Dynamics of the 9,10-Dihydroanthracene Type Inversion of the Six-membered Palladocycle in Chloro(ligand)[2-(2′-pyridylmethyl)phenyl]palladium(II) Complexes

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The dynamics of inversion of the six-membered palladocycle in chloro(ligand)[2-(2′-pyridylmethyl)-phenyl]palladium(II) complexes, where ligand = substituted pyridine, PPh_3, or $PMePh_2$, has been studied by ^1H n.m.r. spectroscopy in $CDCl_3$ in the temperature range 213—323 K. The pseudo-first-order rate constants for the inversion are independent of the total concentration of the complex as well as of the concentration of added free pyridine. Although the inversion proceeds without dissociation of N-bound pyridines, the free energies of activation, $\Delta G^{\ddagger}$, are virtually insensitive to electronic effects brought about by pyridine substituents. The proposed inversion mechanism involves the formation of a planar intermediate or transition state without any bond breaking. The role of steric factors was demonstrated by the measuring rates of isomerisation of the phosphine complexes. The results obtained are discussed in connection with the dynamic behaviour of 9,10-dihydroanthracenes.

Hiraki *et al.*[1] first, and then we, using another approach,[2] reported the preparation of six-membered cyclopalladated derivatives of 2-benzylpyridine. Among this family of compounds, of particular interest are monomeric complexes of the type chloro(ligand)[2-(2′-pyridylmethyl)phenyl]palladium(II), where ligand stands for ring-substituted pyridines or tertiary phosphines, which show a dynamic behaviour due to the 9,10-dihydroanthracene-type inversion of the six-membered palladocycle (Scheme). The temperature-dependent ^1H n.m.r. spectra of the complexes (**1**) and (**2**) provide an excellent subject for kinetic investigation of this inversion, analysing the line broadening of signals from the geminal protons. In the case of 9,10-dihydroanthracenes the inversion is usually characterised by very low activation barriers[3] and such measurements cannot give values of the free energies of activation, which have been evaluated only in a few special cases.[4] The goal of the present work was to obtain kinetic data on the inversion of the six-membered palladocycle, which could be of use not only for elucidating the mechanism of this particular inversion, but might also throw some light on general aspects of the dynamic behaviour of 9,10-dihydroanthracenes.

Experimental

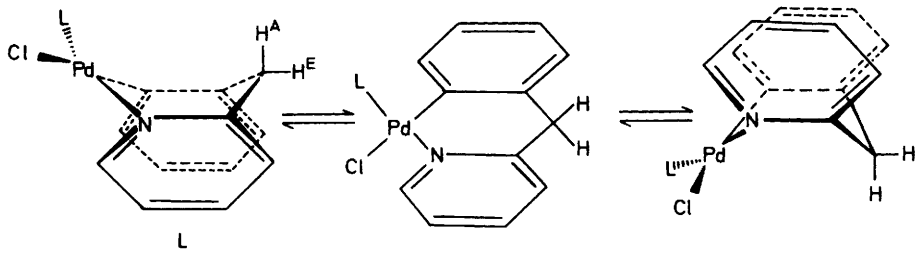
Materials.—2-Benzylpyridine was a Reakhim reagent. This was converted into the dimeric complex di-μ-chloro-bis[2-(2′-pyridylmethyl)phenyl]dipalladium(II), (**3**), by reaction with di-μ-chloro-bis(2-dimethylaminomethylphenyl)dipalladium(II) in acetic acid–chloroform as described.[2] All monomethyl- and dimethyl-pyridines as well as 4-dimethylaminopyridine were Fluka reagents. 2,4,6-Trimethylpyridine was an Erkner product. 4-Methoxycarbonylpyridine was prepared by oxidation and subsequent esterification from 4-methylpyridine according to the literature procedures.[5] Freshly distilled pyridines were used throughout. Triphenylphosphine was a Chemapol reagent, while methyldiphenylphosphine was kindly provided by Dr. A. B. Permin.

