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Ion Pairing and Salt Structure in Organic Salts through Diffusion, Overhauser, DFT and X-ray Methods

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Abstract: Pulsed gradient spin-echo (PGSE) diffusion characteristics for a) the new [brucinium][X] salts 6a-f [a: $X = BF_4^-$; b: $X = PF_6^-$; c: X =MeSO₃⁻, **d**: $X = CF_3SO_3^-$; **e**: X =BArF⁻; **f**: $X = PtCl_3(C_2H_4)^{-}$], b) 4-tertbutyl-N-benzyl analogue, 7 and c) the aryl carbocations $(p-R-C_6H_4)_2CH$ 9a $(R = CH_3O)$ and **9b** $(R = (CH_3)_2N)$, (p- $CH_3O-C_6H_4)_xCPh_{3-x}$ + 10 a-c (x = 1-3, respectively) and $(p-R-C_6H_4)_3C^+$ 11 $(R = (CH_3)_2N)$ and 12 (R = H) all in several different solvents, are reported. The solvent dependence suggests strong ion pairing in CDCl₃, intermediate ion pairing in CD₂Cl₂ and little ion pairing in [D₆]acetone. ¹H, ¹⁹F HOESY NMR spectra (HOESY: heteronuclear Overhauser effect spectroscopy) for 6

and **7** reveal a specific approach of the anion with respect to the brucinium cation plus subtle changes, which are related to the anion itself. Further, for carbocations **9–12**, (all as BF_4^- salts) based on the NOE results, one finds marked changes in the relative positions of the BF_4^- anion. In these aryl cationic species the anion can be located either a) very close to the carbonium ion carbon b) in an intermediate position or c) proximate to the N or O atom of the *p*-substituent and remote from the formally positive C atom.

Keywords: carbocations • ion pairs • NMR spectroscopy • salt effect • solvent effects This represents the first example of such a positional dependence of an anion on the structure of the carbocation. DFT calculations support the experimental HOESY results. The solidstate structures for 6c and the novel Zeise's salt derivative, [brucinium]- $[PtCl_3(C_2H_4)]$, **6 f**, are reported. Analysis of ¹⁹⁵Pt NMR and other NMR measurements suggest that the η^2 -C₂H₄ bonding to the platinum centre in 6 f is very similar to that found in K[PtCl₃- (C_2H_4)]. Field dependent T_1 measurements on $[brucinium][PtCl_3(C_2H_4)]$ and $K[PtCl_3(C_2H_4)]$, are reported and suggested to be useful in recognizing aggregation effects.

Introduction

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The subject of ion pairing is a recurring theme in many areas of chemistry with examples from water-soluble polyanionic dendrimers,^[1] sulfated glycoproteins^[2] and alkali metal complexes of ionophore antibiotics,^[3] all having recently appeared. In addition, there are an increasing number of studies on transition metal salts and we note examples from iridium,^[4,5] cobalt,^[6] ruthenium,^[7] manganese,^[8] palladium,^[9] and titanium,^[10] to name just a few.

Although UV, Raman and (aspects of) NMR spectroscopy are powerful tools for the investigation of the solution structure, these methods are not always suitable for investigating ion pairing. Alternative techniques, such as dielectric or ultrasonic relaxation, which can detect various ion-pair types have been suggested.^[11] However, there is an increasing NMR literature involving diffusion studies, that suggests that pulsed gradient spin-echo (PGSE) techniques or the two-dimensional variant, diffusion-ordered spectroscopy

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(DOSY), may be the methods of choice and the applications of these methodologies have been recently reviewed.^[12,13] It is important to recognize that PGSE and DOSY methods are currently widely in use, usually (but not exclusively) in connection with estimating relative molecular volumes.^[14-23] A recent novel biological application of diffusion methods concerns the use of He-3 PGSE diffusion methods in the lungs.^[23]

Assuming that the diffusion characteristics of the anion and cation can be measured separately (using ¹H signals from the cations, and ¹⁹F resonances, from, for example, the BF₄⁻ or PF₆⁻ anions), inspection of the Diffusion constants (D values) is instructive. Since the D value for the (normally) larger cation is often fairly small, the observation of identical D values usually results from complete ion pairing. If the two values are different, the extent of the difference reflects the degree of ion pairing. Strongly solvated ions (from e.g., aqueous solutions) will reveal two very different diffusion constants. However, given that many reactions and measurements are carried out in solvents, such as acetone, dichloromethane and chloroform, it is useful to understand how these solvents can affect ion pairing. We have begun PGSE studies on a variety of transition metal complexes in $CD_2Cl_2\ solution^{[24,25]}$ and suggested that the charge distribution and the ability of the anion to approach the positively charged positions (steric effects owing to molecular shape) are the determining factors in deciding the amount of ion pairing.[24]

We show here that the previously observed solvent dependence of the *D* values in these three solvents can be extended to organic salts and specifically to a number of brucinium salts, as well as salts from seven aryl carbocations. Brucinium salts were chosen as they represent moderately complicated organic structures. Further, ¹H, ¹⁹F HOESY NMR methods (HOESY: heteronuclear Overhauser effect spectroscopy) reveal both subtle and gross changes in the positions of the anions with respect to the cations.

Results and discussion

Model species and solvent dependence: One goal of this study concerns a generalization of the effect of the three selected solvents on ion pairing. To appreciate the trends in the new diffusion data derived from the organic cations, we show in Table 1 new and old diffusion constants (*D* values, $\times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) for three very different inorganic salts, **1–3**.

From this table it can be seen that in CDCl₃, the *D* values for the cation and anion are almost identical, consistent with complete or almost complete ion pairing. In CD_2Cl_2 the *D* values for the cation and anion are somewhat different and thus reflect intermediate ion pairing, whereas in $[D_6]$ acetone, one finds markedly different *D* values suggesting little or no ion pairing in this solvent. We give additional new solvent dependent diffusion data for the salts $[PPh_4]$ - $[PF_6]$ (4) and $[PPh_4][BPh_4]$ (5) in Table S1 in the Supporting Information. Table 1. Some D values $(10^{-10} \text{ m}^2 \text{s}^{-1})$ for three very different salts **1–3** in the solvents CDCl₃, CD₂Cl₂ and [D₆]acetone.



Brucinium salts: The new brucinium salts, **6a–f** in Figure 1, were prepared by standard procedures, e.g., by addition of HCl to brucine and then extraction of the chloride with a suitable reagent. Potentially all of these salts can demonstrate differing degrees of solvent dependent ion pairs and/ or hydrogen bonding (see for example Scheme 1 for **6a**).

To obtain a feeling for the ion pairing to be expected (in the absence of possible hydrogen bonding) we have prepared the 4-*tert*-butyl-*N*-benzylbrucinium phosphorous hexa-



fluoride salt, 7, and show these diffusion results, as well as the D values for **6a–f**, in Table 2.

