPh_3–$NaBH_4$ (1 : 2 : 1)	50 : 1	6	20	85	2	6	75	17
	$NiCl_2$–$PhP(OPr^i)_2$–$NaBH_4$ (1 : 2 : 1)	50 : 1	9	20	11	14	77	8	1
	$NiCl_2$–(O-*o*-tolyl)$_3$P–$NaBH_4$ (1 : 2 : 1)	50 : 1	8	20	44	3	27	64	6
	$NiCl_2$–(O-*o*-biphenylyl)$_3$P–$NaBH_4$ (1 : 2 : 1)	50 : 1	9	20	18			85	15
	$CoCl_2$–PPh_3–$NaBH_4$ (1 : 1.5 : 1)	5 : 2	8	20	98	10	90		
	$CoCl_2$–PPh_3–$NaBH_4$ (1 : 3 : 0.5)	20 : 3	8	20	98	9	83	7	1
	$CoCl_2$–PPh_3–$NaBH_4$–$Al(OPr^i)_3$ (1 : 3 : 4 : 16)	40 : 1	15½	100	60	12	29	54	5
	$CoCl_2$–PPh_3–$NaBH_4$–$Al(OPr^i)_3$ (1 : 3 : 4 : 16)	40 : 1	15½	75	37	8	13	71	8
	$IrCl_3$	93 : 1	16	75	76	5	14	60	21
	$IrCl_3$–HCl (1 : 1)	93 : 1	16	75	100	5	12	62	21
	$RhCl_3$	130 : 1	16	75	77	26	70	4	
	$RhCl_3$–PPh_3 (1 : 1)	130 : 1	15	75	83	12	26	57	5
	$RhCl_3$–PPh_3 (1 : 3)	130 : 1	18	75	33	29	21	45	5
	$RhCl_3$–$AsPh_3$ (1 : 1)	130 : 1	16	75	91	6	42	51	1
	$RhCl_3$–Et_3N (1 : 3)	130 : 1	16	75	98	25	73	2	
	$RhCl_3$–$AsPh_3$ (1 : 3)	130 : 1	16	75	81	2	30	66	2
	$RhCl_3$–$(C_6H_{11})_3P$ (1 : 1)	130 : 1	16	75	74	55	45		
Di-n-propylamine	$CoCl_2$–PPh_3–$NaBH_4$ (1 : 1 : 1.5)	5 : 2	11	20	66	29	55	8	8
	$CoCl_2$–PPh_3–$NaBH_4$–$Al(OPr^i)_3$ (1 : 3 : 4 : 16)	40 : 1	16	100	35	22	20	54	4
	$IrCl_3$–HCl (1 : 1)	93 : 1	16	100	100	10	22	61	7
	$RhCl_3$–Et_3N (1 : 1)	130 : 1	16	75	68	90	3	4	3
	$RhCl_3$–$AsPh_3$ (1 : 3)	130 : 1	16	75	66	9	12	79	
	$RhCl_3$	130 : 1	15	75	43	70	18	12	
	$RhCl_3$–PPh_3 (1 : 1)	130 : 1	15	75	49	10	23	67	
	$NiCl_2$–PPh_3–$NaBH_4$ (1 : 2 : 4)	13 : 1	6	20	46	5	2	84	9
Diethylamine	$CoCl_2$–PPh_3–$NaBH_4$–$Al(OPr^i)_3$ (1 : 3 : 4 : 16)	40 : 1	16	100	44	14	42	41	3
Pyrrolidine	$IrCl_3$	93 : 1	16	75	82	5	19	53	23
Piperidine	$IrCl_3$	93 : 1	16	75	100	8	13	44	35
$PhNH_2$	$IrCl_3$–HCl	93 : 1	16	100	32	24	40	23	5 *
	$RhCl_3$	130 : 1	15	75	6	19	81		
	$CoCl_2$–Ph_3P–$NaBH_4$ (1 : 1 : 1.5)	5 : 2	11	20	5		100		

* Unknown (8%).

