

Synthesis, Characterization, and PGSE (^1H and ^{19}F) NMR Diffusion Studies on Cationic $(\eta^6\text{-Arene})\text{Mn}(\text{CO})_3^+$ Complexes: Boron Counterion, Ion Pairing, and Solvent Dependences

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The synthesis, characterization, and PGSE (^1H and ^{19}F) NMR diffusion studies on the cationic $[(\eta^6\text{-arene})\text{Mn}(\text{CO})_3][\text{X}]$ (arene = anisole, 4-chloroanisole, and 1,3,5-trimethoxybenzene; $\text{X} = \text{BPh}_4$ and BArF) are reported. The tetraphenyl borate complexes of anisole and 4-chloroanisole show surprisingly strong ion pairing in dichloromethane solution, whereas the BArF salts do not. ^1H , ^1H -NOESY data support this anion selectivity. In chloroform solution one finds the usual strong ion pairing for both anions. The solid-state structure of $[(\eta^6\text{-1,3,5-trimethoxybenzene})\text{Mn}(\text{CO})_3][\text{BPh}_4]$ has been determined. ^{13}C NMR and IR data for the new complexes are reported. The observed IR frequencies are higher for the BArF complexes than for the BPh_4 complexes.

Introduction

It is now clear that anion effects play a role in the kinetics of a number of stoichiometric and catalytic processes.¹ Specifically, for the Rh(I)-catalyzed Pauson–Khand reaction,² the Ru(II)- or Cu(II)-catalyzed Diels–Alder³ reaction, or the Ir(I)-catalyzed hydrogenation of polysubstituted olefins,⁴ among others,⁵ the anion associated with the transition metal cation can markedly affect the rate of reaction. The source of these effects is often completely unknown and may be related to coordination effects, ion pairing effects, or both, among other possible explanations.

^1H and ^{19}F pulsed gradient spin–echo (PGSE) diffusion studies,^{6–16} together with NOE measurements,^{17–27} are

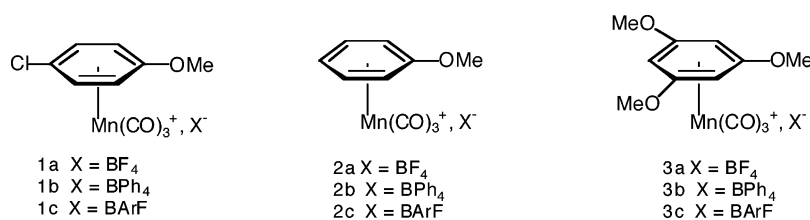
rapidly becoming the methods of choice for recognizing how anions and cations interact in solution. This stems, partially, from the ability to use a multinuclear diffusion approach²⁸

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Scheme 1



(i.e., ¹H and ¹⁹F NMR methods for the cation and anion, respectively, combined with ¹H and ¹⁹F HOESY data) to follow how and where the anions and cations interact. This approach has also been extended to salts (and compounds) containing other nuclei, including, ⁷Li,²⁹ ³¹P,³⁰ ²⁹Si,⁹ ³⁵Cl,³⁰ and recently, ¹⁹⁵Pt.³¹ Despite the recent surge in interest, the applications of the PGSE method to the problems of ion pairing remain sparse, and there are few systematic studies for transition metal complexes in different solvents.

Organometallic Mn compounds enjoy wide synthetic applications. Indeed, the increased reactivity of aromatic molecules coordinated to electron-deficient metal fragments, such as M(CO)₃ (M = Cr or Mn⁺), is associated with versatile synthetic intermediates in organometallic and organic chemistry.³² Interestingly, the applications of cationic manganese complexes remain relatively undeveloped compared to their isoelectronic, neutral chromium counterparts. The two main reasons for this are as follows: (a) preparation of the functionalized complexes by direct complexation of the arenes to the Mn(CO)₃ is difficult³³ (access to the salts, [(η⁶-arene)Mn(CO)₃][X]-substituted by electron-withdrawing or conjugated substituents, has only recently become available³⁴ using a multistep synthesis strategy) and (b) the lack

of solubility of these cationic complexes in most of the usual organic solvents. Moreover, they cannot be purified by column chromatography which strongly limits their use and the subsequent development of new reactions. However, in a recent report, the routine anions, PF₆ and BF₄, have been replaced by the TRISPHAT anion, resulting in the new salts being soluble in organic solvents of modest polarity.³⁵

