A Dinuclear Palladium(II) Complex of the $\{N(SPPh_2)_2\}^-$ Ligand – Synthesis and Structure

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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

The synthesis and characterization including the crystal structure of the dinuclear palladium(II) complex $[(\kappa\text{-S},S')\text{-}\{N(SPPh_2)_2\}Pd(\mu\text{-}\{\kappa^2\text{-}S'',S'''\})\text{-}\{N(SPPh_2)_2\}PdCl_2]$ (**1**) are reported. Compound **1** was obtained from the reaction of $[PdCl_2(COD)]$ (COD = 1,5-cyclooctadiene) and $HN(SPPh_2)_2$ in a 1 : 1 molar ratio in CH_2Cl_2. The $\{N(SPPh_2)_2\}^-$ ligands act both as bridging and/or terminally chelating units.

Key words: Bimetallic Complex, Palladium, PNP Ligand, S Donor Ligand

Introduction

The coordination chemistry of the anionic ligand $\{N(SPPh_2)_2\}^-$ and its chalcogenide congeners $\{N(EPPh_2)_2\}^-$ (E = O, Se, Te) has attracted much attention during the last two decades. In this context numerous compounds of the main group elements as well as of the transition metals and *f* elements were reported [1 – 6]. Due to the sulfur donor set of $\{N(SPPh_2)_2\}^-$, this ligand is considered to be a soft analog of the acetylacetonato ligand (acac) in terms of Lewis basicity (Fig. 1). In contrast to acac, the $\{N(SPPh_2)_2\}^-$ system possesses a high degree of geometric and electronic flexibility since it can readily deviate from planarity without substantial disruption of the P–S π bonds [7]. Although a large number of coordination and organometallic compounds of the late transition metals containing the $\{N(SPPh_2)_2\}^-$ ligand can be found in the literature, mainly complexes in which the ligand adopts a S,S'-chelation mode were described [1 – 18], whereas the S,S'-bridging mode has hitherto been observed only in a tetranuclear copper cluster, a dinuclear rhenium, and a trinuclear osmium complex [16, 19, 20].

In this contribution, we report the preparation and crystallographic characterization of a dinuclear Pd(II) complex in which the $\{N(SPPh_2)_2\}^-$ ligand adopts
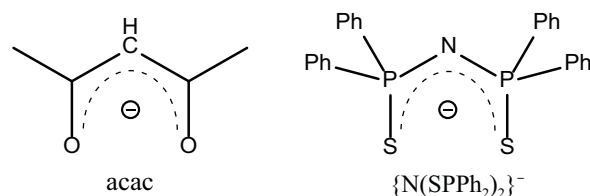

Fig. 1. The ligands acac *vs.* $\{N(PSPh_2)_2\}^-$.

both the common S,S'-chelation mode and the less common S,S'-bridging mode.

Results and Discussion

The reaction of $[PdCl_2(COD)]$ (COD = 1,5-cyclooctadiene) and $HN(SPPh_2)_2$ in a 1 : 1 molar ratio in CH_2Cl_2 leads to the formation of $[(\kappa\text{-S},S')\text{-}\{N(SPPh_2)_2\}Pd(\mu\text{-}\{\kappa^2\text{-}S'',S'''\})\text{-}\{N(SPPh_2)_2\}PdCl_2]$ (**1**) (Scheme 1). Reactions of $HN(SPPh_2)_2$ with other palladium compounds were reported earlier [12, 21]. The reaction of Pd metal, $HN(SPPh_2)_2$, and I_2 and the reaction of $Na_2[PdCl_4]$ and $[Na\{N(SPPh_2)_2\}]$ resulted in both cases solely in the homoleptic compound $[Pd(\kappa\text{-S},S')\text{-}\{N(SPPh_2)_2\}_2]$ [12, 21]. Compound **1** was obtained as bright-orange crystals in high yield and was characterized by standard
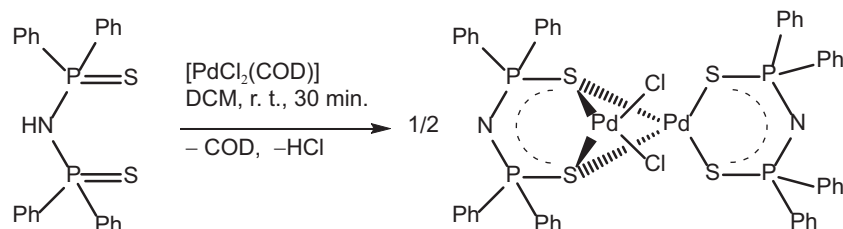
Scheme 1. Synthesis of **1**.