TABLE 2

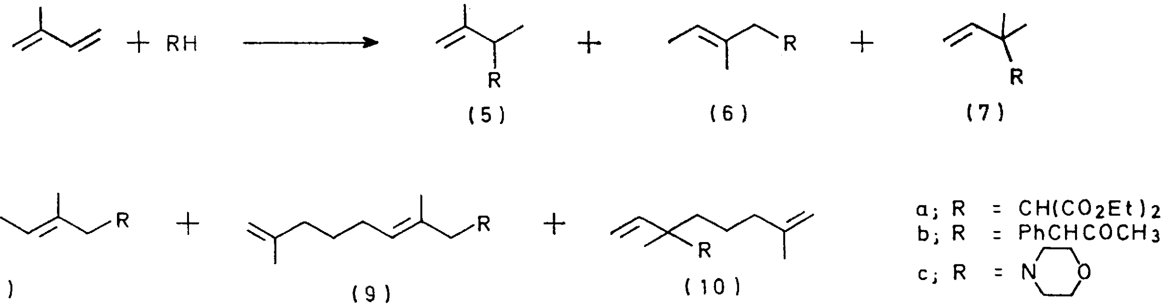
Reactions of active methylene compounds with buta-1,3-diene

Substrate	Conditions	Substrate: metal salt	Time (h)	Temp. (°C)	Yield (%)	1 : 1 adduct		1 : 2 adduct	
						(1)	(2)	(3)	(4)
$PhCH_2COCH_3$	$NiCl_2$–Ph_3P–$NaBH_4$ (1 : 2 : 1)	50 : 1	8	20	72	7	8	76	9
$CH_2(CO_2Et)_2$	$NiCl_2$–Ph_3P–$NaBH_4$ (1 : 2 : 1)	50 : 1	8	20	85	2	7	67	24
$Na^{+-}CH(CO_2Et)_2$	$CoCl_2$–Ph_3P–$NaBH_4$ (1 : 1 : 1.5)	5 : 2	12	20	55	3	12	35	34 *

* 3 : 1 Adduct (4%), 4 : 1 adduct (12%).

was found and with Co : Al ratios of 1 : 8, 1 : 16, and 1 : 24, conversions were 45, 60, and 72%.

In sharp contrast to the range of systems which can be used to catalyse reactions of amines with 1,3-dienes only the two systems $NiCl_2$–PPh_3–$NaBH_4$ and $CoCl_2$–PPh_3–$NaBH_4$ can be used for reactions of active methylene compounds and 1,3-dienes. No reactions were found between these two reagents in the presence of the iridium- or rhodium-containing catalytic systems. Even with the cobalt system only the sodium salt of diethyl malonate gave reaction to mainly the 1 : 2 adduct (Table 2). The reactivity of the $NiCl_2$–PPh_3–$NaBH_4$ system with active methylene compounds is also extremely limited and no reaction was observed between ethyl acetoacetate or acetylacetone and butadiene other than reduction of the carbonyl compounds.



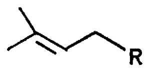
The high specificity for formation of octadienyl adducts from active hydrogen compounds and butadiene using the nickel chloride–triphenylphosphine–sodium borohydride catalyst system was also followed, to a smaller extent, in corresponding reactions with isoprene. Reaction of diethyl malonate and isoprene at 20° gave 64% reaction to produce products comprising more than 64% 1 : 2 adducts (Table 3)

TABLE 3

Reactions of active hydrogen compounds with isoprene in the presence of $NiCl_2$–Ph_3P–$NaBH_4$ [a]

Substrate (RH)	Temp. (°C)	Time (h)	Yield (%)	(5)	(6)	(7)	(8)	(9)
$PhCH_2COCH_3$ [b]	20	24	50	50	17		10	7
$CH_2(CO_2Et)_2$ [c]	20	24	64	14	17		39	10
Morpholine	20	90	98	20	12	41	17	10
Morpholine	50	22	98	30	30	23	9	8

[a] $NiCl_2$ (3.3 mmol), Ph_3P (6.6 mmol), $NaBH_4$ (13.3 mmol), EtOH (20 ml). Substrate (0.043 mol), isoprene (0.13 mol). [b] (A) (16%) also formed. [c] (10a) (15%) and (A) (5%) also formed.

