Kinetics and Mechanism of Ortho-palladation of Ring-substituted *NN*-Dimethylbenzylamines

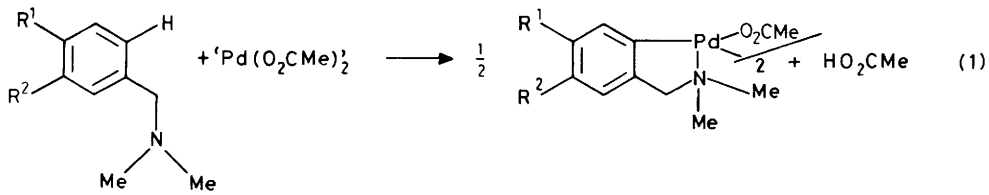
Alexander D. Ryabov,* Inna K. Sakodinskaya, and Anatoly K. Yatsimirsky *
Department of Chemistry, Moscow State University, 119 899 GSP, Moscow V-234, U.S.S.R.

Addition of excess of *NN*-dimethylbenzylamine to a chloroform solution of $[Pd_3(O_2CMe)_6]$ leads to instantaneous depolymerisation of the trimer giving the monomer *trans*-$[Pd(O_2CMe)_2(PhCH_2NMe_2)_2]$. Reversible dissociation of the amine from the latter affords a pseudo-three-co-ordinate 14-electron intermediate $[Pd(O_2CMe)_2(PhCH_2NMe_2)]$ which undergoes subsequent rate-limiting ortho-palladation to form the cyclopalladated acetato-bridged dimer $[\{Pd(O_2CMe)(C_6H_4CH_2NMe_2)\}_2]$. The rate-limiting step is electrophilic in character; the slope of the corresponding Hammett plot for differently ring-substituted *NN*-dimethylbenzylamines is −1.6. The kinetic isotope effect, k_H/k_D, for $PhCH_2NMe_2$ is 2.2 ± 0.2. The activation entropy for the rate-limiting step is very negative, *ca.* −250 J K^{-1} mol^{-1} for $PhCH_2NMe_2$, suggesting a highly ordered tight transition state. This dissociative path is a factor of *ca.* 100 faster than a parallel one, involving the 16-electron monomer *trans*-$[Pd(O_2CMe)_2(PhCH_2NMe_2)_2]$ but without loss of the amine. Ortho-palladation is not rate-limiting in acetic acid solvent, where slow cleavage of acetate bridges in polynuclear palladium species occurs, affording a vacant co-ordination site for subsequent rapid ortho-palladation. A comparison of intra- and inter-molecular activations of carbon–hydrogen bonds in arenes by palladium(II) in terms of 'effective molarities' shows that the ratio k_{intra}/k_{inter} is not less than 3.6 × 10^2 mol dm^{-3}.

Considerable attention has recently been devoted to the mechanistic study of intramolecular organic reactions.[1] An important feature of these, compared with chemically related intermolecular counterparts, is the remarkably high relative rates due to proximity effects.[2] Similar effects could be responsible for the apparent preference for intramolecular (cyclometallation) *versus* intermolecular activation of carbon–hydrogen bonds by transition-metal complexes. The literature, however, contains only a few comparative investigations of intra- and inter-molecular activation of such bonds by metal centres, which have been briefly summarised.[3]

Intermolecular activation of carbon–hydrogen bonds by metal complexes is the key step in various catalytic reactions.[4] In particular, the cleavage of aromatic C–H bonds by palladium(II) to form σ-bound arylpalladium intermediates is involved in oxidative coupling and vinylation of arenes, the kinetics of which has been studied.[5,6] Ortho-palladation might be a suitable intramolecular counterpart for the two processes with which to study the rate-determining C–H bond rupture. At the same time cyclopalladation, which has been intensively explored in recent years[7] with special relevance to organic syntheses,[8] has not been kinetically studied in detail. To our knowledge the only such study reported was of the intramolecular cyclisation of *trans*-$[PdCl_2(PhN{=}NPh)_2]$ to give di-μ-chloro-bis[2-(phenylazo)phenyl-C^1,N]dipalladium(II), revealing a general base catalysis in the course of the C–H bond cleavage.[9] In several other works cyclopalladation was shown to be electrophilic in character.[10] This was deduced from the preference for attack of palladium(II) on a more electron-rich aromatic ring, when substrates with two or more rings with different electron densities were involved. Deeming and Rothwell[11] demonstrated that cyclopalladation would occur in the co-ordination plane of Pd^{II} and suggested the existence of a three-co-ordinate intermediate.

For the present kinetic study we chose the interaction of ring-substituted *NN*-dimethylbenzylamines with palladium(II) acetate in chloroform as solvent [equation (1)]. The reaction was thought to occur through initial N-co-ordination of *NN*-dimethylbenzylamines, with subsequent intramolecular attack of Pd^{II} on C–H bonds. Thus, the kinetic study of reaction (1)



(1) (2) (1)

(a) R^1 = Me, R^2 = H
(b) R^1 = R^2 = OMe
(c) R^1 = R^2 = H
(d) R^1 = OMe, R^2 = H
(e) R^1 = Cl, R^2 = H
(f) R^1 = NO_2, R^2 = H

allows one to discuss the mechanistic features of cyclopalladation as well as to evaluate the magnitude of the proximity effect in electrophilic aromatic substitution by palladium(II). We have also studied reaction (1) in acetic acid media, since this solvent is usually employed for activation of arenes by palladium(II) acetate in catalytic reactions.[4b]

Experimental

Instrumentation.—U.v. spectra were recorded on a Hitachi 356 spectrophotometer, i.r. spectra for KBr discs or Nujol mulls on a JASCO 200 spectrophotometer, and 60-MHz ^{1}H n.m.r. spectra on a Tesla BS-467 instrument in $CDCl_3$ as solvent using tetramethylsilane as internal standard. Melting points were determined with a VEB Analytic Dresden PHMK apparatus and are uncorrected.

Reagents.—*NN*-Dimethylbenzylamine (**1c**) and *NN*-diethylbenzylamine were Koch-Light and Reakhim reagents, respectively. All other ring-substituted *NN*-dimethylbenzylamines, as well as the deuteriated amine $C_6D_5CD_2NMe_2$, were prepared as described previously.[12] Palladium(II) acetate was obtained according to the procedure of Wilkinson *et al.*[13]

Preparation of Cyclopalladated Complexes (**2**).—The synthesis and characterisation of di-μ-acetato-bis[(*o*-dimethylaminomethylphenyl-*C*,*N*)palladium(II)] (**2c**) was reported previously.[14,15] We have found that all the amines (**1**) readily undergo ortho-palladation at ambient temperature in chloroform as solvent. A representative small-scale procedure is given below.

Palladium(II) acetate (0.060 g, 0.27 mmol) was dissolved in chloroform (5 cm^3) and *NN*-dimethyl-4-nitrobenzylamine (**1f**) (0.05 cm^3, 0.31 mmol) was added. The mixture was allowed to stand overnight at room temperature. The solvent was then removed *in vacuo* and the residue was dissolved in acetic acid (3 cm^3). Addition of water (3 cm^3) to this solution caused precipitation of a greenish compound which was filtered off, washed with water, and air dried. The compound was then dissolved in chloroform (1 cm^3) and precipitated by addition of hexane. The precipitate was filtered off, washed with hexane, and air dried to afford 0.030 g (22%) of di-μ-acetato-bis[(2-dimethylaminomethyl-5-nitrophenyl-C^1,*N*)palladium(II)] (**2f**) (Found: C, 37.7; H, 4.0; N, 8.2. $C_{22}H_{24}N_4O_8Pd_2$ requires C, 38.5; H, 3.5; N, 8.2%). The spectral characteristics of (**2f**) and all the other cyclopalladated complexes (**2**), prepared as yellow solids, are summarised in Table 1.