analytical/spectroscopic methods. Compound **1** is a homodinuclear species, in which a $PdCl_2$ fragment is bonded to the two sulfur atoms of a $[Pd(\kappa\text{-}S,S')\text{-}\{N(SPPh_2)_2\}_2]$ scaffold. The $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ shows two signals of equal intensity giving evidence for the stability of **1** in solution. The signal at $\delta = 38.7$ ppm can be assigned to the two equivalent phosphorus atoms of the terminal $\{N(SPPh_2)_2\}^-$ ligand, which is in accordance with the reported value for the homoleptic complex $[Pd(\kappa\text{-}S,S')\text{-}\{N(SPPh_2)_2\}_2]$ (38.7 ppm) [12]. The signal for the two equivalent phosphorus atoms of the bridging $\{N(SPPh_2)_2\}^-$ ligand is found at $\delta = 37.1$ ppm and is in the same region as observed for $[Os_3H(CO)_9\{\mu\text{-}(\kappa^2\text{-}S,S')\text{-}N(SPPh_2)_2\}]$ (35.4 ppm) or $[Re_2(CO)_6(\mu\text{-}Br)\{\mu\text{-}(\kappa^2\text{-}S,S')\text{-}N(SPPh_2)_2\}]$ (41.0 ppm), as well as for $[Re_2(CO)_6\{\mu\text{-}(\kappa^2\text{-}S,S')\text{-}N(SPPh_2)_2\}\{\mu\text{-}(\kappa^2\text{-}Se,Se')\text{-}N(SePPh_2)_2\}]$ (38.0 ppm) [19, 20]. Both signals are shifted upfield by approximately 20 ppm as compared to the neutral ligand $HN(SPPh_2)_2$ (55.1 ppm) [22]. Recording an NMR spectrum at elevated temperature in $[D_6]DMSO$ resulted in decomposition of compound **1**. The IR spectrum of **1** shows the characteristic asymmetric P–N–P stretching at $\nu_{asym} = 1161$ cm^{-1} and the P–S stretching at $\nu = 569$ cm^{-1}. These values are matching well with those reported for $[Pd(\kappa\text{-}S,S')\text{-}\{N(SPPh_2)_2\}_2]$ ($\nu_{asym,P-N-P} = 1161$ cm^{-1}, $\nu_{P-S} = 571$ cm^{-1}) or $[Ni(\kappa\text{-}S,S')\text{-}\{N(SPPh_2)_2\}_2]$ ($\nu_{asym,P-N-P} = 1150$ cm^{-1}, $\nu_{P-S} = 565$ cm^{-1}) [12, 21]. However, it is not possible to discriminate the two different coordinating ligands by the obtained IR data.