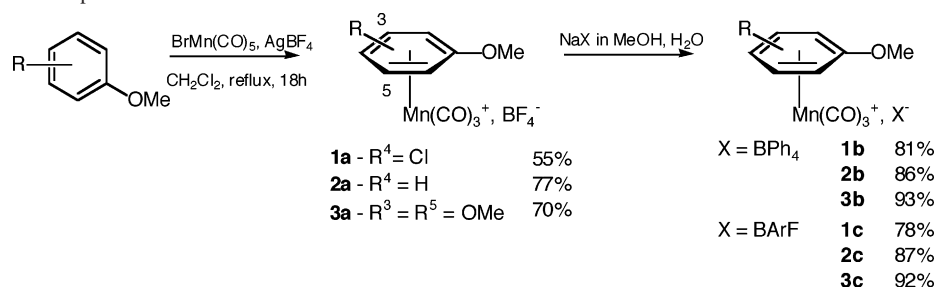
We report here the preparation and spectroscopic characterization of the new cationic manganese complexes [(η⁶-arene)Mn(CO)₃][X] (arene = 4-chloroanisole (**1**), anisole (**2**), and 1,3,5-trimethoxybenzene (**3**) with X = BPh₄ (**b**) and BARf (B[3,5-(CF₃)₂C₆H₃]₄) (**c**)) (Scheme 1) as well as PGSE diffusion studies on these complexes. The latter measurements are designed to shed light on possible differences caused by ion pairing. Our results represent the first examples of PGSE measurements on organometallic Mn compounds and demonstrate a surprising difference between the anions BPh₄ and BARf.

Results and Discussion

Syntheses of Complexes 1–3. We are only aware of two publications concerning [(η⁶-arene)Mn(CO)₃]⁺ cationic complexes^{36,37} as tetraphenylborate salts. One of these³⁷ reports a general method for the introduction of the desired counterion using an anion metathesis reaction and was applied to the synthesis of complexes of benzene, toluene, and mesitylene. We chose to prepare the tetrafluoroborate salts **1a–3a** as these were easily obtained via a well-known versatile procedure.^{38a,b} These BF₄ salts were soluble in polar solvents such as acetone and acetonitrile but were only very poorly soluble in THF or CH₂Cl₂. The new anions, BPh₄[–] and BARf[–],³⁹ the latter being known for its beneficial effect

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Scheme 2. Syntheses of Complexes **1a–3c****Table 1.** IR Spectral Data (neat, cm^{-1}) for Complexes **1b,c–3b,c**

cation	anion	complex	$\nu(\text{A1})$	$\Delta\nu(\text{A1})^a$	$\nu(\text{E})$	$\Delta\nu(\text{E})^b$
1	BPh_4	1b	2072	15	2012	24
	BArF	1c	2087		2036	
2	BPh_4	2b	2069	14	2013	16
	BArF	2c	2083		2029	
3	BPh_4	3b	2057	16	1989	23
	BArF	3c	2073		2012	

^a $\Delta\nu(\text{A1}) = \nu(\text{A1}, \text{BArF}) - \nu(\text{A1}, \text{BPh}_4)$. ^b $\Delta\nu(\text{E}) = \nu(\text{E}, \text{BArF}) - \nu(\text{E}, \text{BPh}_4)$.

on the stability of the related complexes,^{40,41} were introduced via their sodium salts.

The BPh_4 and BArF salts were prepared by treating **1a–3a**, dissolved in a minimum of water, by a saturated methanolic solution of NaX ($\text{X} = \text{BPh}_4, \text{BArF}$). The new complexes, **1b–3b** ($\text{X} = \text{BPh}_4$) or **1c–3c** ($\text{X} = \text{BArF}$) precipitated and were isolated as light yellow powders, either by filtration of the mixture or by extraction in CH_2Cl_2 , in good to excellent yields (see Scheme 2). The absence of any residual BF_4^- anion was confirmed by mass spectrometry analysis (negative mode): only the new X^- counterion was detected.

It is noteworthy that the new complexes with BPh_4 and BArF as counterions are soluble in CH_2Cl_2 and THF and can be purified by silica gel chromatography.

