Journal of

The Chemical Society,

Chemical Communications

NUMBER 10/1975 21 MAY

Ring Opening and Insertion Reactions of *endo*-Alkoxy-tetraphenylcyclobutenylpalladium(II) Derivatives

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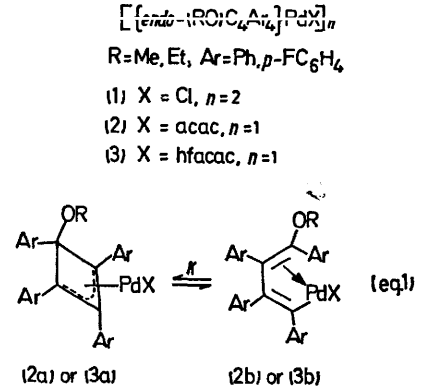
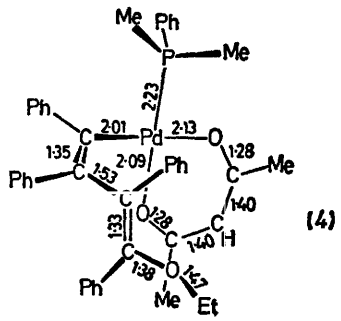
Summary *endo*-Alkoxy-tetraphenylcyclobutenylpalladium(II) β-diketonates readily undergo a stereospecific ring opening to give 4-alkoxytetraphenylbuta-1-*cis*,3-*trans*-dienylpalladium complexes which undergo insertion reactions with unsaturated hydrocarbon substrates.

The reaction of diphenylacetylene with $PdCl_2$ in alcohols to yield *endo*-alkoxytetraphenylcyclobutenylpalladium chloride dimer (**1**) proceeds *via* a stereospecific pathway.[1] We report that under suitable conditions, the ring closing step in the formation of the *endo*-alkoxy-cyclobutenyl ligand is readily reversible.



Treatment of (**1**) with the appropriate thallium(I) salt gives the acetylacetonate and hexafluoroacetylacetonate derivatives (**2**) and (**3**) respectively. The low temperature ^1H and ^{19}F n.m.r. spectra of these complexes in a variety of solvents demonstrate the presence of two isomeric structures in solution, one corresponding with the cyclobutenyl structure [(**2a**) or (**3a**)] and the other with a ring-opened



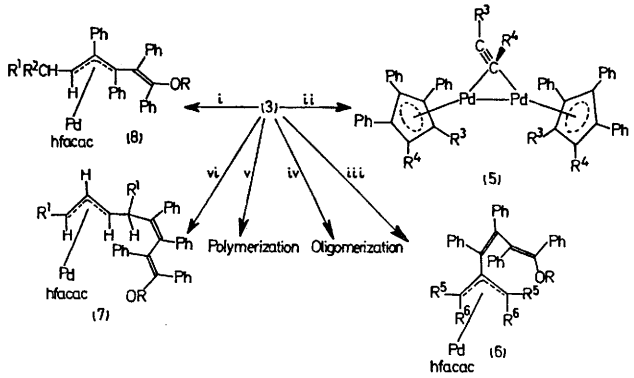
(4)

Figure. Molecular structure of (**4**) as determined by *X*-ray crystallography; $R = 8{\cdot}3\%$.

butadienyl structure [(**2b**) or (**3b**)].† At 245 K the ratio of (**2a**) : (**2b**) or (**3a**) : (**3b**) (*K* in equation 1) lies in the range 0·6—1·0:1 and is relatively insensitive to changes in concentration, solvent, and temperature. The stereochemistry of the ring opening (equation 1) has been unambiguously defined by an *X*-ray structural study of the adduct [{(EtO)-C_4Ph_4}Pd(acac)PMe_2Ph] (**4**) formed from the reaction of (**2**; R = Et) with Me_2PhP (see Figure). The stereochemistry of the '-PhC–CPhOEt' part of the σ-bonded '4-EtOPh$_4$-

† e.g. The low temperature n.m.r. spectra of (**3a**; R = Me, Ar = *p*-C_6H_4F) contains singlet resonances assignable to a hexafluoroacetylacetone (hfacac) central proton and a methoxy group (^1H n.m.r.) and four resonances with intensity ratios 1:1:2 (C_6H_4F):6(hfacac CF_3) (^{19}F n.m.r.) and that of (**3b**; R = Me, Ar = *p*-C_6H_4F) contains singlet signals assignable to a hfacac central proton and a methoxy group (^1H n.m.r.) and six resonances with intensity ratios 1:1:1:1(C_6H_4F):3:3(non-equivalent CF_3) (^{19}F n.m.r.).