Before discussing the new measurements, one should note that D values are viscosity dependent and, consequently, it is normal to discuss the data from diffusion measurements in different solvents by using the measured D value to solve the Stokes–Einstein relation [Eq. (1)] for the hydrodynamic radii, $r_{\rm H}$.

$$r_{\rm H} = \frac{kT}{6\pi\eta D} \tag{1}$$

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Figure 1. The new brucinium salts: **6**, R = H **6a**, $X = BF_4^-$; **6b**, $X = PF_6^-$; **6c**, $X = MeSO_3^-$; **6d**, $X = CF_3SO_3^-$ (=OTf); **6e**, $X = BArF^-$; **6f**, $X = PtCl_3(C_2H_4)^-$; **7**, R = 4-tert-butyl-N-benzyl, $X = PF_6^-$.



Scheme 1. An example of ion pairs and/or hydrogen bonding.

The Stokes–Einstein relation has been subject to criticism,^[26] in that the value 6 is often too large. One normally makes a semi-empirical correction to afford $r_{\rm H}^{\rm corr}$, which is always slightly larger. In Table 2 we show both values. In addition, we show a relatively new parameter, the ratio D_c/D_a , which we have recently introduced,^[24] as a reflection of the amount of ion pairing. This ratio is most useful when the two ions have very different sizes so that values close to unity reflect very substantial ion pairing. A D_c/D_a ratio in the range 0.4–0.6 suggests relatively little ion pairing.

Returning to 7, the observed solvent dependence of the Dand $r_{\rm H}^{\rm corr}$ values as well as the $D_{\rm c}/D_{\rm a}$ ratios follow the same pattern as found for salts 1-3. The ion pairing is complete in chloroform, weaker, but still significant in CD₂Cl₂, and very weak or absent in $[D_6]$ acetone. Specifically, the observed D and calculated $r_{\rm H}^{\rm corr}$ values for the PF₆⁻ anion in 7 in acetone, 25.44 and 4.4 Å, respectively, are typical for this anion in this solvent (see Figure 2 for a comparison with complex 8). We find a relatively large $r_{\rm H}^{\rm corr}$ value of 7.2 Å for the cation in 7 in acetone, and believe that this observation reflects the presence of the large 4-tert-butyl-N-benzyl group. Based on literature crystallographic data^[27] for brucinium salts, one expects a value of \approx 5.2–5.6 Å. The ¹H, ¹⁹F HOESY NMR spectrum for 7 in CD_2Cl_2 is given on the left portion of Figure 3. The strongest contact to the anion arises from the ortho protons of the tBu benzyl ring. One also finds crosspeaks stemming from aromatic proton H1, methoxy-methyl group, H2' and methine proton H16 (rather weak). Taken together, these Overhauser data suggest a specific approach in which the anion nears the formally positively charged N atom of the cation from the same side as the methine proton H16, and close H1 and H2' (see structure 7 above).

Turning to the brucinium salts, **6a–f**, we find equivalent D values for the cations and anions in CDCl₃ and CD₂Cl₂ (except for the BArF salt, BArF⁻=tetra(3,5-ditrifluoromethyl)phenyl borate). This suggests that hydrogen bonding between the NH and the anion is an important contributor in this latter solvent as the ion pairing is not normally sufficient to keep the ions together. In [D₆]acetone the solvent overcomes the hydrogen bonding in most of the salts and the anions are now well separated; however, for CH₃SO₃⁻, the ions remain together (the D_c/D_a ratio is 0.96). The large BArF⁻ anion in **6e** is strongly associated in CDCl₃ and represents an intermediate case in CD₂Cl₂. Based on the r_H

> value of 5.9 Å in [D₆]acetone (the $r_{\rm H}$ value for NaBArF in [D₄]MeOH lies between 5.8 and 6.0 Å), the BArF anion does not feel the cation.

> The right side of Figure 3 shows the ¹H, ¹⁹F HOESY NMR spectrum for the PF_6^- salt, **6b** in CD_2Cl_2 . The NOE contact to H16 is now *much* stronger than in **7** and consistent with a closer approach of the anion, owing to the hydro-

gen bonding. Moreover there is now a strong contact to H18' as well as to H1 (see Figure 3). 1

Summarizing this section, in the absence of hydrogen bonding, the diffusion data for the brucinium salt **7** show the now typical solvent dependence of the ion pairing in all three solvents. The ¹H, ¹⁹F HOESY results suggest that the anion is somewhat remote from the cation, but approaches in a specific fashion. However, for the BF₄⁻, PF₆⁻ and CF₃SO₃⁻ salts **6**, in CDCl₃ and CD₂Cl₂, the NH-(anion) hydrogen bond holds the anion close to the cation (as indicated by both the D_c/D_a ratios and the relatively strong NOE's in CD₂Cl₂). The PGSE data for BF₄⁻, PF₆⁻, and CF₃SO₃⁻ salts of **6** in acetone suggest that the solvent can separate the ions. A more detailed analysis of **6 f**, the Zeise's salt analogue, will be given below.

Carbocations: To extend our studies on organic cations we have prepared and measured NMR data for the known^[28] seven aryl cations **9–12**, all as BF_4^- salts (see Scheme 2 and Tables 3 and 4).

The ¹H chemical shifts in Table 3 are informative in that they support a classical view of charge delocalization from the ring-containing the electron-donating substituents towards the cationic carbon.

¹ The HOESY spectra for the BF_4^- salt shows more intense cross-peaks to the same cites, For $CF_3SO_3^-$ the cross-peaks are much weaker and restricted primarily to H1, H2' and H16. We find no contacts from the $MeSO_3^-$ to the cation in **6c**. There is a rather weak cross-peak in the HOESY spectrum of the BArF analog from the CF₃ groups to the CH₃O protons, H2'.

