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Sulfur-assisted chloride and triphenylphosphine dissociation of palladium(II) complex [Pd(PPh_3)$_2$(η^1-$SCNMe_2$)(Cl)]. X-ray structures of [Pd(PPh_3)$_2$(η^1-$SCNMe_2$)(Cl)], [Pd(PPh_3)(Cl)]$_2$ (μ, η^2-$SCNMe_2$)$_2$, and [Pd(PPh_3)$_2$(η^2-$SCNMe_2$)][PF_6]

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Abstract

Treatment of Pd(PPh_3)$_4$ with $Me_2NC({=}S)Cl$ in dichloromethane at −20 °C produces the complex [Pd(PPh_3)$_2$(η^1-$SCNMe_2$)(Cl)], **2**. Variable temperature ^1H and $^{31}P\{H\}$ NMR experiments of complex **2** shows the dissociation of either the chloride or the triphenylphosphine ligand to form complex [Pd(PPh_3)$_2$(η^2-$SCNMe_2$)][Cl], **3** or the dipalladium complex [Pd(PPh_3)Cl]$_2$(μ, η^2-$SCNMe_2$)$_2$, **4**. The reaction of complex **2** with $NaPF_6$ affords complex [Pd(PPh_3)$_2$(η^2-$SCNMe_2$)][PF_6], **5**. Complexes **2**, **4**, and **5** are characterized by X-ray diffraction analyses.

Keywords: Dissociation behaviour; *N*,*N*-dimethylthiocarbamoyl; Palladium; Sulfur-assisted; X-ray diffraction

The study of transition-metal compounds containing the *N*,*N*-dialkylthiocarbamonyl ligand ($^-SCNR_2$) is of interest in that this ligand may behave like a mono- or bidentate in ether, resulting in novel structural and chemical features [1]. We have recently been investigating the chemistry of sulfur-containing heteroallenes and related molecules with mono- and binuclear systems in order to obtain a better understanding of how these molecules interact with the metal center [2]. In this paper, we report the preparation and properties of palladium complexes with the $^-SCNMe_2$ containing ligand.

Treatment of Pd(PPh_3)$_4$, **1** with $Me_2NC({=}S)Cl$ in dichloromethane at −20 °C yields the yellow complex [Pd(PPh_3)$_2$(η^1-$SCNMe_2$)(Cl)], **2** (Scheme 1). The variable temperature ^1H and $^{31}P\{^1H\}$ NMR spectra of **2** show three sets of methyl resonances of $SCNMe_2$ and three sets of triphenylphosphine resonances at 233 K in $CDCl_3$. As depicted in Fig. 1, the three sets of resonances are assigned to the **2** and the dissociation of either the chloride of **2** to form the mononuclear complex [Pd(PPh_3)$_2$(η^2-$SCNMe_2$)][Cl], **3** or the triphenylphosphine ligand of **2** to form the dipalladium complex [Pd(PPh_3)Cl]$_2$(μ, η^2-$SCNMe_2$)$_2$, **4**. Continuous stirring dichloromethane solution of complex **2** at room temperature for 8 h produces complex **4** as the ultimate product. The spectroscopic [3] and analytical data of **2**–**4** are obtained. Complex [Pd(PPh_3)$_2$(η^1-CH_2SCH_3)Cl] [4a] is the one only reported example including the dissociation observation to form monomer complexes [Pd(PPh_3)(η^2-CH_2SCH_3)Cl] and [Pd(PPh_3)$_2$(η^2-CH_2SCH_3)][Cl]. From the above description, one can conclude that the sulfur atom of $SCNMe_2$ ligand assists triphenylphosphine or chloride dissociation of **2** to form **4** or **3**.