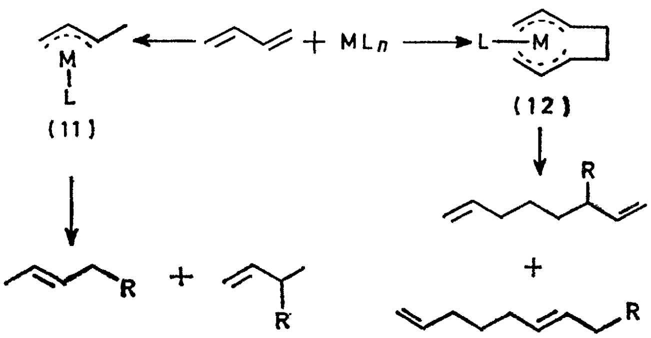


(A)

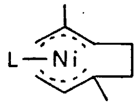
of which the main product was (8a) (61%). The structure of (8a) was assigned on the basis of its n.m.r. spectrum, τ 4.40 (1H, m, vinylic), 4.85 (1H, t, vinylic), 5.10 (2H, dd, terminal olefinic), 5.85 (4H, q, J 7 Hz, OCH_2), 6.62 and 6.82 (1H, 2 × t, J 8 Hz, methyne), 7.50 (2H, m, allylic β-ester), 7.90—8.20 (3H, m, allylic), 8.40 (3H, s, olefinic methyl), 8.76 (6H, t, J 7 Hz, methyl), 8.55—8.80 (2H, m, methylene), and 9.00 (3H, d, J 6 Hz, methyl). On the basis of the two triplets at τ 6.62 and 6.82 the compound has been assessed as a mixture of *cis*- and *trans*-isomers around the double bond.

DISCUSSION

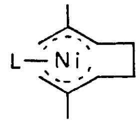
As in previous studies, it is clear 1 : 1 and 1 : 2 adducts arise through π-allylmetal (11) and bis-π-allylmetal (12) complexes [7–11] and the reactions are generally shown in the Scheme.



The selectivity for formation of the head-to-tail isoprene dimer adduct with dimethyl malonate is indicative of a more favourable formation of the bis-π-allylnickel (13) over (14) in agreement with the work of Wilke *et al.*[12]



(13)



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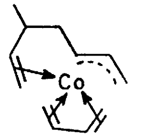

(15)

The striking feature of reactions of amines and butadiene in the presence of the NiX_2–R_3P–$NaBH_4$ catalyst system is the large amount of octadienyl adducts formed compared to that found with the nickel salt–dialkoxyphenylphosphine system previously reported.[7] Clearly, although a reduced nickel species is formed in both systems the 'ML$_n$' complexes produced

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[12] B. Barnett, B. Bussemeier, P. Heimbach, P. W. Jolly, C. Kruger, I. Tkatchenko, and G. Wilke, *Tetrahedron Letters*, **1972**, 1457.

yield different product proportions due to the differences in associated ligands. Either a hydride or hydroborate species could be involved in the reactions with the nickel salt and sodium borohydride[13] but no direct evidence has been obtained as to the nature of the catalytically active species. The large amount of C_8 adducts produced might argue against a direct involvement of a hydrido-species in reaction with butadiene since this might be anticipated to yield more C_4 adduct through the π-allylnickel intermediate. The change in product distribution with ligand must depend upon a number of factors since competitive formation of (11) and (12) will be determined to a large extent by ligand dissociation. Tolman has demonstrated that this is primarily determined by the steric bulk of the ligands.[14] Whilst this is undoubtedly important, other factors such as the electronic effect associated with the ligands will also be involved in formation of (11) and (12).

Selective formation of the C_8 adducts was also observed on reaction of butadiene with benzyl methyl ketone and diethyl malonate in presence of $NiCl_2$–PPh_3–$NaBH_4$. Again this is in sharp contrast to the results with the nickel salt–di-isopropoxyphenylphosphine catalyst system which yields substantial amounts of the C_4 adduct with benzyl methyl ketone and almost exclusive C_4 adduct with diethyl malonate.[8]

