[24] The geometries of the four independent molecules of **3** in the unit cell show very similar values for the Co–Si distances. However, small deviations between 2.25 Å (Co–Si1) and 2.26 Å (Co–Si2) are observed within each molecule in the unit cell.
[25] The steric effect of the more bulky $SiEt_3$ group in the Rh complex elongates the Rh–Si bond distance increasing the expected difference between Rh–Si and Co–Si (see Table 1).
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[27] For calculations of energies and gradients we used the hybrid nonlocal density functional according to Becke and Lee, Yang, and Parr (B3LYP). For all calculations the program Gaussian94 was used with the fine integration grid option. For geometry optimization a gradient convergence criterion of 0.1 E – 6 was used. For C, H, and Si we used the 6-31G* split-valence basis set supplied by the program. For Co we used an effective core potential basis set according to Hay and Wadt with double zeta quality in the valence region.
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[35] Orbital population analysis revealed that the main bonding contribution between the metal atom and the hydrido and silyl ligands arises from their σ bonds. A very small π backbonding from a metal d_{xz} orbital into a Si p_x orbital (about 2 % of the σ bond) also contributes to the Co–Si bond. Some contribution to the stability of the complex appears to arise from the overlap population of Si and the hydrido ligands of 0.1 electrons.
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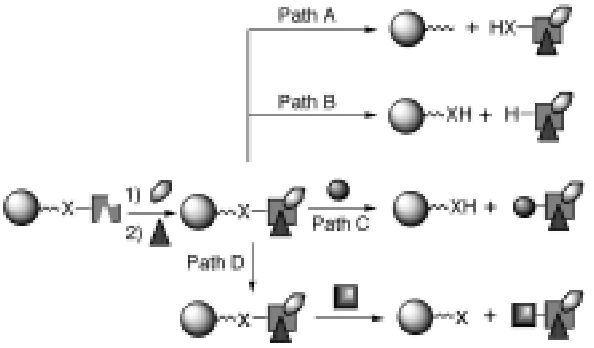
Traceless, Solid-Phase Synthesis of Biarylmethane Structures through Pd-Catalyzed Release of Supported Benzylsulfonium Salts**

Cécile Vanier, Franz Lorgé, Alain Wagner,* and Charles Mioskowski*

Solid-phase synthesis (SPS) has attracted much attention from the scientific community during the past decade, particularly by pharmaceutical companies in their race to speed up drug discovery. Solid-phase chemistry evolved from peptide chemistry and gradually became a field on its own in chemistry.[1] Multi-step processes were automated in a peptide-like fashion, and gave birth to the so-called high-throughput synthesis (HTS).

Under this impulse, new tools for SPS were rapidly developed, for example, new generations of robots and synthesizers, resins, linkers, reactions, and building blocks. However, most of the chemistry performed derives from solution and peptide synthetic studies and do not make full benefit of the use of the solid-support technique. In particular, the most frequently used linkers were designed for peptide-like synthesis. Substrates are therefore linked to the solid support through either an ester, amide, or ether bond. Thus, the cleaved products contain an acid, amide, or hydroxyl residue, respectively, at the former linkage site (Scheme 1, path A).[2]



Scheme 1. Anchoring – cleavage strategies used in SPS.

To avoid a residual functionality on the cleaved product, traceless cleavage strategies were developed (Scheme 1 path B).[3] These strategies result in the formation of a carbon – hygrogen or heteroatom – hydrogen bond and often rely on cyclization/cleavage or *ipso*-aromatic-substitution reactions.[4]

Recently developed synthetic procedures for SPS have allowed the introduction of diversity concomitantly with the release of the target compound (Scheme 1, path C).[5] These advantageous double transformations are generally achieved through nucleophilic cleavage. The resin is thus used both as a protecting group during all preliminary SPS steps, and as a leaving group during the cleavage. These two properties, stability during SPS and reactivity towards cleavage, are somewhat antinomic. The linkages so far reported for such functionalizing cleavage suffer from an enhanced reactivity that forbids the use of many reaction conditions during the SPS sequence.