	Х	Solvent	Fragment	D	$D_{\rm c}/D_{\rm a}$	$r_{\rm H}$	$r_{\rm H}^{\rm corr}$
6a	BF_4	CDCl ₃	cation	6.72	0.99	6.1	6.8
			anion	6.81		6.0	6.7
		CD_2Cl_2	cation	10.06	1.01	5.3	5.9
			anion	9.98		5.3	6.0
		[D ₆]acetone	cation	12.70	0.60	5.6	6.3
			anion	21.08		3.4	4.6
6b	PF_6	CDCl ₃	cation	6.99	0.99	5.9	6.6
	-	-	anion	7.03		5.8	6.5
		CD_2Cl_2	cation	10.00	0.99	5.3	6.0
			anion	10.10		5.2	5.9
		[D ₆]acetone	cation	12.48	0.58	5.7	6.4
			anion	21.60		3.3	4.6
6c	CH ₂ SO ₂	CDCl	cation	6.99	1.00	5.9	6.6
υc		,	anion	6.99		5.9	6.6
		CD ₂ Cl ₂	cation	9.64	1.00	5.5	61
			anion	9.61	1.00	5.5	6.1
		[D_lacetone	cation	12 33	0.96	5.8	6.4
		[D ₆]acctone	anion	12.33	0.90	5.6	63
			union	12.02		5.0	0.0
6 d	CF ₃ SO ₃	CDCl ₃ (6 mм)	cation	6.97	1.01	5.9	6.6
			anion	6.89		6.0	6.6
		CDCl ₃	cation	7.04	1.00	5.8	6.5
		-	anion	7.03		5.8	6.5
		CD_2Cl_2	cation	10.09	0.99	5.2	5.9
			anion	10.17		5.2	5.9
		[D ₆]acetone	cation	12.65	0.67	5.7	6.3
			anion	19.01		3.8	4.9
6e	BArF	CDCl	cation	5 61	1.02	73	78
oc	Dim	ebel,	anion ^[b]	5 48	1.02	75	8.0
			anion	5 51		74	8.0
		CD.Cl.	cation	8.95	1.09	59	6.5
			anion ^[b]	8 21	1.09	64	7.0
			anion	8 23		64	7.0
		[D_lacetone	cation	12.98	1.08	5.5	62
		[D ₆]ucctone	anion	12.06	1.00	5.9	6.6
6 F	PtCl (C H)	CDCI	cation	7 25	0.00	56	62
01	$1(C_3(C_2)_{4})$		anion	7 30	0.77	5.5	63
		CD CI	anion	10.29	0.00	5.5	5.0
		CD_2CI_2	anion	10.26	0.99	5.1	5.9
		[D]acetone	cation	12.30	0.68	5.0	5.0 6.5
			anion	12.52	0.08	3.0	5.0
			amon	10.09		5.9	5.0
7	PF_6	CDCl ₃	cation	5.43	1.00	7.6	8.1
			anion	5.41		7.6	8.1
		CD_2Cl_2	cation	8.18	0.90	6.5	7.0
			anion	9.12		5.8	6.4
		[D ₆]acetone	cation	10.69	0.42	6.7	7.2
			anion	25.44		2.8	4.4

Table 2. $D [10^{-10} \text{ m}^2 \text{s}^{-1}]$ and $r_{\rm H}$ [Å] values for the [brucinium][X] salts **6a–f** and **7** in several solvents^[a]



For example, in the set **12**, **10 c**, **10 b** (Figure 4), the *para* proton of the unsubstituted C_6H_5 aryl ring shifts to lower frequency, as the number of CH₃O groups increases. The signals of the protons *ortho* to the CH₃O groups in **10 a–c**



Figure 2. The observed D and calculated $r_{\rm H}^{\rm corr}$ values for the PF₆⁻ ion in 8.

move progressively to higher frequency, as the number of methoxy groups decreases (since with more CH_3O groups each of the substituents need not donate quite so much) and of course the carbonium ion CH signal of **9a** is found at higher frequency relative to **9b** as the Me₂N group is expected to be a better donor (Figure 5).

The PGSE results for salts **9–11** are shown in Table 4. We know of only one other organic carbocation salt, $13^{[29]}$ for which PGSE diffusion data have been reported. Some of the



salts 9-12 decompose over the few hours necessary to make the measurements in $[D_6]$ acetone. However, when they are stable, the trend in the D values is clear. In CDCl₃ 9b, 10a, **10b** and **11** show ≈ 100 % ion pairing and the ratio D_c/D_a is close to unity. The $r_{\rm H}^{\rm corr}$ values are all relatively large (if compared to those for CD₂Cl₂ and [D₆]acetone). In CD₂Cl₂ all the salts, 9-11, show varying degrees of intermediate ion pairing. Interestingly, the bis-salt, $[(4-(CH_3)_2N-C_6H_4)_2CH]$ - $[BF_4]$, **9b**, shows more ion pairing, $D_c/D_a = 0.95$, than the tris salt, $[(4-(CH_3)_2N-C_6H_4)_3C][BF_4]$, **11**, $D_c/D_a = 0.71$, suggesting more charge delocalization in 11, and we shall return to this point during the HOESY discussion. In [D₆]acetone the data for 11, with a ratio $D_c/D_a = 0.45$, strongly support little or no ion pairing in that this is one of the smallest ratios we have found. Summarizing, for the BF₄⁻ salts 9-11, the overall solvent dependent ion pairing picture, is rather similar to that for 7, discussed above, and fits into the general picture found for 1-3 and many other salts.

To explore the structural side of the ion pairing for 9-12 in CD_2Cl_2 , we have measured ¹H, ¹⁹F HOESY spectra for all seven salts and Figure 6 shows a comparison of the results

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Figure 3. ¹H, ¹⁹F HOESY spectra for **7** (left) and **6b** (right) in CD_2Cl_2 . Note that a) in **7** the cross-peaks are much weaker, especially for H16 and b) in **6b**, there is now a readily visible contact to H18' (CD_2Cl_2 , 400 MHz, 10 mM).



Scheme 2. Aryl carbonium ions as BF₄⁻ salts

for the two bis-aryl cations **9a** and **9b**. For **9a** there is no contact to the MeO groups and a fairly strong contact to the carbonium CH proton and the *ortho* protons of the rings.

This result for **9a** suggests that the anion approaches the central carbon, in a fashion related to known^[30] structures from Xray data, for example, **13**. On



the other hand, in 9b, the strongest cross-peak now arises from contacts to the methyl groups of the 4-(CH₃)₂N substituents, as well as strong contacts to both the ortho and meta ring protons. Further, the cross-peak for the carbonium CH is very much weaker. It would seem that on going from 9a to 9b, the BF4⁻ anion moves increasingly away from the formally positive carbon atom towards the N atoms of the $4-(CH_3)_2N$ groups. Presumably, this partially reflects the decrease of positive charge on the carbonium ion carbon, owing to the delocalization via the aryl rings.

The ¹H, ¹⁹F HOESY results for **10a–c** are shown in Figure 7. In the tris salt **10a** (left), one finds strong contacts to the methoxy and both ring protons. The contacts to the *meta* protons (immediately ad-

jacent to the CH₃O groups) are slightly more intense (see Figure 8 bottom, for projections of the NOE intensities). In 10b and 10c there are only very weak interactions with the unsubstituted C₆H₅ ring, and the same type of strong contacts to the CH₃O-substituted ring. In 10c it is clear that the cross-peaks to the CH₃O groups and the meta protons are the strongest (see Figure 8, top trace, for the relative intensities). We conclude that there is a specific salt solution structure and that, for example, the anion definitely prefers to be close to the methoxy substituents in 10c. We note that Bleasdale et al, in their X-ray studies of 10b and 10c write^[28f] "Thus there is a clear tendency for 4-methoxysubstituted phenyl rings to be more nearly coplanar with the carbenium centre in these mixed systems. This is because the methoxy group offers greater stabilization of the carbenium centre than does an H atom." This greater stabilization is also reflected in the position of the anion.





[a] CH 9.05 ppm. [b] CH 7.87 ppm.

¹H, ¹⁹F HOESY results for **11** and **12** are shown in Figure 9. For the trityl cation, **12**, all three ring protons show cross-peaks with the *ortho* and *meta* contacts as the strongest. In **11**, there is, again selectivity in favor of the $(CH_3)_2N$ groups and the *meta* protons. Note that there is only a very weak contact to the *ortho* protons. Clearly in **11**, the anion is positioned close to the amine function.

