Synthesis, Dissociation Behavior and Crystal Structures of Palladium(II) Complexes with N,N-dimethylthiocarbamoyl, $Me_2NC{=}S$, Containing Ligand: Structures of $[Pd(PPh_3)_2(\eta^1\text{-}SCNMe_2)(Cl)]$, $[Pd(PPh_3)(Cl)]_2(\mu,\eta^2\text{-}SCNMe_2)_2$, $[Pd(PPh_3)_2\{\eta^1\text{-}C(SMe)(NMe_2)\}(\eta^2\text{-}S_2CO)]$, and $[Pd\{\eta^1\text{-}SC(O)NMe_2\}Pd(Cl)](\mu,\eta^2\text{-}SCNMe_2)(\mu,\eta^2\text{-}dppm)_2$

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Treatment of $Pd(PPh_3)_4$ with N,N-dimethylthiocarbamoyl chloride, $Me_2NC(=S)Cl$, in dichloromethane at -20 °C produces complex $[Pd(PPh_3)_2(\eta^1\text{-}SCNMe_2)(Cl)]$ (**1**). In solution state, complex **1** shows the intramolecular dissociation of the chloride or intermolecular dissociation of the triphenylphosphine ligands to form η^2-thiocarbamoyl complex $[Pd(PPh_3)_2(\eta^2\text{-}SCNMe_2)][Cl]$ (**2**) or the bridging η^2-thiocarbamoyl dipalladium complex $[Pd(PPh_3)Cl]_2(\mu,\eta^2\text{-}SCNMe_2)_2$ (**3**). Treatment of **1** with $MeOCS_2K$ yields $[Pd(PPh_3)\{\eta^1\text{-}C(SMe)(NMe_2)\}(\eta^2\text{-}S_2CO)]$ (**5a**). The Fischer-type carbene-complex **5a** is formed via methyl migration of the methyldithiocarbonate to thiocarbamoyl ligand. Complex **1** reacts with $EtOCS_2K$ resulting in the formation of η^2-dithiocarbonate complex $[Pd(PPh_3)(\eta^1\text{-}SCNMe_2)(\eta^2\text{-}S_2COEt)]$ (**4b**) and carbene-complex $[Pd(PPh_3)\{\eta^1\text{-}C(SEt)(NMe_2)\}(\eta^2\text{-}S_2CO)]$ (**5b**) with ratios of 10:1 from the integration of $^{31}P\{^1H\}$ NMR spectra. By continuously stirring the mixtures **4b** and **5b** in CH_2Cl_2 solution for 2 h, complex **5b** was formed as the final product. Complex $[Pd(\eta^1\text{-}SCNMe_2)(\eta^2\text{-}Phen)(Cl)]$ (**6**) or $[Pd\{\eta^1\text{-}SC(O)NMe_2\}Pd(Cl)](\mu,\eta^2\text{-}SCNMe_2)(\mu,\eta^2\text{-}dppm)_2$ (**7**) is accessible by the reaction of **1** with phen (1,10-phenanthroline) or dppm {bis(diphenylphosphino)methane} in dichloromethane at room temperature. All of the complexes are identified by spectroscopic methods and complexes **1**, **3**, **5a**, and **7** are determined by single-crystal X-ray diffraction. The complexes **1** and **3** crystallize in the monoclinic space group $P2_1/n$ and $P2_1/c$ with $Z = 4$, respectively, whereas **5a** and **7** belong to the triclinic space group $P\bar{1}$ with $Z = 2$. The cell dimensions are as follows: for **1**, a = 12.8248(1) Å, b = 18.6358(2) Å, c = 14.9692(1) Å, β = 105.1513(4)°; for **3**, a = 9.8782(1) Å, b = 11.7238(1) Å, c = 20.7353(2) Å, α = 103.9126(5)°, β = 97.8453(3)°, γ = 104.9669(5)°; for **5a**, a = 16.3638(2) Å, b = 9.3374(1) Å, c = 15.7117(2) Å, β = 98.2957(6)°; for **7**, a = 12.1128(1) Å, b = 14.0133(2) Å, c = 17.7873(2) Å, α = 82.1939(5), β = 79.6190(6)°, γ = 80.9551(5)°.

Keywords: N,N-dimethylthiocarbamoyl chloride; Intramolecular intermolecular dissociation; η^2-thiocarbamoyl; Fischer-type carbene; Methyl migration; Palladium complex.

INTRODUCTION

Thiocarbamoyl (thiocarboxamide) complexes have previously been prepared by a variety of synthetic routes[1] from the reaction of metal carbonylates with N,N-dimethylthiocarbamoyl chloride, $Me_2NC(=S)Cl$, via nucleophilic displacement of chloride,[2] nucleophilic attack by an amine on an electrophilic thiocarbonyl complex,[3] reaction of hydrosulfide with haloaminocarbene[4] or isonitrile[5] ligands, electrophilic attack at a coordinated isothiocyanate,[6] cleavage of a dithiocarbamate ligand,[7] or C-H activation of thioformamides.[8] Oxidative addition[9] of both chloride and N,N-dimethylthiocarbamoyl ligand to metal complex is most generally used and is relevant to the work to be described herein. The thiocarbamoyl metal complexes are known in Nb, Ta (VB),[10] Mo, W (VIB),[7b,11] Ru, Rh, and Ir (VIIIB),[9c,12] although rare Pd thiocarbamoyl complex has also been studied.

In a previous communication,[13] we have reported that

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the first N,N-dimethylthiocarbamoyl, S_2CNMe_2, complexes of palladium metal are accessible via the oxidative addition reaction of tetrakis(triphenylphosphine)palladium with thiocarbamoyl chloride. In contrast to thiocarbamoyl complexes of the above-mentioned metals, the palladium examples are a particularly reactive species. Especially, in solution state, the sulfur atom of the thiocarbamoyl ligand assists the dissociation of either the chloride or the triphenylphosphine ligand to form the η^2-thiocarbarmoyl complexes. Because of the ability of amino lone pair to contribute via conjugation to the metal-ligand bonding, the thiocarbamoyl ligands show a strong tendency to adopt bidentate coordination.

On the basis of these experimental results, we report the dissociation behavior and reactions of $[Pd(PPh_3)_2(\eta^1\text{-}SCNMe_2)(Cl)]$ (**1**) with anionic dithio, neutral nitrogen and phosphorus ligands as well as the novel carbene-complexes formation from the alkyl-thiocarbamoyl coupling reaction in this article. Four X-ray crystal structure analyses have been carried out to provide accurate structural parameters.