The specificity towards formation of C_4 and C_8 adducts is also demonstrated by comparison of the two cobalt-containing systems used. In the presence of $CoCl_2$–PPh_3–$NaBH_4$, reaction of butadiene and morpholine at 20° yields only C_4 adduct whilst reaction in presence of $CoCl_2$–PPh_3–$NaBH_4$–$Al(OPr^i)_3$ at 75° yields 80% of the C_8 adduct. The octadienyl adducts produced were shown to be identical to those formed in the nickel-catalysed reaction and did not have the methylheptatriene skeleton which might have been anticipated from the previous studies on butadiene dimerisation.[15,16] Predominantly 3-methylhepta-1,4,6-triene and a small amount of octa-1,3,6-triene was obtained from dimerisation of butadiene in presence of $Co(acac)_3$–Et_3Al.[15,16] The complex $CoC_{12}H_{19}$ (15), believed to be the intermediate in the cobalt catalysed oligomerisation reactions, has also been prepared and characterised from reaction of cobalt(II) chloride, sodium borohydride, and butadiene in ethanol at −30°. It is clear that (15) is not the active intermediate in the present reaction. In the presence of triphenylphosphine a different active complex must be formed in solution.

Separate comments must be made about the two different cobalt-containing systems used in the present reaction. Reactions (1)—(3) are probable in the system $CoCl_2$–PPh_3–$NaBH_4$. Hydridotris(triphenylphosphine)cobalt (16) may be the active catalyst but is unstable and has **not** been isolated.[17] A cobalt hydride with 1,2-bis(diphenylphosphino)ethane (L′) as ligand has been

$$CoCl_2 + 2\,PPh_3 \xrightarrow{EtOH} CoCl_2(PPh_3)_2 \qquad (1)$$

$$2\,CoCl_2(PPh_3)_2 + 2\,PPh_3 + 2\,NaBH_4 \longrightarrow 2\,CoCl(PPh_3)_3 + 2\,NaCl + B_2H_6 + H_2 \qquad (2)$$

$$2\,CoCl(PPh_3)_3 + 2\,NaBH_4 \xrightarrow{EtOH} 2\,\underset{(16)}{CoH(PPh_3)_3} + 2\,NaCl + B_2H_6 \qquad (3)$$

prepared by reaction of cobaltous bromide with the diphosphine and lithium aluminium hydride in tetrahydrofuran at room temperature.[17]

If (16) is the active species then the present reactions can be envisaged to proceed through the π-allyl- and bis-π-allyl-cobalt complexes analogously to the nickel-catalysed reactions. The low yield of octadienyl adducts produced in these reactions would be consistent with the presence of the hydride in the active intermediate which would favour formation of a π-allylcobalt intermediate. The best yields were also obtained with a threefold excess of ligand to cobalt which would favour formation of a $CoHL_3$ complex.

Almost stoicheiometric quantities of the system $CoCl_2$–PPh_3–$NaBH_4$ were required for reaction and formation of the active complex was required at low temperature before addition of butadiene and the amine. We were prompted to search for a more active system, preferably where a catalytic species could be produced *in situ*. Reactions between buta-1,3-diene and amines could be effected at 100° with ratios of 1 : 40 of Co : amine with the system $CoCl_2$–PPh_3–$NaBH_4$–$Al(OPr^i)_3$ (1 : 3 : 4 : 16). In the absence of aluminium alkoxide, no alkylation of morpholine was observed, but hydrocarbons were produced comprising 3-methylhepta-1,4,6-triene (10%), 4-vinylcyclohexene (38%), 1,5-cyclooctadiene (10%), and higher oligomers. Aluminium t-butoxide could also be used as an activator but no reaction was obtained if other aluminium salts such as the ethoxide, hydroxide, and acetate were used. Sodium phenoxide was also found to be unsuitable as an activating agent. Other reactions catalysed by cobalt-containing systems have been shown to require the presence of an 'activating' reagent. Thus the formation of hexadienes by reaction of butadiene and ethylene is catalysed by dichloro-[1,2-bis(diphenylphosphino)ethane]cobalt in the presence of triethylaluminium but not diethylaluminium ethoxide.[18] The reaction is catalysed by the same cobalt complex in the presence of a Grignard complex and ethanol but no reaction is observed in the absence of ethanol.[19] Hydridobis-[1,2-bis(diphenylphosphino)ethane]cobalt also catalysed reaction of butadiene and ethylene when large

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[15] G. Allegra, F. L. Giudice, G. Natta, U. Giannini, G. Fagherazzi, and H. Pino, *Chem. Comm.*, 1967, 1263.