To overcome this drawback a tether that is stable during SPS steps but becomes reactive after selective activation is used (Scheme 1, path D). An example of such a strategy is the safety-catch linker of Kenner et al.,[6] which is unreactive towards nucleophiles as such, but becomes electrophilic upon activation with diazomethane. Other linkers such as the REM or hydrazide linkers were recently developed based on the same principle.[7] Although they allow efficient cleavage, they are highly specific and can not be used generally.

To the best of our knowledge, no strategy so far reported for the safety-catch linkers enables concomitant formation of a carbon – carbon bond and functionalization within the cleavage step. During the course of our study on the SPS of

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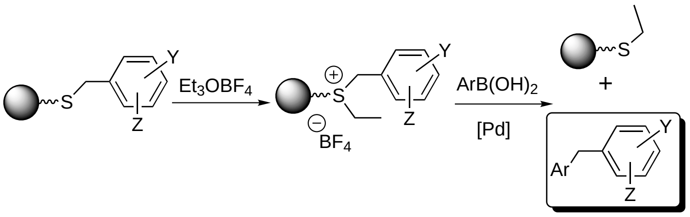
biarylmethane compounds, we were challenged by the problem of attachment and traceless release of these structures. Herein we describe an efficient anchoring/activation/cleavage sequence for traceless, solid-phase synthesis of biarylmethane derivatives. Of particular interest is that, in contrast to biphenyl, biarylmethane structures are rarely found in pharmaceutical compounds, which makes this process attractive for the preparation of original libraries.

A functional arene scaffold is linked to the resin through a benzylic carbon–sulfur bond. This C–S bond is known to be stable under many reaction conditions classically used in SPS, namely acidic, basic, nucleophilic, mild electrophilic, and oxophilic conditions. The activation step consists of the alkylation of the sulfur atom leading to a sulfonium salt. Cleavage from the resin is carried out subsequently by treatment of the resulting supported sulfonium salt through palladium catalysis in the presence an aryl boronic acid. This key reaction allows both the release and the synthesis of the biaryl moiety by formation of a carbon–carbon bond (Scheme 2).

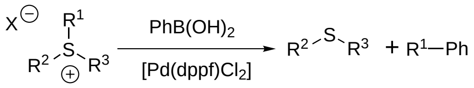


Scheme 2. Coupling–release strategy, which relies on a sulfur/sulfonium switch. Y, Z = functional groups or building blocks.

Very few examples of the use of sulfonium salts as appropriate substrates for Pd-catalyzed cross-coupling reactions are reported in the literature. A recent study performed in the solution phase has demonstrated that aryl- and benzyl-substituted cyclic tetramethylenesulfonium salts can undergo a coupling reaction with boronic acids.[8] However, no mention was made of the relative ease of palladium insertion in the aryl versus the benzyl bond and on the reactivity of acyclic sulfonium salts. Since cyclic tetramethylenesulfonium salts are prepared in one step from a thiol and 1,4-dibromobutane, this sulfonium structure could not be used in the envisioned solid-support sequence. Therefore, before running our strategy, we first carried out a series of experiments to develop and understand the chemistry of acyclic sulfonium salts. To determine a general relative reactivity of aryl–, benzyl–, and alkyl–sulfur bonds towards Pd-catalyzed cross-coupling, several sulfonium salts were synthesized and tested in solution.[9] The most representative results are summarized in Table 1.

