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PAPER

Reaction of a heterotopic P,SAs ligand with group 10 metal(II) complexes: As–S bond cleavage and the formation of two unusual trinuclear structural isomers for Pd and Pt†

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The synthesis of the heterotopic P,SAs ligand, 1-$Ph_2AsSC_6H_4$-2-PPh_2 (**1**) and its reaction with [$PdCl_2$(cod)], [PtI_2(cod)] (cod = 1,5-cyclooctadiene) and $NiCl_2 \cdot 6H_2O$ is reported. Cleavage of the As–S bond of **1** and coordination of the resulting phosphanylthiolato ligand $(SC_6H_4\text{-2-}PPh_2)^-$ (SC_6H_4-2-PPh_2 = P,S) was observed with formation of [M(P,S)$_2$] (M = Ni, Pd, Pt). In the case of Pd and Pt, not only the mononuclear complexes [M(P,S)$_2$] formed, but also the trimers of [MX(P,S)] ([MX{(μ-*S*-SC_6H_4-2-PPh_2)-κ^2*S*,*P*}]$_3$ [M = Pd, X = Cl (**2**) and M = Pt, X = I (**4**)]). Formation of **2** and **4** was preceded by the trinuclear isomeric intermediates [(*cis*-M{(μ-*S*-SC_6H_4-2-PPh_2)-κ^2*S*,*P*}$_2$)-MX_2-MX{(μ-*S*-SC_6H_4-2-PPh_2)-κ^2*S*,*P*}] [M = Pd, X = Cl (**3**) and M = Pt, X = I (**5**)]. The crystal structures of **1–5** and a possible reaction mechanism that leads to **2** and **4** are presented.

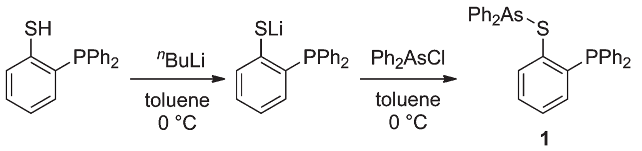
Introduction

Various derivatives of phosphanyl- and arsanyl thiolates have been explored as heterotopic ligands in transition metal complexes.[1] One of the most prominent E,S (E = P, As) ligands is HSC_6H_4-2-EPh_2, in which the thiol group is rapidly deprotonated and may serve as a versatile donor in phosphanyl- and arsanyl thiolato complexes.[2,3] These mixed-donor (E,S) ligands tend to form mononuclear metal complexes [M(E,S)$_2$].[1,3] On the other hand, the reaction of the structurally isomeric thioarsines and thiophosphines EPh_2(SPh) (E = P, As)[4,5] with metal carbonyls resulted in metal-mediated E–S bond cleavage. Thus, reactions with [$Fe(CO)_5$], [$FeCp(CO)_2$]$_2$ (Cp = C_5H_5), [$Co_2(CO)_8$], [Co_2(μ-HCCH)$(CO)_6$], [$Mn_2(CO)_{10}$] and complexes with mixed metal centers (Co–Mo) usually lead to a variety of sulfur- and phosphorus- or arsenic-containing metallacycles.[6,7] We now report the synthesis of heterotopic P,SAs ligand, 1-$Ph_2AsSC_6H_4$-2-PPh_2 (**1**), which may not only combine the properties of phenylthio(diphenyl)arsine and 2-diphenylphosphanylbenzenethiol, but may also exhibit a wide range of possible bonding modes and may allow the effect of the PPh_2 group in the *ortho* position on the cleavage of the As–S bond to be studied. Furthermore, **1** could act as a potentially tridentate ligand for a wide range of metals. Here, the synthesis, spectroscopic characterization and reactions of **1** with palladium(II), platinum(II) and nickel(II) complexes are reported.

Results and discussion

The synthesis of **1** starts with the *ortho*-lithiation of the thiophenol followed by reaction with Ph_2PCl.[2,8] The mono-lithiation of the resulting phosphanylarylthiol, HSC_6H_4-2-PPh_2, allowed introduction of the third donor group through reaction with Ph_2AsCl (Scheme 1).

Crystals of **1** were obtained from a saturated solution of **1** in diethyl ether. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with two independent molecules in the asymmetric unit (Table 4). They differ mainly in the orientation of one phenyl substituent at the arsenic position and, thus, further discussion will focus on only one molecule (Fig. 1). The phosphorus and arsenic atoms are in a slightly distorted trigonal–pyramidal environment (Table 1). The C–E–C bond angles are similar to those found in phosphanylarylthiols,[9] *o*-(diphenylphosphanyl)thioanisole[10] and thioacylsulfanylarsines.[11] The P–C bond lengths are in the expected range.[12] The As–S bond length



Scheme 1 Synthesis of 1-$Ph_2AsSC_6H_4$-2-PPh_2 (**1**).

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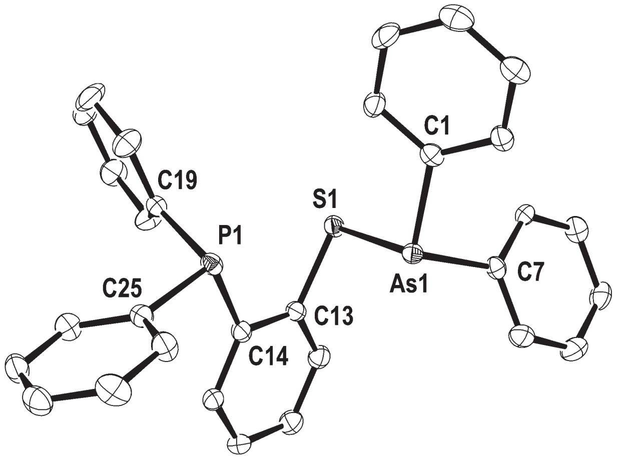


Fig. 1 Molecular structure of 1-Ph_2AsS-2-PPh_2-C_6H_4 (**1**). Only one of the two independent molecules is shown. Hydrogen atoms are omitted for clarity.