Returning briefly to ion pairing observations for the $(CH_3)_2N$ -salts, **9b** and **11**, in CD_2Cl_2 , presumably the three strong donor $(CH_3)_2N$ groups result in sufficient positive charge dispersal so that the ion pairing $(D_c/D_a=0.71 \text{ for } 11 \text{ vs. } D_c/D_a=0.95 \text{ for } 9\text{ b})$, is significantly reduced.^[24] However, the three aryl rings of **11** with their known propeller shape,^[28d-g] will sterically hinder the approach of the anion relative to **9b**, that contains only two rings. This may also contribute to the observed differences in the ion pairing.

Summarizing the HOESY results, there is clearly a change in the anion position as a function of the structure of

	Solvent	Fragment	D	$D_{\rm c}/D_{\rm a}$	$r_{\rm H}$	$r_{\rm H}^{\rm corr}$
9 a ^[b,c]	CDCl ₃	cation	8.75		4.7	5.6
		anion				
	CD_2Cl_2	cation	12.74	0.88	4.2	5.1
		anion	14.41		3.7	4.7
9b	CDCl ₃	cation	8.42	1.00	4.9	5.7
		anion	8.38		4.9	5.8
	CD_2Cl_2	cation	12.40	0.95	4.3	5.2
		anion	13.11		4.0	5.0
	[D ₆]acetone	cation	15.54	0.67	4.6	5.5
		anion	23.30		3.1	4.5
10 a	CDCl ₃	cation	7.51	0.97	5.5	6.2
	-	anion	7.76		5.3	6.1
	CD_2Cl_2	cation	10.52	0.81	5.0	5.8
		anion	13.01		4.1	5.0
	[D ₆]acetone	cation	13.48	0.48	5.3	6.0
		anion	27.84		2.6	4.3
10b ^[b]	CDCl ₃	cation	7.93	0.98	5.2	6.0
		anion	8.11		5.1	5.9
	CD_2Cl_2	cation	11.12	0.82	4.8	5.5
		anion	13.62		3.9	4.9
10 c ^[b]	CDCl ₃	cation	8.18	0.92	5.0	5.8
	5	anion	8.88		4.6	5.5
	CD_2Cl_2	cation	11.54	0.85	4.6	5.4
	2 2	anion	13.62		3.9	4.9
11	CDCl ₃	cation	7.06	0.98	5.8	6.5
	5	anion	7.20		5.7	6.4
	CD_2Cl_2	cation	10.05	0.71	5.3	5.9
		anion	14.13		3.7	4.8
	[D ₆]acetone	cation	12.46	0.45	5.8	6.4
		anion	27.92		2.6	4.3
F 1 4 11	- D - 1					

Table 4. $D [10^{-10} \text{ m}^2 \text{s}^{-1}]$ and $r_{\text{H}} [\text{\AA}]$ values for the carbocationic salts 9–

11^[a]

[a] All at 2 mM. For the calculation of r_H , the viscosity of the nondeuterated solvent at 299 K was used. η (CHCl₃)= 0.53×10^{-3} kgs⁻¹m⁻¹; η (CH₂Cl₂)= 0.41×10^{-3} kgs⁻¹m⁻¹; η (acetone)= 0.31×10^{-3} kgs⁻¹m⁻¹. r_H was calculated using the Stokes–Einstein equation while $r_H^{\rm corr}$ was calculated using a semiempirical estimation of $c_1^{[50]}$ [b] Decomposes slowly in [D₆]acetone. [c] ¹⁹F signal of the anion in CDCl₃ too broad for an accurate measurement.



Figure 5. The ¹H chemical shifts of carbonium protons.



Figure 4. The ¹H chemical shifts of protons para (top) and ortho (bottom) to CH₃O groups.

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the aryl carbocation. We believe this to be the first example of such an anion/cation structure relationship in organic salts.

DFT calculations: To refine our understanding of the aryl carbonium ion BF_4^- salts, **9–12**, the relative positions and geometries of the individual ions were

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Figure 6. ¹H, ¹⁹F HOESY spectra for (left) **9a** and (right) **9b** in CD₂Cl₂. Note that in **9a** there is no contact to the CH₃O or *meta* protons, but a fairly strong contact to the carbonium CH. In **9b** the cross-peak for the $(CH_{3})_2N$ is now the strongest and the cross-peak for the carbonium CH is much weaker $(CD_2Cl_2, 400 \text{ MHz}, 10 \text{ mM})$.

calculated by means of DFT methods.[31] Equal optimization procedures were used in all cases, starting from equivalent initial geometries, thereby giving significance to the observed differences. In addition, the geometry calculations included solvent effects (see the Computational Details). The optimized structures obtained for the ions of salts 9a and 9b are represented in Figure 10. The results indicate a clear difference in the spatial arrangements calculated for 9a and 9b. In the case of 9a the anion approaches the three-coordinated carbon atom in such a way that one F atom establishes a bridge between the carbonium ion carbon atom and the B atom in the anion. This view is supported by the corresponding distances: $d_{C-F} = 1.51$ Å, and $d_{B-F} = 1.76$ Å. In this salt the anion makes the closest approach to the carbocation. The separation of 2.82 Å between the boron atom and the carbon atom is the shortest of the entire series.

In the case of **9b**, the calculated structure shows a completely different arrangement for the two ions. The $BF_4^$ anion moves considerably away from the formally positive C atom, resulting in a B–C separation of 5.48 Å. Interestingly, the BF_4^- anion lies almost in the same plane as the carbocation, with a 0.38 Å deviation of the B atom from the mean plane defined by the carbonium C atom and the three atoms directly attached to the carbocation. In addition, there is an asymmetrical arrangement in the ion pair, in that the anion approaches the NMe₂ substituent of one of the two aryl groups, as demonstrated by two clearly different B–N distances: 5.19 and 6.97 Å. An attempt was made to optimize a geometry for **9b** equivalent to that obtained for **9a** (i.e., with a C-F-B bridge). The result was separation of the two ions, demonstrating that the arrangement observed for the ion pair in **9a** is not favorable when the aryl substituents are NMe₂ groups.

The structures calculated for the salts **10a–c**, with methoxy substituted aryl groups, are represented in Figure 11.

The spatial arrangements obtained for **10a** and **10b** are rather similar. The calculated separations between the ions are equivalent ($d_{B-C}=3.49$ Å and 3.48 Å, for **10a** and **10b**, respectively), and considerably larger than the 2.82 Å distance found for **9a**. The BF₄⁻ anion is situated above the carbonium ion mean plane in a more or less symmetrical way. Possible distortions in the relative position of the two ions in each pair can be assessed by means of a

comparison of the distance between the boron atom and each of the C₆-rings centroids (noted for convenience as "X"). In **10a**, one finds three essentially equivalent distances $(d_{B-X}=4.50, 4.53 \text{ and } 4.54 \text{ Å})$, denoting an almost perfectly symmetrical arrangement. In **10b**, the anion approaches one of the substituted rings, $(d_{B-X}=4.47 \text{ Å})$, although not to a very marked extent relative to the other two aryl ring separations $(d_{B-X}=4.51 \text{ and } 4.61 \text{ Å})$. It is interesting to note that in **10b** the ring without a methoxy substituent, is the one furthest away from the anion $(d_{B-X}=4.61 \text{ Å})$.