[16] H. Bonneman, Ch. Grard, N. Kopp, and G. Wilke, I.U.P.A.C., XXIIIrd International Congress, Boston, 1971, vol. 6.

[17] F. Zingales, F. Canziani, and A. Chiesa, *Inorg. Chem.*, 1963, **2**, 1303.

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excesses of some phenols were added as co-catalysts.[20] Activation in this case was suggested to be due to formation of a co-ordinately unsaturated cobalt complex by interaction of the phosphorus atoms of the ligands and phenol. Both this form of interaction and also that between the phosphorus atoms in the complex and the electrophilic aluminium is probably the role of the co-catalyst in the present reactions. This could explain the specialist role of aluminium alkoxides, which possess both electrophilic aluminium and donor oxygen atoms, compared to other aluminium salts and also the critical nature of the added organophosphorus compound.

The most striking feature of the iridium trichloride catalysed reactions is the enhancement of reaction in the presence of hydrochloric acid. Although we have no direct information on the catalytic species it is most likely a hydridoiridium species [reactions (4) and (5)].[21,22]

$$IrCl_3,H_2O \xrightarrow{EtOH} L_3IrCl + CH_3CHO + 2HCl + H_2O \tag{4}$$

$$IrClL_3 + HCl \longrightarrow HIrCl_2L_3 \tag{5}$$

The overall reduction and oxidative addition has been exemplified by reaction (6) of tris(triethylphosphine)-iridium trichloride with ethanol in the presence of potassium hydroxide.[23] A similar reaction has been

$$IrCl_3(PEt_3)_3 \xrightarrow{EtOH-KOH} HIrCl_2(PEt_3)_3 + CH_3CHO + KCl + H_2O \tag{6}$$

observed with rhodium trichloride trihydrate in ethanol which catalyses the addition of butadiene and ethylene. This catalyst system has been shown to have an induction period.[24,25] which can be eliminated by use of a rhodium(I) compound and hydrogen chloride in methanol.[24] Acid promotion of a nickel-catalysed reaction of butadiene and amines has been noted and ascribed to formation of a nickel hydride species.[26,27]

Unlike the rhodium-catalysed reactions the addition of ligands such as triphenylphosphine completely arrested reaction, probably due to the stability of the iridium complexes formed. The stability of iridium-amine complexes produced in the reaction could also be an important criterion in controlling the efficiency of the reaction; no reaction was observed with strongly complexing amines such as n-butylamine and ammonia.

EXPERIMENTAL

General details of the separation and spectroscopic characteristics of products and the purification of reagents have been described.[7,8]

General Reaction Procedures.—$NiCl_2$–Ph_3P–$NaBH_4$ *System.* The catalyst was preformed from nickel chloride (3.3 mmol), triphenylphosphine (6.6 mmol), sodium borohydride (13.3 mmol), ethanol (20 ml), and a small amount of buta-1,3-diene (*ca.* 15.0 mmol). Initial mixing of these reagents under nitrogen atmosphere at −70° produced no observable reaction. A rise in temperature caused the yellow colour of the nickel chloride particles to disappear, and the solution gradually turned brown. On reaching room temperature, a deep red-brown solution had formed. Morpholine (0.043 mol) and butadiene (0.13 mol) were added to this catalyst solution and after 6 h at room temperature, 2N-hydrochloric acid (50 ml) was added, and the solution stirred for 30 min. A 95% conversion was realised to (1a) (8%), (2a) (8%), (3a) (65%), and (4a) (19%).

$CoCl_2$–Ph_3P–$NaBH_4$ *System.* The catalyst solution was prepared from anhydrous cobalt(II) chloride (0.02 mol), triphenylphosphine (0.02 mol), sodium borohydride (0.01 mol), and butadiene (*ca.* 0.1 mol) in ethanol (50 ml) at −70°. Morpholine (0.05 mol) and butadiene (0.15 mol) were added and the reaction mixture was warmed to room temperature whilst stirring for 8 h; the solution turned from brown to green. The solution was extracted with ether and a quantitative yield of (1a) (10%) and (2a) (90%) was obtained.

