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A STUDY OF *trihapto–pentahapto* EQUILIBRIA IN HEPTADIENYL-PALLADIUM(II) COMPLEXES AND THE POSSIBLE ROLE OF SUCH COMPLEXES IN METAL COMPLEX CATALYSED 1,4-POLYMERIZATIONS OF 1,3-BUTADIENE

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SUMMARY

^{1}H and ^{13}C NMR spectroscopy and molecular weight studies of a series of hepta-2,6-dienylpalladium(II) carboxylate complexes have demonstrated the existence in solution of an equilibrium between *trihapto*-dimeric complexes with bridging carboxylates and *pentahapto*-monomeric complexes with terminal carboxylate ligands. At constant temperature, the position of equilibrium is a function of carboxylate ligand, substituents at position 6 on the heptadienyl ligand, and the solvent. The dimer $\rightleftharpoons$ monomer rearrangement is fast on the ^{1}H NMR time scale. These observations together with previously reported data concerning the reactivity of allyl and carboxylate ligands coordinated to palladium(II) are considered as model systems for the π-allylnickel carboxylate catalysed *cis*-1,4-polymerization of 1,3-butadiene. A mechanism is proposed that provides a rationalization for the majority of the factors affecting the initial rate of the nickel complex catalysed polymerization of 1,3-butadiene as reported by Dawans.

INTRODUCTION

A series of papers by Dawans *et al.*[1–6] has shown π-allylnickel carboxylate complexes to be extremely efficient homogeneous catalysts for the 1,4-polymerization of 1,3-butadiene. The authors have noted that several factors affect the observed initial rates of polymerization. For the series of complex catalysts $[(\pi\text{-allyl})Ni(O_2CR)]_2$ the initial rate of polymerization decreased in the order: $R = CF_3 > CCl_3 > CHCl_2 > CHCl_2 > CH_3$[3]. For the catalysts $[(\pi\text{-All})Ni\text{–}O_2CCF_3]_2$ the initial rate decreased in the order: All = allyl > 2-methylallyl > 1-methylallyl[1]. These catalytic systems are also sensitive to apparently subtle changes in the area of solvent effects with both the initial rate and the mode of 1,4-polymerization (*cis* or *trans*) being affected by a change in the solvent system[1]. The mechanism of these nickel catalysed polymerizations however is still not clear. We have recently shown that the reaction of the π-allylic palladium complexes (I) [$M = Pd$; $X = Cl$, Br, O_2CR ($n = 2$); Acac, Hfacac ($n = 1$)]

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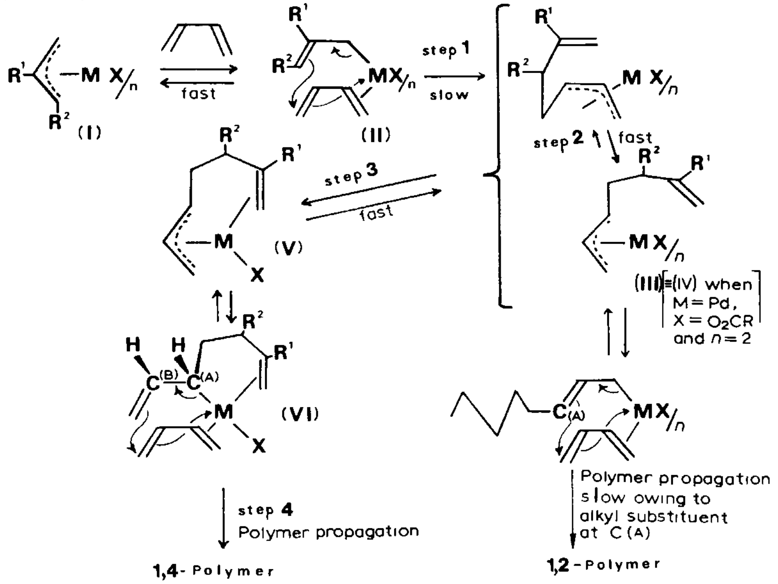
SCHEME 1

Proposed mechanism for the metal complex catalysed 1,4-polymerization of 1,3-butadiene based on structural and kinetic studies of the reactions of π-allylic palladium(II) complexes[7-11,14] and π-allylic nickel(II) carboxylates[1-6] with 1,3-butadiene.



