Structure and Reactivity of *cis*- and *trans*-Bis-[{5-carbomethoxy-(1,2,3-η)-cyclohexenyl}palladium]. Evidence for a (σ-Allyl)palladium Intermediate in the *cis*-Migration of Acetate from Palladium to Coordinated π-Allyl

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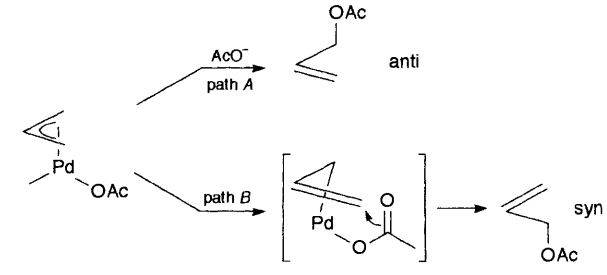
The mode of attack by acetate on a (π-allyl)palladium complex depends not only on the ligands on palladium, but also on the structure of the complexes; for the bis-[{5-carbomethoxy-(1,2,3-η³)-cyclohexenyl}palladium] complexes, the structures of which were determined by X-ray crystallography and NMR spectroscopy, the *cis* isomer preferably reacted by external attack whereas the *trans* isomer, under identical conditions, preferred internal migration.

Attack by acetate on (π-allyl)palladium complexes occurs in catalytic reactions such as the synthetically useful allylic oxidation[1] and 1,4-diacetoxylation[2] processes. An interesting aspect of acetate as nucleophile is that it can attack the (π-allyl) ligand *via* two different steric modes (Scheme 1),[3] either in an external *trans* fashion (path *A*), or, if acetate is coordinated to palladium, *via* internal *cis* migration (path *B*). A (σ-allyl)palladium intermediate has been proposed for the latter pathway,[2] and attempts have been made to observe such intermediates in related reactions by NMR spectroscopy.[4]

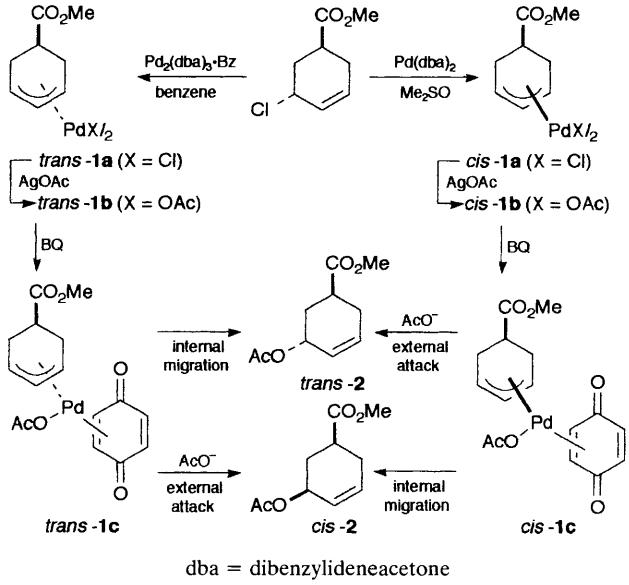
We have now studied the mechanism for the attack by acetate on the (π-allyl)palladium complexes, *cis*- and *trans*-**1a**,[5] according to Scheme 2. The structures of these complexes were determined by X-ray crystallography† and NMR spectroscopy.‡

The (π-allyl)palladium complex *trans*-**1a** was found to exist in a chair-type conformation whereas *cis*-**1a** possesses a boat-type conformation in the crystalline state (Fig. 1 and Table 1). ^{1}H NOE measurements and H–H coupling constants‡ are in agreement with these structures but indicate a less pronounced chair and boat, respectively, in solution than in the crystalline state. It has been shown by NMR spectroscopy that a chair-type conformation is preferred in unsubstituted (π-allyl)palladium complexes,[7] and both boat- and chair-type conformations have been reported for substituted systems.[4a,8]

