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Reactions of Benzyl t-Butyl Sulfide with Palladium(II)-chloride and -acetate. Unusual Sulfur–Carbon Bond Cleavage and Cyclopalladation

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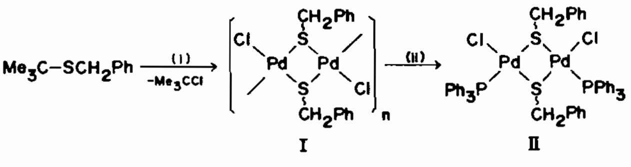
Cyclometallated complexes containing a sulfur-donor ligand are less popular [1] than those containing a nitrogen- or a phosphorus-donor one [2]. Only a few reports have been published about oxypalladation reactions of allylic sulfides [3], about cyclopalladation of thiopivaloylferrocene [4], thiobenzophenone [5], and 2,2-dimethylpent-4-enyl methyl sulfide [6], and about carbopalladation of α, β-unsaturated thioamides [7]. It has been reported that attempts to obtain new cyclopalladated complexes by the reaction of benzyl sulfides with tetrachloropalladate(II) ion were unsuccessful and only the addition products, dichlorobis(benzyl sulfide)-palladium(II) complexes, were produced [3, 8]. In the course of the investigation of the reactions of metal compounds with sulfur-donor ligands, benzyl t-butyl sulfide was found to undergo both an unusual sulfur–carbon bond cleavage with palladium(II) chloride and a cyclopalladation reaction with palladium(II) acetate. This letter deals with these two reactions and the resulting palladium(II) complexes.

A methanol suspension containing equimolar amounts of palladium(II) chloride and benzyl t-butyl sulfide was heated under reflux for 6 h to give an orange suspension. After filtration, orange precipitates were separated and washed with diethyl ether to give $[\{PdCl(SCH_2Ph)\}_n]$ (I), which is insoluble in common organic solvents. The IR spectrum of I lacked two bands at 2960 1170 cm^{-1} characteristic of the C–H stretching and the skeletal vibrations of t-butyl group, respectively. Furthermore, it was confirmed by gas chromatography that the filtrate contained t-butyl chloride in an amount nearly equimolar to palladium(II) chloride. On the basis of these results and the characterization of the derivative of I as stated later, I can be assigned to a polynuclear type complex, *catena*-μ-benzylthio-μ-chloropalladium(II) [9]. Lindoy *et al.* have reported such a metal-assisted cleavage of sulfur–carbon bond in sulfides such as 2-methylthioaniline [10], 8-methylthioquinoline [11], and dimethyl(2-methylthiophenyl)arsine [12], but these reactions were accompanied by a chelate formation and most of them were carried out in considerably drastic conditions: refluxing dimethylformamide for 8 h. It is noteworthy that the sulfur–carbon bond cleavage of benzyl t-butyl sulfide by palladium(II) chloride proceeded almost quantitatively under the milder condition, in refluxing methanol for 6 h.

Triphenylphosphine cleaved the chloro-bridge rather than the sulfido-one in I, and afforded di-μ-benzylthio-*ae*-dichloro-*bf*-bis(triphenylphosphine)dipalladium(II) (II) [9] (Scheme 1). The ^1H NMR spectrum of II showed a singlet at δ 3.00 ppm (2H) and a triplet at δ 4.54 ppm ($^4J_{PH}$ = 6 Hz, 2H), which were ascribed to two magnetically nonequivalent methylene groups, situated at *cis* and *trans* positions



Scheme 1. Reactions of benzyl t-butyl sulfide with palladium(II) chloride. (i) $PdCl_2$, MeOH, reflux; (ii) PPh_3, CH_2Cl_2, 15–20 °C.

TABLE I. Yields and Some Properties of the Palladium(II) Complexes.

Complex	Yield %	Color	MP °C	^1H NMR (δ value from TMS)^c CH_2
I	92	Orange	245	–
II	71	Yellow	226–234(dec)	d 3.00 s, 4.54 t ($^4J_{PH}$ = 6 Hz)
III	56	Yellow	103	e 3.8 br
IV	29^a, 20^b	Lemon yellow	190 (dec)	e 2.79 q (Δδ = 0.65, $^2J_{HH}$ = 18 Hz)
V	95	Pale yellow	200–205 (dec)	f 4.1 br
VI	62	Yellow white	145–165 (dec)	f 4.09 br s

[a] Based on II. [b] Based on $Pd(O_2CMe)_2$. [c] Measured at room temperature. [d] In $CDCl_3$. [e] In CCl_4. [f] In CD_2Cl_2.

