Cyclopalladation of 4-Methyl-4′-nitrodibenzyl Sulphide

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4-Methyl-4′-nitrodibenzyl sulphide reacts with palladium(II) acetate to afford the complex $[\{Pd[C_6H_3(Me\text{-}5)CH_2SCH_2C_6H_4NO_2\text{-}4'](\mu\text{-}O_2CMe)\}_2]$ (1). A chloro-bridged analogue, $[\{Pd[C_6H_3(Me\text{-}5)CH_2SCH_2C_6H_4NO_2\text{-}4'](\mu\text{-}Cl)\}_2]$ (2), prepared by the metathetical reaction of (1) with lithium chloride, undergoes a bridge-splitting reaction with 3,5-dimethylpyridine to give a mononuclear cyclopalladated complex, $[Pd\{C_6H_3(Me\text{-}5)CH_2SCH_2C_6H_4NO_2\text{-}4'\}Cl(NC_5H_3Me_2\text{-}3,5)]$ (3). Analysis of the proton n.m.r. spectrum of (3) indicates that the cyclopalladation by palladium(II) acetate proceeds *via* an electrophilic attack on the aryl group.

Many articles have appeared concerning the cyclometallation of aryl-substituted bases having nitrogen, phosphorus, or sulphur donor atoms.[1] These reactions may be defined as aromatic substitutions in which a co-ordinated ligand undergoes intramolecular metallation resulting in the formation of a new metal–carbon σ bond.

We [2–7] have reported several new cyclopalladations of aryl-substituted Lewis bases, and have shown that palladium(II) acetate is a better starting material than $[PdCl_4]^{2-}$ or a $[PdCl_4]^{2-}$–$MeCO_2^-$ system. As for the mechanistic feature of cyclopalladation, it has been reported that $PdCl_2$ and $[PdCl_4]^{2-}$ behave as electrophilic reagents.[8,9,†] However, palladium(II) acetate has shown different reactivities compared to $PdCl_2$ or $[PdCl_4]^{2-}$. Palladium(II) acetate reacted with 1-ethyl-2-phenylimidazole [2] and 2-phenylthiazole [3] to afford cyclopalladated complexes, whereas $[PdCl_4]^{2-}$ gave addition complexes of the corresponding bases. In the case of benzyl t-butyl sulphide, cyclopalladation took place with palladium(II) acetate,[4,5] but a carbon–sulphur bond cleavage occurred with $PdCl_2$.[4]

It is interesting to investigate whether palladium(II) acetate behaves as an electrophilic or nucleophilic reagent in the cyclopalladation process. Recently, Newkome and co-workers [10] suggested that palladium(II) acetate acts as an electrophilic reagent on the basis of only the yields of the cyclopalladated complexes of substituted 2-phenylpyridines. In order to obtain more reliable information about the mechanistic features, we report herein the reaction of palladium(II) acetate with 4-methyl-4′-nitrodibenzyl sulphide, which involves both an electron-attracting and an electron-withdrawing group in the *para*-positions of the phenyl moieties. Reports concerning cyclopalladation of dibenzyl sulphide [11] and benzyl isobutyl sulphide [5] have appeared recently.

Results and Discussion

The reaction of palladium(II) acetate and 4-methyl-4′-nitrodibenzyl sulphide in acetic acid at 70 °C afforded, as yellow-brown crystals, an acetato-bridged binuclear cyclopalladated complex, $[\{Pd[C_6H_3(Me\text{-}5)CH_2SCH_2C_6H_4NO_2\text{-}4'](\mu\text{-}O_2CMe)\}_2]$ (1) Complex (1) was converted to the analogue, $[\{Pd[C_6H_3(Me\text{-}5)CH_2SCH_2C_6H_4NO_2\text{-}4'](\mu\text{-}Cl)\}_2]$ (2) by reaction with excess LiCl. Compound (2) was treated