The acetate analogues of **1a**, *trans*- and *cis*-**1b**, prepared by stirring **1a** with AgOAc (1 equiv. per Pd) in [$^2H_4$]acetic acid and subsequent removal of AgCl, were treated with 1,4-benzoquinone (BQ) at various concentrations (0–2 mol dm^{-3}) of LiOAc·2H$_2$O at temperatures ranging from 23



Scheme 1



dba = dibenzylideneacetone

Scheme 2

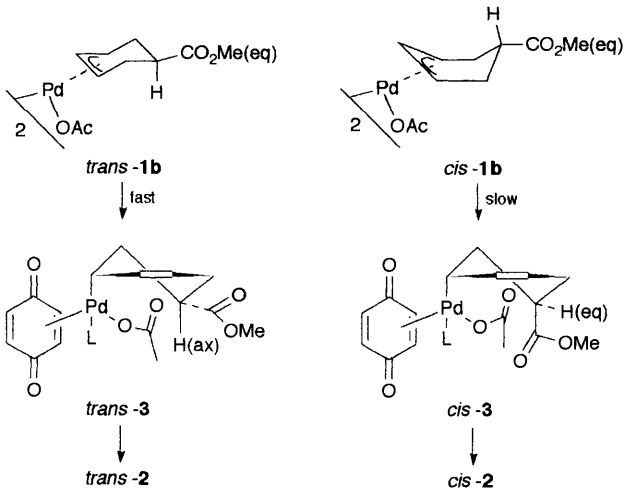
† *Crystal data* for **1a**: $C_{16}H_{22}Cl_2O_4Pd_2$, M = 562.05. *Trans*-**1a**: triclinic, space group $P\bar{1}$, a = 6.973(2), b = 12.913(6), c = 5.591(2) Å, α = 101.38(2), β = 100.15(2), γ = 99.51(3)°, V = 475.2(3) Å^3, Z = 1, D_c = 1.964 g cm^{-3}, R = 0.034; crystal size 0.15 × 0.02 × 0.30 mm. *Cis*-**1a**: monoclinic, space group $P2_1/n$, a = 5.987(4), b = 14.836(6), c = 10.614(5) Å, β = 97.16(5)°, V = 935.3(8) Å^3, Z = 2, D_c = 1.995 g cm^{-3}, R = 0.067; crystal size 0.30 × 0.05 × 0.02 mm.

All X-ray measurements were made on a Rigaku AFC6R diffractometer with graphite monochromated Mo-Kα radiation and a 12 kW rotating anode generator. The data were collected at a temperature of 23 ± 1 °C using the ω − 2θ scan technique to a maximum 2θ value of 50.0°. The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 3 rescans) and the counts were accumulated to assure good counting statistics. Intensities of three reflections measured after every 150 reflections remained cosntant throughout data collection, indicating crystal and electronic stability. An empirical absorption correction, based on azimuthal scans of several reflections, was applied. The data were corrected for Lorentz and polarization effects.