with 1,3-butadiene proceeds via a (π-1,3-diene) σ-allyl PdX_n intermediate (II) in which an electrocyclic mechanism of C–C σ-bond formation, as shown, leads to the insertion product (III) (Scheme 1, steps 1 and 2)[7]. It is possible that a similar mechanism of carbon–carbon bond formation may be involved in the $[(\pi\text{-All})NiO_2CR]_2$-catalysed 1,4-polymerization of 1,3-butadiene via the general reaction sequences outlined in Scheme 1 ($M = Ni$; $X = O_2CR$). The extreme reactivity towards further insertion of the products obtained from the "insertion" of one molecule of 1,3-butadiene into the allyl–nickel bond makes the possibility of their isolation and the direct study of such compounds difficult[1-6]. However, by analogy with studies on similar palladium systems[7], the rate of an electrocyclic addition of 1,3-butadiene to $[(\pi\text{-All})NiO_2CCF_3]_2$ (Scheme 1, step 1) would be predicted to decrease in the order observed for the initial rates of polymerization namely All = allyl > 2-methylallyl > 1-methylallyl. The effect of the carboxylate ligand on the initial rate may be associated with the ease with which the carboxylate bridges in $[(\pi\text{-All})NiO_2CR]_2$ may be cleaved to give a species containing monodentate carboxylates. Such a property would be important in facilitating steps 3 and 4 of the proposed mechanism where three of the four possible coordination sites are required by the reactant hydrocarbons. We have previously shown that for complexes of the type $[(\pi\text{-All})PdO_2CR]_2$[8,9] and $[(EMe_2Ph)XMO_2CR]_2$[8] ($E = P, As$; $X = Cl, Br, I$; $M = Pd, Pt$) that the rates of bridge cleavage reactions decrease in the order: $CF_3 \approx CCl_3 > CHCl_2 > CH_2Cl' > CH_3$ which parallels the initial rate studies of Dawans[3] (see above). Previous studies on palladium(II) complexes have shown the *syn–anti* isomerization of (III) (step 2 of proposed scheme) to be very facile[7,10].

To further assess the validity of the proposed reaction scheme for the [(π-All)-$NiO_2CR]_2$ catalysed 1,4-polymerization of 1,3-butadiene we have investigated the effect of solvents on the solution structure of the palladium(II) complexes (IV) (R = CH_3, CH_2Cl, $CHCl_2$, CF_3; W = H, Me, Cl) Complexes (IV) may be considered as model compounds for the product derived from the initial addition of one 1,3-butadiene molecule across the allyl–nickel bond of [(π-All)$NiO_2CR]_2$ catalysts. The results of this study provide supporting evidence for step 3 of the proposed Scheme for 1,4-polymerization and also provide some insight into the role of the solvent in the overall reaction mechanism.

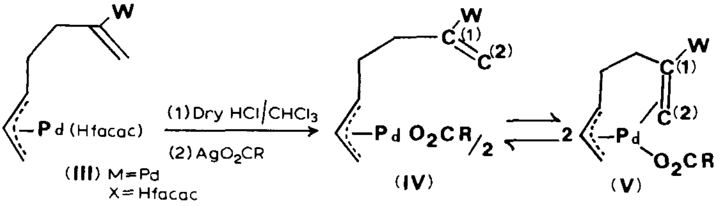
EXPERIMENTAL

Instrumentation

^1H NMR spectra were obtained using a Varian Associates A56/60D spectrometer. ^{13}C NMR spectra were obtained using a Varian Associates XL-100-15 spectrometer, operating in the Fourier Transform mode, and utilising a Varian 620*i* computer with a 16K memory. Molecular weight data were obtained using a Mechrolab 301A osmometer.

Preparation of complexes

Complexes (III) (X = Hfacac) were prepared from the appropriate π-allylic Pd(Hfacac) complex (I) and butadiene by previously reported methods[7]. Treatment of complexes (III) [X = Hfacac] with an equimolar amount of dry HCl in benzene gave quantitative conversion to the previously characterised[11] chloride-bridged complexes (III) (X = Cl) (see ref. 7 for experimental details).



Complexes (IV) (W = H, CH_3, Cl; R = CH_3, CH_2Cl, $CHCl_2$, CF_3) were prepared by reaction of complexes (III) (X = Cl) with the appropriate silver carboxylate; *e.g.* a solution of di-μ-chlorobis[π-1-*syn*-(but-3′-enyl)allyl]dipalladium(II) (0.520 g) in dichloromethane (25 ml) was treated with silver trifluoroacetate (0.520 g). The resultant mixture was shaken vigorously (15 min) and then filtered. Evaporation of the filtrate under reduced pressure followed by recrystallisation of the residue from a benzene/petroleum ether (b.p. 30–60°) mixture, yielded cream coloured prisms (0.600 g; 87%), m.p. 42–45°. (Found: C, 34.53; H, 3.63. $[C_9H_{11}F_3O_2Pd]_n$ calcd.: C, 34.37; H, 3.53%.)

