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Article

Genuine Examples of Tetrahedral Tetradentate Sulfide Ligand Bridging Four Pd Atoms: Controlled Formation of $[(\mu_4\text{-S})\{(\mu_2\text{-X})Pd_2(C^\wedge N)_2\}_2]$ (X = OH or Cl; $HC^\wedge N$ = p-$C_2H_5OC_6H_4CH{=}NC_6H_4$-$p$-$C_2H_5$) Complexes

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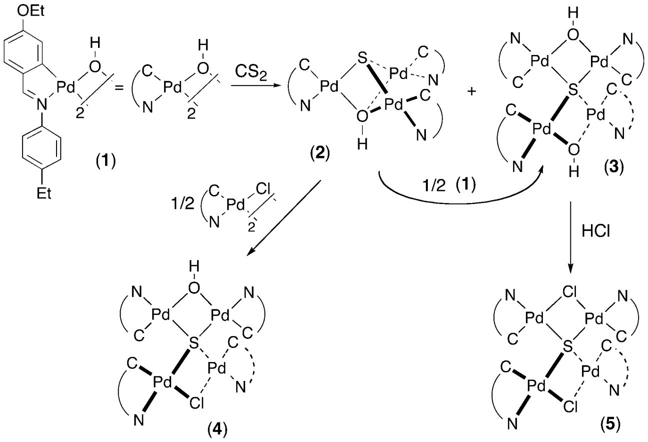
A smooth reaction of $[(\mu_3\text{-S})(\mu_3\text{-OH})Pd_3(C^\wedge N)_3]$ (**2**) with $[(\mu_2\text{-X})_2Pd_2(C^\wedge N)_2]$ (2:1; $HC^\wedge N$ = p-$C_2H_5OC_6H_4CH{=}NC_6H_4$-$p$-$C_2H_5$, X = OH, Cl) provides $[(\mu_4\text{-S})\{(\mu_2\text{-OH})Pd_2(C^\wedge N)_2\}_2]$ (**3**) and $[(\mu_4\text{-S})(\mu_2\text{-Cl})(\mu_2\text{-OH})Pd_4(C^\wedge N)_4]$ (**4**). Treatment of **3** with HCl (molar ratio 1:2) leads to the corresponding tetranuclear complex $[(\mu_4\text{-S})(\mu_2\text{-Cl})_2Pd_4(C^\wedge N)_4]$ (**5**). The three complexes contain a $(\mu_4\text{-S})Pd_4$ core. A density functional theory study of the bonds in **3** supports that the bonding of the S atom can be described in terms of four two-center two-electron S–Pd bonds, in contrast to most other $(\mu_4\text{-S})M_4$ systems in the literature, where the presence of M–M bonds prevents a bond-localized description of the molecule. The X-ray structures of **2**, **3**, and **5** are reported.

Introduction

The residual nucleophilicity of the bridging sulfido ligand in $[(\mu_2\text{-S})_2Pt_2(PR_3)_4]_2$ compounds has provided a significant number of homo- and heterometallic clusters and aggregates with (μ_3-S) bridging sulfide.[1] Sulfido-bridged trinuclear palladium complexes are much more scarce because of the absence of a suitable sulfido precursor. Nevertheless, there are a few examples of complexes with a $(\mu_3\text{-S})Pd_3$ core. These have been isolated from reactions with compounds with a $(\mu\text{-S})_2Pd_2$ core,[2] the reaction of a Pd–Cl complex with Na_2S[3] or $S(SiMe_3)_2$,[4] cleavage of a S–C bond on a thiocyanate complex,[5] thermolysis of a $Pd(S_2C_2O_2)$ complex,[6] or reactions of palladium complexes with SH_2, COS,[7] or NaSH.[8] The possibility of further exploiting the residual nucleophilicity of S in a $(\mu_3\text{-S})Pd_3$ system remains unexplored.

Scheme 1



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10.1021/ic061367t CCC: $37.00

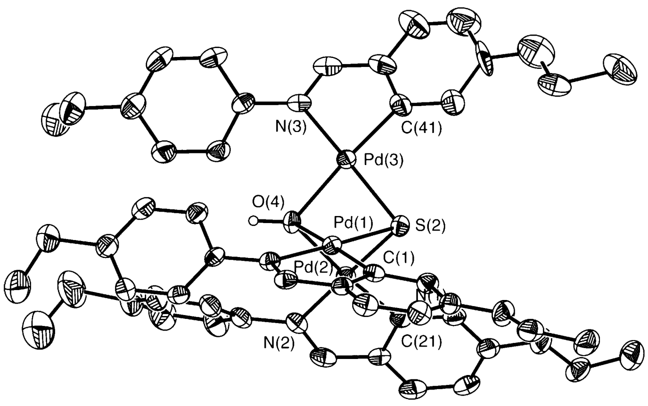

Figure 1. Molecular structure of **2** with thermal ellipsoids (30% probability).