Table 1 Selected bond lengths (pm) and angles (°) in **1**

As(1)–S(1)	226.6(1)	C(1)–As(1)–C(7)	100.7(5)
S(1)–C(13)	178.4(4)	C(1)–As(1)–S(1)	99.2(2)
P(1)–C(19)	183.7(4)	C(7)–As(1)–S(1)	98.3(2)
P(1)–C(14)	183.8(4)	C(13)–S(1)–As(1)	94.4(2)
P(1)–C(25)	184.3(4)	C(19)–P(1)–C(14)	102.2(2)
		C(19)–P(1)–C(25)	103.2(2)
		C(14)–P(1)–C(25)	100.7(2)

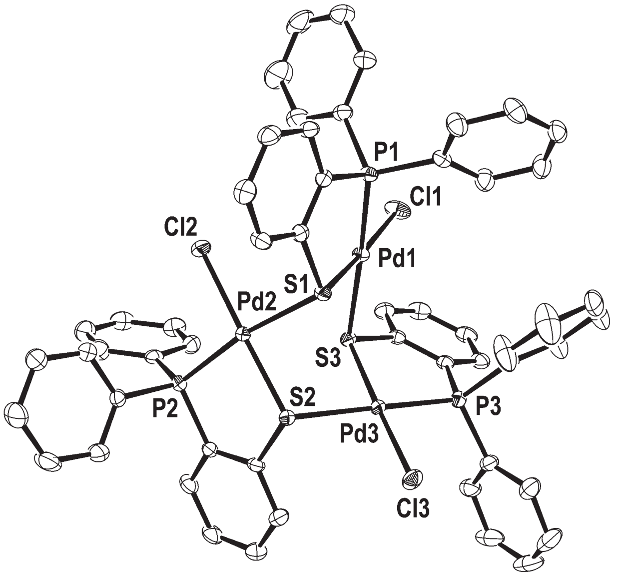


Fig. 2 Molecular structure of $[PdCl\{(\mu\text{-}S\text{-}SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa^2S,P\}]_3$ (**2**). Hydrogen atoms and solvent molecules are omitted for clarity.

and the C–S–As bond angle show no remarkable deviations from other organic arsenic(III) compounds (As–S: 222.8(5) pm[13] to 233.0(6) pm;[14] C–S–As: 92(1)° to 105.8(2)°).[11,15]

Palladium(II) and platinum(II) complexes **2–5** were synthesized by reaction of **1** with $[MX_2(cod)]$ (M = Pd, X = Cl; M = Pt, X = I; cod = 1,5-cyclooctadiene) in a 1 : 1 ratio. Shorter reaction times (4 h, M = Pd; 1 week, M = Pt) gave the trinuclear complexes $[(cis\text{-}M\{(\mu\text{-}S\text{-}SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa^2S,P\}_2)\text{-}MX_2\text{-}MX\{(\mu\text{-}S\text{-}SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa^2S,P\}]$ [M = Pd, X = Cl (**3**); M = Pt, X = I (**5**)], while the trimeric trinuclear isomers $[MX\{(\mu\text{-}S\text{-}SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa^2S,P\}]_3$ [M = Pd, X = Cl (**2**); M = Pt, X = I (**4**)] were obtained after reaction times of two weeks. The isolated trinuclear isomeric products, **2** and **4** or **3** and **5**, contain only the P,S-coordinating phosphanylarylthiolato ligand. The eliminated $AsPh_2$ group was observed in the filtrate after isolation of **2–5** by MS-ESI spectrometry, which showed different oxidized species of dimerized $AsPh_2$. Scission of the As–S bond has been observed also in reactions of thioarsines with different metal carbonyls, leading to a variety of metal-, sulfur- and arsenic-containing cyclic products.[7] The metal-mediated breaking of the As–S bonds in inorganic molecules, such as As_4S_4, has received considerable attention,[16] but the cleavage of As–S bonds in thioarsines has been less explored. The $^{31}P\{^1H\}$ NMR spectra of palladium complex **2** showed a singlet at δ = 55.7; for platinum complex **4** a singlet at δ = 32.5 with the corresponding satellites ($J_{P,Pt}$ = 3285 Hz) was observed. In both reactions, the formation of intermediates can be observed by $^{31}P\{^1H\}$ NMR spectroscopy. After 4 h, the reaction mixture of the palladium complex showed three singlets with the same intensity at δ = 53.7, 48.8 and 47.2, which can be attributed to trinuclear palladium complex **3**. After 24 h, the peak for symmetric trimer **2** was also visible. Trinuclear complex **3** was isolated as dark orange crystals from the reaction medium after a reaction time of 4 h. Once re-dissolved, transformation of pristine **3** into trimer **2** commences. At room temperature, full conversion takes approximately three weeks. During the formation of **2**, a signal at δ = 48.6 with a minor intensity rises as well. This peak is characteristic for the presence of the *cis* bis-chelate, which has already been reported in the literature.[17] The $^{31}P\{^1H\}$ NMR spectra of the reaction medium of the platinum complex after 4 h showed two singlets with corresponding satellites at δ = 50.2 ($J_{P,Pt}$ = 2646 Hz) and δ = 32.5 ($J_{P,Pt}$ = 3285 Hz); the former can be assigned to the *trans* bis-chelate based on the chemical shift and coupling constants, the latter was found to belong to trimeric platinum complex **4**. After a few days, *trans*/*cis* isomerization of the bis-chelate complex can be observed in solution; the appearance of a signal for the *cis* isomer at δ = 42.3 ($J_{P,Pt}$ = 2915 Hz) is accompanied by a decrease of the peak for the *trans* isomer. Three additional signals of equal intensity with satellites are observed at δ = 35.0 ($J_{P,Pt}$ = 3131 Hz), δ = 33.1 ($J_{P,Pt}$ = 3419 Hz) and δ = 30.3 ($J_{P,Pt}$ = 2989 Hz) for trinuclear complex **5**. Complex **5** was isolated as dark orange crystals. Transformation into the more stable isomeric symmetric trimer takes place at room temperature over two weeks. In contrast, the 1 : 1 reaction of **1** and $NiCl_2 \cdot 6\ H_2O$ resulted in scission of the As–S bond and formation of the known complex, $trans\text{-}[Ni\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa^2S,P\}_2]$[18,19] (**6**), in just a few hours as the only phosphorus-containing compound, even after prolonged standing in solution. Complexes **2–4** crystallize in the monoclinic space group $P2_1/c$ and compound **5** in $P2_1/n$ with four molecules in the unit cell (Table 4). They consist of a six-membered M_3S_3 ring (M = Pd, Pt), in which the S atoms of the phosphanylthiolato ligand act as bridges between two metal atoms. In the case of the symmetric trimeric complexes **2** (Fig. 2) and **4** (Fig. 3), each P atom additionally binds to one metal center resulting in MSC_2P rings.

