

Reviving the Coordination Chemistry of Sulfonium Cations

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ABSTRACT: More than a century old, sulfonium ions are still intriguing species in the landscape of organic chemistry. On one hand they have found broad applications in organic synthesis and material science, but on the other hand, while isoelectronic to the ubiquitous tertiary phosphine ligands, their own coordination chemistry has been neglected for the last three decades. Here we report the synthesis and full characterization of the first Rh(I) and Pt(II) complexes of sulfonium. Moreover, for the first time, coordination of an aromatic sulfonium has been established. A thorough computational analysis of the exceptionally short S-Rh bonds obtained attests for the strongly π -accepting nature of sulfonium cations and places them among the best π -acceptor ligands available today. Our calculations also show that embedding within a pincer framework enhances their π -acidity even further. Therefore, in addition to the stability and modularity that these frameworks offer, our pincer complexes might open the way for sulfonium cations to become powerful tools in π -acid catalysis.

Rethinking the coordination chemistry of main group elements has often led to breakthroughs in metal-based homogeneous catalysis. For instance, extending the chemistry of B, Al, Ga, Sn, and Bi gave birth to the concept of σ -acceptor (aka Z-type) ligands,¹ which have been successfully applied for such fundamentally important processes as N₂ fixation,² CO₂ reduction,³ and H₂ activation.⁴

The electron-withdrawing nature of Z-type ligands also offered new opportunities for π -acid catalysis, leading to preparation of novel σ -acceptor ligands based on boranes,⁵ antimony,⁶ and carbenium⁷ cation. π -acid catalysis was also significantly advanced by stretching to an extreme the π -acceptor property of phosphines⁸ and arsines⁹ through the introduction of positively charged substituents.

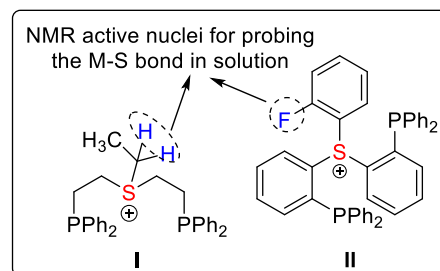
While seeking to unravel new facets of main group chemistry, the coordination properties of another main-group species, sulfonium cations, have been greatly overlooked. Yet, sulfonium salts are at the forefront of fundamental and applied research¹⁰ due to their countless applications as precursors for sulfur ylides,¹¹ alkyl and aryl group sources in cross-coupling reactions,¹² photoacids,¹³ and many others.¹⁴

Compared to the isoelectronic and isostructural tertiary phosphines, sulfonium ions have their lone pair stabilized by their positive charge, while their low-lying S-C σ^* -orbitals can accept electron density. Therefore, together with sulfoxonium, they have attracted the attention as non-metal Lewis acids¹⁵ and have been utilized as such for catalysis and anion sensing.¹⁶ However, while tertiary phosphines are perhaps the most iconic family of ligands, only a handful of crystallographically characterized sulfonium complexes of Mo(0), W(0), and Mn(I) were reported decades ago,¹⁷ where these ligands exhibited strongly π -acidic character. Yet, no sulfonium complexes relevant to catalysis, have ever been reported, even though formation of transient metal-coordinated sulfonium intermediates during Pd catalyzed cross-coupling reactions of sulfonium salts has been suggested.^{12a}

Here we report the first synthesis and characterization of a series of complexes of both aliphatic and aromatic sulfonium cations with Rh(I) and Pt(II), two metals of the Pt-group, which lies at the core of today's homogeneous catalysis. Our in-depth theoretical analysis of sulfonium-metal interaction demonstrated it to be dominated by π -back bonding. This strongly π -acidic character is further enhanced by the pincer frameworks, which also provide our complexes with structural robustness and modularity, both properties of pivotal importance in catalysis.¹⁸