IR Spectroscopy. Because IR ν_{CO} shifts are known to be very sensitive to changes in electron density at the metal and reflect π -back-bonding into the $\text{CO } \pi^*$ orbitals,⁴² we have recorded the spectra for **1–3** and show these data in Table 1. The observed IR frequencies are higher for the BArF complexes than for the BPh_4 complexes with the differences ranging from 14 to 16 cm^{-1} for the A1 mode frequency and from 16 to 24 cm^{-1} for the E mode frequency. Although the source of this difference is not immediately clear, the data suggest less π -back-bonding for the BArF salts and thus, less electron density at the metal than for the BPh_4 analogues.

X-ray Study on Complex 3b. Crystals of complex **3b** were grown by slow diffusion of petroleum ether into a

Table 2. Crystal Data for Complex **3b**

formula	$\text{C}_{36}\text{H}_{32}\text{BMnO}_6$
fw	626.39
cryst syst	triclinic
a (Å)	10.4965(11)
b (Å)	11.9045(16)
c (Å)	14.029(2)
α (deg)	74.428(15)
β (deg)	88.031(14)
γ (deg)	71.735(10)
V (Å ³)	1601.2(3)
Z	2
space group	$\bar{P}1$
cryst shape	parallelepiped
cryst color	yellow
μ (cm^{-1})	4.57
ρ (g cm^{-3})	1.30
diffractometer	KAPPA CCD Enraf Nonius
radiation	$\text{Mo K}\alpha$ ($\lambda = 0.71073$ Å)
scan type	$\omega/2\theta$
scan range (deg)	$0.8 \geq \theta \geq 0.345$
θ limits (deg)	2–30
octants collected	–14, 14; –12, 16; –19, 18
no. of data collected	17662
no. of unique data collected	9229
no. of unique data used for refinement	$4311(F_o)^2 > 3\sigma(F_o)^2$
merging R	0.12
R_1^a	0.0529
$R_2^{b,c}$	0.0596
absorption correction	difabs ($T_{\min} = 0.80, T_{\max} = 1.08$)
secondary extinction coefficient	none
GOF	1.086
no. of variables	398
$\Delta\rho_{\min}$ ($\text{e}/\text{\AA}^3$)	–0.468
$\Delta\rho_{\max}$ ($\text{e}/\text{\AA}^3$)	0.454

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$. ^c Weighting scheme of the form $w = w'[1 - (|F_o| - |F_c|)/6\sigma(F_o)]^2$ with $w' = 1/S_r A_r T_r(X)$ with coefficients of 0.477, 0.326, and 0.227 for a Chebyshev series for which $X = F_o/F_{c(\max)}$.

concentrated acetone solution of **3b**. Crystal data^{43,44} are reported in Table 2, and Figure 1 shows a CAMERON⁴⁵ view of the salt along with some selected bond lengths and angles. The $\text{Mn}(\text{CO})_3$ moiety exhibits the well-known regular piano-stool geometry.³³ The three $\text{Mn}-\text{C}(\text{CO})$ bonds are perfectly eclipsed by the $\text{C}-\text{O}$ bonds stemming from the arene carbons bearing the methoxy groups. The six $\text{Mn}-\text{C}$ arene bonds have almost the same lengths with the values ranging from 2.20 to 2.25 Å, in line with those found for the previously described (1,2,3-trimethoxybenzene) $\text{Mn}(\text{CO})_3$ isomeric complex,⁴⁶ whose values range from 2.14 to 2.28 Å. The three $\text{Mn}-\text{C}(\text{CO})$ separations fall in the range 1.804(4)–1.816(4) Å. There seems to be no obvious contact between the two ions with the $\text{Mn} \cdots \text{B}$ distance > 7 Å.

Diffusion studies for [(Arene) $\text{Mn}(\text{CO})_3$][X]. Diffusion constants, D , from the ^1H and ^{19}F PGSE measurements in

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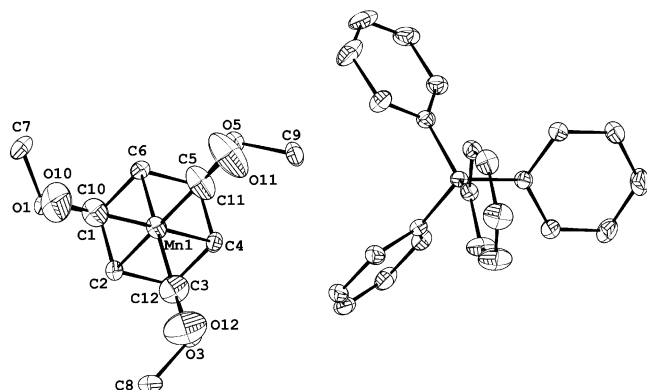


