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Thiocarbarmoyl-Assisted Formation of a New Type of α- and β-Isomer Paddlewheel Pd_2^{4+} Compounds. Synthesis, Characterization, and Crystal Structures of [Pd(η^1-SCNMe$_2$)(η^2-Tp)(PPh$_3$)], [Pd$_2$(μ-Hdppa)$_2$(μ-SCNMe$_2$)$_2$][Cl]$_2$, [Pd$_2$(μ-dppa)$_2$(μ-SCNMe$_2$)$_2$], and [Pd{η^2-S$_2$P(OEt)$_2$}]$_2$(μ-dppa)(μ-SCNMe$_2$)

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The reaction of the doubly thiocarbamoyl-bridged boat-form complex [Pd(PPh$_3$)(Cl)]$_2$-(μ-SCNMe$_2$)$_2$, **1**, with dithio (SS) and tris(pyrazoyl-1-yl)borate (Tp) ligands produces the monomer η^1-thiocarbamoyl complexes [Pd(PPh$_3$)(η^1-CSNMe$_2$)(η^2-SS)] (SS = Et$_2$NCS$_2$, **2a**; (EtO)$_2$PS$_2$, **2b**) and [Pd(PPh$_3$)(η^1-CSNMe$_2$)(η^2-Tp)], **3**, respectively. Treatment of **1** with dialkyldithiocarbonate, ROCS$_2^-$, yields Fischer-type carbene complexes [Pd(PPh$_3$){η^1-C(SR)(NMe$_2$)}(η^2-S$_2$CO)] (R = Me, **4a**; Et, **4b**). The carbene complexes **4a** and **4b** are formed via alkyl migration of the alkyldithiocarbonate ligand to the thiocarbamoyl ligand. The organometallic α-isomer paddlewheel-type Pd_2^{4+} dipalladium complex without axial ligation, [Pd$_2$(μ-Hdppa)$_2$(μ-SCNMe$_2$)$_2$][Cl]$_2$, **5**, is prepared by the reaction of Hdppa (Hdppa = bis(diphenylphosphino)amine) with **1**. Treatment of **5** with anionic oxygen, nitrogen, or carbon reagents (KOH, NaN$_3$, NaNH$_2$, NaCCH), instead of forming axial ligation complex, yields the deprotonation of the Hdppa ligand of **5** to obtain the α-isomer paddlewheel Pd_2^{4+} complex [Pd$_2$(μ-dppa)$_2$(μ-SCNMe$_2$)$_2$], **6**. Protonation of **6** by HBF$_4$ or HCl gave **5** quantitatively as the BF$_4^-$ and Cl$^-$ salts, respectively. In the reaction of **5** with KTp, instead of forming a Tp-Pd complex, complex **6** was formed. The β-isomer paddlewheel complexes containing a Pd_2^{4+} core, [Pd(η^2-dithio)]$_2$(μ-dppa)(μ-SCNMe$_2$) (dithio = S$_2$P(OEt)$_2$, **7a**; S$_2$COEt, **7b**; S$_2$CNC$_4$H$_8$, **7c**), are prepared by reactions of **5** with various dithio ligands, [NH$_4$][S$_2$P(OEt)$_2$], [K][S$_2$COEt], and [NH$_4$][S$_2$CNC$_4$H$_8$], in methanol at ambient temperature, respectively. X-ray structures of the new type of α- and β-paddlewheel Pd_2^{4+} species have been determined.

Introduction

Paddlewheel-type metal complexes with bridging ligands are a remarkable and important new class of homogeneous catalysts.[1] The α-isomer paddlewheel-type dipalladium complexes without axial ligation are known in pyt (pyridine-2-thionate),[2] dpb (*N*,*N*′-diphenylbenzamidinate),[3] mhp (6-methyl-2-hydroxypyridinate),[4] and hpp (1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidinate)[5] bridging ligands. α-Isomers were reported for the paddlewheel-type Pd_2^{4+} complexes Pd(DPhBz)$_4$[3] (DPhBz = *N*,*N*′-diphenylbenzamidinate), Pd$_2$(TPG)$_4$[6] (TPG = *N*,*N*,*N*′-triphenylguanidinate), and Pt$_2$(DArF)$_4$[7] (DArF = diarylformamidinate), whereas the β-isomers were reported for [Pd(TBT)]$_2$(μ-acetate)$_2$ (TBT = tolylbenzothiazole)[8] and Pd$_2$[μ-(C$_6$X$_4$)PPh$_2$]$_2$(μ-O$_2$CR)$_2$. All four ligands in the α-isomer bridge the dimetal unit to form a paddlewheel, and in the β-isomer, two bridging and two chelating ligands coordinate to the metal centers. Notably, these dipalladium complexes can be stabilized by these bridging ligands with N, O, or S atoms, and no metal−carbon bonded α-, β-isomer paddlewheel-type dipalladium complexes have been synthesized and characterized.