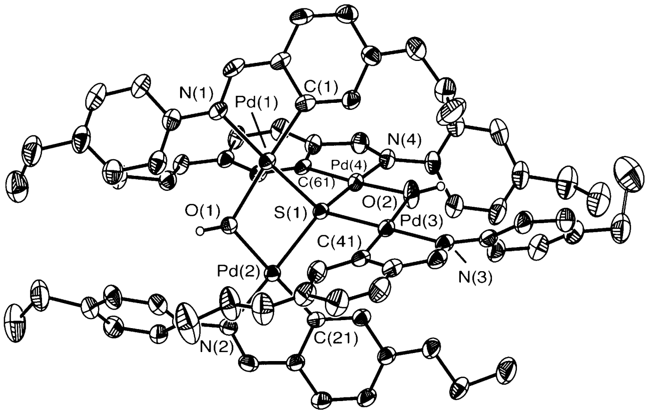

Figure 2. Molecular structure of **3** with thermal ellipsoids (30% probability).

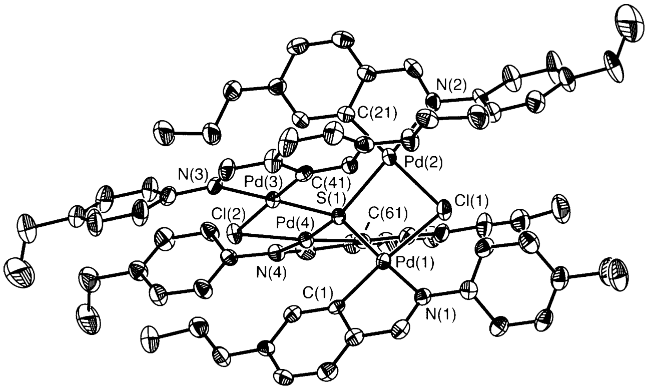

Figure 3. Molecular structure of **5** with thermal ellipsoids (30% probability).

Recently, we discovered a new synthetic route that affords trinuclear palladium orthometalated complexes $[(\mu_3\text{-S})(\mu_3\text{-OH})Pd_3(C^\wedge N)_3]$ ($HC^\wedge N = p\text{-}C_nH_{2n+1}OC_6H_4CH{=}NC_6H_4O\text{-}p\text{-}C_nH_{2n+1}$, $n = 2, 10$) by the reaction of $[(\mu\text{-OH})_2Pd_2(C^\wedge N)_2]$ with CS_2.[9] The complexes contain unprecedented $(\mu_3\text{-S})(\mu_3\text{-OH})$ bridges holding together the three metal atoms. These asymmetric bridges induce an all-cis arrangement of the three orthometalated ligands. Their structure could not be perfectly assessed by X-ray diffraction methods because of the poor quality of the crystals obtained, but a partial resolution confirmed the arrangement of the molecular core.

In the present study, we report the results arising from a change of the imine in the starting complex $[(\mu\text{-OH})_2Pd_2(C^\wedge N)_2]$ (to $HC^\wedge N = p\text{-}C_2H_5OC_6H_4CH{=}NC_6H_4\text{-}p\text{-}C_2H_5$) looking for better single crystals. This change not only afforded the synthesis of a new trinuclear palladium orthometalated complex with asymmetrical bridges, $(\mu_3\text{-S})(\mu_3\text{-OH})$, for which the crystal structure could be solved, but also provided the controlled formation of unprecedented $(\mu_4\text{-S})Pd_4$ complexes, also supported by a crystal structure.