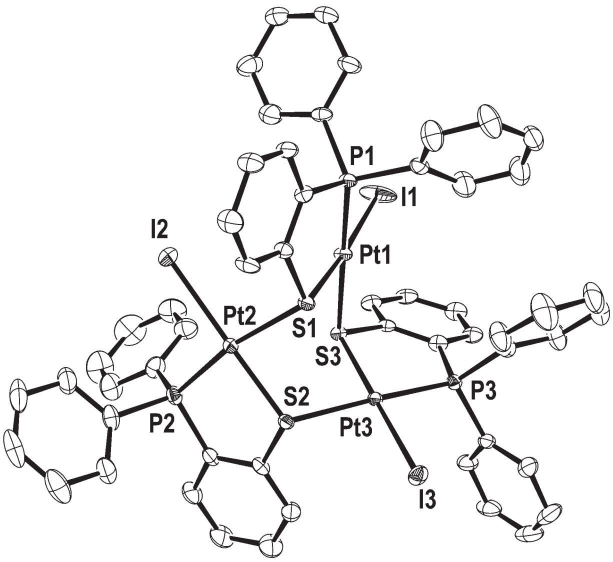


Fig. 3 Molecular structure of [PtI{(μ-*S*-SC$_6$H$_4$-2-PPh$_2$)-κ^2*S,P*}]$_3$ (**4**). Hydrogen atoms and solvent molecules are omitted for clarity.

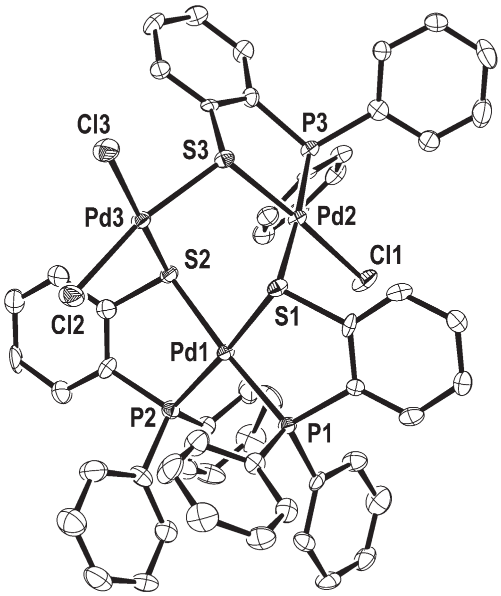


Fig. 4 Molecular structure of [(*cis*-Pd{(μ-*S*-SC$_6$H$_4$-2-PPh$_2$)-κ^2*S,P*}$_2$)-PdCl$_2$-PdCl{(μ-*S*-SC$_6$H$_4$-2-PPh$_2$)-κ^2*S,P*}] (**3**). Hydrogen atoms and solvent molecules are omitted for clarity.

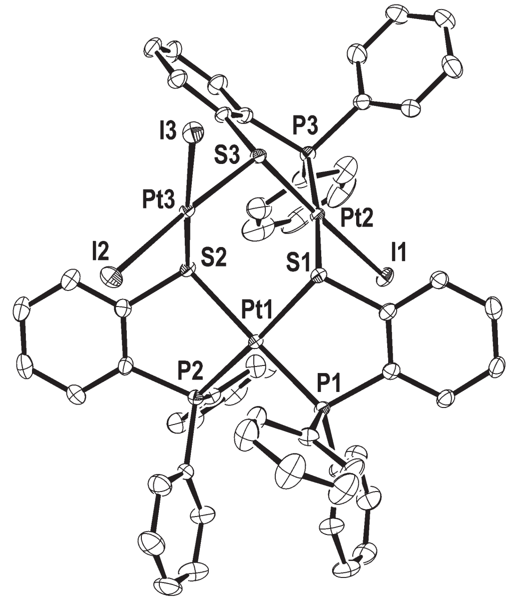


Fig. 5 Molecular structure of [(*cis*-Pt{(μ-*S*-SC$_6$H$_4$-2-PPh$_2$)-κ^2*S,P*}$_2$)-PtI$_2$-PtI{(μ-*S*-SC$_6$H$_4$-2-PPh$_2$)-κ^2*S,P*}] (**5**). Hydrogen atoms and solvent molecules are omitted for clarity.

Table 2 Selected bond lengths (pm) and angles (°) for **2** and **4**

	2 (M = Pd)	**4** (M = Pt)
M(1)–P(1)	223.0(6)	222.8(1)
M(1)–S(1)	228.8(6)	230.2(1)
M(1)–S(3)	242.5(6)	242.8(1)
M(2)–P(2)	223.4(6)	223.6(1)
M(2)–S(2)	227.3(5)	227.3(1)
M(2)–S(1)	237.3(6)	237.3(1)
M(3)–P(3)	223.4(7)	223.5(2)
M(3)–S(3)	228.7(6)	228.8(1)
M(3)–S(2)	240.5(6)	238.7(1)
P(1)–M(1)–S(1)	86.1(2)	86.3(4)
S(1)–M(1)–S(3)	91.2(2)	91.1(4)
P(2)–M(2)–S(2)	86.7(2)	88.2(4)
S(2)–M(2)–S(1)	84.4(2)	81.9(4)
P(3)–M(3)–S(3)	86.5(2)	88.1(4)
S(3)–M(3)–S(2)	93.1(2)	91.6(4)
C(2)–S(1)–M(1)	105.6(8)	105.2(2)
C(20)–S(2)–M(2)	105.4(8)	105.2(2)
C(38)–S(3)–M(3)	105.3(8)	103.8(2)
M(1)–S(1)–M(2)	97.3(2)	99.8(4)
M(2)–S(2)–M(3)	105.6(2)	109.7(4)
M(3)–S(3)–M(1)	103.9(2)	100.4(4)

