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Heteropolytopic Arsanylarylthiolato Ligands: Cis−Trans Isomerism of Nickel(II), Palladium(II), and Platinum(II) Complexes of 1-AsPh$_2$-2-SHC$_6$H$_4$

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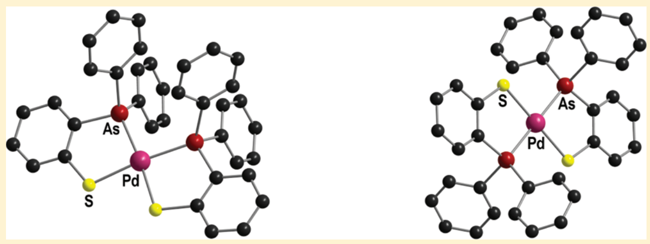
Supporting Information

ABSTRACT: Heteropolytopic arsanylthiolato ligands 1-AsPh$_2$-2-SHC$_6$H$_4$ (**AsSH**), PhAs(2-SHC$_6$H$_4$)$_2$ (**AsS$_2$H$_2$**), and As(2-SHC$_6$H$_4$)$_3$ (**AsS$_3$H$_3$**) have been prepared by lithiation−electrophilic substitution procedures. The 2:1 reaction of **AsSH** with NiCl$_2$·6H$_2$O, Na$_2$[PdCl$_4$], and [PtI$_2$(cod)] (cod = 1,5-cyclooctadiene) in the presence of NEt$_3$ afforded the square-planar complexes *trans*-[Ni{(**AsS**)-κ^2*S*,*As*}$_2$] (**1**), *cis*-[Pd{(**AsS**)-κ^2*S*,*As*}$_2$] (**2**), *trans*-[Pd{(**AsS**)-κ^2*S*,*As*}$_2$] (**3**), and *cis*-[Pt{(**AsS**)-κ^2*S*,*As*}$_2$] (**4**). In the cases of nickel and platinum, only one isomer was isolated. With palladium, initially the cis isomer **2** is formed and undergoes slow isomerization to the trans isomer **3** in solution. Small amounts of the trinuclear complex [{PtI(1-AsPh$_2$-μ-2-S-C$_6$H$_4$-κ^2*S*,*As*)}$_3$] (**5**) are also formed besides the mononuclear platinum bis-chelate complex **4**. Density functional theory calculations support a dissociative mechanism for the isomerization of the palladium(II) complexes.



INTRODUCTION

The search for new and more efficient catalytically active transition-metal complexes is based on the design and synthesis of appropriate ligands. While phosphorus-based ligands have been widely explored,[1] the combination of arsenic and one or more sulfur-donor atoms in the same ligand is not widely exploited. There are, however, examples of transition-metal complexes of triorganoarsines that are at least as good or even more efficient catalysts in organic synthesis than the phosphorus-containing analogues in Stille[2a,b] and Suzuki−Miyaura coupling reactions,[2c,d] hydroformylation of terminal alkenes,[2e] Heck olefination,[2f] carbonylation,[2g] and asymmetric Wittig olefination.[2h]

Recently, our attention focused on the polytopic 10-(*o*-alkoxyphenyl)phenoxarsines[3] (2-alkoxy- or 2-hydroxyphenyl)-diphenylarsine[4] and (2-alkoxyphenyl)dicyclohexylarsine[5] and the arsanylarylthiolates 1-AsPh$_2$-2-SHC$_6$H$_4$ (**AsSH**), PhAs(2-SHC$_6$H$_4$)$_2$ (**AsS$_2$H$_2$**), and As(2-SHC$_6$H$_4$)$_3$ (**AsS$_3$H$_3$**) and preliminary studies on their coordination chemistry.[6] Early studies on arsenic/sulfur-containing derivatives were dedicated to the coordination chemistry of arsanylarylthioethers.[7−10] The mono- and bis-chelate complexes of dimethyl-*o*-methylthiophenylarsine 1-AsMe$_2$-2-SMe-C$_6$H$_4$ (**Me$_2$AsSMe**), [PdX$_2$-{(**Me$_2$AsSMe**)-κ^2*S*,*As*}], (X = Cl, Br, I), [PtI$_2${(**Me$_2$AsSMe**)-κ^2*S*,*As*}], and [Pt{(**Me$_2$AsSMe**)-κ^2*S*,*As*}$_2$][PtX$_4$] (X = Cl, Br) were reported by Livingstone et al.[7a,b] S-Demethylation of the ligand occurs when these compounds are heated under reflux in dimethylformamide (DMF),[7c−e] and an X-ray crystal structure analysis of [Pt{(**Me$_2$AsS**)-κ^2*S*,*As*}$_2$] revealed a trans arrangement of the ligands.[7f] No isomerization of these complexes was observed upon heating in DMF.

The coordination chemistry of the phosphanylarylthiolate analogues 1-PPh$_2$-2-SHC$_6$H$_4$ (**PSH**), PhP(2-SHC$_6$H$_4$)$_2$ (**PS$_2$H$_2$**), and P(2-SHC$_6$H$_4$)$_3$ (**PS$_3$H$_3$**) is well established.[1,6,11] They were synthesized by the reaction of lithium 2-lithiobenzenethiolate, 1-Li-2-SLi-C$_6$H$_4$, with chlorophosphines PCl$_n$Ph$_{3-n}$ (n = 1−3).[12,13] Most of the known complexes of nickel, palladium, and platinum with phenylene-bridged phosphanylthiolato ligands have been prepared by dealkylation of the corresponding thioether complexes.[8d,14] *trans*-[Ni{(**PS**)-κ^2*S*,*P*}$_2$] has been structurally characterized in green (monoclinic)[15] and brown (triclinic)[16] modifications. Both cis and trans isomers of [Pd{(**PS**)-κ^2*S*,*P*}$_2$] were obtained from the reaction of 2 equiv of **PSH** with Na$_2$[PdCl$_4$] in the presence of a base.[17] *trans*-[Pd{(**PS**)-κ^2*S*,*P*}$_2$] was described previously also as the product of S-dealkylation of the cationic thioether complex.[14a,18] The structure of [Pt{(**PS**)-κ^2*S*,*P*}$_2$] has been assumed to be trans, but no molecular structure was reported.[18b,c] *cis*-[M{(**PS**)-κ^2*S*,*P*}$_2$] (M = Ni, Pd, Pt) was synthesized by transmetalation reactions of [MCl$_2$(NCPh)$_2$] (M = Pd, Pt) and NiCl$_2$·6H$_2$O with [SnR$_2${(**PS**)-κ*S*}$_2$] (R = Ph, ^{n}Bu, ^{t}Bu).[19] However, the cis geometry of the nickel complex

