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SYNTHESIS AND CHARACTERIZATION OF PALLADIUM COMPLEXES WITH BIS(BENZYLTHIO)METHANE

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Abstract—Reactions of $Na_2[PdCl_4]$ with one equivalent and two equivalents of bis(benzylthio)methane (btm) yield *trans*-$[PdCl_2(\mu\text{-btm})]_n$ (**1**) and *trans*-$[PdCl_2(\text{btm-}S)_2]$ (**2**), respectively. Treatment of **2** with $[PdCl_2(NCMe)_2]$ gives the face-to-face type palladium(II) complex, *trans*-$[Pd_2Cl_4(\mu\text{-btm})_2]$ (**3**), whereas the reaction of **2** with $[Pd(dba)_2]$ (dba = dibenzylideneacetone) produces the side-by-side type palladium(I) complex, $[Pd_2Cl_2(\mu\text{-btm})_2]$ (**4**). Treatment of **4** with dimethyl acetylenedicarboxylate gives the A-frame type complex $[Pd_2Cl_2\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-btm})_2]\cdot 1/2CH_2Cl_2$ (**5**). The complexes obtained in this study were characterized by elemental analysis, IR and NMR spectroscopy.

There has been interest recently in binuclear complexes containing the "short-bite" ligands such as bis(diphenylphosphino)methane[1] and 2-(diphenylphosphino)pyridine,[2] etc. In our previous papers, we have reported the synthesis of mono- and bimetallic complexes of palladium[3] and rhodium[4] containing the unsymmetrical "short-bite" ligand, (benzylthiomethyl)diphenylphosphine. Syntheses have also been reported of various metal complexes with symmetrical "short-bite" sulphur donor ligands; specifically thioether ligands, $RSCH_2SR$ (R = Me, Ph).[5–12] These dithioether ligands are mostly coordinated in unidentate or bidentate chelating modes in metal complexes. As for the bidentate bridging coordination mode of dithioether ligands, few have been reported: the platinum complexes of $[(PtXMe_3)_2(\mu\text{-}MeSCH_2SMe)]$[8,9] and the rhodium complex of $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}PhSCH_2SPh)_2]$[10] are two examples.

Here, we wish to report the synthesis of palladium complexes with a dithioether ligand, bis(benzylthio)methane (btm), including the side-by-side type bimetallic complex of $[Pd_2Cl_2(\mu\text{-btm})_2]$, the face-to-face type complex of $[Pd_2Cl_4(\mu\text{-btm})_2]$ and the A-frame type complex of $[Pd_2Cl_2\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-btm})_2]$.

RESULTS AND DISCUSSION

The new reactions of bis(benzylthio)methane are summarized in Scheme 1. Yields, melting points and analytical data are listed in Table 1, while ^1H and ^{13}C NMR data are summarized in Table 2.

Reactions of $Na_2[PdCl_4]$ *with* btm

Treatment of btm with one or a half equivalent of $Na_2[PdCl_4]$ yielded *trans*-$[PdCl_2(\mu\text{-btm})]_n$ (**1**) and *trans*-$[PdCl_2(\text{btm-}S)_2]$ (**2**), respectively. The ^1H NMR spectrum of **1** was not obtained due to its poor solubility in common solvents. However, the far-IR spectrum showed a single band at 361 cm^{-1} assigned to $\nu(Pd—Cl)$, suggesting a *trans* con-

