Inorganica Chimica Acta, *174* (1990) 209–215

Isolation of Palladium(II) Quinoline-2-thione (HqnS) and Quinoline-2-thiolate (qnS) Complexes: Crystal Structures of $Pd(HqnS)(PMe_3)Cl_2$, $[Pd(HqnS)_2(PMe_3)Cl][Cl]$ and *vic*-$Pd_2(\mu,N\text{-}S\eta^2\text{-}qnS)_2(\eta^1\text{-}qnS)_2(PMe_3)_2$

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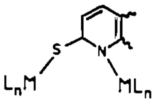
(Received February 14, 1990)

Abstract

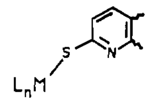
Reaction of 2-quinolinethione, HqnS, with $[PdCl(PR_3)\mu\text{-}Cl]_2$ (**1**) in acetone solution produces $Pd(HqnS)(PMe_3)Cl_2$ (**2**) or under more forcing conditions, $[Pd(HqnS)_2(PMe_3)Cl][Cl]$ (**3**). Reaction of **1** with the conjugate anion, quinoline-2-thiolate, qnS, in ethanol gives rise to the unusual N-heterocycle-2-thiolate bridged dipalladium complex, *vic*-$Pd_2(\mu,N\text{-}S\eta^2\text{-}qnS)_2(\eta^1\text{-}qnS)_2(PMe_3)_2$ (**4**). The crystal and molecular structures of **2**, $\mathbf{3}\cdot CH_2Cl_2$ and **4** have been determined. Crystallographic data for **2**: monoclinic $P2_1/n$, $Z = 4$; $a = 11.027(4)$, $b = 11.230(6)$, $c = 12.676(6)$ Å; $\beta = 92.32(3)°$; $V = 1568.4(1)$ Å^3, $\rho_{calc} = 1.756$ g/cm^3. Crystallographic data for **3**: triclinic $P\bar{1}$, $Z = 2$; $a = 8.902(3)$, $b = 12.858(4)$, $c = 13.303(6)$ Å; $\alpha = 89.28(3)$, $\beta = 71.24(3)$, $\gamma = 72.54(2)°$; $V = 1369.4(8)$ Å^3, $\rho_{calc} = 1.597$ g/cm^3. Crystallogrphic data for **4**: monoclinic $P2_1/n$, $Z = 4$ $a = 8.902(3)$, $b = 12.858(4)$, $c = 13.303(6)$ Å; $\beta = 107.25(3)°$; $V = 4216(3)$ Å^3, $\rho_{calc} = 1.585$ g/cm^3.

Introduction

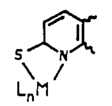
The major product of the reaction of thiols with $[PdCl(PR_3)\mu\text{-}Cl]_2$ is generally [1] a dipalladium mono(μ-thiolate) complex. By contrast, we have found quinoline-2-thiol preferentially reacts with $[PdCl(PMe_3)\mu\text{-}Cl]_2$ (**1**) as the tautomeric 1H-quinoline-2-thione, HqnS, to produce S-coordinated η^1-HqnS complexes; either $Pd(HqnS)(PMe_3)Cl_2$ (**2**) or under more forcing conditions, $[Pd(HqnS)_2(PMe_3)Cl][Cl]$ (**3**). This reactivity parallels the dominant coordination chemistry of pyridine-2-thiol [2–4]. Reaction of **1** with four equivalents of the conjugate anion, quinoline-2-thiolate (qnS), gives rise to a dipalladium complex, *vic*-$Pd_2(\mu,N\text{-}S\eta^2\text{-}qnS)_2(\eta^1\text{-}qnS)_2(PMe_3)_2$ (**4**). The μ,η^2 coordination (as in **A**) of heterocycle-2-thiolate liquands in this complex is rare [3, 5–8] as these anions generally [4, 9–15] coordinate either η^1 through S as in **B** or η^2 in a terminal η^2 chelating mode as in **C** which is believed [3] to be less strained than the bridging mode, **A**. We wish to report the syntheses and the results of the first X-ray structural determinations of HqnS and qnS complexes.



A



B



C

Experimental

General Details

The following were purchased from Aldrich Chemical Co. and used without further purification: 2-quinolinethiol, acetone (reagent-grade), dichloromethane-d_2 and dichloromethane (reagent-grade). The complex, $[PdCl(PMe_3)\mu\text{-}Cl]_2$ was prepared by a method analogous to the synthesis of $[PdCl(PEt_3)\mu\text{-}Cl]_2$ by Chatt and Venanzi [16].

The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Nicolet NT300 spectrometer at 300 and 122 MHz, respectively. The ^1H NMR data are listed in ppm downfield from TMS at 0.00 ppm. ^{31}P NMR chemical shifts were measured relative to the deuterium resonance of the solvent by using the internal frequency lock of the spectrometer so that the resonance from a capillary of 85% H_3PO_4, centered in 5 mm NMR tube containing the deuterated solvent, appeared at 0.0 ppm at 20 °C. Microanalyses were performed by Oneida Research Services Inc. (Whitesboro, NY).