The geometry calculated for **10c** is markedly different from **10a** and **10b**. In the case of **10c**, the BF₄⁻ anion is the most distant from the carbonium ion carbon (d_{B-C} =4.09 Å, relative to the ≈ 3.5 Å separations calculated for **10a** and **10b**). This corresponds to an increase of practically 0.6 Å in the distance between the B atom and the formally positive carbon atom. Perhaps most important is the fact that, in **10c** the anion clearly moves towards the only methoxy-substituted aryl ring, resulting in a markedly asymmetrical arrangement. The calculated B–X separations are 3.50, 5.19 and 5.75 Å, with the 3.50 Å distance associated with the aryl with the methoxy substituent.

The structures and geometries calculated for the two remaining aryl carbocation salts, **11** and **12**, are represented in Figure 12. The structures calculated for the two tris-aryl salts, **11** and **12**, are quite different. For the trityl salt **12**, the two ions are relatively close with a B–C distance of 3.61 Å.



Figure 7. ¹H, ¹⁹F HOESY spectra for (from left to right) **10a–c** in CD_2Cl_2 . For both **10b** and **10c**, the cross-peaks to the C_6H_5 rings are very weak. In **10c**, the *meta* protons (b) afford the strongest contacts (CD_2Cl_2 , 400 MHz, 10 mM).



Figure 8. 1D projections of the cross-peaks for 10a-c (from bottom to top). Note the relatively intense signals in the upper most trace for the CH₃O or *meta* protons in **10c**. Whereas for **10a** (bottom trace) all of the signals have similar intensities.

This is only slightly longer than the values observed in **10a** and **10b**. The spatial arrangement of the ions in **12** is slightly distorted, with distances between the boron atom and each of the C₆-ring centroids within 0.9 Å (d_{B-X} =4.13, 4.79 and 5.00 Å).

In the case of salt **11**, the anion is remote from the carbocation centre, affording a B–C separation of 5.46 Å. This distance is comparable to the value found in **9b**, but longer than that in the methoxy salt **10c**, d_{B-C} =4.09 Å. In **11**, the B atom in the anion is situated only 1.68 Å away from the plane defined by the carbonium C atom and the three proximate C atoms, indicating a tendency towards co-planarity between the two ions, similar to what was observed for **9b**. In addition, the general arrangement between the two ions is very asymmetrical, with the BF₄⁻ anion moving towards one side of the carbocation, approaching the NMe₂ substituent of one aryl group. This is shown quite clearly by the three B–N distances: 4.75, 6.12 and 10.97 Å.

In summary, the DFT results presented above qualitatively support the experimental data obtained in solution by means of ¹H, ¹⁹F HOESY NMR spectra analysis. The calculations indicate quite clearly that the most favorable geometric arrangement in the ion pair is dictated by the nature

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Figure 9. ¹H, ¹⁹F HOESY spectra for **11** (left) and **12** (right) in CD_2Cl_2 . In **11** note the weak signals for the *ortho* protons, suggesting that the anion is remote from the carbonium ion central carbon (CD_2Cl_2 , 400 MHz, 10 mM).



Figure 10. Optimized geometries for the salts **9a** and **9b**.

and structure of the cation, and, thus, there is not one well defined anion position common to all salts.

[Brucinium][PtCl₃(C₂H₄)] (6f): Although Zeise's salt, K-[PtCl₃(C₂H₄)], is one of the oldest known organometallic species, 6f represents the first example of this anion together with a cation derived from a natural product. Based on the PGSE results we find that there is complete ion pairing in both CDCl₃ and CD₂Cl₂, and, much less in [D₆]acetone. To study the possible influence of the brucinium cation on the bonding in the anion we have obtained the ¹⁹⁵Pt (I=1/2,abundance = 33.7%) natural chemical shifts (via 195Pt, 1H correlations) for both K[PtCl₃- (C_2H_4)] and the brucinium salt, **6 f**, in $[D_6]$ acetone. The two ¹⁹⁵Pt chemical shifts, -2270 ppm and -2243 ppm, respectively, are very similar. The range of ¹⁹⁵Pt chemical shifts is of the order of 10000 ppm with small steric effects often changing the position of the metal resonance by several tens of ppm.^[32] Consequently, a change of 27 ppm is very modest and supports the view that the anions in both salts are well separated in acetone and that the cation does not markedly affect the anion. Along the same lines, the value for ${}^{1}J({}^{195}\text{Pt}, {}^{13}\text{C})$ in **6 f** is 193 Hz



(in CD_2Cl_2) whereas the literature values for Zeise's salt fall in the range 192–195 Hz.^[33]

The solid-state structure of 6 f has been determined and a view of the salt, along with selected metric data, is given in Figure 13a. The close proximity of the two ions is indicated in Figure 13b. The literature contains a number of brucinium structures^[27] and the values for our cation seem very similar to the reported data. The structure of the anion of Zeise's salt appears in many textbooks.^[34] In **6 f**, the immediate coordination sphere of the Pt atom contains the three complexed Cl⁻ anions and the η^2 complexed ethylene. The local geometry is pseudo square planar with the ethylene C-C bond approximately perpendicular to the plane defined by the metal and the three halogens. The C-C bond length of 1.376(7) Å is in exact agreement with that found in the early structure of Zeise's salt.^[33] The metal-halogen bond distance, Pt-Cl1, trans to the olefin, Pt-Cl1=2.315(1) Å is, as expected, slightly larger than the average value for the two Pt-Cl bond lengths *cis* to the olefin, 2.295(1) Å. We note that the N-H bond of the cation interacts with the trans chloride of the Pt-anion. The separation between N19 and Cl1 is \approx 3.24 Å. This halogen hydrogen-bond selectivity is presum-



Figure 11. Optimized geometries for the salts 10 a-c.

ably a consequence of the stronger *trans* influence of the olefin resulting in a slightly more anionic character of Cl1 relative to Cl2.

 T_1 values: Given that the brucinium Pt-salt **6f** shows a rather substantial D_c/D_a ratio in CD₂Cl₂ but much less in [D₆]acetone, we were curious as to whether one could detect differences in, e.g., the olefin ¹H spin-lattice relaxation time, T_1 .

These ¹H T_1 data for the complexed ethylene of **6f** in two solvents and at two concentrations is shown in Table S3. For the 2 mM solution, T_1 of 1.6 s is much shorter in CD₂Cl₂ than in [D₆]acetone, 4.2 s (even allowing for the different solvent viscosities: η (CH₂Cl₂)/ η (acetone) \approx 1.4). Assuming that the dipole–dipole relaxation dominates,^[35] and thus that T_1^{-1} is proportional to the molecular correlation time, τ_c , then the increased association in CD₂Cl₂ (as a consequence of the



Figure 12. Optimized geometries for the salts 11 and 12.