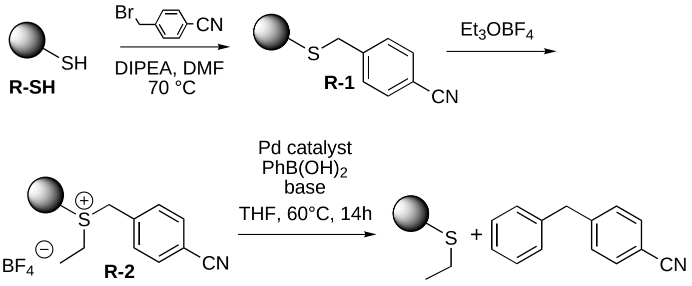
The phenyltetramethylenesulfonium salt (entry 1) underwent efficient Pd-catalyzed cross-coupling to give biphenyl in 85% yield, as described.[8] When the cyclic phenylsulfonium structure was replaced by an acyclic one, namely, homobenzyl and ethyl (entry 2), no coupling reaction was observed. Only partial dealkylation by loss of the ethyl group occurred. Dealkylation of a sulfonium salt has already been reported on a solid support.[10] Interestingly, the sulfonium salt bearing both phenyl and benzyl residues reacted exclusively at the benzylic position (entry 3). Moreover, in contrast to the aryldialkylsulfonium salt (entry 2), the benzyldialkylsulfonium salt (entry 4) gave the coupling product in high yield. Thus, we have shown that acyclic benzylsulfonium salts can undergo this Pd coupling reaction and that they are ideal intermediates for the development of our original safety-catch strategy. According to these results, it appeared appropriate to link the arene scaffold through a benzylic bond to a alkylthiol resin (**R-SH**).[11]

Table 1. Relative reactivity of different carbon–sulfur bonds towards Pd-catalyzed cross coupling with phenyl boronic acid.



Entry	R¹	R²	R³	Yield
1	phenyl	$-(CH_2)_4-$		85
2	phenyl	homobenzyl	ethyl	0
3	benzyl	phenyl	ethyl	68
4	benzyl	homobenzyl	ethyl	85

A series of experiments using a model system was then carried out to optimize the reaction conditions on a solid support (Scheme 3). 4-Cyano-benzylbromide was linked to the alkylthiol resin under classical SPS conditions.[12] The **R-SH** resin was swelled in DMF (1 g per 10 mL), the benzylbromide derivative (3 equiv/resin loading) and *N,N*-diisopropylethylamine (DIEA) (3 equiv/resin loading) were added successively and the slurry heated for 10 h at 70 °C.



Scheme 3. Model system and optimized conditions to carry out the grafting/activation/cleavage sequence.

To validate this first step of the SPS resin **R-1** was subjected to spectral analysis. The ^{13}C NMR spectrum was recorded by using a procedure we recently reported.[13] Each carbon atom of the linker could be identified, with the sulfur-substituted benzyl and alkyl carbon atoms at $\delta = 40.5$ and 35.5, respectively, being especially clear. Though not quantitative, NMR spectroscopy gave good evidence that both the preparation of the alkylthiol resin and the substrate grafting proceeded efficiently without any significant formation of side products.

Starting from resin **R-1**, the activation step was carried out by alkylating the sulfur atom under conditions that are analogous to those used in solution chemistry. The sulfide resin (200 mg, 1 equiv) was allowed to swell in dichloromethane (2 mL) and then cooled down to 0 °C. Five equivalents of triethyloxonium tetrafluoroborate were added. The resulting slurry was swirled for eight hours at room temperature. The activated resin **R-2** was washed with CH_2Cl_2 and MeOH, and finally dried under vacuum.