Preparation of $Pd(HqnS)(PMe_3)Cl_2$ *(2)*

A solution of $[PdCl(PMe_3)\mu\text{-}Cl]_2$ (2.000 g, 3.95 mmol) in acetone (150 ml) is treated with 2-quinolinethiol (2.547 g, 15.80 mmol). The initially orange solution becomes green–yellow within 15 min and is stirred at room temperature for 24 h. The resulting green–yellow solid is isolated by filtration from the reaction mixture. Purified product

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(2.701 g, 82.5% yield) is obtained as a microcrystalline solid following recrystallization from dichloromethane. ^{1}H NMR (CD_2Cl_2): δ 15.24 (br s, 2H N*H*); 7.96(m), 7.80(m), 7.55(m) (6H, aromatic); 1.64 (d, J_{P-H} = 12 Hz, P(C*H*$_3$)$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 3.8(s). *Anal.* Calc.: C, 34.76; H, 3.86; N, 3.38. Found: C, 34.60; H, 3.81; N, 3.22%.

Preparation of [Pd(HqnS)$_2$(PMe$_3$)Cl] [Cl] (3)

A solution of [PdCl(PMe$_3$)μ-Cl]$_2$ (1.317 g, 2.60 mmol) in acetone (150 ml) is treated with 2-quinolinethiol (1.653 g, 10.03 mmol) and refluxed for 2 h; the initially orange solution changes color to red–orange. Upon cooling to room temperature, the resulting orange product is isolated from the reaction mixture by filtration. Purified product (1.841 g, 93.5% yield) is obtained as a microcrystalline solid following recrystallization from dichloromethane. ^{1}H NMR (CD_2Cl_2): δ 15.25 (br s, 2H N*H*); 8.70(m), 7.90(m), 7.79(m), 7.52(m) (12H aromatic); 1.75 (d J_{P-H} = 12 Hz, 18H, P(C*H*$_3$)$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 1.8 (s). *Anal.* Calc.: C, 43.80; H, 4.00; N, 4.87. Found: C, 43.86; H, 3.82; N, 4.81%.

Preparation of Pd(μ,N-Sη^2-qnS)$_2$(η^1-qnS)$_2$(PMe$_3$)$_2$ (4)

An ethanolic solution of sodium ethoxide under nitrogen (prepared by dissolving 0.051 g, 2.21 mmol of Na in 25 ml of absolute ethanol) is treated with 2-quinolinethiol (0.334 g, 2.07 mmol). Under nitrogen purge, [PdCl(PMe$_3$)μ-Cl]$_2$ (0.250 g, 0.49 mmol) is added to the clear, red solution arising upon completion of the heterocycle deprotonation and the resulting suspension is allowed to stir overnight. The resulting orange product is isolated by filtration from the reaction mixture. Purified product (0.475 g, 95.7% yield) is obtained as a microcrystalline solid following recrystallization from dichloromethane. ^{1}H NMR (CD_2Cl_2): δ 8.28(m), 7.73(m), 7.60(m), 7.52(m), 7.30(m) (24H, aromatic) 1.58 (d, J_{P-H} = 12 Hz, P(C*H*$_3$)$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −0.9 (s).

Crystallographic Studies

Crystals suitable for X-ray diffraction were obtained by slow evaporation of dichloromethane solutions of the respective compounds. The crystals were mounted on glass fibers with epoxy and centered on a Nicolet P3 automated diffractometer. The unit-cell parameters were obtained by least-square refinement of the setting angles of 20 reflections. Crystal and instrument stability were monitored with a set of three standard reflections measured every 97 reflections; in all cases no significant variations were found. Details of other crystal data and relevant information are summarized in Table 1.

TABLE 1. Summary of crystal data

	2	3·CH_2Cl_2	4
Formula	$PdC_{12}H_{16}Cl_2PSN$	$PdC_{22}H_{25}PS_2Cl_4N_2$	$Pd_2C_{42}H_{42}P_2S_4N_4$
Formula weight	414.6	660.8	1005.8
Crystal dimensions (mm)	0.2 × 0.2 × 0.6	0.1 × 0.1 × 0.4	0.1 × 0.1 × 0.1
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a (Å)	11.027(4)	8.902(3)	12.837(5)
b (Å)	11.230(6)	12.858(4)	17.136(7)
c (Å)	12.676(6)	13.303(6)	20.069(9)
α (°)	90	89.28(3)	90
β (°)	92.32(3)	71.24(3)	107.25(3)
γ (°)	90	72.54(2)	90
V (Å^3)	1568(1)	1369.4(8)	4216(3)
Z	4	2	4
ρ_{calc} (g/cm^3)	1.756	1.597	1.585
λ (Å) (Mo Kα radiation)	0.71073	0.71073	0.71073
T (K)	295	296	297
Scan type	$2\theta-\theta$	$2\theta-\theta$	ω
Scan rate (°/min)	1.5–15	1.5–15	1.5–15
2θ range (°)	4.0–55.0	4–55.0	4–40.0
μ (cm^{-1})	17.24	12.54	11.42
Transmission coefficient	0.4735–0.5412	0.6278–0.6831	0.734–0.870
Extinction correction	0.00066(9)	0.00023(3)	N/A
Reflections collected	4280	5327	4561
Unique data with $I > 3\sigma(I)$	3218	3980	2304
R^a	2.53	2.84	4.46
$R_w{}^b$	2.81	3.04	4.68
Goodness of fit^c	1.73	2.68	1.22

[a] $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [b] $R_w = [w\Sigma(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [c] $GOF = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$.