The dissociation of the chloride ligand from **2** also can be confirmed by the shorter reaction time of **2** with

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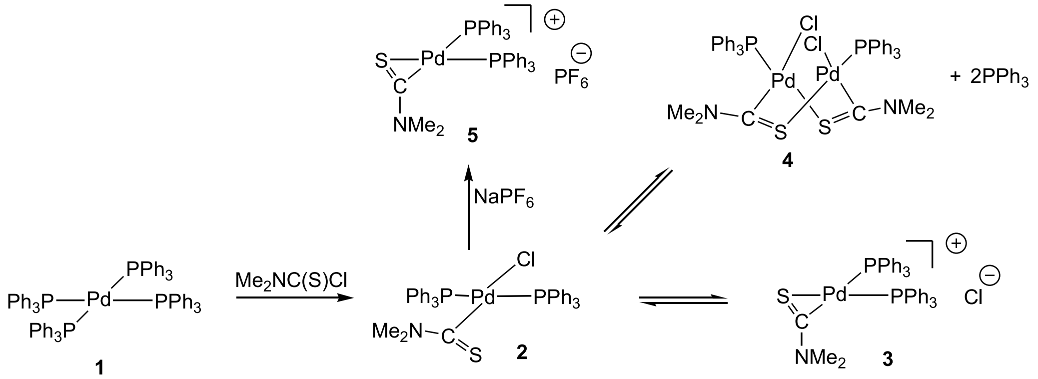

Scheme 1.

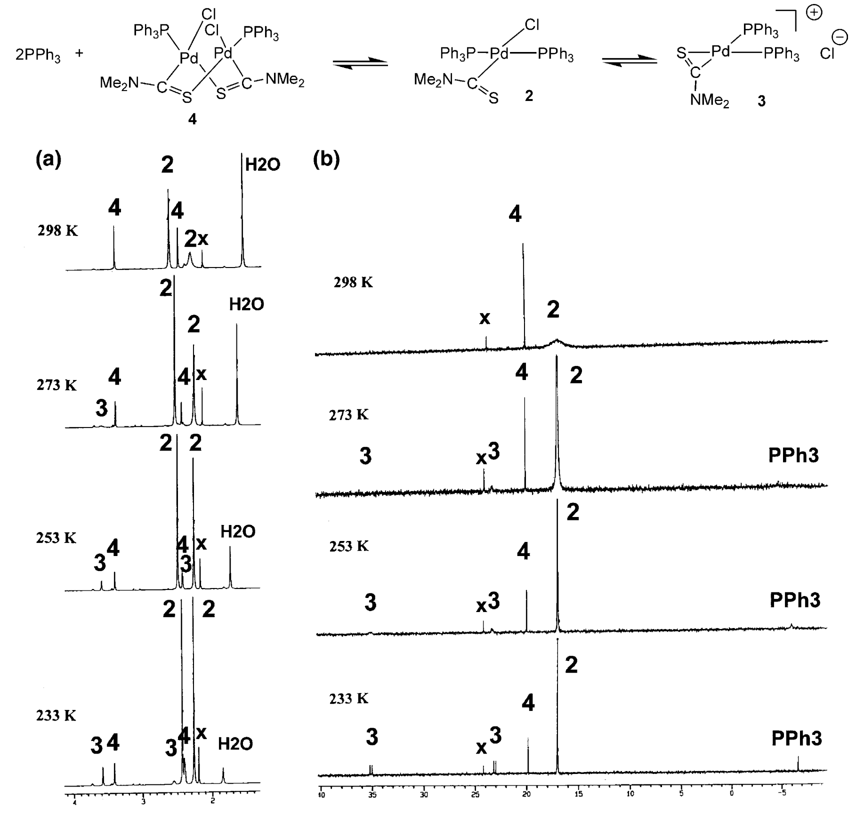

Fig. 1. Variable-temperature ^1H (a) and $^{31}P\{^1H\}$ NMR (b) spectra of the mixtures **2**, **3**, and **4** in $CDCl_3$ (x as the impurity).

