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Preliminary communication

Insertion of 1,2-dienes into π-homoallylic complexes of palladium(II)

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Recent results have shown that 6-methoxynorbornenyl complexes of palladium(II) and platinum(II) may be considered as having π-homoallylic–metal bonding[1]. Thus addition of ligands such as pyridine or tertiary phosphines to these complexes results in the formation of 5-methoxynortricycl-3-enyl complexes which may be considered as the homo-allylic analogues of σ-allyl complexes[2–4]. With a view to elucidating the extent to which such an analogy is valid and to obtaining new mechanistic information on the insertion of olefins into palladium–carbon bonds we have investigated the reaction of a variety of 6-substituted norbornenylpalladium(II)-hexafluoroacetylacetonates (I) with olefins, 1,2-dienes and 1,3-dienes.

Addition of one mol of PPh_3, $AsPh_3$, $SbPh_3$, or pyridine to $CHCl_3$ solutions of (I) gives compounds which structurally analyse as the nortricyclenyl derivatives (II) (*e.g.* for L = pyridine; R = CH_3CO. Found: C, 40.89; H, 3.18; N, 2.64. $C_{18}H_{17}F_6NO_4Pd$. calcd.: C, 40.66; H, 3.22; N, 2.64%. PMR data: no resonances due to olefinic protons; complex peak system τ7.5–9 characteristic of nortricyclenyl moiety[2]).

Addition of one mol of mono-olefins or 1,3-dienes to $CHCl_3$ solution of (I) give PMR spectra consistent with the presence of an equilibrium mixture of (I) and (II) (L = olefin or 1,3-diene) in solution. The concentrations of (I), (II), and olefin (or diene) can be measured by integrating the spectrum, thus providing a direct route to the equilibrium constants (*K*) shown in Table 1. For systems in which L = 1,3-diene, the values of *K* decrease in the order 1,3-butadiene ~ *trans*-1,3-pentadiene ~ *cis*-1,3-pentadiene > isoprene* > 2,3-dimethylbutadiene > 2,5-dimethyl-2,4-hexadiene. This order is only consistent with preferential coordination of the least substituted olefinic function of the diene to palladium.

Addition of allene, 1-methylallene, 1,1-dimethylallene, or 1,3-dimethylallene to $CHCl_3$ solutions of (I) also gave initial PMR spectra sonsistent with the formation of (II) where L is a coordinated 1,2-diene. However, complex (II) [L = 1,2-diene] undergoes a further reaction whereby migration of the nortricyclenyl ligand from palladium to the coordinated 1,2-diene occurs to give the π-2-nortricyclenylallylpalladium(II)-hexafluoroacetylacetonate complexes (III). Complexes (III) were readily isolated and

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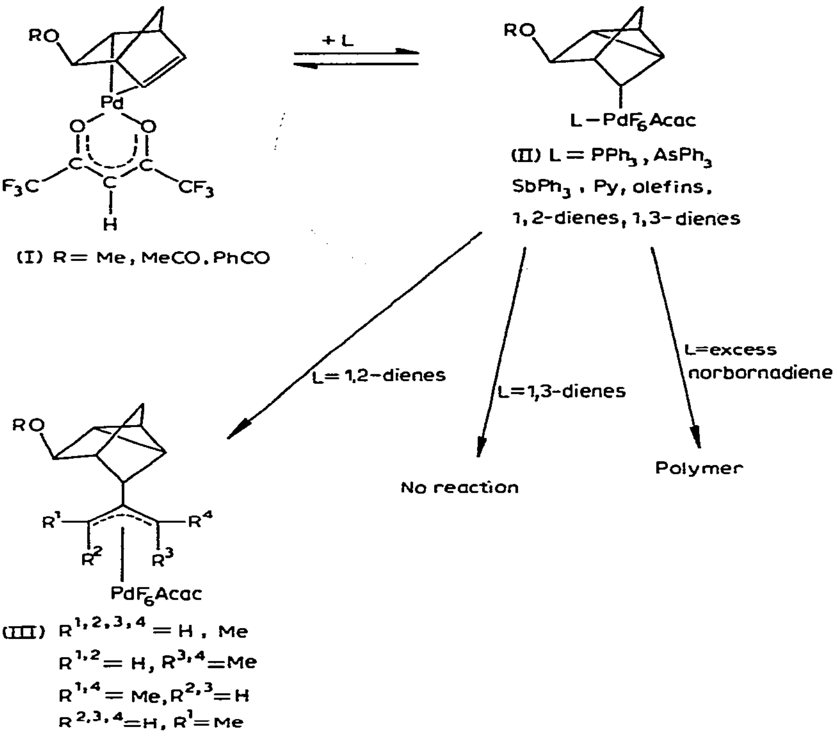
*The reason for a smaller equilibrium constant when the 1,3-diene is isoprene relative to those of other 1,3-dienes containing a monosubstituted olefin function is probably a steric factor.