Results and Discussion

Synthesis and Characterization. The reaction of $[(\mu\text{-OH})_2Pd_2(C^\wedge N)_2]$ (**1**) with the $HC^\wedge N$ in CH_2Cl_2, with 3 mol equiv of carbon disulfide at room temperature for 2 h, produced a mixture of two complexes (Scheme 1; molar ratio **2**:**3** = 48:52), which could be characterized in the ^1H NMR spectrum of the mixture in $CDCl_3$. The trinuclear complex $[(\mu_3\text{-S})(\mu_3\text{-OH})Pd_3(C^\wedge N)_3]$ (**2**) displays a set of ^1H NMR resonances for the orthopalladated imine and a singlet at −2.55 ppm, with the intensity corresponding to one μ_3-OH group for three imines. The other compound, $[(\mu_4\text{-S})\{(\mu_2\text{-OH})Pd_2(C^\wedge N)_2\}_2]$ (**3**), shows just one set of ^1H NMR resonances, proving the chemical equivalence of the four orthopalladated imine ligands. Worth noting are the doublet observed for H^3 at very low field (9.28 ppm) and a singlet at −3.82 ppm, with intensity OH:imine = 1:2. This is consistent with a tetranuclear palladium compound made of two $(C^\wedge N)Pd(\mu_2\text{-OH})Pd(C^\wedge N)$ moieties linked by one μ_4-bridging sulfide. A trans arrangement of the sulfide and the iminic N atoms is expected in the thermodynamically preferred isomer.[10]

Complexes **2** and **3** could be separated by recrystallization from CH_2Cl_2/toluene. Their analytical and spectroscopic data (see the Experimental Section) were consistent with the formulation given in Scheme 1. Both structures were unambiguously confirmed by single-crystal X-ray diffraction analyses (see below).[11]

In order to obtain information on the possible pathways of the generation of the tetrametallic compound **3**, the reaction of **1** with a large excess of CS_2 (Pd:CS_2 = 1:30) was studied. This resulted in the formation of **2** as the main product (molar ratio **2**:**3** = 91:9) after 25 min of reaction. On the other hand, when the proportion of CS_2 was reduced to Pd:CS_2 = 1:0.5, complex **1** gave, after 24 h, a mixture where the tetrapalladium complex was the major product (molar ratio **2**:**3** = 20:80). These results suggest a reaction pathway where **2** is generated initially. Then, its reaction with still unreacted **1** affords **3**, in a rearrangement where the lone pair of the sulfido in **2** would act as a nucleophile to split the OH bridges in **1**. In effect, the reaction of **2** with **1** in dichloromethane (molar ratio 1:0.5) for 6 h at room

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compound **2**

S(2)−Pd(1)	2.3029(17)	Pd(1)−S(2)−Pd(2)	79.40(5)
S(2)−Pd(2)	2.3037(16)	Pd(1)−S(2)−Pd(3)	86.05(5)
S(2)−Pd(3)	2.2941(16)	Pd(2)−S(2)−Pd(3)	81.18(5)
O(4)−Pd(1)	2.139(3)	Pd(1)−O(4)−Pd(2)	86.02(13)
O(4)−Pd(2)	2.175(4)	Pd(1)−O(4) −Pd(3)	94.30(14)
O(4)−Pd(3)	2.139(4)	Pd(2)−O(4)−Pd(3)	87.82(14)
Pd(1)−Pd(2)	2.943(2)		
Pd(2)−Pd(3)	2.992(2)		
Pd(1)−Pd(3)	3.137(2)		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound **3**[a]

S(1)−Pd(1)	2.2889(14)	Pd(1)−S(1)−Pd(2)	93.93(5)
S(1)−Pd(2)	2.2881(14)	Pd(1)−S(1)−Pd(3)	123.35(6)
S(1)−Pd(3)	2.2946(14)	Pd(1)−S(1)−Pd(4)	115.54(6)
S(1)−Pd(4)	2.2915(16)	Pd(2)−S(1)−Pd(3)	119.55(6)
O(1)−Pd(1)	2.119(3)	Pd(2)−S(1)−Pd(4)	112.59(6)
O(1)−Pd(2)	2.117(4)	Pd(4)−S(1)−Pd(3)	93.34(5)
O(2)−Pd(3)	2.103(5)	Pd(2)−O(1)−Pd(1)	104.33(16)
O(2)−Pd(4)	2.098(4)	Pd(4)−O(2)−Pd(3)	105.16(18)
Pd(1)−Pd(2)	3.346(3)		
Pd(3)−Pd(4)	3.336(2)		

[a] For the sake of comparison, the distance Pd···Pd in the optimized structure is 3.424 Å and those in [(μ_4-S){(μ_2-η^3-C_3H_5)$Pd_2(PH_3)_2$}$_2$] are 2.668 and 2.669 Å.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound **5**