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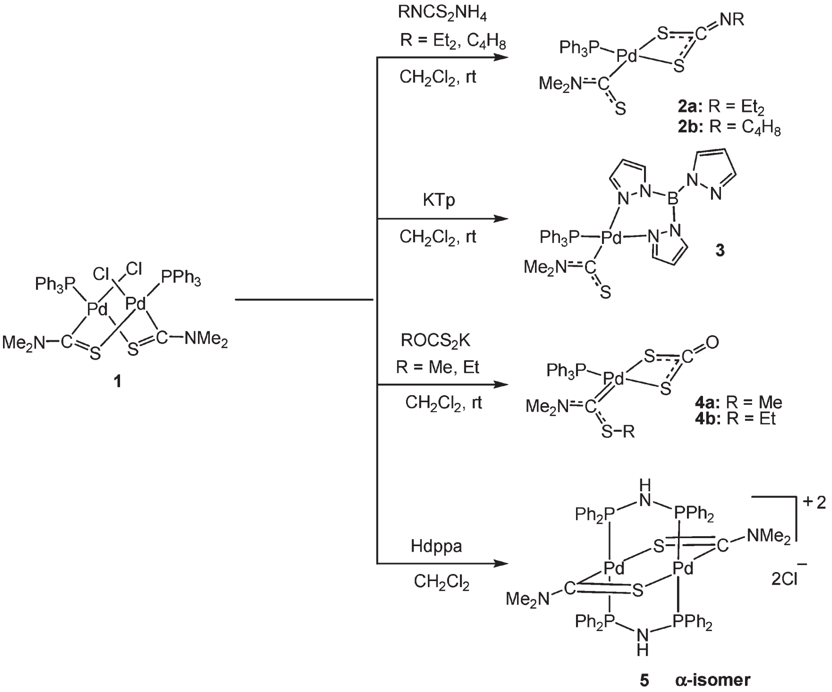
Scheme 1



All the characterized Pd(I) complexes are diamagnetic and have at least dinuclear,[9] side-by-side,[10] or A-frame[11] structures with a metal−metal bond, which allows the coupling of the unpaired electron on each metal. The Pd_2^{4+} paddlewheel complexes with d^8 configurations of each Pd atom lead to a Pd−Pd bond order of zero.

In an early study,[12] variable-temperature ^1H and ^{31}P NMR experiments of the thiocarbamoyl-Pd complex show the sulfur-assisted dissociation reaction to form mono- and dinuclear thiocarbamoyl-Pd complexes. In this paper, we report the synthesis, characterization, electronic spectra, and X-ray crystal structure analyses of a new type of α- and β-isomer paddlewheel Pd_2^{4+} compound formed in a thiocarbamoyl-assisted mechanism.

Results and Discussion

Syntheses. Thiocarbamoyl chloride, $Me_2NC(S)Cl$, has been used to prepare the Pd-carbon complex $[Pd(PPh_3)_2(\eta^1\text{-SCNMe}_2)(Cl)]$[13a] and the intermolecular dissociation reaction of complex $[Pd(PPh_3)_2(\eta^1\text{-SCNMe}_2)(Cl)]$, forming the doubly thiocarbamoyl-bridged boat-form dipalladium complex $[Pd(PPh_3)(Cl)]_2(\mu\text{-SCNMe}_2)_2$, **1**.[13b] Treatment of **1** with diethyldithiocarbamate and diethyldithiophosphate ligands in dichloromethane at ambient temperature produced the monomer η^1-thiocarbamoyl complexes $[Pd(PPh_3)(\eta^1\text{-CSNMe}_2)(\eta^2\text{-SS})]$ (SS = Et_2NCS_2, **2a**; $(EtO)_2PS_2$, **2b**) with 85% and 87% isolated yield (Scheme 1). Complexes **2a** and **2b** can also be obtained from the reaction of $[Pd(PPh_3)_2(\eta^2\text{-SCNMe}_2)][PF_6]$[12a] with dithio ligands, respectively. In the reaction of **1** and tris(pyrazoyl-1-yl)borate, the η^1-thiocarbamoyl complex $[Pd(PPh_3)(\eta^1\text{-CSNMe}_2)(\eta^2\text{-Tp})]$, **3**, is produced with 80% isolated yield. Treatment of **1** with alkyldithiocarbonate, $ROCS_2^-$, yields Fischer-type carbene complexes $[Pd(PPh_3)\{\eta^1\text{-C(SR)(NMe}_2)\}(\eta^2\text{-S}_2CO)]$ (R = Me, **4a**; Et, **4b**) with 72% and 75% isolated yield. No dinuclear Fischer-type carbene complexes have been found in the reaction. Fischer-type carbene complexes can also be synthesized by the reaction of $[Pd(PPh_3)_2(\eta^1\text{-SCNMe}_2)(Cl)]$[12b] or $[Pd(PPh_3)_2(\eta^2\text{-SCNMe}_2)][PF_6]$ with alkyldithiocarbonate ligands in methanol. Complexes **4a** and **4b** both include a dithiocarbonate group, S_2CO^{2-}. Dithiocarbonate metal complexes have previously been prepared by a variety of synthetic routes including reactions of metal carbonyl sulfide complexes with COS,[14] reactions of metal carbon disulfide complexes with dioxygen,[15] dealkylation,[16] iodide abstraction,[17] and hydrolysis[18] of alkoxydithiocarbamate metal complexes. Syntheses of carbene complexes by the reaction of Pd thiocarbamoyl and thio ester complexes with