^1H NMR, ^{13}C NMR, and molecular weight studies showed this material to exist in solution as a mixture of di-μ-trifluoroacetatobis[π-1-*syn*-(but-3′-enyl)allyl]dipalladium(II) and trifluoroacetato-1,2,3,6,7-*pentahapto*-heptadienylpalladium(II).

Treatment of complexes (IV) with one molar equivalent of dry HCl in benzene gave quantitative regeneration of previously characterised complexes (III) (X = Cl)[7,11].

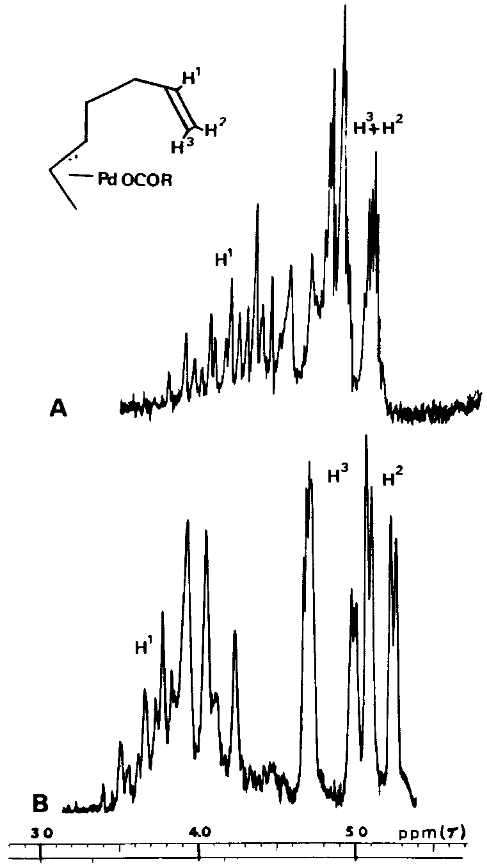
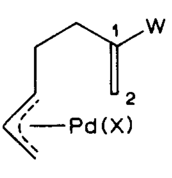


Fig. 1 ^{1}H NMR spectra (60 MHz; CDCl$_3$, 34°) of the olefinic protons of complexes (IV) A, W = H, R = CH$_3$, B, W = H, R = CF$_3$.

TABLE 1

^{13}C CHEMICAL SHIFT DATA[a] FOR C(1) AND C(2) OF SEVERAL HEPTA-2,6-DIENYLPALLADIUM(II) COMPLEXES (III) [(IV) WHEN X = O$_2$CR]

	Solvent	*W*	*X*	*δ(ppm)*	
				C(1)	*C*(2)
	CDCl$_3$	H	Cl	136.1	114.4
	C$_6$D$_6$	H	Cl	137.1	114 8
	CDCl$_3$	H	Hfacac	137.9	115.2
	CDCl$_3$	H	CH$_3$CO$_2$	136.5	114.4
	CDCl$_3$	H	CF$_3$CO$_2$	133 9	102.7
	C$_6$D$_6$	H	CF$_3$CO$_2$	135 3	116 2
	CDCl$_3$	Cl	Hfacac	141.2	113 5
	CDCl$_3$	Cl	CF$_3$CO$_2$	140 8	112 7

[a] Recorded in CDCl$_3$ and C$_6$D$_6$ solutions at 34° Shifts are quoted in ppm downfield from a TMS internal standard.

RESULTS AND DISCUSSION

Trihapto and pentahapto-hepta-2,6-dienyl complexes of palladium(II)

Complexes (IV) (W = H, CH_3, Cl; R = CH_3, CH_2Cl, $CHCl_2$, CF_3) were prepared by treatment of the previously reported[7] analogous Hfacac complexes (III) (M = Pd, X = Hfacac) with dry HCl to yield the dimeric chloride-bridged species, followed by reaction with the appropriate silver carboxylate. Analogous complexes (IV) (W = H; R = CH_3, CF_3) have been reported as the products of butadiene insertion into the allyl–palladium bonds of complexes (I) [*i.e.* (III) M = Pd; X = CH_3CO_2 (*n* = 2)][11].