Obviously, coordination of sulfonium cation is hindered by an electrostatic repulsion between its positive charge and that of a metal center (even if partial). So far, the preparation of sulfonium complexes was achieved by alkylation of corresponding sulfide complexes. We adopted here a more systematic approach, where the aliphatic or aromatic sulfonium moieties were incorporated within pincer frameworks (**I** and **II**, respectively), bearing chelating phosphine arms. A similar strategy was used earlier to achieve coordination of the nitrenium cation.¹⁹

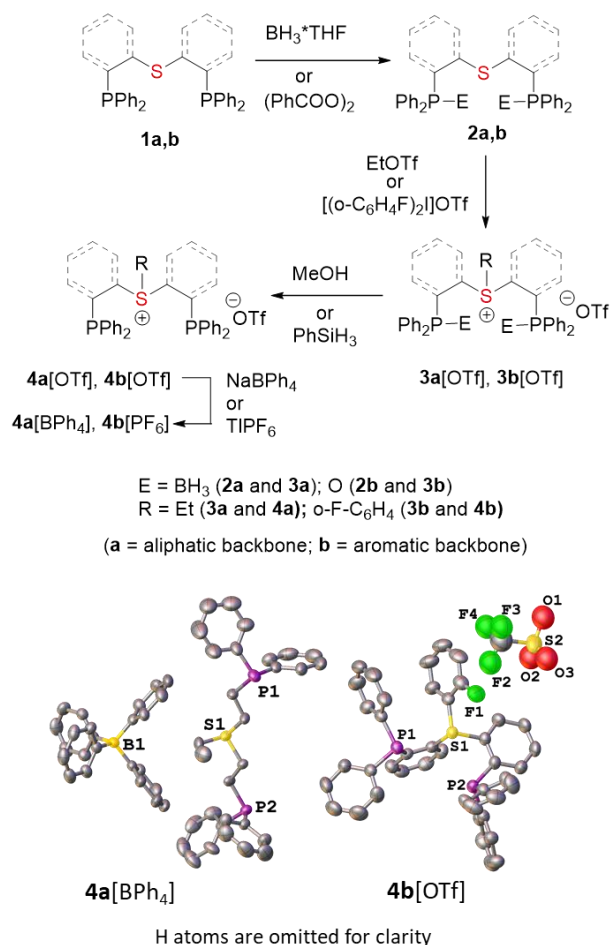
Chart 1: Design of sulfonium-based pincer ligands.



We designed aliphatic and aromatic sulfonium ligands with NMR active nuclei in the vicinity of the sulfur, namely methylene protons in **I** and a fluorine atom in **II**, that would allow detecting the formation of an S-M bond in solution, by tracing

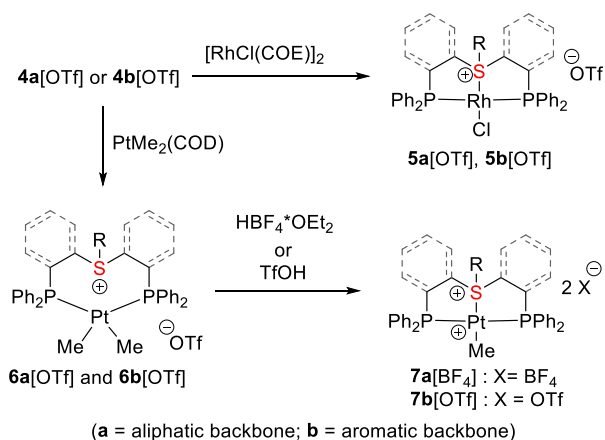
their chemical shifts and magnetic coupling to NMR-active metal centers, ^{103}Rh and ^{195}Pt .

Scheme 1: Synthesis and XRD structures of sulfonium pincer ligands



Both sulfonium pincer ligands were prepared by alkylation or arylation of the corresponding bis-phosphine sulfide ligands,²⁰ protected as borane adducts or as phosphine oxides (Scheme 1). Their deprotection resulted in ligands **4a[OTf]** and **4b[OTf]**. To obtain single crystals of the ligands and their complexes suitable for XRD analysis, the triflate counterions were in some cases exchanged to tetraphenylborate or hexafluorophosphate.

