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PAPER

Sulfonate-tagged 1,4-diazabutadiene (DAD^S) ligands and their noble-metal complexes – synthesis, characterization and immobilization in ionic liquids†

Benjamin Oelkers and Jörg Sundermeyer*

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A series of sulfonate-tagged 1,4-diazabutadiene (DAD^S) ligands was prepared as salts with typical ionic liquid (IL) cations ($[EMIM]^+$, $[BMIM]^+$, $[BMMIM]^+$, Bu_4N^+, Bu_3PMe^+, [Gua-4,4-4,4-4,1]$^+$). Complexation behaviour of the ligands was investigated by preparing complexes of the types $[BMMIM]_2[MCl_2(DAD^S)]$ (M = Pd, Pt), $[BMMIM][Rh(COD)(DAD^S)]$ and $[BMMIM]_2[Mo(CO)_4(DAD^S)]$. Using UV-Vis spectroscopy, the latter sulfonate-tagged chromophore was shown to be well soluble in the sulfonate IL [BMIM]OTf and completely insoluble in toluene, resulting in perfect immobilization. The crystal structures of $[HNEt_3]_2$[2,6-Me_2-Me-DAD^S], $[BMIM]_2$[2,6-Me_2-Me-DAD^S], $[BMMIM]_2$[2,4,6-Me_3-Me-DAD^S], $[BMMIM]_2$[2,6-*i*Pr_2-Me-DAD^S] and $[HNEt_3]_2[PdCl_2$(2,6-Me_2-Me-DAD^S)] were determined. Regarding the diimine fragment, they show geometries similar to the respective non-sulfonated parent compounds.

Introduction

Ionic liquids (ILs) are most promising media for multiphasic catalysis.[1] They offer high polarity that is often needed to stabilize reactive intermediates in combination with an aprotic environment as required in many organometallic transformations. Consequently, it is possible to combine advantages of multiphasic aqueous catalysis with the unique "designer-solvent" properties of ILs.[2] Among the criteria for transition-metal complexes to be applied as catalysts in multiphasic IL-based processes, selective solubility in the IL is one of the most important ones. Only if the catalyst is completely immobilized in the IL by some means it can be retained efficiently and thus be recycled easily.[3] Learning again from aqueous biphasic catalyst systems,[4] the modification of the ligand periphery with ionic substituents such as imidazolium[5] or sulfonate groups[6] has been used successfully for the immobilization of phosphorous and bipyridine ligands and their transition-metal complexes in ILs.[7]

While some work has been done concerning the immobilization of phosphanes using cationic or anionic tags, much less is known about immobilization of azaligand complexes with anionic tags in ionic liquids. Sulfonate-tagged derivatives of bipyridine,[8] phenanthroline[9] and pyridylimine[10] are well known, but have mainly been applied as sodium salts for aqueous catalysis. Concerning sulfonated 1,4-diazadiene (DAD^S) ligands, three studies have been published. Sun and co-workers showed that the sodium salts of these modified ligands can be used to stabilize active palladium species in the aerobic alcohol oxidation and in the Suzuki coupling under aqueous conditions.[11] One tetrabutylammonium salt and two $[BMIM]^+$ salts were also prepared using salt metathesis protocols. However, such ligands and the corresponding complexes often show slow degradation in water-based applications due to hydrolysis of the diimine moiety.[12] The potential stability benefit of non-aqueous, IL-based azaligand catalyst systems has not been exploited so far. Plenio and co-workers presented similar DAD^S sodium salts as intermediates in the synthesis of water-soluble *N*-heterocyclic carbenes. These were applied as ligands for palladium-catalyzed Suzuki coupling in water.[13]

Regarding the choice of anionic tags, sulfonates are used most often as they show a range of favourable characteristics, *i.e.* relatively low nucleophilicity, thermal stability under aprotic as well as aqueous conditions, good stability towards oxidation and reduction. Salts of sulfonate-tagged ligands bearing sodium or similar inorganic cations usually show sufficient solubility in ILs to serve as catalysts. Nevertheless, the preparation of salts bearing IL-typical onium cations (*e.g.* alkyl substituted imidazolium, ammonium, phosphonium) seems worthwhile because they most likely prevent problems concerning low solubility, increasing viscosity due to ion pairing effects or side reactions associated with "foreign" ions. We present here a general approach towards DAD^S ligands with various onium cations *via* acid–base reactions and towards their noble-metal complexes. The solubility and immobilization of such complexes in ILs is quantitatively shown *via* photometric measurements using a chromophoric Mo(0) DAD^S complex in a toluene/[BMIM]OTf biphasic mixture as model system.

Philipps-Universität Marburg, Fachbereich Chemie, Hans-Meerwein-Straße, 35032, Marburg, Germany. E-mail: jsu@staff.uni-marburg.de; Fax: +49 (0)6421 28-25711; Tel: +49 (0)6421 28-25693

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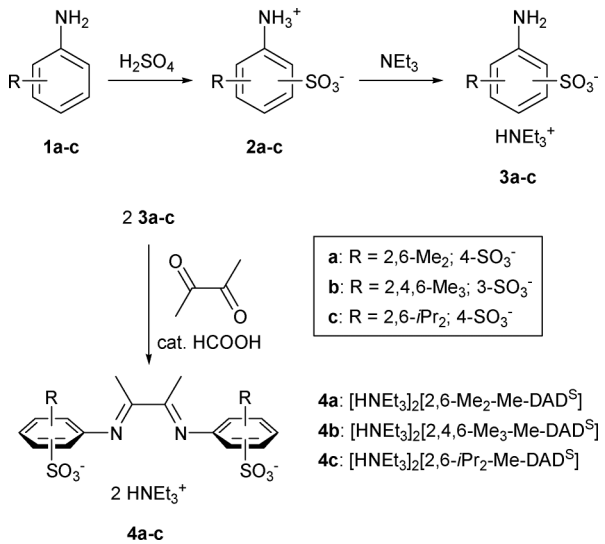
Results and discussion

Ligand synthesis

The preparation of triethylammonium salts **4a–c** of sulfonate-tagged 1,4-diazabutadiene (DAD^S) ligands is outlined in Scheme 1. Commercially available alkylated anilines **1a–c** were transformed into the corresponding sulfanilic acids **2a–c** by sulfonation according to known procedures.[14] After preparation of the corresponding triethylammonium salts **3a–c** the desired DAD^S ligands were obtained by condensation with butane-2,3-dione in methanol. All studied DAD^S ligands were obtained as yellow solids.

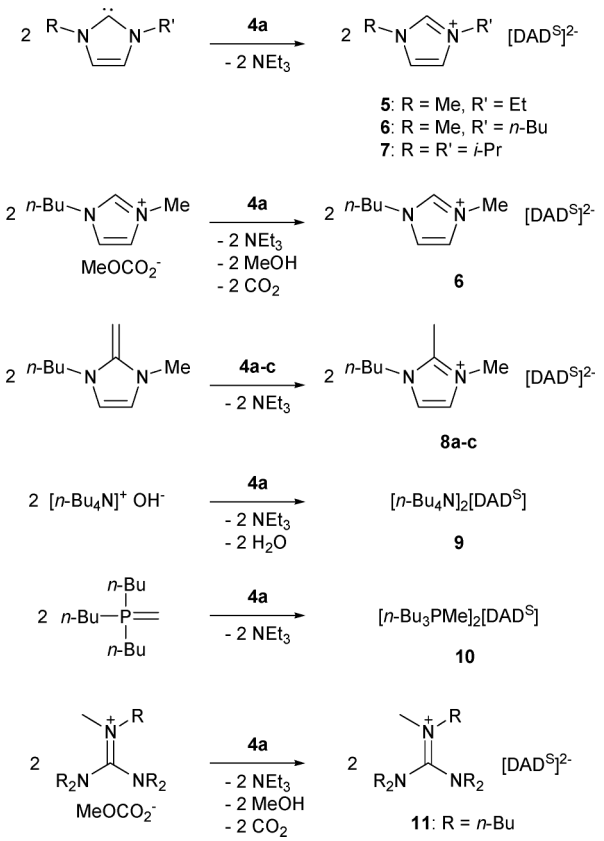


Scheme 1 Synthesis of DAD^S ligands.

While it has been shown that the disodium salts of DAD^S ligands can be used to introduce the desired onium-cations *via* salt metathesis,[11] we discarded this method because it needs accurately tuned reaction conditions for each ligand and cation to be introduced, otherwise complicated salt mixtures are obtained.

The reason for these problems was found to be the very polar and hydrophilic nature of the doubly charged DAD^S anions. In order to completely avoid contamination of the products with halide and alkali metal ions, acid–base reactions were chosen instead of salt metathesis as the key step of the ligand synthesis. A number of basic cation precursors that are also used in high-purity syntheses of ILs themselves was utilized for the transformation of the triethylammonium salts **4a–c** as shown in Scheme 2.

In all cases, the desired onium-salts **5–11** were obtained in high yield and purity upon reaction of the appropriate $HNEt_3$ salt with two equivalents of the respective cation precursor in acetonitrile. For the highly reactive and (partly) temperature-sensitive *N*-heterocyclic carbenes,[15] *N*,*N*-ketenediacetals[16] and *P*-ylides,[17] the reactions were carried out at –40 °C, while the ammonium hydroxides, imidazolium methylcarbonates and guanidinium methylcarbonates[18] were used at room temperature. Triethylamine is released as byproduct of the reaction and can easily be removed *in vacuo*. All other byproducts (if any) are volatile as well and no contamination of the ligand salts with "simple" inorganic ions such as alkali metal or halide ions is possible, thus eliminating this often most difficult issue arising from salt metathesis protocols.



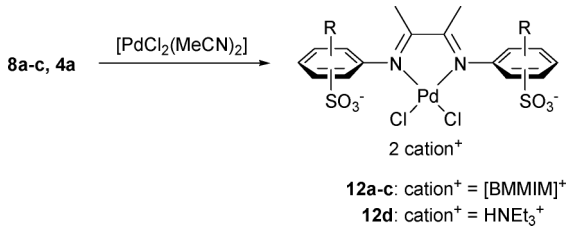
Scheme 2 Cation exchange with basic cation precursors.

Synthesis of complexes

To demonstrate the potential scope of applications, a number of prominent noble-metal complexes were synthesized starting from the $[BMMIM]_2[DAD^S]$ ligands **8a–c**. The 1-butyl-2,3-dimethylimidazolium cation ($[BMMIM]^+$) was chosen instead of the more common 1-butyl-3-methylimidazolium cation ($[BMIM]^+$) because the latter is known to easily form carbene complexes, especially in combination with palladium(II) precursors.[19] Furthermore, molybdenum tetracarbonyl complexes were chosen to probe the immobilization concept *via* UV-Vis spectroscopy.

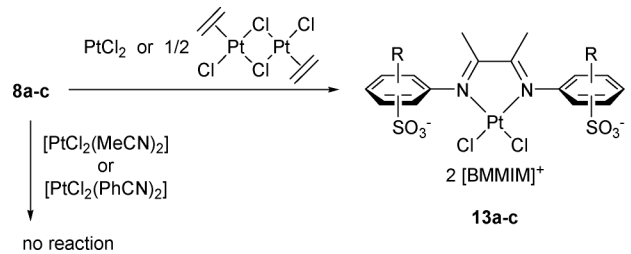
Palladium dichloro complexes. Palladium complexes of aza-ligands are most versatile catalysts for a variety of important synthetic transformations.[20–23] Examples that have been shown for DAD ligand-based systems are olefin polymerization,[22] CO/styrene copolymerization,[23] cyclooligomerization of alkynes,[24] $C(sp^2)$–$C(sp^2)$ bond formation[11,25] and aerobic alcohol oxidation.[11] Hence we decided to investigate whether the coordination behaviour of the DAD^S ligands is considerably different from that of the well-known DAD ligands by synthesizing the corresponding dichloro complexes (Scheme 3).

Similar to known procedures,[26] the complexes **12a–d** are obtained in high yield upon reaction of $[PdCl_2(MeCN)_2]$ or $[PdCl_2(PhCN)_2]$ with the appropriate ligand at room temperature. Acetonitrile proved useful as solvent for this as well as most of the other complexation reactions. It combines sufficient polarity to (partly) dissolve the salt-like ligands and complexes with inertness towards most reactions catalyzed by the formed complexes.



Scheme 3 Synthesis of complexes of the type $[BMMIM]_2[PdCl_2(DAD^S)]$ (**12a–c**) and $[HNEt_3]_2[PdCl_2(2,6\text{-}Me_2\text{-}Me\text{-}DAD^S)]$ (**12d**).

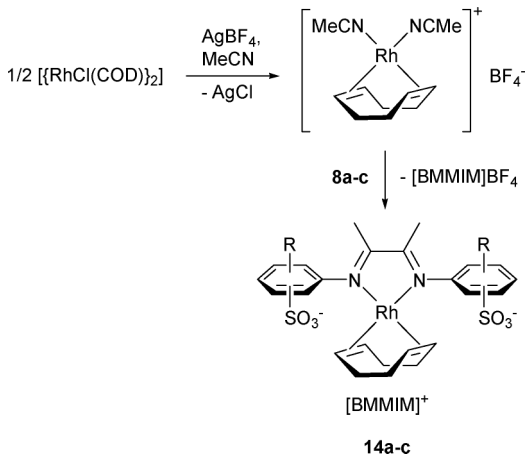
Platinum dichloro complexes. Platinum(II) complexes of DAD ligands are of growing interest as they are known to activate C–H bonds.[27,28] As they are much more inert towards ligand substitution than their palladium analogues, formation of the DAD^S dichloro complexes **13a–c** was investigated as an example of more subtle choice of metal source (Scheme 4).



Scheme 4 Reactivity of DAD^S ligands **8** towards different $PtCl_2$ synthons.

In order to avoid side reactions, all attempts to prepare the complexes $[BMMIM]_2[PtCl_2(DAD^S)]$ (**13a–c**) were conducted at room temperature. The simplest possible precursor for the desired platinum dichloro complexes, $PtCl_2$, was found to react rather slowly with a solution of the appropriate ligand **8**, presumably because of its hexameric nature.[29] The better soluble nitrile adducts $[PtCl_2(MeCN)_2]$ and $[PtCl_2(PhCN)_2]$ were completely unreactive towards ligand substitution in acetonitrile solution, thus showing a distinctive difference in reactivity compared to the corresponding palladium precursors (*vide supra*). $[PtCl_2(COD)]$ and $[PtCl_2(SMe_2)_2]$ are reported to show little reactivity in similar complex formations with DAD ligands[27,30] and were not tested. In contrast to that, Zeise's salt, $K[PtCl_3(C_2H_4)]\cdot H_2O$, is known as labile precursor for dichloro complexes.[27,31] However, it was dismissed in this case because it inevitably introduces further ions into the reaction mixture. This, in turn, is likely to cause problems such as contamination of the product with foreign ions or even complete formation of an undesired salt due to solubility effects. Alternatively, Zeise's dimer, $[\{PtCl_2(C_2H_4)\}_2]$, was chosen as labile starting material.[27] The desired complexes **13a–c** were formed in high yields by reaction of this platinum source with the appropriate ligand in methanol at room temperature. Stirring was continued for three days to assure complete reaction (Scheme 4); however, much shorter reaction times are sufficient when gentle heating is applied.