The structures were solved by direct methods using SHELX PLUS computer programs (Nicolet Instrument Corp.) and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic temperature coefficients. The positions of all hydrogen atoms in 2 and 3 were clearly visible in difference Fourier maps phased on the non-hydrogen atoms, and the coordinates and isotropic thermal parameters for hydrogens were varied in the final cycles of refinement. In the case of 4, the hydrogen atoms were introduced in fixed calculated positions and the full-matrix least-squares refinement of the non-hydrogen atoms was completed.

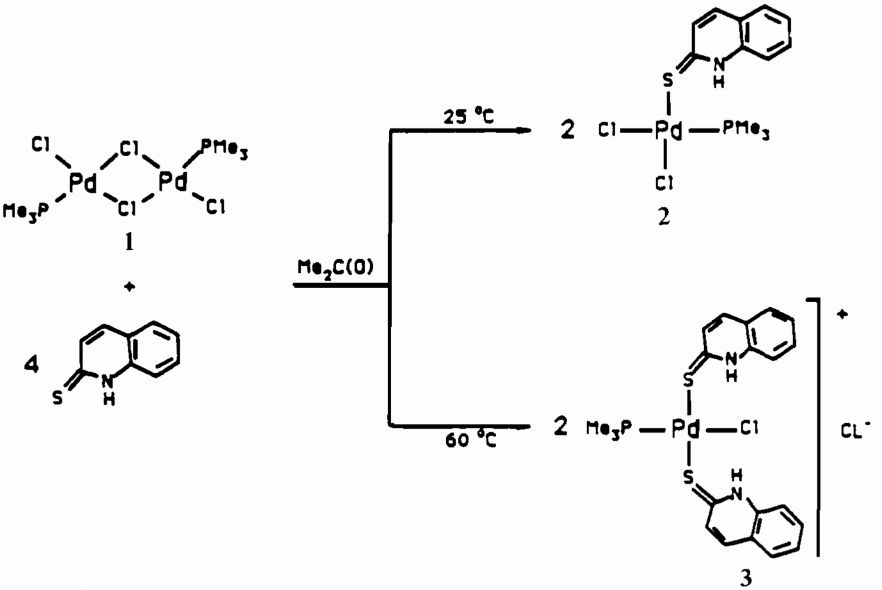
During the refinement of 3, a group of peaks, not associated with the palladium complex or the chloride anion became apparent in the difference Fourier maps. The peaks were refined as a methylene chloride solvate. One chloride of this molecule is twofold disordered about a Cl–C–H mirror plane and refined with occupancies of 0.612 and 0.388 in the Cl(4) and Cl(4)′ sites, respectively.

Results and Discussion

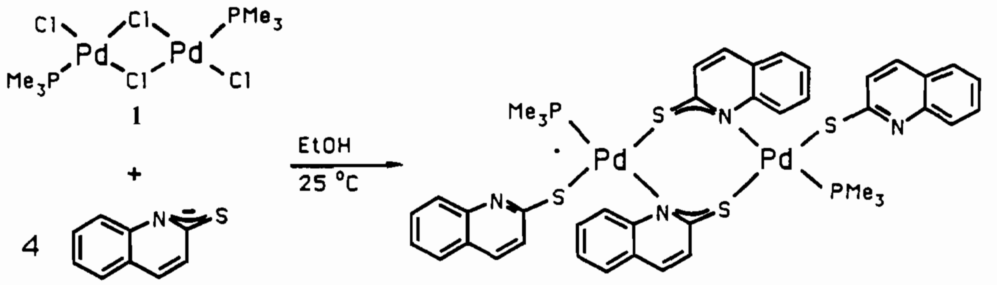
Syntheses

The HqnS complexes, 2 and 3, are obtained by reaction of acetone solutions of 1 with 4 equivalents of HqnS, as illustrated in Scheme 1. The mono-HqnS complex, 2, is obtained from the reaction at 25 °C while the bis-HqnS complex, 3, is obtained under the more forcing conditions of acetone reflux. Cleavage of the chloro bridges of 1 by HqnS matches the reactivity of other neutral ligands such as phosphines, carbon monoxide and amines [17].