Preparation of Chloro(ligand)[2-(2′-pyridylmethyl)phenyl]-palladium(II) Complexes (**1**) *and* (**2**).—The procedure was essentially the same as described earlier.[1,2] The dimeric complex (**3**) (0.100 g, 0.323 mmol) was suspended in chloroform (1.5—2.0 cm^3) and to this mixture a ligand in 20—50% excess was added. The mixture was usually stirred with gentle heating (40—50 °C) for *ca.* 1—2 h, but 2 d were necessary to achieve complete dissolution of the dimer in the case of 2,4,6-trimethylpyridine due to conversion into the monomeric species chloro(ligand)[2-(2′-pyridylmethyl)phenyl]palladium. Solutions were then filtered and the monomeric species were precipitated by slow addition of hexane (*ca.* 10 cm^3). These were filtered off, washed with hexane, and dried *in vacuo*. The white microcrystalline solids were characterised by ^1H n.m.r. and i.r. spectral data (Table 1 and Figure 1).

Instrumentation and Total Line Shape Analysis.—Proton n.m.r. spectra were obtained on Tesla BS-497 (100 MHz) and Bruker WM (500 MHz) instruments. Unless otherwise stated, all measurements were made in $CDCl_3$ as solvent with tetramethylsilane as an internal standard. Chemical shifts are given in p.p.m. downfield from $SiMe_4$. Kinetic data were obtained using the 100-MHz instrument equipped with a temperature-control device, calibrated by use of chemical shifts for MeOH. Experimental line shapes for the geminal proton signals in the temperature range 213—323 K were matched against those calculated for different exchange rate constants $k_{obs.}$ using the Binsch computer program.[6] Parameters of the limiting slow-exchange spectra of complexes (**1**) and (**2**) (peak widths and positions) were obtained from several spectra recorded at temperatures at which the exchange was slow on the n.m.r. time-scale. The geminal coupling constants were found to be virtually independent of the temperature over the whole range studied. Values of T_2^* (spin–spin relaxation time) were obtained from the spectra recorded at the slow- and fast-exchange limits, while those in the exchange-broadened region were evaluated by linear interpolation. The Arrhenius and Eyring equations were used to evaluate E_a, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ from $k_{obs.}$.

Results and Discussion

Geometry of the Complexes.—Only one isomer is observed for complexes (**1**) and (**2**) in which the pyridine nitrogen of the cyclopalladated ligand and the N or P donors of L are mutually *trans*. This is evident from inspection of the low-field parts of the ^1H n.m.r. spectra. A representative spectrum of complex (**1g**) is shown in Figure 1. This has similar general features to that of complex (**1d**) reported earlier,[1] nevertheless a few brief



L

(1a) 4MeO$_2$C-py
(1b) py
(1c) 4Me-py
(1d) 3,5Me$_2$-py
(1e) 3,4Me$_2$-py
(1f) 2,4,6,Me$_3$-py
(1g) 4Me$_2$N-py
(2a) PPh$_3$
(2b) PMePh$_2$

Scheme.

