Syntheses and Characterization of the Cyclopalladated Complexes of Benzyl Butyl Sulphides

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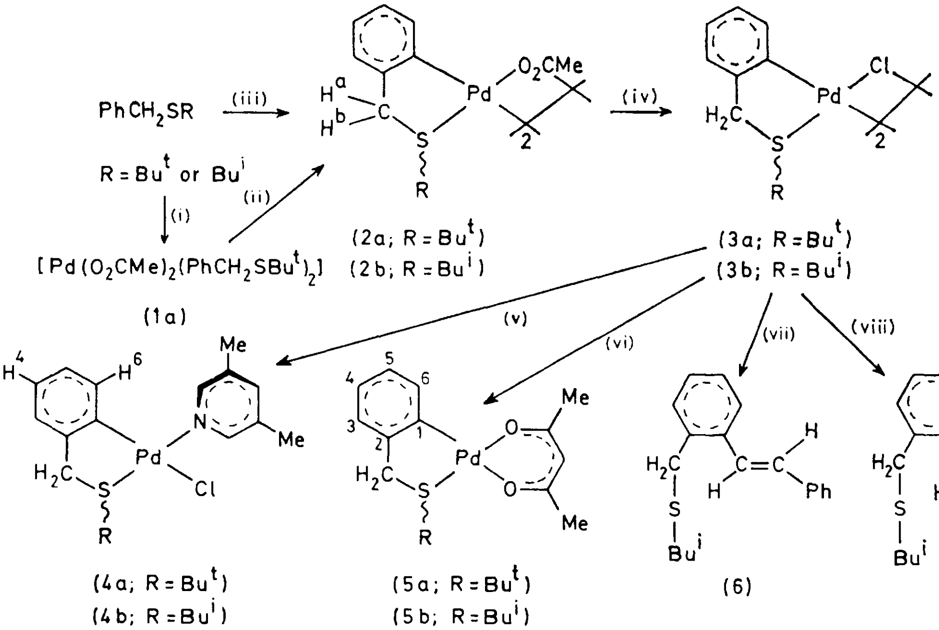
Reactions of benzyl t- and iso-butyl sulphides with palladium(II) acetate result in the formation of the acetato-bridged binuclear cyclopalladated complexes, $[\{Pd(C_6H_4CH_2SR)(O_2CMe)\}_2]$ (R = Bu^t or Bu^i). These complexes are easily converted into the chloro-bridged analogues, $[\{Pd(C_6H_4CH_2SR)Cl\}_2]$, by metathetical reaction with LiCl. The chloro-bridged complexes undergo bridge cleavage with 3,5-dimethylpyridine (dmpy) and thallium(I) acetylacetonate, Tl[acac], to give the corresponding mononuclear cyclopalladated complexes, $[Pd(C_6H_4CH_2SR)Cl(dmpy)]$ and $[Pd(C_6H_4CH_2SR)(acac)]$ respectively. All complexes are characterized by means of elemental analysis, i.r., n.m.r., and mass spectroscopy. Temperature-dependent ^1H n.m.r. spectra are observed for all the cyclopalladated complexes and are attributed to the inversion of the butyl group at the sulphur atom.

CYCLOMETALLATED complexes are increasingly used for organic syntheses.[1,2] Various substituents can be introduced regiospecifically onto the palladated carbon position by reactions of cyclopalladated complexes with various reagents, *e.g.* carbon monoxide, vinyl compounds, or halogens.[3-5] A previous communication [6] dealt with two different reaction modes of benzyl t-butyl sulphide ($PhCH_2SBu^t$) towards palladium(II) chloride and palladium(II) acetate, resulting in the formation of *catena*-μ-benzylthio-μ-chloro-palladium(II) and di-μ-acetato-bis{[2-(t-butylthiomethyl)phenyl-C^1,*S*]palladium(II)}, $[\{Pd(C_6H_4CH_2SBu^t)(O_2CMe)\}_2]$ (2a), respectively.