RESULTS AND DISCUSSION

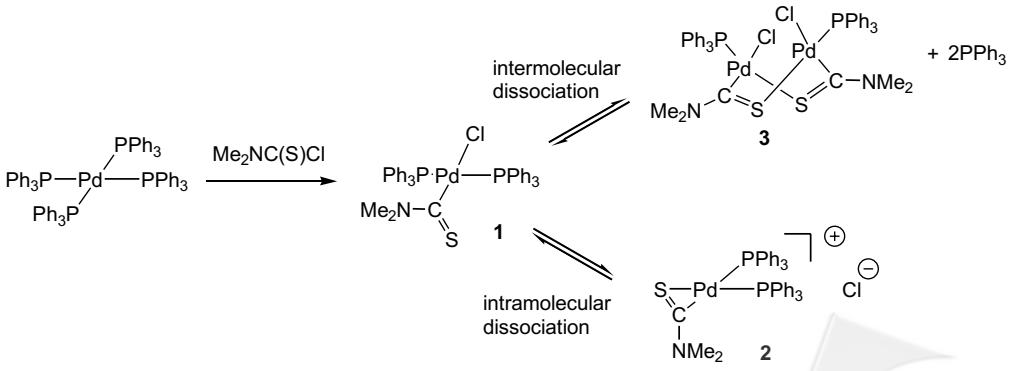
Syntheses

Treatment of $Pd(PPh_3)_4$ with N,N-dimethylthiocarbamoyl chloride, $Me_2NC(=S)Cl$, in dichloromethane at -20 °C yields the air-stable yellow complex $[Pd(PPh_3)_2(\eta^1\text{-}SCNMe_2)(Cl)]$ (**1**) with 92% isolate yield (Scheme I). The air-stable yellow compound **1** is soluble in dimethylsulfoxide, dichloromethane and acetonitrile, slightly soluble in methanol, and insoluble in *n*-hexane and diethyl ether.

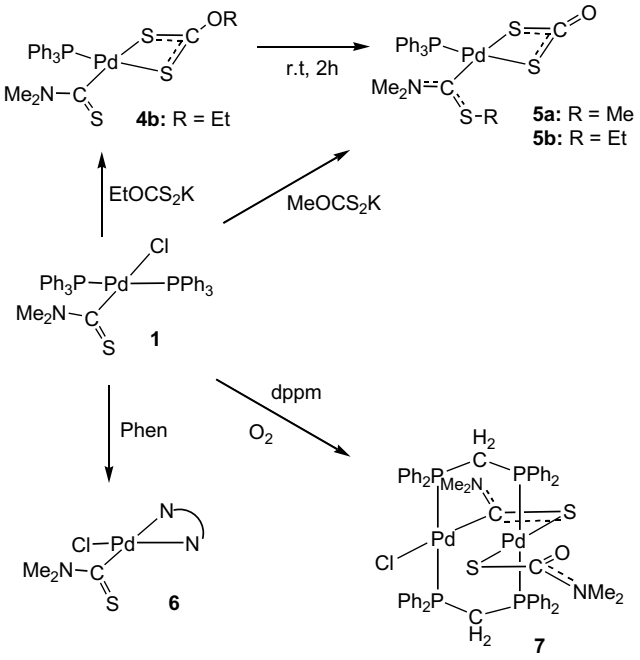
The dichloromethane solution of **1** processes intra- and intermolecular dissociation of either the chloride of **1** to form the chelating η^2-thiocarbarmoyl complex $[Pd(PPh_3)_2(\eta^2\text{-}SCNMe_2)][Cl]$ (**2**) or the triphenylphosphine ligand of **1** to form the bridging η^2-thiocarbarmoyl dipalladium complex $[Pd(PPh_3)Cl]_2(\mu,\eta^2\text{-}SCNMe_2)_2$ (**3**). Continuous stirring of dichloromethane solution of these mixtures at room temperature for 8 h produces complex **3** with 93% isolate yield. We did not isolate complex **2** in the dissociative reaction because it can be synthesized from the reaction of **1** and ammonium hexafluorophosphate, NH_4PF_6, in acetone with 92% isolate yield at ambient temperature.[14] The yellow complex **3** is more stable and has poorer solubility in common solvents than that of **1**. Only one example, $[Pd(PPh_3)_2(\eta^1\text{-}CH_2SCH_3)Cl]$,[15] is known, the dissociation of either the phosphine or the chloride ligand occurred in CH_2Cl_2 solution to form monomer complexes $[Pd(PPh_3)(\eta^2\text{-}CH_2SCH_3)Cl]$ and $[Pd(PPh_3)_2(\eta^2\text{-}CH_2SCH_3)][Cl]$. From the above description, one can conclude that the sulfur atom of the thiocarbamoyl ligand assists triphenylphosphine or chloride dissociation of **1** to form **3** or **2**.

Nucleophilic displacement of the chloride in **1** with anionic dithiocarbonate ligands, $MeOCS_2^-$ or $EtOCS_2^-$, in methanol at room temperature produces carbene-complex $[Pd(PPh_3)\{\eta^1\text{-}C(SMe)(NMe_2)\}(\eta^2\text{-}S_2CO)]$ (**5a**) with 90% isolate yield (Scheme II) or the mixtures of η^2-dithiocarbonate complex $[Pd(PPh_3)(\eta^1\text{-}SCNMe_2)(\eta^2\text{-}S_2COEt)]$, **4b** and carbene-complex $[Pd(PPh_3)\{\eta^1\text{-}C(SEt)(NMe_2)\}(\eta^2\text{-}S_2CO)]$ (**5b**) in good yields with a 10:1 ratio according to the integration of $^{31}P\{^1H\}$ NMR spectrum (Fig. 1). The dichloromethane solution of **4b** slowly undergoes ethyl-thiocarbamoyl coupling reaction at ambient temperature for 2 h to give **5b** in 75% yields. The air-stable yellow-orange compounds **5a** and **5b** are soluble in polar solvent, and insoluble in diethyl ether and *n*-hexane. Both complexes **5a** and **5b** include a dithiocarbonate, S_2CO^{-2}, group. Dithiocarbonate metal complexes have previously been prepared by a variety of syn-

Scheme I



Scheme II



thetic routes including reactions of (i) metal carbonyl sulfide complexes with COS[16] (ii) metal carbon disulfide complexes with dioxygen[17] (iii) dealkylation,[18] iodide abstraction,[19] and hydrolysis[20] of alkoxydithiocarbamate metal complexes. To our knowledge, formation of dithiocarbonate carbene-complex from the alkyl-thiocarbamoyl coupling reaction is the first example in the literature.