Diacetatobis(NN-*dimethylbenzylamine*-N]*palladium*(II).—Palladium(II) acetate (0.091 g, 0.404 mmol) was dissolved in acetone (15 cm^3) and *NN*-dimethylbenzylamine (0.13 cm^3, 0.867 mmol) was added. The solution was stirred at room temperature for 1 min and diethyl ether (50 cm^3) was then added. The resulting solution was kept at *ca.* −5 °C for 2 h, producing orange crystals. These were filtered off, washed with hexane, and dried in the air to yield 0.054 g (27%) of the unstable product which slowly loses acetic acid even in the solid state, transforming into the cyclopalladated dimer (**2c**). Its i.r. spectrum, recorded immediately after preparation, showed bands for unidentate acetato-ligands[13,16,17] at 1 625, 1 370, and 1 315 cm^{-1}.

Kinetic Measurements.—These were made in acetic acid and chloroform as solvents. The former was purified by the standard procedure.[18] Acetic acid solutions of palladium(II) acetate in the presence of sodium acetate were kept for at least 24 h at 50 °C in order to equilibrate oligomeric forms of the palladium salt.[19] Reproducible kinetic data in chloroform were obtained when the solvent was purified according to the following procedure. Commercially available chloroform (Kiev Khimfarmzavod) was washed three times with water, dried over $MgSO_4$, and kept in the dark. It was distilled before use and utilized within a day. Freshly prepared chloroform solutions of palladium(II) acetate were used throughout.

Unless otherwise stated the reaction progress was monitored spectrophotometrically by measuring the increase in absorbance due to formation of cyclopalladated dimers (**2**) at the wavelength of the maximum absorption (usually at 330 nm). All runs were made under pseudo-first-order conditions with at least a 10-fold excess of compound (**1**) over the total concentration of Pd^{II}, in 10-mm quartz cells, placed in the thermostatted cell compartment of the spectrophotometer. The reactions were initiated either by addition of the amines to solutions of palladium(II) acetate ($MeCO_2H$–NaO_2CMe system) or by addition of palladium(II) solutions to the amines dissolved in pure acetic acid or chloroform. In acetic acid solvent good first-order plots of absorbance *versus* time were obtained which were analysed by plotting $\ln[A_\infty/(A_\infty - A)]$ *versus* time. In chloroform, biphasic kinetic curves were obtained. The first fast process arising from monomerisation of the palladium species (see below) was complete within 1—2 min of mixing the reagents. The second one leading to the final products gave good first-order plots which were analysed as above. Some less accurate kinetic measurements were also made using a ^{1}H n.m.r. technique in $CDCl_3$ as solvent. Compound (**1c**) or (**1f**) was added to a frozen solution of palladium(II) acetate in the presence of nitromethane (as a reference) in a 5-mm n.m.r. tube. The solution was then warmed to 25 °C and the reaction progress was followed by integrating the downfield resonance of the N–CH_3 protons of the cyclopalladated complexes (**2**). In these experiments much higher concentrations of both palladium(II) acetate (0.1 compared with 0.001 mol dm^{-3} monitored by spectrophotometry) and the amines were employed.

Form of the Amines in Acetic Acid.—Since it is known[20] that nitrogen-containing ligands can exist in acetic acid in free non-protonated form, we undertook a qualitative study of *NN*-dimethylbenzylamine in different solvents. In non-protonating methanol, compound (**1c**) had an absorption maximum at 262 nm (ε 120 dm^3 mol^{-1} cm^{-1}). Addition of perchloric acid to this solution caused a shift of the maximum to 268 nm (ε = 180 dm^3 mol^{-1} cm^{-1}). The same spectrum was obtained in pure acetic acid ($\lambda_{max.}$ = 268 nm, ε = 180 dm^3 mol^{-1} cm^{-1}), addition of $HClO_4$ having no effect in this case. This result shows that *NN*-dimethylbenzylamine undergoes protonation in acetic acid and equilibrium (2) (R = substituted phenyl group) is strongly shifted to the left in this solvent.

$$[RCH_2NHMe_2]^+O_2CMe^- \overset{K_2}{\rightleftharpoons} RCH_2NMe_2 + HO_2CMe \quad (2)$$

Results and Discussion

Analysis of the Products.—Examination of Table 1 shows that the ring-substituted ortho-palladated *NN*-dimethylbenzylamines show minor variations in spectral properties compared to the unsubstituted complex (**2c**), which has been reported previously.[14,15] These dimeric acetato-bridged compounds have an *ab,hg* (*trans*) configuration as is seen from the single ^{1}H n.m.r. resonance of the acetate methyls and only one AB quartet for RCH_2N protons, *cf.* ref. 11*b*. The i.r. data confirm the bridging character of the acetato-ligands.[21] Addition of [$^2H_5$]pyridine to $CDCl_3$ solutions of the dimers (**2**) leads to a marked simplification of the ^{1}H n.m.r. spectra, indicative of conversion of folded boat-type dimers into planar monomeric

Table 1. Some data for ortho-palladated complexes (**2**)

Compound	Yield/%	M.p./°C	U.v. spectra[a] $\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})	I.r. spectra (cm^{-1})	^{1}H N.m.r.[b]
(**2a**)	80	144—146	340(1 090) 330(960)	1 560, 1 410 (O_2CMe)	6.85—6.75 (m, R), 3.58 and 3.02 (d, *J* 13, RCH_2N), 2.80 and 2.05 (s, NCH_3), 2.23 (s, RCH_3), 2.05 (s, O_2CMe)
(**2b**)	60	138—140 (decomp.)	340(2 110) 340(1 650)	1 575, 1 415 (O_2CMe)	6.58 and 6.53 (s, R), 3.83 and 3.80 (s, OCH_3), 3.61 and 3.12 (d, *J* 13, RCH_2N), 2.83 and 2.08 (s, NCH_3), 2.08 (s, O_2CMe)
(**2c**)	30	210—211[c]	330(1 240) 330(1 015)	1 590, 1 570, 1 415 (O_2CMe)	7.00—6.83 (m, R), 3.62 and 3.09 (d, *J* 14, RCH_2N), 2.79 and 2.06 (s, NCH_3), 2.06 (s, O_2CMe)
(**2d**)	70	164—166	330(1 420) 330(1 450)	1 580, 1 418 (O_2CMe)	6.62—6.53 (m, R), 3.75 (s, OCH_3), 3.63 and 3.08 (d, *J* 13, RCH_2N), 2.80 and 2.05 (s, NCH_3), 2.05 (s, O_2CMe)
(**2e**)	75	186—188 (decomp.)	330(1 650) 330(1 590)	1 585, 1 575, 1 415 (O_2CMe)	7.00—6.75 (m, R), 3.60 and 3.15 (d, *J* 13, RCH_2N), 2.83 and 2.15 (s, NCH_3), 2.12 (s, O_2CMe)
(**2f**)	22	194—196 (decomp.)	330(4 720)[d] 330(4 800)[d]	1 575, 1 420 (O_2CMe); 1 515, 1 335 (NO_2)	7.95 [dd, $^3J(H^4H^3)$ 8, $^4J(H^4H^6)$ 2], 7.85 (s, H^6), 7.06 (d, *J* 8, H^3), 3.75 and 3.29 (d, *J* 15, RCH_2N), 2.83 and 2.14 (s, NCH_3), 2.14 (s, O_2CMe)

[a] First value in acetic acid solvent, second in chloroform. [b] In $CDCl_3$; *J* in Hz. [c] Ref. 14. [d] Shoulder.