Figure 1. ORTEP view of the structure of complex **3b** with 30% thermal ellipsoid probability. Selected bond lengths (Å) and selected angles (deg) are as follows: Mn–C1, 2.253(3); Mn–C3, 2.247(3); Mn–C5, 2.237(3); Mn–C2, 2.198(3); Mn–C4, 2.201(3); Mn–C6, 2.198(3); Mn–C10, 1.816(4); Mn–C11, 1.804(4); Mn–C12, 1.816(4); C10–Mn–C11, 90.0(2); C10–Mn–C12, 91.2(2); and C11–Mn–C12, 91.1(2)

chloroform, dichloromethane, and acetone are given in Table 3.

$$r_H = \frac{kT}{6\pi\eta D}$$

The hydrodynamic radii, r_H , are obtained from the Stokes–Einstein relationship⁴⁷ (above) where k is the Boltzmann constant and η is the viscosity. This calculated r_H value permits a direct comparison between diffusion measurements in different solvents, as it corrects for the different solvent viscosities.

We make the assumption that, when the cation and anion reveal identical D values, whose magnitudes produce r_H values which are substantially greater than those estimated either by crystallography or calculations,⁴⁸ then we are dealing with ion pairing. Further, as an estimate of the r_H value of the solvated cation or anion, we use the measured

D (and then calculate the r_H) values in either water or methanol as these solvents are normally sufficiently polar to separate and solvolyse the ions.

Organometallic cations are not routinely soluble in water; however, both the BF_4 salts of **1a** and **2a** are soluble in aqueous solution so that their D and r_H values for the cations ($D = 7.04$ and $r_H = 3.5$ Å for **1a** and $D = 7.68$ and $r_H = 3.2$ Å for **2a**) could be determined. These r_H values for the cations are relatively small but reasonable.⁴⁷ From a methanolic solution of NaBPh_4 , we find $D = 8.08$ and $r_H = 5.1$ Å for the BPh_4 anion, in good agreement with what we observed from the X-ray data for **3b**. Further, from a methanolic solution of **3b**, the diffusion measurements for the anion give $D = 7.75$ and $r_H = 5.4$ Å. Alcohols as solvents may induce some ion pairing,^{20b,27,31} so we assumed that a value of ca. 5.1 Å is reasonable for the BPh_4 anion. In the absence of ion pairing, the BARf anion often shows r_H values in the region of 5.8–6.1 Å.^{28c,f}

The data in Table 3 show D and r_H values for 2 mM solutions of **1–3** as their BPh_4 and BARf salts, in three solvents, chloroform, dichloromethane, and acetone. As expected,²⁸ there is very substantial (often 100%) ion pairing in chloroform for **1–3**. Reasonably enough, the BARf ion pair is larger in volume than the BPh_4 analogues. We consider the 6.2 Å values for **1b** in chloroform to be slightly large; perhaps these are the result of increased solvation (hydrogen bonding) from the chloroform to the Cl atom.

In a direct comparison of the BPh_4 and BARf salts **1–3** in dichloromethane, the solvent often used in homogeneously catalyzed reactions, we find that the tetraphenyl borate complexes show complete ion pairing for **1b** and **2b** and substantial ion pairing for **3b**, whereas the BARf analogues appear to have little or no ion pairing. The r_H values for the cations in **1b** and **2b**, 5.6 Å, are much larger than the measurements on the cation models described above (3.2–3.5 Å). We believe this to be the first clear example of this kind of ion pairing selectivity in tetraphenyl borate anions. We note that the r_H values for the cations in these BARf salts (4.3–4.7 Å) are much closer to what one might expect for a solvated cation in dichloromethane, instead of water. Presumably, the electron-withdrawing trifluoromethyl groups delocalize the negative charge so that the ion pairing is no longer very favorable. Moreover, these results are consistent with the variations observed for the carbonyl stretching frequencies, which suggest an increase in electron density at the metal center for the BPh_4 complexes.