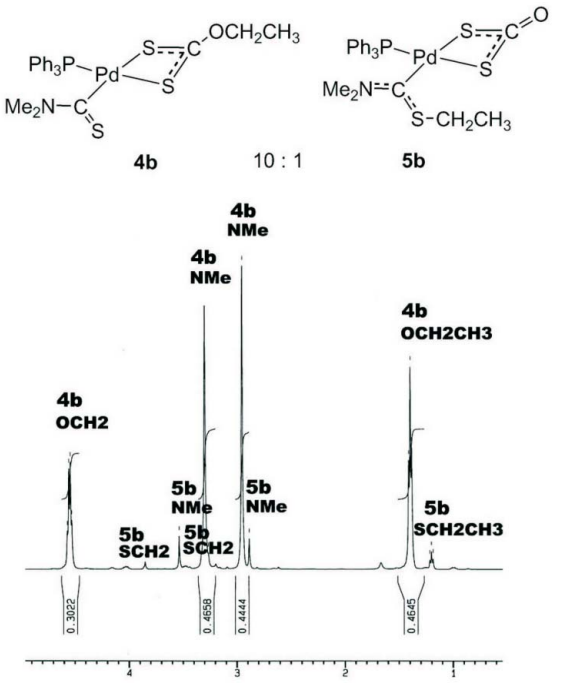


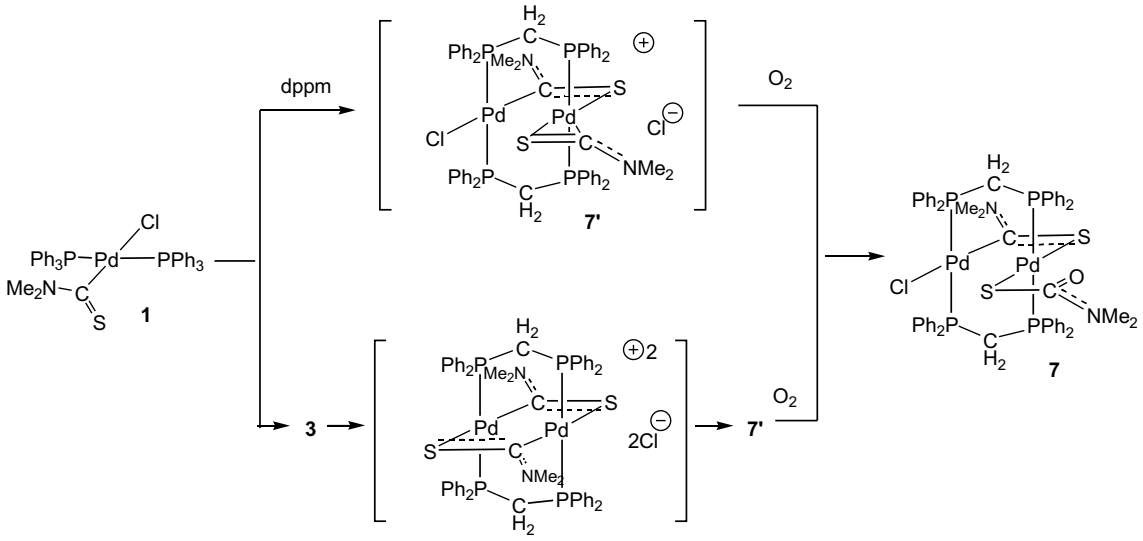
Fig. 1. ^{1}H NMR spectra of the mixtures **4b** and **5b** in $CDCl_3$.

The respective reactions of **1** and phen or dppm in dichloromethane results in the isolation of [Pd(η^1-SCNMe$_2$)(η^2-Phen)(Cl)] (**6**) or [Pd{η^1-SC(O)NMe$_2$}Pd(Cl)](μ,η^2-SCNMe$_2$)(μ,η^2-dppm)$_2$ (**7**) with 73% or 45% isolate yield. We expected the reaction of **1** with phen would produce a triphenylphosphine and chloride displaced complex [Pd(PPh$_3$)(η^1-SCNMe$_2$)(η^2-Phen)][Cl]. Instead, the product of this reaction was found to be a two triphenylphosphine ligands displaced complex **6** that was confirmed by spectroscopic data (described below). Another 20% yield of unidentified product was detected that includes similar spectroscopic data as that of **7**. Formation of thiocarbamate complex **7** is proposed to proceed via one triphenylphosphine displacement by sulfur atom of thiocarbamoyl of **1** to afford a bridging thiocarbamoyl dimetal complex, followed by one chloride and three triphenylphosphines displacement by two dppm ligands to form an unstable species containing bridging thiocarbamoyl, dppm and a chelating thiocarbamoyl intermediate **7'** (Scheme III) or via intermolecular dissociation of two triphenylphosphine ligands forming **3**, followed by two chloride and two triphenylphosphine displacement by two dppm ligands to form [Pd$_2$(μ,η^2-SCNMe$_2$)$_2$(μ,η^2-dppm)$_2$]-[Cl]$_2$ and then one of the chloride re-coordinated to metal forming complex **7**'. In isolation and recrystallization, complex **7'** reacted with oxygen to give the final thiocarbamate product **7**. The air-stable brown and yellow complexes **6** and **7** are soluble in chlorinated solvents and DMSO, and insoluble in diethyl ether and *n*-hexane. The isolated compounds **1**, **3-7** were already of good purity, but analytically pure samples could be obtained by slow *n*-hexane diffusion into a dichloromethane solution at +4 °C. All characterization data are consistent with the proposed constitution.

IR and MS Spectroscopy

In the infrared spectra of **1**, **4-6** the C-N stretches for the SCNMe$_2$ group are in the region of 1429-1436 cm^{-1}, typical for a η^1-bound SCNMe$_2$ group[21] with partially multiple C-N bond of the thiocarbamoyl ligand. The peaks at 1516 and 1526 cm^{-1} in the IR spectra of **5a** and **5b** indicate a delocalized C(SR)NMe$_2$ group. The IR spectra of **5a** and **5b** show the C=O stretching band of the co-ordinated carbonate ligand at 1675, 1603 and at 1681, 1605 cm^{-1}, respectively, which are indicative of a chelate dithiocarbonate ligand.[16-20] The FAB mass spectra of **1**, **3-5** show parent peaks with the typical Pd isotope distribution corresponding to [M$^+$] molec-

Scheme III



ular masses, respectively. In the FAB mass spectra, base peaks with the typical Pd isotope distribution are respectively in agreement with the $[M^+ - Cl]$ and $[M^+ - dppm - O]$ molecular masses of **6** and **7**.

NMR Spectroscopy

The room-temperature ^1H NMR spectra of **1** are complicated because of the dissociation of either the chloride or the triphenylphosphine ligand of **1** to form the mononuclear complex $[Pd(PPh_3)_2(\eta^2\text{-}SCNMe_2)][Cl]$ (**2**) or the dipalladium complex $[Pd(PPh_3)Cl]_2(\mu,\eta^2\text{-}SCNMe_2)_2$ (**3**). Clear spectra of complex $[Pd(PPh_3)_2(\eta^2\text{-}SCNMe_2)][PF_6]$ and **3** and variable-temperature (298-233 K) ^1H NMR spectra of the mixture distinguished the three complexes unambiguously (Supporting Information, spectrum A). Two methyl resonances of the $SCNMe_2$ ligand are observed in the ^1H NMR spectra of complexes **1-7**, consistent with hindered rotation about the partially multiple C-N bond. The $^{13}C\{^1H\}$ NMR spectra of the methyl signals of complexes **1-7** are in the region from δ 38.9 to δ 53.4. The low-field section of the $^{13}C\{^1H\}$ NMR spectra consists of one resonance attributable on intensity grounds to the thiocarbamoyl carbon atom in the region from δ 212.8 to δ 234.3. In the ^1H NMR spectra of **5a** and **5b**, one resonance at δ 2.88 and three resonances at δ 1.20 and 3.45, 4.03 and the corresponding $^{13}C\{^1H\}$ NMR signals at δ 21.2 and at δ 13.4, δ 33.4 are attributed to the $S\text{-}CH_3$[22] and the $S\text{-}CH_2CH_3$[23] groups, respectively. The $^{13}C\{^1H\}$ NMR spectra of **5a** and **5b** reveal two singlets at lowest field, which are assigned to the carbon atoms of the carbene (δ 247.9 and δ 246.7) and dithiocarbonate (δ 199.0 and δ 199.1) carbon nuclei, respectively.

The $^{31}P\{^1H\}$ NMR spectrum of **3** 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 relatively more downfield resonance than those of **1** (δ 16.6), **3** (δ 19.8), **4b** (δ 24.8), and **7** (δ 1.97, 9.91) shows the cationic character of **2**. From the description, it is clear that the compound **2** is side-on bound through the C-S moiety of the $SCNMe_2$ ligand.