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Table 1. Crystal Data and Refinement Details for 1−5

	1	2	3	4	5
empirical formula	$C_{36}H_{28}As_2NiS_2$	$C_{36}H_{28}As_2PdS_2 \cdot CH_2Cl_2$	$C_{36}H_{28}As_2PdS_2$	$C_{36}H_{28}As_2PtS_2 \cdot CH_2Cl_2$	$C_{54}H_{42}As_3I_3Pt_3S_3 \cdot 2CH_2Cl_2$
fw	733.25	865.87	780.94	954.56	2147.64
temp (K)	208(2)	208(2)	210(2)	210(2)	210(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$
unit cell dimensions					
a (Å)	9.7440(7)	15.498(2)	9.726(3)	15.479(4)	23.988(2)
b (Å)	12.898(1)	9.532(1)	12.768(3)	9.526(2)	11.4987(9)
c (Å)	12.783(1)	22.842(3)	12.877(3)	22.771(5)	24.100(2)
α (deg)	90	90	90	90	90
β (deg)	107.552(2)	91.746(3)	108.045(4)	91.836(4)	112.635(1)
γ (deg)	90	90	90	90	90
volume (Å^3)	1531.7(2)	3372.7(8)	1520.4(7)	3355.8(14)	6135.5(8)
Z	2	4	2	4	4
density (calcd) (Mg m^{-3})	1.590	1.705	1.706	1.889	2.325
abs coeff (mm^{-1})	2.939	2.807	2.933	6.449	10.251
F(000)	740	1720	776	1848	3960
cryst size (mm^3)	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.05	0.20 × 0.10 × 0.10	0.40 × 0.20 × 0.04	0.2 × 0.1 × 0.1
$\theta_{min}/\theta_{max}$ (deg)	2.19/28.79	1.61/29.44	2.20/29.18	2.32/29.36	1.70/29.45
index ranges	$-12 \le h \le 10$	$-11 \le h \le 21$	$-12 \le h \le 13$	$-20 \le h \le 20$	$-29 \le h \le 31$
	$-17 \le k \le 17$	$-12 \le k \le 12$	$-16 \le k \le 16$	$-13 \le k \le 11$	$-15 \le k \le 15$
	$-14 \le l \le 17$	$-30 \le l \le 30$	$-17 \le l \le 17$	$-31 \le l \le 24$	$-33 \le l \le 32$
reflns collected	8746	20825	14358	20678	57526
indep reflns	3631 [*R*(int) = 0.0408]	8346 [*R*(int) = 0.0513]	14358 [*R*(int) = 0.0000]	8307 [*R*(int) = 0.0637]	15654 [*R*(int) = 0.0568]
completeness to θ_{max} (%)	90.9	89.3	91.5	90.1	91.2
restraints/param	0/187	0/397	0/196	0/397	0/649
GOF on F^2	1.213	1.012	0.923	1.017	1.151
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0548, wR2 = 0.0945	R1 = 0.0437, wR2 = 0.0930	R1 = 0.0544, wR2 = 0.1325	R1 = 0.0394, wR2 = 0.0969	R1 = 0.0574, wR2 = 0.1020
R indices (all data)	R1 = 0.0765, wR2 = 0.1007	R1 = 0.0874, wR2 = 0.1063	R1 = 0.0927, wR2 = 0.1392	R1 = 0.0550, wR2 = 0.1024	R1 = 0.0835, wR2 = 0.1092
largest diff peak and hole (e Å^{-3})	1.060 and −0.754	1.583 and −0.941	1.015 and −1.288	1.992 and −1.922	3.289 and −1.233
twin fraction (ratio domain *a*/*b*)			0.60(1)/0.40(1)[a]		

[a]Twin law by rows: −1.00, 0.00, −0.47; 0.00, 1.00, 0.00; 0.00, 0.00, −1.00.

could not be unequivocally confirmed by X-ray diffraction studies.[19]

We report here the synthesis of three heteropolytopic arsanylthiolates **AsSH**, **AsS_2H_2**, and **AsS_3H_3**. Complexes (1:2) of nickel(II), palladium(II), and platinum(II) with **AsS**$^-$ were prepared and characterized by spectroscopic methods and X-ray diffraction. In addition, a trimeric complex (Pt:L = 3:3; L = **AsS**$^-$) has been obtained.

■ EXPERIMENTAL SECTION

All manipulations were carried out by standard Schlenk and vacuum-line techniques under an atmosphere of dry nitrogen with dry and oxygen-free solvents. Ph_2AsCl,[20] $PhAsCl_2$,[21] and [PtI_2(cod)] (cod = 1,5-cyclooctadiene)[22,23] were prepared according to the literature. All other chemicals were used as purchased.

The IR spectra were recorded on a Perkin-Elmer System 2000 Fourier transform infrared spectrometer by scanning between 400 and 4000 cm^{-1} using KBr pellets. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX-400 spectrometer. ^{1}H and ^{13}C chemical shifts are quoted in parts per million (ppm) at 400.13 and 100.63 MHz, respectively, relative to tetramethylsilane. The mass spectra were recorded on a VG12-520 mass spectrometer (EI-MS, 70 eV, 200 °C). The melting points were determined in sealed capillaries with a Gallenkamp instrument and are uncorrected.

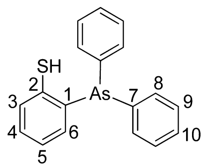
Crystallographic data (Table 1) were collected on a Siemens CCD diffractometer (SMART), ω-scan rotation with Mo Kα radiation (λ = 0.71073 Å). Data reduction was performed with *SAINT* including the programs *SADABS* for empirical absorption correction. Direct methods (compounds **1**−**4**) and Patterson methods (compound **5**) were used to solve the structures. Anisotropic full-matrix least-squares refinement on F^2 of all non-hydrogen atoms was performed with *SHELXL-97*. Hydrogen atoms were calculated on idealized positions. Structure figures were generated with ORTEP (ellipsoids are drawn at 50% probability if not otherwise mentioned).[24] The structure determination of **3** is based on a twinned crystal and was analyzed with the program *GEMINI*.[25] CCDC 859782 (**1**), 859783 (**2**), 859784 (**3**), 859785 (**4**), and 859786 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

All calculations were performed with the *Gaussian 09* program package,[26] using the M06 functional[27] with the mLANL2DZ basis set and effective core potential[28] for the transition-metal atoms and the 6-31G** basis set[29] for all other atoms. Transition-state structures have been located with the combined synchronous transit and quasi-Newton methods.[30]