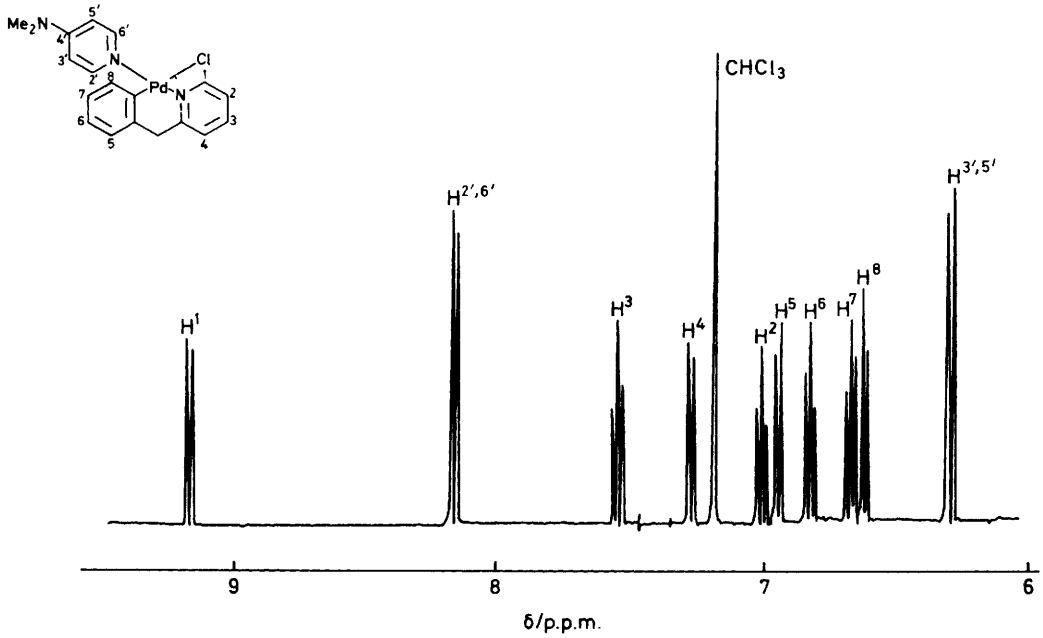


Figure 1. Low-field region of the 500-MHz ^{1}H n.m.r. spectrum of complex (**1g**) in $CDCl_3$

comments can be made. First, there is no indication of the presence of two isomers. The spectrum contains two definite well resolved ABCD patterns from both rings of the cyclopalladated ligand, together with a couple of sets of signals from the 4-dimethylaminopyridine ligand at δ 6.29 and 8.16 arising from the $H^{3',5'}$ and $H^{2',6'}$ protons, respectively. Secondly, the appearance of a doubled doublet at δ 6.61 and a doubled triplet at 6.66 from H^8 and H^7, respectively, conclusively indicates that both the signals experience anisotropic shielding from the ring current of the proximal ('*cis*') pyridine ring[7] and suggests a *trans* geometry for the two N donors. The upfield drift of these signals is somewhat less than in the case of corresponding cyclopalladated *NN*-dimethylbenzylamine derivatives[7,8] due to the puckered structure of (**1**). A study of molecular models has shown that the protons H^8 and H^7 approach only the edge of perpendicularly co-ordinated pyridine ligands, thus the shielding from the ring is not as strong as in the case of planar *NN*-dimethylbenzylamine complexes. The tentative assignment of the remaining low-field signals is depicted in Figure 1. Similar low-field patterns were also observed for other complexes (**1**) and (**2**). In the latter case a long-range coupling of aromatic protons with phosphorus was observed (Table 1).

It is generally accepted that a geminal axial proton appears at higher field compared with an equatorial one due to anisotropy of the C–C bond. In our case this is also supported by the observation that the low-field part of the AB quartet is broader than the high-field one. This can be ascribed to the quadrupole effect of the pyridine nitrogen, since the latter is '*trans*' to the equatorial and '*cis*' to the axial protons, providing noticeable broadening of the equatorial signal.

Dynamic Behaviour.—It has been previously proposed[1] that complexes of type (**1**) undergo inversion of the six-membered palladocycle (Scheme), which is manifested in broadening and coalescence of the signals of the geminal protons. Since pyridines with various electron-donating and electron-withdrawing groups can be introduced, complexes (**1**) are of evident convenience for investigation of the electronic effects in this process.

The rates of exchange of the two equally populated forms of

Table 1. Selected ^{1}H n.m.r. spectral data for complexes (1) and (2) in $CDCl_3$ at 30 °C