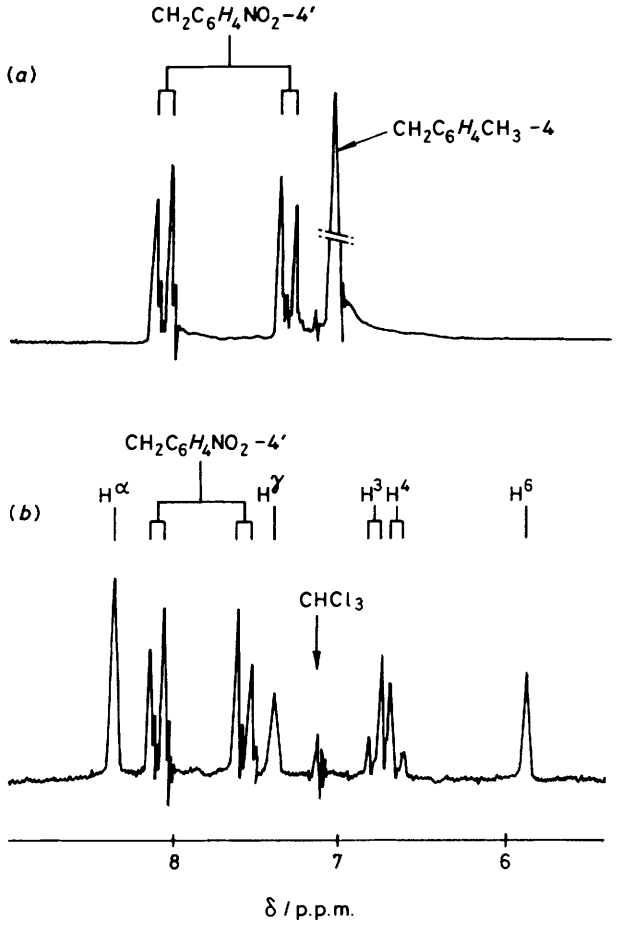


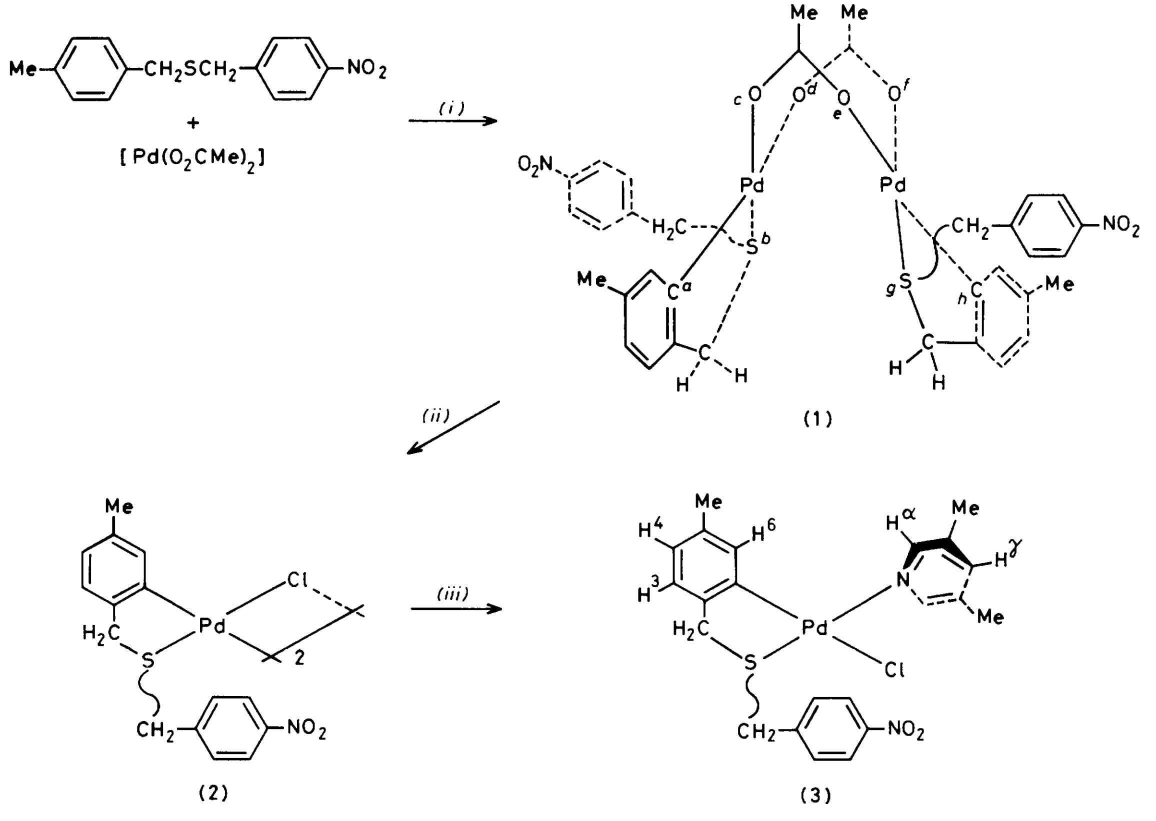
Figure. Low-field region of the ^1H n.m.r. spectra of (*a*) 4-methyl-4′-nitrodibenzyl sulphide at 23 °C and (*b*) complex (3) at −7 °C