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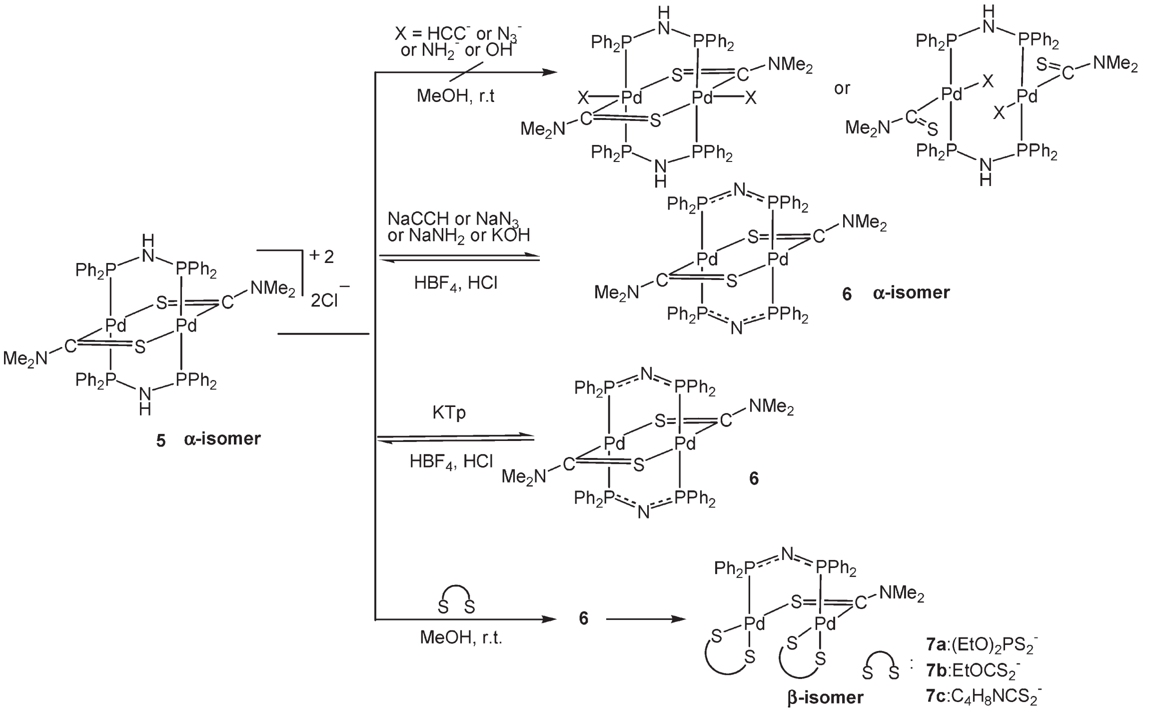
Scheme 2



electrophiles have been reported.[19] To our knowledge, our discussion here of the formation of dithiocarbonate carbene complexes via cleavage of the bridging S−Pd bond to form a monomer alkyldithiocarbonate-Pd complex followed by alkyl migration of the alkyldithiocarbonate ligand to the thiocarbamoyl ligand has not been reported in the literature.

Treatment of **1** with Hdppa (Hdppa = {bis(diphenylphosphino)amine}) in dichloromethane at ambient temperature causes displacement of both chloride and triphenylphosphine ligands from palladium to give a novel paddlewheel-type Pd_2^{4+} complex without exogenous ligation, $[Pd_2(\mu\text{-dppa})_2(\mu\text{-SCNMe}_2)_2][Cl]_2$, **5**, in 82% isolated yield (Scheme 2). Reaction of **5** with KOH, NaN_3, NaCCH, or $NaNH_2$ in methanol yields neither an axial ligation dinuclear compound nor a face-to-face dinuclear complex, but forms the deprotonated Hdppa ligand in **5** to form the Pd_2^{4+} complex $[Pd_2(\mu\text{-dppa})_2(\mu\text{-SCNMe}_2)_2]$, **6**, with 75−98% isolated yield. Protonation of **6** by HBF_4 or HCl give **5** quantitatively as the BF_4^- and Cl^- salts, respectively. The phenomena also take place in the reaction of **5** with KTp. Treatment of **5** with various dithio ligands $[NH_4][S_2P(OEt)_2]$, $[K][S_2COEt]$, and $[NH_4][S_2CNC_4H_8]$ in methanol at ambient temperature undergoes a deprotonation reaction on two Hdppa to form **6** first and then replacement of one Hdppa and one thiocarbamoyl ligand to give the β-isomer paddlewheel Pd_2^{4+} complexes $[Pd\{\eta^2\text{-S}_2P(OEt)_2\}]_2(\mu\text{-dppa})(\mu\text{-SCNMe}_2)$, **7a**, $[Pd(\eta^2\text{-S}_2COEt)]_2(\mu\text{-dppa})(\mu\text{-SCNMe}_2)$, **7b**, and $[Pd(\eta^2\text{-S}_2CNC_4H_8)]_2(\mu\text{-dppa})(\mu\text{-SCNMe}_2)$, **7c**, in 75%, 82%, and 88% isolated yield, respectively (Scheme 2). These air-stable and yellow or red compounds are obtained in high yields and are easily soluble in chlorinated or polar solvents but rather insoluble in nonpolar solvents. No appreciable decomposition of these isolated products was observed even upon prolonged standing of the precipitates in air. An attempt to prepare an axial ligation dinuclear compound or an A-frame dinuclear complex from the reaction of **5** with KSCN, PhC≡CH, or S_8 gave no reaction.

In order to synthesize different bridging ligands of paddlewheel-type Pd_2^{4+} complexes, some doubly nitrogen-bridged boat-form dipalladium complexes of the type $[Pd(PPh_3)(X)]_2(\mu\text{-L})_2$ (X = Cl, Br; L = 4-methylpyridine-2-yl, 3-hydroxypyridine-2-yl, 3-aminopyridine-2-yl, pyrimidine-5-yl, thiazoline-2-yl, phenyloxythiocarbonyl)[20] similar to complex **1** have been prepared, and no paddlewheel-type Pd_2^{4+} complexes without exogenous ligation, $[Pd_2(\mu\text{-dppa})_2(\mu\text{-N})_2][Cl]_2$, were obtained. To our knowledge, thiocarbamoyl-assisted formation of new α- and β-isomer paddlewheel-type Pd_2^{4+} complexes is the first example in the literature.