Complex	Ligand (L)	CH_3	$H^{2',6'}$	$H^{3',5'}$	H^1	H^8	CH_2	$H^{e,a}$	$H^{a,a}$	$^2J(CH_2)$/Hz
(1a)	$4MeO_2C$-py	3.87(s)	8.89(d)	7.77(d)	9.24(dd)	6.36(dd)	4.37(s)	4.85(d)	3.89(d)	14.0
(1b)	py	—	8.79(d)	*b*	9.29(dd)	6.47(dd)	4.45(s)	4.97(d)	4.02(d)	14.3
(1c)	4Me-py	2.29(s)	8.59(d)	8.43(d)	9.27(dd)	6.50(dd)	4.45(s)	4.94(d)	4.02(d)	14.5
(1d)	$3,5Me_2$-py	2.24(s)	8.22(s)	7.24(s)[c]	9.20(dd)	6.64(dd)	4.44(s)	4.90(d)	3.97(d)	14.4
(1e)	$3,4Me_2$-py	2.12(s)	8.33(d)	*b*	9.20(dd)	6.55(dd)	4.37(s)	4.85(d)	3.89(d)	14.0
		2.18(s)	8.49(s)							
(1f)	$2,4,6Me_3$-py	2.20(s)	—	6.87(s)	9.22(dd)	6.32(dd)	4.28(s)	4.68(d)	3.88(d)	14.0
		3.12(s)[d]								
(1g)	$4Me_2N$-py	2.90(s)	8.16(d)	6.29(d)	9.24(dd)	6.61(dd)	4.35(s)	4.83(d)	3.88(d)	13.7
(2a)	PPh_3	—	—	—	9.23(m)[e]	6.23(t)[e]	4.35(s)	4.89(d)	3.99(d)	13.8
(2b)	$PMePh_2$	1.84(d)[f]	—	—	9.02(dd)	6.65(m)[e]	4.27(s)	4.73(d)	3.90(d)	14.0

[a] At −50 °C. [b] Obscured by other resonances. [c] $H^{4'}$. [d] These 2,6-methyl groups at −50 °C give two sharp singlets at δ 3.38 and 2.64 (see text). [e] Due to long-range coupling with phosphorus. [f] ^2J(PH) 9.8 Hz. On decreasing the temperature to 10 °C the doublet collapses into a singlet; further decrease causes separation into a doublet.

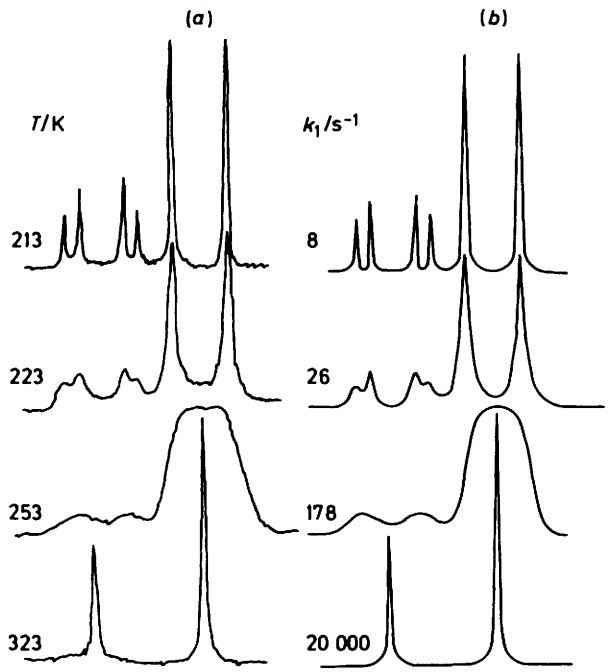


Figure 2. Observed (*a*) and calculated (*b*) spectra of complex (1f) in $CDCl_3$ at various temperatures

complexes (1), Scheme, were measured by line shape analysis of the AB quartet from the geminal CH_2 protons. In the case of (1f), analysis of the line broadening of the signals from pyridine 2,6-methyls can be also used to obtain corresponding $k_{obs.}$ values. An example of the procedure for evaluation of $k_{obs.}$ by comparing experimental and calculated spectra is presented in Figure 2. We have found that $k_{obs.}$ is independent of the concentration of complex (1b) in the range 0.07—0.60 mol dm^{-3}, as well as of the concentration of added pyridine in the range 0.1—1.0 mol dm^{-3}. Thus, the rate is given by equation (1) where

$$\text{Rate} = k_1[(1)][L]^0 \quad (1)$$

$k_{obs.} = k_1$. We also verified that $k_{obs.}$ is independent of the $2,4,6Me_3$-py concentration in the case of complex (1f). For the remaining complexes (1) it was assumed that $k_{obs.} = k_1$, and the representative set of k_1 obtained at 303 K together with the corresponding activation parameters are summarised in Table 2.