Synthesis of AsSH, AsS_2H_2, and AsS_3H_3. *General Procedure.* $Li_2(2\text{-}S\text{-}C_6H_4)(TMEDA)_{1.3}$ was prepared as described in the literature[12] from thiophenol (7 g, 64 mmol), tetramethylethylenediamine

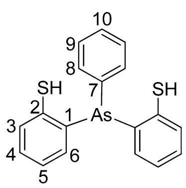
(TMEDA; 21 mL, 141 mmol), and ^{n}BuLi (2.3 M in *n*-hexane; 62 mL, 141 mmol). $Li_2(2\text{-}S\text{-}C_6H_4)(TMEDA)_{1.3}$ was obtained as a white solid, washed with *n*-hexane, and dissolved in tetrahydrofuran (THF) at −78 °C. The stirred solution of $Li_2(2\text{-}S\text{-}C_6H_4)(TMEDA)_{1.3}$ in THF (100 mL) was treated dropwise with a solution of chlorodiphenylarsine (11.75 g, 44 mmol) in THF (20 mL) at −78 °C. The reaction mixture was warmed to room temperature overnight. The deep-red solution was acidified at 0 °C with degassed dilute sulfuric acid (6%) to ca. pH 3−4 and concentrated in vacuum to one-third of its volume, and the resulting residue was dissolved in diethyl ether (100 mL). The ether phase was washed with degassed water (3 × 50 mL), dried over $MgSO_4$, and concentrated to afford crude **AsSH**. The crude product was dissolved in diethyl ether. Treatment with activated charcoal, filtration, and crystallization from diethyl ether/*n*-hexane (2:1) gave **AsSH** as a colorless solid. Yield: 10.51 g, 31 mmol (71% based on Ph_2AsCl). $\mathbf{AsS_2H_2}$ and $\mathbf{AsS_3H_3}$ were obtained accordingly from phenyldichloroarsine or $AsCl_3$, respectively. $\mathbf{AsS_2H_2}$: yield 3.0 g, 8.1 mmol (56% based on $PhAsCl_2$). $\mathbf{AsS_3H_3}$: yield 3.2 g, 7.9 mmol (42% based on $AsCl_3$).

*Data for **AsSH**.*



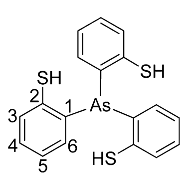
^{1}H NMR (*δ*, $CDCl_3$): 7.34 (m, 10H, aryl-H), 7.19 (m, 2H, aryl-H), 7.05 (t, $^3J_{HH}$ = 8 Hz, 1H, aryl-H), 6.88 (d, $^3J_{HH}$ = 8 Hz, 1H, aryl-H), 3.67 (s, 1H, SH). $^{13}C\{^1H\}$ NMR (*δ*, $CDCl_3$): 140.5 (C^2), 138.3 (C^1), 136.4 (C^7), 134.0 (C^3), 133.8 (C^8), 131.5 (C^6), 129.1 (C^4), 128.8 (C^{10}), 128.7 (C^9), 126.6 (C^5). IR (KBr, cm^{-1}): 2552 (m, ν_{S-H}). EI-MS: *m/z* 338.4 ([M]$^+$). Mp: 91−95 °C.

Data for $\mathbf{AsS_2H_2}$.



^{1}H NMR (*δ*, $CDCl_3$): 7.41−7.36 (m, 5H, aryl-H), 7.31−7.29 (m, 2H, aryl-H), 7.23 (t, $^3J_{HH}$ = 8 Hz, 2H, aryl-H), 7.08 (t, $^3J_{HH}$ = 8 Hz, 2H, aryl-H), 6.85 (d, $^3J_{HH}$ = 8 Hz, 2H, aryl-H), 3.7 (s, 2H, SH). $^{13}C\{^1H\}$ NMR (*δ*, $CDCl_3$): 139.6 (C^2), 137.3 (C^1), 136.6 (C^7), 134.07 (C^3), 134.03 (C^8), 131.7 (C^6), 129.4 (C^4), 129.0 (C^{10}), 128.9 (C^9), 126.8 (C^5). IR (KBr, cm^{-1}): 2564 (m, ν_{S-H}). EI-MS: *m/z* 370.0 ([M]$^+$). Mp: 85−88 °C.

Data for $\mathbf{AsS_3H_3}$.



^{1}H NMR (*δ*, $CDCl_3$): 7.43 (d, $^3J_{HH}$ = 8 Hz, 3H, aryl-H), 7.23 (t, $^3J_{HH}$ = 8 Hz, 3H, aryl-H), 7.09 (t, $^3J_{HH}$ = 8 Hz, 3H, aryl-H), 6.83 (d, $^3J_{HH}$ = 8 Hz, 3H, aryl-H), 3.74 (s, 3H, SH). $^{13}C\{^1H\}$ NMR (*δ*, $CDCl_3$): 138.7 (C^2), 136.9 (C^1), 134.0 (C^3), 131.9 (C^6), 129.6 (C^4), 125.0 (C^5). IR (KBr, cm^{-1}): 2531 (m, ν_{S-H}). EI-MS: *m/z* 402.2 ([M]$^+$). Mp: 117−121 °C.

Synthesis of *trans*-[Ni{(AsS)-κ^2*S*,*As*}$_2$] (1). A solution of $NiCl_2\cdot6H_2O$ (0.08 g, 0.34 mmol) in methanol (5 mL) was added to a solution of **AsSH** (0.24 g, 0.71 mmol) and triethylamine (0.07 g, 0.71 mmol) in methanol (20 mL). The reaction mixture was heated to reflux for 2 h and then stirred overnight. The green precipitate formed was separated by filtration and washed with a small quantity of methanol. Green crystals of **1** were obtained from a CH_2Cl_2/MeOH (4:1) layered system at room temperature. Yield: 0.24 g, 0.32 mmol (97%).

*Data for **1**.* Anal. Calcd for $C_{36}H_{28}As_2NiS_2$ (733.27): C, 58.97; H, 3.85. Found: C, 58.46; H, 3.93. ^{1}H NMR (*δ*, $CDCl_3$): 7.72 (d, $^3J_{HH}$ = 8 Hz, 8H, aryl-H), 7.57 (d, $^3J_{HH}$ = 8 Hz, 2H, aryl-H), 7.47−7.38 (m, 12H, aryl-H), 7.20 (d, $^3J_{HH}$ = 8 Hz, 2H, aryl-H), 7.16 (t, $^3J_{HH}$ = 8 Hz, 2H, aryl-H), 6.94 (t, $^3J_{HH}$ = 8 Hz, 2H, aryl-H). IR (KBr, cm^{-1}): 3051 (m), 2986 (w), 1953 (w), 1878 (w), 1806 (w), 1579 (m), 1566 (vs), 1550 (m), 1480 (s), 1438 (vs), 1424 (vs), 1304 (w), 1238 (m), 1184 (m), 1157 (w), 1123 (w), 1090 (s), 1081 (s), 1033 (m), 1025 (m), 998 (m), 911 (w), 858 (w), 806 (w), 755 (s), 734 (vs), 715 (m), 690 (vs), 674 (m), 504 (w), 468 (vs), 454 (s), 431 (m). EI-MS: *m/z* 733.4 ([M]$^+$). Mp: 295 °C.