The olefinic regions of the ^1H NMR spectra of complexes (IV) (W = H; R = CH_3 or CF_3), in $CDCl_3$ solution, are shown in Fig. 1 The pattern of the olefinic region of the acetate complex (IV) (W = H; R = CH_3) is typical of the ABC portion of an $ABCX_2$ pattern and is identical to that observed for the analogous complexes (III) (W = H; X = Hfacac, Cl)[7] (Fig. 1A). The olefinic region of the spectrum of (IV) (W = H; R = CF_3) however, appears as the AGM portion of an $AGMX_2$ pattern (Fig. 1B), and is highly reminiscent of the ^1H NMR spectrum of complex (VII) containing a coordinated vinyl olefin[12]. In C_6D_6 solution however the olefinic resonances of (IV) (W = H, R = CF_3) revert to an ABC pattern analogous to that of (IV) (W = H; R = CH_3). The vinylidene proton resonances of complex (IV) (W = Cl; R = CF_3) in $CDCl_3$ solution are unchanged from those in the analogous Hfacac complex. The vinylidene proton resonances of (IV) (W = H; R = CH_2Cl and $CHCl_2$) in $CDCl_3$ solution are intermediate in pattern and chemical shift to those where R = CH_3 and CF_3.

The ^{13}C NMR chemical shifts for the olefinic carbon atoms of complexes (IV) (W = H, Cl; R = CH_3, CF_3) and complexes (III) (W = H; X = Hfacac, Cl) in $CDCl_3$ and C_6D_6 solution are presented in Table 1. The resonances of C(1) and C(2) for complex (IV) (W = H; R = CF_3) in $CDCl_3$ show an upfield shift compared to the values for the same complex in C_6D_6, and the values for C(1) and C(2) in complexes (IV) (W = H; R = CH_3) and (III) (W = H; X = Cl, Hfacac) in $CDCl_3$ or C_6D_6. The upfield shift, which is more pronounced for C(2) than C(1), is compatible with a coordinated olefinic function[13]. The values of $\delta(^{13}C)$ for C(1) and C(2) for complex (IV) (W = Cl; R = CF_3) are virtually identical to those of its "Hfacac analogue" suggesting that in $CDCl_3$ at 34° the olefin in this complex is not coordinated to the Pd.

TABLE 2

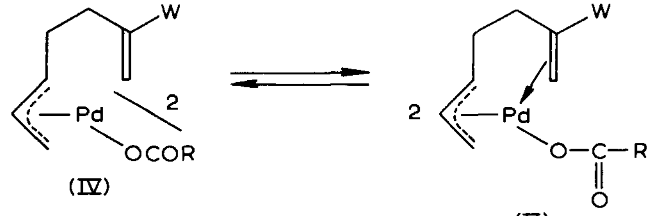
MOLECULAR WEIGHT DATA OF COMPLEXES (IV)[a]

W	*R*	*Calcd for monomer*	*Calcd. for dimer*	*Observed*	
		(V)	*(IV)*	*$CHCl_3$*	*C_6H_6*
H	CH_3	260	520	505	
H	CH_2Cl	295	590	464	
H	$CHCl_2$	329.5	659	470	621
H	CF_3	314.5	629	399	604
Me	CF_3	328	656	436	619
Cl	CF_3	349	698	606	703

[a] Determined in $CHCl_3$ and C_6H_6 at 37° at a concentration of 0.054 g-atoms of Pd per litre (*i.e.* 0.027 *M* if dimeric in solution).

Molecular weight studies of complexes (IV) (W=H, CH_3, Cl; R=CF_3, $CHCl_2$, CH_2Cl, CH_3) in $CHCl_3$ and C_6H_6 solution at 37° yielded the results shown in Table 2. For R=CF_3, W=H the observed value is close to that expected for a monomeric species whilst in C_6H_6 the observed value is closer to that expected for the dimer molecule (IV).

The above results only seem compatible with a monomer–dimer equilibrium in solution for complex (IV) as depicted below*.