Complex (1f) has proved to be highly useful for elucidating some mechanistic features of the process under investigation. First, pyridine 2- and 6-methyls are markedly non-equivalent, the chemical shift separation (Δδ) reaching 0.74 p.p.m. in a low-temperature-limiting spectrum. This anisochronicity serves as additional evidence for a puckered structure of the cyclopalladated ligand. If the complex were planar, the methyl groups would be equivalent. Secondly, these methyl resonances are strongly deshielded compared to free $2,4,6Me_3$-py and observed at δ 3.38 and 2.64 (*cf.* δ 2.36 for the free ligand), probably due to CH • • • Pd interactions *via* the fifth and sixth co-ordination sites of the square-planar palladium(II) polyhedron.[7] Thirdly, the signals in question provide a probe to establish that there is no exchange between co-ordinated and added ligands in solution under the experimental conditions, since over the whole temperature range we do not observe collapse of the 2,6-methyl signals of the free and co-ordinated forms. Even in a high-temperature-limiting spectrum, separate signals are found at δ 3.12 and 2.36 for the co-ordinated and free ligands, respectively. Fourthly, the behaviour of the 2,6-methyl resonances reflects the inversion of the palladocycle, not a rotation of the ligand about the palladium–nitrogen bond as in the case of the system studied by Deeming and Rothwell.[9] This is strongly supported by the observation of identical coalescence temperatures for the *gem*-CH_2 and 2,6-$(CH_3)_2$ signals. The calculated values of $k_{obs.}$ also show excellent agreement, and the coincidence is demonstrated in Figure 3. These findings together with the rate law (1) indicate that the inversion occurs without loss of the co-ordinated pyridine ligand. Thus, electronic effects brought about by the substituted pyridines (pK_a 3.26—9.70) might influence k_1 or the corresponding free energies of activation $\Delta G^{\ddagger}$. Examination of Table 2 reveals, however, that in the case of complexes (1) $\Delta G^{\ddagger}$ is virtually independent of the nature of L, *i.e.* the process is insensitive to electronic effects, suggesting that the reaction mechanism does not involve formation of a polar transition state or intermediates.

We feel that our data are in better agreement with a concerted mechanism involving a planar transition state or intermediate without any bond breaking (Scheme). In other words, the isomerisation resembles a similar inversion in the case of 9,10-dihydroanthracenes. An alternative mechanism, which begins with cleavage of the palladium–nitrogen bond *trans* to L followed by inversion and subsequent re-ligation, can be ruled out on the following grounds. The lack of any dependence of $\Delta G^{\ddagger}$ on the nature of L is inconsistent with the palladium–

Table 2. Kinetic and activation parameters for the inversion of complexes (**1**) and (**2**) in $CDCl_3$

Complex	pK_a of L[a]	$10^{-3}k_1$[b]/s^{-1}	lg A	E_A/kJ mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta G^{\ddagger}$[c]/kJ mol^{-1}
(**1a**)	3.26	1.1	10.4 ± 1.0	43.6 ± 6.0	41.6 ± 4.0	−51.7 ± 3.0	57.1
(**1b**)	5.21	0.79	9.0 ± 1.0	37.5 ± 5.0	35.1 ± 1.6	−74.4 ± 4.0	57.3
(**1c**)	6.03	1.1	11.4 ± 1.0	49.3 ± 4.0	46.8 ± 4.2	−33.9 ± 6.0	56.9
(**1d**)	6.15	1.1	9.9 ± 0.6	40.1 ± 3.0	37.6 ± 4.0	−62.3 ± 6.2	56.9
(**1e**)	6.46	1.2	11.2 ± 1.0	44.3 ± 4.0	41.4 ± 3.3	−50.6 ± 3.0	56.6
(**1f**)	7.43	8.3	10.5 ± 0.6	40.1 ± 4.0	38.0 ± 4.0	−50.2 ± 5.0	53.1
(**1g**)	9.70	1.0	12.1 ± 1.0	53.9 ± 6.0	51.4 ± 6.0	−21.7 ± 3.0	57.9
(**2a**)		0.0034	13.5 ± 1.1	76.5 ± 10.0	73.6 ± 10.0	+4.2 ± 1.3	72.3
(**2b**)		3.7	8.4 ± 0.9	28.8 ± 6.0	26.3 ± 6.0	−91.1 ± 10.0	53.9