$NaPF_6$ in acetone at room temperature to form complex $[Pd(PPh_3)_2(\eta^2\text{-}SCNMe_2)][PF_6]$, **5** (5 min) than those of chloride abstraction reaction of complex $[C_6H_4CH_2NMe_2)Pd(Cl)(2,6\text{-dimethoxyphenyl})diphenylphosphine]$ [4b] with $NaPF_6$ (3 h) and $[Pd(PPh_3)_2(CH_2SCH_3)Cl]$ with NH_4PF_6 (15 min) in the same reactive conditions. The spectroscopic [5] and analytical data of **5** are in good agreement with the formulation. The ^1H and $^{31}P\{^1H\}$ NMR spectra of **5** are similar to those of **3**. In the ^1H NMR spectrum of **5**, the two methyl protons of the $SCNMe_2$ ligand exhibit two resonances at δ 2.54 and δ 3.61. The corresponding $^{13}C\{^1H\}$ NMR signals are at δ 45.9 and δ 53.9. The $^{31}P\{^1H\}$ NMR spectrum of **5** shows two doublet resonances at δ 23.1 and δ 35.1 due to the chemical inequivalence of the two PPh_3 ligands and the relative downfield resonance than that of **2** (δ 16.6) which shows the cationic character of **5**. From the description, it is clear that the palladium of **5** is side-on bound through the C–S moiety of the $SCNMe_2$ ligand. The compounds **2**, **4**, and **5** were recrystallized from CH_2Cl_2/*n*-hexane (1:10) and were isolated in 98%, 93% and 92% yield, respectively.

Single crystals of **2**, **4**, and **5** suitable from X-ray diffraction studies [6] were grown by slow *n*-hexane diffusion into a dichloromethane solution at 4 °C. ORTEP plots of **2**, **4**, and **5** are shown in Figs. 2–4. In

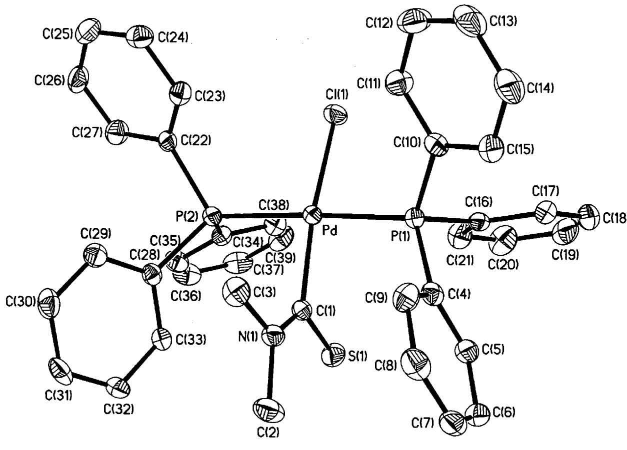

Fig. 2. An ORTEP drawing with 30% thermal ellipsoids and atom-numbering scheme for the complex $[Pd(PPh_3)_2(\eta^1\text{-}SCNMe_2)(Cl)]$, **2**. Selected bond distances (Å) and angles (°) are as follows: Pd–P(1) 2.3531(9), Pd–P(2) 2.3401(9), Pd–Cl(1) 2.4067(9), Pd–C(1) 1.982(3), C(1)–S(1) 1.679(4), C(1)–N(1) 1.320(4), C(2)–N(1) 1.458(5), C(3)–N(1) 1.457(5); C(1)–Pd–Cl(1) 166.32(10), P(1)–Pd–P(2) 173.75(3), Cl(1)–Pd–P(1) 93.50(3), Cl(1)–Pd–P(2) 91.13(3), C(1)–Pd–P(1) 87.50(10), C(1)–Pd–P(2) 89.00(10), S(1)–C(1)–Pd 111.61(18), S(1)–C(1)–N(1) 124.7(3), N(1)–C(1)–Pd 123.6(3).