$CoCl_2$–Ph_3P–$Al(OPr^i)_3$–$NaBH_4$ *System.* A mixture of anhydrous cobalt(II) chloride (0.7 mmol), triphenylphosphine (2.1 mmol), sodium borohydride (2.8 mmol), aluminium isopropoxide (0.0112 mol), morpholine (0.025 mol), and butadiene (0.075 mol) in ethanol (6 ml) was heated for 15.5 h at 100° in a Carius tube. A 60% conversion to (1a) (12%), (2a) (29%), (3a) (54%), and (4a) (5%) was obtained.

$RhCl_3$–Ph_3As *System.* A mixture of rhodium trichloride trihydrate (0.38 mmol), triphenylarsine (0.38 mmol), morpholine (0.05 mol), and butadiene (0.15 mol) was heated in deoxygenated ethanol (10 ml) in a Carius tube for 15 h at 75°. A 90% conversion to a mixture of (1a) (6%), (2a) (42%), (3a) (51%), and (4a) (1%) was obtained.

$IrCl_3$ *System.* Iridium chloride (0.54 mmol), pyrrolidine (50 mmol), butadiene (150 mmol), and ethanol (10 ml) were heated at 75° in a Carius tube for 16 h. An 81.5% conversion to a mixture of (1b) (5%), (2b) (19%), (3b) (53%), and (4b) (23%) was obtained.

Reaction of Isoprene and Diethyl Malonate in the Presence of $NiCl_2$–Ph_3P–$NaBH_4$.—A catalyst solution was prepared from anhydrous nickel chloride (3.3 mmol), triphenylphosphine (6.6 mmol), sodium borohydride (13.3 mol), ethanol (20 ml), and a small quantity of isoprene (*ca.* 15.0 mmol) at −70°. After warming to room temperature, diethyl malonate (0.43 mol) and more isoprene (0.13 mol) were added and the reaction was stirred for 24 h at 20°. After filtration the products were separated by fractional distillation to yield a 64% conversion to (5a) (14%), (6a) (17%), (8a) (39%), (9a) (10%), (10a) (15%), and an unidentified product (5%). After removal of ethanol and diethyl malonate a fraction of b.p. 76—82° at 0.6 mmHg contained a mixture of (5a) and (6a). A mixture of (8a)—(10a) in a ratio of 1 : 3 : 1 was obtained at 140—150° and 0.5 mmHg from which the products were isolated by preparative g.l.c. (25% SE 30 at 230°).

The mixture of (5a) and (6a) had *m/e* 228 (*M*), 115, 81, 69, 67, 55, 43, 41, 39, and 29 (100%), $\nu_{max.}$ 2 950, 1 730,

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1 640, 1 460, 1 440, 1 370, 1 200, 1 030, 960, 910, and 860 cm^{-1}, τ (CCl_4) 4.00—5.20 (2H and 1H, m), 5.85 (4H and 4H, q, *J* 7 Hz), 8.70 (6H and 6H, t, *J* 7 Hz), 6.70 (1H, d, *J* 11 Hz), 6.75 (1H, d, *J* 7 Hz), 7.20—7.70 (1H and 2H, m), 8.30—8.45 (3H and 6H, m), and 8.95 (3H, d, *J* 6 Hz). Compound (8a) had *m/e* 268 (vw), 160 (41), 121 (26), 118 (23), 81 (23), 79 (33), 67 (64), 55 (36), 41 (46), 29 (100), and 27 (31%), $\nu_{max.}$ 2 950, 1 740, 1 640, 1 450, 1 370, 1 250—1 150, 1 040, 970, 910, 790, and 760 cm^{-1}. Compound (10a) had *m/e* 268 (vw), 81 (20), 79 (20), 67 (45), 55 (37), 54 (20), 53 (33), 43 (23), 41 (83), 39 (38), 29 (100), and 27 (80%), $\nu_{max.}$ 2 950, 1 730, 1 640, 1 450, 1 370, 1 260, 1 150, 1 030, 910, and 860 cm^{-1}, τ (CCl_4) 4.10—4.70 (1H, m), 4.80—5.20 (4H, m), 5.85 (4H, q, *J* 7 Hz), 6.80 (1H, s), 7.85 (2H, m), 8.35 (3H, s), 8.60 (4H, m), 8.80 (6H, t, *J* 7 Hz), and 9.00 (3H, d, *J* 7 Hz).

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