NH…Cl hydrogen bond) results in a larger species which will have a larger τ_c , and thus afford a smaller T_1 . We note that increasing the concentration of **6 f** from 2 to 10 mM further decreases T_1 from 1.6 to 0.9 s and assume that this is a reflection of salt aggregation.^[17,26] We believe this to be the first example of the use of T_1 values in an anion to support the idea of differences in aggregation. The ¹H T_1 values for the C_2H_4 in the smaller salt K[PtCl₃(C₂H₄)] in [D₆]acetone are considerably larger, \approx 7–9 s than the value of 4.2 s for **6 f**. Perhaps the protons of the brucinium cation contribute to the ethylene relaxation.

Table S3 also shows ¹⁹⁵Pt T_1 values. The relaxation mechanism for ¹⁹⁵Pt is known to be chemical shift anisotropy (CSA).^[32] Consequently, one expects (and finds) a B_0^2 dependence of T_1 on the applied magnetic field strength, with values much shorter at the higher B_0 fields. However, in this relaxation mechanism, as well, T_1^{-1} is proportional to the molecular correlation time τ_c .^[32] Therefore the metal relaxation should show a similar solvent dependence. For **6f** at 9.4 T (400 MHz for ¹H), a) the ¹⁹⁵Pt T_1 in CD₂Cl₂ is much shorter than in [D₆]acetone and b) the ratio of the two ¹⁹⁵Pt T_1 's, in the two solvents, 60 ms/27 ms=2.2, is close to that found in the ¹H case, 4.2 s/1.6 s=2.6. Consequently, we conclude that the metal T_1 is also capable of providing an indication of differences in aggregation and this represents the

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Figure 13. a) A view of salt **6f**. Selected bond lengths and bond angles: Pt-C2l=2.116(5); Pt-C1l=2.126(4); C1l-C2l=1.376(7); Pt-C1l=2.3150(11); Pt-Cl2: 2.2878(10); Pt-Cl3=2.2947(11); Cl2-Pt-Cl3=178.92(4); Cl3-Pt-C1l=90.66(4): Cl2-Pt-C1l-C2l=-88.7(3); Cl3-Pt-C1l-C2l=90.2(3). b) Space-filling model showing the relationship for the two ions.

first example of the use of $^{195}\mbox{Pt}$ relaxation characteristics for this purpose. $^{[36]}$

X-ray study of 6c: Relative to the $CF_3SO_3^-$ anion, the $CH_3SO_3^-$ anion is not frequently used. Consequently we have determined the solid-state structure of salt **6c** and show this in Figure 14a along with selected bond lengths and bond angles. The local geometry at the S atom of the anion is distorted tetrahedral although one of the angles around sulfur, O3s-S-O2s is rather large, $\approx 117^\circ$. The various S–O bond distances are found in the range $\approx 1.39-1.46$ Å. Unfortunately, the structure contains a number of water molecules (see Figure 14b). One of these is hydrogen bonded to both N19 and an O atom of the $CH_3SO_3^-$ anion. The separation between the O(water) and O2s is about 2.73 Å.



Figure 14. a) A view of $CH_3SO_3^-$ salt **6c**. Selected bond lengths and bond angles N9–C10, 1.355(7); N9–C5, 1.430(6); N9–C8, 1.490(6); N19–C20, 1.496(7); N19–C18, 1.500(8); N19–C16, 1.531(7); S–O3s, 1.394(5); S–O2s, 1.426(4); S–O1s, 1.458(6); S–C1s, 1.702(8); O3s-S-O2s 117.0(3); O3s-S-O1s, 109.1(5); O2s-S-O1s, 108.7(3); O3s-S-C1s, 109.7(4); O2s-S-C1s, 108.5(4); O1s-S-C1s, 103.0(5). b) Representation indicating the water molecules and the hydrogen-bonding networks.

Conclusions

The diffusion results indicate that (for a number of routine anions such as BF_4^- , PF_6^- or $CF_3SO_3^-$) whether one considers ammonium, phosphonium, brucinium or carbocations, there is a similar solvent dependence of the ion pairing for the three solvents acetone, dichloromethane and chloroform. When taken together with the modestly large PGSE data base for transition metal complexes,^[12,13] it would seem that one can suggest a general trend: complete (or almost complete) ion pairing in CDCl₃, intermediate in CD₂Cl₂, and weak in [D₆]acetone.

The ¹H, ¹⁹F HOESY spectra can indicate both subtle and marked changes in the solution structures of related salts.

For the various aryl carbocations 9-12, we find a number of different positions for the BF_4^- anion. As suggested by the NMR measurements, and supported by DFT calculations, the anion can be situated either in a position, close to the C⁺ center, or along the aryl groups or even very close to the para-substituent and thus quite remote from the formally positive carbon atom. The DFT calculations nicely complement the solution results and provide details of the salt structures not readily available via NMR. For the protonated brucinium salts 6, the hydrogen bonding holds the anion close to the NH-function; however, when the N atom is quaternized with a large substituent, as in 7, the ion pairing is weaker and (although there is a specific approach of the anion), the anion is further away, relative to 6. Although PGSE data may provide the most reliable estimation of aggregation effects,^[26] one can use ¹H and even metal T_1 data as a supplement to these.

Experimental Section

All air-sensitive reactions and manipulations were performed under a N_2 or Ar atmosphere, respectively. Solvents were dried and distilled following standard procedures and stored under N_2 . Deuterated chloroform and dichloromethane were distilled over CaH₂ and degassed using two freeze-pump-thaw cycles and stored under N_2 . [D₆]acetone was prepared analogously over CaSO₄. All commercially available starting materials were purchased from commercial sources and used as received unless otherwise stated. NMR spectra were recorded with Bruker Avance-400 and DPX-500 MHz at ambient temperature and at 303 K, respectively. Elemental analyses and mass spectroscopic studies were performed at ETHZ.

Computational details: All calculations were performed by using the Gaussian 03 software package,[37] and the PBE1PBE functional, without symmetry constraints. That functional uses a hybrid generalized gradient approximation (GGA), including 25% mixture of Hartree-Fock^[38] exchange with DFT^[31] exchange-correlation, given by Perdew, Burke and Ernzerhof functional (PBE),^[39] and has proven to perform well in the description of nonbonded interactions.^[40] The optimized geometries were obtained with a standard 6-31G(d,p)^[41] basis set. Solvent (CH₂Cl₂) effects were considered in the geometry optimizations by means of the polarizable continuum model (PCM) initially devised by Tomasi and co-workers^[42] as implemented on GAUSSIAN 03.^[43] The molecular cavity was based on the united atom topological model applied on UAHF radii, optimized for the HF/6-31G(d) level. Equivalent starting geometry and optimization procedures were used for all ion pairs, to allow comparison between the different salts. Thus, the initial guess for the geometry calculations corresponded, in all cases, to the BF_4^- anion placed above the carbocation plane with one B-F bond directed to the carbonium C atom and a F-C distance of 4 Å. This initial geometry was first optimized in vacuum and, then, re-optimized with inclusion of solvent effects to yield the final ion pair geometry.