Every metal atom is thus coordinated by two S, one P and one terminally bound X atom [X = Cl (**2**), I (**4**)] in a distorted square planar fashion, with the two sulfur atoms in a *cis* arrangement. The M$_3$S$_3$ ring has a twist-boat conformation. Complexes **3** (Fig. 4) and **5** (Fig. 5) are built up of three subunits: a *cis* bis-chelate M(P,S)$_2$ is connected through the S atoms to an MX(P,S) and an MX$_2$ unit to form the M$_3$S$_3$ ring. As expected for a chelate ligand, due to the fixed geometry, the smallest bond angle at each metal atom is the intrachelate P–M–S angle (Tables 2 and 3), which is in the range found for *cis* bis-chelates.[17,20] Complexes **2** and **4** have a very small S–M–S bond angle, possibly due to steric constraints in the six-membered ring. However, the two other corresponding S–M–S bond angles are larger and the average value is close to 90°, as expected for a square planar environment at Pd and Pt. The S–M–S bond angle in the *cis* bis-chelates [M(P,S)$_2$] (M = Pd, Pt)[17,20] is well below 90° due to the relatively bulky PPh$_2$ fragments, but in complexes **3** and **5** this angle exceeds 90° (Table 3), which facilitates the formation of the M$_3$S$_3$ ring. Each trigonal–pyramidal sulfur atom coordinates to two metal atoms with one shorter and one longer bond. The intramolecular M···M distances are all greater than 356 pm, indicating no metal–metal bonding.

The structures of several trinuclear platinum[3,21–23] and palladium[24,25] complexes with bridging sulfur atoms have been described, but none of them contain the $(SC_6H_4\text{-}2\text{-}PPh_2)^-$ ligand. Related structures to **2** and **4** were found in $[PtBr\{(\mu\text{-}S\text{-}CH_2CH_2NMe_2)\text{-}\kappa^2 N,S\}]_3$, with nearly symmetric Pt–S–Pt thiolato bridges[22] in $[Pd\{2\text{-}CH_2\text{-}5\text{-}MeC_6H_3C(H){=}NN{=}C(S)NHEt\}]_3$, in which the S–Pd–S angles were almost identical,[25] and in $[PtI\{(\mu\text{-}S\text{-}SC_6H_4\text{-}2\text{-}AsPh_2)\text{-}\kappa^2 S,As\}]_3$[3] and $[PtI\{(\mu\text{-}S\text{-}SC_6H_4\text{-}2\text{-}P(Biph)\}\text{-}\kappa^2 S,P\}]_3$ (Biph = 1,1′-biphenyl).[23] However, the distortion of the ring is more pronounced in $[PtI\{(\mu\text{-}S\text{-}SC_6H_4\text{-}2\text{-}P(Biph))\text{-}\kappa^2 S,P\}]_3$ due to the greater rigidity introduced by the biphenyl groups.

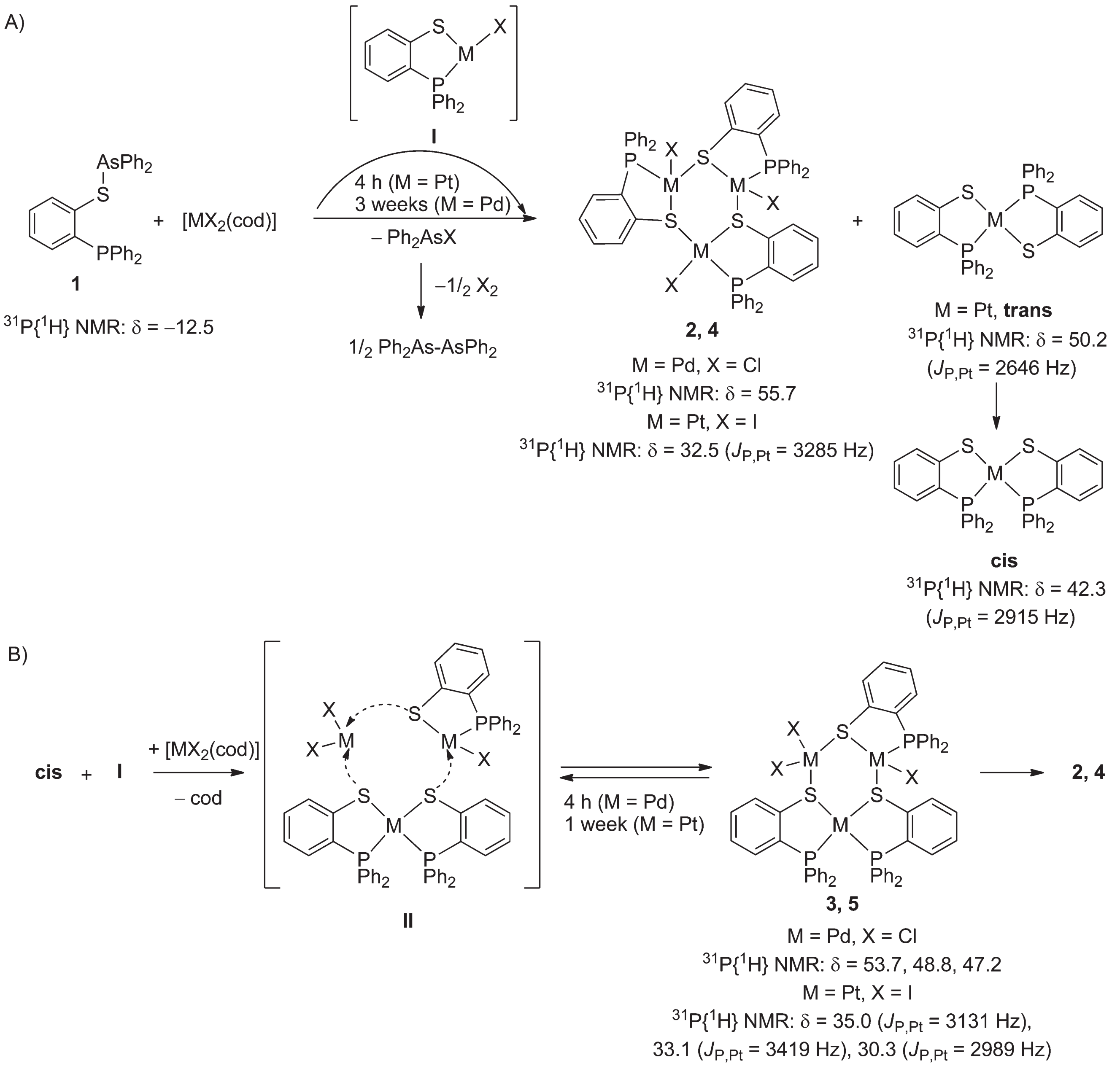
Table 3 Selected bond lengths (pm) and angles (°) for **3** and **5**