NMR Spectroscopy. The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra of complexes **2a**,**b** and **4a**,**b** are compared to our previous reports[12a,b] to confirm the formula. Complex **3** shows broad singlets for CH of pyrazole protons; because of fast intramolecular exchange of the pyrazolyl groups, the five-membered-ring inversion is too fast on the NMR time scale. The ^1H NMR spectra of α-isomers **5** and **6** in $CDCl_3$ solution show two singlet resonances for the methyl groups of the thiocarbamoyl ligands in the region of δ values from 1.54 to 2.15 ppm and the corresponding $^{13}C\{^1H\}$ NMR signals from δ 38.3 to δ 54.9. The low-field section of the $^{13}C\{^1H\}$ NMR spectra consists of one sharp resonance attributable on intensity grounds to the thiocarbamoyl carbon atom in the region from δ 242 to δ 245. The $^{31}P\{^1H\}$ NMR spectra of **5** and **6** show singlet resonance at δ 58.2 and 50.1, respectively.

The ^1H NMR spectra of β-isomers **7a**, **7b**, and **7c** in $CDCl_3$ solution also show two singlet resonances for the methyl groups of the thiocarbamoyl ligands in the region of δ values

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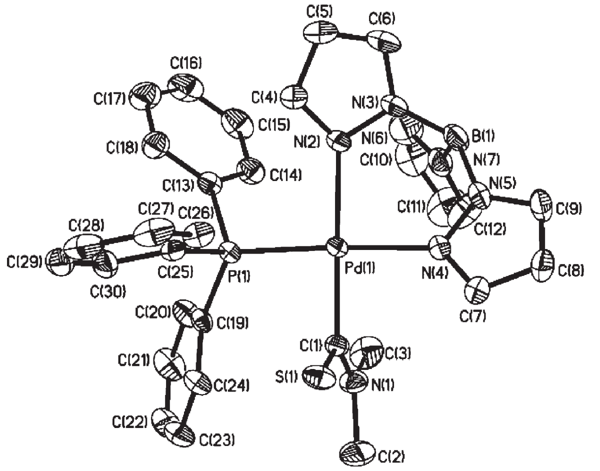

Figure 1. ORTEP drawing with 30% thermal ellipsoids and atom-numbering scheme for the cationic complex [Pd(PPh$_3$)(η^1-SCNMe$_2$)(η^2-Tp)], **3**. Selected bond distances (Å) and angles (deg): Pd(1)−C(1) 1.980(3), Pd(1)−N(4) 2.101(2), Pd(1)−N(2) 2.138(2), Pd(1)−P(1) 2.2725(7), S(1)−C(1) 1.676(3), N(1)−C(1) 1.318(4), C(1)−Pd(1)−N(4) 88.63(11), C(1)−Pd(1)−N(2) 170.64(11), N(4)−Pd(1)−N(2) 88.29(9), C(1)−Pd(1)−P(1) 88.75(8), N(4)−Pd(1)−P(1) 176.27(7), N(2)−Pd(1)−P(1) 94.71(7).

from 2.80 to 3.28 ppm and the corresponding ^{13}C{^{1}H} NMR signals from δ 41.3 to δ 50.1 ppm. The low-field section of the ^{13}C{^{1}H} NMR spectra consist of one resonance attributable on intensity grounds to the thiocarbamoyl carbon atom in the region from δ 231.6 to δ 242.0 ppm. The ^{31}P{^{1}H} NMR spectra of **7a**, **7b**, and **7c** show two doublet resonances attributed to the different chemical environment of the two phosphorus atoms of the dppa ligand and two singlet resonances for two (EtO)$_2$PS$_2$ ligands of **7a**.

X-ray Single-Crystal Structures of 3, 5, 6, and 7a. The novel complexes **3**, **5**, **6**, and **7a** were analyzed by X-ray diffraction studies and are shown in Figures 1−4, respectively.

In Figure 1, the X-ray diffraction study of **3** reveals a square-planar geometry for palladium with the poly(pyrazol-1-yl)borate ligands in bidentate mode, and the uncoordinated pyrazole group lies above the coordination plane. The poly(pyrazol-1-yl)borate ligands form a chelate angle of 88.29(9)° and adopt a boat-form conformation for the six-membered PdN$_4$B ring. In complex **3**, the Pd(1)−C(1), Pd(1)−N(2), and Pd(1)−N(4) bond distances (1.980(3), 2.101(2), and 2.138(2) Å) are consistent with the values reported for Pd^{II}−C and Pd−N systems. The Pd(1)−N(2) distance (*trans* to carbon) is slightly longer than Pd(1)−N(4) (*trans* to phosphorus) because of the higher *trans* influence induced by the thiocarbamoyl group than the triphenylphosphine group. The N(2)−Pd−N(4) bond angle (88.29(9)°) is larger than that reported for the same ligand in Pd(3-C$_{10}$H$_6$CH$_2$NMe)(η^2-Tp) (85.52(8)°),[21a] Pd{2-CH$_2$C$_6$H$_4$-P(o-tolyl)$_2$}(η^2-Tp) (86.3(1)°), Pd(C$_6$H$_4$C$_5$H$_4$N)(η^2-Tp) (85.7(3)°),[21b] and PdPh(PPh$_3$)(η^2-Tp) (87.1(3)°) but smaller than that of Pd(allyl)(η^2-Tp)[21c] (92.2(3)°).