S(1)−Pd(1)	2.3189(19)	Pd(1)−S(1)−Pd(2)	98.17(7)
S(1)−Pd(2)	2.3196(19)	Pd(1)−S(1)−Pd(3)	107.67(7)
S(1)−Pd(3)	2.3067(19)	Pd(1)−S(1)−Pd(4)	125.13(9)
S(1)−Pd(4)	2.3092(18)	Pd(2)−S(1)−Pd(3)	116.35(8)
Cl(1)−Pd(1)	2.434(2)	Pd(2)−S(1)−Pd(4)	112.24(8)
Cl(1)−Pd(2)	2.466(2)	Pd(3)−S(1)−Pd(4)	98.37(7)
Cl(2)−Pd(3)	2.459(2)	Pd(1)−Cl(1)−Pd(2)	91.33(6)
Cl(2)−Pd(4)	2.432(2)	Pd(3)−Cl(2)−Pd(4)	91.17(6)
Pd(1)−Pd(2)	3.505(2)		
Pd(3)−Pd(4)	3.494(2)		

temperature does afford cleanly the tetranuclear complex **3**. Moreover, **2** also reacts with [Pd(C^N)(μ-Cl)]$_2$ (molar ratio 1:0.5), affording [{Pd_2(C^N)$_2$(μ_2-OH)}{Pd_2(C^N)$_2$(μ_2-Cl)}$_2$-(μ_4-S)] (**4**). The ^{1}H NMR spectrum of **4** showed the expected two sets of ^{1}H NMR resonances for the two nonequivalent types of orthometalated imine and a singlet at −3.63 ppm (with intensity 1 for four imines) due to the presence of the μ-OH group.

Treatment of **3** with HCl (molar ratio 1:2) led to the displacement of the two bridging hydroxo ligands by chloro, giving the corresponding tetranuclear complex [(μ_4-S)(μ_2-Cl)$_2$$Pd_4(C^N)_4$] (**5**). Its ^{1}H NMR spectrum shows just one set of ^{1}H NMR signals for the orthopalladated imine ligand, proving the chemical equivalence of the imine ligands and the isomeric purity of the complex. The expected ligand arrangement with the sulfide trans to the iminic N atoms, as found for **3**, was unambiguously confirmed for **5** by single-crystal X-ray diffraction.

Crystal Structures. Detailed crystallographic data are summarized in Table 4. ORTEP drawings of the molecules **2**, **3**, and **5** are shown in Figures 1−3, respectively, and selected bond distances and angles are listed in Tables 1−3.

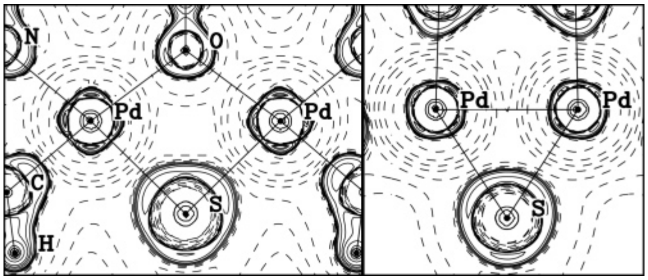
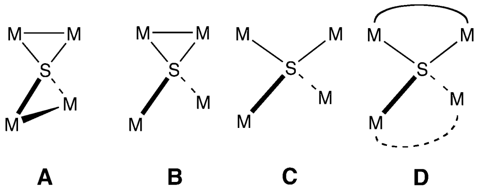


Figure 4. Partial representation of the Laplacian function for the modeled compound **3** (left) and [Pd_4(μ-S)(η^3-allyl)$_2$(PH_3)$_4$] (right) in a plane of Pd_2S. Complete graphics of the Laplacian function and the electron densities are available as the Supporting Information.

Chart 1



The molecule of **2** consists of three Pd(C^N) moieties linked by one μ_3-sulfide and one μ_3-hydroxo ligand. The cyclometalated C is coordinated trans to the O atoms of the bridging hydroxo groups, and a cis arrangement of the three imine moieties is found. The three Pd atoms describe an isosceles triangle with distances that do not suggest significant intermetallic interaction [2.943(1)−3.137(1) Å]. The distortion observed from the ideal equilateral to an isosceles triangle might originate from a second-order Jahn−Teller effect[12] or more probably from packing effects.[2e]