	3 (M = Pd)	**5** (M = Pt)
M(1)–P(2)	225.9(2)	225.3(9)
M(1)–P(1)	227.5(2)	225.7(8)
M(1)–S(1)	234.6(2)	235.7(8)
M(1)–S(2)	233.9(2)	236.1(8)
M(2)–P(3)	222.3(2)	222.4(9)
M(2)–S(3)	227.6(2)	228.6(8)
M(2)–S(1)	237.1(2)	237.8(8)
M(3)–S(2)	228.6(2)	230.7(8)
M(3)–S(3)	230.7(2)	231.0(8)
P(2)–M(1)–P(1)	98.4(7)	99.9(3)
P(2)–M(1)–S(2)	85.6(6)	84.5(3)
P(1)–M(1)–S(1)	84.1(6)	88.9(3)
S(2)–M(1)–S(1)	92.1(6)	91.9(3)
P(3)–M(2)–S(3)	87.7(6)	86.9(3)
S(3)–M(2)–S(1)	86.1(6)	84.7(3)
S(2)–M(3)–S(3)	89.1(6)	87.3(3)
C(2)–S(1)–M(1)	104.6(2)	104.7(1)
M(1)–S(1)–M(2)	92.8(6)	91.4(3)
C(20)–S(2)–M(1)	104.6(2)	103.1(1)
M(3)–S(2)–M(1)	102.8 (7)	103.6(3)
C(38)–S(3)–M(2)	105.0(2)	104.6(1)
M(2)–S(3)–M(3)	107.5(7)	110.2(3)

Ligands containing mixed donors (P,S) are known to form mononuclear complexes $[M(P,S)_2]$.[1] Thus, $HSC_6H_4\text{-}2\text{-}PPh_2$ reacts with palladium(II) and platinum(II) complexes in the presence of a base (NEt_3), which facilitates the deprotonation of the S atom, to give the bis-chelates.[17,26,27] In the present study, the reaction of **1** with $[PdCl_2(cod)]$ and $[PtI_2(cod)]$ resulted in the formation of trimers. Formation of the bis-chelates seems to be kinetically more favored, as the $^{31}P\{^1H\}$ NMR spectra of the reaction mixture of the Pt complex shows the *trans* bis-chelate complex as the major reaction product after 4 h. To facilitate formation of the trinuclear complex, the *trans* bis-chelate complex must isomerize to the *cis* form (Scheme 2A). During the isomerization process, which could occur through an unbinding–binding mechanism and in illustration of the hemilabile properties of the P,S ligand, not only the conversion of the *trans* bis-chelate into the *cis* isomer occurs; the formation of monomeric $[MX(P,S)]$ is facilitated as well, due to the presence of unconverted $[MX_2(cod)]$ in solution. However, no signal is visible in the $^{31}P\{^1H\}$ NMR spectrum for $[MX(P,S)]$, that is, the subsequent formation of trinuclear complexes **3** and **5** is very fast. Rearrangement to the more stable trimeric form, the final thermodynamic products **2** and **4**, occurs over about three weeks at room temperature in THF (Scheme 2B). The formation of *trans*-