Scheme 2: Synthesis of Rh(I) and Pt(II) complexes



The coordinative behavior of the aliphatic sulfonium ligand **4a[OTf]** towards Rh(I) was tested by reacting it with $[\text{RhCl}(\text{COE})_2]_2$ (Scheme 2). A full conversion to a symmetric Rh(I) complex was evident by ^{31}P NMR, as the chemical shift moved from a singlet at -18.2 ppm to a doublet at +46.4 ppm ($1/J_{\text{Rh-P}} = 127.8 \text{ Hz}$). In the ^1H NMR spectrum, significant downfield shifts of all aliphatic signals is observed. Each of the methylene protons signals **a** and **b** (Figure 1), divides upon coordination into two (**a*** and **b*** pairs, respectively), indicating formation of a rigid structure with no rotation around C-C bonds. Furthermore, an additional splitting of 1.3 Hz appears in the quartet assigned to the ethyl tail methylene protons (**c***). By means of ^1H - ^{103}Rh HMBC (Figure S3), this splitting was attributed to a through-bonds $^3J_{\text{Rh-H}}$ interaction. The latter is only possible if sulfonium is coordinated to the Rh center.

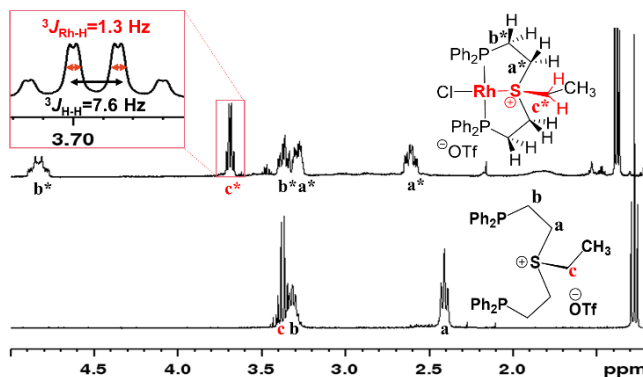


Figure 1: Aliphatic region of ^1H NMR spectra of **4a[OTf]** and **5a[OTf]**.

Encouraged by these results, we then turned to the aromatic ligand **4b[OTf]** (Scheme 2). Here also, a full conversion of the ligand to a symmetric Rh(I) complex **5b[OTf]** was evident from the ^{31}P NMR spectrum, where the chemical shift changed from a singlet at -12.9 ppm to a doublet of doublets at +48.6 ppm ($1/J_{\text{Rh-P}} = 126.7 \text{ Hz}$; $5/J_{\text{F-P}} = 6.0 \text{ Hz}$). Interestingly, the P-F interaction unobservable in the spectrum of the free ligand, became noticeable after coordination, perhaps due to the additional rigidity of the formed complex.

The ^{19}F NMR spectrum of **5b[OTf]** showed only a small downfield shift compared to the free ligand (-104.1 vs -105.3 ppm, respectively) and no additional splitting by ^{103}Rh could be identified. Likewise, no ^{19}F - ^{103}Rh interactions could be detected by HMBC, hence in this case, metal coordination to aromatic sulfonium moiety could not be validated by NMR alone.

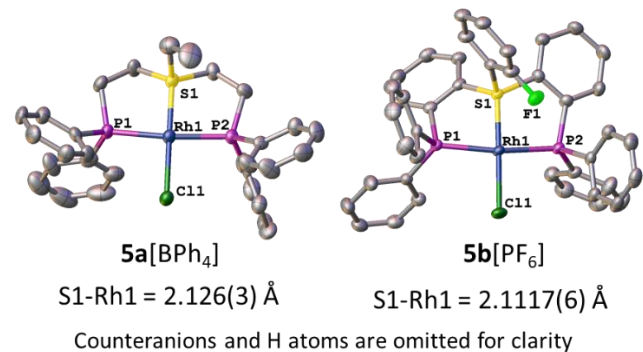


Figure 2: XRD structures of Rh(I)-sulfonium complexes, **5a[BPh₄]** and **5b[PF₆]**.