Reaction of 1 with 4 equivalents of the conjugate anion, qnS, in ethanol solution gives 4 as illustrated in eqn. (1). Although N-heterocycle-2-thiolate complexes have been obtained through oxidative-addition reactions of neutral heterocycle-2-thiols with metal complexes [3, 4, 6, 12, 15], the present case in which synthesis is achieved through prior deprotonation of the heterocycle-2-thiol and subsequent substitution of halide(s) at the metal centers by the resulting anion is more common [7, 8, 10, 13, 14, 18].



Scheme 1.



4 (1)

Structure of $Pd(HqnS)(PMe_3)Cl_2$ *(2)*

An ORTEP projection of the molecular structure of 2 is seen in Fig. 1. Selected bond angles and distances are presented in Table 2; the final fractional atomic coordinates are given in Table 3. The complex exhibits nearly square-planar geometry; the chlorides having a *cis* orientation. The HqnS ligand is bound to the palladium η^1 through sulfur. This mode of coordination has generally been found for pyridine-2-thiol which also coordinates as the tautomeric thione and demonstrates the generality of the η^1-coordination of heterocycle-2-thiols as their 2-thione tautomers.

The atom H(1N) was located but the protonation of the nitrogen atom can also be inferred by the C(11)–N(1)–C(19) angle of 124.4(2)° which is within the range expected [19] for protonated N-heterocycles. Additionally, a signal for the N-bound hydrogen is observed in the ^{1}H NMR spectrum of 2 at 15.24 ppm.

The C(11)–S(1) distance of 1.713(3) Å is within the 1.69–1.72 Å range which has been reported previously [2, d, e, f; 3, 4, 20] for the S=C bond of η^1-1H-pyridine-2-thione complexes and significantly shorter than the 1.72–1.86 Å distances which have been reported [4, 7, 10–15] for the S–C bond of pyridine-2-thiolato, pyS$^-$, groups.

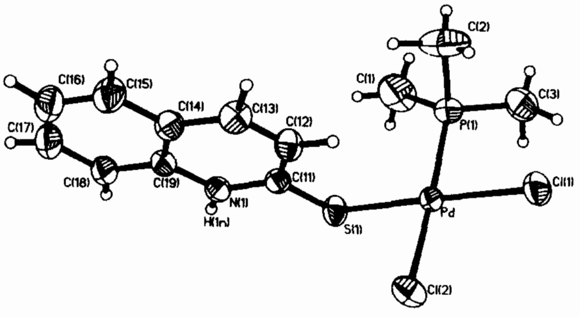


Fig. 1. ORTEP projection of $Pd(HqnS)(PMe_3)Cl_2$, thermal ellipsoids at 50% probability.

TABLE 2. Selected bond distances (Å) and angles (°) for $Pd(HqnS)(PMe_3)Cl_2$

Distances			
Pd–Cl(1)	2.311(1)	Pd–S(1)	2.297(1)
Pd–Cl(2)	2.401(1)	S(1)–C(11)	1.713(3)
Pd–P(1)	2.238(1)		
Angles			
Cl(1)–Pd–S(1)	176.9(1)	Cl(2)–Pd–S(1)	90.4(1)
Cl(2)–Pd–P(1)	171.3(1)	P(1)–Pd–S(1)	92.1(1)
Cl(1)–Pd–Cl(2)	90.3(1)	Pd–S(1)–C(11)	105.5(1)
Cl(1)–Pd–P(1)	87.5(1)	C(11)–N(1)–C(19)	124.4(2)

TABLE 3. Atomic coordinates and equivalent isotropic displacement coefficients[a] for $Pd(HqnS)(PMe_3)Cl_2$

	x	y	z	U_{eq}
Pd	0.2305(1)	0.6320(1)	0.0904(1)	0.029(1)
Cl(1)	0.1001(1)	0.7920(1)	0.1029(1)	0.055(1)
Cl(2)	0.3833(1)	0.7603(1)	0.0228(1)	0.041(1)
S(1)	0.3542(1)	0.4698(1)	0.0701(1)	0.036(1)
P(1)	0.0956(1)	0.5247(1)	0.1771(1)	0.039(1)
C(1)	0.1129(5)	0.3653(3)	0.1816(5)	0.081(2)
C(2)	0.1047(5)	0.5698(6)	0.3137(3)	0.080(2)
C(3)	−0.0614(3)	0.5445(4)	0.1368(3)	0.061(1)
N(1)	0.5539(2)	0.4012(2)	0.1708(2)	0.031(1)
C(11)	0.4616(2)	0.4784(2)	0.1712(2)	0.030(1)
C(12)	0.4588(3)	0.5608(2)	0.2566(2)	0.036(1)
C(13)	0.5459(3)	0.5574(2)	0.3355(2)	0.038(1)
C(14)	0.6399(2)	0.4719(2)	0.3360(2)	0.035(1)
C(15)	0.7301(3)	0.4619(3)	0.4178(2)	0.048(1)
C(16)	0.8153(3)	0.3738(3)	0.4139(3)	0.055(1)
C(17)	0.8150(3)	0.2935(3)	0.3298(2)	0.050(1)
C(18)	0.7310(3)	0.3025(3)	0.2472(2)	0.040(1)
C(19)	0.6424(2)	0.3915(2)	0.2509(2)	0.032(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Structure of $[Pd(HqnS)_2(PMe_3)Cl][Cl]$ *(3)*

An ORTEP projection of the molecular structure of 3 is seen in Fig. 2. Selected bond angles and distances are in Table 4; the final fractional atomic coordinates are given in Table 5. The complex exhibits nearly square-planar geometry, however a highly distorted S(1)–Pd(1)–S(2) angle of 165.5(1)° is found between the *trans* quinolinethione ligands which apparently allows the establishment of the NH···Cl hydrogen bonding interactions.