Synthesis of *cis*-[Pd{(AsS)-κ^2*S*,*As*}$_2$] (2) and *trans*-[Pd{(AsS)-κ^2*S*,*As*}$_2$] (3). $Na_2[PdCl_4]$ was prepared from NaCl (66 mg, 1.13 mmol) and $PdCl_2$ (100 mg, 0.56 mmol) in water (25 mL) by stirring the reactants at 40 °C, cooling to room temperature, and evaporating to dryness. $Na_2[PdCl_4]$ was dissolved in MeOH (25 mL) and added to a solution of **AsSH** (0.4 g, 1.2 mmol) in MeOH (20 mL) and NEt_3 (1.2 mmol). A yellow-orange solid formed immediately. The reaction mixture was heated to reflux for 2 h. The light-orange solid was separated by filtration, washed with methanol, and dried in a vacuum. Slow crystallization from a 2:1 mixture of CH_2Cl_2/MeOH at room temperature afforded orange crystals of *cis*-[Pd{(**AsS**)-κ^2*S*,*As*}$_2$] (**2**). Yield: 0.39 g, 0.49 mmol (89%).

*Data for **2**.* Anal. Calcd for $C_{36}H_{28}As_2PdS_2$ (781.00)·$^1/_4CH_2Cl_2$: C, 54.27; H, 3.58. Found: C, 54.37; H, 3.73. ^{1}H NMR (*δ*, $CDCl_3$): 7.70 (d, $^3J_{HH}$ = 8 Hz, 6H, aryl-H), 7.66 (d, $^3J_{HH}$ = 8 Hz, 2H, aryl-H), 7.47−7.40 (m, 10H, aryl-H), 7.23−7.14 (m, 8H, aryl-H), 6.99 (t, $^3J_{HH}$ = 8 Hz, 2H, aryl-H). IR (KBr, cm^{-1}): 3047 (s), 1953 (w), 1880 (w), 1809 (w), 1616 (w), 1566 (vs), 1546 (m), 1480 (s), 1438 (vs), 1421 (vs), 1306 (m), 1241 (m), 1183 (m), 1158 (m), 1121 (w), 1090 (s), 1080 (s), 1033 (m), 1025 (m), 998 (m), 915 (w), 847 (w), 805 (w), 736 (vs), 718 (m), 690 (vs), 656 (w), 503 (w), 470 (vs), 434 (m). EI-MS: *m/z* 780.4 ([M]$^+$). Mp: 308−312 °C.

In solution, complex **2** undergoes slow isomerization to *trans*-[Pd{(**AsS**)-κ^2*S*,*As*}$_2$] (**3**). **3** was separated as light-red crystals from a CH_2Cl_2 solution of **2** after standing for 1 week at room temperature.

*Data for **3**.* Anal. Calcd for $C_{36}H_{28}As_2PdS_2$ (781.00)·$^1/_4CH_2Cl_2$: C, 54.27; H, 3.58. Found: C, 54.37; H, 3.73. ^{1}H NMR (*δ*, $CDCl_3$): 7.70−7.64 (m, 8H, aryl-H), 7.45−7.40 (m, 10H, aryl-H), 7.24−7.11 (m, 8H, aryl-H), 6.98 (t, $^3J_{HH}$ = 7.5 Hz, 2H, aryl-H). IR (KBr, cm^{-1}): 3051 (m), 2961 (w), 1568 (vs), 1548 (m), 1482 (s), 1439 (vs), 1423 (vs), 1307 (w), 1261 (m), 1242 (m), 1184 (m), 1158 (m), 1083 (vs), 1032 (s), 1000 (m), 803 (m), 738 (vs), 718 (m), 468 (vs), 435 (m). EI-MS: *m/z* 781.0 ([M]$^+$). Mp: 334−336 °C.

Synthesis of *cis*-[Pt{(AsS)-κ^2*S*,*As*}$_2$] (4) and Formation of [{PtI(1-AsPh$_2$-*μ*-2-S-C$_6$H$_4$-κ^2*S*,*As*)}$_3$] (5). ***a. From [PtI$_2$(cod)] and AsSH.*** A solution of **AsSH** (0.34 g, 1 mmol) and NEt_3 (1 mmol) in methanol (20 mL) was added to a suspension of [PtI_2(cod)] (0.28 g, 0.5 mmol) in methanol (20 mL). The reaction mixture was heated to reflux for 3 h to give a yellow solution and a yellow precipitate, which was separated by filtration, washed with methanol, and dried in a vacuum. Yield: 0.33 g. Recrystallization from CH_2Cl_2/MeOH at 8 °C yielded yellow crystals of **4**. A few crystals of **5** were also isolated from the CH_2Cl_2/MeOH solution. Complex **5** was characterized by X-ray crystallography, IR spectroscopy, and fast atom bombardment mass spectrometry (FAB-MS). The amount of pure substance was insufficient for other characterization methods.

b. From K$_2$[PtCl$_4$] and AsSH. A solution of **AsSH** (0.11 g, 0.34 mmol) and NEt_3 (0.34 mmol) in methanol (20 mL) was added to a suspension of $K_2[PtCl_4]$ (0.07 g, 0.17 mmol) in methanol (20 mL). The reaction mixture was heated to reflux for 1 h and stirred at room temperature overnight. The yellow precipitate formed was separated by filtration, washed with methanol, and dried in a vacuum. Crystallization from CH_2Cl_2/MeOH at 8 °C yielded yellow crystals of **4**. Yield: 0.11 g, 0.13 mmol (74%).