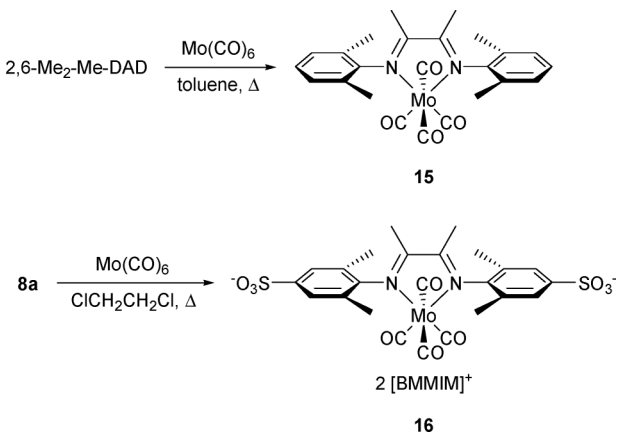
Rhodium cyclooctadiene complexes. Rhodium(I) complexes of azaligands are well-known as catalysts for (asymmetric) transfer hydrogenation[32] and hydrosilylation[33] of ketones. We chose rhodium(I) DAD^S cyclooctadiene complexes $[Rh(DAD^S)(COD)]^-$ as an example of a formally monocationic metal centre that is incorporated into an anion due to the doubly charged DAD^S ligand system. The participation of ions not belonging to the final product cannot be avoided in this case. The complexation was achieved using $[Rh(COD)(MeCN)_2]BF_4$, prepared *in situ* from $[\{Rh(COD)Cl\}_2]$ and $AgBF_4$ in acetonitrile at room temperature (Scheme 5). Therefore, the stoichiometric byproduct was $[BMMIM]BF_4$, which could be separated from the less lipophilic complexes **14a–c** by washing the product mixture with dichloromethane–ether (1 : 1).



Scheme 5 Synthesis of complexes of the type [BMMIM]-$[Rh(COD)(DAD^S)]$ (**14a–c**).

Molybdenum tetracarbonyl complexes. Molybdenum carbonyl complexes with DAD ligands are well-known and have been extensively studied, mainly in terms of their optical properties.[34]

For the evaluation of the immobilization concept, both a complex with a "classical", non-sulfonated DAD ligand (**15**) and its counterpart incorporating a DAD^S ligand (**16**) were prepared by heating the free ligand with $Mo(CO)_6$ in a suitable solvent, *i.e.* toluene and 1,2-dichloroethane, respectively (Scheme 6).



Scheme 6 Synthesis of molybdenum tetracarbonyl complexes.

Spectroscopic properties

NMR spectroscopy. The ^1H and ^{13}C NMR spectra of both the free ligands (**4–11**) and the various complexes (**12–14**, **16**) in DMSO-d_6 or CD_3CN show the typical signals belonging to the

Table 1 Comparison of ^{1}H and ^{13}C NMR shifts (δ (ppm), DMSO-d_6, 298 K) for DAD and DAD^{S} ligands

	N=CCH_3	N=CCH_3	N=CCH_3	C_{ipso}	$C_{ortho}CH_3$	$C_{ortho}CH_3$	$CH(CH_3)_2$	$CH(CH_3)_2$	$C_{para}CH_3$	$C_{para}CH_3$
(2,6-Me_2-Me-DAD)	167.6	15.5	1.95	148.0	17.3	1.96	—	—	—	—
(2,4,6-Me_3-Me-DAD)	167.9	15.6	1.93	145.6	17.3	1.92	—	—	20.3	2.23
(2,6-*i*Pr_2-Me-DAD)	167.9	16.3	1.98	145.6	28.0[a]	2.66[a]	1.09/1.15[b]	22.4/22.8[b]	—	—
[BMMIM]$_2$[2,6-Me_2-Me-DAD^{S}]	167.6	15.6	1.96	147.9	17.3	1.97	—	—	—	—
[BMMIM]$_2$[2,4,6-Me_3-Me-DAD^{S}]	167.7	15.5	1.90	146.6	15.8/15.9[b] 17.2/17.3[b]	2.22/2.23[b] 1.87/1.89[b]	—	—	22.7	2.50
[BMMIM]$_2$[2,6-*i*Pr_2-Me-DAD^{S}]	168.0	16.3	1.99	145.7	28.0[a]	2.66[a]	1.09/1.15[b]	22.3/22.7[b]	—	—

[a] Values correspond to $CH(CH_3)_2$ and $CH(CH_3)_2$, respectively. [b] Two rotamers are observed.

respective cation. The anions seem to have little influence on the cations' signals and *vice versa*. This behaviour indicates a truly ionic nature of the investigated substances; no extensive ion pairing effects were observed in any of the NMR spectra.

The NMR signals corresponding to the respective anion of the free DAD^{S} ligands are rather similar to those obtained for the classical, non-sulfonated DAD ligands concerning all resonances that are not directly affected by the differing aromatic substitution patterns (Table 1). Resonances of the diimine backbone are found at around 168 ppm in DMSO-d_6 for all three ligands **8a**, **8b** and **8c**. A single imine signal is present in all cases for both the free ligands and metal complexes presented herein. The ligands and complexes carrying isopropyl substituents invariably show two signals for the corresponding methyl groups due to restricted rotation of the *i*Pr groups. In contrast to that, two sets of signals belonging to the aromatic *ortho*-methyl groups are observed only for the mesitylamine-derived free ligands (**4b** and **8b**) and the rhodium(I) complex **14b** but not for the palladium(II) and platinum(II) complexes (**12b** and **13b**). This finding can presumably be attributed to *syn*/*anti* isomerism regarding the orientation of the sulfonate groups (*vide infra*).

Although the free ligands' NMR spectra do not show significant differences compared to their non-sulfonate tagged parent compounds in the case of *para*-sulfonated aromatics (Table 1), an electron-withdrawing effect especially of the *para*-sulfonate groups on the diimine fragment has to be expected. It has been shown for a series of aromatic DAD ligands bearing different substituents in the *para*-position that the electronic environment of coordinated palladium is clearly affected by the aromatic substitution pattern while there is little difference in the NMR spectra of the free ligands.[35]

Upon complexation of the Lewis-acidic fragment $PdCl_2$, a significant downfield shift of approximately 14 ppm is observed for the imine carbon signal. While the rhodium(I) COD complexes **14a–c** show an almost identical downfield shift, the platinum(II) dichloro complexes **13a–c** exhibit a slightly smaller deshielding of the imine carbon atoms (12–13 ppm).

Comparison of the ^{195}Pt NMR signals of the complexes **13a–c** with known values[30] shows that the electronic influence of the aryl groups' substitution is by far less pronounced than that of the diimine backbone (Table 2). Electron-withdrawing substituents at the imine carbons cause a greater π-acidity of the ligand and thus a less electron-rich metal centre. Regarding the aryl substitution pattern, no clear trend is found. The overall electronic situation at the metal centre seems to be more affected by the bulkiness of the aromatic substituents than by the presence or absence of *para*-sulfonate groups.

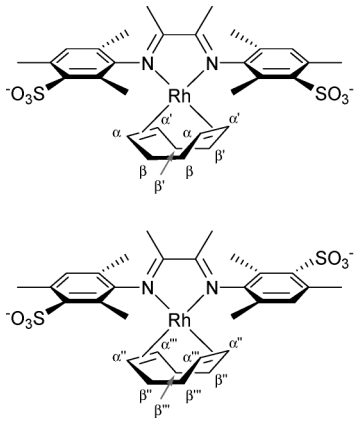
The rhodium(I) COD complexes **14a** and **14c** show three broad signals of equal intensity in the ^{1}H NMR spectra belonging to the two diastereotopic sets of methylene protons and the four equivalent olefinic protons. For the mesitylamine-derived complex **14b** two signals for the olefinic protons are observed, showing the two inequivalent faces of the metal–ligand plane caused by the non-symmetric substitution of the aromatic ring (Scheme 7). In the case of **14a** and **14c**, the ^{13}C NMR spectra show two signals for the COD ligand, of which the olefinic resonance at around 89 ppm features a $^{1}J_{RhC}$ coupling constant of about 11–12 Hz that is also observed for similar rhodium COD complexes.[36] In the case of **14b**, two sets of these signals could be identified due to the above-mentioned reason. However, additional splitting of the signals is expected in the case of *syn*/*anti* isomers (Scheme 7), which could not be clearly resolved from the obtained NMR spectra.

Mass spectrometry. All ligands and complexes were characterized by high-resolution electrospray ionization-mass spectrometry (HR ESI-MS) using acetonitrile as solvent. The cations of the

Table 2 ^{195}Pt NMR shifts (δ (ppm), DMSO-d_6, 298 K) for complexes of the types [$PtCl_2$(DAD)] and [$PtCl_2$(DAD^{S})]$^{2-}$

	Substituents at		
	Aryl	Diimine	^{195}Pt (δ (ppm))
[$PtCl_2$(2,6-Me_2-CF_3-DAD)]	2,6-Me_2	CF_3	−1183[a]
[$PtCl_2$(2,6-Me_2-H-DAD)]	2,6-Me_2	H	−2100[a]
[$PtCl_2$(2,6-Me_2-Me-DAD)]	2,6-Me_2	Me	−2179[a]
[BMMIM]$_2$[$PtCl_2$(2,6-Me_2-Me-DAD^{S})] (**13a**)	2,6-Me_2, 4-SO_3^-	Me	−2193
[BMMIM]$_2$[$PtCl_2$(2,4,6-Me_3-Me-DAD^{S})] (**13b**)	2,4,6-Me_3, 3-SO_3^-	Me	−2192
[BMMIM]$_2$[$PtCl_2$(2,6-*i*Pr_2-Me-DAD^{S})] (**13c**)	2,6-*i*Pr_2, 4-SO_3^-	Me	−2169

[a] Ref. 30.



Scheme 7 Possible conformers of **14b**. While the *syn* conformer has C_s symmetry, the *anti* conformer shows C_2 symmetry. Both conformers have two different α and β positions; up to four sets of COD signals can be distinguished in total.

respective salts were identified in positive ionization mode while the anions were observed in negative ionization mode. In the case of doubly charged anions the dominating mass peak was attributed to $[anion]^{2-}$. Apart from this anion peak, small clusters of the form $[anion + cation]^-$ were found with medium to low intensity in some cases.

Crystal structures

Single-crystal analyses could be obtained for four salts of the free ligands, covering all three different DAD^S anions, as well as for the palladium complex **12d** (Fig. 1–5). Selected bond lengths and angles are shown in Table 3 and in the legend of Fig. 5, respectively. Full details are available in ESI†.

All four crystal structures of the free DAD^S ligands have an asymmetric unit that contains only half a formula unit. The anions are each completed by an inversion centre in the middle of the central carbon–carbon bond (C101–C101′). Because of that, the planar diimine moieties of the DAD^S ligands show perfect *anti* conformation. They are not coplanar with the aromatic substituents but show torsion angles of 82–90°. All bond lengths are in the expected ranges of single and double bonds, respectively (Table 3). The overall geometry of the anions is thus quite similar

Table 3 Selected bond lengths (pm) and angles (°) of the DAD^S ligands. Symmetry operations for equivalent atoms are given at Fig. 1–4

	4a	6	8b	8c
C101–N101	126.3(3)	127.4(2)	127.1(2)	122.8(5)
C101–C101′	150.3(4)	150.0(3)	149.2(4)	149.7(7)
C101–C102	149.3(3)	149.2(3)	149.8(3)	152.9(7)
N101–C103	143.2(3)	142.5(2)	142.7(2)	144.6(4)
C101–N101–C103	121.3(2)	120.1(2)	120.9(2)	122.2(4)
N101–C101–C101′	116.6(3)	116.4(2)	116.6(2)	120.4(6)
N101–C101–C102	125.9(2)	126.0(2)	125.7(2)	125.7(4)
C102–C101–C101′	117.5(3)	117.6(2)	117.7(2)	113.9(5)
N101–C101–C101′–N101′	180[a]	180[a]	180[a]	180[a]
C102–C101–C101′–C102′	180[a]	180[a]	180[a]	180[a]
C101–N101–C103–C104	84.7(3)	90.2(2)	87.8(2)	82.2(6)
C101–N101–C103–C108	101.4(3)	95.8(2)	95.7(2)	108.8(5)

[a] Restricted due to crystal symmetry.

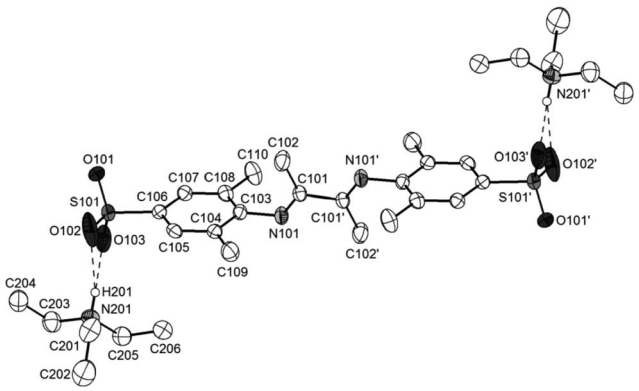


Fig. 1 Molecular structure of **4a**. Displacement ellipsoids are shown for 50% probability, carbon-bound hydrogen atoms are omitted for clarity. Symmetry-equivalent atoms are generated by ′ = –*x*, –*y*, 1 – *z*.

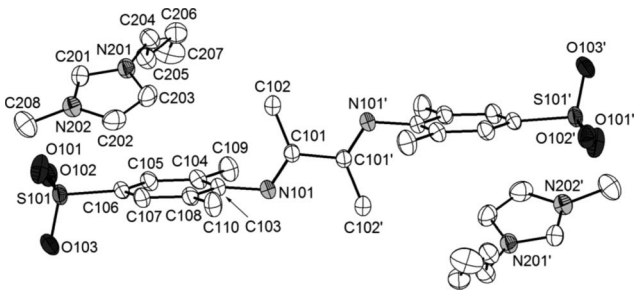


Fig. 2 Molecular structure of **6**. Displacement ellipsoids are shown for 50% probability, hydrogen atoms are omitted for clarity. Symmetry-equivalent atoms are generated by ′ = 2 – *x*, –*y*, –*z*.

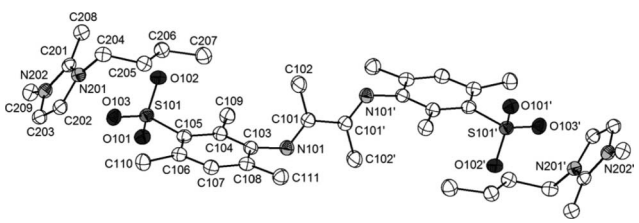


Fig. 3 Molecular structure of **8b**. Displacement ellipsoids are shown for 50% probability, hydrogen atoms are omitted for clarity. Symmetry-equivalent atoms are generated by ′ = 1 – *x*, –*y*, 2 – *z*.