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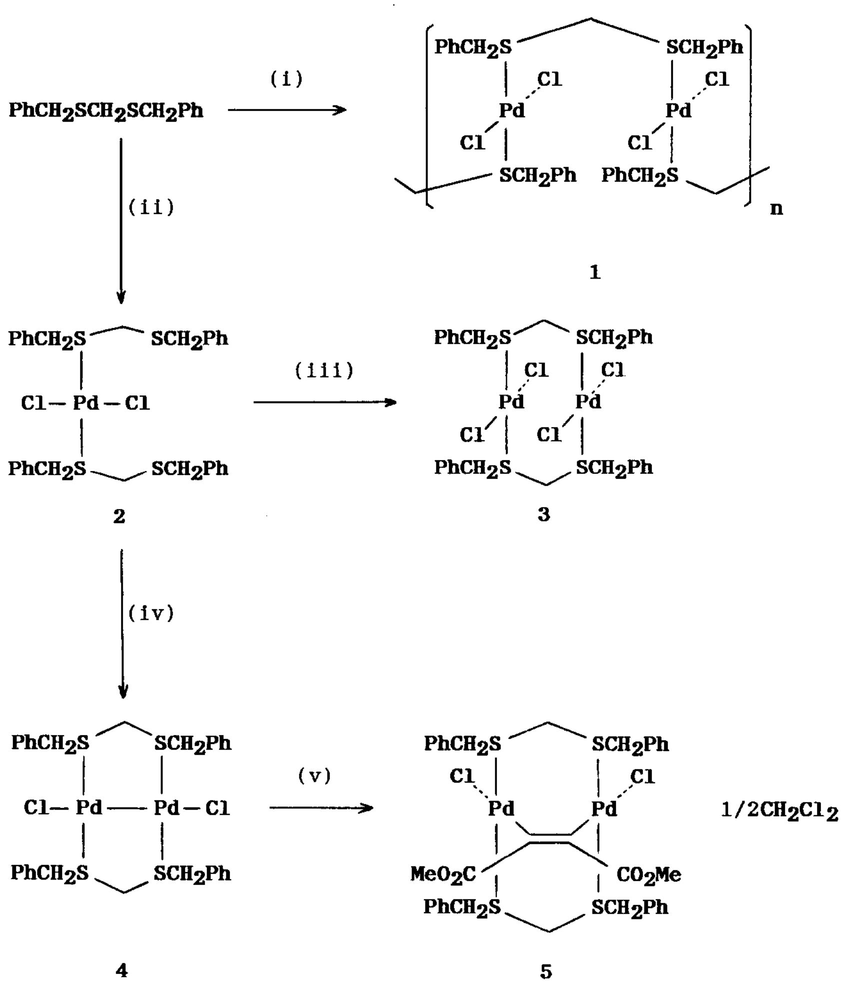

Scheme 1. Formation and reactions of btm complexes of palladium: (i) one equivalent of $Na_2[PdCl_4]$; (ii) a half equivalent of $Na_2[PdCl_4]$; (iii) $[PdCl_2(NCMe)_2]$; (iv) $[Pd(dba)_2]$; (v) $MeO_2CC{\equiv}CCO_2Me$.

figuration of the chloro ligands. On the basis of these results and the elemental analysis, **1** was assigned an oligomeric structure in which btm acts as a bidentate bridging ligand, as shown in Scheme 1.

As for **2**, the elemental analysis supported the formulation of $[PdCl_2(btm\text{-}S)_2]$ and the far-IR spectrum indicated a *trans* configuration of the chloro ligands [ν(Pd—Cl) 362 cm^{-1}]. Complex **2** showed temperature-dependent ^1H NMR spectra, as shown in Fig. 1. At 50°C, two singlets appeared at δ 4.11 and 3.81 due to CH_2Ph and SCH_2S, respectively. The former singlet broadened at 25°C and then at -10°C separated into two broad resonances at δ 4.25 and 3.95. Furthermore, at -50°C the resonance at δ 4.25 became sharp (δ 4.28), whereas the signal at δ 3.95 separated into two resonances at δ 3.95 and 3.90. In contrast, the SCH_2S resonance, observed at δ 3.81 at 50°C, broadened at -10°C and then at -50°C separated into two humps at δ 3.8 and 3.6. These phenomena could be explained in terms of 1,3-intramolecular metal shifts between the four ligand sulphur atoms and the pyramidal inversions of the ligated sulphur atoms, as illustrated in Fig. 2. At 50°C, the 1,3-metal shifts and the

Table 1. Yields, melting points and analytical data

Complex	Yield (%)	Melting point (°C)	Analysis (%)[b]	
			C	H
1	87	166	40.8(41.2)	3.6(3.7)
2	75	100	51.1(51.6)	4.6(4.6)
3	80	105	41.0(41.2)	3.7(3.7)
4	50	128	44.3(44.8)	3.9(4.0)
5	50	165	44.6(44.3)	4.1(4.0)

[a] With decomposition.