*Data for **4**.* Anal. Calcd for $C_{36}H_{28}As_2PtS_2$ (869.66): C, 49.72; H, 3.25. Found: C, 49.40; H, 3.51. ^{1}H NMR (*δ*, $CDCl_3$): 7.77 (d, $^3J_{HH}$ = 8 Hz, 2H, aryl-H), 7.28 (m, 4H, aryl-H), 7.20 (d, $^3J_{HH}$ = 8 Hz, 8H,

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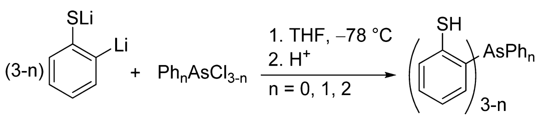
aryl-H), 7.14–7.05 (m, 12H, aryl-H), 6.82 (t, $^3J_{HH}$ = 8 Hz, 2H, aryl-H). IR (KBr, cm^{-1}): 3048 (m), 2988 (w), 1952 (w), 1878 (w), 1812 (w), 1570 (s), 1547 (m), 1480 (s), 1438 (vs), 1422 (vs), 1306 (m), 1267 (m), 1242 (s), 1182 (w), 1158 (m), 1123 (w), 1091 (s), 1080 (vs), 1037 (m), 1024 (m), 998 (m), 915 (w), 852 (w), 807 (w), 734 (vs), 720 (m), 690 (vs), 656 (w), 616 (w), 504 (w), 473 (vs), 449 (m), 435 (s). EI-MS: *m/z* 869 ([M]$^+$). Mp: 381 °C.

*Data for **5***. IR (KBr, cm^{-1}): 3051 (m), 2963 (s), 1960 (w), 1889 (w), 1814 (w), 1618 (w), 1570 (s), 1481 (s), 1440 (vs), 1424 (s), 1308 (w), 1262 (vs), 1182 (m), 1157 (m), 1093 br (vs), 1124 br (vs), 866 (m), 805 br (vs), 738 (vs), 692 (vs), 616 (w), 550 (w), 502 (w), 472 (vs), 437 (m), 405 (w). FAB-MS: *m/z* 1979.2 ([M]$^+$), 1851.5 ([M − I]$^+$).

■ RESULTS AND DISCUSSION

The new ligands containing both thiol and arsanyl groups were prepared by lithiation–electrophilic substitution procedures.[12,13] Treatment of THF solutions of lithium 2-lithiobenzenethiolate (1-Li-2-SLi-C_6H_4) at −78 °C with the appropriate electrophile gives, after acidic workup, the 2-mercaptophenyl derivatives as white solids, which are relatively air-stable in the solid state (Scheme 1).

Scheme 1. Synthesis of Arsanylarylthiols



AsSH, **AsS_2H_2**, and **AsS_3H_3** show signals in the ^{1}H NMR spectra in the range of 6.8–7.4 ppm corresponding to the aromatic protons and a singlet around 3.7 ppm assigned to the SH protons.

Treatment of **AsSH** with $NiCl_2·6H_2O$, $Na_2[PdCl_4]$, and $[PtI_2(cod)]$ in a 2:1 ratio and in the presence of NEt_3 (Scheme 2) led to the corresponding square-planar nickel, palladium, and platinum complexes **1**–**4**. Only one isomer was isolated in the case of nickel, compound **1**, and platinum, compound **4**. In the case of palladium, orange crystals were formed by slow crystallization from CH_2Cl_2/MeOH and identified as **2**. In solution, **2** undergoes slow isomerization to **3**, and in a few days at room temperature, light red crystals of **3** formed. A similar behavior was observed for the corresponding nickel, palladium, and platinum complexes of **PSH**.[14a,15,17,19]

The ^{1}H NMR spectra for **1**–**4** show only signals of the aromatic rings. The absence of the S–H vibration at about 2550 cm^{-1} in the IR spectra indicates that deprotonation of the thiol has occurred and that the ligands are coordinated in their anionic form. Electron impact mass spectrometry (EI-MS) spectra exhibit the signal corresponding to the molecular ion peak with the appropriate isotopic distribution.

Besides mononuclear platinum complex **4**, a few dark-orange crystals of another product were isolated from the 2:1 reaction of **AsSH** with $[PtI_2(cod)]$. These were identified by X-ray structure analysis as trimeric platinum complex **5** (Figure 1).

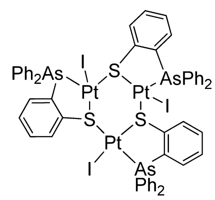
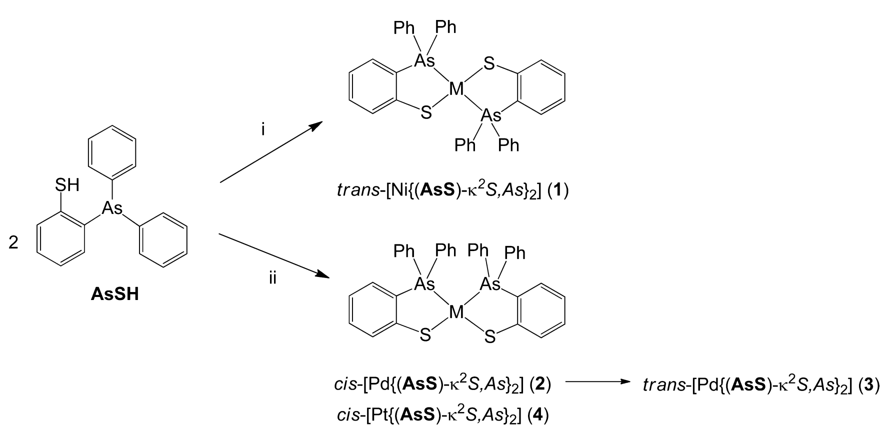


Figure 1. Schematic drawing of $[\{Pt(I)L\}_3]$, L = **AsS**$^-$ (**5**).

Attempts to obtain exclusively the trinuclear complex by a 1:1 reaction of **AsSH** with $[PtI_2(cod)]$ led to the formation of the bis-chelate **4** and only a very small amount of orange crystals of trimer **5** (Figure 1). A similar reaction was observed for 1-P(Biph)-2-SHC_6H_4 (Biph = 1,1′-biphenyl-2,2′-diyl) with $[PtI_2(cod)]$, which gave *cis*-[Pt{(1-P(Biph)-2-S-C_6H_4)-κ^2*S*,*P*}$_2$] and small amounts of the trinuclear complex [{PtI(1-P(Biph)-μ-2-S-C_6H_4-κ^2*S*,*P*)}$_3$].[31] Subsequently, it was found that the 1:1 reaction of the heterotopic P,SAs ligand 1-PPh_2-2-SAsPh_2-C_6H_4 with $[PtI_2(cod)]$ resulted in cleavage of the As–S bond and coordination of the resulting phosphanylthiolato ligand $(SC_6H_4\text{-}2\text{-}PPh_2)^-$ with formation of a similar trimeric compound to **5**. It was shown that this trimer is not formed as an intermediate on the way to formation of the bis-chelate, but it is (besides the cis bis-chelates) the major product formed. The proposed mechanism for the formation of this trimer involves generation of trinuclear species [(*cis*-Pt{(μ-*S*-SC_6H_4-2-PPh_2)-κ^2*S*,*P*}$_2$)–PtI_2–PtI{(μ-*S*-SC_6H_4-2-PPh_2)-κ^2*S*,*P*}], which rearranges with formation of the trimer [PtI{(μ-*S*-SC_6H_4-2-PPh_2)-κ^2*S*,*P*}]$_3$.[32]