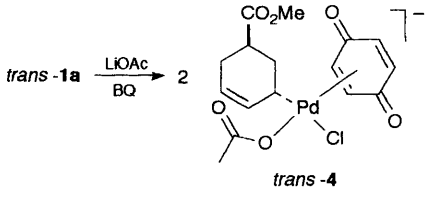
The structures were solved by direct methods.[6a] In both cases, the crystallographic centre of symmetry coincided with the centre of the molecule. The non-hydrogen atoms were refined anisotropcially. Neutral atom scattering factors were taken from Cromer and Waber.[6b] Anomalous dispersion effects were included in F_{calc},[6c] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[6d] All calculations were performed using the TEXSAN[6e] crystallographic software package of Molecular Structure Corporation.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ ^{1}H NMR spectra were recorded for $CDCl_3$ solutions on a Varian 300 MHz spectrometer with Me_4Si as internal standard. For *trans*-**1a**: δ 5.48 (t, 1 H, H-2, $J_{2,3}$ 6.4 Hz), 5.03 (ddd, 2 H, H-1,3, $J_{1,2}$ 6.4, $J_{3,4ax}$ 4.0, $J_{3,4ex}$ 3.0 Hz) 3.39 (tt, 1 H, H-5, $J_{5,4eq}$ 6.5, $J_{5,4ax}$ 7.7 Hz) 2.22 (ddd, 2 H, H-4, 6_{eq}, $J_{4eq,4ax}$ 17.0, $J_{4eq,5}$ 6.5, $J_{4eq,3}$ 3.0 Hz) 1.74 (ddd, 2 H, H-4, 6_{ax}, $J_{4ax,4eq}$ 17.0, $J_{4ax,5}$ 7.7, $J_{4ax,3}$ 4.0 Hz). NOE: {H-5}: H-4$_{eq}$ 5%; {H-4$_{eq}$}: H-4$_{ax}$ 22%, H-3 5%, H-5 22%; {H-4$_{ax}$}: H-4$_{eq}$ 30%, H-3 11%, H-5 4%. For *cis*-**1a**: δ 5.55 (t, 1 H, H-2, $J_{2,3}$ 6.0 Hz) 5.20 (dd, 2 H, H-1, 3, $J_{3,4eq}$ 6.7, $J_{3,2}$ 6.0 Hz) 2.26 (dd, 2 H, H-4, 6_{eq}, $J_{4eq,4ax}$ 12.2, $J_{4eq,3}$ 6.7 Hz) 2.06 (t, 1 H, H-5, $J_{5,4ax}$ 6.2 Hz) 2.02 (dd, 2 H, H-4, H-6, 6_{ax}, $J_{4ax,4eq}$ 12.2, $J_{4ax,5}$ 6.2 Hz). NOE: {H-4$_{eq}$}: H-3 13%, H-4$_{ax}$ and H-5 22%; {H-4$_{ax}$ and H-5} H-3 4%, H-4$_{eq}$ 37%.