[b] Calculated values in parentheses.

Table 2. NMR spectral data

Complex	^{1}H NMR^a	^{13}C{^{1}H} NMR^a
2	3.81 (s, SCH_2S); 4.11 (s, CH_2Ph); 7.2–7.4 (m, Ph)	37.93 (SCH_2S); 38.45 (CH$_2$Ph); 128.03 (*para*-Cs); 128.92 (*meta*-Cs); 129.77 (*ortho*-Cs)^b
3	3.9 (br s, SCH_2S); 4.35 (br s, CH_2Ph); 7.1–7.5 (m, Ph)	—^{c}
4	3.96 (s, SCH_2S); 4.29 (s, CH_2Ph); 7.1–7.4 (m, Ph)	38.12 (SCH$_2$S); 42.89 (CH$_2$Ph); 128.89 (*para*-Cs); 129.14 (*meta*-Cs); 129.55 (*ortho*-Cs); 133.60 (*ipso*-Cs)
5	2.73 [d, ^2J(HH) 12.1 Hz, SCH_2S]; 3.43 [d, ^2J(HH) 12.1 Hz, SCH_2S]; 3.69 [s, OCH_3]; 4.38 [d, ^2J(HH) 13.9 Hz, CH_2Ph]; 4.45 [d, ^2J(HH) 13.9 Hz, CH_2Ph]; 5.28 (s, CH_2Cl$_2$)	31.51 (SCH$_2$S); 41.31 (CH$_2$Ph); 52.23 (CO$_2$$CH_3$); 128.61 (*para*-Cs); 129.22 (*meta*-Cs); 129.65 (*ortho*-Cs); 133.65 (*ipso*-Cs); 163.47 (CO$_2$CH$_3$)^d

[a] Spectra obtained in $CDCl_3$ at 50°C. s = singlet, d = doublet, m = multiplet and br = broad.
[b] *Ipso*-Cs could not be detected.
[c] Not measured (see text).
[d] Olefinic carbons could not be detected.

pyramidal inversions were supposed to take place rapidly, and these motions caused two differential sited CH_2Ph groups to resonate as one singlet at δ 4.11. At −10°C, the 1,3-metal shifts seem to be quenched, while the pyramidal inversions are still occurring. Accordingly, at this temperature two different environmental CH_2Ph groups appeared as two signals. Finally, at −50°C, when the pyramidal inversions were nearly quenched, the CH_2Ph groups directly attached to the ligated sulphur atoms further split into two signals owing to the presence of diastereomers, DL and *meso* (Fig. 2). Corresponding to this fact, at −50°C SCH_2S separated into two humps. Further measurements below −50°C were