(IV) (V)

The position of the equilibrium is dependent on: (*i*) the substituent (W) in that this substituent affects the coordinative ability of the olefinic function towards Pd^{II}; (*ii*) the nature of R, since an electronegative CF_3 group on the carboxylate ligand reduces the tendency of the carboxylate ligand to occupy two coordination sites and would also be expected to increase the electrophilicity of the Pd towards the olefinic function, thereby increasing the amount of monomer (V) relative to when R=CH_3; and (*iii*) the solvent. The role of the solvent in this system is not clear as yet, but probably reflects the increased ability of $CHCl_3$ (relative to C_6H_6) to effectively solvate and hence stabilize a monodentate carboxylate ligand. The deviation from monomeric (V) (W=H) behaviour towards the dimeric structure (IV) in $CHCl_3$ solution decreases linearly with the pK_a of the carboxylate used in the order R = CH_3 > CH_2Cl > CCl_2H > CF_3 (see Fig. 2) paralleling the ability of these carboxylate moieties to act as bridging, or chelating ligands[8]. Thus the $CF_3CO_2^-$ ligand has a considerably greater tendency to be monodentate than does the $CH_3CO_2^-$ ligand.

The PMR spectra of the equilibrium mixture of (IV) and (V) (R=CH_2Cl, $CHCl_2$ and CF_3) in $CDCl_3$ do not exhibit resonances assignable to the individual isomers even at −50° indicating that the monomer–dimer interchange is very rapid. The molecular weight studies of the (IV)$\rightleftharpoons$(V) equilibria in $CHCl_3$ solution are only slightly affected by changes in the palladium concentration. This suggests that solvation effects are a major factor in determining the equilibrium position, [*i.e.* solvation of (V) > (IV) and hence ΔS is small].

The mechanism of cis-1,4-*polymerization catalysed by π-allylnickel carboxylates*

The above and previous studies on the nature and reactivity of carboxylate and allylic ligands bonded to palladium(II) provide strong supporting evidence for an electrocyclic mechanism for the 1,4-polymerization of 1,3-butadiene catalysed by $[\pi\text{-AllNi}(O_2CR)]_2$ of the type outlined in the proposed scheme (M = Ni; X = O_2CR).

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* The tendency of dimeric μ-fluoroacetate complexes to adopt monomeric structures in solution has been previously noted for several platinum(II) complexes[16]. Complex (V) is structurally similar to a series of *pentahapto*-hepta-2,6-dienyl(ligand)palladium(II) cations recently reported by Takahashi *et al*[17].

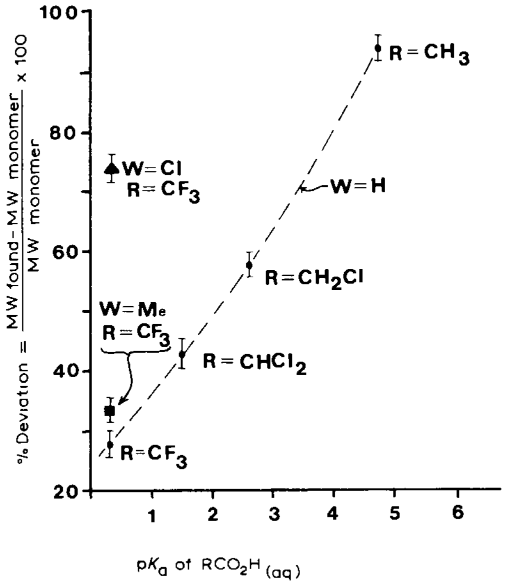

Fig 2 The % deviation from the monomeric structure (V) as a function of R and W. The data are for $CHCl_3$ solutions with a concentration of 0.054 g-atoms of Pd per litre. (See Table 2)

Essential requirements for this mechanism are (*i*) the availability of 3 coordination sites for the reactant hydrocarbons* and (*ii*) a side chain olefin attached to the π-allyl ligand such that intermediates (V) and (VI) (step 3) are readily generated**. It is remarkable that the fastest initial rates of polymerization of 1,3-butadiene reported by Dawans *et al.* were obtained using a catalyst derived from the reaction of HO_2CCF_3 with 1,6,10-dodecatrien-1,12-diylnickel(II)[6] and presumably of structure (VIII)***, *i.e.*, once a side chain olefin function is available to generate intermediate (V) polymerization is reasonably fast. Thus the probable rate determining factor in the initial rate studies with $[(\pi\text{-All})Ni(O_2CCF_3)]_2$[1] is the electrocyclic 1,4-addition of the first 1,3-butadiene across the σ-allyl–Ni system (Scheme 1, step 1) to give (III) (M = Ni; $X = O_2CCF_3$) which now contains a side chain olefin. This accounts for the observed dependence of the initial rates on the nature of the allylic ligand in the $[(\pi\text{-All})Ni(O_2CCF_3)]_2$ catalysts. The effect of the carboxylate ligand in these systems may be rationalized in terms of its ability to become monodentate, and thus provide an additional coordination site at the catalyst centre thereby facilitating the generation of intermediates such as (V) and (VI). The nature of the solvent molecules can thus have a marked effect on the number of available coordination sites, not necessarily by