Crystallography: Colorless crystals of [brucinium][MeSO₃] (**6c**) were obtained by crystallization from EtOH/H₂O, while pale yellow crystals of [brucinium][PtCl₃(C₂H₄)] (**6f**) were obtained by crystallization from CH₂Cl₂. Details of the X-ray measurements can be found in Table 5.

The crystals were mounted on a Bruker diffractometer, equipped with a CCD detector, for the unit cell and space group determinations. Crystals of **6f** were cooled, using a cold nitrogen stream, to 180 K for the data collection. Selected crystallographic and other relevant data are listed in Table 5 and in the Supporting Information. Data were corrected for Lorentz and polarization factors with the data reduction software SAINT^[44] and empirically for absorption using the SADABS program.^[45] The structures were solved by direct methods and refined by full matrix least-



Table 5. Experimental data for the X-ray diffraction study of the brucinium salts $6c\text{-}3\,H_2O$ and $6\,f.^{[a]}$

	6 c •3H ₂ O	6 f
formula	C24H36N2O10S	C ₂₅ H ₃₁ Cl ₃ N ₂ O ₄ Pt
$M_{ m w}$	544.61	724.96
T [K]	293 (2)	180 (2)
crystal system	orthorhombic	orthorhombic
space group (no.)	$P2_{1}2_{1}2_{1}$ (19)	$P2_{1}2_{1}2_{1}$ (19)
<i>a</i> [Å]	8.2164(8)	12.3858(8)
<i>b</i> [Å]	12.697(1)	13.2250(9)
<i>c</i> [Å]	24.998(2)	15.181(1)
a [°]	90	90
β [°]	90	90
γ [°]	90	90
V [Å ³]	2607.9(4)	2488.1(3)
Ζ	4	4
$\rho_{\text{calcd}} [\text{g cm}^{-3}]$	1.526	1.935
μ [cm ⁻¹]	1.83	59.98
θ range [°]	$1.63 < \theta < 18.94$	$2.04 < \theta < 29.26$
data collected	14763	31 1 46
independent data	2082	6428
observed reflections (n_0)	1942	5807
$[F_{o} ^{2} > 2.0\sigma(F ^{2})]$		
parameters refined (n_v)	341	331
absolute structure parameter	0.07(2)	0.001(4)
$R_{\rm int}^{\rm [b]}$	0.0374	0.0443
$R \text{ (obsd reflns)}^{[c]}$	0.0408	0.0258
wR^2 (obsd reflns) ^[d]	0.1077	0.0449
GOF ^[e]	1.077	0.992

[a] Work completed by using a Bruker SMART diffractometer using Mo_{Ka} radiation (graphite monochrom., $\lambda = 0.71073$ Å). [b] $R_{int} = \Sigma |F_o^2 - \langle F_o^2 \rangle |/\Sigma F_o^2\rangle$. [c] $R = \Sigma (|F_o - (1/k)F_c|)/\Sigma |F_o|$. [d] $wR^2 = \{\Sigma [w(F_o^2 - (1/k)F_c^2)^2]/\Sigma w |F_o^2|^2]\}^{1/2}$. [e] GOF = $[\Sigma_w(F_o^2 - (1/k)F_c^2)^2/(n_o - n_v)]^{1/2}$.

squares^[46] (the function minimized being $\Sigma[w(F_o^2-1/kF_c)^2]$). For all structures, no extinction correction was deemed necessary. The scattering factors used corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.^[47] All calculations were carried out by using the PC version of SHELX-97,^[46] WINGX and ORTEP programs.^[48]

Structural study of [brucinium][MeSO₃] ($6c \cdot 3H_2O$): The space group was unambiguously determined from the systematic absences, while the cell constants (at RT) were refined by least-squares, at the end of the data collection, using 4219 reflections ($\theta_{max} \leq 18.8^{\circ}$). The data were collected using ω scans, in steps of 0.5°. For each of the 1440 collected frames, counting time was 30 s All crystals of 6c-3H2O were diffracting very weakly so that no significant scattered intensity could be found for $\theta >$ 20°. Thus only data up to $\theta_{\text{max}} \leq 18.94^{\circ}$ have been used for the refinement. The least-squares refinement was carried out using anisotropic displacement parameters for all non-hydrogen atoms. From the difference Fourier maps three clathrated water molecules were found and their oxygen atoms refined anisotropically; however, the hydrogen atoms of these water molecules could not be located. The contribution of the hydrogen atoms, in their calculated positions, $(C-H=0.96(\text{\AA}), B(H)=a \times$ $B(C_{bonded})(Å^2)$, in which a=1.5 for the hydrogen atoms of the methyl groups and 1.2 for the others), was included in the refinement using a riding model. Refining the Flack's parameter tested the handedness of the structure.[48c]

Structural study of [brucinium][PtCl₃(C_2H_4)] (**6f**): The space group was determined from the systematic absences and the low temperature cell constants were refined by least-squares at the end of the data collection, using 9861 reflections ($\theta_{max} \le 27.4^{\circ}$). The data were collected by using ω scans, in steps of 0.3°. For each of the 1560 collected frames, counting time was 30 s. The least-squares refinement was carried out using anisotropic displacement parameters for all non-hydrogen atoms, while the H atoms were included in the refinement as described above. The handedness of **6 f** was determined by refining the Flack's parameter.^[4&c]

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CHEMISTRY

NMR measurements: Samples of **9**, **10** and **12** where prepared in an Argon dry box. All the PGSE diffusion measurements were performed at a concentration of 2 mM by using the standard stimulated echo pulse sequence by using 400 MHz Bruker Avance spectrometer equipped with a microprocessor-controlled gradient unit and an inverse multinuclear probe with an actively shielded Z-gradient coil. The shape of the gradient pulse was rectangular, its duration δ was 1.75 ms and its strength varied automatically in the course of the experiments. The calibration of the gradients was carried out via a diffusion measurement of HDO in D₂O. In the ¹H-PGSE experiments, $\Delta^{[13]}$ was set to 117.75 ms and 167.75 ms, respectively. The number of scans varied between 8 and 32 per increment with a recovery delay of 10 to 24 s. Typical experimental times were 2–8 h. For ¹⁹F, Δ was set to 117.75 and 167.75 ms, respectively. 16 scans were taken with a recovery delay of 12 to 24 s, and a total experimental time of ≈ 2.5 –6 h.

All the spectra were acquired using 32 K points and a spectral width of 2796.4–4006.4 Hz (¹H) and 1882.5 Hz (¹⁹F) and processed with a line broadening of 1 Hz (¹H) and 2 Hz (¹⁹F). The slopes of the lines, *m*, were obtained by plotting their decrease in signal intensity vs G^2 using a standard linear regression algorithm. Normally, 12–20 points have been used for regression analysis and all of the data leading to the reported *D* values afforded lines whose correlation coefficients were >0.999. The gradient strength was incremented in 2–4% steps from 2–4% to 40–80%. A measurement of ¹H and ¹⁹F T_1 was carried out before each diffusion experiment and the recovery delay set to (at least) 5 times T_1 . We estimate the experimental error in *D* values at ±2%. The hydrodynamic radii, $r_{\rm H}$, were estimated using the Stokes–Einstein equation (c=6) or by introducing a semi-empirical estimation of the *c* factor.^[49,50]

The ¹H, ¹⁹F HOESY measurements were acquired using the standard four-pulse sequence^[51] on a 400 MHz Bruker Avance spectrometer equipped with a doubly tuned (¹H, ¹⁹F) TXI probe. A mixing time of 800 ms was used. The number of scans was 8–16 and the number of increments in the F1 dimension 512. The delay between the increments was set to 0.8 s. The concentration of the sample was 10 mM unless otherwise stated.