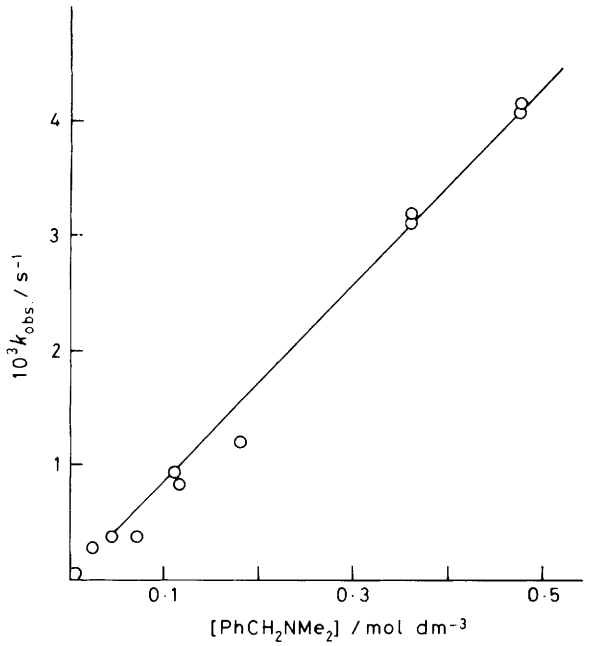


Figure 1. The dependence of $k_{obs.}$ on the concentration of *NN*-dimethylbenzylamine for palladation of the amine by $[Pd_3(O_2CMe)_6]$ in acetic acid at 50 °C

species $[Pd(O_2CMe)(C_6H_4CH_2NMe_2)([^2H_5]py)]$, see also ref. 17. For example, in the case of complex (**2c**) an AB quartet for the methylene protons transforms into a singlet at δ 3.95, while the N–CH_3 groups become equivalent and appear at δ 2.80. Since such monomeric species exist only in solution,[17] we did not attempt to isolate the complexes as solids. It is noteworthy that palladium(II) acetate proved to be a more powerful metallating agent compared with sodium tetrachloropalladate(II). While the latter does not give an ortho-palladated derivative of compound (**1f**),[22] the former affords the nitro-substituted complex (**2f**) in 22% yield.[23]

Kinetics of Palladation by $[Pd_3(O_2CMe)_6]$ *in Acetic Acid.*—When compound (**1**) is present in large excess, the conversion of palladium(II) acetate into complex (**2**) is usually not less than 85% complete. The dependence of the pseudo-first-order rate constant, $k_{obs.}$, on *NN*-dimethylbenzylamine concentration is shown in Figure 1. The reaction is first-order in the amine concentration over the range 0.005—0.5 mol dm^{-3}, $k_{obs.}$ being independent of the total concentration of palladium(II) acetate in the range (0.5—2.0) × 10^{-3} mol dm^{-3}. Thus, the reaction rate follows equation (3) where $k_3 = k_{obs.}/[(\mathbf{1})]$. The ring-substi-

$$d[(\mathbf{2})]/dt = k_3[(\mathbf{1})][Pd^{II}] \quad (3)$$

tuted amines also follow this rate law. The second-order rate constants k_3 are summarised in Table 2. These are virtually independent of the nature of compound (**1**). The kinetic isotope effect, $k_3(PhCH_2NMe_2)/k_3(C_6D_5CD_2NMe_2) = 1.1 \pm 0.1$, is too small to be considered as primary. This indicates that under these particular conditions the activation of *ortho* C–H bonds of compound (**1**) is not rate-determining. Taking into account that (*i*) the amines exist in protonated form in acetic acid [equation (2)], (*ii*) palladium(II) acetate is a trimer in this solvent[13,19] having six non-labile bridging acetates,[24] and (*iii*) we obtained no spectrophotometric evidence for the formation of intermediates, we assume the rate-determining step to be the rupture of bridging acetates in $[Pd_3(O_2CMe)_6]$ by $[RCH_2NHMe_2]^+$-O_2CMe^- to produce species either with vacant co-ordination sites or with more labile terminal acetates in which subsequent rapid ortho-palladation occurs. The nucleophilic attack of sodium and lithium acetates on $[Pd_3(O_2CMe)_6]$ has been

Table 2. Kinetic and thermodynamic parameters of reaction (1) under various conditions

Substrate		$[Pd_3(O_2CMe)_6]$ θ_c/°C	$[Pd_3(O_2CMe)_6]$ 10^3k_3/dm^3 mol^{-1} s^{-1}	$Na_2[Pd_2(O_2CMe)_6]$ 10^4k_5[a]/s^{-1}	$[Pd(O_2CMe)_2(RCH_2NMe_2)_2]$ θ_c/°C	$[Pd(O_2CMe)_2(RCH_2NMe_2)_2]$ 10^2K_{10}/mol dm^{-3}	$[Pd(O_2CMe)_2(RCH_2NMe_2)_2]$ 10^3k_{11}/s^{-1}
4-$MeC_6H_4CH_2NMe_2$	(**1a**)	50	7.8 ± 0.7	4.2 ± 0.3	25	1.5 ± 0.2	5.0 ± 0.7
3,4-$(MeO)_2C_6H_3CH_2NMe_2$	(**1b**)	50	8.3 ± 0.7	4.4 ± 0.3	25	2.7 ± 0.3	3.05 ± 0.35
$PhCH_2NMe_2$	(**1c**)	40	3.3 ± 0.2[b]	7.6 ± 0.4	25	1.35 ± 0.10[c]	4.3 ± 0.5[c]
		50	8.7 ± 0.4[b]		40	8.9 ± 0.9[c]	5.5 ± 0.7[c]
		55	11.5 ± 0.6[b]				
4-$MeOC_6H_4CH_2NMe_2$	(**1d**)	50	6.3 ± 0.4	3.5 ± 0.2	25	2.0 ± 0.2	2.7 ± 0.3
4-$ClC_6H_4CH_2NMe_2$	(**1e**)	50	6.8 ± 0.3	14.8 ± 0.9	25	2.9 ± 0.3	1.0 ± 0.1
$C_6D_5CD_2NMe_2$		50	7.8 ± 0.4	7.2 ± 0.5	25		1.9 ± 0.2[d]
$PhCH_2NEt_2$		60	2.0 ± 0.1				

[a] At 50 °C. [b] $\Delta H_3^{\ddagger}$ = 69 ± 5 kJ mol^{-1}, $\Delta S_3^{\ddagger}$ = −71 ± 16 J K^{-1} mol^{-1}. [c] ΔH_{10}° = 97 ± 10 kJ mol^{-1}, ΔS_{10}° = 290 ± 34 J K^{-1} mol^{-1}; $\Delta H_{11}^{\ddagger}$ = 11 ± 12 kJ mol^{-1}, $\Delta S_{11}^{\ddagger}$ = −254 ± 40 J K^{-1} mol^{-1}. [d] Calculated assuming the same value of K_{10} for (**1c**) and its deuteriated analogue.

proposed[19] as rate-limiting for the conversion of the trimer into the dimeric species $M_2[Pd_2(O_2CMe)_6]$ [equation (4)], and the

$$2[Pd_3(O_2CMe)_6] + 6MO_2CMe \rightleftharpoons 3M_2[Pd_2(O_2CMe)_6] \quad (4)$$

reported second-order rate constants at 25 °C are 2.7 × 10^{-3} and 2.9 × 10^{-3} dm^3 mol^{-1} s^{-1} for LiO_2CMe and NaO_2CMe, respectively. The latter can be compared with k_3 for compound (**1c**) when extrapolated to 25 °C using data from Table 2. The resulting value of 0.9 × 10^{-3} dm^3 mol^{-1} s^{-1} is somewhat lower than those above, probably due to a steric effect of a more bulky counter ion $[RCH_2NHMe_2]^+$, since salts are likely to occur in associated form in acetic acid as solvent.[20] Evidently, the steps of interest occur only after the rate-limiting cleavage of acetato-bridges in $[Pd_3(O_2CMe)_6]$, and this system is of no use for elucidating the intimate mechanism of ortho-palladation. In order to obtain more informative kinetic data we turned to the palladium species $Na_2[Pd_2(O_2CMe)_6]$ formed by reaction (4), since the dimer possesses terminal, readily substituted,[25] acetato-ligands.