Molecular Structures of the Square-Planar Nickel, Palladium, and Platinum Complexes of AsSH. Crystals of **1**–**4** suitable for X-ray crystallography were obtained from a

Scheme 2. Syntheses of the Nickel, Palladium, and Platinum Complexes of AsSH[a]



[a](i) $NiCl_2·6H_2O$, NEt_3; (ii) $Na_2[PdCl_4]$ or $[PtI_2(cod)]$, NEt_3.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in 1−4

compound	M−S	M−As	As−M−S	As−M−S′	S−M−S′	As−M−As′
1	2.188(1)	2.2709(4)	88.96(3)	91.04(3)	180	180
2[a]	2.319(1)	2.3625(6)	87.30(4)	174.61(4)	87.28(5)	98.08(2)
	2.322(1)	2.3648(6)	87.36(4)	173.95(4)		
3	2.314(1)	2.3604(6)	86.82(3)	93.18(3)	180	180
4[a]	2.313(1)	2.3530(7)	87.62(4)	173.86(4)	86.75(5)	98.04(3)
	2.314(1)	2.3524(7)	87.62(4)	174.33(4)		

[a]In Figure 3 (left), the prime notation was employed, even though the corresponding atoms are not symmetry-related, to facilitate a comparison of the related structures.

CH_2Cl_2/MeOH double-layer system. Selected bond lengths and angles for **1−4** are given in Table 2. Structures of compounds **1** and **3** or **2** and **4**, respectively, are isotypic.

The molecular structure of green prisms of **1** is shown in Figure 2.

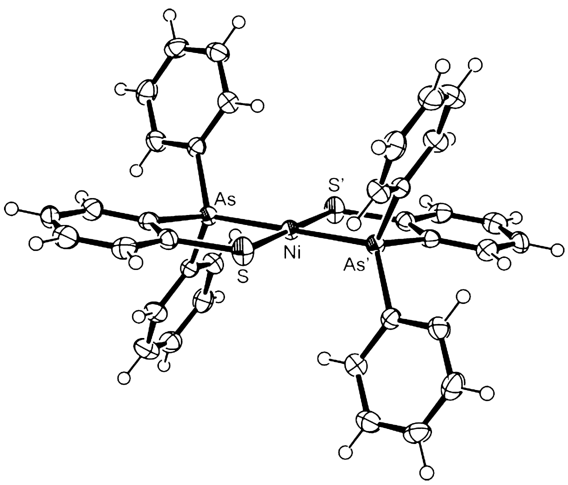


Figure 2. Molecular structure of **1**.

The nickel atom is located on a crystallographic inversion center and is coordinated by two sulfur atoms and two arsenic atoms, giving a strictly planar arrangement (As−Ni−As′ 180° and S−Ni−S′ 180°). The sulfur atoms are in a trans disposition, and the As−Ni−S′ bond angles between the adjacent ligands are close to 90° (Table 2). The chelate angle S−Ni−As [88.96(3)°] and the Ni−S bond length of 2.188(1) Å are in the range reported for other thiolato complexes of this type.[15,16,33] The Ni−As bond length of 2.2709(4) Å is close to the values found in other tertiary arsine complexes: 2.253(2) Å in 1-(diphenylarsanyl)-2-(diphenylphosphanyl)ethane(*o*-methyl dithiophosphate)nickel(II),[34,35] 2.255(1) Å in tetrakis(μ_3-sulfido)tris(η^5-methylcyclopentadienyl)(triphenylarsine)-trimolybdenum−nickel *p*-toluenesulfonate[35], and 2.218(2) and 2.325(2) Å in (bis(*o*-diphenylarsinophenyl)(*o*-methylthiophenyl)-arsine)bromonickel(II) perchlorate.[36] The arsenic atoms are surrounded in a slightly distorted tetrahedral fashion with bond angles between 103.04(2)° and 119.19(1)°.

The molecular structure of **2** (Figure 3, left) reveals strong interactions between the phenyl rings of the *cis*-diphenylarsanyl groups caused by the rigidity of the chelating ligand and the square-planar coordination of palladium(II). The molecules of **2** accommodate the bulky diphenylarsanyl groups by widening the As−Pd−As′ bond angle to 98.08(2)°, reducing the S−Pd−S′ bond angle to 87.28(5)°, and arranging the interfering phenyl rings parallel to each other (av. phenyl−phenyl distance 4.184 Å).

The palladium atom is in a slightly distorted square-planar environment [As−Pd−S′ 173.95(4)° and As′−Pd−S 174.61(4)°], with this distortion being due to the cis arrangement of both **AsS**$^-$ ligands. The bite angles of the chelate ligand [As−Pd−S 87.30(4) and 87.36(4)°] are similar to that found for the corresponding phosphorus-containing analogue **PS**$^-$ [P−Pd−S chelate angles 87.06(3)° and 87.24(3)°]. Most bond lengths and angles in **2** [Pd−S 2.319(1) and 2.322(1) Å and Pd−As 2.3648(6) and 2.3625(6) Å] are not very different from those found in *cis*-[Pd{(**PS**)-κ^2S,P}$_2$] (Pd−S 2.32 Å and Pd−P 2.28 Å).[17]

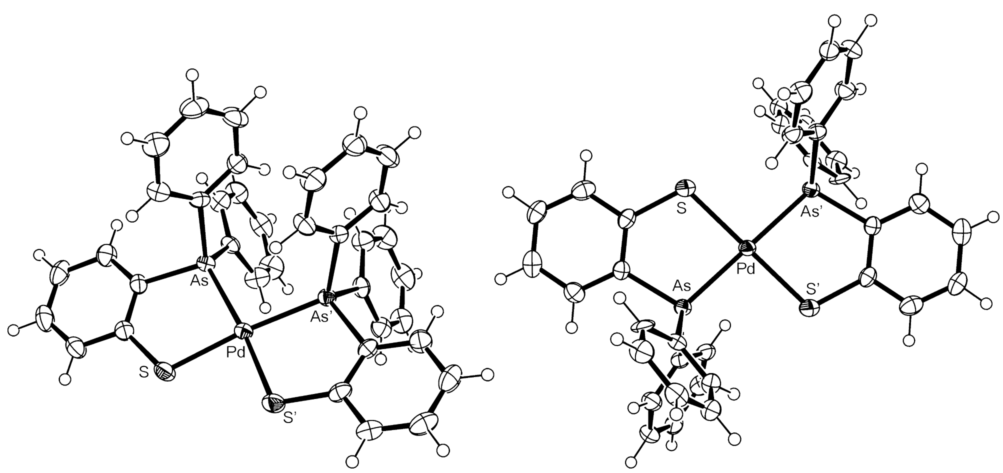


Figure 3. Molecular structures of **2** (left) and **3** (right).