Recently, Shaw and co-workers [7] reported that cyclopalladation by sodium tetrachloropalladate(II) did not occur on reaction with $PhCH_2SBu^t$ in the presence of sodium acetate, but did with 1,3-bis(t-butylthiomethyl)benzene, a more sterically demanding benzyl sulphide, under the same conditions. The fact that $PhCH_2SBu^t$ is readily cyclopalladated by palladium(II) acetate is of great significance, therefore. In this paper, we report on the cyclopalladation reactions of not only $PhCH_2SBu^t$, but also of a less bulky benzyl sulphide, benzyl isobutyl sulphide ($PhCH_2SBu^i$) by palladium(II) acetate, and also some new complexes derived from (2a) and its isobutyl analogue, $[\{Pd(C_6H_4CH_2SBu^i)(O_2CMe)\}_2]$.

RESULTS AND DISCUSSION

Syntheses and General Properties of the Cyclopalladated Complexes.—Palladium(II) acetate reacted with an excess of $PhCH_2SBu^t$ in benzene at room temperature to afford diacetatobis(benzyl t-butyl sulphide)palladium(II) (1a) as yellow crystals. This compound was then converted into the cyclopalladated binuclear complex, $[\{Pd(C_6H_4CH_2SBu^t)(O_2CMe)\}_2]$ (2a), in refluxing methanol for 30 min. Complex (2a) was also obtained directly from the reaction of $PhCH_2SBu^t$ with palladium(II) acetate in



SCHEME (i) $Pd[O_2CMe]_2$ in benzene for $PhCH_2SBu^t$; (ii) in refluxing methanol; (iii) $Pd[O_2CMe]_2$ in MeOH for $PhCH_2SBu^t$ and in acetic acid for $PhCH_2SBu^i$; (iv) LiCl in tetrahydrofuran–water; (v) 3,5-dimethylpyridine in CH_2Cl_2; (vi) Tl[acac] in CH_2Cl_2; (vii) styrene in *o*-xylene for (3b) (accompanied by the formation of $PhCH_2SBu^i$); (viii) methyl vinyl ketone in benzene for (3b) (accompanied by the formation of $PhCH_2SBu^i$)

refluxing methanol. Benzyl isobutyl sulphide also reacted with palladium(II) acetate in refluxing acetic acid to afford an analogous cyclopalladated complex, [{Pd-$C_6H_4CH_2SBu^i$)(O_2CMe)}$_2$] (2b). It should be noted that no (2a) was isolated from the reaction between $PhCH_2SBu^t$ and palladium(II) acetate in refluxing acetic acid, whereas $PhCH_2SBu^i$ reacted with palladium(II) acetate and chloride in refluxing methanol to give palladium black accompanied by a very small amount of (2b) and [$PdCl_2(PhCH_2SBu^i)_2$] respectively.

TABLE 1

Yields and elemental analyses of the palladium complexes

Complex	Yield/%	Colour	M.p. (θ_c/°C)	Analysis [a] (%) C	Analysis [a] (%) H
(1a)	56	Yellow	103	53.95 (53.35)	6.75 (6.55)
(2a)	29,[b] 34	Lemon-yellow	190 [c]	45.75 (45.3)	5.35 (5.25)
(2b)	63	Yellow	188 [c]	45.25 (45.3)	5.20 (5.25)
(3a)	95	Pale yellow	200—205 [c]	40.95 (41.15)	4.75 (4.70)
(3b)	81	Pale yellow	188	41.3 (41.15)	4.65 (4.70)
(4a)	62	Yellow-white	145—165 [c]	[d] 50.65 (50.45)	5.80 (5.65)
(4b)	54	Yellow-white	116—119	[e] 51.05 (50.45)	5.70 (5.65)
(5a)	70	Yellow	101 [c]	49.8 (49.95)	5.85 (5.75)
(5b)	45	Yellow	129—130	50.05 (49.95)	5.85 (5.75)

[a] Calculated values are given in parentheses. [b] Based on (1a). [c] With decomposition. [d] N, 3.10 (3.25). [e] N, 3.10 (3.25).