Kinetics of Palladation by $Na_2[Pd_2(O_2CMe)_6]$ *in Acetic Acid.*—Conversion of $[Pd_3(O_2CMe)_6]$ into $Na_2[Pd_2(O_2CMe)_6]$ is nearly complete at $[NaO_2CMe]$ = 0.1 mol dm^{-3} and the concentration of the dimer shows little variation with further increase in $[NaO_2CMe]$ up to 0.4 mol dm^{-3}.[19] Under these conditions the rate of reaction (1) can easily be measured at 50 °C. The reaction proceeds without formation of any intermediates according to spectrophotometry. As in the case of $[Pd_3(O_2CMe)_6]$, the pseudo-first-order rate constant shows no variance with the total palladium(II) concentration over the range (0.5—2.0) × 10^{-3} mol dm^{-3}, and $k_{obs.}$ is a linear function of [*NN*-dimethylbenzylamine] in the range (0.08—2.0) × 10^{-1} mol dm^{-3}. Figure 2 shows that an increase in $[NaO_2CMe]$ from 0.1 to 0.5 mol dm^{-3} results in a decrease in the second-order rate constant, $k_{obs.}/[(\mathbf{1c})]$. A plot of $k_{obs.}/[(\mathbf{1c})]$ *versus* $[NaO_2CMe]^{-1}$ (not shown) was found to be linear without any significant intercept. These findings suggest the rate expression (5), where $k_5 = k_{obs.}[NaO_2CMe]/[(\mathbf{1})]$. The ring-substituted

$$d[(\mathbf{2})]/dt = k_5[(\mathbf{1})][Pd^{II}]/[NaO_2CMe] \quad (5)$$

NN-dimethylbenzylamines behave quite similarly, and the corresponding rate constants k_5 are summarised in Table 2. Measurements with $C_6D_5CD_2NMe_2$ reveal the absence of a primary kinetic isotope effect, k_H/k_D = 1.05 ± 0.1. The value of k_5 displays a moderate, but definite, dependence on the electron-donor properties of the amines. As shown in Figure 3,

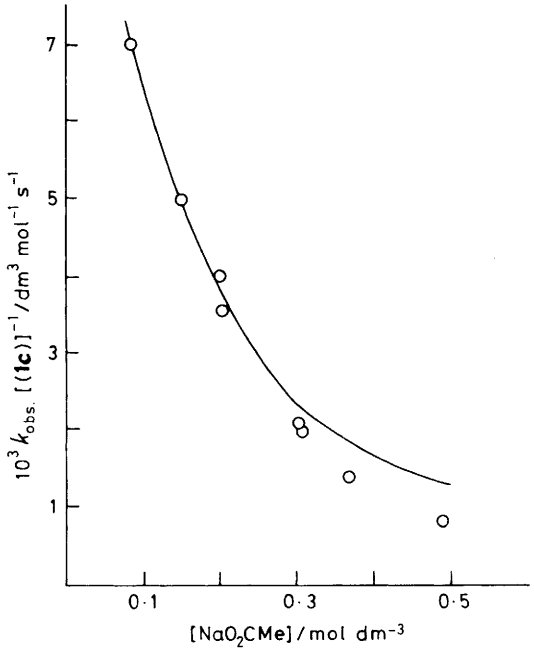
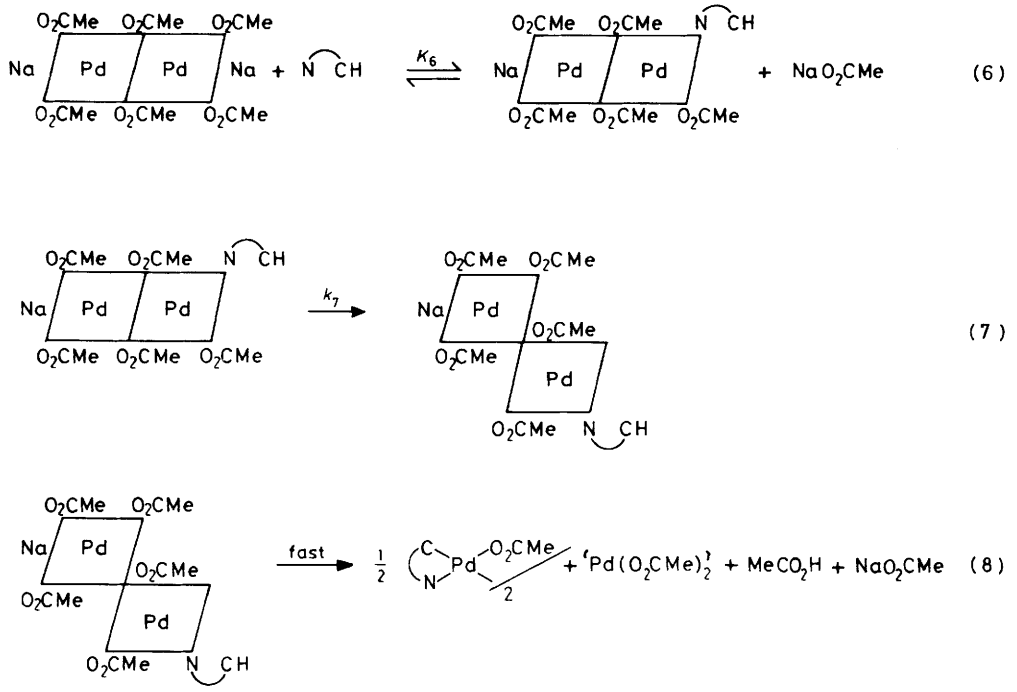


Figure 2. Plot of the second-order rate constant $k_{obs.}/[(\mathbf{1c})]$ *versus* $[NaO_2CMe]$ for palladation of *NN*-dimethylbenzylamine by $Na_2[Pd_2(O_2CMe)_6]$ in acetic acid at 50 °C

electron-withdrawing substituents result in higher rates of reaction; the slope of the Hammett plot of log k_5 against σ_p is +1.4. At the same time the correlation between log k_5 and σ_m is very poor.

The rate law (5) appears to be general for reactions involving $Na_2[Pd_2(O_2CMe)_6]$.[25] The inverse dependence of the rate on $[NaO_2CMe]$ suggests a pre-equilibrium co-ordination of the amine to palladium followed by a rate-determining step. We believe that, as in the case discussed above, the latter is not ortho-palladation of amine (**1**), but rather the creation of a vacant co-ordination site for subsequent rapid cyclisation *via* either partial acetate-bridge cleavage[26] or loss of terminal acetate.[25b] Of the two we prefer a partial dissociation as proposed by Powell[26,27] for acetate-bridge inversion (Scheme 1). Three observations confirm that ortho-palladation is not rate-determining: (*i*) too low a magnitude of kinetic isotope effect; (*ii*) a positive slope of the Hammett plot, which is inconsistent with the electrophilic nature of cyclopalladation; and (*iii*) a good correlation between log k_5 and σ_p, Figure 3,



Scheme 1.