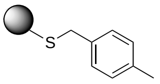
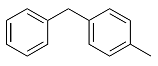
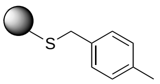
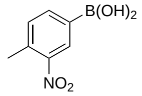
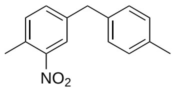
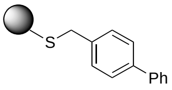
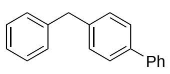
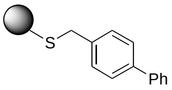
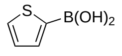
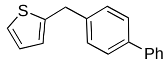
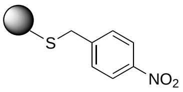
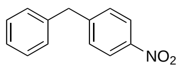
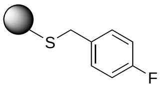
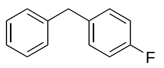
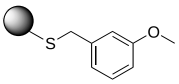
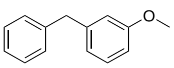
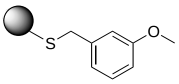
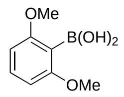
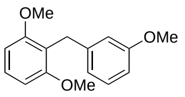
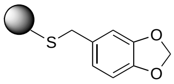
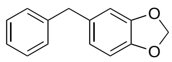
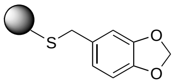
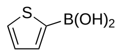
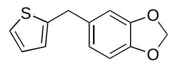
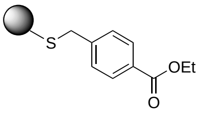
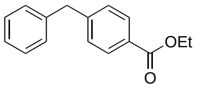
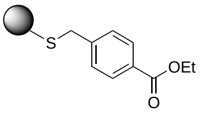
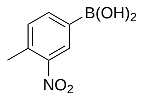
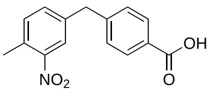
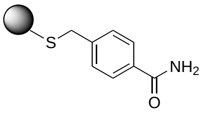
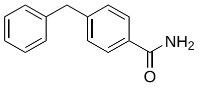
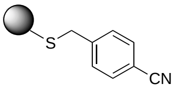
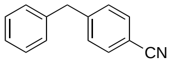
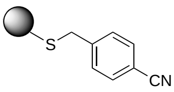
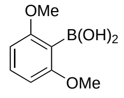
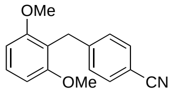
The functionalizing release was carried out under standard palladium coupling conditions. Analysis of the resulting crude mixtures showed the presence of two compounds: the desired biarylmethane along with a biaryl product that was derived from homo-coupling of the boronic acid.[14] Several combinations of catalyst and base were tested to optimize the yield and lower formation of the side product. Treatment of the sulfonium resin with $Pd(OAc)_2$ in the presence of triphenylphosphane or triphenylphosphane sulfide, K_2CO_3 as base, and three equivalents of phenylboronic acid never gave the desired biarylmethane in more than 73 % yield after chromatographic purification, the crude product being contaminated by 50 % of the biaryl side product. A better efficiency was obtained with $[Pd(dppf)Cl_2]$ in association with K_2CO_3 (dppf = 1,1′-bis(diphenylphosphanyl)ferrocene). By using this catalytic system the yield of the desired product was raised to 97 %, the crude product still being contaminated by 50 % of the biaryl product. Although it was not possible to completely avoid formation of the biphenyl derivative, the use of only two equivalents of phenylboronic acid enabled its amount to be reduced to only 20 % in the cleavage mixture without decreasing the yield in the biarylmethane. The crude cleavage product was purified by preparative layer chromatography using ethyl acetate/hexane (1/9) as eluant and the biphenylmethane was recovered in 97 % yield. An additional confirmation of the efficacy of the cleavage was given by IR analysis of the resulting resin where no IR band corresponding to the nitrile group could be detected.

Different combinations of resin-bound benzylic substrates and boronic acids were tested under the optimized conditions to determine the scope of this process (Table 2).

To establish the limitations of this novel, traceless linker strategy, we focused on two areas. First, we wanted to determine if the reaction proceeded both with electron-rich and electron-deficient benzylthiols. Second, we explored which type of functional groups would tolerate the cleavage reaction. Therefore, we introduced several electron-withdrawing and electron-donating groups (entries 1–8) onto the resin as mimics for the potential building blocks and we prepared resins with readily derivatizable aromatic structures: acetal (entries 9, 10), ester (entries 11, 12), amide (entry 13), and nitrile moieties (entries 14, 15).