Table 4 Crystallographic data for compounds **1–5**

	1	**2**	**3**	**4**	**5**
Formula	$C_{30}H_{24}AsPS$	$C_{54}H_{42}Cl_3P_3Pd_3S_3{\cdot}CH_2Cl_2$	$C_{54}H_{42}Cl_3P_3Pd_3S_3{\cdot}2CH_2Cl_2$	$C_{54}H_{42}I_3P_3Pt_3S_3{\cdot}2CH_2Cl_2$	$C_{54}H_{42}I_3P_3Pt_3S_3{\cdot}2.5CHCl_3$
M_r	522.44	1390.44	1475.37	2015.79	2144.36
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/pm	1048.30(2)	1963.05(2)	1707.82(4)	2333.81(4)	1421.75(2)
b/pm	987.97(3)	1140.76(1)	1194.68(3)	1144.52(1)	2306.16(3)
c/pm	4848.1(1)	2395.33(2)	2835.40(7)	2393.86(4)	2029.71(3)
α/°	90	90	90	90	90
β/°	93.390(2)	96.739(1)	100.312(2)	112.458(2)	105.754(1)
γ/°	90	90	90	90	90
V/nm^3	5.0123(2)	5.32697(8)	5.6916(2)	5.9093(2)	6.4050(2)
Z	8	4	4	4	4
D_{calcd}/g cm^{-3}	1.385	1.734	1.722	2.266	2.224
μ(MoKα)/mm^{-1}	1.520	1.498	1.499	9.057	8.505
F(000)	2144	2760	2928	3744	3988
Crystal size/mm^3	0.4 × 0.4 × 0.07	0.2 × 0.2 × 0.1	0.38 × 0.05 × 0.03	0.27 × 0.11 × 0.09	0.3 × 0.15 × 0.15
θ range/°	2.84–30.51	2.81–30.51	2.87–26.37	2.83–30.51	2.83–30.51
hkl range	$-14 \le h \le 10$ $-14 \le k \le 14$ $-60 \le l \le 69$	$-21 \le h \le 28$ $-15 \le k \le 16$ $-34 \le l \le 29$	$-21 \le h \le 21$ $-14 \le k \le 14$ $-35 \le l \le 35$	$-32 \le h \le 33$ $-16 \le k \le 16$ $-34 \le l \le 34$	$-20 \le h \le 20$ $-32 \le k \le 32$ $-28 \le l \le 28$
Refl. collected	45 613	45 773	44 068	72 568	3988
Refl. unique	15 249 [R_{int} = 0.0457]	16 241 [R_{int} = 0.0402]	11 622 [R_{int} = 0.0999]	18 027 [R_{int} = 0.0424]	19 523 [R_{int} = 0.0396]
Param. refined	595	634	649	649	724
GoF on F^2	1.124	0.809	1.080	1.025	1.040
R_1 [$I > 2\sigma(I)$]	R_1 = 0.0721 wR_2 = 0.1300	R_1 = 0.0303 wR_2 = 0.0486	R_1 = 0.0691 wR_2 = 0.1048	R_1 = 0.0347 wR_2 = 0.0637	R_1 = 0.0264 wR_2 = 0.0462
R indices (all data)	R_1 = 0.0989 wR_2 = 0.1355	R_1 = 0.0561 wR_2 = 0.0511	R_1 = 0.1129 wR_2 = 0.1182	R_1 = 0.0478 wR_2 = 0.0684	R_1 = 0.0370 wR_2 = 0.0493
$\Delta\rho_{fin}$/e Å^{-3}	1.127 and −1.000	1.627 and −1.173	2.449 and −0.925	7.210 and −4.345	1.769 and −1.728



Scheme 2 The possible steps involved in the formation of complexes **2–5**.

$[Ni\{(SC_6H_4\text{-}2\text{-}PPh_2)\text{-}\kappa^2S,P\}_2]$ (**6**) as the only P-containing reaction product is probably due to the smaller atomic radius of nickel making it more difficult to accommodate both the diphenylphosphanylthiolato ligands in a *cis* conformation. Since the $AsPh_2$ group is eliminated and does not participate in coordination to the metal center, the reaction of $HSC_6H_4\text{-}2\text{-}PPh_2$ with $[PdCl_2(cod)]$ and $[PtI_2(cod)]$ was reinvestigated. The 2 : 1 or 1 : 1 reactions conducted in the presence of NEt_3 always led to the formation of *cis* and *trans* bis-chelates. When the deprotonating agent was excluded from the reaction mixture, exclusive formation of the trinuclear complex was preferred in the reaction with $[PdCl_2(cod)]$, while the reaction with $[PtI_2(cod)]$ led to *cis*- and *trans*-$[M(P,S)_2]$ complexes as the main reaction products and traces of trimeric complex **2**. However, reactions of $[PtI_2(cod)]$ with $HSC_6H_4\text{-}2\text{-}AsPh_2$ or $HSC_6H_4\text{-}2\text{-}P(Biph)$ in the presence of NEt_3 resulted in small amounts of the corresponding trimeric complexes, $[PtI\{(\mu\text{-}S\text{-}SC_6H_4\text{-}2\text{-}AsPh_2)\text{-}\kappa^2S,As\}]_3$ or $[PtI\{(\mu\text{-}S\text{-}SC_6H_4\text{-}2\text{-}P(Biph))\}\text{-}\kappa^2S,P\}]_3$, besides the mononuclear platinum complexes.[3,23] Due to the continuous interconversion of the metal complexes and their poor solubility in common solvents, their separation in a pure form proved to be very difficult and prevented the recording of $^{13}C\{^1H\}$ NMR spectra.

Conclusions

Reactions of **1** with group 10 metal dihalides occurred with cleavage of the As–S bond and coordination of the resulting phosphanylthiolato ligand $(SC_6H_4\text{-}2\text{-}PPh_2)^-$. However, reactions with

[MX_2(cod)] (M = Pd, X = Cl; M = Pt, X = I) led to trinuclear complexes [(*cis*-M{(μ-*S*-SC_6H_4-2-PPh_2)-κ^2*S*,*P*}$_2$)-MX_2-MX{(μ-*S*-SC_6H_4-2-PPh_2)-κ^2*S*,*P*}] [M = Pd, X = Cl (**3**); M = Pt, X = I (**5**)] as the kinetic products, followed by formation of the thermodynamic products [PtI{(μ-*S*-SC_6H_4-2-PPh_2)-κ^2*S*,*P*}]$_3$ (M = Pd, X = Cl (**2**); M = Pt, X = I (**4**)). The isomerization process was observed by $^{31}P\{^1H\}$ NMR spectroscopy; all the structural isomers were isolated and characterized by X-ray structure analysis. In contrast, the reaction of **1** with $NiCl_2 \cdot 6H_2O$ led only to the bis-chelate complex, *trans*-[Ni{(SC_6H_4-2-PPh_2)-κ^2*S*,*P*}$_2$] (**6**).

Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and distilled prior to use by described procedures or by use of a solvent purification system (MB SPS-800). $PdCl_2$ and $H_2[PtCl_6] \cdot 6H_2O$ were used as received and Ph_2AsCl,[28] HSC_6H_4-2-PPh_2,[8] [$PdCl_2$(cod)][29] and [PtI_2(cod)][29] were prepared according to the published procedures. All other reagents were used as received.