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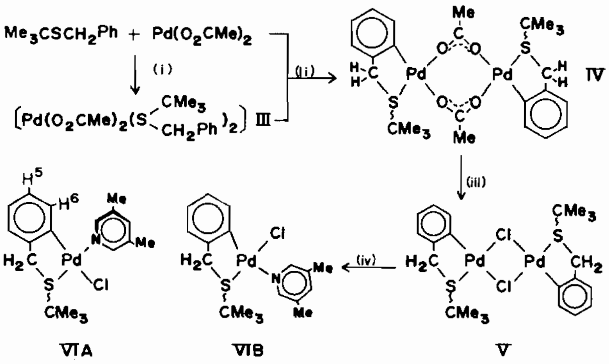
to two one-sided phosphine ligands, respectively. No *af*-dichloro type binuclear complex was obtained. This result agrees very closely with that of Chatt and Hart [13].

Palladium(II) acetate reacted with an excess amount of benzyl t-butyl sulfide to produce yellow crystals, diacetatobis(benzyl t-butyl sulfide)palladium(II) (III) [9]. A methanol solution of III was refluxed for 30 min. Resulting palladium black was filtered off, and the filtrate was passed through a silica gel column (10 cm length) with diethyl ether. A yellow fraction was evaporated to dryness, and the residue was washed with hexane to give lemon-yellow crystals, di-μ-acetato-bis[(t-buthylthiomethyl)phenyl, 1-*c,s*] dipalladium(II) (IV) [9]. Complex IV was also obtained from equimolar amounts of palladium(II) acetate and the sulfide in refluxing methanol for 1 h.

The IR spectra of III and IV showed a medium band at 1165 cm^{-1} due to the skeletal vibration of the t-butyl group, indicating that both complexes have the t-butyl group different from I. Complex III exhibited two bands at 1635 and 1300 cm^{-1} characteristic of the COO stretching vibrations of unidentate acetato groups, whereas IV showed two bands at 1575 and 1420 cm^{-1} for those of bridged acetato groups. The ^1H NMR spectrum of IV exhibited an AB quartet due to methylene protons at δ 2.79 (2H) and complicated *o*-phenylene signals near δ 6.5–6.9 and 7.2–7.3 (total 4H), which are quite different from the phenyl proton resonances of benzyl t-butyl sulfide (multiplet near δ 7.1–7.4, 5H). These facts indicate that IV contains cyclopalladated benzyl moieties.



Scheme 2. Reactions of benzyl t-butyl sulfide with palladium(II) acetate. (i) benzene 15–20 °C; (ii) MeOH, reflux; (iii) LiCl, THF–H_2O, 15–20 °C; (iv) lut, CH_2Cl_2, 15–20 °C.

Complex IV reacted with an excess amount of lithium chloride in THF-H_2O mixture at room temperature to yield the chloro-bridged analogue (V) [9]. This complex underwent a bridge splitting reaction with 3,5-lutidine (lut) to afford a mononuclear complex (VI) [9]. In the ^1H NMR spectrum of VI, t-butyl protons were observed as two singlets at δ 1.20 (1.8H) and 1.54 (7.2H), indicating that VI has two isomers, VI-A and VI-B, as shown in Scheme 2 (the population ratio of VI-A: VI-B = 8:2). As far as the *o*-phenylene protons are concerned, a doublet and a triplet resonance ascribable to 6-H and 4-H (or 5-H) were observed at δ 6.16 ($^3J_{HH}$ = 8 Hz, 0.8H) and 6.62 ($^3J_{HH}$ = 8 Hz, 1H), respectively. The former resonance, which appeared at a significantly higher field, is associated with the anisotropic shielding from the adjacent lutidine ring [14]. In the ^1H NMR spectrum of V, a doublet resonance due to 3-H or 6-H was also observed at δ 7.14 ($^3J_{HH}$ = 8 Hz, 1H). These results confirm unambiguously the cyclopalladated structure of V and VI.

In this letter we revealed that benzyl t-butyl sulfide displays two different reaction modes towards palladium(II) chloride and palladium(II) acetate. It seems likely that the reaction modes depend upon the ability of the ligating anions (*i.e.* chloro or acetato anion) to capture either the t-butyl cation or the *ortho*-proton of the benzyl group. The chloro anion captures easily the t-butyl cation instead of the *ortho*-proton owing to its weak basicity to give I, whereas the acetato one does the *ortho*-proton owing to the relatively strong basicity to produce IV.

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