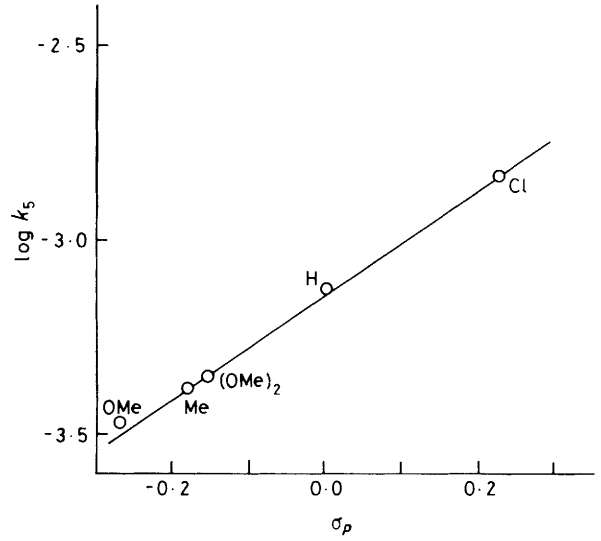


Figure 3. Hammett plot of log k_5 *versus* σ_p

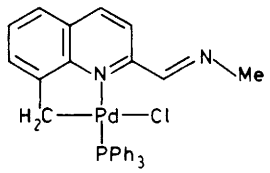
without any statistical correction for compound (**1b**). Such a correction would be necessary if ortho-palladation is rate-limiting, since only position 6 of (**1b**) is attacked by palladium(II),[28] while both positions 2 and 6 are available for all the remaining amines. On the basis of Scheme 1, and taking into account that equation (5) contains the total concentration of compound (**1**) which is protonated in the acid solvent, one obtains equation (9). The value of K_2 should increase on going

$$k_5 = K_2K_6k_7 \qquad (9)$$

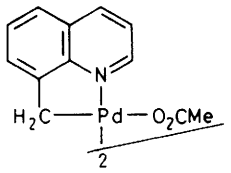
to *NN*-dimethylbenzylamines with electron-withdrawing ring substituents, since pK_a for similarly substituted benzylamines follows the Hammett correlation with a negative slope.[29] Nothing is known about substituent effects on K_6 and k_7, but if the effect on K_2 dominates, the observed dependence in Figure 3 could readily be explained by an increase in the concentration of the free non-protonated form of (**1**) with increasing acceptor strength of the ring substituents.

Cyclometallation by Palladium(II) *Acetate in Chloroform.—Spectral studies.* N-Donor ligands resistant to cyclopalladation are known to react rapidly with palladium(II) acetate in a number of solvents to afford N-bound complexes.[13,16,17,30] When the ratio [ligand]/[Pd^{II}] is $\geqslant 2:1$, bis adducts of the type *trans*-[$Pd(O_2CMe)_2L_2$] are formed, but when the ratio is *ca.* 1:1 binuclear acetato-bridged dimers [{$Pd(O_2CMe)_2L$}$_2$] can be isolated. Obviously, these species can readily be formed in the course of cyclopalladation of N-donor ligands. Thus, the question arises as to whether such N-bound species are reactive intermediates or not. In particular, it has been demonstrated[31] that when 8-methylquinoline-2-carbaldehyde-*N*-methylimine (mqa) is treated with palladium(II) acetate for 1 min the bis adduct [$Pd(O_2CMe)_2(mqa)_2$] forms, co-ordination occurring through the imine nitrogen. An increase in both time and temperature leads to formation of cyclopalladated species which, after work-up, have been isolated and characterised as (**3**). On the other hand, it has also been reported[11b] that palladation of 8-methylquinoline to afford complex (**4**) proceeds with no detectable intermediate. This is why we started with a low-temperature ^1H n.m.r. investigation of an interaction between palladium(II) acetate and amines (**1**) in $CDCl_3$ solvent in the hope of characterising species formed prior to ortho-palladation.

The interaction between 1 molar equivalent of palladium(II) acetate and 2 molar equivalents of amine (**1c**) was followed by ^1H n.m.r. spectroscopy (Figure 4). The first spectrum [Figure 4(*a*)] was recorded immediately after warming the frozen solution of the reactants to −40 °C. Analysis of the 'methylene' and 'acetate' group regions of the spectrum reveals the presence of two major species. In the 'acetate' region two signals of approximately equal intensity are observed at δ 2.04 and 1.79, which can be ascribed to bridging and terminal acetates, respectively, of the dimer complex [{$Pd(O_2CMe)_2(PhCH_2$-



(3)



(4)

$NMe_2)\}_2]$.[16,17,30] A signal at δ 1.92 can be assigned to terminal acetates of the monomer $[Pd(O_2CMe)_2(PhCH_2NMe_2)_2]$. A singlet at δ 3.80 and the broader one at δ 3.50 refer to the methylene ($PhCH_2N$) protons of the monomer and the dimer, respectively. Both signals are shifted downfield compared to that of free amine (**1c**) (δ 3.40), reflecting co-ordination of nitrogen to the metal. The relative concentration of the dimer exceeds that of the monomer by 25%. There is another complex in solution, its concentration being much lower than that of the dimer and the monomer. It has an apparent AB quartet centred at δ 4.30 (J = 13 Hz) and a signal at δ 2.55, which is presumably a downfield part of a N-methyl doublet. At present we have no adequate interpretation of these signals. The spectrum shown in Figure 4(*b*) was recorded at −40 °C after 35 min. It can be seen that the dimer slowly transforms into the monomer, resulting in an increase in intensities of the signals at δ 3.80 and 1.92 with a concomitant decrease in those at δ 3.50, 2.04, and 1.79. An increase in temperature to 0 °C leads to almost complete conversion of the dimer into $[Pd(O_2CMe)_2(PhCH_2NMe_2)_2]$, the ratio [monomer]/[dimer] being *ca.* 11:1, Figure 4(*c*). The next spectrum [Figure 4(*d*)], recorded after 30 min at the same temperature, demonstrates that new signals begin to develop due to formation of the product (**2c**), *cf.* data in Table 1. On the other hand, the resonances due to the dimer have practically disappeared. Further warming of the solution to 30 °C [Figure 4(*e*)] leads to rapid ortho-palladation to form the acetato-bridged binuclear complex (**2c**) together with $[PhCH_2NHMe_2]^+O_2CMe^-$. Broad signals at δ 3.72 and 2.37 refer to the methylene and methyl protons of the protonated amine, respectively, while an AB quartet centred at δ 3.35 (J = 14 Hz) and a singlet at δ 2.79 arise from methylene and downfield methyl protons of ortho-palladated *NN*-dimethylbenzylamine. The most intense signal at δ 2.04 is a superposition of the acetate from $[PhCH_2NHMe_2]^+O_2CMe^-$, bridging acetate, and upfield N-methyl, the latter two from complex (**2c**). This spectrum shows no variation with time.* The nitro-substituted amine (**1f**) interacts with palladium(II) acetate in a similar fashion. At 0 °C the monomer $[Pd(O_2CMe)_2(4\text{-}NO_2C_6H_4CH_2NMe_2)_2]$ has distinct resonances at δ 3.75 (RCH_2N), 2.43 ($N\text{–}CH_3$), and 1.90 (O_2CMe). All these spectral observations suggest that an interaction between trimeric palladium acetate and *NN*-dimethylbenzylamines can be represented by Scheme 2 where the major identified species are shown. The most important conclusion is that formation of the ortho-palladated complex (**2**) in the presence of excess of the ligand is preceded by nearly quantitative conversion of $[Pd_3(O_2CMe)_6]$ into the monomer $[Pd(O_2CMe)_2(RCH_2NMe_2)_2]$.