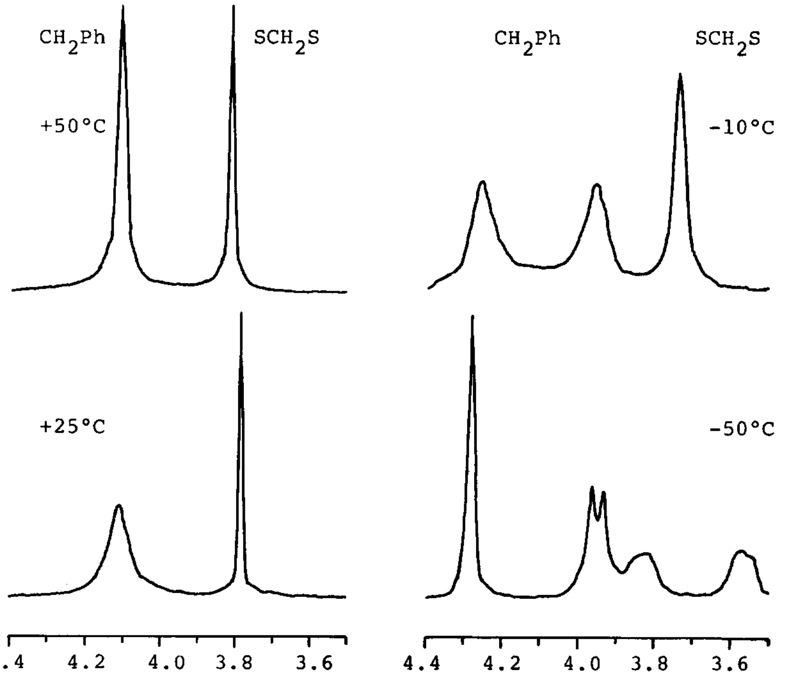

Fig. 1. Temperature-dependent ^{1}H NMR spectra of $[PdCl_2(btm\text{-}S)_2]$ (**2**) in $CDCl_3$.

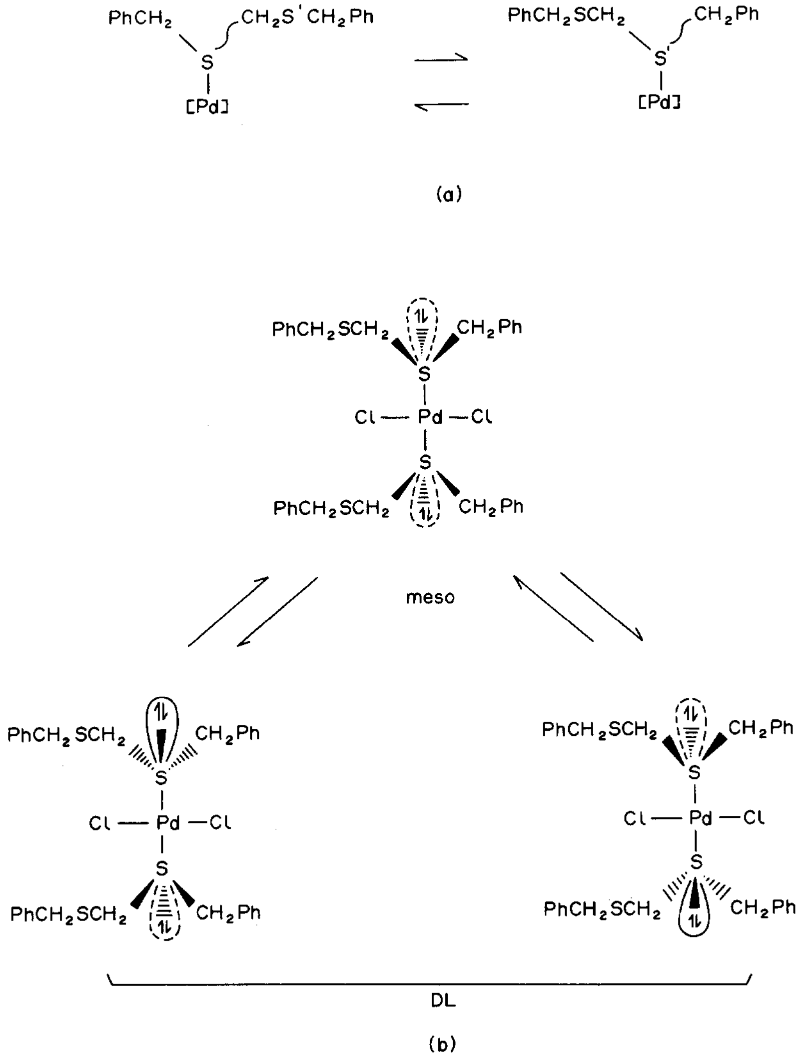

Fig. 2. (a) The 1,3-intramolecular metal shifts and (b) the pyramidal inversions of ligated sulphur atoms and invertomers of $[PdCl_2(btm\text{-}S)_2]$ (**2**).

unsuccessful due to precipitation of solids from the NMR sample solution. Precise studies on the 1,3-intramolecular metal shifts between the ligand sulphur atoms and the pyramidal inversions of the sulphur atoms have been reported by the groups of Abel[5] and Kuhn.[11] In the $^{13}C\{^{1}H\}$ NMR spectrum at 50°C, two methylene carbons due to CH_2Ph and SCH_2S were observed at δ 38.45 and 37.93, respectively.