The ¹H and ¹⁹⁵Pt spin-lattice relaxation times T_1 were measured for K[PtCl₃(C₂H₄)] in [D₆]acetone (2 mM and 15 mM) and for **6f** in [D₆]acetone (2 mM and 10 mM) and CD₂Cl₂ (2 mM and 10 mM), respectively. The sample temperature was calibrated to 303 K.

The ¹H spin-lattice relaxation times T_1 were determined by the inversionrecovery experiment. A recovery delay of 6 s was used and 13 different delay times τ where applied. The number of sampling points was 72k, and the observed frequency range was 6.4 kHz, resulting in a digital resolution of 0.087 Hz.

The ¹⁹⁵Pt spin-lattice relaxation times T_I were determined using the inversion-recovery experiment followed by a polarization transfer to ¹H.^[52] The ¹⁹⁵Pt π (hard) pulse was calibrated prior to the measurement. T_1 values were determined at a magnetic field corresponding to a proton frequency of 400, 500 and 700 MHz, respectively. A recovery delay of 1 s was used and 10 different delay times τ where applied. The number of sampling points was 16k, and the frequency range was 1.6 kHz, resulting in a digital resolution of 0.098 Hz.

General procedure for the synthesis of brucinium salts 6 a-f and 7:

[Brucinium][CI]: In a two-neck flask brucine (600 mg) was dissolved in CH_2Cl_2 (40 mL). HCl (g), evolving from the slow addition of H_2SO_4 to NaCl using a dropping funnel, was flushed for 1.5 h trough the reaction solution at RT. The solution was then slowly concentrated under vacuum and the resulting precipitate filtrated off.

[Brucinium][X] (X = BF₄, PF₆, OMs, OTf) (6a-d): In a typical procedure bruciniumchloride (0.2 mmol) was dissolved in CH₂Cl₂ (2 mL) and added to a solution of AgX (1 equiv) in CH₃CN (0.3 mL). An immediate precipitate was formed and the reaction solution stirred for 4 h at RT in the dark. After filtration of the suspension through Celite the filtrate was



slowly concentrated under vacuum. The resulting crude was triturated with ${\rm Et}_2O$ and dried under vacuum affording a white powder.

[Brucinium][BArF] (6e): CH₂Cl₂ (2 mL) was added to a Schlenk containing BruciniumBF₄ (**6a**) (51 mg, 0.092 mmol). After addition of NaBArF (79.7 mg, 0.092 mmol) a crystalline precipitate formed and the mixture was stirred for 3 h at RT and subsequently filtrated through Celite. The filtrate was slowly concentrated under vacuum and Et₂O was added. The solution was stored at 4°C for 2 days and the formed crystals separated from the solution. The solution was concentrated under vacuum and the resulting crude was washed with hexane (59 mg, 58%). Elemental analysis calcd (%) for C₅₅H₃₉N₂O₄BF₂₄ (1258.7): C 52.48, H 3.12, N 2.23; found: C 52.30, H 3.01, N 2.27.

[Brucinium][**PtCl₃(C₂H₄)] (6 f)**: Acetone (35 mL) was added to a Schlenk containing bruciniumchloride (103.6 mg, 0.24 mmol). Addition of MeOH (2 mL) provided a clear solution. K[PtCl₃(C₂H₄)] (88.6 mg, 0.264 mmol) was added upon which a white precipitate formed. The suspension was stirred for 14 h at RT and filtrated. The filtrate was evaporated to dryness and extracted with CH₂Cl₂ (2×2 mL). The solution was concentrated under vacuum affording a yellow solid (109 mg, 63%). Elemental analysis calcd (%) for C₂₅H₃₁N₂O₄PtCl₃ (725.0): C 41.42, H 4.31, N 3.86; found: C 41.63, H 4.32, N 3.80; MS (MALDI): m/z: 395.2 (M^+).

[*N*-(4-*t*Bu-benzyl)brucinium][PF₆] (7): To a solution of brucine (134.1 mg, 0.34 mmol) in CH₂Cl₂ (6 mL) a solution of 4-*t*Bu-benzylbromide in CH₂Cl₂ (5 mL) was added dropwise. The reaction solution was stirred for 3 h at RT. Addition of Et₂O resulted in a white precipitate which was filtered, washed with Et₂O and Et₂O/CH₂Cl₂ (1:1) and dried under vacuum. The resulting *N*-(4-*t*Bu-benzyl)bruciniumbromide (172.4 mg, 82%), was reacted with Ag[PF₆] as described for **6a–d**, yield-ing (**7**) (26.1 mg, 78%).

Carbonium ions 9–12: 4,4'-Bis(dimethoxy)benzhydrilium tetrafluoroborate (**9a**),^[28a] and 4,4',4"-Trimethoxytrityl tetrafluoroborate (**10a**)^[28b] were synthesized following literature procedures.

4,4'-Bis(dimethylamino)benzhydrilium tetrafluoroborate (9b): 9b was prepared by a modified version of Dauben's^[28c] procedure. **4,4'-Bis(dimethylamino)benzhydrol (105.3 mg, 0.39 mmol) was dissolved in CH₂Cl₂ (3 mL). Addition of HBF₄·OEt₂ (57 \muL, 0.39 mmol) resulted in a deep blue solution. The solution was stirred at RT for 15 min and then in an ice bath for 30 min. Addition of Et₂O resulted in a dark blue precipitate which was filtered, washed with Et₂O and dried under vacuum (106 mg, 80%).**

4,4'-Dimethoxytrityl tetrafluoroborate (10b) and 4,4',4"-Tris(dimethylamino)trityl tetrafluoroborate (11) were prepared from the chloride salts as described for 6–9.

4-Methoxytrityl tetrafluoroborate (10 c): 4-Methoxytrityl alcohol was recrystallized from hot hexane/Et₂O (10:1) prior to use. 4-Methoxytrityl alcohol (228.5 mg, 0.79 mmol) was dissolved in Ac₂O (1.5 mL). Addition of HBF₄·OEt₂ (196 μ L, 1.58 mmol) resulted in an orange solution, which was stirred at RT for 60 min. Addition of Et₂O lead to an orange precipitate which was filtered and washed with Et₂O until the washing solution was colorless. The orange powder was dried under vacuum (262 mg, 92%).

Carbonium ions 9, 10 and 12 were stored in an Ar dry box at 243 K.

Model compounds: CPh_4 was recrystallized from hot benzene prior to use. $[PPh_4][PF_6]$ was prepared as described elsewhere.^[24]

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