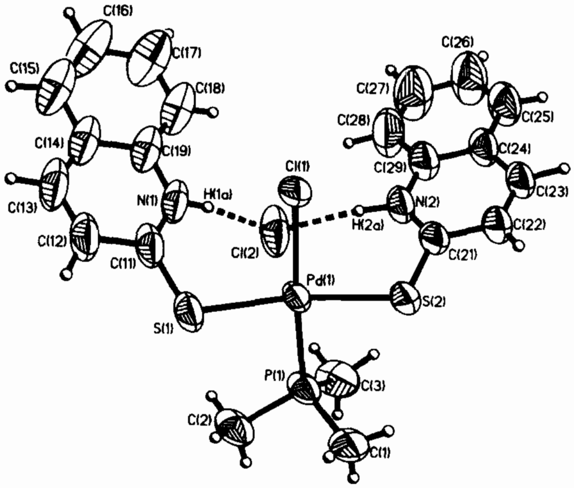


Fig. 2. ORTEP projection of $[Pd(HqnS)_2(PMe_3)Cl][Cl]$, thermal ellipsoids at 50% probability.

TABLE 4. Selected bond lengths (Å) and angles (°) for $[Pd(HqnS)_2(PMe_3)Cl][Cl] \cdot CH_2Cl_2$

Distances			
Pd(1)–Cl(1)	2.399(2)	Pd(1)–P(1)	2.249(2)
Pd(1)–S(1)	2.328(2)	S(1)–C(11)	1.696(6)
Pd(1)–S(2)	2.326(2)	S(2)–C(21)	1.703(4)
Angles			
Cl(1)–Pd(1)–P(1)	175.8(1)	Cl(1)–Pd(1)–S(1)	93.3(1)
S(2)–Pd(1)–S(1)	165.5(1)	Cl(1)–Pd(1)–S(2)	90.2(1)
P(1)–Pd(1)–S(2)	86.3(1)	Pd(1)–S(1)–C(11)	110.7(2)
P(1)–Pd(1)–S(1)	90.6(1)	Pd(1)–S(2)–C(21)	112.0(2)
P(1)–Pd(1)–S(2)	86.3(1)	C(21)–N(2)–C(29)	123.8(4)
		C(11)–N(1)–C(19)	125.5(5)

As was the case with 2, structural and spectroscopic data suggest the heterocycle ligand is coordinated as the 2-thione tautomer. The hydrogens on the nitrogen atoms, H(1A) and H(2A) were located and the protonation of the nitrogen atoms can also be inferred by the C(21)–N(2)–C(29) and C(11)–N(1)–C(19) angles of 123.8(4) and 125.5(5)°, respectively which are within the range expected [19] for protonated N-heterocycles. Additionally, a signal for the N-bound hydrogen is observed in the ^1H NMR spectrum of 2 at 15.25 ppm. The C(11)–S(1) and C(22)–S(2) distances of 1.696(6) and 1.703(4) Å, respectively, are similar to the above noted C–S distance in 2.

The H(1A)–Cl(2) and H(2A)–Cl(2) distances of 2.470(5) and 2.332(5) Å, respectively indicate that non-coordinated chloride is involved in NH···Cl hydrogen bonding. Although the Pd–Cl(2) distance of 3.375(2) Å clearly demonstrates the lack of a coordinative interaction, the NH···Cl hydrogen bonding interactions result in Cl(2) being located in an apical position of an approximately square pyramidal geometry about the palladium center.

TABLE 5. Atomic coordinates and equivalent isotropic displacement parameters[a] for $[Pd(HqnS)_2(PMe_3)Cl][Cl] \cdot CH_2Cl_2$