[a] Taken from D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, London, 1965. [b] Obtained at 303 K. [c] Calculated at 300 K.

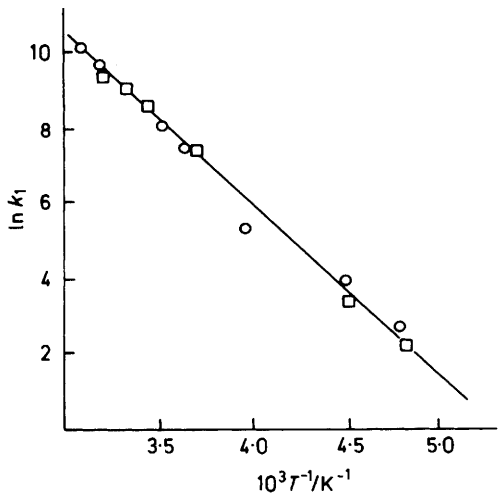


Figure 3. Arrhenius plot for complex (**1f**). The rate constants k_1 were calculated from analysis of the geminal CH_2 resonances (□) and 2,6-methyl resonances (○)

nitrogen bond breaking being rate-limiting.* The leaving ligand might experience an influence from ancillary ones, especially when they are *trans*. A mechanism in which the Pd–N bond breaking is fast, but subsequent inversion is slow, can also be discarded. It is inconsistent with the rate law (1), since pyridine from the bulk solvent should compete with 'intramolecular' pyridine ligand resulting in an apparent decrease in the activation barrier, *cf.* ref. 11. On the other hand, the dechelated intermediate should invert at least no slower than 9,10-dihydroanthracenes, since the constraints (see below) are much lower in this case. The rates of inversion of 9,10-dihydroanthracenes, however, are usually so fast that they cannot be measured by n.m.r. spectroscopy.[3] Thus, a mechanism *via* the rate-limiting inversion of dechelated intermediates appears to be ruled out.

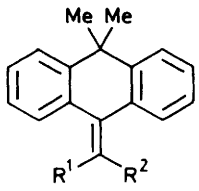
Investigation of molecular models suggests that the process is sterically unhindered if the ancillary pyridine L is strictly perpendicular to the palladium plane. Otherwise, interactions between C–H[8] and C–H$^{2'(6')}$ bonds and/or stacking ones between adjacent aromatic rings may slow down the inversion. Evidently, the steric requirements could be higher in the case of complex (**1f**), where the 2,6-methyl groups are much bulkier than C–H$^{2'(6')}$. However, the inversion of (**1f**) is characterised by an even lower activation barrier (by *ca.* 4 kJ mol^{-1} in terms of $\Delta G^{\ddagger}$) compared with other pyridine complexes, demonstrating that the 2,6 substituents favour the inversion. We believe that these methyl groups, which interact with palladium(II) through axial sites, serve as anchors fixing the most favourable perpendicular co-ordination of this ligand.† It should be noted that the relative lowering of the activation barrier in the case of complex (**1f**) is not high, indicating that some kind of additional stabilisation of the perpendicular co-ordination takes place. This could be a back donation from the metal d_{xy} orbital to the pyridine ligands. Such back bonding, which might be stronger for electron-poor pyridines, must hinder the rotation around the pyridine nitrogen–palladium bond, providing a free channel for the conformational change through the planar intermediate or transition state.

