1,3-Shifts in Fluxional η^3-Dienylpalladium(II) Complexes

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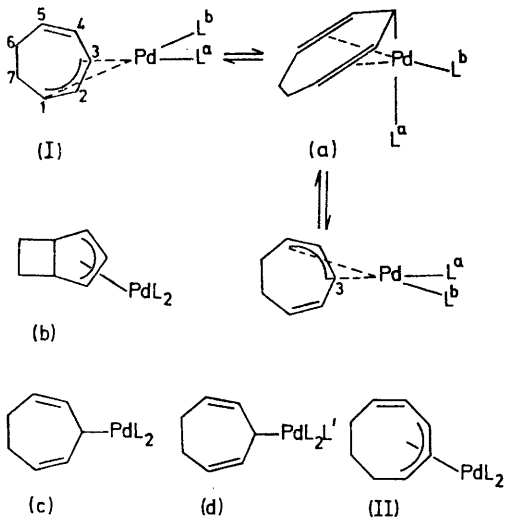
Summary η^3-Cyclohepta-2,4-dienylpalladium complexes are fluxional in solution owing to interchange of C(1) and C(5), C(2) and C(4), and C(6) and C(7); a 1,3-shift mechanism is indicated for the interchange and there is a direct relation between $\Delta G^{\ddagger}$ and the *trans*-effectiveness of L in $[Pd(C_7H_9)L_2]$ or $[Pd(C_7H_9)L_2]PF_6$.

We[1,2] recently described n.m.r. spectroscopic behaviour of some non-rigid allylic and benzylic palladium complexes which was difficult to reconcile with either of the two well established dynamic processes for π-bonded complexes, the η^3-η^1-η^3 or the 1,2-shift mechanism.[3] These investigations have now been extended to related systems in which a double bond is conjugated to the η^3-allylic unit and we present here evidence for a 1,3-shift mechanism.

A variety of neutral and cationic η^3-cyclohepta-2,4-dienylpalladium(II) complexes (Table) were prepared by standard methods from the known compound $[Pd(C_7H_9)$-

Cl]$_2$.[4] Variable temperature ^{13}C n.m.r. studies indicated all the complexes to be fluxional and to show exchange (process A) between C(1) and C(5), C(2) and C(4), and C(6) and C(7); C(3)[†] remained unchanged. Values of $\Delta G^{\ddagger}$ for process A were determined for the series (Table) and the enthalpy and entropy of activation were also measured for $[Pd(C_7H_9)(AsEt_3)_2]PF_6$ ($\Delta H^{\ddagger}$ +9·7 ± 0·2 kcal mol^{-1};[‡] $\Delta S^{\ddagger}$, −0·6 ± 0·7 cal K^{-1} mol^{-1} $[Pd(C_7H_9)(Ph_2AsCH_2CH_2AsPh_2)]PF_6$ ($\Delta H^{\ddagger}$, +9·0 ± 0·3 kcal mol^{-1}; $\Delta S^{\ddagger}$, +0·7 ± 1·2 cal K^{-1} mol^{-1}), and $[Pd(C_7H_9)(acac)]$ ($\Delta H^{\ddagger}$, +14·8 ± 0·7 kcal mol^{-1}; $\Delta S^{\ddagger}$, −5·9 ± 2·2 cal K^{-1} mol^{-1}) (acacH = acetylacetone).



SCHEME

Over the temperature range investigated this was the only dynamic process occurring for most of the complexes, but there was some evidence for a second dynamic process involving the ligands L in $[Pd(C_7H_9)(MeSCH_2CH_2SMe)]PF_6$ and $[Pd(C_7H_9)(S_2CNMe_2)]$ and there was no differentiation between the ends of the ligand L_2 in $[Pd(C_7H_9)(CH_3COCHCOCH_3)]$ and $[Pd(C_7H_9)(CF_3COCHCOCF_3)]$. In each case, however, the rates of these secondary processes were clearly different to that of process A. For both $[Pd(C_7H_9)(AsEt_3)_2]PF_6$ and $[Pd(C_7H_9)(acac)]$ the rates of process A were independent of concentration (over a 3-fold range) and of solvent {acetone and dichloromethane, and also benzene for $[Pd(C_7H_9)(acac)]$}. Addition of an excess of $AsEt_3$ did not affect the rate of process A for $[Pd(C_7H_9)(AsEt_3)_2]PF_6$.

These observations rule out (i) transition states (b) and (c) since either would require L_2 interconversion to take place at the same rate as process A, and (ii) bimolecular mechanisms and intermediates such as (d) (see Scheme).