An attempt to isolate the monomer was partially successful. The compound proved to be unstable even in the solid state. However, its i.r. spectrum gives sufficient information to claim that the aromatic ring in $[Pd(O_2CMe)_2(PhCH_2NMe_2)_2]$ is not

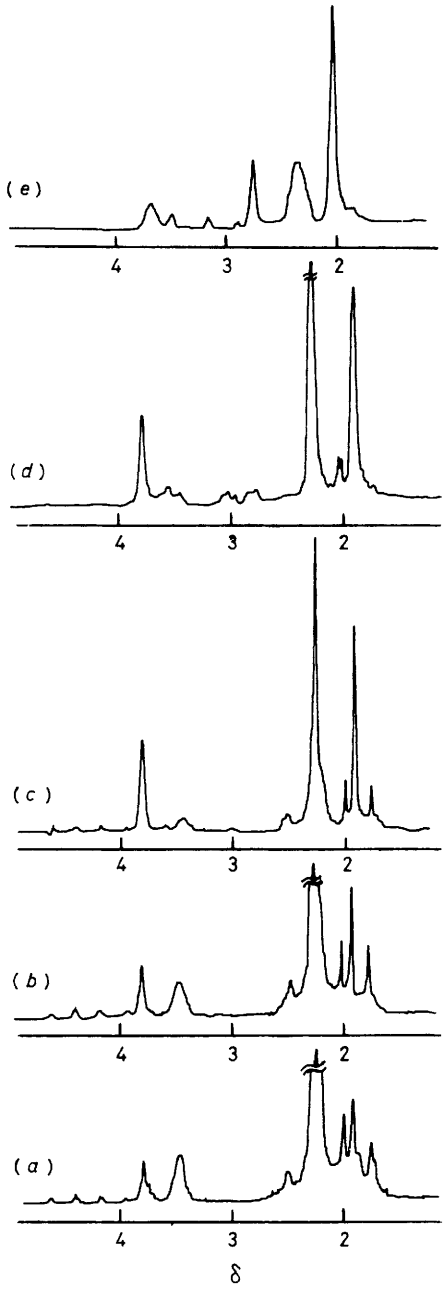


Figure 4. Interaction of 1 molar equivalent palladium(II) acetate with 2 molar equivalents of *NN*-dimethylbenzylamine in $CDCl_3$ as studied by ^1H n.m.r. spectroscopy. Spectra: (*a*) immediately after warming the frozen solution to −40 °C; (*b*) after 35 min at −40 °C; (*c*) after increasing the temperature to 0 °C; (*d*) after 30 min at 0 °C; (*e*) at 30 °C. For details see text

palladated (two bands at 750 and 705 cm^{-1} due to C–H deformational vibrations of the monosubstituted ring[33]) and the acetates are unidentate[13] (1 625, 1 370, and 1 315 cm^{-1}). For comparison, the corresponding ortho-palladated dimer (**2c**) has the following bands in the same regions: 740 (1,2-disubstituted ring); 1 590, 1 570, and 1 415 cm^{-1} (bridging acetates). The geometry of the monomer is probably *trans*, at least when there is an excess of amine (**1**) over Pd^{II}. Since the dipole moment of $[Pd(O_2CMe)_2(PhCH_2NMe_2)_2]$ cannot be measured because of rapid ortho-palladation, we base our arguments on spectral data. The absorption spectrum of the complex, obtained in

* After submission of this manuscript a brief account of a ^1H n.m.r. study of the interaction between *equimolar* amounts of palladium(II) acetate and amine (**1c**) was published.[32] The same species were observed in solution prior to ortho-palladation, but none of them dominates under these conditions.

$$[Pd_3(O_2CMe)_6] + RCH_2NMe_2$$
$$\downarrow -40\ ^\circ C$$
$$[Pd(O_2CMe)_2(RCH_2NMe_2)_2] + [\{Pd(O_2CMe)_2(RCH_2NMe_2)\}_2]$$
$$\downarrow 0\ ^\circ C$$
$$[Pd(O_2CMe)_2(RCH_2NMe_2)_2]$$
$$\downarrow 30\ ^\circ C$$
$$[\{Pd(O_2CMe)(R'CH_2NMe_2)\}_2] + [RCH_2NHMe_2]^+O_2CMe^-$$

Scheme 2. R′ = R minus *ortho*-H

$CHCl_3$ at 8 °C and [(**1c**)] = 0.22 mol dm^{-3}, has a maximum at 355 nm (ε = 340 dm^3 mol^{-1} cm^{-1}). It might be compared with electronic spectra of related complexes of the type $[PdX_2(amine)_2]$, where $X^- = I^-$ or SCN^-.[34] The *trans* form of these is characterised by maximum absorptions at *ca.* 360 nm, shifted by *ca.* 60 nm to higher wavelengths compared with the *cis* species. A similar trend is also observed in the case of phosphine complexes $[PdX_2(PR_3)_2]$, where X is halide[35] or acetate.[36] If the same is true for corresponding amine–acetate complexes,* one may argue that the spectrum of $[Pd(O_2CMe)_2(PhCH_2NMe_2)_2]$ is consistent with a *trans* configuration.

Kinetics.—The evidence presented above demonstrates that with excess of amine (**1**) over palladium(II) acetate the monomeric complex *trans*-$[Pd(O_2CMe)_2(RCH_2NMe_2)_2]$ should be considered as a starting material in reaction (1). Thus, we are dealing with intramolecular activation of C–H bonds in a square-planar complex of the type $M^{II}A_2B_2$. Such species have recently been used for mechanistic studies of various catalytically important processes, namely reductive[38] and β elimination[39] from palladium, thermal decomposition,[40] cyclometallation,[41] and hydrogenolysis[42] in platinum complexes.

In our case $k_{obs.}$ is independent of the total concentration of palladium(II) acetate in the range (0.5—2.0) × 10^{-3} mol dm^{-3}. Figure 5 shows the dependence of $k_{obs.}$ on *NN*-dimethylbenzylamine concentration. The plot is in remarkable contrast to the corresponding dependencies obtained in acetic acid as solvent. Instead of first-order kinetics in amine (**1**) in acetic acid, the reaction obeys an inverse dependence on [(**1**)] in $CHCl_3$ suggesting that dissociation of the ligand occurs prior to the rate-determining step. The existence of the linear dependence between $k_{obs.}$ and $[(\mathbf{1})]^{-1}$ with non-zero intercept at the highest concentrations of *NN*-dimethylbenzylamine indicates that the experimental rate expression is $k_{obs.} = \{a + b[(\mathbf{1})]\}/\{c + [(\mathbf{1})]\}$. A plausible reaction pathway is shown in Scheme 3. Here

$$trans\text{-}[Pd(O_2CMe)_2(RCH_2NMe_2)_2] \overset{K_{10}}{\rightleftharpoons} [Pd(O_2CMe)_2(RCH_2NMe_2)] + (\mathbf{1}) \quad (10)$$

$$[Pd(O_2CMe)_2(RCH_2NMe_2)] \xrightarrow{k_{11}} \text{products} \quad (11)$$

$$trans\text{-}[Pd(O_2CMe)_2(RCH_2NMe_2)_2] \xrightarrow{k_{12}} \text{products} \quad (12)$$

Scheme 3.

* A difference in the spectra of *trans* and *cis* forms of the amine complexes is definitely manifested when the anionic ligands are rather bulky, *e.g.* I^- and SCN^-.[34] In the case of chloride, the spectra of both forms are similar.[37] Evidently, acetate is much bulkier than chloride and at least comparable with I^- and SCN^-.