The X-ray structures of **3** and **5** confirm that these molecules contain four Pd(C^N) moieties connected by two μ_2-hydroxo bridging ligands (in compound **3**) or two μ_2-chloro bridging ligands (in compound **5**) and by a central μ_4-sulfide. The two Pd(C^N) moieties linked by a μ_2 ligand are coplanar. The two planes, each containing two Pd(C^N) moieties, are arranged perfectly perpendicular to each other in compound **3** [the angle between these two planes is 89.7-(5)°], but they form an angle of 81.9(5)° in compound **5**. The coordination of the central μ_4-sulfide is distorted tetrahedral. The angles Pd−S−Pd are 93.64° on average for Pd atoms linked additionally by the μ_2-hydroxo group in compound **3** and 98.27° on average when they are linked by the μ_2-chloro ligand in compound **5**. The angles Pd−S−Pd range from 112.59° to 123.35° when they are not bridged by OH in compound **3** and from 107.67° to 125.13° when they are not bridged by Cl in compound **5**.

Density Functional Theory (DFT) Studies. Distorted tetrahedral coordination of sulfides is not uncommon. It is found in the infinite structure of PdS.[13] It can be found also in many sulfide-containing molecular clusters of a variety of metals. However, a closer look at all of the X-ray structures available with the help of a search in the Cambridge Crystallographic Database reveals that, with very few exceptions, these sulfides are always connecting two metals bonded by a metal−metal bond, which leads to an acute M−S−M angle and distorts the ideal tetrahedron. For

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Table 4. Crystal and Structure Refinement Data for **2**, **3**, and **5**

	2	**3**	**5**
empirical formula	$C_{102}H_{110}N_6O_8Pd_6S_2$	$C_{68}H_{64}N_4O_6Pd_4S$	$C_{68}H_{72}Cl_2N_4O_4Pd_4S$
fw	2250.48	1490.89	1537.86
T (K)	298(2)	298(2)	298(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$
a (Å)	9.123(4)	10.4576(17)	18.395(4)
b (Å)	15.099(6)	13.229(2)	16.080(3)
c (Å)	18.519(7)	23.965(4)	22.437(5)
α (deg)	69.010(9)	85.723(3)	90
β (deg)	86.773(9)	81.829(4)	104.752(5)
γ (deg)	76.679(9)	72.474(4)	90
V (Å^3)	2316.5(16)	3127.7(9)	6418(2)
Z	1	2	4
D_{calc} (g cm^{-3})	1.613	1.583	1.592
abs coeff (mm^{-1})	1.245	1.219	1.269
F(000)	1136	1496	3096
cryst size (mm)	0.22 × 0.11 × 0.03	0.14 × 0.14 × 0.05	0.13 × 0.08 × 0.03
θ range for data collection (deg)	1.18−23.38	0.86−23.26	1.14−23.29
reflns collcd	10936	14871	30661
indep reflns	6675	8952	9214
abs correction	SADABS	SADABS	SADABS
max, min transmn factor	1.000000, 0.779657	1.000000, 0.851928	1.000000, 0.843978
data/restraints/param	6675/0/568	8952/1/774	9214/28/825
GOF on F^2	1.002	1.025	1.003
R1 [$I > 2\sigma(I)$]	0.0348	0.0368	0.0382
wR2 (all data)	0.1012	0.0982	0.1294

instance, bis(μ-η^3-allyl)-μ_4-sulfidotetrakis(triphenylphosphine)-tetrapalladium (two Pd−Pd), corresponding to the structural type **A** in Chart 1, shows two short Pd−Pd interactions at 2.625 and 2.639 Å associated with two acute Pd−S−Pd angles, 68.2° and 68.5°. The other four angles defining the distorted tetrahedron around the S atom are 144.0°, 140.47°, 123.5°, and 119.01°.[14] The degree of distortion can be estimated by the S_T parameter.[15] The only molecular compound containing a sulfide ligand fairly close to a tetrahedral arrangement yet involving a M−M bond is $[S(AuPPh_3)_2\{Au(C_6F_5)_3\}_2]$. In spite of the fact that this gold compound corresponds to the structural type **B**, in Chart 1, the Au−Au bond is very long (3.224 Å), which makes it compatible with an Au−S−Au bond angle of 87.75° in front of the Au−Au bond (the values for the other five angles around S are 104.84°, 108.14°, 115.70°, 116.50°, and 119.67°).[16] The angle between the two Au−S−Au planes (with and without the Au−Au bond) is 82.48°, but still all of these distortions lead to a very high degree of tetrahedricity ($S_T = 1.63$). Only two compounds were found that, exceptionally, contain tetrahedrally coordinated sulfide connected to four metal atoms not involved in M−M bonds. These are $[Cr_4S(O_2CCH_3)_8(H_2O)_4](BF_4)_2{\cdot}H_2O$ (obtained in 20% yield; $S_T = 0.18$)[17] and $[Fe(DMF)Cl(Cl_4\text{-cat})_2Mo_2Fe_2S_4(PEt_3)_2ClFe_4S_4(PEt_3)_3(CO)_6Cl]$ (obtained in 0.9% yield; $S_T = 0.94$),[18] for which the metal coordination environment and the oxidation state of the metal prevent M−M interaction (Chart 1, **C**).