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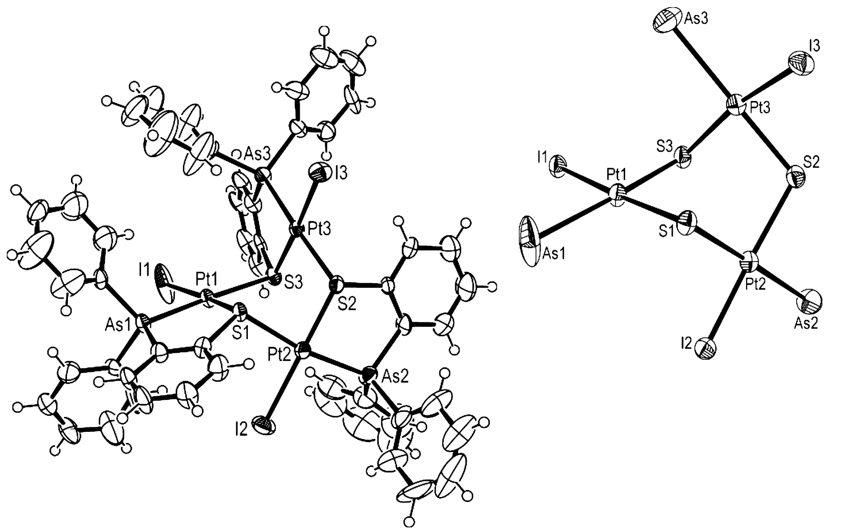

Figure 4. Molecular structures of the trinuclear complex **5** and structure fragment showing the central Pt_3S_3 six-membered ring and the square-planar coordination around the platinum atoms.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in 5

Pt1−S1	2.306(2)	S1−Pt1−As1	86.12(5)	S3−Pt3−As3	87.36(6)
Pt2−S2	2.284(2)	S1−Pt1−S3	91.95(7)	S3−Pt3−S2	91.50(7)
Pt3−S3	2.292(2)	P1−Pt1−S3	177.18(6)	As3−Pt3−S2	175.20(5)
Pt1−S3	2.398(2)	S1−Pt1−I1	172.71(6)	S3−Pt3−I3	176.66(5)
Pt2−S1	2.344(2)	As1−Pt1−I1	86.99(3)	As3−Pt3−I3	92.30(3)
Pt3−S2	2.365(2)	S3−Pt1−I1	95.01(5)	S2−Pt3−I3	89.11(5)
Pt1−As1	2.3343(8)	S2−Pt2−P2	87.84(6)	C2−S1−Pt1	107.7(3)
Pt2−As2	2.340(1)	S2−Pt2−S1	83.18(7)	C2−S1−Pt2	111.4(3)
Pt3−As3	2.3455(9)	As2−Pt2−S1	169.55(6)	Pt1−S1−Pt2	101.43(8)
Pt1−I1	2.6021(7)	S2−Pt2−I2	177.58(5)	C20−S2−Pt2	107.5(3)
Pt2−I2	2.6208(7)	As2−Pt2−I2	93.30(3)	C20−S2−Pt3	104.0(3)
Pt3−I3	2.6148(7)	S1−Pt2−I2	95.89(5)	Pt2−S2−Pt3	109.43(8)
				C38−S3−Pt3	106.3(3)
				C38−S3−Pt1	107.6(3)
				Pt3−S3−Pt1	98.79(8)

In solution, **2** undergoes slow isomerization to **3** (Figure 3). In **3**, the palladium atom is situated in a strictly square-planar environment (As−Pd−As′ 180° and S−Pd−S′ 180°). The bite angle As−Pd−S of 86.82(3)° is slightly smaller than those found for the cis isomer **2**.

Deep-yellow prisms of **4** crystallized with one molecule of dichloromethane in the asymmetric unit. The structure is isotypic to that of the palladium complex **2** (Figure 3, left). The platinum atom is in a distorted square-planar arrangement [As−Pt−S′ 173.86(4)°, As′−Pt−S 174.33(4)°] (Table 2). The arsenic atoms are in a cis position, and the average distance between the phenyl rings in the molecule is 4.177 Å. The Pt−S (av. 2.31 Å) and Pt−As (av. 2.35 Å) bond distances and the bite angle As−Pt−S of 87.62(4)° are similar to those found in the methyl-substituted analogue *trans*-[Pt{(1-$AsMe_2$-2-S-C_6H_4)-κ^2*S*,*As*}$_2$] [Pt−S 2.308(3) Å and Pt−As 2.354(1) Å; As−Pt−S 87.7°][7f] and in the phosphorus analogue *cis*-[Pt{(**PS**)-κ^2*S*,*P*}$_2$] (2.31 Å).[19]

Molecular Structure of 5. Trinuclear complex **5** contains a six-membered Pt_3S_3 ring with a twist−boat conformation and nonsymmetrical Pt−S−Pt thiolato bridges (Figure 4 and Table 3). Each ligand chelates one platinum atom to give a $PtSC_2As$ ring. The sulfur atoms bridge the platinum atoms to give a central Pt_3S_3 ring. The fourth coordination site at platinum is occupied by a terminally bonded iodo ligand.

The structures of several trinuclear complexes of platinum with bridging sulfur atoms have been described;[37,38] however, none contain an arsanylthiolato ligand. Geometry-related structures were found in the platinum complex of 2-(dimethylamino)ethanethiol, [{PtBr(μ-S-$CH_2CH_2NMe_2$-κ^2*N*,*S*)}$_3$], which contains a central Pt_3S_3 ring with nearly symmetrical Pt−S−Pt thiolato bridges [Pt1−S1 2.255(4) Å and Pt1−S3 2.285(4) Å][38] and in trimeric complexes [{PtI(1-P(Biph)-μ-2-S-C_6H_4-κ^2*S*,*P*)}$_3$][31] and [PtI{(μ-*S*-SC_6H_4-2-PPh_2)-κ^2*S*,*P*}]$_3$.[32]

In **5**, each sulfur atom is coordinated to two platinum atoms with one shorter (trans to iodine av. 2.29 Å) and one longer bond (trans to arsenic av. 2.37 Å; Table 3). The Pt−S bond lengths are in the range observed for dimeric platinum(II) complexes containing nonchelating thiolato bridges of the type [{PtX(μ-SR′)(PR_3)}$_2$] (X = Cl, I; R = Pr, Ph; R′ = Et, $CH_2CH_2CMe{=}CH_2$).[39,40] The Pt−I bond lengths are comparable to those found in [{PtI(μ-$SCH_2CH_2CMe{=}CH_2$)-(PPh_3)}$_2$] (2.62 Å).[40] The distances between the platinum atoms in **5** are all greater than 3.56 Å and thus indicate no metal−metal bonding.