C_4-' ligand is *trans*, confirming an initial *trans*-attack of an alcohol on a co-ordinated diphenylacetylene in the formation of (**1**), as previously suggested.[1]



SCHEME. Products obtained from the reaction of (**3**; Ar = Ph) with several unsaturated hydrocarbons at 25 °C in $CDCl_3$. (unless otherwise stated).‡

R^1 = H, Me; R^2 = H, Me, Ph; R^3 and R^4 = Me, Et, Ph; R^5 and R^6 = H, Me.

i, $R^1R^2C{=}CH_2$, hydride shift; ii, $R^3C{\equiv}CR^4$ in MeOH; iii, $R^5R^6C{=}C{=}CR^5R^6$; iv, $Me_2C{=}C{=}CH_2$; v, norbornadiene; vi, $R^1CH{=}CHCH{=}CHR^1$.

Whilst (**2b**) and (**3b**) are fluxional with respect to Me or CF_3 site exchange in the β-diketonate ligand, no evidence of site exchange between (**2a**) ⇌ (**2b**) or (**3a**) ⇌ (**3b**) has been observed in the n.m.r. spectra on warming to 60 °C in $CDCl_3$. An estimated minimum for $\Delta G^{\ddagger}$ of the ring opening process (equation 1) is 80 kJ mol^{-1}.

Compounds (**2**) and (**3**) react readily with unsaturated hydrocarbons to give a variety of insertion products [see Scheme for (**3**; R = Me)]. Reaction with disubstituted acetylenes in alcohols gives a series of dinuclear penta-substituted cyclopentadienylpalladium(I) complexes (**5**) structurally similar to the product derived from PhC≡CPh and $Pd(OAc)_2$ in MeOH.[2] Allenes give either π-allylic products (*e.g.* **6**) or result in oligomerizations depending on the structure of the allene used. 1,3-Dienes give π-allylic products (*e.g.* **7**) *via* an insertion process that is stereochemically different to that observed for the 'insertion' of 1,3-dienes into allyl–Pd bonds.[3] Olefins also react with (**2**) or (**3**) to yield π-allylic derivatives, the reaction proceeding *via* a 'hydride shift' mechanism (*e.g.* **8**).

Under suitable conditions, (**1**) and its acetate analogue also undergo ring opening and insertion reactions although with (**1**) the reactions proceed much more slowly.

The *exo*-alkoxytetraphenylcyclobutenylpalladium(II) analogues of (**1**), (**2**), and (**3**) do not undergo thermal ring opening easily and are unreactive towards unsaturated hydrocarbons. Equation (**1**) can be considered as a con-rotatary ring opening of a *cis*-3,4-disubstituted tetraphenylcyclobutene.[1] An explanation of the non-reactivity of the *exo*-cyclobutenyl complexes may be steric inhibition between phenyl groups in the transition state of a con-rotary ring opening process leading to a bidentate 4-alkoxytetraphenylbuta-1-*cis*,3-*cis*-dienyl complex [the analogue of (**2b**) and (**3b**)].

We thank the National Research Council of Canada for financial support.

(*Received*, 10*th March* 1975; *Com.* 290.)

‡ Complexes (**2**)—(**4**) and (**6**)—(**8**) exhibit rapid, concentration-independent site exchange of non-equivalent acac Me's and hfacac CF_3's in their high temperature n.m.r. spectra. Complexes (**7**) and (**8**) consist of two conformational isomers in $CDCl_3$ solution (possibly *syn*- and *anti*-conformational isomers) which equilibrate rapidly at room temperature on the n.m.r. time scale. All the complexes described have been fully characterised by microanalysis, molecular weight and mass, i.r., and n.m.r. spectroscopy.

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