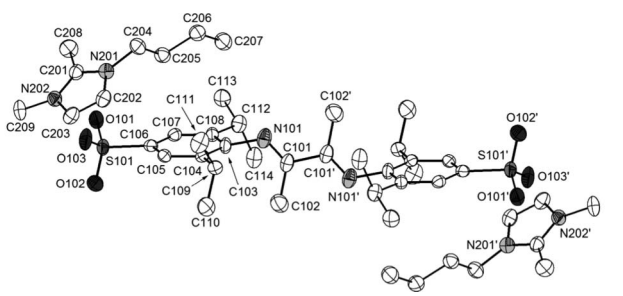


Fig. 4 Molecular structure of **8c**. Displacement ellipsoids are shown for 50% probability, hydrogen atoms are omitted for clarity. Symmetry-equivalent atoms are generated by ′ = 2 – *x*, –*y*, –*z*.

to that of non-sulfonated DAD ligands[37,38] and of $[BMIM]_2$[2,6-Et_2-Me-DAD^S].[11]

The palladium dichloro complex **12d** shows an essentially square-planar coordination geometry with an acute N–Pd–N

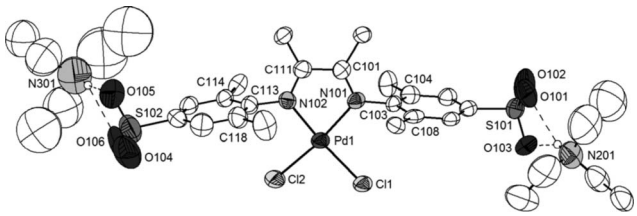


Fig. 5 Molecular structure of **12d**. Displacement ellipsoids are shown for 50% probability, carbon-bound hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and angles (°): Pd1–N101 202.2(4), Pd1–N102 201.2(4), Pd1–Cl1 231.8(2), Pd1–Cl2 228.2(2), C101–N101 128.6(6), C111–N102 129.5(6), C101–C111 148.4(8), N101–C103 140.8(7), N102–C113 143.4(7); N101–Pd1–N102 79.5(2), N101–Pd1–Cl1 95.4(2), N102–Pd1–Cl2 94.3(2), Cl1–Pd1–Cl2 91.1(1), C101–N101–Pd1 113.8(4), C111–N102–Pd1 116.0(4), C103–N101–Pd1 125.5(3), C113–N102–Pd1 124.0(3), C101–N101–C103 120.6(4), C111–N102–C113 119.9(4); N101–C101–C111–N102 3.0(6), C101–N101–C103–C104 83.6(6), C101–N101–C103–C108 98.0(5), C111–N102–C113–C114 90.4(6), C111–N102–C113–C118 92.5(6).

angle of 79.5°. Due to the chelating metal coordination, *cis* conformation is found for the diimine moiety. The aromatic substituents feature torsion angles towards the diimine fragment that are similar to the free ligands (84 and 91°, respectively). All main geometric characteristics are thus comparable to palladium dichloro complexes of non-sulfonated DAD ligands such as [$PdCl_2$(2,6-*i*Pr_2-Me-DAD)][38] and [$PdCl_2$(2,6-*i*Pr_2-H-DAD)].[39]

As expected for acidic ammonium salts, **4a** and **12d** clearly show N–H···O hydrogen bonding (N···O = 299–334 pm). For all imidazolium-based salts, a relatively short contact between the *N*-methyl group and the sulfonate groups is found (C···O = 310–318 pm). In the case of **6**, additional short contacts exist between all three imidazolium carbon atoms and the sulfonate groups (319–322 pm), indicating C–H···O hydrogen bonding.

Both **8b** and **8c** show short contacts between the sulfonate moieties and C201 (C···O = 295 and 304 pm) as well as C202 (C···O = 319 and 309 pm). Interestingly, no such interaction is found for C203 and C208, although the latter position is selectively deprotonated with strong bases, yielding the corresponding *N*,*N*-ketenediacetals (*cf*. Scheme 2).

The crystal packings of **4a**, **8b**, **8c** and **12d** form layered structures with alternating polar (anionic and cationic head groups) and unpolar layers (aromatics, diimine motif and *N*-butyl groups) as shown for **8c** in Fig. 6.

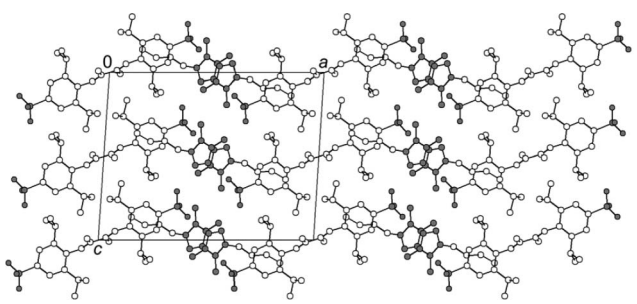


Fig. 6 Crystal packing of **8c**, view along the *b* axis. Sulfonate and imidazolium groups are shown in grey, diimines, aromatics and butyl groups in white. Hydrogens are omitted.

Immobilization in ILs

The effectiveness of immobilization of the herein described complexes was tested using UV-Vis spectroscopy. As the solvatochromic molybdenum tetracarbonyl complexes **15** and **16** give rise to intensely purple coloured solutions due to MLCT transitions,[34] solubility and phase distribution behaviour can easily be monitored. Another interesting feature of the chosen complexes is their rather unpolar metal environment, rendering leaching out of the highly polar IL phase facile in the case of non-immobilizing ligands.

Solutions of the solvatochromic complexes **15** and **16** in [BMIM]OTf both showed the same absorption maximum of 525 nm. Combined with their quite similar high-energy CO stretching modes (1993 and 1996 cm^{-1}, respectively) and the nearly identical carbon NMR shifts of the carbonyl ligands this is a strong indication that the electronic influence of the additional sulfonate groups towards the metal centre is neglectable at least in this case.

The saturation limit of the immobilized complex **16** was found to be considerably higher for the IL than that of the "classical" complex **15** without sulfonate tags (Table 4). As shown in Fig. 7, the molybdenum tetracarbonyl complex **15** not bearing sulfonate-tagged ligands is soluble in both phases arising from the mixture [BMIM]OTf/toluene[40] and thus shows strong leaching while complex **16** having a sulfonated DAD^S ligand is completely retained in the polar, IL-rich phase. No visible leaching of **16** into the toluene layer was observed even in contact to concentrated IL solutions. As this intensely coloured complex is clearly visible at concentrations of about 0.1 mmol L^{-1} and the saturation limit in pure [BMIM]OTf exceeds 100 mmol L^{-1}, the distribution ratio of the DAD^S complex **16** can be estimated to be at least 1000 : 1 in favour of the IL phase.

Fig. 7 Different distribution behaviour of molybdenum carbonyl complexes in [BMIM]OTf/toluene for a "classical", non-sulfonated DAD ligand (left, **15**) and a sulfonated DAD^S ligand (right, **16**).

Table 4 Solubility of molybdenum carbonyl complexes in [BMIM]OTf

	15	**16**
DAD ligand	(2,6-Me_2-Me-DAD)	[BMMIM]$_2$[2,6-Me_2-Me-DAD^S]
λ_{max}/nm	525	525
ε/M^{-1} cm^{-1}	6290	5340
Solubility[a]/g L^{-1}	3.3	104
w_{max}/mg g^{-1}	2.6	80
c_{max}[a]/mmol L^{-1}	6.8	108

[a] Density (solution) = density (pure IL) is assumed.

Conclusions

Sulfonate-tagged diazadiene (DAD^S) ligands have been shown to be easily accessible, versatile building blocks for transition-metal catalysts in multiphasic IL systems. Prominent basic cation precursors also used in the high-purity synthesis of ILs provide a reliable route towards completely halide-free and metal-free DAD^S ligands with onium cations. These well IL-soluble ligands show similar behaviour in complexation reactions as the corresponding neutral parent compounds and can thus be used to generate prominent catalyst precursor analogues with optimised solubility and retention in ILs. Additional studies will be undertaken in the future regarding further catalytically attractive metal complexes and their evaluation in biphasic homogeneous catalysis based on ILs. Preliminary results suggest that zwitterionic DAD^S complexes of Pd(II) and Pt(II) bearing neutral coligands are potentially valuable catalyst precursors. The pronounced solvatochromic behaviour of DAD and DAD^S molybdenum carbonyl complexes offers another interesting subject for further studies on the polarity of ILs as compared to conventional solvents.

Experimental

General remarks

Manipulation of air- and moisture-sensitive substances was carried out using standard Schlenk- and glovebox-techniques. Solvents were dried using standard procedures[41] and stored over Al_2O_3/molecular sieve 3 Å/R3-11G catalyst (BASF).

Sulfanilic acids,[14] imidazoline-2-ylidenes,[15] 2-methylidene-imidazolines,[16] methylidenephosphoranes[17] and guanidinium methylcarbonates[18] were prepared according to the literature. [BMIM]OTf (99%, MERCK) was degassed and stored in a glovebox. Other starting materials were obtained from commercial sources (SIGMA-ALDRICH, MERCK, IOLITEC) and used as received.

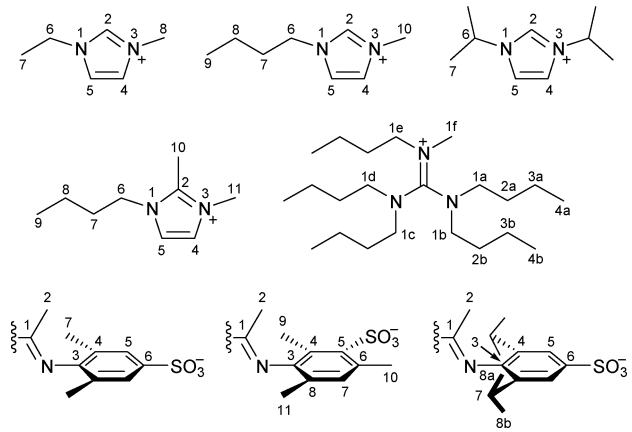
NMR spectra were recorded at 300 K on a BRUKER AC 300, DRX 400 or DRX 500 using CD_3CN or DMSO-d_6 as solvent. Chemical shifts are given with respect to tetramethylsilane (^{1}H, ^{13}C), phosphoric acid (^{31}P) and $Na_2[PtCl_6]$ (^{195}Pt), respectively. Calibration of ^{1}H and ^{13}C NMR spectra was accomplished with the solvent signals, ^{31}P and ^{195}Pt NMR spectra were calibrated externally.

For facile differentiation of anion and cation signals the former are denoted with the subscript "$_A$" while the latter are identified using the subscript "$_C$". The applied numbering schemes are shown in Scheme 8. Only half a molecule is shown for the DAD^S ligand anions because of the magnetic equivalence of both moieties that was observed for all ligands and complexes.

ESI mass spectra were recorded on a THERMO FISHER SCIENTIFIC LTQ FT Ultra using acetonitrile as solvent. *m/z* values are given together with their relative intensities. Isotopic patterns were in all cases consistent with natural abundances.

IR spectra were recorded on a BRUKER Alpha FT-IR spectrometer using neat samples with an ATR measurement setup (diamond cell) at room temperature.

Elemental analysis was done on a CHN/S vario MICROcube (ELEMENTAR). Values are given in weight percent. Satisfactory analyses could not be obtained for all new compounds. In most aberrant cases, the measured values were too low by a factor of 0.95 to 0.98 for all four elements. These differences are most likely attributed to the poor combustion of the ionic compounds.



Scheme 8 Numbering of cations and anions.

UV-Vis spectra were taken on a Novaspec II spectrophotometer at room temperature. Absorption at λ_{max} (525 nm) was measured for six calibration standards in the concentration range of 0.1 to 1 mg mL^{-1} for both complexes. Saturated solutions of the complexes were obtained by stirring an excess of the solute with 1 mL of the IL for three days at room temperature, followed by filtration *via* 0.45 µm syringe filters. Weighted samples of these stock solutions were diluted using [BMIM]OTf to give absorptions similar to the calibration standards and measured. Concentrations were determined according to Lambert–Beer's law.

Synthesis of compounds

Triethylammonium dialkylsulfanilates

General procedure for the preparation of triethylammonium dialkylsulfanilates (3a–c). The appropriate sulfanilic acid **2** (1.0 eq) was suspended in a sufficient amount of methanol to allow for magnetic stirring. Triethylamine (1.1–1.3 eq) was added and the mixture was stirred for 15 min at room temperature. Any insoluble matter was removed by filtration; the resulting solution was concentrated and dried *in vacuo*. The obtained crude product was extracted with ether and dried *in vacuo*.

Triethylammonium 2,6-dimethylaniline-4-sulfonate (3a). Prepared from 2,6-dimethylaniline-4-sulfonic acid (**2a**) (12.00 g, 59.6 mmol, 1.00 eq) and triethylamine (7.24 g, 71.6 mmol, 1.20 eq): 17.21 g (95%) light brown powder. Anal. calc. for $C_{14}H_{26}N_2O_3S$ (302.43 g mol^{-1}) C 55.60, H 8.67, N 9.26, S 10.60%; found C 55.08, H 8.83, N 8.84, S 9.74%. ^{1}H NMR (300 MHz, D_2O) δ = 1.15 (t, 9H, $^3J_{HH}$ = 7.3 Hz, C2$_C$-H), 2.10 (s, 6H, C5$_A$-H), 3.02 (q, 6H, $^3J_{HH}$ = 7.3 Hz, C1$_C$-H), 7.32 (s, 2H, C3$_A$-H) ppm; ^{13}C NMR (75 MHz, D_2O) δ = 8.4 (C2$_C$), 17.1 (C5$_A$), 46.9 (C1$_C$), 123.2 (C2$_A$), 125.5 (C3$_A$), 132.4 (C4$_A$), 145.8 (C1$_A$) ppm. MS (ESI+) *m/z* (%) = 102.1252 (100, $C_6H_{16}N$ requires 102.1277, [cation]$^+$); MS (ESI–) *m/z* (%) = 200.0375 (100, $C_8H_{10}NO_3S$ requires 200.0387, [anion]$^-$). IR (neat) ν = 3459 (w), 3366 (w), 2982 (w), 2695 (br w), 1632 (w), 1481 (m), 1458 (w), 1443 (w), 1389 (w), 1294 (w), 1210 (s), 1180 (m), 1151 (s), 1115 (s), 1029 (vs), 1011 (m), 886 (w), 840 (w), 748 (w), 634 (vs), 612 (m) cm^{-1}.

Triethylammonium 2,4,6-trimethylaniline-3-sulfonate (3b). Prepared from 2,4,6-trimethylaniline-3-sulfonic acid (2b) (20.00 g, 92.9 mmol, 1.00 eq) and triethylamine (10.12 g, 100 mmol, 1.08 eq): 28.61 g (97%) light brown powder. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 1.16 (t, 9H, $^3J_{HH}$ = 7.3 Hz, C2$_C$-H), 2.04, 2.38, 2.40 (3 × s, 3 × 3H, C7-9$_A$-H), 3.04 (q, 6H, $^3J_{HH}$ = 7.3 Hz, C1$_C$-H), 4.29 (s, 2H, NH_2), 6.60 (s, 1H, C5$_A$-H), 9.46 (br s, 1H, NH^+) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 8.5 (C2$_C$), 15.4, 17.7, 22.7 (C7-9$_A$), 45.7 (C1$_C$), 120.0, 121.1, 122.9 (C2$_A$, C4$_A$ and C6$_A$), 130.4 (C5$_A$), 142.4 (C3$_A$), 143.2 (C1$_A$) ppm. MS (ESI+) m/z (%) = 102.1278 (100, $C_6H_{16}N$ requires 102.1277, [cation]$^+$), 418 (24, [2 × cation + anion]$^+$); MS (ESI–) m/z (%) = 214.0540 (100, $C_9H_{12}NO_3S$ requires 214.0543, [anion]$^-$). IR (neat) ν = 3381 (w), 3016 (br w), 2980 (w), 2702 (br w), 1623 (w), 1476 (w), 1459 (m), 1387 (w), 1303 (w), 1221 (m), 1201 (m), 1178 (m), 1151 (m), 1051 (s), 1010 (m), 986 (m), 897 (w), 841 (w), 812 (w), 669 (vs), 599 (m), 577 (m), 546 (s), 519 (m), 470 (m) cm^{-1}.