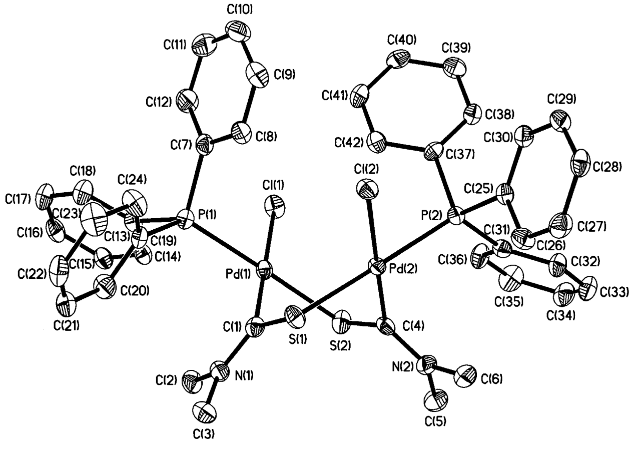

Fig. 3. An ORTEP drawing with 50% thermal ellipsoids and atom-numbering scheme for the complex $[Pd(PPh_3)Cl]_2$ $(\mu,\eta^2\text{-}SCNMe_2)_2$, **4**. Selected bond distances (Å) and angles (°) are as follows: Pd(1)···Pd(2) 3.334(2), Pd(1)–P(1) 2.3046(10), Pd(2)–P(2) 2.3013(9), Pd(1)–Cl(1) 2.3721(10), Pd(2)–Cl(2) 2.3677(9), Pd(1)–C(1) 1.969(4), Pd(2)–C(4) 1.989(4), C(1)–S(1) 1.731(4), C(4)–S(2) 1.718(4); C(1)–Pd(1)–Cl(1) 178.55(11), C(4)–Pd(2)–Cl(2) 178.05(10), Cl(1)–Pd(1)–P(1) 87.26(3), Cl(2)–Pd(2)–P(2) 84.95(3), C(1)–Pd(1)–P(1) 93.41(11), C(4)–Pd(2)–P(2) 93.51(10), S(1)–C(1)–Pd(1) 116.93(19), S(2)–C(4)–Pd(2) 117.7(2).

complex **2**, the $SCNMe_2$ ligand is σ-bounding to Pd atom through the carbon atom of the thiocarbonyl group. The S–Pd bond distance of 3.033 Å in **2** indicates no bonding interaction between the sulfur atom and palladium metal atom. Complex **4** is a dimer with each $SCNMe_2$ unit bridging through carbon atom of thiocarbonyl group to one metal center and sulfur atom to the other metal. Within the $SCNMe_2$ ligands themselves,