Elemental analysis was performed with a VARIO EL-Heraeus microanalyzer. The melting points were determined in sealed capillaries and are uncorrected. The IR spectra were recorded on a Perkin–Elmer System 2000 FTIR spectrometer scanning between 4000 and 400 cm^{-1} using KBr disks. ^1H (400 MHz), ^{13}C (100 MHz) and ^{31}P NMR (162 MHz) spectra were recorded at 24 °C in $CDCl_3$ on a Bruker Avance DRX-400 instrument with TMS as an internal standard (^1H NMR) and 85% H_3PO_4 as an external standard (^{31}P NMR). The mass spectra were recorded on a VG12-520 mass spectrometer (EI-MS, 70 eV, 200 °C) and an FT-ICR-MS Bruker Daltonics ESI mass spectrometer (APEX II, 7 T). The data for the X-ray structures were collected on a Gemini diffractometer (Agilent Technologies) with MoKα radiation (λ = 71.073 pm) and ω-scan rotation. Data reduction was performed with CrysAlisPro including the program SCALE3 ABSPACK for empirical absorption correction (**1**, **2**, **3** and **5**)[30] and a model based on expressions derived by Clark and Reid[31] for the analytical numeric absorption correction using a multifaceted crystal (**4**). The structures were solved by direct methods with the program SIR92 (**1**, **2**, **3** and **5**) or by Patterson methods (**4**) with the program SHELXS-97.[32] Anisotropic refinement of all non-hydrogen atoms was performed with SHELXL-97, except for the disordered solvent molecules in complex **2**. All hydrogen atoms were calculated on idealized positions using the riding model. An analysis with SQUEEZE[33] revealed a small cavity (approximately 20 Å^3 for the asymmetric unit) in the structure of **3** that may be occupied to approximately 28% by water or a similar small molecule. This effect is responsible for the relatively high residual electron density (2.45 e Å^{-3}) and was not taken into account. In the structure of **5**, two of the $CHCl_3$ molecules are disordered. One of them was difficult to localize and was treated as threefold disordered; the other is disordered on a special position (the center of inversion). All 61 restraints were used to model these two molecules. Structure figures were generated with ORTEP.[34] Thermal ellipsoids are drawn at 50% probability unless otherwise mentioned. CCDC 856663 (**1**), 856664 (**2**), 856665 (**3**), 856666 (**4**) and 856667 (**5**) contain the supplementary crystallographic data for this paper.

Synthesis of 1-$Ph_2AsSC_6H_4$-2-PPh_2 (1)

n-Butyllithium (7.72 mL of a 2.2 M solution in *n*-hexane, 16.98 mmol) was slowly added at 0 °C to a stirred solution of HSC_6H_4-2-PPh_2 (5.00 g, 16.98 mmol) in toluene (65 mL). The reaction mixture was stirred for 20 h and allowed to attain room temperature. A pale yellow suspension formed. The reaction vessel was cooled to 0 °C and a solution of chlorodiphenylarsine (2.88 mL, 16.13 mmol) in toluene (5 mL) was slowly added (over 15 min) to the stirred suspension. The solution was stirred for 40 h, until the reaction was completed. The organic phase was separated from the LiCl precipitate by filtration and concentrated *in vacuo*. The oily residue was dissolved in diethyl ether and layered with *n*-hexane. 1-$Ph_2AsSC_6H_4$-2-PPh_2 (**1**) precipitated as a pale yellow solid. Crystals suitable for X-ray structure analysis were obtained from a saturated diethyl ether solution at room temperature over one week. Yield: 7.14 g (84.7%). M. p. 95 °C. Anal. $C_{30}H_{24}AsPS$ (522.44 g mol^{-1}): found (calcd): C 68.56 (68.96); H 4.60 (4.63)%. ^1H NMR: δ = 7.36 (m, 5 H, aryl-H), 7.20 (m, 16 H, aryl-H), 7.06 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H, aryl-H), 6.99 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, aryl-H), 6.65 (d, $^3J_{H,H}$ = 7.2 Hz, 1 H, aryl-H). $^{13}C\{^1H\}$ NMR: δ = 141.44 (d, $J_{C,P}$ = 7.9 Hz), 140.94 (d, $J_{C,P}$ = 28.8 Hz), 140.23, 136.82 (d, $J_{C,P}$ = 11.7 Hz), 134.03 (m), 133.40, 132.84, 129.16, 128.88, 128.49 (m), 127.95, 127.70, 127.46, 127.20. $^{31}P\{^1H\}$ NMR: δ = −12.5 (s). IR (cm^{-1}, KBr disks): 3065 (m), 3046 (m), 1478 (m), 1433 (s), 1091 (m), 1038 (m), 1024 (m), 998 (m), 742 (s), 693 (s), 499 (m), 457 (m), 418 (m). MS-EI: *m*/*z* = 522 (M^+, 7%), 445 (M^+ − Ph, 18%), 293 (M^+ − $AsPh_2$, 95%), 229 ($AsPh_2^+$, 26%), 215 (M^+ − 4Ph, 100%), 183 (M^+ − PPh_2 − 2Ph, 70%), 152 ($AsPh^+$, 35%), 108 (PPh^+, 15%), 77 (Ph^+, 35%).

Synthesis of [PdCl{(μ-*S*-SC_6H_4-2-PPh_2)-κ^2*S*,*P*}]$_3$ (2)

A THF solution (10 mL) of [$PdCl_2$(cod)] (41 mg, 0.143 mmol) was added to a stirred solution of **1** (75 mg, 0.143 mmol) in THF (15 mL). The resulting solution was stirred for two weeks. A pale orange precipitate formed, which was isolated and washed with methanol. Recrystallization from a two-layer solvent system (dichloromethane–*n*-hexane) afforded complex **2** as pale orange crystals in two days at room temperature. Yield: 23.5 mg (12.6%). M.p. 285 °C (decomp.). Anal. $C_{54}H_{42}P_3S_3Pd_3Cl_3$ (1305.65 g mol^{-1}): found (calcd for $C_{54}H_{42}P_3S_3Pd_3Cl_3$ + CH_2Cl_2): C 47.16 (47.50); H 3.27 (3.19); S 7.33 (6.92)%. ^1H NMR: δ = 7.87 (d, $^3J_{H,H}$ = 8 Hz, 3 H, aryl-H), 7.76 (q, $^3J_{H,H}$ = 7.4 Hz, 12 H, aryl-H), 7.37 (m, 21 H, aryl-H), 7.13 (t, $^3J_{H,H}$ = 6.7 Hz, 3 H, aryl-H), 7.04 (t, $^3J_{H,H}$ = 8.4 Hz, 3 H, aryl-H). $^{31}P\{^1H\}$ NMR: δ = 55.7 (s). MS-ESI: *m*/*z* = 1320.80 [M + O]$^+$. The eliminated $AsPh_2$ group was observed in the filtrate by ESI-MS as $(Ph_2AsO)_2$: *m*/*z* = 491.00 [M + H]$^+$.