Triethylammonium 2,6-diisopropylaniline-4-sulfonate (3c). Prepared from 2,6-diisopropylaniline-4-sulfonic acid monohydrate (**2c**) (12.17 g, 44.2 mmol, 1.00 eq) and triethylamine (5.31 g, 53.0 mmol, 1.20 eq): 15.50 g (98%) light brown powder. Anal. calc. for $C_{18}H_{34}N_2O_3S$ (358.54 g mol^{-1}) C 60.30, H 9.56, N 7.81, S 8.94%; found C 60.02, H 9.45, N 7.71, S 8.45%. ^{1}H NMR (300 MHz, D_2O) δ = 1.17 (d, 12H, $^3J_{HH}$ = 6.7 Hz, C6$_A$-H), 1.18 (t, 9H, $^3J_{HH}$ = 7.3 Hz, C2$_C$-H), 2.94 (sept, 2H, $^3J_{HH}$ = 6.8 Hz, C5$_A$-H), 3.07 (q, 6H, $^3J_{HH}$ = 7.3 Hz, C1$_C$-H), 7.45 (s, 2H, C3$_A$-H) ppm; ^{13}C NMR (75 MHz, D_2O) δ = 8.3 (C2$_C$), 21.8 (C6$_A$), 27.3 (C5$_A$), 46.7 (C1$_C$), 120.4 (C3$_A$), 132.9 (C4$_A$), 133.9 (C2$_A$), 143.0 (C1$_A$) ppm. MS (ESI+) m/z (%) = 102.1276 (100, $C_6H_{16}N$ requires 102.1277, [cation]$^+$); MS (ESI–) m/z (%) = 256.1009 (100, $C_{12}H_{18}NO_3S$ requires 256.1002, [anion]$^-$). IR (neat) ν = 3440 (w), 3362 (w), 3266 (w), 2964 (m), 2637 (br w), 2495 (w), 1641 (m), 1461 (m), 1437 (m), 1384 (w), 1357 (w), 1285 (w), 1202 (s), 1150 (s), 1119 (m), 1072 (s), 1026 (vs), 885 (w), 838 (w), 759 (w), 636 (vs), 616 (s), 535 (m) cm^{-1}.

Triethylammonium DAD^S

General procedure for the preparation of triethylammonium salts of DAD^S ligands (4a–c). A solution of the appropriate triethylammonium sulfanilate **3** (2.0 eq), butane-2,3-dione (1.0–1.5 eq) and formic acid (0.05 eq) in methanol (100 mL) was heated to 40 °C for 24 h. The resulting brown solution was evaporated to dryness. The crude product was suspended in ether and sonicated until a powdery solid had formed. After drying, this solid was recrystallized from acetonitrile or acetonitrile/ether. In most cases, two or three additional crops of product were obtained from the mother liquor upon cooling and further addition of ether.

Bis(triethylammonium) *N*,*N*′-bis(2,6-dimethyl-4-sulfonatophenyl)butane-2,3-diimine (4a) [HNEt$_3$]$_2$[2,6-Me$_2$-Me-DAD^S]. Prepared from triethylammonium 2,6-dimethylaniline-4-sulfonate (**3a**) (10.61 g, 35.1 mmol, 2.00 eq) and butane-2,3-dione (2.4 mL, 26.9 mmol, 1.53 eq): 5.11 g (44%) yellow powder. Anal. calc. for $C_{32}H_{54}N_4O_6S_2$ (654.92 g mol^{-1}) C 58.68, H 8.31, N 8.55, S 9.79%; found C 58.36, H 8.46, N 8.46, S 9.47%. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 1.17 (t, 18H, $^3J_{HH}$ = 7.3 Hz, C2$_C$-H), 1.96 (s, 6H, C2$_A$-H), 1.97 (s, 12H, C7$_A$-H), 3.09 (dq, 12H, $^3J_{HH}$ = 4.9, 7.3 Hz, C1$_C$-H), 7.34 (s, 4H, C5$_A$-H), 8.97 (br s, 2H, NH^+) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 8.5 (C2$_C$), 15.6 (C2$_A$), 17.3 (C7$_A$), 45.7 (C1$_C$), 123.3 (C4$_A$), 125.3 (C5$_A$), 142.8 (C6$_A$), 148.2 (C3$_A$), 167.7 (C1$_A$) ppm. MS (ESI+) m/z (%) = 102.1276 (100, $C_6H_{16}N$ requires 102.1277, [cation]$^+$); MS (ESI–) m/z (%) = 225.0455 (100, $C_{20}H_{22}N_2O_6S_2$ requires 225.0465, [anion]$^{2-}$), 451 (23, [anion + H]$^-$). IR (neat) ν = 2983 (w), 2691 (br w), 1641 (m), 1473 (m), 1453 (w), 1393 (w), 1362 (w), 1224 (s), 1157 (s), 1123 (m), 1107 (s), 1032 (vs), 886 (m), 839 (w), 786 (w), 647 (vs), 628 (vs), 589 (m), 554 (m), 523 (m), 497 (m), 444 (w) cm^{-1}.

Bis(triethylammonium) *N*,*N*′-bis(2,4,6-trimethyl-3-sulfonatophenyl)butane-2,3-diimine (4b) [HNEt$_3$]$_2$[2,4,6-Me$_3$-Me-DAD^S]. Prepared from triethylammonium 2,4,6-trimethylaniline-3-sulfonate (**3b**) (1.00 g, 3.16 mmol, 2.00 eq) and butane-2,3-dione (0.14 mL, 1.59 mmol, 1.02 eq): 0.44 g (41%) yellow powder. Anal. calc. for $C_{34}H_{58}N_4O_6S_2$ (682.98 g mol^{-1}) C 59.79, H 8.56, N 8.20, S 9.39%; found C 59.44, H 8.39, N 8.06, S 9.03%. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 1.17 (t, 18H, $^3J_{HH}$ = 7.3 Hz, C2$_C$-H), 1.88, 1.89 (2 × s, 6H, C11$_A$-H, conformers), 1.91 (s, 6H, C2$_A$-H), 2.22, 2.24 (2 × s, 6H, C9$_A$-H, conformers), 2.51 (s, 6H, C10$_A$-H), 3.08 (q, 12H, $^3J_{HH}$ = 7.3 Hz, C1$_C$-H), 6.85 (s, 2H, C7$_A$-H), 9.08 (br s, 2H, NH^+) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 8.6 (C2$_C$), 15.57, 15.59 (C2$_A$, conformers), 15.8, 15.9 (C9$_A$, conformers), 17.2, 17.3 (C11$_A$, conformers), 22.7 (C10$_A$), 45.8 (C1$_C$), 123.2, 123.29, 123.32, 123.4, 130.2 (C4$_A$, C6$_A$ and C6$_A$, conformers), 130.6 (C7$_A$), 143.9 (C5$_A$), 146.6 (C3$_A$), 167.8 (C1$_A$) ppm. MS (ESI+) m/z (%) = 102.1277 (100, $C_6H_{16}N$ requires 102.1277, [cation]$^+$); MS (ESI–) m/z (%) = 239.0619 (100, $C_{22}H_{26}N_2O_6S_2$ requires 239.0622, [anion]$^{2-}$), 479 (28, [anion + H]$^-$). IR (neat) ν = 2982 (w), 2926 (w), 2698 (br w), 1649 (m), 1451 (m), 1401 (w), 1360 (w), 1223 (s), 1166 (vs), 1125 (m), 1049 (s), 1014 (m), 991 (s), 869 (w), 803 (w), 751 (w), 695 (m), 658 (vs), 628 (s), 595 (w), 578 (m), 559 (m), 543 (s), 523 (m), 467 (w) cm^{-1}.

Bis(triethylammonium) *N*,*N*′-bis(2,6-diisopropyl-4-sulfonatophenyl)butane-2,3-diimine (4c) [HNEt$_3$]$_2$[2,6-*i*Pr$_2$-Me-DAD^S]. Prepared from triethylammonium 2,6-diisopropylaniline-4-sulfonate (**3c**) (3.02 g, 8.40 mmol, 2.00 eq) and butane-2,3-dione (0.6 mL, 6.46 mmol, 1.54 eq): 0.58 g (18%) yellow powder. Anal. calc. for $C_{40}H_{70}N_4O_6S_2$ (767.14 g mol^{-1}) C 62.63, H 9.20, N 7.30, S 8.36%; found C 62.21, H 9.06, N 7.23, S 7.99%. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 1.10 (d, 12H, $^3J_{HH}$ = 6.9 Hz, C8a$_A$-H), 1.16 (d, 12H, $^3J_{HH}$ = 6.9 Hz, C8b$_A$-H), 1.17 (t, 18H, $^3J_{HH}$ = 7.2 Hz, C2$_C$-H), 2.00 (s, 6H, C2$_A$-H), 2.68 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, C7$_A$-H), 3.09 (dq, 12H, $^3J_{HH}$ = 4.7, 7.3 Hz, C1$_C$-H), 7.44 (s, 4H, C5$_A$-H), 8.98 (br s, 2H, NH^+) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 8.6 (C2$_C$), 16.3 (C2$_A$), 22.2 (C8a$_A$), 22.7 (C8b$_A$), 28.0 (C7$_A$), 45.8 (C1$_C$), 120.4 (C5$_A$), 133.7 (C4$_A$), 143.6 (C6$_A$), 145.9 (C3$_A$), 168.0 (C1$_A$) ppm. MS (ESI+) m/z (%) = 102.1278 (100, $C_6H_{16}N$ requires 102.1277, [cation]$^+$); MS (ESI–) m/z (%) = 281.1084 (100, $C_{28}H_{38}N_2O_6S_2$ requires 281.1091, [anion]$^{2-}$), 563 (4, [anion + H]$^-$). IR (neat) ν = 2967 (w), 2705 (br w), 1655 (w), 1465 (w), 1430 (w), 1361 (w), 1224 (m), 1166 (s), 1151 (s), 1118 (m), 1070 (m), 1029 (vs), 888 (w), 847 (w), 801 (w), 650 (m), 639 (s), 618 (s), 607 (m), 556 (w), 538 (w), 520 (w), 497 (w), 467 (w), 445 (w) cm^{-1}.

Imidazolium DAD^S and related

General procedure for the preparation of onium-salts of DAD^S ligands (5–8, 10) from imidazoline-2-ylidenes, 2-methylideneimidazolines or methylidenephosphoranes. A solution or suspension of the appropriate triethylammonium DAD^S **4** (0.2–5 g, 1.0 eq) in acetonitrile (10–40 mL) was cooled to –40 °C. The appropriate cation precursor (2.2 eq) was slowly added *via* syringe. The mixture was allowed to warm to room temperature overnight. After removal of all volatiles *in vacuo* the crude product was washed with ether and dried at 10^{-2} mbar.

The obtained ligand salts can be further purified by recrystallization from acetonitrile/ether or dichloromethane/ether, if necessary.

General procedure for the preparation of onium-salts of DAD^S ligands (6, 9, 11) from ammonium hydroxides, imidazolium methylcarbonates or guanidinium methylcarbonates

The same procedure as above was applied, except that no cooling of the reaction mixture was needed with these less sensitive cation precursors. Thus, the reaction was carried out at room temperature.

Bis(1-ethyl-3-methylimidazolium) *N*,*N*′-bis(2,6-dimethyl-4-sulfonatophenyl)butane-2,3-diimine (5) [EMIM]$_2$[2,6-Me$_2$-Me-DAD^S]. Prepared from **4a** (2.09 g, 3.18 mmol, 1.00 eq) and 1-ethyl-3-methylimidazoline-2-ylidene (0.77 g, 6.99 mmol, 2.20 eq): 1.91 g (89%) light yellow powder. Anal. calc. for $C_{32}H_{44}N_6O_6S_2$ (672.86 g mol^{-1}) C 57.12, H 6.59, N 12.49, S 9.53%; found C 56.92, H 6.64, N 12.44, S 9.18%. ^{1}H NMR (300 MHz, CD_3CN) δ = 1.44 (t, 6H, $^3J_{HH}$ = 7.3 Hz, C7$_C$-H), 1.99 (s, 6H, C2$_A$-H), 2.01 (s, 12H, C7$_A$-H), 3.83 (s, 6H, C8$_C$-H), 4.17 (q, 4H, $^3J_{HH}$ = 7.3 Hz, C6$_C$-H), 7.34, 7.39 (2 × s, 2 × 2H, C4$_C$-H and C5$_C$-H), 7.45 (s, 4H, C5$_A$-H), 8.80 (s, 2H, C2$_C$-H) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 15.6 (C2$_A$), 16.2 (C7$_C$), 18.0 (C7$_A$), 36.7 (C8$_C$), 45.7 (C6$_C$), 125.1 (C4$_A$), 126.4 (C5$_A$), 144.6 (C6$_A$), 149.7 (C3$_A$), 169.2 (C1$_A$) ppm. MS (ESI+) *m*/*z* (%) = 111.0916 (100, $C_6H_{11}N_2$ requires 111.0917, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 225 (6, [anion]$^{2-}$), 451.1011 (100, $C_{20}H_{23}N_2O_6S_2$ requires 451.1003, [anion + H]$^-$). IR (neat) ν = 3096 (w), 1646 (w), 1574 (w), 1457 (br w), 1363 (w), 1209 (m), 1180 (s), 1127 (m), 1105 (m), 1035 (s), 888 (w), 872 (w), 835 (w), 784 (w), 645 (s), 621 (s), 587 (m), 554 (w), 522 (w), 498 (w) cm^{-1}.

Bis(1-*n*-butyl-3-methylimidazolium) *N*,*N*′-bis(2,6-dimethyl-4-sulfonatophenyl)butane-2,3-diimine (6) [BMIM]$_2$[2,6-Me$_2$-Me-DAD^S]. Prepared from **4a** (215 mg, 0.33 mmol, 1.00 eq) and a methanolic solution (50%) of 1-*n*-butyl-3-methylimidazolium methylcarbonate (0.3 mL, corresponds to 0.68 mmol, 2.05 eq): 238 mg (99%) light yellow powder. Anal. calc. for $C_{36}H_{52}N_6O_6S_2$ (728.97 g mol^{-1}) C 59.31, H 7.19, N 11.53, S 8.80%; found C 58.64, H 7.34, N 11.56, S 7.88%. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.89 (t, 6H, $^3J_{HH}$ = 7.3 Hz, C9$_C$-H), 1.24 (psext, 4H, $^3J_{HH}$ = 7.5 Hz, C8$_C$-H), 1.75 (pquint, 4H, $^3J_{HH}$ = 7.4 Hz, C7$_C$-H), 1.95 (s, 6H, C2$_A$-H), 1.96 (s, 12H, C7$_A$-H), 3.84 (s, 6H, C10$_C$-H), 4.15 (t, 4H, $^3J_{HH}$ = 7.2 Hz, C6$_C$-H), 7.33 (s, 4H, C5$_A$-H), 7.71 (t, 2H, $^3J_{HH}$ = 1.7 Hz, C4$_C$-H), 7.78 (t, 2H, $^3J_{HH}$ = 1.7 Hz, C5$_C$-H), 9.15 (s, 2H, C2$_C$-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 13.2 (C9$_C$), 15.6 (C2$_A$), 17.3 (C7$_A$), 18.7 (C8$_C$), 31.3 (C7$_C$), 35.7 (C10$_C$), 48.4 (C6$_C$), 122.2 (C5$_C$), 123.2 (C4$_A$), 123.6 (C4$_C$), 125.2 (C5$_A$), 136.5 (C2$_C$), 143.3 (C6$_A$), 148.0 (C3$_A$), 167.7 (C1$_A$) ppm. MS (ESI+) *m*/*z* (%) = 139.1229 (100, $C_8H_{15}N_2$ requires 139.1230, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 225 (100, [anion]$^{2-}$), 451.0982 (17, $C_{20}H_{23}N_2O_6S_2$ requires 451.0992, [anion + H]$^-$), 589 (7, [anion + cation]$^-$). IR (neat) ν = 3094 (w), 2959 (w), 2872 (w), 1631 (w), 1569 (w), 1456 (w), 1359 (w), 1233 (w), 1209 (m), 1173 (s), 1124 (m), 1103 (m), 1035 (s), 886 (w), 877 (w), 853 (w), 783 (w), 641 (s), 629 (m), 619 (s), 586 (m), 556 (m), 522 (m), 497 (m) cm^{-1}.