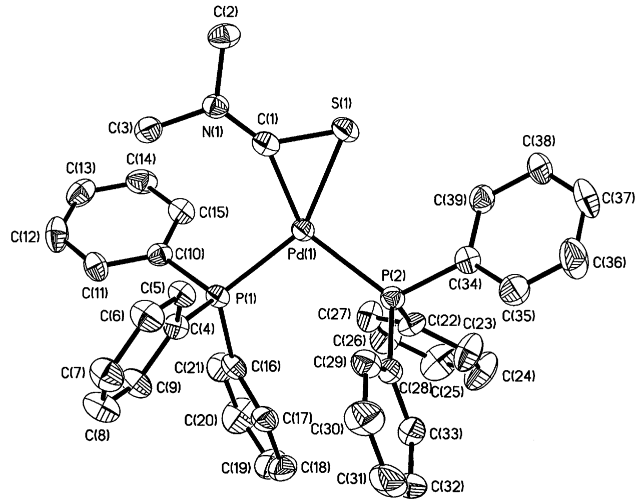

Fig. 4. An ORTEP drawing with 30% thermal ellipsoids and atom-numbering scheme for the cationic complex $[Pd(PPh_3)_2(\eta^2\text{-}SCNMe_2)]$ $[PF_6]$, **5**. Selected bond distances (Å) and angles (°) are as follows: Pd–P(1) 2.3125(15), Pd–P(2) 2.3660(16), Pd–S(1) 2.3243(15), Pd–C(1) 2.003(6), C(1)–S(1) 1.667(6), C(1)–N(1) 1.303(7), C(2)–N(1) 1.468(7), C(3)–N(1) 1.466(7); C(1)–Pd–S(1) 44.54(16), P(1)–Pd–P(2) 103.66(5), S(1)–Pd–P(1) 151.36(6), S(1)–Pd–P(2) 104.92(5), C(1)–Pd–P(1) 106.82(16), C(1)–Pd–P(2) 149.15(16), S(1)–C(1)–Pd 78.0(2), S(1)–C(1)–N(1) 131.5(4), N(1)–C(1)–Pd 150.5(4), C(1)–S(1)–Pd 57.4(2).

the geometries are consistent with significant partial double bond character in the C–S and SC–N bonds. Thus, the C–S bond distances (1.679(4) Å of **2**, 1.731(4) and 1.718(4) Å of **4**, and 1.667(6) Å of **5**) are comparable to the C–S double bond in ethylenethiourea although they are longer than those in free CS_2 (1.554 Å). The SC–N bond distances (1.320(4) Å of **2**, 1.316(5) and 1.318(5) Å of **4**, and 1.303(7) Å of **5**) are typical for a C–N bond having partial double bond character and are certainly much shorter than the normal C–N (1.47 Å) single bond. The Me–N distances are normal for single bonds and are significantly longer than those of SC–N bonds, which, as noted, have multiple bond character.

In complex **5**, the Pd atom and its neighboring atoms, P(1), P(2), S(1), and C(1) lie in a distorted squared plane. The distortion is mainly due to the short bite of the C=S linkage [C–Pd–S, 44.54(16)°]. A least-squares plane cal culation reveals that the planarity of the P(2)P(1)C(1) S(1) core (largest deviation 0.031(1) Å). The C(1)–S(1) bond distance of 1.667(6) Å is similar to the corresponding carbon–sulfur bond distance observed in η^2-CS_2 (sp^2) transition-metal complexes [1.65(3) Å in $[(PPh_3)_2Pd(\eta^2\text{-}CS_2)]$ [7]. The Pd–S(1) distance of 2.3243(5) Å is within the normal Pd–S length range (2.23–2.32 Å) [8]. Our interest in the M–C(S)NMe_2 and M–C(S)OPh moieties are due to their analogies with metallocarboxylic acid esters (M–C(O)OR) and metallocarboxylic acids themselves. Metallocarboxylic acids have been proposed to be the key intermediates in the homogeneous catalysis of the water gas shift reaction

[9]. Reactions and different bonding modes of **2** and nucleophiles are currently under investigation.

Acknowledgements

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[3] Spectroscopy for **2**: ^{31}P {^{1}H} NMR: δ 16.6 (br, PPh$_3$). ^{1}H NMR: δ 2.34, 2.64 (s, 6H, NCH_3), 7.31–8.05 (m, 30H, Ph). ^{13}C{^{1}H} NMR: δ 41.5 (s, NCH$_3$), 128.4–135.8 (m, C of Ph), 223.5 (s, CS). Anal. Calcd. for $C_{39}H_{36}ClNP_2SPd$: C, 62.08; H, 4.81; N, 1.86%. Found: C, 62.10; H, 4.81; N, 1.84. Spectroscopy for **3**: ^{31}P{^{1}H} NMR: δ 23.1, 35.1 (d, $^2J_{P-P} = 40.7$). ^{1}H NMR: δ 2.39, 3.58 (s, 6H, NCH_3), 7.31–8.05 (m, 30H, Ph). ^{13}C{^{1}H} NMR: δ 46.1, 53.4 (s, NCH$_3$), 128.4–135.8 (m, C of Ph). Spectroscopy for **4**: ^{31}P{^{1}H} NMR: δ 19.8 (s, PPh$_3$). ^{1}H NMR: δ 2.51, 3.44 (s, 6H, NCH_3), 7.28–8.05 (m, 15H, Ph). ^{13}C{^{1}H} NMR: δ 39.9, 49.1 (s, NCH$_3$), 128.4–135.8 (m, C of Ph), 234.4 (s, CS). Anal. Calcd. for $C_{42}H_{42}Cl_2N_2P_2S_2Pd_2$: C, 51.23; H, 4.30; N, 2.85%. Found: C, 51.28; H, 4.21; N, 2.80.

