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Palladium dimethylsilanedithiolato complex: a precursor for Ti–Pd and Ti–Pd_2 heterometallic complexes†

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Received (in Cambridge, UK) 15th February 2002, Accepted 21st March 2002

The silanedithiolato complex $Pd(S_2SiMe_2)(PEt_3)_2$ 1 reacted with $(C_5H_5)TiCl_3$ and $TiCl_4(thf)_2$ to produce the heterometallic clusters $(C_5H_5)TiCl(\mu\text{-}S)_2Pd(PEt_3)_2$ 2 and $TiCl_2(S)(\mu\text{-}S)_2Pd_2(PEt_3)_4$ 3 along with silicon–sulfur bond cleavage, respectively.

The bis-silylated sulfides $(R_3Si)_2S$ have been widely used to prepare a variety of metal sulfide clusters, because these reagents exploit the strength of the Si–O and Si–Cl bond to replace a halide, alkoxide, acetate or oxide with a sulfido ligand under very mild and controlled conditions. Therefore, a metal–silanethiolato complex (*e.g.*, M–$SSiR_3$) would be expected to serve as a synthetic precursor of homo- and hetero-metallic sulfido clusters.[1] However, compounds containing the silanethiolato ligand are less common compared with alkylthiolato complexes.[2,3] Herein we report the synthesis of a palladium dimethylsilanedithiolato complex and its cluster forming reactions with $(C_5H_5)TiCl_3$ and $TiCl_4(thf)_2$.

Reaction of palladium(II) acetate with 1 equiv of cyclotrisilathiane in the presence of triethylphosphine resulted in formation of the dimethylsilanedithiolato complex $Pd(S_2SiMe_2)(PEt_3)_2$ **1** (Scheme 1), which was isolated as yellow crystals in 88% yield.‡ The compound is characterized by analytical, spectroscopic, and crystallographic methods. In the $^{29}Si\{^1H\}$ NMR spectrum, the signal due to the silanedithiolato ligand appears as a triplet at δ 36.1 ($^3J_{SiP}$ 2 Hz). This resonance is shifted to a lower field than that of cyclotrisilathiane (δ 21.4). Compound **1** consists of a chelating $S_2SiMe_2^{2-}$ ligand and two phosphine ligands arranged in a square planar structure (Fig. 1).§ The Pd–S(1)–Si–S(2) ring is planar, and this coordination geometry is similar to that found in $(C_5H_4Me)_2Ti(S_2SiMe_2)$.[2] The Pd–S distances of 2.362(1) and 2.392(1) Å are at the longer end of the range for palladium(II) thiolato complexes (2.25–2.37 Å).[4]

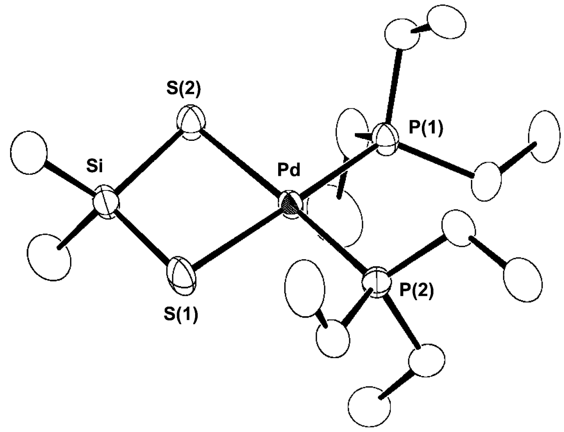
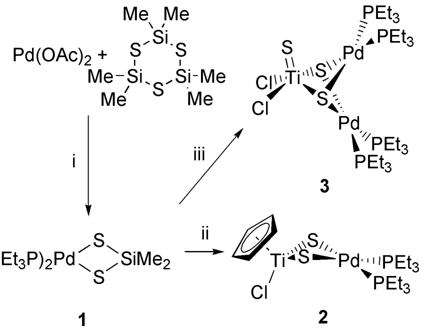


Fig. 1 Molecular structure of **1**. Selected interatomic distances (Å) and angles (°): Pd–S(1) 2.362(1), Pd–S(2) 2.392(1), S(1)–Si 2.099(1), S(2)–Si 2.108(1), Pd–P(1) 2.304(1), Pd–P(2) 2.290(1); S(1)–Pd–S(2) 85.80(3), P(1)–Pd–P(2) 98.09(3).