Since the activation is carried out using triethyloxonium tetrafluoroborate one might fear alkylation of the linked substrate might occur. Miscellaneous functions such as ether (Table 2, entries 7, 8), acetal (entries 9, 10), nitro (entry 5), ester (entries 11, 12), or nitrile (entries 14, 15) were compatible with these conditions. None of them were affected by the triethyloxonium tetrafluoroborate. Interestingly, the

Table 2. Coupling–release of various functionalized resins.

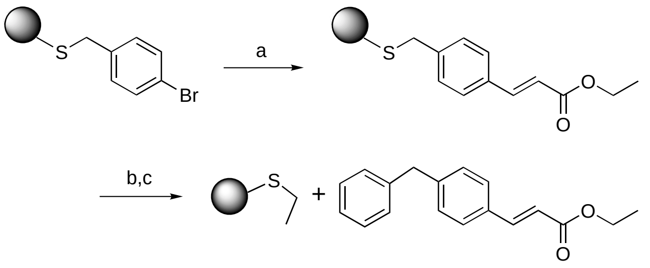
Entry	Resin	Boronic acid	Product	Yield [%][a]
1		$PhB(OH)_2$		46
2				99
3		$PhB(OH)_2$		96
4				80
5		$PhB(OH)_2$		55
6		$PhB(OH)_2$		42
7		$PhB(OH)_2$		82.5
8				62
9		$PhB(OH)_2$		79
10				24
11		$PhB(OH)_2$		98
12				99[b]
13		$PhB(OH)_2$		80
14		$PhB(OH)_2$		97
15				63

[a] Yields of isolated products based on the loading of the **R-SH** resin (0.8 mmol g^{-1}). All compounds were purified by flash chromatography on silica gel. [b] The ester was hydrolyzed to the corresponding acid with LiOH in H_2O/dioxane (1/1) and the undesired homo-coupling product was extracted with diethyl ether. The aqueous phase was acidified and the acid was extracted with EtOAc.

primary amide and the nitrile also proved to be compatible with our procedure (Table 2, entries 13, 14, 15).

The cleavage reaction proceeds under conditions very similar to those already described and extensively used in SPS. Moreover, since the boronic acid is never in contact with the alkylating reagent there is no problem of compatibility. Thus, an important diversity can be introduced through this functionalizing cleavage. For instance, substituted aromatic and heteroaromatic boronic acids could be used without any difficulty (Table 2, entries 4, 8, 12) and the coupling was shown not to be affected by steric hindrance (entries 8, 15).

Finally, to illustrate the versatility of this activation/cleavage sequence, two successive Pd-catalyzed reactions (widely used in SPS to introduce further diversity) were carried out. 4-Bromobenzylbromide was linked to the alkylthiol resin **R-SH**. A Heck coupling reaction involving ethyl acrylate was then performed under standard conditions (Scheme 4), to afford the supported ethyl cinnamate. The sulfide link was activated with triethyloxonium tetrafluoroborate and subsequent cleavage gave the biarylmethane cinnamate derivative in 57 % yield.



Scheme 4. Pd-catalyzed Heck coupling performed in the presence of the sulfide link and Pd-catalyzed cleavage after activation of the sulfide bond. Reagents and conditions: a) $Pd(OAc)_2$ (0.2 equiv), PPh_3 (0.4 equiv), ethyl acrylate (4 equiv), K_2CO_3 (2 equiv), DMF, 70 °C, 14 h. b) $Et_3O^+BF_4^-$ (5 equiv), CH_2Cl_2, 0 °C → RT, 8 h. c) $[Pd(dppf)Cl_2]$ (0.2 equiv), $PhB(OH)_2$ (1 equiv), K_2CO_3 (3 equiv), THF, 60 °C, 14 h.

As no cleavage was observed during the Heck reaction, it emphasizes that, prior to the activation step, the sulfide link is totally stable towards the Pd-catalyzed coupling reaction, while after alkylation, the resin-bound sulfonium group undergoes efficient cleavage.