This leaves the transition state (a), where the double bond C(4)–C(5) has now also become co-ordinated and where L^a remains *trans* to C(3), as the most plausible to explain process A, which may be defined as a η^3-η^5-η^3 interchange or a 1,3-shift.

TABLE

^{13}C N.m.r. chemical shifts of C(3) and $\Delta G^{\ddagger}$ for a series of fluxional η^3-cycloheptadienylpalladium complexes (I) in CH_2Cl_2.

	δ C(3) p.p.m.	$\Delta G^{\ddagger}$ kcal mol^{-1}
$[Pd(C_7H_9)(CH_3COCHCOCH_3)]$	71·7	16·6
$[Pd(C_7H_9)(CF_3COCHCOCF_3)]$	75·2	15·5
$[Pd(C_7H_9)(Me_2NCH_2CH_2NMe_2)]^+$	76·1	14·7
$[Pd(C_7H_9)(S_2CNMe_2)]$	77·1	14·8
$[Pd(C_7H_9)Cl]_2$	78·8	15·1
$[Pd(C_7H_9))(bipyridyl)]^+$	78·9	14·9
$[Pd(C_7H_9)Br]_2$	80·9	14·0
$[Pd(C_7H_9)I]_2$	84·3, 84·8[a]	13·0
$[Pd(C_7H_9)(MeSCH_2CH_2SMe)]^+$	85·7	11·8
$[Pd(C_7H_9)(AsEt_3)_2]^+$	86·5	9·8
$[Pd(C_7H_9)(PEt_3)_2]^+$	87·7	9·5
$[Pd(C_7H_9)(Ph_2AsCH_2CH_2AsPh_2)]^+$	87·9	8·9
$[Pd(C_7H_9)(Ph_2PCH_2CH_2PPh_2)]^+$	88·5	8·8
$[Pd(C_7H_9)(\eta^4$-hexamethylbicyclo-[2.2.0]hexadiene$)]^+$	89·2	8·7
$[Pd(C_7H_9)\{P(OMe)_3\}_2]^+$	91·6	8·2
$[Pd(C_7H_9)(\eta^4$-cyclo-octa-1,5-diene$)]^+$	93·7	ca. 6·8[b]
$[Pd(C_7H_9)(\eta^4$-cyclo-octatetraene$)]^+$	95·7	ca. 7·1[b]

[a] Two isomers are present owing to the asymmetry of the allyl ligands in the dimer. [b] Estimated values at −89 °C; limiting low temperature spectra could not be achieved.

For the three compounds examined $\Delta S^{\ddagger}$ was very small (particularly for the two containing arsenic ligands where greatest accuracy was possible) and it is generally likely that $\Delta G^{\ddagger} \approx \Delta H^{\ddagger}$. There is a nearly linear relation between the ^{13}C chemical shifts of C(3) in the complexes and their $\Delta G^{\ddagger}$'s for process A and the order of increasing $\Delta G^{\ddagger}$ parallels closely the *trans*-effect series for the liganding atoms L in (I). This suggests that the rate of interchange A is largely a function of the *trans*-labilising ability of L.

The mechanism proposed for process A accounts for the puzzling features of our earlier observations,[1,2] and also for the behaviour of the related cyclo-octa-2,4-dienyl (cod) complexes (II). Here however the rates are very much slower than for the corresponding C_7 compounds; for example for the cationic cyclo-octa-1,5-diene complexes $\Delta G^{\ddagger}$ is 6·8 kcal mol^{-1} for $[Pd(C_7H_9)(cod)]PF_6$ and 13·5 for $[Pd(C_8H_{11})(cod)]PF_6$. Indeed many of the cyclo-octadienyl complexes are static over the normal temperature range. Models indicate that it is much more difficult for the C_8 ring to achieve the co-ordination of C(1)–C(5) needed for the transition state corresponding to (a), a point which is well illustrated by the *X*-ray structure of the rigid $[Pd(C_8H_{11})(acac)]$ which shows the unco-ordinated double bond to be twisted well away from conjugation with the η^3-allylic unit.[6]

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[†] For example, for $[Pd(C_7H_9)(AsEt_3)_2]PF_6$ these resonances occurred at δ 87·3, 136·6, 111·7, 123·2, 42·0, 28·2, and 86·5 p.p.m. respectively at −97 °C in CD_2Cl_2–CH_2Cl_2.

[‡] 1 cal = 4·184 J.

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