The same product was obtained from **4a** (1.96 g, 3.00 mmol, 1.00 eq) and 1-*n*-butyl-3-methylimidazoline-2-ylidene (0.87 g, 6.30 mmol, 2.10 eq): 1.30 g (59%) yellow powder.

Bis(1,3-diisopropylimidazolium) *N*,*N*′-bis(2,6-dimethyl-4-sulfonatophenyl)butane-2,3-diimine (7) [DIIM]$_2$[2,6-Me$_2$-Me-DAD^S]. Prepared from **4a** (1.00 g, 1.53 mmol, 1.00 eq) and 1,3-diisopropylimidazoline-2-ylidene (0.50 g, 3.28 mmol, 2.14 eq): 1.13 g (98%) light yellow powder. Anal. calc. for $C_{38}H_{56}N_6O_6S_2$ (757.02 g mol^{-1}) C 60.29, H 7.46, N 11.10, S 8.47%; found C 59.93, H 7.40, N 11.18, S 7.88%. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 1.47 (d, 24H, $^3J_{HH}$ = 6.6 Hz, C7$_C$-H), 1.96 (s, 6H, C2$_A$-H), 1.97 (s, 12H, C7$_A$-H), 4.62 (sept, 4H, $^3J_{HH}$ = 6.7 Hz, C6$_C$-H), 7.34 (s, 4H, C5$_A$-H), 7.93 (d, 4H, $^4J_{HH}$ = 1.2 Hz, C4$_C$-H and C5$_C$-H), 9.32 (s, 2H, C2$_C$-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 15.6 (C2$_A$), 17.3 (C7$_A$), 22.3 (C7$_C$), 52.2 (C6$_C$), 120.6 (C4$_C$ and C5$_C$), 123.2 (C4$_A$), 125.2 (C5$_A$), 133.6 (C2$_C$), 143.3 (C6$_A$), 148.0 (C3$_A$), 167.7 (C1$_A$) ppm. MS (ESI+) *m*/*z* (%) = 153.1387 (100, $C_9H_{17}N_2$ requires 153.1386, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 225.0455 (100, $C_{20}H_{22}N_2O_6S_2$ requires 225.0465, [anion]$^{2-}$), 603 (5, [anion + cation]$^-$). IR (neat) ν = 3087 (w), 3039 (w), 2977 (w), 1639 (m), 1556 (w), 1464 (w), 1435 (w), 1377 (w), 1357 (w), 1271 (w), 1236 (m), 1210 (s), 1185 (s), 1152 (m), 1107 (m), 1038 (s), 883 (m), 784 (w), 662 (w), 641 (s), 628 (s), 608 (w), 587 (w), 555 (w), 522 (w), 497 (w) cm^{-1}.

Bis(1-*n*-butyl-2,3-dimethylimidazolium) *N*,*N*′-bis(2,6-dimethyl-4-sulfonatophenyl)butane-2,3-diimine (8a) [BMMIM]$_2$[2,6-Me$_2$-Me-DAD^S]. Prepared from **4a** (2.02 g, 3.08 mmol, 1.00 eq) and 1-*n*-butyl-2-methylidene-3-methylimidazoline (1.13 g, 7.40 mmol, 2.40 eq): 2.28 g (98%) yellow powder. Anal. calc. for $C_{38}H_{56}N_6O_6S_2$ (757.02 g mol^{-1}) C 60.29, H 7.46, N 11.10, S 8.47%; found C 59.80, H 7.35, N 11.01, S 8.20%. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.90 (t, 6H, $^3J_{HH}$ = 7.3 Hz, C9$_C$-H), 1.27 (psext, 4H, $^3J_{HH}$ = 7.6 Hz, C8$_C$-H), 1.68 (pquint, 4H, $^3J_{HH}$ = 7.5 Hz, C7$_C$-H), 1.96 (s, 6H, C2$_A$-H), 1.97 (s, 12H, C7$_A$-H), 2.57 (s, 6H, C10$_C$-H), 3.74 (s, 6H, C11$_C$-H), 4.10 (t, 4H, $^3J_{HH}$ = 7.3 Hz, C6$_C$-H), 7.31 (s, 4H, C5$_A$-H), 7.62 (d, 2H, $^3J_{HH}$ = 2.1 Hz, C4$_C$-H), 7.65 (d, 2H, $^3J_{HH}$ = 2.1 Hz, C5$_C$-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 9.1 (C10$_C$), 13.3 (C9$_C$), 15.6 (C2$_A$), 17.3 (C7$_A$), 18.8 (C8$_C$), 31.1 (C7$_C$), 34.6 (C11$_C$), 47.2 (C6$_C$), 120.8 (C5$_C$), 122.3 (C4$_C$), 123.1 (C4$_A$), 125.2 (C5$_A$), 143.4 (C6$_A$), 144.2 (C2$_C$), 147.9 (C3$_A$), 167.6 (C1$_A$) ppm. MS (ESI+) *m*/*z* (%) = 153.1386 (100, $C_9H_{17}N_2$ requires 153.1386, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 225.0460 (100, $C_{20}H_{22}N_2O_6S_2$ requires 225.0465, [anion]$^{2-}$), 603 (13, [anion + cation]$^-$). IR (neat) ν = 3097 (w), 2960 (w), 1652 (w), 1589 (w), 1542 (w), 1462 (w), 1436 (w), 1361 (w), 1193 (vs), 1108 (m), 1039 (s), 889 (w), 875 (w), 794 (m), 670 (w), 646 (s), 627 (m), 609 (w), 587 (w), 554 (w), 519 (w), 498 (w), 441 (w) cm^{-1}.

Bis(tri-*n*-butylmethylphosphonium) *N*,*N*′-bis(2,6-dimethyl-4-sulfonatophenyl)butane-2,3-diimine (9) [$Bu_3PMe]_2$[2,6-Me_2-Me-DAD^S]. Prepared from **4a** (301 mg, 0.46 mmol, 1.00 eq) and tri-*n*-butylmethylidenephosphorane (200 mg, 0.92 mmol, 2.02 eq): 370 mg (91%) light yellow powder. Anal. calc. for $C_{46}H_{82}N_2O_6P_2S_2$ (885.23 g mol^{-1}) C 62.41, H 9.34, N 3.16, S 7.24%; found C 61.90, H 9.18, N 3.49, S 6.87%. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.91 (t, 18H, $^3J_{HH}$ = 6.9 Hz, $C4_C$-H), 1.33–1.52 (m, 24H, $C3_C$-H and $C2_C$-H), 1.79 (d, 6H, $^2J_{PH}$ = 14 Hz, $C5_C$), 1.96 (s, 6H, $C2_A$-H), 1.97 (s, 12H, $C7_A$-H), 2.08–2.21 (m, 12H, $C1_C$-H), 7.33 (s, 4H, $C5_A$-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 3.1 (d, $^1J_{PC}$ = 51 Hz, $C5_C$), 13.2 ($C4_C$), 15.6 ($C2_A$), 17.3 ($C7_A$), 18.9 (d, $^1J_{PC}$ = 49 Hz, $C1_C$), 22.6 (d, $^2J_{PC}$ = 4.4 Hz, $C2_C$), 23.3 (d, $^3J_{PC}$ = 16 Hz, $C3_C$), 123.2 ($C4_A$), 125.2 ($C5_A$), 143.4 ($C6_A$), 148.0 ($C3_A$), 167.7 ($C1_A$) ppm; ^{31}P NMR (121 MHz, DMSO-d_6) δ = 32.2 ppm. MS (ESI+) *m*/*z* (%) = 217.2079 (100, $C_{13}H_{30}P$ requires 217.2080, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 225.0455 (100, $C_{20}H_{22}N_2O_6S_2$ requires 225.0465, [anion]$^{2-}$), 668 (5, [anion + cation]$^-$). IR (neat) ν = 2959 (w), 2931 (w), 2906 (w), 2869 (w), 1651 (w), 1464 (w), 1209 (m), 1188 (s), 1123 (w), 1105 (m), 1035 (s), 1003 (w), 941 (m), 931 (m), 909 (w), 898 (w), 879 (w), 783 (w), 645 (s), 626 (s), 588 (m), 553 (w), 520 (w), 498 (w) cm^{-1}.

Bis(tetra-*n*-butylammonium) *N*,*N*′-bis(2,6-dimethyl-4-sulfonatophenyl)butane-2,3-diimine (10) [$Bu_4N]_2$[2,6-Me_2-Me-DAD^S]. Prepared from **4a** (510 mg, 0.78 mmol, 1.00 eq) and tetra-*n*-butylammonium hydroxide (3.6 mL of a 12.5 wt% solution in methanol, 1.39 mmol, 1.78 eq): 640 mg (88%) yellow powder. Anal. calc. for $C_{52}H_{94}N_4O_6S_2$ (935.46 g mol^{-1}) C 66.76, H 10.13, N 5.99, S 6.86%; found C 66.79, H 10.19, N 5.59, S 5.41%. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.93 (t, 24H, $^3J_{HH}$ = 7.3 Hz, $C4_C$-H), 1.30 (psext, 16H, $^3J_{HH}$ = 7.4 Hz, $C3_C$-H), 1.52–1.62 (m, 16H, $C2_C$-H), 1.96 (s, 6H, $C2_A$-H), 1.97 (s, 12H, $C7_A$-H), 3.14–3.20 (m, 16H, $C1_C$-H), 7.33 (s, 4H, $C5_A$-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 13.4 ($C4_C$), 15.6 ($C2_A$), 17.3 ($C7_A$), 19.2 ($C3_C$), 23.0 ($C2_C$), 57.5 ($C1_C$), 123.1 ($C4_A$), 125.2 ($C5_A$), 143.5 ($C6_A$), 147.9 ($C3_A$), 167.7 ($C1_A$) ppm. MS (ESI+) *m*/*z* (%) = 242.2829 (100, $C_{16}H_{36}N$ requires 242.2842, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 225.0455 (100, $C_{20}H_{22}N_2O_6S_2$ requires 225.0465, [anion]$^{2-}$), 693 (12, [anion + cation]$^-$). IR (neat) ν = 2958 (m), 2873 (w), 1634 (w), 1488 (w), 1463 (m), 1380 (w), 1364 (w), 1235 (w), 1212 (m), 1185 (s), 1123 (w), 1105 (m), 1033 (s), 883 (m), 714 (w), 646 (s), 627 (s), 606 (w), 586 (w), 552 (w), 521 (w), 496 (w) cm^{-1}.

Bis(*N*,*N*,*N*′,*N*′,*N*″-penta-*n*-butyl-*N*″-methylguanidinium) *N*,*N*′-bis(2,6-dimethyl-4-sulfonatophenyl)butane-2,3-diimine (11) [Gua-4,4-4,4-4,1]$_2$[2,6-Me_2-Me-DAD^S]. Prepared from **4a** (199 mg, 0.30 mmol, 1.00 eq) and *N*,*N*,*N*′,*N*′,*N*″-penta-*n*-butyl-*N*″-methylguanidinium methylcarbonate (259 mg, 0.60 mmol, 2.01 eq): 342 mg (98%) yellow powder. Anal. calc. for $C_{64}H_{118}N_8O_6S_2$ (1159.80 g mol^{-1}) C 66.28, H 10.25, N 9.66, S 5.53%; found C 65.92, H 10.11, N 9.58, S 5.15%. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.86–0.92 (m, 30H, C4a-e_C-H), 1.17–1.72 (m, 40H, C3a-e_C-H and C2a-e_C-H), 1.96 (s, 6H, $C2_A$-H), 1.97 (s, 12H, $C7_A$-H), 2.87 (s, 6H, C1f_C-H), 2.91–3.30 (m, 20H, C1a-e_C-H), 7.32 (s, 4H, $C5_A$-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 13.46 (C4a-d_C), 13.51 (C4e_C), 15.6 ($C2_A$), 17.3 ($C7_A$), 19.3, 19.4, 19.5 (C3a-e_C), 28.6, 28.7, 28.8, 29.0, 29.2 (C2a-e_C), 37.6 (C1f_C), 48.2, 48.5, 48.6, 49.0 (C1a-d_C), 51.9 (C1e_C), 123.1 ($C4_A$), 125.2 ($C5_A$), 143.5 ($C6_A$), 147.9 ($C3_A$), 163.2 (C_{Gua}), 167.7 ($C1_A$) ppm. MS (ESI+) *m*/*z* (%) = 354.3842 (100, $C_{22}H_{48}N_3$ requires 354.3843, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 451.1015 (100, $C_{20}H_{23}N_2O_6S_2$ requires 451.1003, [anion + H]$^-$), 804 (20, [anion + cation]$^-$). IR (neat) ν = 2956 (m), 2930 (m), 2871 (w), 1644 (w), 1537 (m), 1457 (m), 1376 (w), 1360 (w), 1313 (w), 1270 (w), 1235 (w), 1196 (vs), 1106 (m), 1035 (vs), 886 (m), 738 (w), 645 (s), 627 (s), 605 (w), 587 (w), 553 (w), 520 (w), 497 (w) cm^{-1}.