On the basis of the results mentioned above, together with the molar conductance (Λ_M 2.4 S cm^2 mol^{-1} in acetone), **2** was assigned to *trans*-$[PdCl_2(btm\text{-}S)_2]$ in which two btm ligands are coordinated in a unidentate fashion. Two sulphur atoms in each btm ligand in **2** are coordinatively free, and **2** reacted to form bimetallic complexes (see below).

The face-to-face type complexes $[Pd_2Cl_4(\mu\text{-}btm)_2]$ (**3**)

Treatment of **2** with one equivalent of $[PdCl_2(NCMe)_2]$ afforded **3** which had the same composition as **1** by elemental analysis. However, the molecular weight of **3** was 804.5 (determined by osmometry in benzene at 42°C; calc. for $C_{30}H_{32}Cl_4Pd_2S_4$: 875.5). In contrast with **1**, **3** is soluble in benzene, chloroform and dichloromethane, but is not as stable under conditions of prolonged standing or heating in solution due to gradual conversion back to **1**. For this reason, the ^{13}C NMR spectrum could not be measured. Temperature-dependent ^{1}H NMR spectra were observed for **3**. At 50°C, **3** showed a nearly high-temperature limiting spectrum exhibiting two kinds of methylene proton due to CH_2Ph and SCH_2S moieties. These occurred as slightly broad singlets at δ 4.35 and 3.9, respectively. However, the low-temperature limiting spectra were very complicated owing to a number of conformers caused by the pyramidal inversions of the ligated sulphur atoms. Complete analysis of the temperature-dependent spectra will be reported elsewhere in due course. The ^1H NMR spectra of **4** and **5**, showed similar situations to **3**, but only high-temperature limiting spectra are described in this paper (see below).

On the basis of these results and the far-IR spectrum [ν(Pd—Cl) 357 cm^{-1}], **3** was assigned to the face-to-face type palladium(II) complex, $[Pd_2Cl_4(\mu\text{-btm})_2]$, as illustrated in Scheme 1.

The side-by-side type complex $[Pd_2Cl_2(\mu\text{-btm})_2]$ (4)

Treatment of **2** with one equivalent of $[Pd(bda)_2]$ (dba = dibenzylideneacetone) afforded **4** as orange–brown microcrystals. The high-temperature limiting ^1H NMR spectrum at 50°C exhibited singlets at δ 4.29 and 3.96 due to CH_2Ph and SCH_2S, respectively. The $^{13}C\{^1H\}$ NMR spectrum at 50°C exhibited two methylene carbon signals at δ 42.89 (CH_2Ph) and 38.12 (SCH_2S). On the basis of these results, elemental analysis, its deep colour and the reactivity towards dimethyl acetylenedicarboxylate (see below), **4** was assigned to the side-by-side type palladium(I) complex $[Pd_2Cl_2(\mu\text{-btm})_2]$.

The A-frame type complex $[Pd_2Cl_2\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-btm})_2]$ (5)

The reaction of **4** with dimethyl acetylenediacarboxylate yielded the A-frame type complex **5**. The IR spectrum showed a ν(C=O) band at 1700 cm^{-1} and a ν(C=C) band at 1580 cm^{-1}. The ^1H NMR spectrum was measured at 50°C, a temperature at which the pyramidal inversions occurred rapidly. Together with the OCH_3 resonance at δ 3.69, CH_2Ph and SCH_2S appeared as AB quartets at δ 4.45 (d) and 4.38 (d), and δ 3.43 (d) and 2.73 (d), respectively. As this complex is an A-frame type, the two protons of the SCH_2S moieties are originally non-equivalent and CH_2Ph are diastereotopic even when rapid pyramidal inversions of the ligated sulphur atoms occur, and they were observed as AB quartets. In the $^{13}C\{^1H\}$ NMR spectrum at 50°C, all carbons except for the olefinic carbons formed by the insertion of the acetylene were clearly detected (Table 2).