The ^1H NMR spectrum of **6** shows eight resonances with the same ratios and the $^{13}C\{^1H\}$ NMR spectrum exhibits twelve singlet resonances, which are attributed to the inequivalent environments of the phen ligand. The relative down-field $^{13}C\{^1H\}$ NMR spectrum of **1**, appears as one singlet resonance at δ 221.6 for the carbon atom of the thiocarbamoyl group.

The methyl group of the $SCNMe_2$ ligand in **7** shows similar ^1H NMR and $^{13}C\{^1H\}$ NMR resonances as those of **1**-**6**, two singlet resonances appear at δ 173.2 and δ 223.0 which are assigned to the carbon atoms of the $SCNMe_2$ and $SC(=O)NMe_2$ ligands, respectively.

X-ray single-crystal structures of 1, 3, 5a, and 7

To confirm the first thiocarbamoyl palladium and the methyl-thiocarbamoyl coupling carbene-complex, the aforementioned compounds **1**, **3**, **5a**, and **7** have been performed by single-crystal X-ray diffraction studies. Single crystals of **1**, **3**, **5a**, and **7** were grown by slow *n*-hexane diffusion into a dichloromethane solution at +4 °C. ORTEP plots with atom labels of **1**, **3**, **5a** and **7** are shown in Figs. 2-5. Crystal data and refinement details, selected interatomic distances (Å)

and angles (deg), and atomic coordinates and equivalent isotropic displacement coefficients for important atoms of complexes **1**, **3**, **5a** and **7** are listed in Tables 1, 2 and 3, respectively.

In complex **1**, the $SCNMe_2$ ligand is σ bound to Pd atom through the carbon atom of the thiocarbamoyl group. The S-Pd bond distance of 3.033 Å in **1** indicates no bonding interaction between the sulfur atom and palladium metal atom. The palladium atom has a distorted square planar geometry in which two triphenylphosphine and the carbon atom of the thiocarbamoyl ligand and the chloride ligand are in *trans* positions: P(2)-Pd-P(1), 173.75(3)°; Cl(1)-Pd-C(1), 166.32(10)°.

Complex **3** is a dimer with each $SCNMe_2$ unit bridging through a carbon atom of the thiocarbamoyl group to one metal center and sulfur atom to the other metal forming a six-membered ring and boat-form geometry. Within the $SCNMe_2$ ligands themselves, the geometries are consistent with significant partial double bond character in the C-S and

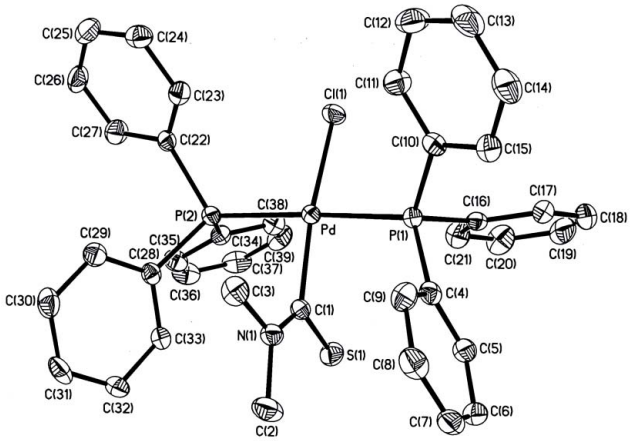


Fig. 2. An ORTEP drawing with 50% thermal ellipsoids and atom-numbering scheme for the complex [[$Pd(PPh_3)_2(\eta^1$-$SCNMe_2)(Cl)$] (**1**).

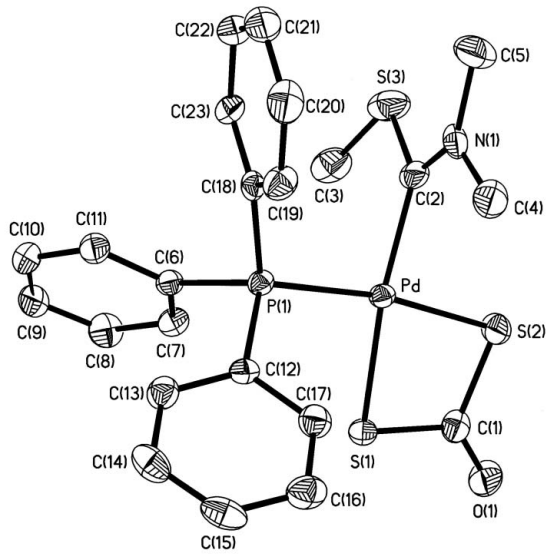


Fig. 4. An ORTEP drawing with 50% thermal ellipsoids and atom-numbering scheme for the complex [$Pd(PPh_3)\{\eta^1$-$C(SMe)(NMe_2)\}(\eta^2$-$S_2CO)$] (**5a**).

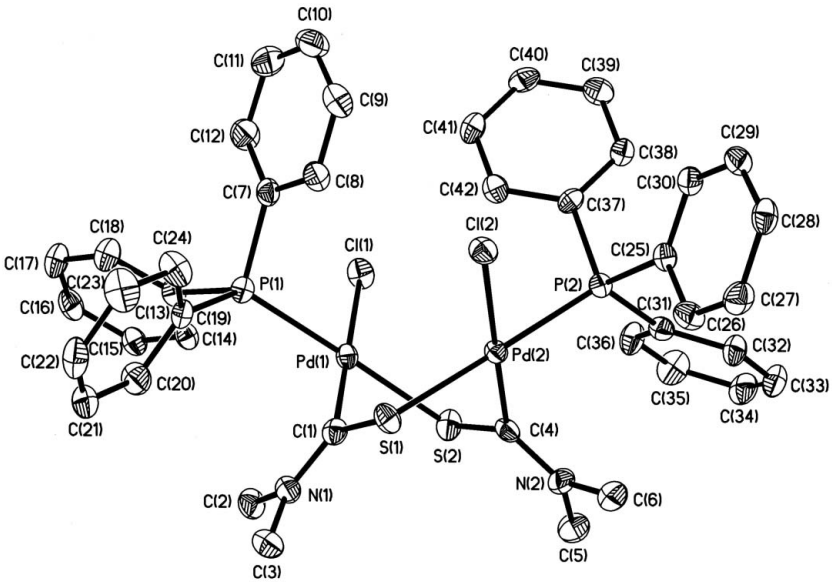


Fig. 3. An ORTEP drawing with 50% thermal ellipsoids and atom-numbering scheme for the complex [$Pd(PPh_3)Cl]_2(\mu,\eta^2$-$SCNMe_2)_2$ (**3**).