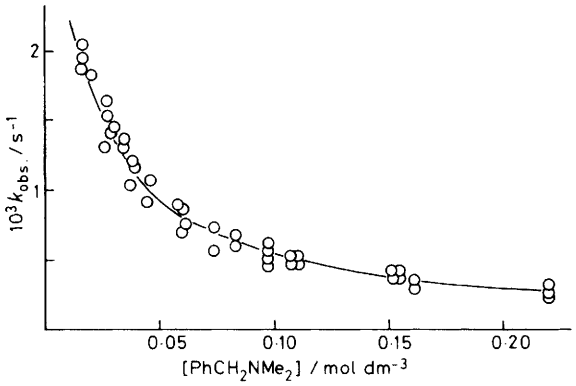


Figure 5. Dependence of $k_{obs.}$ on the concentration of *NN*-dimethylbenzylamine for palladation of the amine in $CHCl_3$ at 25 °C

$[Pd(O_2CMe)_2(RCH_2NMe_2)]$ is a pseudo-three-co-ordinate intermediate. Scheme 3 also contains another pathway, k_{12}, leading to products without pre-dissociation of amine (**1**). The resulting expression for $k_{obs.}$ is (13), which corresponds to the experimental rate equation.

$$k_{obs.} = \frac{k_{11}K_{10} + k_{12}[(\mathbf{1})]}{K_{10} + [(\mathbf{1})]} \quad (13)$$

A computer fitting of the data in Figure 5 to equation (13) using a weighted non-linear least-squares program gave the following numerical values: K_{10} = 1.35 × 10^{-2} mol dm^{-3}, k_{11} = 4.3 × 10^{-3} s^{-1}, and k_{12} = 3.1 × 10^{-5} s^{-1} at 25 °C. An important point here is that the inhibition by the added amine is caused by the dissociation (10), not because of the kinetically indistinguishable formation of unreactive complexes $[Pd(O_2CMe)(RCH_2NMe_2)_3]O_2CMe$, the reactive species being *trans*-$[Pd(O_2CMe)_2(RCH_2NMe_2)]$. If such unreactive species were formed at [(**1c**)] = 1.8 mol dm^{-3} and K_{10} = 1.35 × 10^{-2} mol dm^{-3} the ratio $[Pd(O_2CMe)_2(PhCH_2NMe_2)_2]/[\{Pd(O_2CMe)(PhCH_2NMe_2)_3\}O_2CMe]$ should be 0.0075, thus $[Pd(O_2CMe)(PhCH_2NMe_2)_3]O_2CMe$ would be a dominant species and could be detected by ^1H n.m.r. spectroscopy. However, we did not obtain any n.m.r. evidence indicating formation of higher complexes even in the presence of a large excess of amines (**1c**) and (**1f**) over palladium(II). In this context, in a solvent such as chloroform, dissociation of the amines seems to be more probable than formation of charged species of the type $[Pd(O_2CMe)(RCH_2NMe_2)_3]^+$.

The kinetic data indicate also that the dominant pathway is intramolecular and external amine is not included in the transition state. Evidently, if the rate-limiting step were (14) a

$$[Pd(O_2CMe)_2(RCH_2NMe_2)] + (\mathbf{1}) \xrightarrow{k_{14}} \text{products} \quad (14)$$

combination of steps (10) and (14) would give $k_{obs.} = k_{14}K_{10}[(\mathbf{1})]/\{K_{10} + [(\mathbf{1})]\}$, and no inhibition by the amines should be observed.

It should be pointed out that the accuracy of determining k_{12} is rather low, since the corresponding pathway becomes significant only at high concentrations of amine (**1c**), when a pronounced change in solvent composition takes place and the reaction is very slow, *cf.* ref. 40*b*. However, the k_{12} path is real and support for it has been obtained by less precise kinetic measurements using n.m.r. spectroscopy, which allows higher concentrations of (**1c**) than those shown in Figure 5. At 25 °C, [(**1c**)] = 2.7 mol dm^{-3}, and total $[Pd^{II}]$ = 0.105 mol dm^{-3}, $k_{obs.}$ is *ca.* 0.9 × 10^{-4} s^{-1}. The value calculated using k_{11} and K_{10}

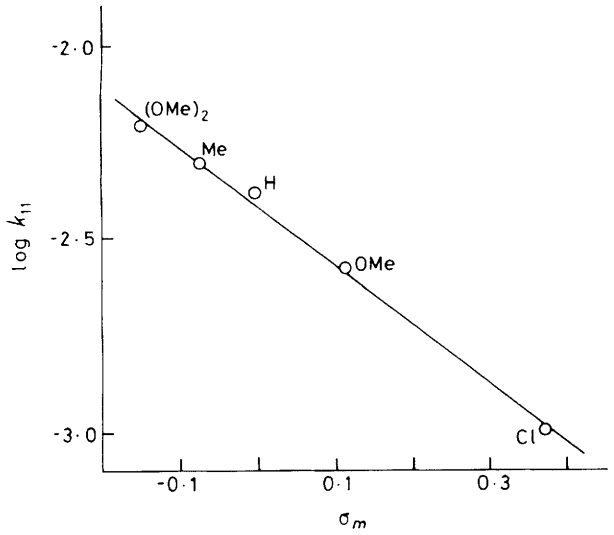
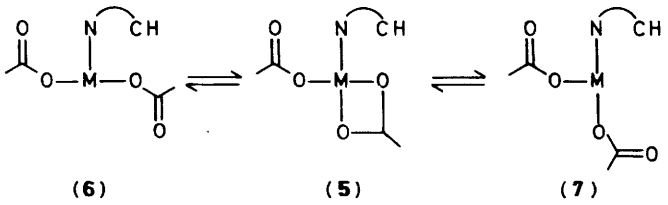


Figure 6. Hammett plot of log k_{11} against σ_m

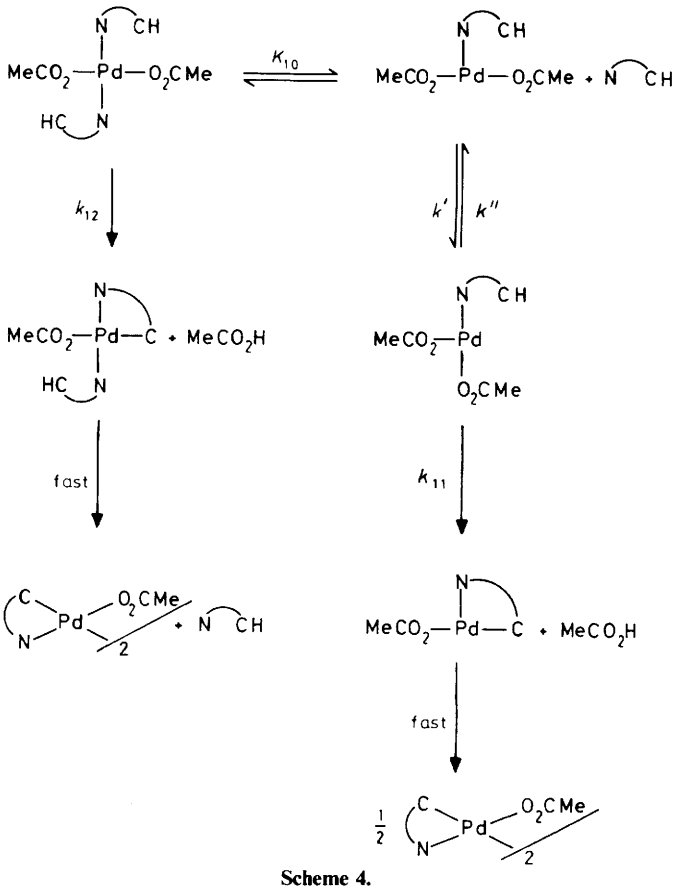
without taking into account a contribution from the k_{12} path is 0.23×10^{-4} s^{-1}, while with this path the value is 0.54×10^{-4} s^{-1}, showing a more satisfactory agreement with the $k_{obs.}$ value measured by n.m.r. spectroscopy.