Conclusions

The dithioether ligand, btm, was found to coordinate to palladium complexes in a unidentate manner in **2**, and a bidentate bridging fashion in **1** to form an oligomeric compound, or in **3** and **4** to produce bimetallic complexes. Complexes **2**–**4** are fairly stable in the solid state, but gradually decomposed in solution under prolonged heating or standing in air, which precluded the growing of suitable crystals for X-ray structural analysis. The ^{13}C NMR spectra could be successfully measured at 50°C. ^1H NMR spectra were all temperature-dependent mainly owing to the pyramidal inversions of the ligated sulphur atoms, and therefore in this paper only high-temperature limiting spectra have been described.

EXPERIMENTAL

General methods were as previously described in a recent paper from our laboratory.[3] Bis(benzylthio)methane was prepared according to a literature method.[13]

Preparation of trans-$[PdCl_2(\mu\text{-btm})]_n$ (1)

A solution of btm (0.097 g, 0.36 mmol) in MeOH (5 cm^3) was added to a solution of $Na_2[PdCl_4]$ (0.100 g, 0.34 mmol) in MeOH (15 cm^3). A yellow precipitate was formed immediately. The resulting suspension was stirred at room temperature for 2 h and filtered to yield **1**.

Synthesis of trans-$[PdCl_2(\text{btm-}S)_2]$ (2)

A solution of btm (0.186 g, 0.71 mmol) in MeOH (10 cm^3) was added to a solution of $Na_2[PdCl_4]$ (0.100 g, 0.34 mmol) in MeOH (15 cm^3). A yellow precipitate which initially formed was dissolved and then a yellow precipitate reappeared. Stirring was continued for at least 1 day at room temperature, and the precipitate was collected to give **2**.

Preparation of $[Pd_2Cl_4(\mu\text{-btm})_2]$ (3)

Solid $[PdCl_2(NCMe)_2]$ (0.037 g, 0.14 mmol) was added to a solution of **2** (0.100 g, 0.14 mmol) in CH_2Cl_2 (10 cm^3). The resulting solution was stirred at room temperature for 2 h, and the volatile materials were removed under reduced pressure. The residue was recrystallized from CH_2Cl_2–Et_2O–hexane to afford **3** as yellow crystals.

Synthesis of [$Pd_2Cl_2(\mu\text{-btm})_2$] (**4**)

Solid [$Pd(dba)_2$] (0.300 g, 0.52 mmol) was added to a solution of **3** (0.363 g, 0.52 mmol) in CH_2Cl_2 (15 cm^3), and the mixture was refluxed for 30 min. After the reaction mixture was evaporated to dryness, the residue was chromatographed on a silica gel column (200 mesh, 200 × 10 mm). The red fraction eluted by CH_2Cl_2 was concentrated and diluted with hexane to give **4** as orange–brown microcrystals.

Preparation of [$Pd_2Cl_2\{\mu\text{-}C_2(CO_2Me)_2\}(\mu\text{-btm})_2$] · $1/2CH_2Cl_2$ (**5**).

An excess of dimethyl acetylenedicarboxylate (0.233 g, 1.57 mmol) was added to a stirred solution of **4** (0.315 g, 0.39 mmol) in CH_2Cl_2 (20 cm^3). The resulting solution was stirred for 1 day, during which time the colour changed from orange–brown to yellow–orange. After the reaction mixture was evaporated to dryness, the residue was chromatographed on a silica gel column (200 mesh, 180 × 10 mm). The yellow–orange fraction eluted by CH_2Cl_2–Et_2O (10 : 1) was collected and recrystallized from CH_2Cl_2–hexane to afford **5**.

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