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[5] Spectroscopy for **5**: IR (KBr, υPF$_6$/cm^{-1}): 839 (vs). ^{31}P{^{1}H} NMR: δ 23.2, 34.8 (d, $^2J_{P-P} = 40.7$, PPh$_3$), −144.0 (sep, $J_{P-F} = 708.6$, PF$_6$). ^{1}H NMR: δ 2.45, 3.61 (s, 6H, NCH_3), 7.24–7.73 (m, 30H, Ph). ^{13}C {^{1}H} NMR: δ 45.9, 53.9 (s, NCH$_3$), 128.8–134.0 (m, C of Ph), 212.1 (d, CS, $^2J_{P-C} = 6.7$). Anal. Calcd. for $C_{39}H_{36}F_6$ NP$_3$SPd: C, 54.21; H, 4.20; N, 1.62 %. Found: C, 54.25; H, 4.18; N, 1.70.

[6] Crystal data for **2**: $C_{39}H_{36}ClN_2P_2PdS$, space group P2$_1$/n, $a = 12.8248(1)$ Å, $b = 18.6358(1)$ Å, $c = 14.9692(1)$ Å, $\beta = 105.1513(4)°$, $V = 3453.28(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.451$ gcm^{-3}, $\mu = 0.797$ mm^{-1}, independent reflections 24,507, $\theta_{range} = 1.78$–27.50°. Total number of parameters: 407. $R = 0.043$, $R_w = 0.090$; GOF = 1.049, Mo-Kα radiation; $\lambda = 0.71073$ Å; $T = 150(1)$ K; $\Delta F = 0.843$, −0.893e Å^3. Crystal data for **4** · CH$_2$Cl$_2$: $C_{43}H_{44}Cl_4N_2P_2Pd_2S_2$, space group $\overline{P1}$, $a = 9.8782(1)$ Å, $b = 11.4238(1)$ Å, $c = 20.7353(2)$ Å, $\alpha = 103.9126(5)°$, $\beta = 97.8453(3)°$ $\gamma = 104.9669(5)°$, $V = 2166.76(4)$ Å^3, $Z = 2$, $D_{calcd} = 1.639$ gcm^{-3}, $\mu = 1.281$ mm^{-1}, independent reflections 39,233, $\theta_{range} = 1.02$–27.50°. Total number of parameters: 497. $R = 0.0409$, $R_w = 0.0969$; GOF = 1.103, Mo-Kα radiation; $\lambda = 0.71073$ Å; $T = 150(1)$ K; $\Delta F = 1.730$, −1.261e Å^3. Crystal data for **5**: $C_{39}H_{36}F_6NP_3PdS \cdot CH_2Cl_2$, space group P2$_1$/c, $a = 9.8101(1)$ Å, $b = 23.5315(3)$ Å, $c = 18.2112(2)$ Å, $\beta = 103.2337(5)°$, $V = 4092.35(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.540$ gcm^{-3}, $\mu = 0.810$ mm^{-1}, independent reflections 27,983, $\theta_{range} = 1.44$–27.50°. Total number of parameters: 498. $R = 0.064$, $R_w = 0.148$; GOF = 1.038, Mo-Kα radiation; $\lambda = 0.71073$ Å ; $T = 150(1)$ K; $\Delta F = 1.543$, −1.136e Å^3. Absorption corrections of **2**, **4**, and **5** have been carried out. These structures were solved by Patterson synthesis and then refined via standard least-squares and difference Fourier techniques. Non-hydrogen atoms were refined by using anisotropic thermal parameters.

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