Single crystals of **1** suitable for X-ray diffraction analysis were obtained from an *n*-pentane-layered CH_2Cl_2 solution. **1** crystallizes in the triclinic space group $P\bar{1}$ as a dinuclear compound featuring a bridging $\{N(SPPh_2)_2\}^-$ moiety (Fig. 2). Moreover, strongly disordered CH_2Cl_2 lattice solvent molecules were localized in the unit cell. In **1** both Pd atoms are coordinated either by two chlorine and two sulfur atoms of the bridging ligand (Pd1) or four sulfur atoms of the bridging and the terminally chelating ligand (Pd2) in a distorted square-planar fashion. The chlorine atoms in **1** are in a *cis*-configuration, and the Pd1–Cl distances (Pd1–Cl1 2.3074(15) Å, Pd1–Cl2 2.2992(13) Å) are similar as compared to the starting material $[PdCl_2(COD)]$ (2.3072 Å, 2.3065 Å) but slightly shorter than reported for the related compounds $[PPh_4][Pd_2\{\mu\text{-}(\kappa^2\text{-}S,S')\text{-}S_3N_2\}Cl_4]$ (2.350–2.370 Å) [25] and $[PdCl_2(\kappa\text{-}S,S')\text{-}dppeS_2]$ (2.3161 Å, 2.3347 Å; dppeS$_2$ = 1,2-bis(diphenylthiophosphinyl)ethane) [26]. The Cl1–Pd1–Cl2 angle of $93.42(5)°$ is comparable to those reported for $[PdCl_2(COD)]$ ($91.84°$), $[PPh_4][Pd_2\{\mu\text{-}(\kappa^2\text{-}S,S')\text{-}S_3N_2\}Cl_4]$ ($95.1°$, $90.6°$) and $[PdCl_2(\kappa\text{-}S,S')\text{-}dppeS_2]$ ($91.17°$) [24–26]. The Pd1–S distances (Pd1–S1 2.3163(12) Å, Pd1–S2 2.2825(14) Å) to the bridging $\{N(SPPh_2)_2\}^-$ ligand are in line with those of $[PPh_4][Pd_2\{\mu\text{-}(\kappa^2\text{-}S,S')\text{-}S_3N_2\}Cl_4]$ (2.280–2.266 Å). The S1–Pd1–S2 angle of $86.06(5)°$ also matches well with those observed for $[PPh_4][Pd_2\{\mu\text{-}(\kappa^2\text{-}S,S')\text{-}S_3N_2\}Cl_4]$ ($85.1°$, $85.3°$) [25]. The bridging S–P–N–P–S fragment adopts an envelope conformation, where N1 deviates slightly from the P1–S1–S2–P2 least-squares plane. This conformation was also found for the $\mu\text{-}(\kappa^2\text{-}S,S')$ coordination mode in $[Os_3H(CO)_9\{\mu\text{-}(\kappa^2\text{-}S,S')\text{-}N(SPPh_2)_2\}]$ and $[Re_2(CO)_6(\mu\text{-}Br)\{\mu\text{-}(\kappa^2\text{-}S,S')\text{-}N(SPPh_2)_2\}]$ [19, 20]. The Pd2–S distances to the bridging ligand (Pd2–S1 2.3552(13) Å, Pd2–S2 2.3375(13) Å) are significantly longer than those to Pd1 and in $[PPh_4][Pd_2\{\mu\text{-}(\kappa^2\text{-}S,S')\text{-}S_3N_2\}Cl_4]$, but in agreement with those in the homoleptic compound $[Pd(\kappa\text{-}S,S')\text{-}\{N(SPPh_2)_2\}_2]$ (2.3478 Å, 2.3333 Å) [12, 25]. The Pd2–S distances to the chelating $\{N(SPPh_2)_2\}^-$ ligand (Pd2–S3 2.3152(13) Å, Pd2–S4 2.3264(14) Å) are in the same range as observed for Pd1–S1/S2 and Pd2–S1/S2, but slightly shorter than in the related mononuclear complex
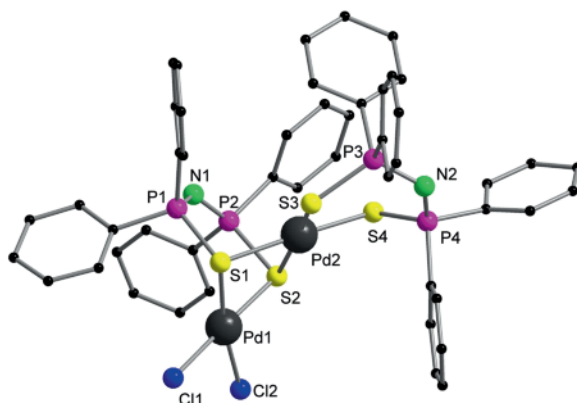
Fig. 2 (color online). Solid-state structure of **1**. Hydrogen atoms and disorder of phenyl rings are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1–S1 2.3163(12), Pd1–S2 2.283(2), Pd1–Cl1 2.307(2), Pd1–Cl2 2.299(2), Pd2–S1 2.355(2), Pd2–S2 2.337(2), Pd2–S3 2.315(2), Pd2–S4 2.327(2), S1–P1 2.083(2), S2–P2 2.088(2), S3–P3 2.038(2), S4–P4 2.030(2), P1–N1 1.585(4), P2–N1 1.577(4), P3–N2 1.605(4), P4–N2 1.585(5); Cl1–Pd1–Cl2 93.42(5), S1–Pd1–S2 83.94(5), Cl1–Pd1–S1 92.23(5), Cl1–Pd1–S2 176.80(5), Cl2–Pd1–S1 171.10(5), Cl2–Pd1–S2 87.96(5), Pd1–S1–Pd2 88.91(5), Pd1–S2–Pd2 90.17(5), S1–Pd2–S2 83.94(5), S1–Pd2–S3 86.6(5), S2–Pd2–S3 169.64(5), S2–Pd2–S4 87.39(5), S3–Pd2–S4 102.14(6), S4–Pd2–S1 171.26(5), Pd1–S1–P1 103.07(6), Pd1–S2–P2 102.80(6), Pd2–S1–P1 97.75(6), Pd2–S2–P2 97.47(6), Pd2–S3–P3 107.71(7), Pd2–S4–P4 104.89(7), S1–P1–N1 115.7(2), S2–P2–N1 116.3(2), S3–P3–N2 115.9(2), S4–P4–N2 117.2(2), P1–N1–P2 132.9(2), P3–N2–P4 122.7(3).