Nevertheless, the irrefutable evidence of sulfonium-Rh bonding in both systems was provided by XRD. Both complexes

5a[BPh₄] and **5b**[PF₆] exhibited a slightly distorted square-planar geometry around the metal, typical of d⁸ complexes (**Figure 2**). The sulfonium-Rh(I) bond lengths of 2.126(3) and 2.1117(6) Å in **5a**[BPh₄] and **5b**[PF₆], respectively, are among the shortest reported S-Rh bonds. These are significantly shorter than in Rh(I) complexes with sulfides (>2.24 Å) and even with sulfoxides (typically, 2.159-2.291 Å).²¹ In fact, shorter Rh(I)-S bonds (2.069-2.100 Å) were only observed with the strongest π -acceptor ligands: SO₂²² and the related N-sulfinylaniline.²³ These exceptionally short bonds in **5a**[BPh₄] and **5b**[PF₆] cannot be explained solely by the grip of the pincer framework. Indeed, in both the analogous aliphatic sulfoxide pincer complex **8** that we prepared (see SI) and the reported aromatic ones,²⁴ the Rh-S bonds are still longer than in their sulfonium counterparts (2.135 and 2.134 Å, respectively).

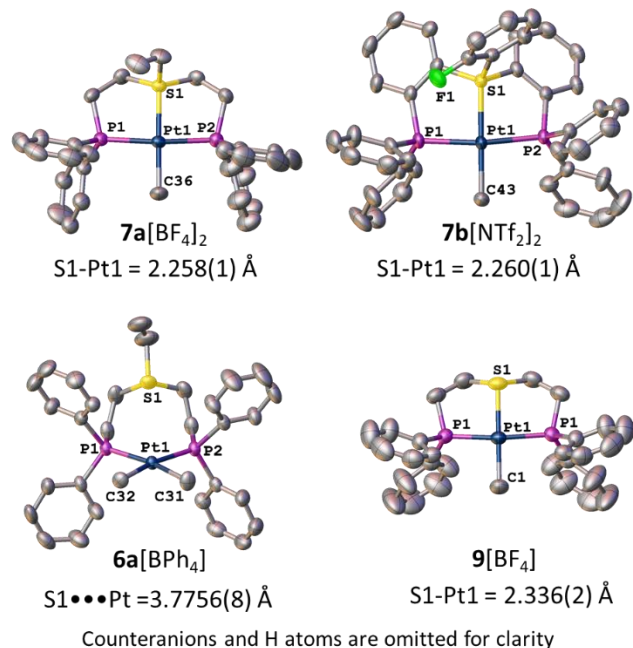


Figure 3: XRD structures of Pt(II) complexes, **6a**[BPh₄], **7a**[BF₄]₂, **7b**[NTf₂]₂, and **9**[BF₄].

Having achieved sulfonium coordination to the neutral RhCl unit, we wondered whether, similarly to cationic nitrenium^{19b} and arenium²⁵ pincers, our frameworks could also induce bonding between a sulfonium cation, and a positively charged metal fragment.

Therefore, we first treated ligands **4a**[OTf] and **4b**[OTf] with Pt(COD)Me₂ which resulted in new compounds (**Scheme 2**), as evident from ³¹P NMR spectrum that exhibited downfield shifted peaks at 11.3 or 16.6 ppm with the characteristic ¹⁹⁵Pt satellites (¹J_{Pt-P}=1813 Hz and 1781 Hz, respectively). In the ¹H NMR signals at 0.42 and 0.65 ppm, were assigned to the methyl protons, confirming the formation of PtMe₂ complexes **6a**[OTf] and **6b**[OTf], respectively. Moreover, these signals appeared as doublets of doublets due to splitting by two magnetically inequivalent P atoms, a configuration only possible when methyl groups are oriented *cis* to each other (**Figures S1, S2**).