Scheme 1 *Reagents and conditions*: i, PEt_3, toluene; ii, $(C_5H_5)TiCl_3$ (1 equiv.), toluene; iii, $TiCl_4(thf)_2$ (0.5 equiv.), CH_2Cl_2, −50 °C to room temperature.

The ability of **1** to serve as a precursor for the formation of heterometallic complexes was investigated through its reactions with titanium compounds. Treatment of **1** with 1 equiv. of $(C_5H_5)TiCl_3$ in toluene gave $(C_5H_5)TiCl(\mu\text{-}S)_2Pd(PEt_3)_2$ **2** as yellow plates in 71% isolated yield.‡ In contrast, **1** did not react with $(C_5H_5)_2TiCl_2$. This is presumably due to electronic factors of the two ancillary ligands bonded to the titanium centre. Compound **2** is very soluble in THF and toluene but only slightly soluble in hexane. The ^1H NMR spectrum of **2** displays a 1 : 2 ratio for the C_5H_5 and PEt_3 ligands, and the $SiMe_2$ proton resonance of **1** (δ 0.57) is absent in the spectrum of compound **2**.

The molecular structure of **2** is determined by X-ray analysis (Fig. 2).§ The two metal centres are linked by two μ-sulfido ligands. The geometry around the palladium atom is square-planar with two sulfido and PEt_3 ligands, while the titanium

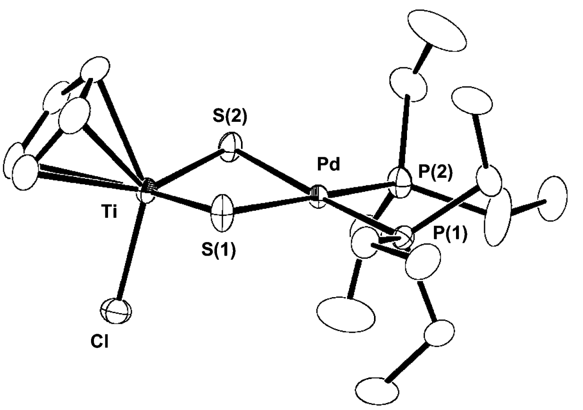


Fig. 2 Molecular structure of **2**. Selected interatomic distances (Å) and angles (°): Ti–Pd 3.014(1), Ti–S(1) 2.224(1), Ti–S(2) 2.222(1), Ti–Cl 2.336(1), Pd–S(1) 2.356(1), Pd–S(2) 2.381(1), Pd–P(1) 2.322(1), Pd–P(2) 2.313(1); S(1)–Ti–S(2) 100.71(4), S(1)–Pd–S(2) 92.59(5), P(1)–Pd–P(2) 100.74(4), Ti–S(1)–Pd 82.24(6), Ti–S(2)–Pd 81.72(3).

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† Electronic supplementary information (ESI) available: experimental details and spectroscopic data for **1**, **2** and **3**. See http://www.rsc.org/suppdata/cc/b2/b201702d/

DOI: 10.1039/b201702d

centre adopts a three-legged piano stool arrangement by coordination to a C_5H_5, a Cl, and two sulfido ligands. The Ti–Pd distance of 3.014(1) Å is long, but it is still in the range where a weak Ti–Pd dative interaction is possible.[5] The presence of a Ti–Pd bond is consistent with the puckered TiS_2Pd quadrilateral. The magnitude of the puckered angle (18.9°) is typical of binuclear μ-sulfur complexes with a metal–metal bond.[5,6] The Pd–S distances (av. 2.369 Å) are similar to those of **1**, and the S–Pd–S angle of **2** is increased. The strong donor ability of the sulfido ligand elongates the Pd–P distances of **2** as compared to those of **1**.