	x	y	z	U_{eq}
Pd(1)	0.1056(1)	0.3510(1)	0.3956(1)	0.058(1)
Cl(1)	0.3736(1)	0.3313(1)	0.4112(1)	0.068(1)
P(1)	−0.1414(1)	0.3560(1)	0.3813(1)	0.065(1)
S(2)	0.814(1)	0.2069(1)	0.5006(1)	0.078(1)
S(1)	0.819(2)	0.5217(1)	0.3299(1)	0.083(1)
N(2)	0.3522(5)	0.769(3)	0.3507(4)	0.069(2)
N(1)	0.3924(6)	0.4340(4)	0.1941(3)	0.074(2)
C(1)	−0.3007(6)	0.3668(5)	0.5082(5)	0.078(3)
C(2)	−0.2387(8)	0.4664(5)	0.3147(6)	0.084(3)
C(3)	−0.1242(8)	0.2343(5)	0.3054(7)	0.094(4)
C(11)	0.2677(7)	0.5239(4)	0.2427(4)	0.079(3)
C(12)	0.2964(9)	0.6261(4)	0.2169(6)	0.098(4)
C(13)	0.445(1)	0.6284(5)	0.1479(5)	0.101(4)
C(14)	0.5736(8)	0.5329(5)	0.1007(4)	0.084(3)
C(15)	0.732(1)	0.5310(7)	0.0287(5)	0.106(4)
C(16)	0.851(1)	0.4342(8)	−0.0119(5)	0.124(5)
C(17)	0.825(1)	0.3330(7)	0.0156(5)	0.118(4)
C(18)	0.6707(9)	0.3332(6)	0.0840(5)	0.093(4)
C(19)	0.5478(8)	0.4317(4)	0.1253(4)	0.076(3)
C(21)	0.2443(6)	0.0904(3)	0.4490(4)	0.062(2)
C(22)	0.2663(6)	0.0025(4)	0.5142(5)	0.068(2)
C(23)	0.3947(6)	−0.0911(3)	0.4772(4)	0.068(2)
C(24)	0.5084(6)	−0.1063(3)	0.3719(4)	0.068(2)
C(25)	0.6432(8)	−0.2021(4)	0.3292(6)	0.093(3)
C(26)	0.744(1)	−0.2111(5)	0.2276(7)	0.129(4)
C(27)	0.716(1)	−0.1267(6)	0.1638(7)	0.147(5)
C(28)	0.5907(9)	−0.0300(6)	0.2021(5)	0.114(4)
C(29)	0.4844(7)	−0.0192(4)	0.3072(4)	0.077(3)
Cl(2)	0.3180(2)	0.2170(1)	0.1506(1)	0.107(1)
Cl(3)	0.8454(3)	0.0791(1)	−0.2527(2)	0.151(1)
Cl(4)	0.9124(7)	0.0162(4)	−0.0618(3)	0.189(4)
C(40)	0.791(2)	0.0215(8)	−0.1320(7)	0.172(7)
Cl(4′)	0.6765(8)	0.0883(3)	−0.0464(4)	0.131(3)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Structure of Pd_2 vic-(μ,N-Sη^2qnS)$_2$(η^1-qnS)$_2$(PMe_3)$_2$ (4)

An ORTEP projection of the molecular structure of 4 is seen in Fig. 3. Bond angles and distances are in Table 6; the final fractional atomic coordinates are given in Table 7. The molecular structure has an approximately C_{2v} symmetry with the two palladium atoms linked through the two μ-qnS ligands which have a vicinal orientation. The coordination geometry about each of the palladium atoms is nearly square-planar. The sulfur atom of the terminal thiolate is oriented *trans* to the sulfur of the bridging thiolate. The Pd(1)–Pd(2) distance of 3.224(2) Å clearly demonstrates the lack of Pd–Pd bonding.

The angles C(11)–N(1)–C(19), C(21)–N(2)–C(29), (C(31)–N(3)–C(39) and C(41)–N(4)–C(49) of 119(2), 118(2), 119(1) and 117(1)°, respectively, are within the range expected [19] for deprotonated N-heterocycles and demonstrate that the terminal as well as the bridging heterocycle-2-thiolate ligands are deprotonated. The C–S distances of the bridging qnS ligands of 1.73(2) and 1.75(2) Å, respectively, as well as those of the terminal qnS ligands, 1.72(2) and 1.73(2) Å, respectively are longer than those found in 2, the HqnS complex. These distances are at the short extreme of those which have been found [4, 7, 10–15] in pyridine-2-thiolate complexes (1.72–1.86 Å).

Conclusions

This work demonstrates the occurrence of simple bridge cleavage upon reaction of the neutral 2-