Scheme 3



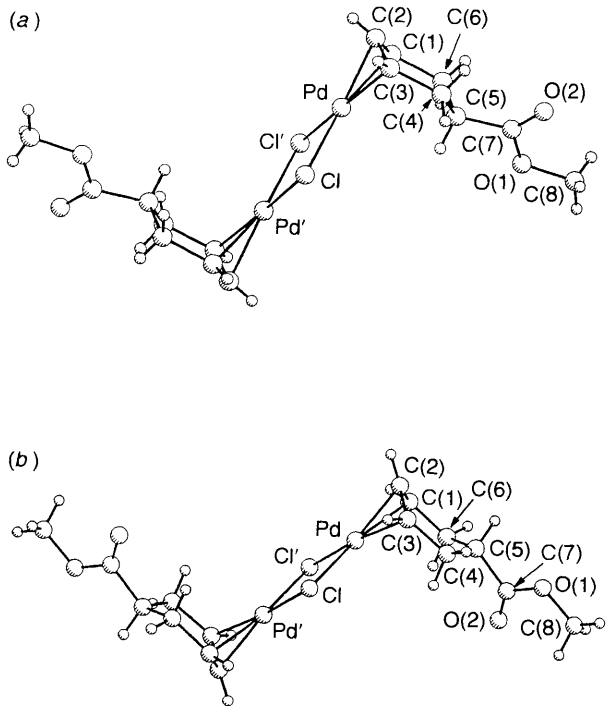


Fig. 1 Structure of (*a*) *trans*-**1a** and (*b*) *cis*-**1a**

Table 1 Selected angles between planes 1 and 2 for *trans*- and *cis*-**1a**

Plane 1	Plane 2	Angle for *trans*-**1a** (°)	Angle for *cis*-**1a** (°)
C-1,2,3	C-1,6,3,4	149.8	151.2
(π-allyl)	C-4,5,6	5.5	65.8
	Pd–Cl–Pd′–Cl′	68.2	111.2
	C-5,CO_2Me	115.8	123.7
C-1,6,3,4	C-4,5,6	144.4	142.9
	Pd–Cl–Pd′–Cl′	81.9	97.6
	C-5,CO_2Me	52.9	54.3
C-4,5,6	Pd–Cl–Pd–Cl′	62.7	45.4
	C-5,CO_2Me	113.8	113.8
Pd–Cl–Pd′–Cl	C-5,CO_2Me	80.9	88.1

to 60 °C. The progress of the reaction was followed by ^{1}H NMR spectroscopy. In the absence of external nucleophiles (LiOAc), both complexes yielded only product from internal *cis* migration, but the difference in reaction rates was large. Complex *trans*-**1b** reacted to yield the allylic acetate *trans*-**2** within one minute at room temperature whereas *cis*-**1b**, under identical conditions, requried 15 to 20 minutes to go to completion. The addition of LiOAc did not affect the stereochemical outcome of the reaction of *trans*-**1b**, but *cis*-**1b** yielded an increasing amount of product *trans*-**2** from external *trans* attack (path *A*, Scheme 1).

These observations are best explained by the structural differences between the two isomers. Both (π-allyl)palladium complexes *trans*- and *cis*-**1** have the carbomethoxy group in a pseudoequatorial position. In the corresponding postulated (σ-allyl) complex, however, the carbomethoxy group of *cis*-**1b** is forced into a pseudoaxial position,§ whereas it will stay in a pseudoequatorial position in the *trans* isomer. Thus, formation of the σ complex *cis*-**3**, which is 1,3-diaxially substituted, is unfavourable compared to the formation of *trans*-**3** from *trans*-**1b** (Scheme 3). Moreover, during the internal migration of acetate in *cis*-**3** a second 1,3-diaxial relationship is created, which will further retard the rate of internal migration for this isomer.

Interestingly, it was found that the chloro complex *trans*-**1a** also preferred to react *via* a highly selective internal migration in the presence of 0.5 mol dm^{-3} LiOAc and benzoquinone, a result which is in contrast to what has been observed previously,[2,3] but in accordance with the facile formation of a reactive (σ-allyl)palladium complex *trans*-**4**. Complex *cis*-**1a**, however, reacted only *via* external attack by acetate under these conditions. Even in the presence of LiCl (3 equiv./Pd), *trans*-**1a** preferred the internal migration pathway.

In the catalytic allylic acetoxylation of 1-methylcyclohex-3-ene,[1a–c] the main product was the *trans* allylic acetate *via* the symmetric (π-allyl)palladium complex, and the same was observed for 1-carbomethoxycyclohex-3-ene.[1a] The two possible stereoisomeric symmetrical (π-allyl) complexes *trans*- and *cis*-**1a** are formed in a ratio close to 1 : 1 from 1-carbomethoxycyclohex-3-ene,[9] but the product acetate is almost 100% *trans*.[1a] Thus, the observed stereochemistry of the product from the catalytic reactions, which take place in the presence of acetate salts,¶ can, in accordance with our results, be explained by a structure–reactivity relationship with fast internal migration from the *trans* complex, and external *trans* attack by acetate on the *cis* complex to yield in both cases the *trans* allylic acetate (*trans*-**2**, *cf.* Scheme 2).

§ In Scheme 3 only the pseudochair conformations of the (σ-cyclohexenyl)palladium complexes are considered. Complex *cis*-**1b** may also rearrange to a σ-allyl complex of boat conformation, in which Pd is axial and CO_2Me equatorial. In this conformation, there will be an unfavourable interaction between the axial proton H-4 and the migrating acetate, a situation similar to that previously discused for a seven-membered ring.[2]

¶ MnO_2 is reduced to $Mn(OAc)_2$.

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