Bis(1-*n*-butyl-2,3-dimethylimidazolium) *N*,*N*′-bis(2,4,6-trimethyl-3-sulfonatophenyl)butane-2,3-diimine (8b) [BMMIM]$_2$[2,4,6-Me_3-Me-DAD^S]. Prepared from **4b** (1.00 g, 1.47 mmol, 1.00 eq) and 1-*n*-butyl-2-methylidene-3-methylimidazoline (0.54 g, 3.53 mmol, 2.40 eq): 1.04 g (91%) yellow powder. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.88 (t, 6H, $^3J_{HH}$ = 7.3 Hz, $C9_C$-H), 1.26 (psext, 4H, $^3J_{HH}$ = 7.5 Hz, $C8_C$-H), 1.66 (pquint, 4H, $^3J_{HH}$ = 7.4 Hz, $C7_C$-H), 1.87, 1.89 (2 × s, 6H, $C11_A$-H, conformers), 1.90 (s, 6H, $C2_A$-H), 2.22, 2.23 (2 × s, 6H, $C9_A$-H, conformers), 2.50 (s, 6H, $C10_A$-H), 2.56 (s, 6H, $C10_C$-H), 3.74 (s, 6H, $C11_C$-H), 4.09 (t, 4H, $^3J_{HH}$ = 7.3 Hz, $C6_C$-H), 6.84 (s, 2H, $C7_A$-H), 7.63 (d, 2H, $^3J_{HH}$ = 1.8 Hz, $C4_C$-H), 7.66 (d, 2H, $^3J_{HH}$ = 1.8 Hz, $C5_C$-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 9.1 ($C10_C$), 13.3 ($C9_C$), 15.5 ($C2_A$), 15.8, 15.9 ($C9_A$, conformers), 17.2, 17.3 ($C11_A$, conformers), 18.8 ($C8_C$), 22.7 ($C10_A$), 31.1 ($C7_C$), 34.6 ($C11_C$), 47.2 ($C6_C$), 120.8 ($C5_C$), 122.3 ($C4_C$), 123.1, 123.2, 130.1 ($C4_A$, $C6_A$ and $C8_A$), 130.6 ($C7_A$), 144.12 ($C5_A$), 144.14 ($C2_C$), 146.6 ($C3_A$), 167.7 ($C1_A$) ppm. MS (ESI+) *m*/*z* (%) = 153.1385 (100, $C_9H_{17}N_2$ requires 153.1386, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 479.1329 (100, $C_{22}H_{27}N_2O_6S_2$ requires 479.1316, [anion + H]$^-$). IR (neat) ν = 3097 (w), 2954 (w), 1646 (w), 1588 (w), 1540 (w), 1457 (w), 1434 (w), 1374 (w), 1360 (w), 1239 (m) 1220 (s), 1181 (vs), 1122 (m), 1049 (s), 1016 (w), 992 (m), 864 (w), 790 (m), 763 (w), 695 (m), 669 (m), 659 (s), 631 (s), 579 (w), 560 (m), 538 (m), 527 (m) cm^{-1}.

Bis(1-*n*-butyl-2,3-dimethylimidazolium) *N*,*N*′-bis(2,6-diisopropyl-4-sulfonatophenyl)butane-2,3-diimine (8c) [BMMIM]$_2$[2,6-*i*Pr_2-Me-DAD^S]. Prepared from **4c** (1.03 g, 1.34 mmol, 1.00 eq) and 1-*n*-butyl-2-methylidene-3-methylimidazoline (0.49 g, 3.20 mmol, 2.39 eq): 0.80 g (69%) yellow powder. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.90 (t, 6H, $^3J_{HH}$ = 7.3 Hz, $C9_C$-H), 1.09 (d, 12H, $^3J_{HH}$ = 6.8 Hz, C8a_A-H), 1.15 (d, 12H, $^3J_{HH}$ = 6.8 Hz, C8b_A-H), 1.28 (psext, 4H, $^3J_{HH}$ = 7.6 Hz, $C8_C$-H), 1.68 (pquint, 4H, $^3J_{HH}$ = 7.4 Hz, $C7_C$-H), 1.99 (s, 6H, $C2_A$-H), 2.58 (s, 6H, $C10_C$-H), 2.66 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, $C7_A$-H), 3.74 (s, 6H, $C11_C$-H), 4.10 (t, 4H, $^3J_{HH}$ = 7.3 Hz, $C6_C$-H), 7.41 (s, 4H, $C5_A$-H), 7.62 (d, 2H, $^3J_{HH}$ = 1.9 Hz, $C4_C$-H), 7.65 (d, 2H, $^3J_{HH}$ = 2.0 Hz, $C5_C$-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 9.1 ($C10_C$), 13.3 ($C9_C$), 16.3 ($C2_A$), 18.8 ($C8_C$), 22.3 (C8a_A), 22.7 (C8b_A), 28.0 ($C7_A$), 31.1 ($C7_C$), 34.6 ($C11_C$), 47.2 ($C6_C$), 120.4 ($C5_A$), 120.8 ($C5_C$), 122.3 ($C4_C$), 133.5 ($C4_A$), 144.0 ($C6_A$), 144.2 ($C2_C$), 145.7 ($C3_A$), 168.0 ($C1_A$) ppm. MS (ESI+) *m*/*z* (%) = 153.1385 (100, $C_9H_{17}N_2$ requires 153.1386, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 281.1085 (100, $C_{28}H_{38}N_2O_6S_2$ requires 281.1091, [anion]$^{2-}$), 563 (4, [anion + H]$^-$), 715.3451 (8, $C_{37}H_{55}N_4O_6S_2$ requires 715.3569, [anion + cation]$^-$). IR (neat) ν = 3091 (w), 2964 (w), 1650 (w), 1590 (w), 1541 (w), 1463 (w), 1436 (w), 1419 (w), 1362 (w), 1261 (w), 1196 (vs), 1152 (w), 1137 (w), 1120 (m), 1099 (w), 1072 (m), 1034 (s), 940 (w), 885 (w), 850 (w), 795 (w), 760 (m), 731 (w), 669 (w), 648 (m), 635 (s), 617 (m), 553 (w), 539 (w), 510 (w), 443 (w) cm^{-1}.

Palladium complexes

General procedure for the preparation of complexes of the type [BMMIM]$_2$[PdCl$_2$(DAD^S)] (12a–d). A mixture of the appropriate DAD^S ligand **8** (0.1–0.2 mmol, 1.0 eq) and [PdCl$_2$(MeCN)$_2$] (1.1 eq) was stirred in acetonitrile (10–20 mL) at room temperature overnight. After removal of all volatiles *in vacuo* the crude product was washed with ether and dried at 10^{-2} mbar.

Bis(1-*n*-butyl-2,3-dimethylimidazolium) {*N*,*N*′-bis(2,6-dimethyl-4-sulfonatophenyl)butane-2,3-diimine-κ^2*N*,*N*′}dichloropalladium(II) (12a) [BMMIM]$_2$[PdCl$_2$(2,6-Me$_2$-Me-DAD^S)]. Prepared from **8a** (155 mg, 0.20 mmol, 1.00 eq) and [PdCl$_2$(MeCN)$_2$] (56 mg, 0.21 mmol, 1.05 eq): 187 mg (98%) light orange powder. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.90 (t, 6H, $^3J_{HH}$ = 7.3 Hz, C9$_C$-H), 1.27 (psext, 4H, $^3J_{HH}$ = 7.5 Hz, C8$_C$-H), 1.67 (pquint, 4H, $^3J_{HH}$ = 7.5 Hz, C7$_C$-H), 2.07 (s, 6H, C2$_A$-H), 2.26 (s, 12H, C7$_A$-H), 2.57 (s, 6H, C10$_C$-H), 3.74 (s, 6H, C11$_C$-H), 4.10 (t, 4H, $^3J_{HH}$ = 7.3 Hz, C6$_C$-H), 7.33 (s, 4H, C5$_A$-H), 7.62 (d, 2H, $^3J_{HH}$ = 2.1 Hz, C4$_C$-H), 7.65 (d, 2H, $^3J_{HH}$ = 2.1 Hz, C5$_C$-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 9.1 (C10$_C$), 13.4 (C9$_C$), 17.8 (C7$_A$), 18.8 (C8$_C$), 19.7 (C2$_A$), 31.1 (C7$_C$), 34.6 (C11$_C$), 47.2 (C6$_C$), 120.8 (C5$_C$), 122.3 (C4$_C$), 125.0 (C5$_A$), 128.7 (C4$_A$), 143.0 (C6$_A$), 144.2 (C2$_C$), 146.9 (C3$_A$), 181.8 (C1$_A$) ppm. MS (ESI+) *m*/*z* (%) = 153.1384 (100, $C_9H_{17}N_2$ requires 153.1386, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 225 (34, [anion – PdCl$_2$]$^{2-}$), 451 (29, [anion – PdCl$_2$ + H]$^-$), 557 (35, [anion – H – 2Cl]$^-$), 595 (22, [anion – Cl]$^-$), 628.9428 (100, $C_{20}H_{23}Cl_2N_2O_6PdS_2$ requires 628.9406, [anion + H]$^-$). IR (neat) ν = 3099 (w), 2958 (w), 1587 (w), 1538 (w), 1463 (w), 1381 (w), 1237 (m), 1195 (vs), 1146 (m), 1106 (m), 1039 (vs), 1015 (m), 878 (w), 755 (w), 668 (w), 649 (s), 632 (vs), 619 (s), 555 (m), 525 (w), 456 (w) cm^{-1}.

Bis(1-*n*-butyl-2,3-dimethylimidazolium) {*N*,*N*′-bis(2,4,6-trimethyl-3-sulfonatophenyl)butane-2,3-diimine-κ^2*N*,*N*′}dichloropalladium(II) (12b) [BMMIM]$_2$[PdCl$_2$(2,4,6-Me$_3$-Me-DAD^S)]. Prepared from **8b** (106 mg, 0.14 mmol, 1.00 eq) and [PdCl$_2$(MeCN)$_2$] (39 mg, 0.15 mmol, 1.11 eq): 115 mg (89%) orange powder. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.89 (t, 6H, $^3J_{HH}$ = 7.3 Hz, C9$_C$-H), 1.26 (psext, 4H, $^3J_{HH}$ = 7.5 Hz, C8$_C$-H), 1.67 (pquint, 4H, $^3J_{HH}$ = 7.5 Hz, C7$_C$-H), 2.03 (s, 6H, C2$_A$-H), 2.20, 2.50, 2.51 (3 × s, 3 × 6H, C2$_A$-H and C9-11$_A$-H), 2.56 (s, 6H, C10$_C$-H), 3.73 (s, 6H, C11$_C$-H), 4.09 (t, 4H, $^3J_{HH}$ = 7.3 Hz, C6$_C$-H), 6.88 (s, 2H, C7$_A$-H), 7.61 (d, 2H, $^3J_{HH}$ = 1.9 Hz, C4$_C$-H), 7.64 (d, 2H, $^3J_{HH}$ = 1.9 Hz, C5$_C$-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 9.1 (C10$_C$), 13.4 (C9$_C$), 16.3 (C9$_A$), 17.8 (C11$_A$), 18.8 (C8$_C$), 19.5 (C2$_A$), 22.9 (C10$_A$), 31.1 (C7$_C$), 34.6 (C11$_C$), 47.2 (C6$_C$), 120.8 (C5$_C$), 122.3 (C4$_C$), 127.8, 128.4 (C4$_A$ and C8$_A$), 130.5 (C7$_A$), 135.0 (C6$_A$), 141.9 (C5$_A$), 144.0 (C3$_A$), 144.2 (C2$_C$), 181.5 (C1$_A$) ppm. MS (ESI+) *m*/*z* (%) = 153.1384 (100, $C_9H_{17}N_2$ requires 153.1386, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 238 (10, [anion – PdCl$_2$]$^{2-}$), 479 (26, [anion – PdCl$_2$ + H]$^-$), 583 (100, [anion – H – 2Cl]$^-$), 656.9748 (44, $C_{22}H_{27}Cl_2N_2O_6PdS_2$ requires 656.9718, [anion + H]$^-$). IR (neat) ν = 2958 (w), 2928 (w), 2871 (w), 1586 (w), 1537 (w), 1450 (w), 1420 (w), 1377 (w), 1192 (br vs), 1136 (m), 1052 (s), 1019 (m), 985 (m), 872 (w), 750 (w), 706 (w), 687 (m), 664 (m), 634 (s), 578 (w), 558 (m), 542 (m), 523 (m) cm^{-1}.

Bis(1-*n*-butyl-2,3-dimethylimidazolium) {*N*,*N*′-bis(2,6-diisopropyl-4-sulfonatophenyl)butane-2,3-diimine-κ^2*N*,*N*′}dichloropalladium(II) (12c) [BMMIM]$_2$[PdCl$_2$(2,6-*i*Pr$_2$-Me-DAD^S)]. Prepared from **8c** (109 mg, 0.13 mmol, 1.00 eq) and [PdCl$_2$(MeCN)$_2$] (36 mg, 0.14 mmol, 1.08 eq): 115 mg (88%) light brown powder. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.90 (t, 6H, $^3J_{HH}$ = 7.3 Hz, C9$_C$-H), 1.19 (d, 12H, $^3J_{HH}$ = 6.8 Hz, C8a$_A$-H), 1.27 (psext, 4H, $^3J_{HH}$ = 7.6 Hz, C8$_C$-H), 1.36 (d, 12H, $^3J_{HH}$ = 6.7 Hz, C8b$_A$-H), 1.67 (pquint, 4H, $^3J_{HH}$ = 7.4 Hz, C7$_C$-H), 2.22 (s, 6H, C2$_A$-H), 2.57 (s, 6H, C10$_C$-H), 3.20 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, C7$_A$-H), 3.73 (s, 6H, C11$_C$-H), 4.10 (t, 4H, $^3J_{HH}$ = 7.3 Hz, C6$_C$-H), 7.45 (s, 4H, C5$_A$-H), 7.61 (d, 2H, $^3J_{HH}$ = 2.1 Hz, C4$_C$-H), 7.64 (d, 2H, $^3J_{HH}$ = 2.1 Hz, C5$_C$-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 9.1 (C10$_C$), 13.3 (C9$_C$), 18.8 (C8$_C$), 20.7 (C2$_A$), 23.3 (C8a$_A$), 23.5 (C8b$_A$), 28.2 (C7$_A$), 31.1 (C7$_C$), 34.6 (C11$_C$), 47.2 (C6$_C$), 120.7 (C5$_A$), 120.8 (C5$_C$), 122.3 (C4$_C$), 138.7 (C4$_A$), 140.3 (C6$_A$), 144.2 (C2$_C$), 147.9 (C3$_A$), 181.9 (C1$_A$) ppm. MS (ESI+) *m*/*z* (%) = 153.1385 (100, $C_9H_{17}N_2$ requires 153.1386, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 370 (100, [anion]$^{2-}$), 891.1975 (15, $C_{37}H_{55}Cl_2N_4O_6PdS_2$ requires 891.1980, [anion + cation]$^-$), 1043.3268 (2, $C_{46}H_{71}Cl_2N_6O_6PdS_2$ requires 1043.3294, [anion + 2 × cation – H]$^-$). IR (neat) ν = 2959 (w), 2929 (w), 2869 (w), 1586 (w), 1537 (w), 1462 (w), 1416 (w), 1382 (w), 1193 (s), 1070 (m), 1032 (s), 1012 (m), 885 (w), 748 (w), 657 (w), 635 (vs), 539 (w), 523 (w) cm^{-1}.