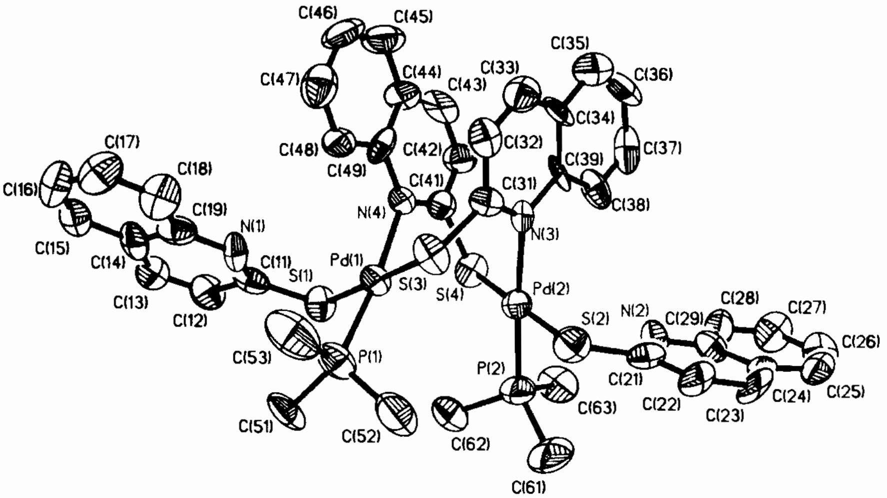


Fig. 3. ORTEP projection of *vic*-$Pd_2(\mu,N\text{-}S\eta^2\text{-}qnS)_2(\eta^1\text{-}qnS)_2(PMe_3)_2Cl_2$, thermal ellipsoids at 50% probability. The hydrogen atoms have been omitted for clarity.

TABLE 6. Selected bond distances (Å) and angles (°) for *vic*-$Pd_2(\mu,N\text{-}S\eta^2\text{-}qnS)_2(\eta^1\text{-}qnS)_2(PMe_3)_2$

Distances			
Pd(1)–S(1)	2.325(5)	Pd(2)–N(3)	2.14(1)
Pd(1)–S(3)	2.363(5)	Pd(2)–P(2)	2.244(5)
Pd(1)–N(4)	2.15(1)	S(1)–C(11)	1.72(2)
Pd(1)–P(1)	2.233(5)	S(2)–C(21)	1.73(2)
Pd(2)–S(2)	2.335(5)	S(3)–C(31)	1.73(2)
Pd(2)–S(4)	2.337(5)	S(4)–C(41)	1.75(2)
Angles			
S(1)–Pd(1)–S(3)	176.8(2)	S(4)–Pd(2)–P(2)	85.4(2)
P(1)–Pd(1)–N(4)	172.9(4)	S(4)–Pd(2)–N(3)	93.4(3)
S(1)–Pd(1)–P(1)	91.7(2)	Pd(1)–S(1)–C(11)	104.2(7)
S(1)–Pd(1)–N(4)	89.0(4)	Pd(1)–S(2)–C(21)	105.0(7)
S(3)–Pd(1)–P(1)	86.3(2)	Pd(1)–S(3)–C(31)	103.7(6)
S(3)–Pd(1)–N(4)	92.7(4)	Pd(2)–S(4)–C(41)	104.0(6)
S(2)–Pd(2)–S(4)	176.1(2)	C(11)–N(1)–C(19)	119(2)
P(2)–Pd(2)–N(3)	174.8(4)	C(21)–N(2)–C(29)	118(2)
S(2)–Pd(2)–P(2)	92.3(2)	C(31)–N(3)–C(39)	119(1)
S(2)–Pd(2)–N(3)	88.5(3)	C(41)–N(4)–C(49)	117(1)

quinolinethione with the chlorobridged palladium dimer (**1**) and that dimetallic integrity is maintained *only* when **1** is reacted with the conjugate anion. Although several examples of μ,η^2 and μ,η^3 coordination of heterocycle-2-thiolates have recently been structurally elucidated [3, 5–7, 21] or established by ^1H NMR spectroscopy [8], the formation of such complexes remains unpredictable. However, we note that precedent for the synthesis of the dimetallic μ,η^2-heterocycle-2-thiolate complex (**4**) through reaction of the μ-chloro dimetallic complex (**1**) with a heterocycle-2-thiolate anion is provided by the synthesis of $Rh_2(\mu,N\text{-}S\eta^2\text{-}pyS)(\mu,S\eta^2\text{-}pyS)(diolefin)_2$ complexes [7] as well as $Pd_2(dmp)_2$-

TABLE 7. Atomic coordinates and equivalent isotropic displacement coefficients[a] for *vic*-$Pd_2(\mu,N\text{-}S\eta^2\text{-}qnS)_2(\eta^1\text{-}qnS)_2(PMe_3)_2$