In conclusion, a reactivity study of acyclic sulfonium salts toward Pd-catalyzed cross coupling has been reported. The reaction allowed us to develop an original and useful safety-catch linker for the SPS of biarylmethane structures. We have shown that the benzyl carbon – sulfur bond is an advantageous link for organic synthesis on a solid support. Since the sulfide bond is compatible with most SPS reaction conditions this resin – substrate linkage is suitable for use in various types of reactions. Moreover, since Pd-catalyzed cross-couplings are well established reactions for the introduction of diversity in SPS and since the pool of commercially available boronic acids is increasing, this new protocol appears to be a powerful tool that might be employed for the synthesis of many libraries.

Experimental Section

Typical procedure for the traceless cleavage: A conical flask was successively charged under argon, with $[Pd(dppf)Cl_2]$ (0.2 equiv), aryl boronic acid (2 equiv), resin **R-2** (200 mg, 1 equiv), potassium carbonate (3 equiv), and THF (2 mL). The resulting suspension was degassed by gently bubbling argon and the flask was hermetically closed. The reaction was carried out at 60 °C for 14 h. After cooling the resin, it was filtered and washed successively with THF (2 × 5 mL), and then 5 times alternately with CH_2Cl_2 (5 mL) and MeOH (5 mL). The combined filtrates were evaporated to dryness to yield a redish brown solid, which was filtered over a bed of silica with dichloromethane and methanol used to remove palladium residues.

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[9] The phenyltetramethylenesulfonium salt was synthesized by the reaction of thiophenol (1 equiv) with 1,4-dibromobutane (2 equiv) in the presence of triethylamine (1.5 equiv) in diethyl ether. The insoluble salt was purified by trituration with ethanol/diethyl ether. All other salts were prepared by alkylation (methylation or ethylation) of the corresponding sulfide. Several alkylating agents were

tested. The use of methyl iodide, even in large excess, gave very slow and incomplete reactions. Very good results were obtained with methyl triflate. However, this method was found to be expensive and not practical to carry out. Thus, triethyloxonium tetrafluoroborate was preferred for a quick (1 or 2 h) and quantitative synthesis of sulfonium salts. Purifications of the salts were performed by trituration in ethanol/diethyl ether.

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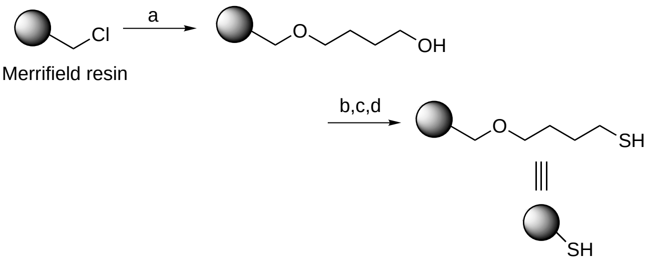
[11] This resin was prepared from commercially available Merrifield resin ($1.2\,\mathrm{mmol\,g^{-1}}$, 200–400 mesh) in four steps. a) 1,4-Butanediol (10 equiv), NaH (5 equiv), DMF, RT, 14 h (an analogous transformation is described in ref. [4f]; b) methanesulfonyl chloride (5 equiv), Et_3N (5 equiv), CH_2Cl_2, RT, 15 h; c) thiourea (5 equiv), DMF, 70 °C, 17 h; d) benzylamine (3 equiv), toluene, 70 °C, 14 h.



[12] Reagents and conditions for the grafting of the substrate on the solid support: 4-cyanobenzylbromide (3 equiv), DIEA (3 equiv), DMF, 70 °C, 14 h.