The bonding in compounds of type **A** and **B** cannot be described in a simple way as containing a sp^3-hybridized sulfide involved in four two-center S−M bonds. Only type **C** (or **D** in our case if other bridging ligands are represented) can be described that way. A closer view of the electronic structure of compounds **3** (type **D**) and $[(\mu_4\text{-S})\{(\mu_2\text{-}\eta^3\text{-}C_3H_5)Pd_2(PPh_3)_2\}_2]$ (type **A**) was achieved using DFT calculations with appropriate models, including a topological analysis of the electron density for their optimized geometries,[19] together with an analysis of Continuous Symmetry Measures of tetrahedral shape, S_T (more details in the Supporting Information).

The coordination of the S atom in **3** is tetrahedral, having a low distortion from the ideal shape by only $S_T = 2.3$. Its Laplacian function (Figure 4) shows clearly that the four-membered ring S−Pd−O−Pd has bond critical points between the Pd and S atoms and between the Pd and O atoms, indicative of the presence of a chemical bond, with electron densities $r = 0.080$ and 0.073 for the Pd−S and Pd−O bonds, respectively. These four maxima are situated at 1.23 Å from S and are very near a tetrahedral disposition ($S_T = 2.2$). Consequently, the bonding in this compound can be adequately described in terms of a sp^3-hybridized sulfide giving rise to four M−S localized bonds, as illustrated in Figure 5.

In contrast, compound $[(\mu_4\text{-S})\{(\mu_2\text{-}\eta^3\text{-}C_3H_5)Pd_2(PH_3)_2\}_2]$ with two Pd−Pd bonds shows an important loss of tetrahe-

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(15) The Continuous Symmetry Measures provide quantitative information of how much the environment deviates from an ideal polyhedron. A zero value of S_T would indicate a perfect match to the ideal tetrahedron; larger values reflect increasing deviations from the ideal tetrahedral shape. Thus, a distortion of a tetrahedron to reach a square plane corresponds to $S_T = 33.3$. Cirera, J.; Alemany, P.; Alvarez, S. *Chem.—Eur. J.* **2004**, *10*, 190.

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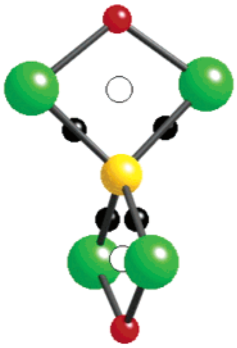

Figure 5. Localization of the critical points around a bridging sulfido ligand. The bond critical points are represented by black circles and the ring critical points by white circles.

dricity around the sulfido bridge ($S_T = 13.5$). The electronic structure is further characterized by bond critical points, corresponding to the presence of Pd−Pd interactions in addition to Pd−S ones ($r = 0.047$ and 0.069, respectively). At variance with complex **3**, the two maxima in each Pd_2S plane overlap. Consequently, the bonds in $[(\mu_4\text{-S})\{(\mu_2\text{-}\eta^3\text{-}C_3H_5)Pd_2(PH_3)_2\}_2]$ surround a ring critical point at the center of the Pd−S−Pd triangle, $r = 0.040$ (compared to $r = 0.020$ for **3**), and are far from a sp^3 hybridization for the sulfide or from a localized two-center bond conception of the molecule.

Conclusion

In summary, although structures containing S surrounded by four M atoms are not uncommon, **3**−**5** are rare examples of metal sulfides with nondistorted tetrahedral coordination of S, the first of its kind in palladium chemistry. Their existence seems to be helped by the ligands sterically preventing the metals from getting close enough to make M−M interactions. The sulfide uses its four electron pairs in an apparently simple coordination to four Pd acidic centers. Thus, compounds **3**−**5** are genuine examples of sulfide acting as a simple tetradentate ligand to four transition metals.