Table 1. Crystal Data and Refinement Details for Complexes **1**, **3**·CH_2Cl_2, **5a** and **7**·$3CH_2Cl_2$

	1	**3**·CH_2Cl_2	**5a**	**7**·$3CH_2Cl_2$
chemical formula	$C_{39}H_{36}ClNP_2SPd$	$C_{43}H_{44}Cl_4N_2P_2S_2Pd_2$	$C_{23}H_{24}NOPS_3Pd$	$C_{59}H_{62}Cl_7N_2OP_4S_2Pd_2$
formula weight	754.54	1069.46	563.98	1464.06
crystal system	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	12.8248(1)	9.8782(1)	16.3638(2)	12.1128(1)
b, Å	18.6358(2)	11.4238(1)	9.3374(1)	14.0133(2)
c, Å	14.9692(1)	20.7353(2)	15.7117(2)	17.7873(2)
α, deg	90	103.9126(5)	90	82.1939(5)
β, deg	105.1513(4)	97.8453(3)	98.2957(6)	79.6190(6)
γ, deg	90	104.9669(5)	90	80.9551(5)
V, $Å^3$	3453.28(5)	2166.76(4)	2375.56(5)	2914.86(6)
Z	4	2	4	2
ρ_{calcd}, g cm^{-3}	1.451	1.639	1.577	1.668
μ, (Mo Kα), mm^{-1}	0.797	1.281	1.128	1.164
λ, Å	0.71073	0.71073	0.71073	0.71073
T, K	150(1)	150(1)	150(1)	150(1)
θ range, deg	1.78-27.50	1.02-27.50	1.26-27.50	1.48-27.50
Independent rflns	7906	9924	5458	13381
no. of variables	407	497	272	682
R[a]	0.043	0.041	0.039	0.069
R_w[b]	0.090	0.097	0.090	0.181
S[c]	1.0459	1.103	1.119	1.017

[a] $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. [b] $Rw = [\Sigma w(|Fo| - |Fc|)^2]^{1/2}$; $w = 1/s^2(|Fo|)$. [c] Quality-of-fit = $[\Sigma w(|Fo| - |Fc|)^2/(N_{observed} - N_{parameters})]^{1/2}$.

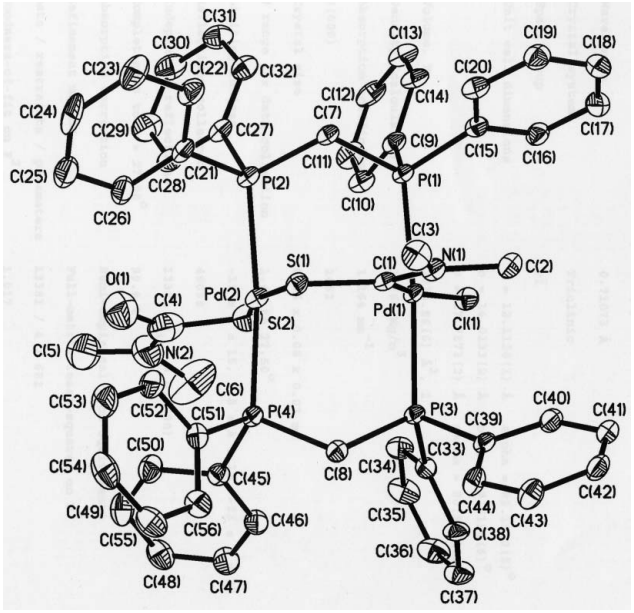
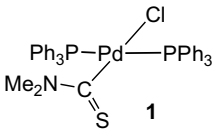


Fig. 5. An ORTEP drawing with 30% thermal ellipsoids and atom-numbering scheme for the complex [Pd{η^1-SC(O)NMe_2}Pd(Cl)](μ,η^2-$SCNMe_2$)(μ,η^2-dppm)$_2$ (**7**).

SC-N bonds. Thus, the C-S bond distances (1.731(4) and 1.718(4) Å) 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 (1.316(5) and 1.318(5) Å) 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.

In complex **5a**, the palladium atom has a distorted square planar geometry and the carbene carbon, Pd, S, and N are coplanar to within 0.030 Å. The bond angles about C(2) (126.7, 113.5, and 119.8°) clearly show the sp^2 character of the carbon. One of the sulfur atoms of dithiocarbonate ligand is *trans* to the triphenylphosphine: S(2)-Pd-P(1), 171.56(3)°, while the other is *trans* to the carbene ligand: S(1)-Pd-C(2), 170.61(10)°. The Pd-C(2) bond distance, 2.043(4) Å, is longer than the other Pd^{II}-carbon(carbonyl) distances, and similar to those of Pd-C(carbene) distances.[24] Within the carbene, C(SMe)(NMe_2), the geometry is consistent with significant partial double bond character in the S(3)-C(2) (1.731(4) Å) and C(2)-N(1) (1.308(4) Å) bonds. This implies P_π-P_π overlap, involving the empty P orbital of C(2) atom. Because of

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **1**, **3**, **5a** and **7**



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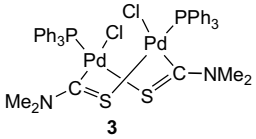

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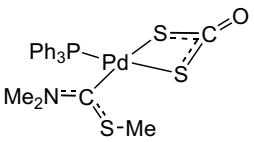
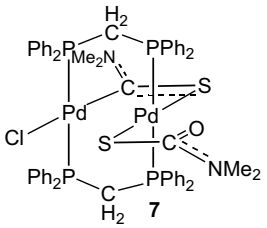


5a



7

Pd-P	2.3531(9), 2.3401(9)	2.3046(10), 2.3013(9)	2.2889(9)	2.3488(16)(av), 2.3345(17)(av)
Pd-Cl	2.4067(9)	2.3721(10), 2.3677(9)	-	2.3579(16)
Pd-C	1.982(3)	1.969(4), 1.989(4)	2.043(4)	2.008(6)
Pd-S	3.033	2.3573(10), 2.3733(9)	2.3306(9), 2.3250(9)	2.317(2), 2.3556(17)
C=S	1.679(4)	1.731(4), 1.718(4)	1.731(4)	1.715(6), 1.692(13)
C-N	1.320(4)	1.316(5), 1.318(5)	1.308(5)	1.315(8), 1.415(15)
N-Me	1.458(5), 1.457(5)	1.465(5)-1.474(5)	1.502(5), 1.441(5)	1.359(15)-1.477(9)
C-Pd-X (Cl, S)	166.32(10)	178.55(11), 178.05(10)	170.61(10)	168.09(18)
Pd-S-C	-	116.93(19), 117.7(2)	88.11(12), 87.91(13)	96.7(2), 105.0(5)
Pd-C-S	111.61(18)	116.93(19), 117.7(2)	119.8(2)	120.6(3)

π-electron donation by both nitrogen and sulfur atoms, the aminothiocarbene is a very weak π-acceptor and has binding properties towards low-valent transition metals similar to those of phosphines or pyridines. The Pd-S(1) bond distance, 2.3306(9) Å, is longer than the Pd-S(2) bond distance, 2.3250(9) Å, due to the high *trans* influence of carbene ligand than PPh_3 ligand and the two Pd-S bonds are within the normal Pd-S length range (2.23~2.32 Å).[25] The bond distances within the dithiocarbonate ligand, S-C(av), 1.773(4) Å, and C(1)-O(1), 1.207(4) Å, fall in the range of values found for other dithiocarbonate complexes, and are indicative of an overall electronic delocalization within the S_2CO group.[16]

Complex **7** consists of two palladium centers bridged by two mutually *trans* dppm groups, with the Cl, $SC(=O)NMe_2$, and $SCNMe_2$ ligands bound in the equatorial plane which is approximately perpendicular to the Pd-P vectors. Pd(1) or Pd(2) has an essentially square-planar coordination in which the two phosphines are mutually *trans* and the chloride or sulfur atom of the $SC(=O)NMe_2$ ligand is *trans* to the carbon or sulfur atom of the bridging $SCNMe_2$ ligand, forming a A-frame type dinuclear compound. Thiocarbamate complex **7** represents a rare example of a binuclear palladium species with M_2^{+3} core, and the two metals can be formally regarded as Pd(II) and Pd(I) with 16- and 17-electron configurations, respectively. The bond distances C(4)-O(1) (1.248(14) Å), C(1)-N(1) (1.315(8) Å), and C(4)-N(2) (1.415(15) Å) are typical for a C-O and C-N bond having partial double bond character and are certainly much shorter than a normal C-O (1.43 Å) and C-N (1.47 Å) single bond.