The acetato-bridged complexes (2a) and (2b) were readily converted into the corresponding chloro-bridged analogues, [{$Pd(C_6H_4CH_2SBu^t)Cl$}$_2$] (3a) and [{Pd-($C_6H_4CH_2SBu^i)Cl$}$_2$] (3b), respectively by treating them with LiCl in a tetrahydrofuran–water solvent. Complexes (3a) and (3b) reacted with 3,5-dimethylpyridine (dmpy) and thallium(I) acetylacetonate, Tl[acac], to afford the corresponding mononuclear cyclopalladated complexes, [$Pd(C_6H_4CH_2SBu)Cl$(dmpy)] [(4a) and (4b)] and [$Pd(C_6H_4CH_2SBu)$(acac)] [(5a) and (5b)] respectively (Scheme).

All the cyclopalladated complexes prepared in this study are stable in air and water, and remain unchanged in an inert atmosphere after more than 6 months. Their elemental analyses and yields are summarized in Table 1. All showed temperature-dependent ^1H n.m.r. spectra, attributable to inversion at the sulphur atom of the co-ordinated sulphide.[8] In all cases, low-temperature limiting spectra were observed, which are listed in Table 2.

Acetato-bridged Binuclear Complexes (2a) *and* (2b).—The i.r. spectra of (2a) and (2b) showed two characteristic bridging acetate bands[9] at 1 575 and 1 420 cm^{-1}, distinct from the terminal ones at 1 635 and 1 300 cm^{-1} of (1a).[10] The ^1H n.m.r. spectra of both (2a) and (2b) at 55 °C showed one singlet due to the methyl protons of the acetate ligands, implying an *ab-hg* type complex and excluding the presence of an *ab-gh* type isomer, detected in di-μ-acetato-bis{[2-(1′-ethylimidazol-2′-yl)-phenyl-C^1,$N^{3'}$]palladium(II)}.[11]

Recently, crystal structures of acetato-bridged dimeric cyclopalladated complexes were elucidated by *X*-ray diffraction analysis, and revealed that two palladium atoms are bridged by two mutually *cis*-μ-acetato-ligands, and that two chelating cyclopalladated moieties are located with a dihedral angle of *ca.* 24°.[12] Assuming

TABLE 2

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

		$C_6H_4CH_2SBu$								
		CH_2				Bu (δ)			Other ligand (δ)	
Complex	θ_c/°C [b]	δ	Δδ	^2J(HH)/Hz	T_c/°C [c]	CH	CH_2	Me	Me	Others
(1a)	26	4.09 (br,s)			*d*			1.1—2.0 [e]	1.1—2.0 [e]	
(2a)	4	2.86 (q)	0.73	16	>55			1.36 (s)	2.14 (s)	
(2b)	4	3.36 (q) [f] 3.42 (q) [f]			36	*ca.* 2.2	*ca.* 2.9	0.98 (d) [f,g] 0.85 (d) [f,g] 0.75 (d) [f,g]	2.09 (s)	
(3a)	−23	3.97 (q)	0.44	16	26			1.46 (s)		
(3b)	5	3.97 (q) [f]	0.46	14	55	2.11 (n)	2.88 (d),[h] 2.85 (d) [h]	1.07 (d) [h]		
(4a)	−20	4.02 (q)	0.44	16	27			1.50 (s)	2.31 (s)	8.38 (s) (dmpy H^{α}), 7.38 (s) (dmpy H^{γ})
(4b)	−10	4.14 (q)	0.36	15	44	*ca.* 2.1	3.10 (dq) [h,i]	1.11 (d) [h]	2.33 (s)	8.48 (s) (dmpy H^{α}), 7 46 (s) (dmpy H^{γ})
(5a)	−10	3.99 (q)	0.21	15	25			1.51 (s)	1.95 (s), 2.08 (s)	5.34 (CH)
(5b)	−10	3.96 (q)	0.49	15	54	*ca.* 2.1	2.84 (dq) [h,j]	1.04 (d) [h]	·1.95 (s), 2.08 (s)	5.36 (CH)

[a] Recorded in $CDCl_3$ except for (1a) (CCl_4) and (3a) (CD_2Cl_2). See text for aromatic protons of (4a) and (4b). s = Singlet, d = doublet, q = quartet, n = nonet, and dq = double quartet. [b] Measured temperature. [c] Coalescence temperature. [d] Measured only at 26 °C. [e] Methyl protons of butyl and acetate groups overlap. [f] See text. [g] ^3J(HH) = 6 Hz. [h] ^3J(HH) = 7 Hz. [i] Δδ = 0.30, ^2J(HH) = 13 Hz. [j] Δδ = 0.19, ^2J(HH) = 12 Hz.