A different type of heterometallic cluster was synthesized by the reaction of **1** with $TiCl_4(thf)_2$ in CH_2Cl_2. This compound **3** was obtained as an orange powder in 84% by addition of Et_2O, and its empirical formula, $TiCl_2(S)(\mu\text{-}S)_2Pd_2(PEt_3)_4$, was confirmed by elemental analysis. The X-ray crystal structure of **3** reveals a $TiPd_2$ triangle core capped by two μ_3-sulfido ligands (Fig. 3).§ Each palladium centre assumes a square-planar geometry. The titanium atom is in a square-pyramidal environment with the terminal sulfido ligand occupying the axial coordination site and the titanium atom located above the basal square plane (0.68 Å above the mean plane). The terminal Ti=S bond of 2.117(1) Å is shorter than the corresponding bonds of $(C_5Me_5)_2Ti(S)(C_5H_5N)$ [2.217(1) Å],[7] $Na_2[(C_5H_5)Ti(\mu\text{-}S)(S)]_2$ [2.187(1), 2.202(1) Å],[8] and $[PhC(NSiMe_3)_2]_2Ti(S)(C_5H_5N)$ [2.139(1) Å][9] but is similar to that of $[NEt_4]_2[Ti(S)Cl_4]$ [2.111(2) Å].[10] The IR spectrum of **3** exhibits a band at 531 cm^{-1} assignable to a Ti=S stretching vibration, which is comparable to those reported for $[PhC(NSiMe_3)_2]_2\text{-}Ti(S)(C_5H_5N)$ (520 cm^{-1})[9] and $[NEt_4]_2[Ti(S)Cl_4]$ (530 cm^{-1}).[10] The Ti–Pd distances are substantially longer than that of **2**, and the Pd–Pd separation [3.315(1) Å] is too long to form a metal–metal bond. The shorter Ti–Pd distances relative to the Pd–Pd distance is reflected in angles at the μ_3-sulfur atoms. The Ti–S–Pd angles are smaller than the Pd–S–Pd angles. Although the molecular structure of **3** is unsymmetrical in crystals, the $^{31}P\{^1H\}$ NMR spectrum of **3** in $CDCl_3$ at room temperature displays one resonance at δ 19.0. Thus the cluster structure is fluxional in solution.

In conclusion, the novel silanethiolato complex **1** has been readily prepared by using cyclotrisilathiane. The formation of **2** and **3** under a mild condition demonstrates that the PdS_2SiMe_2 moiety in **1** can serve as a convenient precursor for heterometallic sulfido clusters. In contrast, the related titanium–silanethiolato complex $(C_5H_4Me)_2Ti(S_2SiMe_2)$ underwent a ligand transfer with L_2MCl_2 [$L_2M = (C_5H_4Me)_2V$, $(PPh_3)_2Pt$] to give $L_2M(S_2SiMe_2)$.[2]

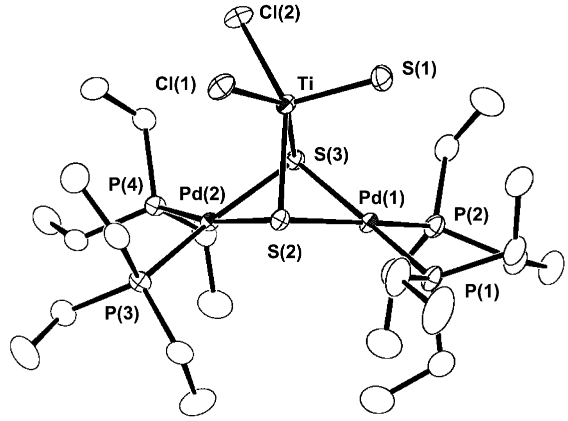

Fig. 3 Molecular structure of **3**. Selected interatomic distances (Å) and angles (°): Ti–Pd(1) 3.130(1), Ti–Pd(2) 3.185(1), Pd(1)–Pd(2) 3.315(1), Ti–S(1) 2.117(1), Ti–S(2) 2.451(1), Ti–S(3) 2.470(1), Pd(1)–S(2) 2.357(1), Pd(1)–S(3) 2.356(1), Pd(2)–S(2) 2.345(1), Pd(2)–S(3) 2.349(1), Pd(1)–P(1) 2.311(1), Pd(1)–P(2) 2.300(1), Pd(2)–P(3) 2.299(1), Pd(2)–P(4) 2.312(1); Ti–S(2)–Pd(1) 81.42(4), Ti–S(3)–Pd(1) 80.83(4), Ti–S(2)–Pd(2) 83.19(3), Ti–S(3)–Pd(2) 82.69(4), Pd(1)–S(2)–Pd(2) 89.91(3), Pd(1)–S(3)–Pd(2) 89.58(4).