To test the importance of steric factors we have prepared a couple of complexes, (**2**), with phosphine ligands of different bulkiness. Tolman's cone angles have been used as a measure of the phosphine bulkiness.[12] Kinetic parameters were obtained in the absence of added ligands (phosphines) in this case. Complex (**2a**) with the less bulky phosphine (cone angle of $PMePh_2$ is 136°) is characterised by an activation barrier which falls in the range of those for pyridine complexes (**1**). However, on going to the much bulkier triphenylphosphine (cone angle 145°), the activation barrier increases by 18 kJ mol^{-1}. A similar trend has recently been observed[13] in the inversion of the four-membered palladocycles [Pd(CHRCOCHR)L_2] (R = COOMe) which is also thought to occur through a planar transition state. In our case the effect is greater due to an increase in the enthalpy of activation, Table 2. This result is in accord with theoretical predictions of Rabideau and co-workers[14] who estimated the relative strain energy as a function of the folding angle for axial to equatorial inversion of 9-alkyl-9,10-dihydroanthracenes. The maximum energy difference on the strain-energy profile (top-to-bottom difference) is *ca.* 29 and 88 kJ mol^{-1} for 9-alkyl = methyl and t-butyl, respectively. In our case the activation enthalpy $\Delta H^{\ddagger}$ is 26 and 73 kJ mol^{-1} for complexes (**2b**) and (**2a**), respectively. Therefore, it can be assumed that the activation enthalpy is associated with the strain energy, *i.e.* enhancement of the strain energy should lead to an increase in the enthalpy of activation.

The large difference in $\Delta S^{\ddagger}$ for (**2a**) and (**2b**) is also worth mentioning. Two factors may be responsible for the much more positive value of $\Delta S^{\ddagger}$ in the former case. The first may be a

* Rate-limiting metal–nitrogen bond rupture was recently proposed[10] to account for the mechanism of topomerisation of [*o*-(diethylaminomethyl)phenyl]halogenodimethylstannanes.

† One of the referees has suggested another possible explanation of this effect. The decrease in the activation barrier in the case of (**1f**) may be due to destabilisation of the ground state, since the axial interactions can be considered[7] as destabilising.



(4)

common compensating effect provided by the much higher value of $\Delta H^{\ddagger}$. The second, and probably more important, can be associated with increased 'disorder' in the transition state in the case of (**2a**) compared with (**2b**). The data in Table 2 suggest that the 'anisotropic' $PMePh_2$ ligand in (**2b**) should be properly oriented in the transition state so as to diminish the unfavourable effect of two bulky phenyl rings by directing them towards the co-ordinated chloride. This seems to be unnecessary in the case of (**2a**), since such a configuration would result in unfavourable interactions between the phenyl rings of PPh_3 and of the palladated ligand.

The absolute values of the activation parameters found can be compared with those obtained previously for 9,10-dihydro-9,9-dimethyl-10-methyleneanthracenes (**4**).[4] Molecules (**1**), (**2**), and (**4**) have a planar function at the 10th position of the 9,10-dihydroanthracene skeleton which, probably, slows down the rate of conformational isomerisation. In the case of (**1**) and (**2**) this is a palladium plane, but in the case of (**4**) this is an exocyclic double-bond fragment $=CR^1R^2$. The rate of inversion became measurable when R^1 = Br and R^2 = Br, Ph, or COOMe, *i.e.* in the case of rather bulky groups. If R^1 = H, the 9,9-dimethyl groups appear as one singlet over the whole temperature range, demonstrating that this isomerisation is also very sensitive to steric effects. In a given R^2 series $\Delta G^{\ddagger}$ decreases from 75 to 64 kJ mol^{-1}, $\Delta H^{\ddagger}$ being constant at 67 kJ mol^{-1}.[4] The highest value of $\Delta G^{\ddagger}$ in Table 2 is 72 kJ mol^{-1} (**2a**) while the lowest is 53 kJ mol^{-1} (**1f**). The values obtained in both systems are similar, confirming the proposed mechanism for inversion of six-membered palladocycles.

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Received 27*th March* 1985; *Paper* 5/512