$[Pd(\kappa\text{-}S,S')\text{-}\{N(SPPh_2)_2\}_2]$. The S–Pd2–S angle to the bridging ligand (S1–Pd2–S2 83.94(5)°) is in the same range as observed for S1–Pd1–S2 and those in $[PPh_4][Pd_2\{\mu\text{-}(\kappa^2\text{-}S,S')\text{-}S_3N_2\}Cl_4]$, whereas the angle to the terminal ligand (S3–Pd2–S4 102.14(6)°) is significantly larger compared to S1–Pd1–S2 and to that in the homoleptic complex $[Pd(\kappa\text{-}S,S')\text{-}\{N(SPPh_2)_2\}_2]$ (98.71°) [12, 25]. The terminal $\{N(SPPh_2)_2\}^-$ ligand forms a six-membered metallacycle (Pd2–S3–P3–N2–P4–S4), which adopts the common twist-boat conformation with S4 and P3 being displaced from the Pd2–S3–N2–P4 least-squares plane [12].

In conclusion, the dinuclear complex $[(\kappa\text{-}S,S')\text{-}\{N(SPPh_2)_2\}Pd(\mu\text{-}\{\kappa^2\text{-}S'',S'''\})\text{-}\{N(SPPh_2)_2\}PdCl_2]$ (**1**) was prepared and characterized. The $\{N(SPPh_2)_2\}^-$ fragment coordinates in the more common chelating fashion in $(\kappa\text{-}S,S')$ mode as well as in the more rare bridging fashion in $(\mu\text{-}\{\kappa^2\text{-}S,S'\})$ mode.

Experimental Section

$HN(SPPh_2)_2$ was prepared according to a literature procedure [22]. NMR spectra were recorded on a Bruker Avance II NMR 300 MHz spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane (^{1}H and ^{13}C{^{1}H}), and 85 % phosphoric acid (^{31}P{^{1}H}). The IR spectrum was obtained on a Bruker

Tensor 37 instrument. Elemental analysis was carried out with an Elementar vario Micro Cube.