Experimental Section

General Procedures. Literature methods were used to prepare $[(\mu_2\text{-OH})_2Pd_2L_2]$ (**1**).[20] C, H, N, and S analyses were carried out on a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded on a Perkin-Elmer FT-1720X spectrometer using Nujol mulls between polyethylene plates. ^{1}H NMR spectra were recorded on a Bruker AC-300 or ARX-300 MHz spectrophotometer.

Reaction of 1 with CS_2. To a suspension of **1** (0.500 g, 0.665 mmol) in dichloromethane (60 mL) was added carbon disulfide (0.120 mL, 2.00 mmol). The mixture was stirred for 2 h at room temperature. The solvent was evaporated off, and the yellow-orange residue, consisting of a mixture of **2** and **3**, was washed with acetone (3 × 5 mL), collected on a frit, and dried in a vacuum. Yield: 0.35 g. The two compounds could be separated by fractional crystallization from CH_2Cl_2/toluene (1:1). In this mixture, **2** is practically insoluble upon cooling to −20 °C, and **3** is very soluble.

$[(\mu_3\text{-S})(\mu_3\text{-OH})Pd_3(C\text{^}N)_3]$ (2). Anal. Calcd for $C_{51}H_{55}N_3O_4Pd_3S$: C, 54.43; H, 4.93; N, 3.73; S, 2.85. Found: C, 54.59; H, 4.76; N, 3.75; S, 3.08. ^{1}H NMR (300 MHz, $CDCl_3$): 7.95 (s, 3H), 7.60 (d, $J = 2.1$ Hz, 3H), 7.23 (d, $J = 8.1$ Hz, 3H), 6.83, 6.72 (AA′BB′ system, $J = 8.2$ Hz, 12H), 6.44 (dd, $J = 8.4$ and 2.1 Hz, 3H), 4.15 (q, $J = 6.9$ Hz, 6H), 2.64 (q, $J = 7.5$ Hz, 6H), 1.46 (t, $J = 7.5$ Hz, 9H), 1.26 (t, $J = 7.5$ Hz, 9H) −2.40 (s, 1H). IR (Nujol, cm^{-1}): ν(O−H) 3622w.

$[(\mu_4\text{-S})\{(\mu_2\text{-OH})Pd_2(C\text{^}N)_2\}_2]$ (3). Anal. Calcd for $C_{68}H_{74}N_4O_6Pd_4S$: C, 54,41; H, 4.97; N, 3.73; S, 2.14. Found: C, 54.16; H, 4.84; N, 3.85; S, 2.51. ^{1}H NMR (300 MHz, $CDCl_3$): 9.28 (d, $J = 2.2$ Hz, 4H), 7.85 (s, 4H), 7.11 (s, AA′BB′ system, 16H), 7.09 (d, $J = 8.2$ Hz, 4H), 6.45 (dd, $J = 8.2$ and 2.2 Hz, 4H), 4.17 (q, $J = 6.9$ Hz, 8H), 2.69 (q, $J = 7.1$ Hz, 8H), 1.28 (t, $J = 7.5$ Hz, 12H), 0.97 (t, $J = 7.0$ Hz, 12H), −3.82 (s, 2H).

$[(\mu_4\text{-S})\{(\mu_4\text{-OH})Pd_2(C\text{^}N)_2\}_2]$ (3). To a solution of **2** (0.050 g, 0.044 mmol) in dichloromethane (25 mL) was added $[(\mu_2\text{-OH})_2Pd_2(C\text{^}N)_2)]$ (0.016 g, 0.022 mmol). The mixture was stirred for 6 h at room temperature. The solvent was evaporated off, and the yellow-orange residue was washed with diethyl ether (2 × 5 mL), collected on a frit, and dried in a vacuum. Yield: 0.045 g.