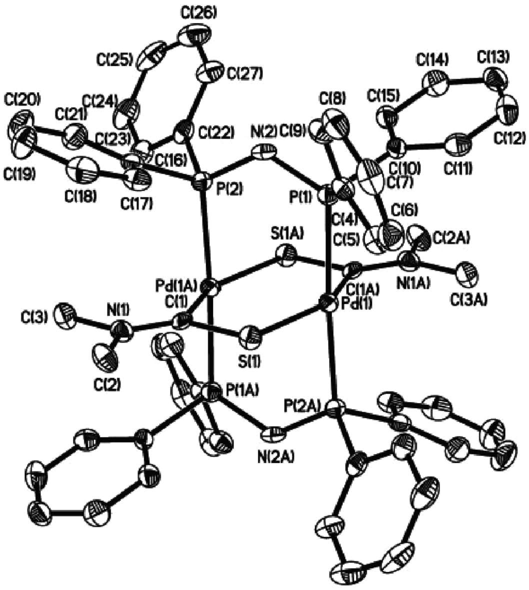

Figure 2. ORTEP drawing with 50% thermal ellipsoids and atom-numbering scheme for the cationic complex [Pd$_2$(μ-dppa)$_2$(μ-SCNMe$_2$)$_2$][Cl]$_2$, **5**. Selected bond distances (Å) and angles (deg): Pd(1)−C(1A) 2.000(4), Pd(1)−P(1) 2.3283(11), Pd(1)−P(2A) 2.3303(11), Pd(1)−S(1) 2.4321(10), Pd(1)−Pd(1A) 2.6908(6), S(1)−C(1) 1.732(4), C(1A)−Pd(1)−P(1) 89.56(12), P(1)−Pd(1)−P(2A) 173.41(4), C(1A)−Pd(1)−S(1) 154.85(12), P(1)−Pd(1)−S(1) 93.29(4), P(2A)−Pd(1)−S(1) 89.53(4), C(1A)−Pd(1)−Pd(1A) 82.13(12).

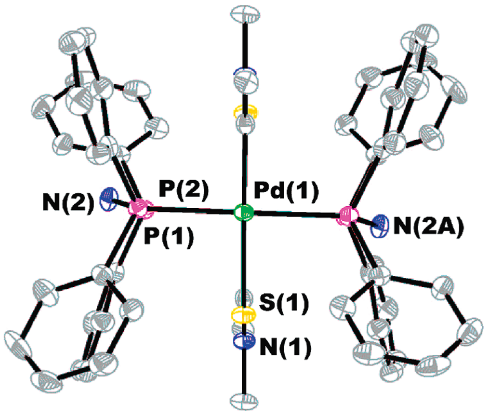

Figure 3. ORTEP drawing with 50% thermal ellipsoids and atom-numbering scheme for the complex [Pd$_2$(μ-dppa)$_2$(μ-SCNMe$_2$)$_2$], **6**. ORTEP view of molecule **6** looking along the Pd−Pd bond, emphasizing the eclipsed geometry of the two PdL$_4$ units. Selected bond distances (Å) and angles (deg): Pd(1)−C(1A) 1.998(5), Pd(1)−P(2A) 2.3409(13), Pd(1)−P(1) 2.3446(13), Pd(1)−S(1) 2.4330(13), Pd(1)−Pd(1A) 2.7113(8), S(1)−C(1) 1.733(5), C(1A)−Pd(1)−P(2A) 90.93(14), C(1A)−Pd(1)−P(1) 88.17(14), P(2A)−Pd(1)−P(1) 176.49(5), C(1A)−Pd(1)−S(1) 154.34(15), P(2A)−Pd(1)−S(1) 89.82(5), P(1)−Pd(1)−S(1) 92.45(5).

In each complex **5** and **6**, the two palladium atoms are bridged by two dppa and two thiocarbamoyl ligands, resulting in a paddlewheel-type structure; no axial coordination of any kind has been found within the molecule or in the lattice. The major changes are in the length of the Pd−Pd and P−N bond distances, but the overall structures do not differ significantly. The Pd$_2$$^{4+}$ electronic configurations of **5** (Figure 2) and **6** (Figure 3) have a bond order of zero. The Pd−Pd

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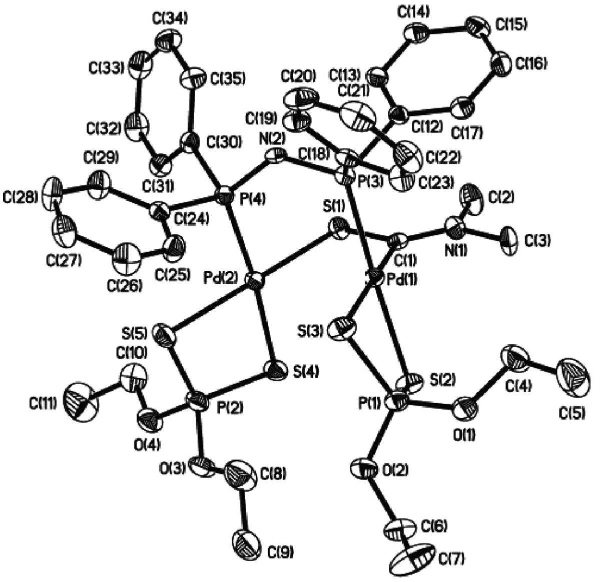

Figure 4. ORTEP drawing with 50% thermal ellipsoids and atom-numbering scheme for the complex $[Pd_2\{\eta^2\text{-}S_2P(OEt)_2\}_2]$-$(\mu\text{-dppa})(\mu\text{-}SCNMe_2)$, **7a**. Selected bond distances (Å) and angles (deg): Pd(1)−C(1) 1.983(4), Pd(1)−P(3) 2.2780(10), Pd(1)−S(3) 2.4063(10), Pd(1)−S(2) 2.4418(10), Pd(1)−P(1) 2.9290(11), Pd(1)−Pd(2) 3.2279(4), C(1)−Pd(1)−P(3) 84.99(11), C(1)−Pd(1)−S(3) 177.16(11), P(3)−Pd(1)−S(3) 97.16(4), C(1)−Pd(1)−S(2) 94.73(11), P(3)−Pd(1)−S(2) 177.67(4), S(3)−Pd(1)−S(2) 83.20(4).