that (2a) and (2b) have similar structures, there are three possible configurations, (A), (B), and (C), of the relative positions of the two butyl groups at low temperature (Figure 1). Molecular models indicate that (2a), containing two sterically bulky t-butyl groups, prefers configuration (A) rather than (B) or (C). In the ^{1}H n.m.r. spectrum of (2a) at 4 °C the t-butyl protons appear as one singlet at δ 1.36 attributable to configuration (A) in the slow-exchange limit. At the same temperature, methylene protons resonate as a refined AB quartet at δ 2.86, indicating that (*i*) the *ortho* position of the benzyl group is fixed, *i.e.* cyclopalladated, and (*ii*) inversion of the t-butyl group has been quenched. At 55 °C, the AB quartet changes into two broad humps. This implies that inversion of the t-butyl groups takes place slowly on the n.m.r. time scale, yielding the quasi-stable configuration (B) in a limited proportion.

FIGURE 1 Possible configurations of the acetato-bridged complexes (2)

At 4 °C, (2b) showed three doublets at δ 0.98 (5.5 H), 0.75 (2.5 H), and 0.85 (4 H) assignable to the methyl protons of the isobutyl group. The doublet at δ 0.98 probably results from configuration (A) with the largest population ratio. Configuration (B) is expected to have two kinds of isobutyl methyl group. Accordingly, both the doublet at δ 0.75 and part of the doublet at δ 0.85 were ascribed to configuration (B), whereas the remaining part of the last doublet was ascribed to (C). These data indicate that (2b) consists of configurational isomers (A), (B), and (C) in a population ratio of 46 : 42 : 12 respectively at the slow-exchange limit. Benzyl methylene protons were observed as two AB quartets at δ 3.36 (2.6 H) and 3.41 (1.4 H) at 4 °C, and associated with two forms of the $C_6H_4CH_2SBu^i$ moiety with the isobutyl group situated inside and outside the dihedral angle, rather than due to configurational isomers.

Chloro-bridged Binuclear Complexes (3a) *and* (3b).—The i.r. spectra of (3a) and (3b) lacked the bands due to the bridging acetato-ligand observed in (2a) and (2b). The chloro-bridged complexes are considered to have three configurations like the acetato-bridged complexes (2a) and (2b), but with a much larger dihedral angle between the two co-ordination planes (*ca.* 121° [13,*]). The ^{1}H n.m.r. spectra of (3b) showed two kinds of isobutyl methylene protons (Table 2) and of benzyl methylene protons [†] at low temperatures, like the benzyl methylene protons in (2b), whereas (3a) exhibited only one resonance.

Vinylation reactions of (3b) were examined as were those of the other cyclopalladated complexes.[4,5,14] Complex (3b) reacted with styrene in the presence of triethylamine in refluxing *o*-xylene to give a mixture of *trans*-2-(isobutylthiomethyl)stilbene (6) (21% yield) and $PhCH_2SBu^i$ (76% yield). Similarly, (3b) was treated with methyl vinyl ketone and triethylamine in refluxing benzene to afford *trans*-2-(isobutylthiomethyl)benzylideneacetone (7) (10% yield) and $PhCH_2SBu^i$ (39% yield). The formation of (6) and (7) indicates clearly the cyclopalladated structure of the $C_6H_4CH_2SBu^i$ moiety in (3b). The details and mechanism of the reactions yielding (6), (7), and $PhCH_2SBu^i$ will be reported in a subsequent paper.

Mononuclear Complexes of the Type [Pd($C_6H_4CH_2SBu$)-Cl(dmpy)] (4a) *and* (4b).—The i.r. spectra of (4a) and (4b) exhibited a medium-intensity band at *ca.* 1 600 cm^{-1} due to the skeletal vibration of the 3,5-dimethylpyridine ring. We [6] previously reported that (4a) consisted of two geometrical isomers, but have found that the minor isomer can be removed by recrystallizing twice from dichloromethane and hexane. In the case of (4b), only one geometrical isomer was detected by the ^{1}H n.m.r. spectrum.