Bis(triethylammonium) {*N*,*N*′-bis(2,6-dimethyl-4-sulfonatophenyl)butane-2,3-diimine-κ^2*N*,*N*′}dichloropalladium(II) (12d) [HNEt$_3$]$_2$[PdCl$_2$(2,6-Me$_2$-Me-DAD^S)]. A mixture of **4a** (213 mg, 0.33 mmol, 1.00 eq) and [PdCl$_2$(MeCN)$_2$] (89 mg, 0.34 mmol, 1.05 eq) was stirred in acetonitrile (30 mL) at room temperature overnight. The precipitated product was isolated by centrifugation, washed with hexane and dried at 10^{-2} mbar. The mother liquor was used for the preparation of single crystals. Yield: 120 mg (44%) yellow powder. Anal. calc. for $C_{32}H_{54}Cl_2N_4O_6PdS_2$ (832.25 g mol^{-1}) C 46.18, H 6.54, N 6.73, S 7.71%; found C 45.32, H 6.38, N 6.50, S 7.51%. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 1.17 (t, 18H, $^3J_{HH}$ = 7.3 Hz, C2$_C$-H), 2.08 (s, 6H, C2$_A$-H), 2.27 (s, 12H, C7$_A$-H), 3.08 (dq, 12H, $^3J_{HH}$ = 4.9, 7.2 Hz, C1$_C$-H), 7.35 (s, 4H, C5$_A$-H), 8.91 (br s, 2H, NH$^+$) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 8.6 (C2$_C$), 17.8 (C7$_A$), 19.7 (C2$_A$), 45.8 (C1$_C$), 125.0 (C5$_A$), 128.8 (C4$_A$), 143.1 (C6$_A$), 146.7 (C3$_A$), 181.7 (C1$_A$) ppm. MS (ESI+) *m*/*z* (%) = 102.1279 (100, $C_6H_{16}N$ requires 102.1277, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 225 (18, [anion – PdCl$_2$]$^{2-}$), 314 (100, [anion]$^{2-}$), 451 (7, [anion – PdCl$_2$ + H]$^-$), 629 (34, [anion + H]$^-$). IR (neat) ν = 2983 (br w), 2698 (br w), 2504 (w), 1457 (w), 1401 (w), 1382 (w), 1217 (m), 1167 (m), 1107 (m), 1037 (s), 1018 (m), 880 (w), 834 (w), 791 (w), 651 (s), 634 (s), 619 (m), 556 (w), 526 (w), 446 (w) cm^{-1}.

Platinum complexes

General procedure for the preparation of complexes of the type [BMMIM]$_2$[PtCl$_2$(DAD^S)] (13a–c). A mixture of the appropriate DAD^S ligand **8** (0.1 mmol, 1.0 eq) and Zeise's dimer, [{PtCl$_2$(C$_2$H$_4$)}$_2$], (0.05 mmol, 0.5 eq) was stirred in methanol (10 mL) for three days at room temperature. After removal of all volatiles *in vacuo* the crude product was washed with ether and dried at 10^{-2} mbar.

Bis(1-*n*-butyl-2,3-dimethylimidazolium) {*N*,*N*′-bis(2,6-dimethyl-4-sulfonatophenyl)butane-2,3-diimine-κ^2*N*,*N*′}dichloroplatinum(II) (13a) [BMMIM]$_2$[PtCl$_2$(2,6-Me$_2$-Me-DAD^S)]. Prepared from **8a** (76 mg, 0.10 mmol, 1.00 eq) and Zeise's dimer (29 mg,

0.05 mmol, 0.50 eq): 93 mg (91%) dark orange powder. Anal. calc. for $C_{38}H_{56}Cl_2N_6O_6PtS_2$ (1023.00 g mol^{-1}) C 44.61, H 5.52, N 8.22, S 6.27%; found C 44.90, H 5.71, N 8.29, S 6.03%. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.90 (t, 6H, $^3J_{HH}$ = 7.3 Hz, C9$_C$-H), 1.27 (psext, 4H, $^3J_{HH}$ = 7.6 Hz, C8$_C$-H), 1.68 (pquint, 4H, $^3J_{HH}$ = 7.4 Hz, C7$_C$-H), 1.76 (s, 6H, C2$_A$-H), 2.22 (s, 12H, C7$_A$-H), 2.57 (s, 6H, C10$_C$-H), 3.74 (s, 6H, C11$_C$-H), 4.10 (t, 4H, $^3J_{HH}$ = 7.3 Hz, C6$_C$-H), 7.39 (s, 4H, C5$_A$-H), 7.62 (d, 2H, $^3J_{HH}$ = 2.0 Hz, C4$_C$-H), 7.65 (d, 2H, $^3J_{HH}$ = 2.0 Hz, C5$_C$-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 9.1 (C10$_C$), 13.4 (C9$_C$), 17.2 (C7$_A$), 18.8 (C8$_C$), 19.3 (C2$_A$), 31.1 (C7$_C$), 34.6 (C11$_C$), 47.2 (C6$_C$), 120.8 (C5$_C$), 122.3 (C4$_C$), 125.0 (C5$_A$), 129.4 (C4$_A$), 143.1 (C6$_A$), 144.2 (C2$_C$), 147.3 (C3$_A$), 180.1 (C1$_A$) ppm; ^{195}Pt NMR (86 MHz, DMSO-d_6) δ = –2193 ppm. MS (ESI+) m/z (%) = 153.1386 (100, $C_9H_{17}N_2$ requires 153.1386, [cation]$^+$); MS (ESI–) m/z (%) = 357.4969 (100, $C_{20}H_{22}Cl_2N_2O_6PtS_2$ requires 357.4978, [anion]$^{2-}$), 868.1328 (18, $C_{29}H_{39}Cl_2N_4O_6PtS_2$ requires 868.1341, [anion + cation]$^-$). IR (neat) ν = 2957 (w), 2871 (w), 1587 (w), 1537 (w), 1458 (br w), 1383 (w), 1237 (w), 1192 (br s), 1105 (m), 1037 (s), 880 (w), 754 (w), 722 (w), 668 (m), 632 (vs), 618 (m), 556 (w), 525 (w), 461 (w), 443 (w) cm^{-1}.

Bis(1-*n*-butyl-2,3-dimethylimidazolium) {*N*,*N*′-bis(2,4,6-trimethyl-3-sulfonatophenyl)butane-2,3-diimine-κ^2*N*,*N*′}dichloroplatinum(II) (13b) [BMMIM]$_2$[PtCl$_2$(2,4,6-Me$_3$-Me-DAD^S)]. Prepared from **8b** (79 mg, 0.10 mmol, 1.00 eq) and Zeise's dimer (29 mg, 0.05 mmol, 0.50 eq): 100 mg (95%) dark orange powder. Anal. calc. for $C_{40}H_{60}Cl_2N_6O_6PtS_2$ (1051.06 g mol^{-1}) C 45.71, H 5.75, N 8.00, S 6.10%; found C 44.71, H 5.76, N 7.84, S 5.46%. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.90 (t, 6H, $^3J_{HH}$ = 7.3 Hz, C9$_C$-H), 1.27 (psext, 4H, $^3J_{HH}$ = 7.6 Hz, C8$_C$-H), 1.67 (pquint, 4H, $^3J_{HH}$ = 7.5 Hz, C7$_C$-H), 1.71 (s, 6H, C2$_A$-H), 2.16, 2.46, 2.56 (3 × s, 3 × 6H, C9-11$_A$-H), 2.57 (s, 6H, C10$_C$-H), 3.74 (s, 6H, C11$_C$-H), 4.10 (t, 4H, $^3J_{HH}$ = 7.3 Hz, C6$_C$-H), 6.94 (s, 2H, C7$_A$-H), 7.62 (d, 2H, $^3J_{HH}$ = 2.0 Hz, C4$_C$-H), 7.65 (d, 2H, $^3J_{HH}$ = 2.0 Hz, C5$_C$-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 9.1 (C10$_C$), 13.4 (C9$_C$), 15.6 (C9$_A$), 17.2 (C11$_A$), 18.8 (C8$_C$), 19.1 (C2$_A$), 22.9 (C10$_A$), 31.1 (C7$_C$), 34.6 (C11$_C$), 47.2 (C6$_C$), 120.8 (C5$_C$), 122.3 (C4$_C$), 128.6, 129.0 (C4$_A$ and C8$_A$) 130.5 (C7$_A$), 135.3 (C6$_A$), 142.0 (C5$_A$), 144.0 (C3$_A$), 144.2 (C2$_C$), 180.3 (C1$_A$) ppm; ^{195}Pt NMR (86 MHz, DMSO-d_6) δ = –2192 ppm. MS (ESI+) m/z (%) = 153.1388 (100, $C_9H_{17}N_2$ requires 153.1386, [cation]$^+$); MS (ESI–) m/z (%) = 371.5128 (100, $C_{22}H_{26}Cl_2N_2O_6PtS_2$ requires 371.5134, [anion]$^{2-}$), 896.1613 (22, $C_{31}H_{43}Cl_2N_4O_6PtS_2$ requires 896.1654, [anion + cation]$^-$). IR (neat) ν = 2957 (w), 2930 (w), 2871 (w), 1587 (w), 1537 (w), 1452 (w), 1379 (w), 1338 (w), 1192 (br vs), 1136 (m), 1053 (s), 1020 (m), 986 (m), 863 (w), 751 (w), 708 (m), 691 (m), 666 (m), 640 (s), 613 (m), 578 (m), 558 (m), 544 (m), 523 (m) cm^{-1}.

Bis(1-*n*-butyl-2,3-dimethylimidazolium) {*N*,*N*′-bis(2,6-diisopropyl-4-sulfonatophenyl)butane-2,3-diimine-κ^2*N*,*N*′}dichloroplatinum(II) (13c) [BMMIM]$_2$[PtCl$_2$(2,6-*i*Pr$_2$-Me-DAD^S)]. Prepared from **8c** (78 mg, 0.09 mmol, 1.00 eq) and Zeise's dimer (28 mg, 0.05 mmol, 0.50 eq): 83 mg (81%) brown powder. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.90 (t, 6H, $^3J_{HH}$ = 7.3 Hz, C9$_C$-H), 1.17 (d, 12H, $^3J_{HH}$ = 6.8 Hz, C8a$_A$-H), 1.27 (psext, 4H, $^3J_{HH}$ = 7.6 Hz, C8$_C$-H), 1.31 (d, 12H, $^3J_{HH}$ = 6.7 Hz, C8b$_A$-H), 1.67 (pquint, 4H, $^3J_{HH}$ = 7.5 Hz, C7$_C$-H), 1.87 (s, 6H, C2$_A$-H), 2.57 (s, 6H, C10$_C$-H), 3.11 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, C7$_A$-H), 3.73 (s, 6H, C11$_C$-H), 4.10 (t, 4H, $^3J_{HH}$ = 7.3 Hz, C6$_C$-H), 7.50 (s, 4H, C5$_A$-H), 7.61 (d, 2H, $^3J_{HH}$ = 2.1 Hz, C4$_C$-H), 7.65 (d, 2H, $^3J_{HH}$ = 2.1 Hz, C5$_C$-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 9.1 (C10$_C$), 13.3 (C9$_C$), 18.8 (C8$_C$), 20.4 (C2$_A$), 23.2 (C8a$_A$), 23.5 (C8b$_A$), 27.6 (C7$_A$), 31.1 (C7$_C$), 34.6 (C11$_C$), 47.2 (C6$_C$), 120.7 (C5$_A$), 120.8 (C5$_C$), 122.3 (C4$_C$), 139.4 (C4$_A$), 140.4 (C6$_A$), 144.2 (C2$_C$), 148.2 (C3$_A$), 180.9 (C1$_A$) ppm; ^{195}Pt NMR (86 MHz, DMSO-d_6) δ = –2169 ppm. MS (ESI+) m/z (%) = 153.1385 (100, $C_9H_{17}N_2$ requires 153.1386, [cation]$^+$); MS (ESI–) m/z (%) = 415 (100, [anion]$^{2-}$), 829 (16, [anion + H]$^-$), 980.2534 (10, $C_{37}H_{55}Cl_2N_4O_6PtS_2$ requires 980.2593, [anion + cation]$^-$). IR (neat) ν = 2958 (w), 2929 (w), 2868 (w), 1586 (w), 1537 (w), 1462 (w), 1418 (w), 1385 (w), 1363 (w), 1332 (w), 1193 (br s), 1070 (m), 1033 (s), 1014 (m), 943 (w), 886 (w), 830 (w), 750 (w), 652 (w), 636 (vs), 565 (w), 539 (w), 524 (w), 480 (w) cm^{-1}.

Rhodium complexes

General procedure for the preparation of complexes of the type [BMMIM][Rh(COD)(DAD^S)] (14a–c). A mixture of silver tetrafluoroborate (0.1–0.2 mmol, 1.0 eq) and [{RhCl(COD)}$_2$] (0.05–0.1 mmol, 0.5 eq) was stirred in acetonitrile (10 mL) for one hour at room temperature. The precipitated silver chloride was removed using a syringe filter (PTFE, 0.45 μm) and the solution was added to a suspension of the appropriate DAD^S ligand **8** (0.1–0.2 mmol, 1.0 eq) in acetonitrile (20 mL). The reaction mixture was then stirred for one hour at room temperature. After removal of all volatiles *in vacuo* the crude product was treated with dichloromethane–ether (1 : 1, 5–10 mL each). The desired complex was isolated by filtration, washed with ether and dried at 10^{-2} mbar.

1-*n*-Butyl-2,3-dimethylimidazolium {*N*,*N*′-bis(2,6-dimethyl-4-sulfonatophenyl)butane-2,3-diimine-κ^2*N*,*N*′}{η^2:η^2-(*Z*,*Z*)-cycloocta-1,5-diene}rhodium(I) (14a) [BMMIM][Rh(COD)(2,6-Me$_2$-Me-DAD^S)]. Prepared from $AgBF_4$ (29 mg, 0.15 mmol, 1.03 eq), [{RhCl(COD)}$_2$] (36 mg, 0.07 mmol, 0.51 eq) and **8a** (109 mg, 0.14 mmol, 1.00 eq): 67 mg (57%) olive-green powder. ^{1}H NMR (500 MHz, DMSO-d_6) δ = 0.90 (t, 3H, $^3J_{HH}$ = 7.4 Hz, C9$_C$-H), 1.28 (psext, 2H, $^3J_{HH}$ = 7.5 Hz, C8$_C$-H), 1.68 (pquint, 2H, $^3J_{HH}$ = 7.4 Hz, C7$_C$-H), 1.82–1.88 (m, 4H, Cβ$_A$-Ha), 2.12 (s, 6H, C2$_A$-H), 2.27–2.34 (m, 4H, Cβ$_A$-Hb), 2.33 (s, 12H, C7$_A$-H), 2.58 (s, 3H, C10$_C$-H), 3.44 (br s, 4H, Cα$_A$-H), 3.74 (s, 3H, C11$_C$-H), 4.10 (t, 2H, $^3J_{HH}$ = 7.4 Hz, C6$_C$-H), 7.44 (s, 4H, C5$_A$-H), 7.61 (d, 1H, $^3J_{HH}$ = 2.1 Hz, C4$_C$-H), 7.65 (d, 1H, $^3J_{HH}$ = 2.1 Hz, C5$_C$-H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6) δ = 9.1 (C10$_C$), 13.4 (C9$_C$), 17.5 (C7$_A$), 18.8 (C8$_C$), 19.3 (C2$_A$), 29.8 (Cβ$_A$), 31.1 (C7$_C$), 34.6 (C11$_C$), 47.2 (C6$_C$), 89.2 (d, $^1J_{RhC}$ = 11.5 Hz, Cα$_A$), 120.8 (C5$_C$), 122.3 (C4$_C$), 125.7 (C5$_A$), 127.7 (C4$_A$), 141.2 (C6$_A$), 144.2 (C2$_C$), 147.2 (C3$_A$), 181.7 (C1$_A$) ppm. MS (ESI+) m/z (%) = 153.1385 (100, $C_9H_{17}N_2$ requires 153.1386, [cation]$^+$); MS (ESI–) m/z (%) = 225 (23, [anion – Rh(COD)]$^{2-}$), 661.0899 (100, $C_{28}H_{34}N_2O_6RhS_2$ requires 661.0919, [anion]$^-$). IR (neat) ν = 2956 (w), 1466 (w), 1430 (w), 1380 (w), 1237 (w), 1216 (s), 1195 (vs), 1151 (w), 1109 (m), 1038 (s), 1010 (m), 994 (m), 968 (m), 880 (w), 650 (s), 633 (s), 619 (s), 555 (w), 524 (w), 429 (w) cm^{-1}.

