

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

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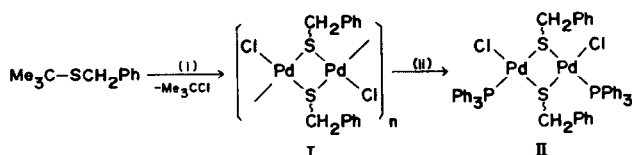
Received June 16, 1980

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], thio-benzophenone [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 precipi-

tates 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)di-palladium(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.

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

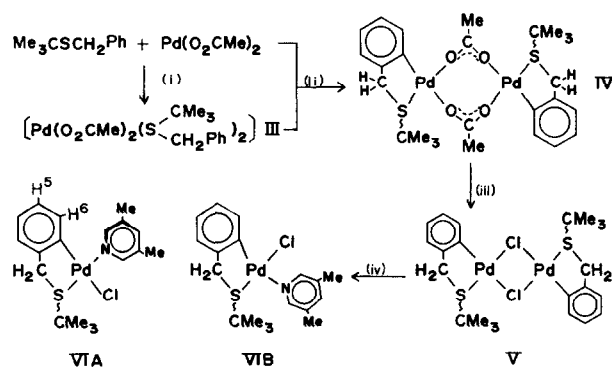
Complex	Yield %	Color	MP °C	1H NMR (δ value from TMS) ^c CH ₂
I	92	Orange	245	—
II	71	Yellow	226–234(dec)	d 3.00 s, 4.54 t ($^4J_{PH} = 6$ Hz)
III	56	Yellow	103	e 3.8 br
IV	29 ^a , 20 ^b	Lemon yellow	190 (dec)	e 2.79 q ($\Delta\delta = 0.65$, $^2J_{HH} = 18$ Hz)
V	95	Pale yellow	200–205 (dec)	f 4.1 br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

^aBased on II. ^bBased on $Pd(O_2CMe)_2$. ^cMeasured at room temperature. ^dIn $CDCl_3$. ^eIn CCl_4 . ^fIn CD_2Cl_2 .

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*-butylthiomethyl)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 $15\text{--}20^\circ\text{C}$; (ii) MeOH, reflux; (iii) LiCl, THF- H_2O , $15\text{--}20^\circ\text{C}$; (iv) lut, CH_2Cl_2 , $15\text{--}20^\circ\text{C}$.

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 ($^3J_{\text{HH}} = 8\text{ Hz}$, 0.8H) and 6.62 ($^3J_{\text{HH}} = 8\text{ Hz}$, 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 ($^3J_{\text{HH}} = 8\text{ Hz}$, 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.

Acknowledgement

We wish to express our gratitude to Mrs. Hisako Mazume and Miss Yumi Kojima of Nagasaki University for their technical assistance.

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