The Pd-PPh_3 bond lengths of **1**, **3** and **5a** are in the region of 2.2889(9) – 2.3531(9) Å, and appear to be normal. The Pd-Cl (2.3579(16) – 2.4067(9) Å) and Pd-S distances are both within the range of values reported for other palladium^{II} complexes.

CONCLUSION

In this article we report the syntheses, dissociation behavior and X-ray crystal structures of thiocarbamoyl Pd complexes. We have prepared $[Pd(PPh_3)_2(\eta^1\text{-}SCNMe_2)(Cl)]$ (**1**) by the oxidative addition of $Me_2NC(=S)Cl$ to $Pd(PPh_3)_4$. The sulfur atom of the thiocarbamoyl ligand assisting the dissociation of either the chloride or the triphenylphosphine ligand to form **2** or **3** has been confirmed. The bridging thiocarbamoyl dinuclear complex $[Pd(PPh_3)Cl]_2(\mu,\eta^2\text{-}SCNMe_2)_2$ (**3**) including six-membered ring is a good starting material for preparation of dinuclear compound. Novel alkyl-thiocarbamoyl coupling reaction produces the first uncyclic N,S-heteroatom Fischer-type carbene-complexes **5a**,**b**[26] from the reaction of **1** with alkyldithiocarbonate ligands. The π interaction between the carbene-carbon and SR or NMe_2 and the more chelate ability of the dithiocarbonate ligand than the alkyldithiocarbonate ligand are two important factors in

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for Important Atoms of **1**, **3**, **5a** and **7**

Atom	*x*	*y*	*z*	B_{eq}
Compound **1**				
Pd	652(1)	1949(1)	7165(1)	17(1)
Cl(1)	671(1)	2746(1)	5905(1)	25(1)
S(1)	-25(1)	406(1)	7332(1)	27(1)
P(1)	2425(1)	1542(1)	7305(1)	18(1)
P(2)	-1061(1)	2358(1)	7203(1)	18(1)
N(1)	753(2)	1157(2)	8875(2)	21(1)
C(1)	479(3)	1132(2)	7962(2)	19(1)
C(2)	668(3)	534(2)	9441(3)	34(1)
C(3)	1085(3)	1816(2)	9395(3)	28(1)
C(4)	2954(3)	887(2)	8214(2)	20(1)
C(10)	3500(3)	2215(2)	7529(2)	21(1)
C(22)	-1228(3)	3333(2)	7154(2)	20(1)
C(28)	-1531(3)	2132(2)	8226(2)	19(1)
Compound **3**				
Pd(1)	3176(1)	4701(1)	1985(1)	18(1)
Pd(2)	1589(1)	5285(1)	3333(1)	17(1)
Cl(1)	2390(1)	5573(1)	1146(1)	27(1)
Cl(2)	-623(1)	3739(1)	3177(1)	24(1)
S(1)	2806(1)	3733(1)	3281(1)	23(1)
S(2)	4183(1)	6715(1)	2742(1)	26(1)
P(1)	2267(1)	2756(1)	1215(1)	20(1)
P(2)	263(1)	6686(1)	3421(1)	18(1)
N(1)	5075(3)	3698(3)	2694(2)	23(1)
N(2)	4014(3)	7473(3)	4017(2)	25(1)
C(1)	3878(4)	4001(3)	2682(2)	21(1)
C(2)	6059(4)	4042(4)	2229(2)	29(1)
C(3)	5541(4)	3020(4)	3146(2)	29(1)
C(4)	3415(4)	6613(3)	3446(2)	20(1)
C(5)	5250(4)	8548(4)	4066(2)	35(1)
C(6)	3518(4)	7389(4)	4655(2)	32(1)
Compound **5a**				
Pd	8143(1)	-264(1)	2500(1)	19(1)
S(1)	7403(1)	-873(1)	3609(1)	25(1)
S(2)	9073(1)	127(1)	3743(1)	30(1)
S(3)	9600(1)	-1049(1)	1356(1)	43(1)
P(1)	7083(1)	-664(1)	1408(1)	18(1)
O(1)	8365(2)	-537(3)	5117(2)	40(1)
N(1)	9062(2)	1515(3)	1348(2)	29(1)
C(1)	8298(2)	-453(4)	4344(2)	27(1)
C(2)	8958(2)	254(4)	1679(2)	29(1)
C(3)	9254(3)	-2663(5)	1831(3)	41(1)
C(4)	8595(3)	2773(4)	1630(2)	37(1)
C(5)	9592(3)	1886(5)	725(3)	50(1)
Compound **7**				
Pd(1)	1586(1)	828(1)	6730(1)	25(1)
Pd(2)	3376(1)	749(1)	7769(1)	31(1)
Cl(1)	-339(1)	800(1)	7264(1)	35(1)
S(1)	4288(1)	891(1)	6480(1)	30(1)
S(2)	2114(2)	522(2)	8902(1)	54(1)
P(1)	1360(1)	2521(1)	6700(1)	27(1)
P(2)	3238(1)	2456(1)	7650(1)	30(1)
P(3)	2004(1)	-877(1)	6764(1)	26(1)
P(4)	3939(1)	-906(1)	7754(1)	29(1)
O(1)	3888(8)	609(7)	9513(5)	95(3)
N(1)	3168(5)	1076(4)	5317(3)	33(1)
N(2)	2416(10)	43(7)	10360(5)	86(3)
C(1)	3099(5)	940(4)	6070(4)	26(1)
C(2)	2197(6)	1138(5)	4913(4)	37(2)
C(3)	4234(6)	1220(6)	4791(4)	44(2)
C(4)	2912(12)	382(8)	9608(7)	80(3)
C(5)	3038(18)	41(11)	10925(10)	141(7)
C(6)	1415(12)	-400(13)	10500(10)	131(7)
C(7)	2644(5)	3013(5)	6793(4)	28(1)
C(8)	3414(5)	-1384(5)	6995(4)	31(1)

E.S.Ds. refer to the last digit printed.

forming the carbene-complexes. Three bonding modes of the thiocarbamoyl ligand have been observed; these include monodentate coordination through carbon atom (complexes **1** and **6**), bidentate through carbon and sulfur atoms by chelation (complex **2**) and bridging between two metal centers (complexes **3** and **7**).

EXPERIMENTAL SECTION

General Procedures

All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. NMR spectra were recorded on a Bruker AM-500 WB FT-NMR spectrometer and are reported in units of δ (ppm) with residual protons in the solvent as an internal standard ($CDCl_3$, δ 7.24; DMSO-d_6, δ 2.45). IR spectra were measured on a Nicolate Avator-320 instrument and were referenced to a polystyrene standard, using cells equipped with calcium fluoride windows. Mass spectra were recorded on a JEOL SX-102A spectrometer. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. *n*-Hexane, diethyl ether, THF and benzene were distilled from sodium-benzophenone. Acetonitrile and dichloromethane were distilled from calcium hydride, and methanol was distilled from magnesium. All other solvents and reagents were of reagent grade and were used as received. Elemental analyses and X-ray diffraction studies were carried out at the Regional

Center of Analytical Instrumentation located at National Taiwan University. $PdCl_2 \cdot xH_2O$ was purchased from Strem Chemical, $EtOCS_2K$, dppm, and 1,10-phenanthroline were purchased from Merck.