[†] It has been reported that a low-valent manganese(I) complex, $[MnMe(CO)_5]$, acts as a nucleophilic reagent towards substituted azobenzenes to give their cyclomanganated complexes.[9]

Table. Proton n.m.r. data [a] of the palladium complexes

	CH_2				Aromatic protons					
Complex	δ	Δδ	^2J(HH)/ Hz	T_c/°C [b]	H^3	H^4	H^6	$H^{2'}$,$H^{6'}$ (H^{α}) [c]	$H^{3'}$,$H^{5'}$ (H^{γ}) [c]	Me
(1)	2.97 (q)	0.20	8		6.90 (d) [d]	6.74 (d) [d]	6.58 (s)	7.11 (d) [e]	7.98 (d) [e]	2.1—2.3 [f]
	3.36 (q)	0.28	14	>55		6.77 (d) [d]				
	3.39 (q)	0.26	10							
	4.00 (q)	0.29	13							
(3)	3.85 (q)	0.19	13	30	6.79 (d) [e]	6.66 (d) [e]	5.88 (s)	7.57 (d) [e]	8.09 (d) [e]	2.35 (s)
	4.42 (q)	0.16	13					8.35 (s) [c]	7.40 (s) [c]	2.03 (s) [c]

[a] Recorded in $CDCl_3$ at −7 °C. s = Singlet, d = doublet, q = quartet. [b] Coalescence temperature. [c] Pertaining to 3,5-dimethylpyridine. [d] ^3J(HH) = 9 Hz. [e] ^3J(HH) = 8 Hz. [f] Methyl protons of C_6H_3(Me-5)CH_2– and acetate groups overlap.



Scheme. (*i*) In acetic acid at 70 °C; (*ii*) LiCl in tetrahydrofuran–water (7 : 1) at 70 °C; (*iii*) 3,5-dimethylpyridine in CH_2Cl_2 at room temperature. Dotted lines represent the groups situated behind the plane of the paper

with 3,5-dimethylpyridine to produce a mononuclear cyclopalladated complex, $[\overline{Pd\{C_6H_3(Me\text{-}5)CH_2S}CH_2C_6H_4NO_2\text{-}4'\}Cl(NC_5H_3Me_2\text{-}3,5)]$ (3) (Scheme).

All three cyclopalladated complexes are stable in air and water. The i.r. spectra of these complexes exhibited two strong bands due to the asymmetric and symmetric NO_2 stretching frequencies at *ca.* 1 520 and 1 345 cm^{-1}, respectively. The ^{1}H n.m.r. spectra of (1) and (3) showed temperature dependency, indicating configurational inversion at the sulphur atom of the co-ordinated sulphide, as in the cyclopalladated complexes of benzyl t- and isobutyl sulphides [5] (Table).

The acetato-bridged complex (1) showed two bands characteristic of the bridging acetato-ligand at 1 570 and 1 415 cm^{-1},[12] which were absent in the chloro-bridged complex (2). The ^{1}H n.m.r. spectrum of (1) at 55 °C showed one singlet (δ 2.12, 6 H) due to the acetato-ligands, indicating that only an (*anti a-C*^{1},*b-S*;*g-S*,*h-C*^{1}) type isomer is present. At −7 °C, methylene protons of the two benzyl moieties appeared as four AB quartets at δ 2.97, 3.36, 3.39, and 4.00 (Table). These quartets are associated with two forms of the C_6H_3(Me-5)-$CH_2SCH_2C_6H_4NO_2$-4′ moiety, having the 4′-nitrobenzyl group situated inside or outside the dihedral angle formed by the two palladium co-ordination planes. The chloro-bridged complex (2) is only sparingly soluble in common organic solvents, but was converted to a soluble mononuclear species (3).