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A Highly Soluble Luminescent Decanuclear Gold(I) Complex with a Propeller-Shaped Structure[**]

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The chemistry of polynuclear d^{10} metal systems has attracted numerous studies in the past few decades, and many of them involved the investigation of their structure and their photoluminescent behavior.[1] These properties are often affected by the presence of weak metal–metal interactions as a result of a relativistic effect that leads to the contraction of the *n*s orbital of the d^{10} metal center.[2] This effect is most prominent for gold and leads to the phenomenon of aurophilicity commonly found in gold complexes, in which aggregation through short sub-van-der-Waals gold–gold contacts of around 3.05 Å occurs.[3] Chalcogenides, with their propensity to bridge metal atoms, could serve as ideal candidates for polynuclear metal complex formation. Although chalcogenido copper(I) and silver(I) clusters are known and a number of them have been structurally characterized, most are insoluble or have low solubility in common organic solvents.[4] Examples of soluble polynuclear d^{10} metal chalcogenides are scarce, especially those of gold.[5–7]

Recently, we reported the isolation of a series of soluble tetranuclear copper(I) and silver(I) chalcogenido complexes with the general formula $[M_4(\mu\text{-dppm})_4(\mu_4\text{-E})]X_2$ (M = Cu, Ag; dppm = bis(diphenylphosphanyl)methane; E = S, Se, Te; X = PF_6, OTf = trifluoromethanesulfonate),[8], as well as the dodecanuclear gold(I) sulfido complex $[Au_{12}(\mu\text{-dppm})_6(\mu_3\text{-S})_4](PF_6)_4$.[6] All were structurally characterized and shown to exhibit rich photophysical properties. Structurally related gold(I) complexes with the general formulas $[E(AuPPh_3)_3]^+$ (E = S, Se, Te) and $[E(AuPPh_3)_4]^{2+}$ (E = S, Se) were also reported.[7] Here we report the synthesis and the structural characterization of a novel soluble, high-nuclearity luminescent μ_3-sulfidogold(I) complex with bridging diphosphanylamine ligands, namely, $[Au_{10}(\mu\text{-PNP})_4(\mu_3\text{-S})_4](PF_6)_2$ (PNP = $Ph_2PN(n\mathrm{Pr})PPh_2$).

Reaction of H_2S with a suspension of $[Au_2Cl_2(PNP)]$[9] in ethanol/pyridine followed by metathesis reaction with NH_4PF_6 in methanol and recrystallization from acetone/diethyl ether afforded $[Au_{10}(\mu\text{-PNP})_4(\mu_3\text{-S})_4](PF_6)_2$ (**1**) as yellow crystals in 72 % yield. The formulation of **1** was confirmed by elemental analyses, positive FAB and ESI mass spectrometry, ^1H and ^{31}P NMR spectroscopy, ^1H–^1H COSY experiments, and measurement of the molar conductivity.[10] The solid-state structure was established by X-ray crystallography (Figure 1).[11]

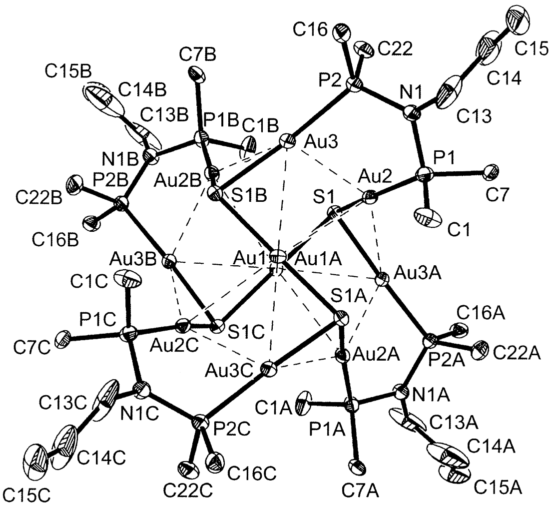

Figure 1. Perspective view of the complex cation of **1** with the atomic numbering scheme. Only the *ipso*-C atoms of the phenyl rings are shown and hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30 % probability level. Atoms with the notations A have coordinates at $(-y+\frac{1}{2}, x+\frac{1}{2}, -z+\frac{1}{2})$, B at $(y-\frac{1}{2}, -x+\frac{1}{2}, -z+\frac{1}{2})$, and C at $(-x, -y+1, z)$.

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