The neutral PtMe₂ fragment in **6a**[OTf] and **6b**[OTf] was then transformed into a cation by protonolysis (by HBF₄·OEt₂ or HOTf) which resulted in the clean formation of complexes **7a**[BF₄]₂ and **7b**[OTf]₂ (**Scheme 2**), as attested by new peaks at 42.4 (¹J_{Pt-P}=2736 Hz) and 44.3 (¹J_{Pt-P}=2768 Hz) ppm, respectively, in ³¹P NMR. In the aromatic complex **7b**[OTf]₂ the ³¹P NMR signals were much sharper than in **6b**[OTf], and similarly

to the Rh(I) complex **5b**[OTf], splitting due to the P-F coupling (⁵J_{P-F}=4 Hz) became observable.

Unlike complexes **6a**[OTf] and **6b**[OTf], in both **7a**[BF₄]₂ and **7b**[OTf]₂, the ¹H NMR signals at 1.21 and 1.56 ppm, corresponding to single methyls, appeared as triplets indicating magnetic equivalence of the two phosphines, only possible in a mutual *trans*-orientation (**Figures S1, S2**). Moreover, the signals of the aliphatic protons in **7a**[BF₄]₂ followed a pattern similar to that of **5a**[OTf] (**Figure 1**), suggesting an analogous structure (**Figure S1**). To further study sulfonium-Pt interaction in solution we applied ¹H-¹⁹⁵Pt HMBC, once again focusing on magnetic interaction between Pt and the methylene protons of the ethyl tail (**Figure S4**). While in **6a**[OTf] this coupling constant is negligible (0.2 Hz, presumably due to ⁶J_{Pt-H}), in **7a**[BF₄]₂ it reaches 7.7 Hz (most likely, due to ³J_{Pt-H}), suggesting the presence of S-Pt bond in **7a**[BF₄]₂, but not in **6a**[OTf]. Similar conclusion about S-Pt bonding in **6b**[OTf] and **7b**[OTf]₂ could be drawn by comparing their ¹⁹F-¹⁹⁵Pt HMBC spectra (**Figure S5**), even though both complexes exhibited nearly identical chemical shifts in ¹⁹F NMR (-102.28 and -102.45 ppm, respectively). The former showed no ¹⁹F-¹⁹⁵Pt correlation, while the latter revealed a prominent cross-peak with a coupling constant of 3.3 Hz, supporting the presence of sulfonium-Pt bond.