At −20 °C the ^{1}H n.m.r. spectrum of (4a) was at the slow-exchange limit (Table 2). Its *o*-phenylene protons appeared as a clear ABCD pattern (Figure 2). A doublet at δ 6.04, resonating at a comparatively high field, was assigned to H^6 and associated with the anisotropic shielding from the 3,5-dimethylpyridine ring.[15,16]

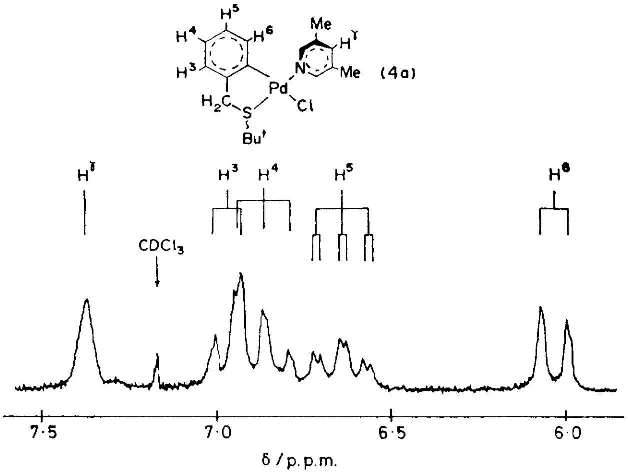


FIGURE 2 Low-field region of the ^{1}H n.m.r. spectrum of (4a)

The ^{1}H n.m.r. spectrum of (4b) at −10 °C exhibited a slow-exchange limit (Table 2), which contained *o*-phenylene proton resonances with an ABCD pattern: a double doublet at δ 6.13 [1 H, ^3J(HH) = *ca.* 8, ^4J(HH) = 2 Hz], a double triplet at δ 6.75 (1 H), a triplet at δ 6.94

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[*] The dihedral angle was apparently not measured in ref. 13, but was calculated using the data of the co-ordinates of the two palladium atoms and two chlorine ones, forming the chloro-bridge.

[†] At −35 °C, the benzyl methylene proton resonance changed into two AB type quartets at δ 3.88 (2.4 H, Δδ = 0.44) and 3.90 (1.6 H, Δδ = 0.48).

(1 H), and a doublet at δ 7.05 (1 H). The first signal was ascribed to H^6 as for (4a). The ABCD patterns in (4a) and (4b) were quite different from the patterns of the phenyl proton resonances in (1a), $PhCH_2SBu^t$, or $PhCH_2SBu^i$, indicating the cyclopalladated nature of the $C_6H_4CH_2SBu$ moieties in (4a) and (4b).[11,16] At the same temperature, isobutyl methylene protons in (4b) exhibited a double AB quartet at δ 3.10 (2 H). This is attributable to two non-equivalent methylene protons of the isobutyl group, which arise from the quenching of rotation of the isobutyl methylene carbon–sulphur bond.

Mononuclear Complexes of the Type $[Pd(C_6H_4CH_2SBu)(acac)]$ (5a) *and* (5b).—The i.r. spectra of (5a) and (5b) showed two bands at 1 575 and 1 520 cm^{-1}, characteristic of *O,O'*-chelation of an acetylacetonato-ligand. The mass spectrum of both (5a) and (5b) gave the parent peak at *m/e* 385 corresponding to ^{106}Pd and fragment peaks at *m/e* 328 $[P - Bu]^+$, 286 $[P - acac]^+$, and 229 $[P - Bu - acac]^+$. These results and the ^1H n.m.r. data (Table 2) support the cyclopalladated structures of the $C_6H_4CH_2SBu$ moieties in (5a) and (5b).

The ^1H-decoupled ^{13}C n.m.r. spectrum of (5b) exhibited two quaternary carbons at δ 147.3 and 149.2, assignable to C^1 and C^2. The other four carbons (C^3—C^6) on the *o*-phenylene group appear at δ 123.0, 124.7, 125.3, and 132.5. These six distinct *o*-phenylene carbons differ from those of the phenyl group of $PhCH_2SBu^i$, and again confirm the cyclopalladated structure of (5b). Carbon signals at δ 21.9 (methyl) 45.0, 47.9 (methylene), and 99.9 (methine) were also observed for the $C_6H_4CH_2SBu^i$ moiety. Two magnetically non-equivalent carbonyl carbons and methyl carbons of the acac chelate appeared at δ 186.3 and 187.9 and δ 27.9 and 28.3 respectively. The methine carbon of the acac chelate overlapped with the methine carbon of the isobutyl group at δ 99.9.