distance of 2.6908(6) Å in **5** is slightly shorter, by ca. 0.0258 Å, than that in **6** (2.7166(6) Å). The crystal structure of **6** has been shown to possess an eclipsed geometry. The Pd−Pd distance of **6** is 0.326 Å longer than the shortest Pd−Pd distance ever reported for any type complex in $Pd_2(hpp)_4Cl_2$ and 0.229 Å longer than that in Pd−Pd-$NCCH_3$.[22]

The metal−carbon-bonded β-isomer paddlewheel Pd_2^{4+} complex **7a** has also been investigated by X-ray crystallography. In Figure 4, one dppa and one thiocarbamoyl bridging ligand are *cis* to each other, with the remaining two dithio ions acting as bidentate chelating ligands, which forms four-membered rings with separate palladium atoms. The thiocarbamoyl ligand shows a strong tendency to adopt bidentate coordination because of the ability of the amino lone pair to contribute via conjugation to the metal−ligand bonding.[23] There are no formal metal−metal bonds in these Pd_2^{4+} complexes; the bridging bulky dppa molecules easily force apart the chelating groups, resulting in the Pd−Pd separation of 3.2279(4) Å in **7a**. The dihedral angle between the $PdCPS_2$ and $PdPS_3$ coordination planes of **7a** is 45°, which is considerably greater than the 24° angle found in the benzoxazole and benzothiazole complexes,[8] indicating much greater steric repulsion in the present cases. In complex **7a**, the three planes of $PdPS_3$, Pd_2CS, and $PdCPS_2$ lie in a distorted square plane. A least-squares plane calculation revealed the planarity of the three planes of **7a** (largest deviation 0.0132−0.0722 Å). In complex **7a**, the Pd(1)−S(3) bond distance, 2.4063(10) Å, is longer than the Pd(2)−S(5) bond distance, 2.3439(11) Å, due to the higher *trans* influence of the carbon than the sulfur atom of the thiocarbamoyl ligand. The P−NH bond distances (1.657(3) and 1.669(4) Å in complex **5**) are longer than the P−N bond distances (in the range 1.596(3)−1.629(4) Å in complexes **6** and **7a**), due to the delocalization of electron density of the dppa ligand in complexes **6** and **7a**.

IR, MS, and UV−Vis Spectroscopy. Spectroscopic and analytical data of **2**−**7** were obtained. In the infrared spectra of **2**−**4**, the C−N stretches for the $SCNMe_2$ group are in the region 1429−1437 cm^{-1}, typical for an η^1-bound $SCNMe_2$ group[24] with a partial multiple C−N bond of the thiocarbamoyl ligand. In the infrared spectra of **5**−**7**, the C−N stretches for the $SCNMe_2$ group are in the region 1536−1556 cm^{-1}, typical for an η^2-bridging-bound $SCNMe_2$ group with partial multiple C−N bonds of the thiocarbamoyl ligand. The peaks at 1520 and 1526 cm^{-1} in the IR spectra of **4a** and **4b** indicate a delocalized $C(SR)NMe_2$ group. The IR spectra of **4a** and **4b** show the C=O stretching band of the coordinated carbonate ligand at 1680, 1612 and at 1683, 1618 cm^{-1}, respectively, which are indicative of a chelate dithiocarbonate ligand.[14−18] In the FAB mass spectra, base peaks with the typical Pd isotope distribution are in agreement with the $[M]^+$ molecular masses of **2**−**7**, respectively.

The UV−visible absorption spectra for α-isomers **5** and **6** and β-isomers **7a**−**c** are obtained. The absorption bands were shown at 406 nm (ε 850 $M^{-1}\,cm^{-1}$) for **5**, 445 nm (ε 406 $M^{-1}\,cm^{-1}$) for **6**, 439 nm (ε 4993 $M^{-1}\,cm^{-1}$) for **7a**, 445 nm (ε 5790 $M^{-1}\,cm^{-1}$) for **7b**, and 383 nm (ε 3740 $M^{-1}\,cm^{-1}$) for **7c**. Such an absorption is similar to that of $[Pd^{II}(bridge)_4Pd^{II}]$-type complexes, since similar absorptions are also found in $[Pd_2(mhp)_4]$ (ca. 370 nm, $\varepsilon = 2200$),[4] $[Pd_2(CH_3CSS)_4]$ (397 nm, $\varepsilon = 2290$),[25] $[Pd_2(form)_4]$ (492 nm, $\varepsilon = 2600$),[26] $[Pd_2(\mu\text{-dbp})_4]$ (500 nm, $\varepsilon = 2500$),[3] and $[Pd_2(pyt)_4]$ (430 nm, $\varepsilon = 2150$).[2]

Conclusion

The doubly thiocarbamoyl-bridged complex **1** is a good starting material for the preparation of paddlewheel dipalladium complexes. We employed Hdppa and three different dithio ligands to investigate the new α- and β-isomer paddlewheel Pd_2^{4+} complexes, respectively. The monodentate anionic oxygen, nitrogen, or carbon ligand improves the formation of α-isomer paddlewheel-type Pd_2^{4+} dipalladium complexes without axial ligation, whereas the bidentate anionic dithio ligands improve the formation of β-isomer paddlewheel-type Pd_2^{4+} dipalladium complexes. The thiocarbamoyl ligand shows a strong tendency to adopt bidentate coordination because of the ability of the amino lone pair to contribute via conjugation to the metal−ligand bonding.