Complex (3) showed a slow-exchange limiting ^{1}H n.m.r. spectrum at −7 °C. Two diastereotopic methylene protons of the C_6H_3(Me-5)CH_2 and 4′-nitrobenzyl groups were observed as AB quartets at δ 3.85 and 4.42 respectively. Aromatic protons of the 4′-nitrobenzyl moiety were observed at δ 7.57(d) and 8.09(d) as a clear A_2B_2 pattern, without virtually changing from the corresponding signals of the starting 4-methyl-4′-nitrodibenzyl sulphide [δ 7.36(d) and 8.10(d); ^3J(HH) = 8 Hz in $CDCl_3$]. On the other hand, a singlet at δ

7.08 (4 H) due to the aromatic protons of the 4-methylbenzyl group in 4-methyl-4′-nitrodibenzyl sulphide changed on cyclopalladation to a clear XYZ pattern at δ 5.88 (s, 1 H), 6.66 (d, 1 H), and 6.79 (d, 1 H) (Figure). These data indicate unambiguously that cyclopalladation occurred only on the more electron-rich 2-position of the 4-methylbenzyl group and not on the electron-poor 2′-position of 4′-nitrobenzyl, and that palladium(II) acetate behaves as an electrophilic reagent towards the aromatic group of the Lewis bases as well as $PdCl_2$ or $[PdCl_4]^{2-}$.

Experimental

General procedures were as described previously.[2]

Preparations.—*4-Methyl-4′-nitrodibenzyl sulphide.* This sulphide was prepared by an analogous method to that for 4-nitrodibenzyl sulphide.[13] Yield 87%, m.p. 87.5 °C (Found: C, 66.0; H, 5.6; N, 5.15. Calc. for $C_{15}H_{15}NO_2S$: C, 65.9; H, 5.55; N, 5.1%). ^1H N.m.r. spectrum: $\delta(CDCl_3)$ 2.32 (s, 3 H, CH_3), 3.56 (s, 2 H, CH_2), 3.62 (s, 2 H, CH_2). For the aromatic protons see text and Figure.

$[\{Pd[C_6H_3(Me\text{-}5)CH_2SCH_2C_6H_4NO_2\text{-}4'](\mu\text{-}O_2CMe)\}_2]$ (1). An acetic acid (15 cm^3) suspension containing palladium(II) acetate (2.67 mmol) and 4-methyl-4′-nitrodibenzyl sulphide (2.94 mmol) was heated at 70 °C for 8 h. The resulting yellow-brown precipitate was filtered off and recrystallized from dichloromethane and hexane to give (1). Yield 68%, m.p. 201—203 °C (Found: C, 45.7; H, 4.0; N, 2.9. Calc. for $C_{34}H_{34}N_2O_8Pd_2S_2$: C, 46.65; H, 3.9; N, 3.2%).

$[\{Pd[C_6H_3(Me\text{-}5)CH_2SCH_2C_6H_4NO_2\text{-}4'](\mu\text{-}Cl)\}_2]$ (2). A tetrahydrofuran–water (7 : 1, 40 cm^3) suspension containing (1) (0.42 mmol) and lithium chloride (2.50 mmol) was heated at 70 °C for 1 h. The resulting mixture was concentrated to about 20 cm^3, and filtered. A pale yellow precipitate resulted which was washed with a small amount of tetrahydrofuran, and dried *in vacuo* to give (2). Yield 52%, m.p. 220—222 °C (Found: C, 43.15; H, 3.4; N, 3.4. Calc. for $C_{30}H_{28}Cl_2N_2O_4Pd_2S_2$: C, 43.5; H, 3.4; N, 3.4%).

$[Pd\{C_6H_3(Me\text{-}5)CH_2SCH_2C_6H_4NO_2\text{-}4'\}Cl(NC_5H_3Me_2\text{-}3,5)]$ (3). A clear solution was obtained immediately by adding 3,5-dimethylpyridine (0.91 mmol) to a suspension of (2) (0.42 mmol) in dichloromethane (10 cm^3). After stirring for 4 h at room temperature, addition of hexane to the mixture gave (3) as a cream powder. Yield 69%, m.p. 168—170 °C (Found: C, 50.15; H, 4.5; N, 5.4. Calc. for $C_{22}H_{23}ClN_2O_2PdS$: C, 50.7; H, 4.45; N, 5.4%).

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