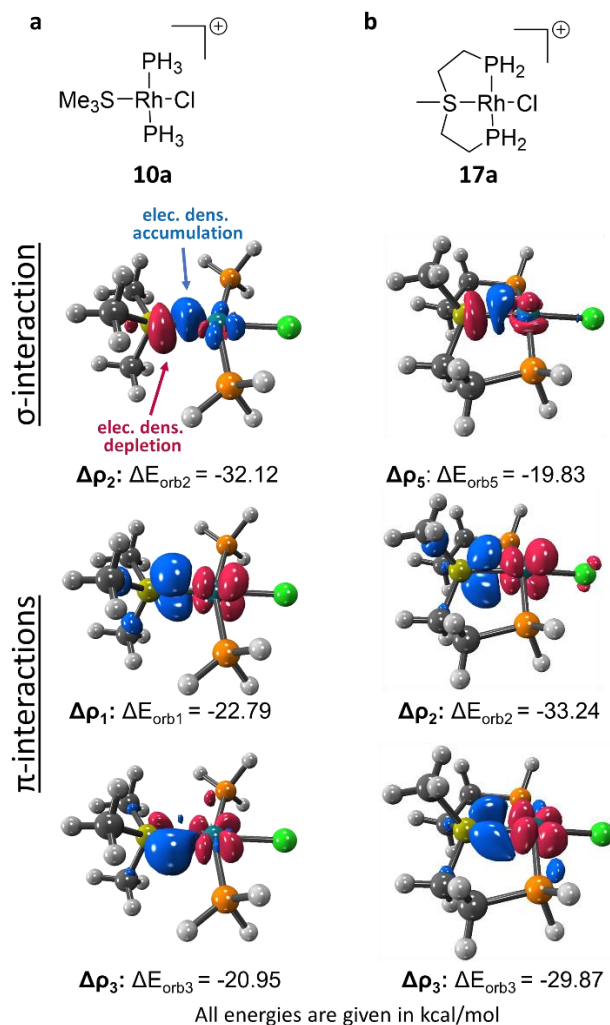


Figure 4: Selected deformation density plots of model complexes **10a** and **17a**.

Ultimately, the solid-state structures of **6a**[BPh₄], **7a**[BF₄]₂, and **7b**[NTf₂]₂ were established by single crystal XRD (**Figure**

3). In **6a**[BPh₄], as expected from the NMR analysis, no Pt-S bond was observed, and the methyl groups indeed exhibited a *cis* configuration. However, in **7a**[BF₄]₂ and **7b**[NTf₂]₂, Pt-S bonds of 2.258(1) and 2.261(1) Å, respectively, were found. Surprisingly, despite electrostatic repulsion between the cationic sulfonium and the PtMe fragment, this bond in **7a**[BF₄]₂ is shorter than that in its neutral sulfide analog **9**[BF₄], 2.336(2) Å, prepared for comparison (**Figure 3**).

The exceptionally short metal-sulfonium bonds mostly observed in our Rh complexes prompted us to undertake a computational investigation by DFT, applying the Energy Decomposition Analysis²⁶ combined with the Natural Orbital for Chemical Valence theory (EDA-NOCV).^{27,28} This method provides a series of density deformation maps ($\Delta\rho_n$) describing the interactions between isolated system components. The energy of the orbital interactions (ΔE_{orb}) is then extracted from the overall interactions (ΔE_{int}) and decomposed into constituents according to their symmetry.

First, we considered the Rh-S bonding interactions in the model monodentate aliphatic and aromatic sulfonium complexes **10a** and **10b** and compared them with analogous complexes of neutral phosphines, sulfides and sulfoxides, as well as with a few representative cationic ligands. By inspecting the deformation density maps of the most significant orbital interactions (ΔE_{orb}), we could identify a single σ -symmetric interaction, which contrary to the reported M \rightarrow L interaction in the isoelectronic telluronium complex,²⁹ has a clear L \rightarrow M donation



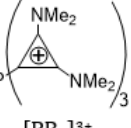
character, and two π -symmetric ones (perpendicular and parallel to the coordination plane) corresponding to the M \rightarrow L back-donation (see representative deformation density maps of **10a** in **Figure 4a**, for other maps see SI).

Table 1 shows that in terms of their BDEs and σ -donation, sulfonium cations are nearly similar to sulfides and sulfoxides. However, sulfonium cations are significantly stronger π -acceptors, with π -back-bonding interaction being predominant. This is quite unusual, and not the case even for the strongly π -acidic perfluorinated phosphines (in complexes **14a-c**), where similarly to common phosphines (in **13a,b**), σ -donation still prevails. This predominance of π -back-donation over σ -donation appears specific only to cationic ligands considered here. Compared to the latter, the π -acidity of sulfonium stands between that of N-heterocyclic nitrenium ([NHN]⁺, in **15a**) and N-heterocyclic phosphonium ([NHP]⁺, in **15b**), and is comparable to Alcarazo's tris-cationic phosphine PR³⁺ (in **15c**). Calculations performed on model Rh complexes **17a,b** (**Table 2**) showed that geometry deformations imposed by the pincer frameworks (**Figures S17, S18** and the explanation therein) further weakens σ -donation, but strengthens π -back donation within the complexes.

With the cationic PtMe fragment in sulfonium complexes **16a,b** (**Table 1**) that are kinetically stable despite their positive BDEs, π -back-bonding is still non-negligible, albeit much weaker than in **10a,b**. Nevertheless, in the corresponding pincer complexes **18a,b** (**Table 2**), it drastically increases, becoming comparable to the σ -donation.