$[(\kappa\text{-}S,S')\text{-}\{N(SPPh_2)_2\}Pd(\mu\text{-}\{\kappa^2\text{-}S'',S'''\})\text{-}\{N(SPPh_2)_2\}PdCl_2]$ (**1**)
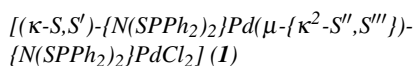
CH_2Cl_2 (10 mL) was added to a mixture of $HN(SPPh_2)_2$ (112 mg, 0.25 mmol) and $[PdCl_2(COD)]$ (71 mg, 0.25 mmol) at room temperature, and the resulting bright-orange solution was stirred for 1 h. The volatile components were evaporated *in vacuo* to leave an orange solid. Recrystallization from CH_2Cl_2-*n*-pentane afforded bright-orange single crystals suitable for X-ray analysis. Yield: 121 mg (82 %). – ^{1}H NMR (CDCl$_3$, 300.13 MHz): δ = 8.13 – 8.06 (m, 4 H, P*Ph*), 7.97 – 7.90 (m, 4 H, P*Ph*), 7.63 – 7.52 (m, 16 H, P*Ph*), 7.50 – 7.45 (m, 8 H, P*Ph*), 7.39 – 7.34 (m, 8 H, P*Ph*) ppm. – ^{13}C{^{1}H} NMR (CDCl$_3$, 75.46 MHz): δ = 133.2 (m, P*Ph*), 132.3 (m, P*Ph*), 131.7 (m, P*Ph*), 131.4 (m, P*Ph*), 128.9 (m, P*Ph*), 128.3 (m, P*Ph*) ppm. – ^{31}P{^{1}H} NMR (CDCl$_3$, 121.49 MHz): δ = 38.7 (chelating), 37.1 (chelating + bridging) ppm. – IR (ATR, cm^{-1}): ν = 3051 (w), 1735, (w), 1585 (w), 1572 (w), 1479 (w), 1435 (m), 1332 (w), 1305 (w), 1279 (w), 1235 (m), 1161 (s), 1107 (s), 1026 (w), 997 (m), 922 (w), 822 (m), 806 (m), 743 (m), 717 (s), 687 (vs), 617 (w), 569 (s), 546 (s), 537 (s), 509 (s). – $C_{48}H_{40}Cl_2N_2P_4S_4Pd_2$ (1180.75 g mol^{-1}): calcd. C 48.83, H 3.41, N 2.37, S 10.86; found C 49.64, H 3.54, N 2.32, S 10.49.

X-Ray structure determination

Data were collected on a diffractometer equipped with a Stoe imaging plate detector system IPDS2 using Mo K_α radiation with graphite monochromatization ($\lambda = 0.71073$ Å) at 153(2) K. Structure solution was performed with Direct Methods and full-matrix least-squares refinement against F^2 using SHELXS-97 and SHELXL-97 software, respectively [27, 28]. The crystal structure contains at least three strongly disordered CH_2Cl_2 lattice solvent molecules. Their effect on the electron density was subtracted mathematically from the intensity data using the SQUEEZE routine integrated in the PLATON program package [29].

Crystal data for 1: $C_{48}H_{40}Cl_2N_2P_4Pd_2S_4$, $M_r = 1180.64$, triclinic, space group $P\bar{1}$, $a = 12.079(2)$, $b = 13.858(3)$, $c = 18.669(4)$ Å, $\alpha = 71.77(3)$, $\beta = 72.97(3)$, $\gamma = 82.56(3)°$,

$V = 2835.6(10)$ Å^3, $T = 153.15$ K, $Z = 2$, $\mu(\text{Mo}\,K_\alpha) = 1.0\,\text{mm}^{-1}$; 29139 reflections measured, 10530 independent reflections ($R_{\text{int}} = 0.049$). The final R_1 value was 0.056 $[I > 2\sigma(I)]$. The final $wR(F^2)$ value was 0.161 (all data). The goodness of fit on F^2 was 1.009. Residual electron density (max / min): 3.26 / -0.92 e Å^{-3}.

CCDC 925481 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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