Experimental Section

Materials. All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. NMR spectra were recorded on a Bruker AM-500 WB

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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; CD_3CN, δ 1.93; C_6D_6, δ 7.15; C_2D_6CO, δ 2.04). IR spectra were measured on a Nicolet 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 the National Taiwan University. $PdCl_2$ and Hdppa were purchased from Strem Chemical. KOH, NaN_3, $NaNH_2$, and NaCCH were purchased from TCI. $NH_4S_2P(OEt)_2$, KS_2COEt, and $NH_4S_2CNC_4H_8$ were purchased from Merck.

[Pd(PPh$_3$)(η^1-SCNMe$_2$)(η^2-Tp)], 3. CH_2Cl_2 (20 mL) was added to a flask (100 mL) containing **1** (0.984 g, 1.0 mmol) and KTp (0.277 g, 1.1 mmol). The solution was stirred for 3 h. The mixture was filtered by filtration (G4) with Celite; then *n*-hexane (30 mL) was added to the solution, and a light yellow precipitate was formed. The precipitate was collected by filtration (G4), washed with *n*-hexane (2 × 10 mL), and then dried in vacuo, yielding 0.535 g (80%) of **3**. Spectroscopic data for **3**: $^{31}P\{^1H\}$ NMR: δ 31.1 (s, PPh_3). ^1H NMR: δ 3.10, 3.28 (s, 6H, NMe), 6.09 (br, 3H, 4-H of pyrazole), 7.05, 7.82 (br, 6H, 3,5-H of pyrazole), 7.27−7.67 (m, 15H, PPh_3). $^{13}C\{^1H\}$ NMR: δ 42.1, 45.5 (s, NCH_3), 128.5 (m, o-C of Ph), 131.1 (s, 4-C of pyrazole), 131.8 (m, p-C of Ph), 132.0 (s, 5-C of pyrazole), 134.2 (m, m-C of Ph), 135.6 (s, 3-C of pyrazole). MS (FAB, NBA, *m*/*z*): 668 (M^+), 601 (M^+ − pyrazole). Anal. Calcd for $C_{30}H_{30}BN_7PSPd$: C, 53.87; H, 4.52; N, 14.66. Found: C, 54.01; H, 4.41; N, 14.58.

[Pd$_2$(μ-Hdppa)$_2$(μ-SCNMe$_2$)$_2$][Cl]$_2$, 5. CH_2Cl_2 (10 mL) was added to a mixture of Hdppa (0.384 g, 1.0 mmol) and complex $[Pd(PPh_3)(Cl)]_2(\mu\text{-}SCNMe_2)_2$, **1** (0.984 g, 1.0 mmol). After 10 min, a yellow solid was formed, which was isolated by filtration (G4), washed with *n*-hexane (2 × 10 mL), and subsequently dried under vacuum, yielding 1.009 g (82%) of $[Pd_2(\mu\text{-}Hdppa)_2(\mu\text{-}SCNMe_2)_2][Cl]_2$, **5**. Spectroscopic data of **5** are as follows: IR (KBr, ν_{CN}/cm^{-1}): 1550(m). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K): δ 58.2 (s, Hdppa). ^1H NMR (500 MHz, $CDCl_3$, 298 K): δ 1.55, 2.11 (s, 12H, NCH_3), 5.74 (s, 2H, NH), 7.11−8.71 (m, 40H, Ph). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K): δ 48.1, 54.9 (s, NCH_3), 127.9−133.2 (m, C of Ph), 245.0 (s, NCS). MS (FAB, NBA, *m*/*z*): 1159 (M^+ − 2Cl). Anal. Calcd for $C_{54}H_{54}Cl_2N_4P_4S_2Pd_2$: C, 52.70; H, 4.42; N, 4.55. Found: C, 52.82; H, 4.46; N, 4.38.

[Pd$_2$(μ-dppa)$_2$(μ-SCNMe$_2$)$_2$], 6. A solution of $[Pd_2(\mu\text{-}Hdppa)_2(\mu\text{-}SCNMe_2)_2][Cl]_2$, **5** (1.059 g, 1.0 mmol), in MeOH (20 mL) was treated with KOH (0.138 g, 3.0 mmol) at ambient temperature. Instantly, the reaction mixture turned red. After 10 min of stirring, a red precipitate was formed. The precipitate was collected by filtration (G4), washed with *n*-hexane (2 × 10 mL), and dried in vacuo to yield 1.136 g (98%) of $[Pd_2(\mu\text{-}dppa)_2(\mu\text{-}SCNMe_2)_2]$, **6**. Spectroscopic data of **6** are as follows: IR (KBr, ν_{CN}/cm^{-1}): 1536(m). $^{31}P\{^1H\}$ NMR (202 MHz, CD_3OD, 298 K): δ 50.1. ^1H NMR (500 MHz, CD_3OD, 298 K): δ 1.54, 2.16 (s, 12H, NCH_3), 7.11−8.71 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD, 298 K): δ 38.3, 49.5 (s, NCH_3), 127.9−133.2 (m, C of Ph), 243.0 (s, NCS). MS (FAB, NBA, *m*/*z*): 1159 (M^+). Anal. Calcd for $C_{54}H_{52}N_4P_4S_2Pd_2$: C, 56.01; H, 4.53; N, 4.84. Found: C, 56.22; H, 4.51; N, 4.78.

Complex **6** can also be synthesized using the same procedure by employing NaN_3, $NaNH_2$, NaCCH, or KTp with complex **5**, respectively.