	x	*y*	*z*	U_{eq}
Pd(1)	0.0925(1)	0.0776(1)	0.3150(1)	0.0471(5)
P(1)	0.0753(4)	0.1991(3)	0.3504(3)	0.064(2)
C(51)	0.182(1)	0.2677(9)	0.3588(9)	0.087(9)
C(52)	−0.043(1)	0.2489(9)	0.299(1)	0.12(1)
C(53)	0.061(2)	0.195(1)	0.4355(9)	0.11(1)
S(1)	0.2675(3)	0.1031(3)	0.3091(2)	0.057(2)
N(1)	0.307(1)	0.0832(7)	0.4453(8)	0.052(6)
C(11)	0.347(1)	0.1002(8)	0.3946(8)	0.049(8)
C(12)	0.461(2)	0.1198(9)	0.411(1)	0.068(9)
C(13)	0.530(1)	0.1154(9)	0.476(1)	0.059(9)
C(14)	0.490(2)	0.0932(9)	0.529(1)	0.056(9)
C(15)	0.551(1)	0.0877(9)	0.600(1)	0.061(9)
C(16)	0.507(2)	0.067(1)	0.6515(9)	0.08(1)
C(17)	0.393(2)	0.052(1)	0.634(1)	0.08(1)
C(18)	0.331(2)	0.057(1)	0.566(1)	0.08(1)
C(19)	0.376(2)	0.0773(9)	0.514(1)	0.059(9)
S(3)	−0.0824(3)	0.0545(2)	0.3272(2)	0.059(2)
N(3)	−0.1267(9)	−0.0402(7)	0.2180(7)	0.042(6)
C(31)	−0.122(1)	−0.0327(9)	0.284(1)	0.048(8)
C(32)	−0.142(1)	−0.097(1)	0.3245(8)	0.053(8)
C(33)	−0.165(1)	−0.168(1)	0.294(1)	0.062(9)
C(34)	−0.167(1)	−0.179(1)	0.225(1)	0.055(9)
C(35)	−0.183(1)	−0.253(1)	0.192(1)	0.07(1)
C(36)	−0.184(1)	−0.259(1)	0.126(1)	0.08(1)
C(37)	−0.173(1)	−0.193(2)	0.0845(9)	0.075(9)
C(38)	−0.155(1)	−0.122(1)	0.116(1)	0.065(9)
C(39)	−0.150(1)	−0.114(1)	0.187(1)	0.045(8)
Pd(2)	−0.0857(1)	0.0572(1)	0.1641(1)	0.0485(6)
P(2)	−0.0472(4)	0.1529(3)	0.0986(2)	0.069(2)
C(61)	−0.141(1)	0.2325(9)	0.0719(9)	0.11(1)
C(62)	0.081(1)	0.1998(9)	0.1368(9)	0.092(9)
C(63)	−0.035(1)	0.1169(9)	0.0168(7)	0.080(9)
S(2)	−0.2551(4)	0.1116(2)	0.1578(2)	0.064(2)

(continued)

TABLE 7. *(continued)*

	x	y	z	U_{eq}
N(2)	−0.293(1)	0.0583(8)	0.0290(9)	0.060(7)
C(21)	−0.335(2)	0.0961(9)	0.0727(8)	0.057(9)
C(22)	−0.444(2)	0.1200(9)	0.052(1)	0.061(9)
C(23)	−0.513(2)	0.107(1)	−0.012(1)	0.07(1)
C(24)	−0.472(2)	0.0678(9)	−0.059(1)	0.053(9)
C(25)	−0.533(2)	0.045(1)	−0.0126(1)	0.07(1)
C(26)	−0.488(2)	0.008(1)	−0.1169(1)	0.08(1)
C(27)	−0.380(2)	−0.016(1)	−0.0152(1)	0.08(1)
C(28)	−0.315(2)	0.002(1)	−0.0828(1)	0.069(9)
C(29)	−0.359(2)	0.045(1)	−0.036(1)	0.055(9)
S(4)	0.0803(3)	0.003(2)	0.1621(2)	0.058(2)
N(4)	0.1152(9)	−0.0435(6)	0.2943(8)	0.045(6)
C(41)	0.110(1)	−0.066(1)	0.2298(9)	0.052(8)
C(42)	0.123(1)	−0.144(1)	0.2118(9)	0.059(8)
C(43)	0.136(1)	−0.1974(9)	0.262(1)	0.065(9)
C(44)	0.136(1)	−0.179(1)	0.331(1)	0.058(9)
C(45)	0.143(1)	−0.233(1)	0.383(1)	0.08(1)
C(46)	0.141(2)	−0.207(2)	0.448(1)	0.10(1)
C(47)	0.139(1)	−0.126(2)	0.462(1)	0.08(1)
C(48)	0.136(1)	−0.074(1)	0.411(1)	0.058(8)
C(49)	0.132(1)	−0.101(1)	0.3445(9)	0.049(8)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

$(\mu,N\text{-}S\eta^2\text{-pyS})_2$ [8] from reaction of μ-chloro dimetallic complexes with heterocycle-2-thiolate anions. We suggest therefore, that reaction of heterocycle-2-thiolate anions with dimetallic μ-chloro complexes may provide a rational method for their incorporation into dimetallic complexes as stabilizing, bridging ligands.

Supplementary Material

Tables of anisotropic thermal parameters, bond distances, bond angles, hydrogen atom coordinates and isotropic thermal parameters for $\mathrm{Pd(HqnS)(PMe_3)Cl_2}$, $\mathrm{[Pd(HqnS)_2(PMe_3)Cl][Cl]\cdot CH_2Cl_2}$ and *vic*-$\mathrm{Pd_2}(\mu,N\text{-}S\eta^2\text{-qnS})_2(\eta^1\text{-qnS})_2(\mathrm{PMe_3})_2$ (16 pages); structure factor tables (32 pages) are available from the authors on request.

Acknowledgements

We thank the University of Hawaii Research Council for the support of this research. The assistance of Professor R. E. Cramer and Mr P. N. Richmann in the X-ray diffraction study is gratefully acknowledged.

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