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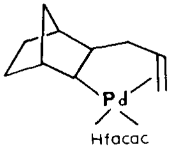
* It is noteworthy that many of the complexes of nickel and palladium which catalyse the 1,2-polymerization of butadiene (*e.g.* allylnickel bromide, $PdCl_2$) promote 1,4-polymerization in the presence of a cocatalyst which can act as a "stripping agent" in the sense that it increases the number of vacant coordination sites on the metal (*e.g.* allylnickel bromide + $AlBr_3$, $PdCl_2 + AlEt_2Cl$)[19,20]

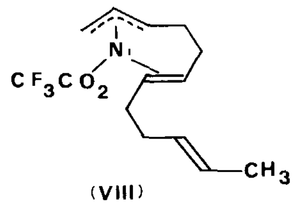
** Anchimeric control of reaction path by the side chain olefinic function in complex (IV) ($R = CH_3$) has recently been shown to occur in the carbon monoxide induced coupling of the coordinated allylic and acetate ligands[18]

*** See Note added in proof

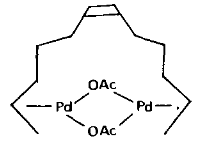
blocking a site through coordination sites, not necessarily by blocking a site through coordination to the metal, as has been suggested[1-6], but by solvation of a ligand attached to the metal such that the ligand is removed from a coordination site [*e.g.* the (IV)$\rightleftharpoons$(V) equilibrium (step 3)].



(VII) .



(VIII)



(IX)

The mechanism outlined in the scheme does not, as yet, explain the observed selectivity for *cis* or *trans* 1,4-polymerization. However it is apparent that for this mechanism the polymer stereochemistry is not determined by the orientation of the 1,3-diene coordinated to the catalyst but rather by the orientation of the σ-allylic ligand in intermediate (VI), carbon C(A) and C(B) being the position at which the olefinic function of the 1,4-polymer is generated. With the most efficient nickel catalyst (VIII) 100% *cis*-1,4-polymer is obtained suggesting that the proposed mechanism may give selectively *cis*-olefinic functions. Molecular models of intermediate(VI) favour a conformation that would lead to the *cis*-1,4-polymer. It may be that the initially formed *cis*-1,4-polymer may undergo a catalysed isomerization to the *trans*-1,4-polymer with prolonged reaction times. A mechanism similar to that outlined in Scheme 1 has been recently suggested by Nelson[14] for the $PdCl_2(PhCN)_2$ catalysed 1,4-polymerization of 2-chloro-1,3-butadiene. Unfortunately the π-allylpalladium carboxylate complexes (IV) and (V) do not readily undergo further insertion of 1,3-butadiene. Instead, as previously reported[11], the major product is (IX) containing a bridging "butadiene trimer" unit. The seven carbon fragment of (IV) [W = H] was shown by Medema and Van Helden[11] to be eliminated as a 1/1 mixture of C_7H_{10} and C_7H_{12} units by a hydrogen transfer mechanism. Thus in the palladium system further insertion of butadiene is apparently thwarted by the efficacy of hydrogen transfer[*]. The same is true for the cobalt(I) catalysed dimerization of butadiene[15].

We are currently investigating other *pentahapto*-1,2,3,6,7-heptadienyl complexes in order to further assess and refine the mechanistic proposals outlined in the scheme, and in particular step 4[**].

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[*] We have found the *pentahapto*-heptadienyl(ligand)palladium(II) cations of the type reported by Takahashi *et al*[17] (ligand = PPh_3, $AsPh_3$) are unactive catalytically towards the 1,4-polymerization of 1,3-butadiene.

[**] See second footnote p 457

ACKNOWLEDGEMENT

We are grateful to the National Research Council of Canada for financial support of this work and for the award of a scholarship to R.P.H.

NOTE ADDED IN PROOF

In the case of nickel the equilibrium between a *trihapto*-dimer and *pentahapto*-monomer may favour the dimer more so than in the case of palladium However, monomers such as (VIII) should be readily accessible

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