EXPERIMENTAL

Benzyl butyl sulphides, $PhCH_2SR$ (R = Bu^t or Bu^i),[17] and Tl[acac] [18] were synthesized according to published methods with slight modifications. General procedures were as described previously.[11]

Preparations.—$[Pd(O_2CMe)_2(PhCH_2SBu^t)_2]$ (1a). Treatment of a suspension of palladium(II) acetate (0.20 g, 0.89 mmol) in benzene (10 cm^3) with an excess of $PhCH_2SBu^t$ (0.64 g, 3.6 mmol) gave an orange-yellow solution, which was stirred for 15 h at room temperature and then filtered. The orange filtrate was concentrated *in vacuo*, and addition of hexane gave 0.52 g of (1a).

$[\{Pd(C_6H_4CH_2SBu^t)(O_2CMe)\}_2]$ (2a). (*i*) A methanol solution (10 cm^3) of (1a) (0.23 g, 0.39 mmol) was refluxed for 30 min. After the resulting palladium black had been filtered off, the filtrate was chromatographed on a silica gel column (200 mesh, 8 × 100 mm). A yellow fraction was eluted with diethyl ether and evaporated to dryness. The residue was washed with a small amount of hexane to afford 0.04 g of (2a).

(*ii*) A mixture of palladium(II) acetate (1.0 g, 4.5 mmol) and $PhCH_2SBu^t$ (0.80 g, 4.5 mmol) in methanol (30 cm^3) was refluxed for 1 h. The product was then obtained in the same way as described for (*i*). Yield, 0.52 g of (2a).

$[\{Pd(C_6H_4CH_2SBu^i)(O_2CMe)\}_2]$ (2b). A mixture of palladium(II) acetate (0.50 g, 2.2 mmol) and $PhCH_2SBu^i$ (0.40 g, 2.2 mmol) in acetic acid (15 cm^3) was refluxed for 30 min. After the resulting solids had been filtered off, the filtrate was diluted with water (150 cm^3) and then set aside overnight. The needles formed were collected and washed with water and diethyl ether to give (2b).

$[\{Pd(C_6H_4CH_2SBu)Cl\}_2]$ (3a) *and* (3b).—Lithium chloride (0.12 g, 2.9 mmol) in water (4 cm^3) was added to a solution of (2a) or (2b) (0.40 g, 0.58 mmol) in tetrahydrofuran (20 cm^3). After stirring for 20 h at room temperature, a pale yellow precipitate was collected and then washed with water and diethyl ether to afford (3a) or (3b) respectively.

Reactions of (3a) *and* (3b).—(*a*) *With* 3,5-*dimethylpyridine*. A pale yellow solution was obtained immediately by adding dmpy (0.07 g, 0.65 mmol) to a suspension of (3a) (0.20 g, 0.31 mmol) in dichloromethane (5 cm^3). After stirring for 2 h at room temperature, addition of hexane to the pale yellow solution gave $[Pd(C_6H_4CH_2SBu^t)Cl(dmpy)]$ (4a). Similarly, a pale yellow solution, obtained from (3b), was evaporated to dryness, and the residue was recrystallized from benzene and hexane to yield $[Pd(C_6H_4CH_2SBu^i)Cl(dmpy)]$ (4b).

(*b*) *With* Tl[acac]. A suspension containing (3a) or (3b) (0.30 g, 0.47 mmol) and Tl[acac] (0.29 g, 0.96 mmol) in dichloromethane (15 cm^3) was stirred for 1 d at room temperature. After centrifuging the resulting milky suspension, the concentrated supernatant solution was passed through a silica gel column (200 mesh, 100 × 80 mm) with dichloromethane. The yellow fraction was evaporated to dryness to give $[Pd(C_6H_4CH_2SBu^t)(acac)]$ (5a) or $[Pd(C_6H_4CH_2SBu^i)(acac)]$ (5b).

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