Preparation of $[Pd(PPh_3)_2(\eta^1\text{-}SCNMe_2)(Cl)]$ (1)

CH_2Cl_2 (20 mL) was added to a flask (100 mL) containing $Pd(PPh_3)_4$ (1.154 g, 1.0 mmol) and $Me_2NC(=S)Cl$ (0.142 g, 1.15 mmol) at -20 °C. The stirred mixture was allowed to warm to room temperature for about 10 min. The solvent was concentrated to 10 mL, and 20 mL of diethyl ether was added to the solution. The yellow solids were formed which were isolated by filtration (G4), washed with *n*-hexane (2 × 10 mL) and subsequently dried under vacuum yielding 0.74 g (98%) of $[Pd(PPh_3)_2(\eta^1\text{-}SCNMe_2)(Cl)]$ (**1**). IR (KBr, cm^{-1}) υ (CN) 1481 (m), 1436 (m). ^1H NMR (500 MHz, $CDCl_3$, 298 K): δ 2.31, 2.62 (s, 6H, NCH_3), 7.30-8.03 (m, 30H, Ph). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K): δ 16.5 (br, PPh_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K): δ 41.2 (br, NCH_3), 128.1-135.3 (m, Ph), 223.5 (s, NCS). MS (FAB, NBA, *m/z*): 754.5 [M^+], 492 [M^+ - PPh_3]. Anal. Calcd. for $C_{39}H_{36}ClNP_2SPd$: C, 62.08; H, 4.81; N, 1.86%. Found: C, 62.10; H, 4.86; N, 1.84.

Preparation of $[Pd(PPh_3)_2(\eta^2\text{-}SCNMe_2)][Cl]$ (2)

^1H NMR (500 MHz, $CDCl_3$, 233 K): δ 2.39, 3.58 (s, 6H, NCH_3), 7.15-7.72 (m, 30H, Ph). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 233 K): δ 23.1, 35.1 (d, $^2J_{P\text{-}P}$ = 40.7 Hz, PPh_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 233 K): δ 46.1, 53.4 (s, NCH_3), 128.1-135.3 (m, Ph), 212.8 (s, NCS).

Preparation of $[Pd(PPh_3)Cl]_2(\mu,\eta^2\text{-}SCNMe_2)_2$ (3)

To $[Pd(PPh_3)_2(\eta^1\text{-}SCNMe_2)(Cl)]$ (**1**) (0.754 g, 1.0 mmol) dissolved in CH_2Cl_2 (10 mL) with continuous stirring under a stream of dry nitrogen for 8 h, 20 mL of *n*-hexane was added, and a yellow precipitate was formed. The precipitate was collected by filtration (G4), washed with *n*-hexane (2 × 10 mL) and then dried in vacuo to yield 0.46 g (93%) of $[Pd(PPh_3)Cl]_2(\mu,\eta^2\text{-}SCNMe_2)_2$ (**3**). IR (KBr, cm^{-1}) υ (CN) 1483 (m), 1436 (m). ^1H NMR (500 MHz, $CDCl_3$, 298 K): δ 2.49, 3.42 (s, 12H, NCH_3), 7.28-8.02 (m, 30H, Ph). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K): δ 19.8 (s, PPh_3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K): δ 39.9, 49.1 (s, NCH_3), 128.4-135.8 (m, Ph), 234.3 (s, NCS). MS (FAB, NBA, *m/z*): 984.5 [M^+], 722.5 [M^+ - PPh_3], 460.5 [M^+ - $2PPh_3$]. 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.

Preparation of $[Pd(PPh_3)_2(\eta^1\text{-}SCNMe_2)(\eta^2\text{-}S_2COEt)]$ (4b)

MeOH (10 mL) was added to a flask (100 mL) containing $[Pd(PPh_3)_2(\eta^1\text{-}SCNMe_2)(Cl)]$ (**1**) (0.754 g, 1.0 mmol) and $EtOCS_2K$ (0.14 g, 1.0 mmol) at room temperature. After stirring for 5 min, a pale-yellow precipitate was formed. The precipitate was collected by filtration (G4) and was washed with MeOH (10 mL) and diethyl ether (2 × 10 mL) and then dried in vacuo yielding 0.51 g (88%) of $[Pd(PPh_3)_2(\eta^1\text{-}SCNMe_2)(\eta^2\text{-}S_2COEt)]$ (**4b**). IR (KBr, cm^{-1}) υ (CN) 1436 (m). ^1H NMR: δ 1.40 (t, 3H, OCH_2CH_3, $^3J_{H\text{-}H}$ = 7.0), 2.95, 3.30 (s, 6H, NCH_3), 4.55 (m, 2H, OCH_2CH_3), 7.37-7.62 (m, 15H, Ph). $^{31}P\{^1H\}$ NMR: δ 24.8 (br, PPh_3). $^{13}C\{^1H\}$ NMR: δ 13.8 (s, OCH_2CH_3), 38.9, 40.8 (s, NCH_3), 67.8, 68.0 (s, OCH_2CH_3), 128.3-134.2 (m, Ph), 210.0 (s, OCS_2), 233.2 (s, NCS). MS (FAB, NBA, *m/z*): 578 [M^+].

Preparation of $[Pd(PPh_3)\{\eta^1\text{-}C(SMe)(NMe_2)\}(\eta^2\text{-}S_2CO)]$ (5a)

MeOH (10 mL) was added to a flask (100 mL) containing $[Pd(PPh_3)_2(\eta^1\text{-}SCNMe_2)(Cl)]$ (**1**) (0.754 g, 1.0 mmol) and $MeOCS_2K$ (0.146 g, 1.0 mmol) at room temperature. After stirring for 5 min, a yellow-orange precipitate was formed. The precipitate was collected by filtration (G4), washed with *n*-hexane (2 × 10 mL) and then dried in vacuo to yield 0.51 g (90%). Of complex $[Pd(PPh_3)\{\eta^1\text{-}C(SMe)(NMe_2)\}(\eta^2\text{-}S_2CO)]$ (**5a**). IR (KBr, cm^{-1}) υ (CO) 1675 (vs), 1603 (vs). ^1H NMR: δ 2.88 (s, 3H, SCH_3), 2.96, 3.52 (s, 6H, $2NCH_3$), 7.30-7.57 (m, 15H, Ph). $^{31}P\{^1H\}$ NMR: δ 28.0 (PPh_3). $^{13}C\{^1H\}$ NMR: δ 21.2 (s, SCH_3), 43.6, 52.0 (s, NCH_3), 128.2-134.2 (m, C of Ph), 199.0 (s, S_2CO), 247.9 (d, NCSMe, $J_{P\text{-}C}$ = 14.6). MS (FAB, NBA, *m/z*): 564 [M^+]. Anal. Calcd for $C_{23}H_{24}NOPS_3Pd$: C, 48.98; H, 4.30; N, 2.48%. Found: C, 49.85; H, 4.56; N, 2.38.