1-*n*-Butyl-2,3-dimethylimidazolium {*N*,*N*′-bis(2,4,6-trimethyl-3-sulfonatophenyl)butane-2,3-diimine-κ^2*N*,*N*′}{η^2:η^2-(*Z*,*Z*)-cycloocta-1,5-diene}rhodium(I) (14b) [BMMIM][Rh(COD)(2,4,6-Me$_3$-Me-DAD^S)]. Prepared from $AgBF_4$ (32 mg, 0.16 mmol,

1.08 eq), [{RhCl(COD)}$_2$] (38 mg, 0.08 mmol, 0.51 eq) and **8b** (119 mg, 0.15 mmol, 1.00 eq): 105 mg (83%) greenish-brown powder. ^{1}H NMR (500 MHz, DMSO-d_6) δ = 0.90 (t, 3H, $^3J_{HH}$ = 7.4 Hz, C9$_C$-H), 1.28 (psext, 2H, $^3J_{HH}$ = 7.6 Hz, C8$_C$-H), 1.68 (pquint, 2H, $^3J_{HH}$ = 7.5 Hz, C7$_C$-H), 1.77–1.91 (m, 4H, Cβ$_A$-Ha), 2.10 (s, 6H, C2$_A$-H), 2.21–2.30 (m, 4H, Cβ$_A$-Hb), 2.27, 2.28 (2 × s, 6H, C11$_A$-H, conformers), 2.54 (s, 6H, C10$_A$-H), 2.56 (s, 6H, C9$_A$-H), 2.58 (s, 3H, C10$_C$-H), 3.32 (br s, 2H, Cα$_A$-H), 3.51 (br s, 2H, Cα′$_A$-H), 3.74 (s, 3H, C11$_C$-H), 4.10 (t, 2H, $^3J_{HH}$ = 7.3 Hz, C6$_C$-H), 7.01 (s, 2H, C7$_A$-H), 7.61 (d, 1H, $^3J_{HH}$ = 2.0 Hz, C4$_C$-H), 7.65 (d, 1H, $^3J_{HH}$ = 2.0 Hz, C5$_C$-H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ = 9.1 (C10$_C$), 13.4 (C9$_C$), 16.2, 16.3 (C9$_A$, conformers), 17.49, 17.53 (C11$_A$, conformers), 18.9 (C8$_C$), 19.2 (C2$_A$), 22.8 (C10$_A$), 29.4, 29.8, 30.2 (Cβ$_A$ and Cβ′$_A$, conformers), 31.2 (C7$_C$), 34.6 (C11$_C$), 47.3 (C6$_C$), 88.7 (d, $^1J_{RhC}$ = 11.7 Hz, Cα$_A$), 89.2 (d, $^1J_{RhC}$ = 11.7 Hz, Cα′$_A$), 120.9 (C5$_C$), 122.3 (C4$_C$), 126.6, 126.7 (C4$_A$, conformers), 127.2, 127.3 (C8$_A$, conformers), 131.3 (C7$_A$), 134.9 (C6$_A$), 140.0 (C5$_A$), 144.2 (C2$_C$), 144.6 (C3$_A$), 181.6 (C1$_A$) ppm. MS (ESI+) *m*/*z* (%) = 153.1385 (100, $C_9H_{17}N_2$ requires 153.1386, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 239 (7, [anion – Rh(COD)]$^{2-}$), 689.1202 (100, $C_{30}H_{38}N_2O_6RhS_2$ requires 689.1232, [anion]$^-$). IR (neat) ν = 2958 (w), 2928 (w), 1536 (w), 1450 (w), 1379 (w), 1243 (w), 1198 (vs), 1053 (s), 1020 (m), 993 (m), 848 (w), 773 (w), 751 (w), 707 (m), 686 (m), 663 (s), 631 (s), 577 (w), 558 (m), 541 (m), 523 (m) cm^{-1}.

1-*n*-Butyl-2,3-dimethylimidazolium {*N*,*N*′-bis(2,6-diisopropyl-4-sulfonatophenyl)butane-2,3-diimine-κ^2*N*,*N*′}{η^2:η^2-(*Z*,*Z*)-cycloocta-1,5-diene}rhodium(I) (14c) [BMMIM][Rh(COD)(2,6-*i*Pr$_2$-Me-DAD^S)]. Prepared from $AgBF_4$ (39 mg, 0.20 mmol, 1.02 eq), [{RhCl(COD)}$_2$] (49 mg, 0.10 mmol, 0.51 eq) and **8c** (170 mg, 0.20 mmol, 1.00 eq): 151 mg (57%) greenish-brown powder. ^{1}H NMR (500 MHz, DMSO-d_6) δ = 0.90 (t, 3H, $^3J_{HH}$ = 7.4 Hz, C9$_C$-H), 1.17 (d, 12H, $^3J_{HH}$ = 6.7 Hz, C8a$_A$-H), 1.28 (psext, 2H, $^3J_{HH}$ = 7.6 Hz, C8$_C$-H), 1.46 (d, 12H, $^3J_{HH}$ = 6.8 Hz, C8b$_A$-H), 1.68 (pquint, 2H, $^3J_{HH}$ = 7.5 Hz, C7$_C$-H), 1.85–1.90 (m, 4H, Cβ$_A$-Ha), 2.18–2.24 (m, 4H, Cβ$_A$-Hb), 2.34 (s, 6H, C2$_A$-H), 2.58 (s, 3H, C10$_C$-H), 3.28 (sept, 4H, $^3J_{HH}$ = 6.7 Hz, C7$_A$-H), 3.53 (br s, 4H, Cα$_A$-H), 3.75 (s, 3H, C11$_C$-H), 4.11 (t, 2H, $^3J_{HH}$ = 7.3 Hz, C6$_C$-H), 7.56 (s, 4H, C5$_A$-H), 7.62 (d, 1H, $^3J_{HH}$ = 2.0 Hz, C4$_C$-H), 7.65 (d, 1H, $^3J_{HH}$ = 2.0 Hz, C5$_C$-H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6) δ = 9.1 (C10$_C$), 13.4 (C9$_C$), 18.8 (C8$_C$), 21.3 (C2$_A$), 23.0 (C8b$_A$), 24.6 (C8a$_A$), 28.4 (C7$_A$), 29.4 (Cβ$_A$), 31.1 (C7$_C$), 34.6 (C11$_C$), 47.2 (C6$_C$), 88.7 (d, $^1J_{RhC}$ = 10.5 Hz, Cα$_A$), 120.8 (C5$_C$), 121.6 (C5$_A$), 122.3 (C4$_C$), 138.1, 138.4 (C4$_A$ and C6$_A$), 144.2 (C2$_C$), 148.3 (C3$_A$), 182.0 (C1$_A$) ppm. MS (ESI+) *m*/*z* (%) = 153.1386 (100, $C_9H_{17}N_2$ requires 153.1386, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 282 (21, [anion – Rh(COD)]$^{2-}$), 773.2143 (100, $C_{36}H_{50}N_2O_6RhS_2$ requires 773.2171, [anion]$^-$). IR (neat) ν = 2961 (w), 2929 (w), 2872 (w), 1463 (w), 1437 (w), 1381 (w), 1200 (s), 1152 (w), 1070 (m), 1034 (s), 1009 (m), 993 (w), 886 (w), 754 (w), 657 (w), 636 (s), 539 (w), 522 (w), 484 (w) cm^{-1}.

Molybdenum complexes

Preparation of {*N*,*N*′-bis(2,6-dimethylphenyl)butane-2,3-diimine-κ^2*N*,*N*′}-tetracarbonylmolybdenum(0) (15) [Mo(CO)$_4$(2,6-Me$_2$-Me-DAD)]. A mixture of *N*,*N*′-bis(2,6-dimethylphenyl)butane-2,3-diimine (1019 mg, 3.48 mmol, 1.00 eq) and molybdenum hexacarbonyl (972 mg, 3.68 mmol, 1.06 eq) was treated with toluene (60 mL) and heated to 95 °C for 20 h. The resulting solution was evaporated to dryness. The almost black crude product was recrystallized from toluene and dried *in vacuo*, yielding 1351 mg (77%) violet crystals with a strong green luster. Anal. calc. for $C_{24}H_{24}MoN_2O_4$ (500.40 g mol^{-1}) C 57.61, H 4.83, N 5.60%; found C 57.54, H 4.83, N 5.59%. ^{1}H NMR (300 MHz, CD_3CN) δ = 2.08 (s, 6H, C2-H), 2.23 (s, 12H, C7-H), 7.11–7.23 (m, 6H, C5-H and C6-H) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 18.5 (C7), 19.9 (C2), 126.9 (C6), 128.2 (C4), 129.8 (C5), 149.8 (C3), 172.8 (C1), 206.8 (CO$_{trans}$), 223.5 (CO$_{cis}$) ppm. MS (ESI+) *m*/*z* (%) = 475.0915 (24, $C_{23}H_{25}MoN_2O_3$ requires 475.0916, [M – CO + H]$^+$), 497 (100, [M – CO + Na]$^+$), 525.0684 (18, $C_{24}H_{24}MoN_2NaO_4$ requires 525.0687, [M + Na]$^+$), 1024.1500 (20, $C_{48}H_{48}Mo_2N_4NaO_8$ requires 1024.1494, [2M + Na]$^+$). IR (neat) ν = 2926 (w), 1993 (s), 1904 (w), 1891 (w), 1847 (br vs), 1588 (w), 1505 (w), 1461 (w), 1440 (w), 1377 (m), 1317 (m), 1217 (m), 1093 (w), 981 (m), 850 (w), 766 (m), 701 (w), 633 (m), 618 (w), 580 (m), 536 (m), 522 (w), 436 (w), 416 (w) cm^{-1}.

Preparation of bis(1-*n*-butyl-2,3-dimethylimidazolium) {*N*,*N*′-bis(2,6-dimethyl-4-sulfonatophenyl)butane-2,3-diimine-κ^2*N*,*N*′}-tetracarbonylmolybdenum(0) (16) [BMMIM]$_2$[Mo(CO)$_4$(2,6-Me$_2$-Me-DAD^S)]. A mixture of **8a** (1156 mg, 1.53 mmol, 1.00 eq) and molybdenum hexacarbonyl (438 mg, 1.65 mmol, 1.08 eq) was treated with 1,2-dichloroethane (60 mL) and heated to reflux for 20 h. The resulting solution was evaporated to dryness. The dark crude product was recrystallized from dichloromethane and dried *in vacuo*, yielding 1225 mg (83%) dark violet powder. ^{1}H NMR (300 MHz, CD_3CN) δ = 0.93 (t, 6H, $^3J_{HH}$ = 7.3 Hz, C9$_C$-H), 1.33 (psext, 4H, $^3J_{HH}$ = 7.5 Hz, C8$_C$-H), 1.72 (pquint, 4H, $^3J_{HH}$ = 7.2 Hz, C7$_C$-H), 2.08 (s, 6H, C2$_A$-H), 2.23 (s, 12H, C7$_A$-H), 2.50 (s, 6H, C10$_C$-H), 3.69 (s, 6H, C11$_C$-H), 4.03 (t, 4H, $^3J_{HH}$ = 7.3 Hz, C6$_C$-H), 7.30 (br s, 4H, C4$_C$-H and C5$_C$-H), 7.55 (s, 4H, C5$_A$-H) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 10.3 (C10$_C$), 13.8 (C9$_C$), 18.5 (C7$_A$), 20.0 (C2$_A$), 20.1 (C8$_C$), 32.3 (C7$_C$), 36.0 (C11$_C$), 49.0 (C6$_C$), 122.0 (C5$_C$), 123.5 (C4$_C$), 127.2 (C5$_A$), 127.8 (C4$_A$), 145.4 (C2$_C$), 147.0 (C6$_A$), 149.7 (C3$_A$), 173.0 (C1$_A$), 206.5 (CO$_{trans}$), 223.5 (CO$_{cis}$) ppm. MS (ESI+) *m*/*z* (%) = 153.1386 (100, $C_9H_{17}N_2$ requires 153.1386, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 315 (44, [anion – CO]$^{2-}$), 329.9884 (100, $C_{24}H_{22}MoN_2O_{10}S_2$ requires 329.9890, [anion]$^{2-}$), 813.1143 (25, $C_{33}H_{39}MoN_4O_{10}S_2$ requires 813.1167, [anion + cation]$^-$). IR (neat) ν = 3103 (w), 2930 (w), 1996 (m), 1882 (s), 1855 (vs), 1588 (w), 1539 (w), 1500 (w), 1463 (w), 1379 (w), 1319 (w), 1274 (w), 1238 (w), 1197 (s), 1144 (m), 1108 (m), 1041 (s), 984 (m), 893 (w), 876 (w), 782 (w), 755 (w), 726 (w), 715 (w), 671 (w), 647 (s), 630 (vs), 615 (m), 579 (m), 557 (m), 522 (m), 462 (m), 428 (w) cm^{-1}.

Single-crystal XRD studies

Crystallographic data are provided in Table 5 and full details are available in ESI†. X-Ray data collection was performed *via* a STOE IPDS I or IPDS II area detector using Mo-Kα-radiation (λ = 71.073 pm). STOE IPDS software[42] was used for integration and data reduction, structure solution and refinement was done with the WinGX program suite[43] using SIR92[44] and SHELX-97.[45] While the complex anion of **12d** showed no unusual features during the refinement, both triethylammonium cations were found to be poorly resolved due to their conformational flexibility or an irresolvable disorder. Bond lengths and 1,3-distances within the cations were fixed to average target values (C–N 1.48 Å,

Table 5 Crystallographic data.

	4a	6	8b	8c	12d
Chemical formula	$C_{32}H_{54}N_4O_6S_2$	$C_{36}H_{52}N_6O_6S_2$	$C_{40}H_{60}N_6O_6S_2$	$C_{46}H_{72}N_6O_6S_2$	$C_{32}H_{54}Cl_2N_4O_6PdS_2$
M/g mol^{-1}	654.91	728.96	785.08	869.22	832.21
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/a$
a/Å	16.7780(14)	8.6734(10)	7.4331(3)	18.7969(13)	13.5983(5)
b/Å	7.2899(9)	9.4661(12)	8.3007(4)	8.4216(6)	7.4017(3)
c/Å	14.6759(11)	11.6547(13)	17.9835(9)	14.6542(11)	38.4451(14)
α/°	90.00	88.301(14)	86.492(4)	90.00	90.00
β/°	101.533(9)	88.487(14)	84.986(4)	93.811(6)	90.841(3)
γ/°	90.00	85.669(15)	65.819(3)	90.00	90.00
V/Å^3	1758.8(3)	953.46(19)	1007.96(8)	2314.6(3)	3869.1(3)
T/K	193(2)	193(2)	100(2)	100(2)	100(2)
Z	2	1	1	2	4
No. reflections measured	13370	8973	8050	12521	22338
No. independent reflections	3200	3378	4158	4879	8201
R_{int}	0.0578	0.0385	0.0616	0.1533	0.1056
Final R_1 values ($I > 2\sigma(I)$)	0.0375	0.0389	0.0446	0.0493	0.0677
Final $wR(F^2)$ values (all data)	0.0828	0.1080	0.1122	0.0785	0.1666

C–C 1.45 Å, N–C–C 2.45 Å, C–N–C 2.49 Å) while the thermal movement was restrained to an approximately isotropic behaviour.

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