The geometry at sulfur is distorted trigonal pyramidal [i.e., C2−S1−Pt1 107.7(3)°, C2−S1−Pt2 111.4(3)°, and Pt1−S1−Pt2 101.43(8)°]. The Pt−As bond lengths and the chelate angle at the platinum atom in **5** are similar to those found in the monomeric complex **4**.

Theoretical Study of Cis−Trans Isomerism. Density functional theory calculations predict practically isoenergetic cis and trans isomers for [Ni{(**AsS**)-$\kappa^2 S,As$}$_2$] (Table 4). However, the trans isomer **1** is slightly favored over the corresponding cis isomer in terms of relative energy. This trend is also in agreement with experimental observations. For [Pt{(**AsS**)-$\kappa^2 S,As$}$_2$], the cis isomer **4** is thermodynamically favored over the corresponding trans isomer (Table 4). This explains why only **4** has been obtained experimentally. For [Pd{(**AsS**)-$\kappa^2 S,As$}$_2$], the cis and trans isomers are again predicted to be isoenergetic (Table 4). To explain the observed cis-to-trans isomerization, the dissociative mechanism suggested by Romeo and co-workers[41] was investigated for the palladium complexes, along with a square planar−tetrahedral (triplet)−square planar pathway. The singlet−triplet splitting energies predict an increasing trend for the isomerization barriers, in the order Ni < Pd < Pt (Table 4). The same trends were also predicted for the related complexes [M{(PBiph)-$\kappa^2 S,P$}$_2$] (M = Ni, Pd, Pt). However, the $\pi-\pi$ interactions between two Biph moieties are much stronger than those between two phenyl rings, as evidenced by experiment and theory.[31] The dissociative cis/trans isomerization mechanism of [Pd{(**AsS**)-$\kappa^2 S,As$}$_2$] involves a Y-shaped transition state (**TS** in Figure 5) lying above **2** by 139.8 kJ mol^{-1} in terms of relative energy (Table 4). This isomerization barrier is lower than the relative energy of the triplet isomer. Thus, the dissociative mechanism is slightly favored over the square planar−tetrahedral−square planar pathway. Following the normal mode associated with the imaginary frequency of **TS** leads to the T-shaped cis- and trans-like intermediates **I** and **II**, respectively (Figure 5). Both intermediates are characterized by a Pd−η^3-AsPh agostic interaction similar to the η^3-metal−benzyl linkage described by Guido et al.[41a] Natural bond orbital analysis[42] of **I** and **II** revealed donation of the electron density from the As−C σ bond to an unoccupied p orbital at Pd as the main contribution to the stabilizing Pd−η^3-AsPh agostic interaction. Additionally, one of the π_{C-C} bonding orbitals of the phenyl ring also donates electron density to the p orbital at Pd. The cis-like intermediate **I** lies at a higher relative energy than the trans-like intermediate **II**; that is, the balance of the cis/trans isomerization reaction is shifted toward the trans isomer.

Table 4. Zero-Point-Energy-Corrected Relative Energies (kJ mol^{-1}) of All Investigated Structures [M{(AsS)-$\kappa^2 S,As$}$_2$] (M = Ni, Pd, Pt)

cis-[Ni{(**AsS**)-$\kappa^2 S,As$}$_2$]	2.8
1	0.0
[Ni{(**AsS**)-$\kappa^2 S,As$}$_2$] (triplet)	78.8
2	0.0
3	2.2
[Pd{(**AsS**)-$\kappa^2 S,As$}$_2$] (triplet)	150.7
I	116.1
TS	139.8
II	91.6
4	0.0
trans-[Pt{(**AsS**)-$\kappa^2 S,As$}$_2$]	10.1
[Pt{(**AsS**)-$\kappa^2 S,As$}$_2$] (triplet)	182.7

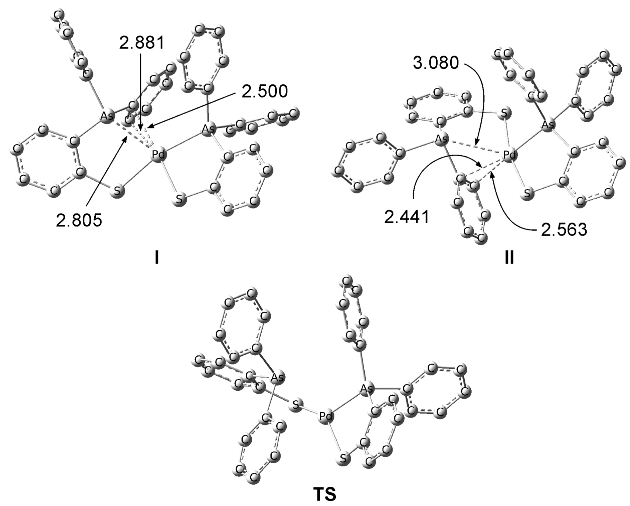

Figure 5. Optimized [Pd{(**AsS**)-$\kappa^2 S,As$}$_2$] intermediates (**I** and **II**) and transition state (**TS**) along the dissociative cis/trans isomerization pathway. The distances between the atoms involved in the Pd−η^3-AsPh agostic interactions are also shown (in Å).

■ CONCLUSIONS

Reactions of the new heteropolytopic arsanylthiolato ligand **AsSH** with group 10 metal(II) complexes in a 2:1 ratio afforded square-planar complexes [M{(1-AsPh$_2$-2-S-C$_6$H$_4$)-$\kappa^2 S,As$}$_2$] ([M{(**AsS**)-$\kappa^2 S,As$}$_2$], M = Ni, Pd, Pt). Only one isomer was isolated in the case of nickel and platinum, **1** and **4**, whereas for palladium, the initially formed cis product **2** undergoes slow isomerization to **3** in solution. Besides mononuclear platinum bis-chelate complex **4**, the unexpected trinuclear complex **5** is also formed.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data of complexes **1**−**5** in CIF format, Table S1 with the computed energies for **1**−**4**, and optimized Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

§Deceased as of Dec 2009. He will be missed.

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