Notes and references

‡ *Selected data* for **1**: yellow crystals, yield 88%. δ_H (500 MHz, $CDCl_3$): 1.87 (dq, 12H, PCH_2CH_3, $^2J_{PH}$ 8.7, $^3J_{HH}$ 7.6 Hz), 1.13 (dt, 18H, PCH_2CH_3, $^3J_{PH}$ 17, $^3J_{HH}$ 7.6 Hz), 0.57 (s, 6H, $SiMe_2$). δ_P (202.35 MHz, $CDCl_3$, 85% H_3PO_4): 20.5 (s). δ_{Si} (99.25 MHz, $CDCl_3$, $SiMe_4$): 36.1 (t, $^3J_{SiP}$ 2 Hz). Anal. Calc. for $C_{14}H_{36}P_2PdS_2Si$: C, 36.16; H, 7.80; S, 13.79. Found: C, 36.07; H, 7.70; S, 13.88%.

Selected data for **2**: yellow crystals, yield 71%. δ_H (500 MHz, $CDCl_3$): 6.38 (s, 5H, C_5H_5), 1.92–2.15 (m, 12H, PCH_2CH_3), 1.13 (dt, 18H, PCH_2CH_3, $^3J_{PH}$ 17, $^3J_{HH}$ 7.6 Hz). δ_P (202.35 MHz, $CDCl_3$): 26.5 (s). Anal. Calc. for $C_{17}H_{35}ClP_2PdS_2Ti$: C, 36.77; H, 6.35; S, 11.55. Found: C, 36.40; H, 6.37; S, 11.30%.

Selected data for **3**: orange powder, yield 84%. δ_H (500 MHz, $CDCl_3$): 1.81–2.03 (m, 24H, PCH_2CH_3), 1.08–1.16 (m, 36H, PCH_2CH_3). δ_P (202.35 MHz, $CDCl_3$): 19.0 (s). IR ν/cm^{-1}: 531 (m, $\nu_{Ti=S}$). Anal. Calc. for $C_{24}H_{60}Cl_2P_4Pd_2S_3Ti\cdot CH_2Cl_2$: C, 30.47; H, 6.34; S, 9.76. Found: C, 30.86; H, 6.70; S, 10.01%.

§ *Crystal data*: for **1**: $C_{14}H_{36}SiP_2S_2Pd$, M = 464.99, monoclinic, space group $P2_1/n$, a = 9.4431(11), b = 17.119(2), c = 14.368(2) Å, β = 108.271(5)°, V = 2205.6(4) $Å^3$, Z = 4, T = 193 K, μ(Mo-Kα) = 12.22 cm^{-1}, Rigaku Mercury CCD diffractometers, 17804 measured reflections ($2\theta_{max}$ = 55.0°). At convergence, $R1$ = 0.032, $wR2$ = 0.040, and GOF = 1.01 for 217 variables refined against all 5037 unique reflections. For **2**: $C_{17}H_{35}P_2S_2ClTiPd$, M = 555.28, monoclinic, space group $P2_1/n$, a = 11.418(5), b = 17.174(8), c = 12.419(6) Å, β = 99.558(7)°, V = 2401(1) $Å^3$, Z = 4, T = 153 K, μ(Mo-Kα) = 14.99 cm^{-1}, 19287 measured reflections ($2\theta_{max}$ = 54.9°). At convergence, $R1$ = 0.031, $wR2$ = 0.078, and GOF = 1.04 for 252 variables refined against all 5430 unique reflections. For **3**·CH_2Cl_2: $C_{25}H_{62}P_4S_3Cl_4TiPd_2$, M = 985.35, monoclinic, space group $P2_1/n$, a = 10.305(3), b = 20.642(7), c = 19.845(7) Å, β = 93.913(4)°, V = 4211(2) $Å^3$, Z = 4, T = 173 K, μ(Mo-Kα) = 16.01 cm^{-1}, 33890 measured reflections ($2\theta_{max}$ = 55.0°). At convergence, $R1$ = 0.030, $wR2$ = 0.070, and GOF = 1.00 for 414 variables refined against all 9627 unique reflections. The structures were solved by Patterson methods for **1** and direct methods for **2** and **3**, and refined on F^2 by full-matrix least-squares procedures using the CrystalStructure package. CCDC reference numbers 180416–180418. See http://www.rsc.org/suppdata/cc/b2/b201702d/ for crystallographic data in CIF or other electronic format.

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