[Pd{η^2-S$_2$P(OEt)$_2$}]$_2$(μ-dppa)(μ-SCNMe$_2$), 7a. To $[Pd_2(\mu\text{-}dppa)_2(\mu\text{-}SCNMe_2)_2]$, **5** (1.159 g, 1.0 mmol), dissolved in MeOH (20 mL) with continuous stirring under a stream of dry nitrogen was added $NH_4S_2P(OEt)_2$ (0.406 g, 2.0 mmol). The color of the solution changed from red to yellow immediately, 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 0.792 g (75%) of $[Pd\{\eta^2\text{-}S_2P(OEt)_2\}]_2(\mu\text{-}dppa)(\mu\text{-}SCNMe_2)$, **7a**. Further purification was accomplished by recrystallization from 1:10 CH_2Cl_2/*n*-hexane. Spectroscopic data of **7a** are as follows: IR (KBr, ν_{CN}/cm^{-1}): 1556(m). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K): δ 31.3, 50.7 (d, dppa, $^2J_{P-P}$ = 21 Hz), 101.2, 111.4 (s, PS_2). ^1H NMR (500 MHz, $CDCl_3$, 298 K): δ 1.15, 1.29 (br, 12H, OCH_2CH_3), 3.10, 3.28 (s, 6H, NCH_3), 3.86, 4.11 (br, 8H, OCH_2), 7.11−8.25 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K): δ 15.8 (s, OCH_2CH_3), 42.1, 47.3 (s, NCH_3), 61.8, 63.0 (br, OCH_2), 127.9−140.8 (m, C of Ph), 242.0 (s, NCS). MS (FAB, NBA, *m*/*z*): 1056.8 (M^+). Anal. Calcd for $C_{35}H_{46}N_2O_4P_4Pd_2S_5$: C, 39.82; H, 4.39; N, 2.65. Found: C, 39.84; H, 4.46; N, 2.60.

[Pd(η^2-S$_2$COEt)]$_2$(μ-dppa)(μ-SCNMe$_2$), 7b. The synthesis and workup were similar to those used in the preparation of complex **7a**. The complex $[Pd(\eta^2\text{-}S_2COEt)]_2(\mu\text{-}dppa)(\mu\text{-}SCNMe_2)$, **7b**, was isolated in 82% yield as a yellow microcrystalline solid. Spectroscopic data of **7b** are as follows: IR (KBr, ν_{CN}/cm^{-1}): 1554(m). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K): δ 57.6, 67.4 (d, dppa, $^2J_{P-P}$ = 76 Hz). ^1H NMR (500 MHz, $CDCl_3$, 298 K): δ 1.54 (s, 6H, OCH_2CH_3), 2.79, 3.07 (s, 6H, NCH_3), 4.52 (br, 4H, OCH_2), 7.08−8.38 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K): δ 13.8 (s, OCH_2CH_3), 41.6, 50.1 (s, NCH_3), 67.2, 67.6 (s, OCH_2), 127.2−132.8 (m, C of Ph), 231.6 (s, NCS). MS (FAB, NBA, *m*/*z*): 926.8 (M^+). Anal. Calcd for $C_{33}H_{36}N_2O_2P_2Pd_2S_5$: C, 42.72; H, 3.91; N, 3.02. Found: C, 42.78; H, 4.00; N, 2.98.

[Pd(η^2-S$_2$CNC$_4$H$_8$)]$_2$(μ-dppa)(μ-SCNMe$_2$), 7c. The synthesis and workup were similar to those used in the preparation of complex **7a**. The complex $[Pd(\eta^2\text{-}S_2CNC_4H_8)]_2(\mu\text{-}dppa)(\mu\text{-}SCNMe_2)$, **7c**, was isolated in 88% yield as a yellow microcrystalline solid. Spectroscopic data of **7c** are as follows: IR (KBr, ν_{CN}/cm^{-1}): 1554(m). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K): δ 55.9, 66.0 (d, dppa, $^2J_{P-P}$ = 80 Hz). ^1H NMR (500 MHz, $CDCl_3$, 298 K): δ 1.84−1.95 (m, 8H, NCH_2CH_2), 2.80, 3.10 (s, 6H, NCH_3), 3.94−3.77 (m, 8H, NH_2), 7.01−8.42 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K): δ 24.3, 24.6, 24.7, 24.8 (s, NCH_2CH_2), 41.3 (s, NCH_3), 48.9, 49.1, 49.4, 49.8 (s, NCH_2), 127.0−132.8 (m, C of Ph), 205.2 (d, NCS_2, $^3J_{P-C}$ = 25.8 Hz), 239.1 (s, NCS). MS (FAB, NBA, *m*/*z*): 979 (M^+). Anal. Calcd for $C_{37}H_{42}N_4P_2Pd_2S_5$: C, 45.44; H, 4.33; N, 5.73. Found: C, 45.52; H, 4.46; N, 5.68.

Single-Crystal X-ray Diffraction Analyses of 3, 5, 6, and 7a. Single crystals of **3**, **5**, **6**, and **7a** 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 **3** 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 1.13° to 27.50°. Cell constants and other pertinent data were collected. Reflection data were collected using the θ/2θ scan method. The θ scan angle was determined for each reflection

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according to the equation 0.70 ± 0.35 tan θ. 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 41 138 unique measured data, of which 14 164 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 $w(|F_o| - |F_c|)^2$, 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 than the equivalent B_{iso} value of the atom to which they were bonded. The final residuals of this refinement were $R = 0.040$ and $R_w = 0.092$.

The procedures for **5**, **6**, and **7a** were similar to those for **3**. The final residuals of this refinement were $R = 0.050$ and $R_w = 0.117$ for **5**, $R = 0.054$ and $R_w = 0.119$ for **6**, and $R = 0.041$ and $R_w = 0.086$ for **7a**.

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Supporting Information Available: ORTEP diagrams and tables of crystal, data collection, and refinement parameters, atomic coordinates, bond distances and bond angles, and isotropic displacement parameters for complexes **3**, **5**, **6**, and **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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