Preparation of $[Pd(PPh_3)\{\eta^1\text{-}C(SEt)(NMe_2)\}(\eta^2\text{-}S_2CO)]$ (5b)

The synthesis and work-up were similar to those used in the preparation of complex **5a**. The complex $[Pd(PPh_3)\{\eta^1\text{-}C(SEt)(NMe_2)\}(\eta^2\text{-}S_2CO)]$ **(5b)** was isolated in 75% yield as a yellow-orange microcrystalline solid. IR (KBr, cm^{-1}) υ (CO) 1681 (vs), 1605 (vs). ^1H NMR: δ 1.20 (t, 3H, SCH_2CH_3, $J_{H\text{-}H}$ = 7.5), 2.89, 3.54 (s, 6H, $2NCH_3$), 3.45, 4.03 (m, 2H, SCH_2), 7.40-7.57 (m, 15H, Ph). $^{31}P\{^1H\}$ NMR: δ 28.0 (PPh_3). $^{13}C\{^1H\}$ NMR: δ 13.4 (s, SCH_2CH_3), 33.4 (s, SCH_2), 43.6,

52.2 (s, N*C*H_3), 128.4-134.0 (m, C of Ph), 199.1 (s, S_2*C*O), 246.7 (d, N*C*SEt, $J_{P\text{-}C}$ = 15.2). MS (FAB, NBA, *m/z*): 578 [M^+]. Anal. Calcd for $C_{24}H_{26}NOPS_3Pd$: C, 49.87; H, 4.53; N, 2.42%. Found: C, 50.15; H, 4.38; N, 2.28.

Preparation of [Pd(η^1-SCNMe$_2$)(η^2-Phen)(Cl)] (6)

CH_2Cl_2 (40 mL) was added to a flask (100 mL) containing [Pd(PPh_3)$_2$(η^1-SCNMe$_2$)(Cl)] (**1**) (0.754 g, 1.0 mmol) and phen (0.18 g, 1.0 mmol), and the solution was stirred at room temperature. After stirring 1 h, MeOH (10 mL) was added to the solution; brown solids were formed which were isolated by filtration (G4), washed with *n*-hexane (2 × 10 mL) and subsequently dried under vacuum yielding 0.30 g (73%) of [Pd(η^1-SCNMe$_2$)(η^2-Phen)(Cl)] (**6**). IR (KBr, cm^{-1}) υ (CN) 1436 (m). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 3.66, 4.06 (s, 6H, NCH_3), 7.50, 7.84, 7.88, 7.94, 8.39, 8.53, 8.63, 8.75 (s, 8H, Phen). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6, 298 K): δ 41.5, 49.4 (s, NCH_3), 125.3, 127.4 (s, 5, 6-C of Phen), 126.6, 127.0 (s, 3, 8-C of Phen), 128.9, 129.6 (s, C of Phen), 139.3, 140.3 (s, 4, 7-C of Phen), 143.3, 144.5 (s, C of Phen), 150.4, 151.7 (s, 2, 9-C of Phen), 221.6 (s, NCS). MS (FAB, NBA, *m/z*): 374 [M^+ - Cl]. Anal. Calcd for $C_{15}H_{14}ClN_3SPd$: C, 43.92; H, 3.44; N, 10.25%. Found: C, 43.80; H, 3.26; N, 10.58.

Preparation of [Pd{η^1-SC(O)NMe$_2$}Pd(Cl)](μ,η^2-SCNMe$_2$)(μ,η^2-dppm)$_2$ (7)

CH_2Cl_2 (30 mL) was added to a flask (100 mL) containing [Pd(PPh_3)$_2$(η^1-SCNMe$_2$)(Cl)] (**1**) (0.754 g, 1.0 mmol) and dppm (0.384 g, 1.0 mmol) at room temperature. After stirring for 2 h, 20 mL of diethyl ether was added to the solution and a yellow precipitate was formed. The precipitate was collected by filtration (G4), washed with diethyl ether (2 × 10 mL) and then dried in vacuo. Further purification was accomplished by slowly diffusion of *n*-hexane (40 mL) to a CH_2Cl_2 solution (5 mL) of the yellow product yielding 0.41 g (45%) of [Pd{η^1-SC(O)NMe$_2$}Pd(Cl)](μ,η^2-SCNMe$_2$)(μ,η^2-dppm)$_2$ (**7**). IR (KBr, cm^{-1}) υ (CN) 1483 (m), 1424 (m). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 3.75, 3.97 (m, PCH_2, 4H), 2.49, 2.91 (s, 12H, NCH_3), 6.65-8.34 (m, 48H, Ph). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 298 K): δ 1.97, 9.91 (m, dppm). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ 30.9 (br, PCH_2), 41.1, 43.4, 47.7 (s, NCH_3), 127.1-135.0 (m, Ph), 173.2 (s, SCO), 223.0 (s, NCS). MS (FAB, NBA, *m/z*): 809 [M^+ - dppm- O], 686 [M^+ - dppm- O - Me_2NCS - Cl], 578 [M^+ - dppm- Me_2NCS - Cl - Pd]. Anal. Calcd for $C_{56}H_{56}ClN_2OP_4S_2Pd_2$: C, 55.62; H, 4.67; N, 2.32%. Found: C, 55.84; H, 4.50; N, 2.28.

Single-Crystal X-ray Diffraction Analyses of 1, 3, 5a and 7

Single crystals of **1**, **3**, **5a**, and **7** suitable for X-ray diffraction analyses were grown by recrystallization from 20/1 *n*-hexane/CH_2Cl_2. The diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. The raw intensity data were converted to structure factor amplitudes and their esd's after corrections for scan speed, background, Lorentz, and polarization effects. An empirical absorption correction, based on the azimuthal scan data, was applied to the data. Crystallographic computations were carried out on a Microvax III computer using the NRCC-SDP-VAX structure determination package.[27]

A suitable single crystal of **1** was mounted on the top of a glass fiber with glue. Initial lattice parameters were determined from 24 accurately centered reflections with θ values in the range from 1.78 to 27.50°. Cell constants and other pertinent data were collected and are recorded in Table 1. Reflection data were collected using the θ/2θ scan method. Three check reflections were measured every 30 min throughout the data collection and showed no apparent decay. The merging of equivalent and duplicate reflections gave a total of 24507 unique measured data, of which 7906 reflections with $I > 2\sigma(I)$ were considered observed. The first step of the structure solution used the heavy-atom method (Patterson synthesis), which revealed the positions of metal atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. The quantity minimized by the least-squares program was $w(|Fo|-|Fc|)^2$, where *w* is the weight of a given operation. The analytical forms of the scattering factor tables for the neutral atoms were used.[28] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry but were not refined in least squares. All hydrogens were assigned isotropic thermal parameters 1-2 Å^2 larger then the equivalent ***B***iso value of the atom to which they were bonded. The final residuals of this refinement were ***R*** = 0.043 and ***Rw*** = 0.090.

The procedures for **3**, **5a** and **7** were similar to those for **1**. The final residuals of this refinement were ***R*** = 0.041 and ***R*w** = 0.097 for **3**, for ***R*** = 0.039 and ***R*w** = 0.090 for **5a** and ***R*** = 0.069 and ***R*w** = 0.181 for **7**. Selected bond distances and an-

gles and selected final atomic coordinates are listed in Tables 2 and 3.

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Supporting Information Available

Plot of VT NMR spectra of the mixtures of **1**, **2** and **3** in $CDCl_3$, X-ray crystallographic files, in CIF format, for the structures of complexes **1**, **3**, **5a**, and **7**.

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