TABLE 1

EQUILIBRIUM CONSTANTS, $K = [(II)] / [(I)]$ [olefin] $(mol^{-1} \cdot l)$ FOR SOLUTIONS OF (I) (R = CH_3CO) IN $CDCl_3$ IN THE PRESENCE OF VARIOUS OLEFINS OR 1,3-DIENES AT 34°.

Olefin	$H_2C{=}CH_2$	$CH_3CH{=}CH_2$	$PhCH{=}CH_2$	*trans*-$CH_3CH{=}CHCH_3$	$(CH_3)_2C{=}CH_2$
K	33 ± 5	4.4 ± 0.5	0.56 ± 0.05	0.29 ± 0.05	<0.03
1,3-Diene	Butadiene	*cis*-Pentadiene	*trans*-Pentadiene	Isoprene	2,3-Dimethylbutadiene
K	2.8 ± 0.5	2.3 ± 0.5	3.4 ± 0.5	0.16 ± 0.05	<0.02



structurally characterized. (*e.g.* (III) R = CH_3CO; $R^{1,2,3,4}$ = H. Found: C, 40.71; H, 3.18; m/e = 504 [P^+]. $C_{17}H_{16}F_6O_4Pd$ calcd.: C, 40.46; H, 3.20% m/e = 504 [P^+]. PMR data: no olefinic resonances; four peaks due to π-allylic protons at τ5.82, 6.00, 6.95, 7.00 [all anisochronous due to the asymmetry of the nortricyclenyl moiety], characteristic nortricyclenyl pattern τ7.5–9[2]). The rate of 'insertion' of allenes into (I) (R = CH_3CO) to give (III) decreased in the order 1,1-dimethylallene > allene > tetramethylallene*
The rate of 'insertion' of these allenes into π-2-chloroallylpalladium hexafluoroacetylacetonate to give new 2-substituted allyl complexes[5] decreases in the same order[6] suggestive of a similar reaction mechanism (*i.e.* direct transfer of the σ-bonded carbon from palladium to the central atom of the coordinated 1,2-diene). Similarly addition of norbornadiene (which readily inserts into the allyl-palladium bond[7]) to $CHCl_3$ solutions of (I) at low temperatures gives PMR spectra which suggest formation of a species such as (II) (L = norbornadiene). At higher temperatures rapid polymerization of the norbornadiene occurs, presumably by successive insertions into Pd—C σ-bonds. 'Insertions' of allenes and norbornadiene into (I) occur more rapidly than the analogous 'insertions' of these molecules into π-2-chloroallylpalladium hexafluoroacetylacetonate[6]. This is consistent with the greater stability of (II) relative to a σ-allylic analogue[8]

Since 1,3-butadiene inserts more rapidly into π-2-chloroallylpalladium hexafluoroacetylacetonate to give a new π-allylic complex than does allene[6,8] it was

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*Reactions of equimolar amounts of complex and diene in $CHCl_3$ solution at 34° were carried out in NMR tubes. Rates were monitored by intigration of the ^1H NMR spectrum at suitable time intervals.

initially surprising to find that although 1,3-dienes readily form the nortricyclenyl complex (II) (L = 1,3-diene) containing a palladium—carbon σ-bond and a coordinated olefin, no further reaction to give a π-allylic product was observed. This result, together with the unusual stereochemistry of 1,3-diene insertion into allyl—palladium bonds[9,10], suggests that this latter insertion reaction does not involve direct transfer of a σ-allyl to a coordinated olefinic function of the 1,3-diene. It is probable that this reaction involves direct participation of the σ-allylic olefinic function in formation of the new carbon—carbon bond[6].

The reaction of allenes with (I) together with carbonylation studies of the chloro-bridged analogues of (I)[11] serve to illustrate that the analogy between the chemistry of norbornenyl complexes and π-allylic complexes of palladium is a good one where reactions occur primarily at palladium—carbon σ-bonds. However, reactions involving participation of a σ-allylic olefinic function are unlikely to have a direct analogue in norbornenyl/nortricyclenyl complexes.

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