Assuming that K_{10} is the same for amine (**1c**) and its deuteriated analogue, from the values of $k_{obs.}$ obtained spectrophotometrically at $[C_6D_5CD_2NMe_2] = (3—7) \times 10^{-2}$ mol dm^{-3}, when the contribution from the k_{12} path is negligible, we have calculated the magnitude of the kinetic isotope effect, $k_H/k_D = 2.2 \pm 0.2$, for the k_{11} path. This indicates that the rate-limiting step of this pathway does involve a cleavage of the carbon–hydrogen bond. In the case of the other amines, equation (13) has also been fitted to values of $k_{obs.}$ as a function of [(**1**)] and the computed parameters K_{10} and k_{11} are summarised in Table 2. Because of pronounced uncertainty in k_{12}, we made no attempt to obtain k_{12} for amines other than (**1c**). The values of K_{10} display a rather weak dependence on the nature of the substituents. The trend in k_{11} is obviously more distinct. Electron-rich amines react more rapidly. The situation is illustrated in Figure 6 where log k_{11} is plotted *versus* Hammett's σ_m constants to give a slope of -1.6. Note that the value $2k_{11}$ for amine (**1b**) is used in accord with rate-limiting ortho-palladation (see above). Figure 6 confirms directly the previous conclusion[10] that cyclopalladation is an electrophilic process.

Intimate Mechanism.—As has already been mentioned, the dissociation of the amine *via* step (10) produces a pseudo-three-co-ordinate intermediate. The prefix 'pseudo' denotes that the intermediate actually contains three co-ordinated ligands, but since acetate can be bidentate,[43] all four co-ordination sites of the palladium plane may be occupied as in structure (**5**). Obviously, rupture of the palladium–oxygen bond *cis* to the co-ordinated amine can easily provide a vacant co-ordination site for subsequent rate-limiting ortho-palladation. If, on the contrary, liberation of the amine leads primarily to 'T'-shaped species (**6**), the necessary configuration (**7**) can be achieved *via* the intermediate containing bidentate acetate, (**5**). Such a movement of a vacant co-ordination site in acetato-complexes should have an extremely low activation barrier since it proceeds through unhindered (**6**) ⟶ (**5**) ⟶ (**7**) interconversions omitting energetically less favourable paths *via* a 'Y'-shaped intermediate or a dissociation–recombination sequence.[44,45]



All the results obtained suggest that the intimate mechanism of ortho-palladation is as presented in Scheme 4. Applying the steady-state approximation to the *cis* 'T'-shaped intermediate



Scheme 4.

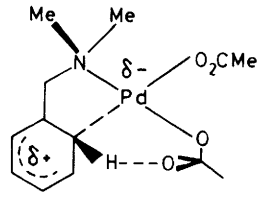
one obtains equation (15) which corresponds to the rate equation (13) as well as to the experimental one. The migration

$$k_{obs.} = \frac{k_{11}k'K_{10} + (k_{11} + k'')k_{12}[(\mathbf{1})]}{\{K_{10} + [(\mathbf{1})]\}(k_{11} + k'') + k'K_{10}} \qquad (15)$$

of a vacant co-ordination site in square-planar complexes is known to proceed rapidly.[45] In the case of rate-limiting ortho-palladation a reasonable assumption is $k'' \gg k_{11}$. If at the same time k' and k'' do not differ markedly ($k'/k'' \approx 1$), the rate constants k_{11} in Table 2 refer directly to the rate-determining cleavage of the C–H bonds.

The dominant 'dissociative' pathway of the reaction involves an unsaturated 14-electron metal system and is characterised by the slope of the Hammett plot, -1.6, and the kinetic isotope effect, $k_H/k_D = 2.2$. Involvement of the three-co-ordinate intermediate suggests that palladation occurs in the metal plane as proposed previously for palladation of 8-alkylquinolines.[11b]

The sensitivity of the electrophilic attack to electronic effects is similar for both intra- and inter-molecular activation of arenes by palladium(II). The Hammett slope of −1.6 found in this work can be compared with those of −1.4 and −2.2 obtained by Fujiwara *et al.*[46] for olefin arylations and by Kozhevnikov[47] for arene couplings. On the other hand, the kinetic isotope effect is significantly lower in the intramolecular process (2.2 *versus ca.* 5[48]). This may reflect an 'early' transition state in the intramolecular reaction (*i.e.* palladium–carbon bond making overtakes cleavage of the carbon–hydrogen bond) and/or a highly non-linear transition state.[49] The former is in accord with a much lower value of $\Delta H_{11}^{\ddagger}$ (11 kJ mol^{-1}) as compared with 73 and 93 kJ mol^{-1} obtained in corresponding intermolecular processes.[5,6] The activation entropy of intramolecular palladation is large and negative, −254 J K^{-1} mol^{-1}. On the basis of these findings for the 'dissociative' pathway of intramolecular palladation of amines (**1**) we propose a tight highly ordered transition state (**8**) in which the leaving



(**8**)

hydrogen is abstracted by acetate but not by external amine (see above).

An interpretation of the pathway governed by k_{12} and involving a 16-electron species is much less obvious. Such a path dominates in β-hydrogen elimination in *trans*-diethylbis(tertiary phosphine)palladium(II) complexes.[39] A five coordinate intermediate has been considered in which the β hydrogen of one of the ethyl groups approaches towards palladium through the space above the molecular plane, bringing the complex configuration close to trigonal bipyramidal. A similar mechanism may operate in the present system. It is partly supported by crystallographic studies of bis(azobenzene-*N*)dichloropalladium(II)[50] and bis(azocyclohexane-*N*)dichloropalladium(II)[51] complexes, where palladium is involved in agostic[52] short intramolecular contacts with '*ortho*' hydrogens through axial sites. Axial CH • • • Pd interactions were studied by Deeming *et al.*[53] by ^{1}H n.m.r. spectroscopy and found to be destabilising. However, it is not yet clear whether this destabilisation facilitates C–H bond cleavage or not.

Comparison of Intra- versus *Inter-molecular Palladation.*—In order to estimate the magnitude of the proximity effect it is interesting to compare rates of intramolecular ortho-palladation with those of intermolecular activations of aromatic C–H bonds by palladium(II) acetate. Activation of benzene by $[Pd(O_2CMe)]^+$ in aqueous acetic acid to afford biphenyl as a final product proceeds according to the rate law[5] (16) with

$$\text{Rate} = k_{16}[Pd(O_2CMe)^+][C_6H_6][MeCO_2H] \qquad (16)$$

k_{16} = 2.1 × 10^{-6} dm^6 mol^{-2} s^{-1} at 25 °C. Extrapolation to pure acetic acid (17.5 mol dm^{-3}) gives a second-order rate constant $k_{16}' = k_{16}[MeCO_2H]$ of 3.7 × 10^{-5} dm^3 mol^{-1} s^{-1}. This has been calculated from the kinetic data obtained under the most favourable conditions for intermolecular palladation in acetic acid solvent. Thus, a comparison of k_{16}' with k_{11} measured in chloroform provides only a lower estimate of the 'effective molarity,'[1] k_{intra}/k_{inter}, which characterises the proximity effect. The rate constant k_{16} is the highest for electrophilic activation of benzene by Pd^{II} because the most electrophilic species $[Pd(O_2CMe)]^+$ is involved. Nevertheless, a fairly high ratio k_{intra}/k_{inter} of 3.6 × 10^2 mol dm^{-3} (statistically corrected) is found in this case. A similar procedure based on kinetic data from ref. 6, where $Na_2[Pd_2(O_2CMe)_6]$ was the reactive species, gave an 'effective molarity' of *ca.* 2 × 10^4 mol dm^{-3}. A similar value was found previously for ortho-palladation of azobenzene by palladium(II) chloride in the presence of carboxylate ions.[9]

These estimations show that the effective molarities in aromatic electrophilic substitution by palladium(II) can be as high as those found in numerous nucleophilic substitutions (10^4—10^6 mol dm^{-3}).[1,2] Evidently, a high effective molarity with metal electrophiles might be responsible for the ease of cyclometallation. On the contrary, when cyclometallation involves oxidative addition to low-valent metal centres, for example in the complex $[Rh^I(C_5Me_5)(PhCH_2PMe_2)]$, the effective molarity is dramatically lowered, being only 5.5 mol dm^{-3}.[3]

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