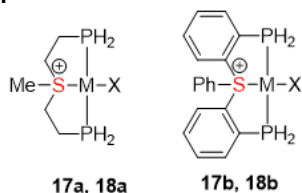
Table 1: EDA-NOCV data for the monodentate [L(PH₃)₂MX]ⁿ⁺ complexes.

MX	RhCl							
Ligand Types	Sulfonium cations		Sulfides		Sulfoxides		Phosphines	
Model Complexes	10a	10b	11a	11b	12a	12b	13a	13b
L	SMe ₃ ⁺	SPh ₃ ⁺	SMe ₂	SPh ₂	DMSO	Ph ₂ SO	PMe ₃	PPh ₃
BDE*	-38.57	-36.96	-36.21	-38.19	-39.82	-44.55	-70.06	-57.77
σ -bonding* (% of $\sigma/\Delta E_{orb}$)	-32.12 (37.3%)	-31.00 (31.0%)	-34.89 (63.5%)	-34.25 (61.0%)	-39.65 (57.1%)	-40.57 (53.5%)	-56.46 (67.3%)	-53.10 (63.3%)
π -backbonding*† (% of $\pi/\Delta E_{orb}$)	-43.74 (50.8%)	-39.24 (39.2%)	-14.83 (27.0%)	-16.04 (28.6%)	-24.31 (35.0%)	-28.80 (38.0%)	-21.98 (26.2%)	-24.08 (28.7%)

MX	RhCl						PtMe ⁺	
Ligand Type	Perfluorinated phosphines			Cationic Ligands			Sulfonium cations	
Model Complex	14a	14b	14c	15a	15b	15c	16a	16b
L								
	PF ₃	P(CF ₃) ₃	P(C ₆ F ₅) ₃	[NHN] ⁺	[NHP] ⁺	[PR ₃] ³⁺	SMe ₃ ⁺	SPh ₃ ⁺
BDE*	-56.76	-53.16	-51.35	-30.55	-57.57	-53.16	+48.60	+30.66
σ -bonding* (% of $\sigma/\Delta E_{orb}$)	-51.61 (51.4%)	-46.69 (49.7%)	-47.59 (55.1%)	-25.20 (40.3%)	-42.75 (44.3%)	-44.25 (42.6%)	-33.60 (57.3)	-32.71 (56.9)
π -backbonding*† (% of $\pi/\Delta E_{orb}$)	-43.42 (43.3%)	-40.58 (43.2%)	-32.08 (37.1%)	-29.07 (46.4%)	-62.16 (52.3%)	-45.99 (44.2%)	-17.12 (29.2%)	-13.48 (23.5)

*Energies are given in kcal/mol, †Sum of the \perp and \parallel π -interactions

Table 2: EDA-NOCV data for the [LMX]⁺ sulfonium pincer complexes.



MX	RhCl		PtMe ⁺	
Model Complex	17a	17b	18a	18b
σ-bonding*	-19.83	-18.10	-46.97	-44.84
π-back bonding*†	-62.11	-58.86	-39.88	-41.4

* Energies are given in kcal/mol, †Sum of the ⊥ and || π-interactions

To summarize, in this paper we have consolidated the status of sulfonium ions among the family of rare cationic ligands demonstrating for the first time that their coordination chemistry can be extended to the Pt group metals. We also prepared

the very first examples of a metal-coordinated aromatic sulfonium cations. These unusual compounds might represent stable analogs of possible transient intermediates forming during Pd-catalyzed cross-coupling of sulfonium salts.

Our calculations suggested that sulfonium cations are among the best π-acceptors available. Moreover, the pincer frameworks which offers an additional robustness also intensify this propensity. These scaffolds might therefore be the key to transform sulfonium complexes from a chemical curiosity into potential π-acid catalysts, the applications of which is currently studied in our lab.

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