$[(\mu_4\text{-S})(\mu_2\text{-Cl})(\mu_2\text{-OH})Pd_4(C\text{^}N)_4]$ (4). To a solution of **2** (0.050 g, 0.044 mmol) in dichloromethane (25 mL) was added $[(\mu_2\text{-Cl})_2Pd_2(C\text{^}N)_2)]$ (0.0018 g, 0.023 mmol). The mixture was stirred for 6 h at room temperature. The solvent was evaporated off, and the yellow-orange residue was washed with diethyl ether (2 × 5 mL), collected on a frit, and dried in a vacuum. Yield: 0.050 g. Anal. Calcd for $C_{68}H_{73}ClN_4O_5Pd_4S$: C, 53,75; H, 4.84; N, 3.69. Found: C, 53.50; H, 4.47; N, 3.55. ^{1}H NMR (300 MHz, $CDCl_3$): 9.54 (d, $J = 2.3$ Hz, 2H), 8.93 (d, $J = 2.3$ Hz, 2H), 7.83 (s, 2H), 7.80 (s, 2H), 7.13 (br, AA′BB′ system, 8H), 7.05 (m, 12H), 6.50 (m, 4H), 4.19 (q, $J = 7.0$ Hz, 4H), 4.04 (q, $J = 7.0$ Hz, 4H), 2.69 (m, 8H), 1.29 (t, $J = 7.6$ Hz, 6H), 1.24 (t, $J = 7.6$ Hz, 6H), 1.10 (t, $J = 7.0$ Hz, 6H), 0.95 (t, $J = 7.0$ Hz, 6H), −3.63 (s, 1H).

$[(\mu_4\text{-S})(\mu_2\text{-Cl})_2Pd_4(C\text{^}N)_4]$ (5). To a solution of **3** (0.05 g, 0.033 mmol) in dichloromethane (10 mL) was added 65 μL of HCl (1 M in diethyl ether). The mixture was stirred for 1 h at room temperature. The solvent was evaporated off, and the residue was crystallized from dichloromethane/diethyl ether. Yield: 0.037 g. Anal. Calcd for $C_{68}H_{72}Cl_2N_4O_4Pd_4S$: C, 53,11; H, 4.72; N, 3.64. Found: C, 52.85; H, 4.56; N, 3.58. ^{1}H NMR (300 MHz, $CDCl_3$): 9.05 (d, $J = 2.3$ Hz, 1H), 7.77 (s, 1H), 6.54 (dd, $J = 2.12$ and 6.1 Hz, 1H), 7.11 (d, $J = 6.4$ Hz, 1H), 7.05, 6.96 (AA′BB′ system, $J = 8.2$ Hz, 4H), 4.09 (q, $J = 6.7$ Hz, 2H), 1.22 (t, $J = 7.8$ Hz, 3H), 2.65 (q, $J = 7.3$ Hz, 2H), 1.07 (t, $J = 6.9$ Hz, 3H). IR (Nujol, cm^{-1}): ν (Pd−Cl) 269w.

X-ray Structures. Crystal and structure refinement data for **2**, **3**, and **5** are collected in Table 4. Data in common: Bruker AXS SMART 1000 CCD diffractometer, ϕ and ω scans, Mo Kα radiation ($\lambda = 0.71073$ Å), graphite monochromator, $T = 295$ K. Raw frame data were integrated with the *SAINT*[21] program. Structures were solved by direct methods with *SHELXTL*.[22] Semiempirical absorption correction was done with *SADABS*.[23] All non-H atoms were refined anisotropically. H atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All calculations were made with *SHELXTL*.

Refinement of the structure of compound **2** proceeded smoothly to give R1 = 0.0348 based on the reflections with $I > 2\sigma(I)$. The ORTEP diagram is represented in Figure 1, and selected distances and angles are collected in Table 1.

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Disorder of two ethyl groups was modeled in the refinement of **3**. An occupancy of 74% was found for C15A and an occupancy of 46% for C57A. H atoms of the disordered parts of **3** (C14, C15A, C15B, C56, C57A, and C57B) were not included in the calculations. A fixed distance of 1.5 Å between C14 and C15B was included as a restraint and the refinement converged to give R1 = 0.0368. The ORTEP diagram is represented in Figure 2, and selected distances and angles are collected in Table 2.

The 4-ethylphenyl group attached to N(2) in compound **5** is disordered and has been modeled with an occupancy of 78% for part A. Part B refinement has been restrained with an instruction SAME (with part A as the reference) and with SIMU and DELU instructions to avoid nonpositive definites. The refinement converged to give R1 = 0.0382. The ORTEP diagram is represented in Figure 3, and selected distances and angles are collected in Table 3.

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Supporting Information Available: X-ray crystallographic data in CIF format and complete graphics of the Laplacian functions and the electron densities for the modeled compounds. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary publications with the following deposition numbers: CCDC 256155, 256156, and 624863 for complexes **2**, **3**, and **5**, respectively. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax (int.) +44-1223/336-033; e-mail deposit@ccdc.cam.ac.uk].

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