Synthesis of [(*cis*-Pd{(μ-*S*-SC_6H_4-2-PPh_2)-κ^2*S*,*P*}$_2$)-$PdCl_2$-PdCl-{(μ-*S*-SC_6H_4-2-PPh_2)-κ^2*S*,*P*}] (3)

A THF solution (10 mL) of [$PdCl_2$(cod)] (41 mg, 0.143 mmol) was added to a stirred solution of **1** (75 mg, 0.143 mmol) in THF (15 mL). The resulting solution was stirred for 4 hours and then concentrated. A red–orange precipitate formed, which was isolated and washed with methanol. Recrystallization from a two-layer solvent system (dichloromethane–*n*-hexane) afforded complex **3** as dark orange crystals in a few hours at room temperature. $^{31}P\{^1H\}$ NMR: δ = 53.7 (s), 48.8 (s), 47.2 (s). MS-ESI: *m*/*z* = 1270.82 $[M - Cl]^+$.

Synthesis of [PtI{(μ-*S*-SC_6H_4-2-PPh_2)-κ^2*S*,*P*}]$_3$ (4)

The compound was synthesized as described for complex **2**. Compound **1** (77 mg, 0.147 mmol) was dissolved in THF (15 mL) and $[PtI_2(cod)]$ (82 mg, 0.147 mmol) in THF (10 mL) was added to the solution, which was stirred for two weeks. A yellow solid formed and was separated by filtration and washed with methanol. Recrystallization from a two-layer solvent system (dichloromethane–*n*-hexane) gave complex **4** as pale orange crystals over one week at room temperature. Yield: 46.9 mg (17.3%). M.p. 354 °C. Anal. $C_{54}H_{42}P_3S_3Pt_3I_3$ (1845.97 g mol^{-1}): found (calcd): C 34.78 (35.13); H 2.44 (2.29); S 5.50 (5.21)%. ^1H NMR: δ = 7.91 (d, $^3J_{H,H}$ = 7.4 Hz, 3 H, aryl-H), 7.69 (q, $^3J_{H,H}$ = 7.6 Hz, 12 H, aryl-H), 7.29 (m, 21 H, aryl-H), 6.99 (m, 6 H, aryl-H). $^{31}P\{^1H\}$ NMR: δ = 32.5 (s, $J_{P,Pt}$ = 3285 Hz). MS-ESI: *m*/*z* = 1718.6 $[M - I + H]^+$. The eliminated $AsPh_2$ group was observed in the filtrate by ESI-MS as $(Ph_2AsO)_2$: *m*/*z* = 491.00 $[M + H]^+$.

Synthesis of [(*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*}] (5)

A THF solution (10 mL) of $[PtI_2(cod)]$ (82 mg, 0.147 mmol) was added under stirring to a solution of **1** (77 mg, 0.147 mmol) in THF (15 mL). The resulting solution was stirred for one week and then concentrated. An orange precipitate formed; the product was isolated and washed with methanol. Recrystallization from a saturated chloroform solution at room temperature overnight afforded complex **5** as dark orange crystals. $^{31}P\{^1H\}$ NMR: δ = 35.0 (m, $J_{P,Pt}$ = 3131 Hz), 33.1 (m, $J_{P,Pt}$ = 3419 Hz), 30.3 (m, $J_{P,Pt}$ = 2989 Hz). Due to the low resolution of the $^{31}P\{^1H\}$ NMR spectra, the $J_{P,P}$ values could not be determined. MS-ESI: *m*/*z* = 1717.7 $[M - I]^+$.

Synthesis of *trans*-[Ni{(SC_6H_4-2-PPh_2)-κ^2*S*,*P*}$_2$] (6)

1 (90 mg, 0.172 mmol) was dissolved in THF (15 mL) and $NiCl_2 \cdot 6H_2O$ (41 mg, 0.172 mmol) in THF (10 mL) was added to this solution, which was stirred overnight. A vivid green solid formed and was separated by filtration and washed with methanol. It proved to be the already reported[18] complex **6**. Yield: 50 mg (45.9%). Anal. $C_{36}H_{28}P_2S_2Ni$ (644.05 g mol^{-1}): found (calcd): C 66.59 (66.90); H 4.66 (4.43); S 10.08 (9.94)%. ^1H NMR: δ = 7.66 (q, $^3J_{H,H}$ = 6 Hz, 8 H, aryl-H), 7.46 (m, 6 H, aryl-H), 7.35 (t, $^3J_{H,H}$ = 7.4 Hz, 8 H, aryl-H), 7.16 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, aryl-H), 7.06 (m, 2 H, aryl-H), 6.89 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, aryl-H). $^{31}P\{^1H\}$ NMR: δ = 55.8. MS-EI: *m*/*z* = 644.2 (M^+, 93%), 293 ($[PPh_2\text{-}S\text{-}C_6H_4]^+$, 53%), 215 ($[PPh\text{-}S\text{-}C_6H_4]^+$, 47%), 183 ($[PPh_2]^+$, 100%). The eliminated $AsPh_2$ group was observed in the filtrate by ESI-MS as $(Ph_2AsO)_2$: *m*/*z* = 491.00 $[M + H]^+$.

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