Normally, acetone as solvent promotes ion separation,^{28c,e,49} relative to either dichloromethane or chloroform, and indeed, we find that, for the BARf salts, **1c–3c**, the D and r_H values for the two ions differ significantly. In **1c** and **2c**, the cations

(43) Data were recorded at room temperature on a Kappa-CCD Enraf-Nonius diffractometer with graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$ Å) and the ω -scan technique. Orientation matrix and lattice parameters were obtained by least-squares refinement of the diffraction data of 52 reflections within the range of $5^\circ < \theta < 20^\circ$. The index ranges of data collection were $-14 \leq h \leq 14$, $-12 \leq k \leq 16$, and $-19 \leq l \leq 18$. Intensity data were collected in the θ range 2.0 – 30° , 4311 have $(F_o)^2 \geq 3\sigma(F_o)^2$. All of the measured independent reflections were used in the analysis. The structure was solved by direct methods and refined with a full-matrix least-squares technique on F using the CRYSTALS^{44} programs. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were either set in calculated positions and isotropically refined. The values of the discrepancy indices R_1 (R_2) for all data were 0.1211 (0.1317), whereas those listed in Table 1 correspond to the data with $I > 3\sigma(I)$. The final Fourier difference map showed maximum and minimum height peaks of 0.454 and -0.468 e Å^{-3} . The values of the number of reflections and number of variable parameters are 398, and that of the goodness-of-fit (GOF) is 1.086. The molecular structure was drawn with the program CAMERON^{45} and is reported in Figure 1.

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(45) Watkin, D. J.; Prout, C. K.; Pearce, L. J. *CAMERON*; Chemical Crystallography Laboratory: OXFORD, UK, 1996.

(46) Gagliardini, V.; Balssa, F.; Rose-Munch, F.; Rose, E.; Susanne, C.; Dromzee, Y. *J. Organomet. Chem.* **1996**, *519*, 281–283.

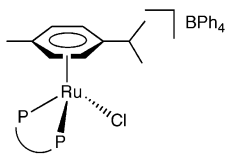
(47) It has been suggested that factor 6 in eq 2 is not valid for small species whose van der Waals radii are < 5 Å (Edward, J. T. *J. Chem. Educ.* **1970**, *47*, 261; Ue, M. *J. Electrochem. Soc.* **1994**, *141*, 3336). To be consistent and facilitate comparisons we have used eq 2 as shown.

(48) The ionic radii can be estimated from crystallographic data, molecular models or both. Modern modelling programs, such as Chem 3D, allow the calculation of the Connolly solvent-excluded volume of a molecule, V_{con} , which is the volume within the surface created when a probe sphere, representing the solvent, is rolled over the molecular mode. M. L. Connolly *J. Mol. Graphics* **1993**, *11*. For more information visit <http://connolly.best.vwh.net/>. We estimate the r_H value of the cation to be between 3.1 and 3.3 Å. For the BARf anion, we estimate an r_H value of ca. 5.8 Å.

Table 3. Diffusion Data for Manganese Carbonyl Complexes^{a-c}

Compound	Fragment	CD_2Cl_2		Acetone		CDCl_3	
		D^a	r_H^b	D^a	r_H^b	D^a	r_H^b
1b	Cations (^1H)	9.52	5.6	14.29	5.0	6.68	6.2
	BPh_4 (^1H)	9.45	5.6	14.36	5.0	6.64	6.2
1c	Cations (^1H)	11.71	4.5	15.67	4.6	6.45	6.4
	BArF (^1H)	8.52	6.2	11.88	6.0	6.10	6.7
2b	Cations (^1H)	9.54	5.6	13.64	5.2	7.20	5.7
	BPh_4 (^1H)	9.36	5.7	13.56	5.3	7.21	5.7
2c	Cations (^1H)	12.34	4.3	16.22	4.4	6.30	6.5
	BArF (^1H)	8.42	6.3	12.06	5.9	6.37	6.4
3b	Cations (^1H)	10.34	5.1	14.31	5.0	6.90	5.9
	BPh_4 (^1H)	9.46	5.6	13.89	5.0	7.06	5.9
3c	Cations (^1H)	11.36	4.7	13.76	5.2	-	-
	BArF (^1H)	8.39	6.3	11.08	6.5	-	-
	BArF (^{19}F)	8.62	6.1	-	-	-	-

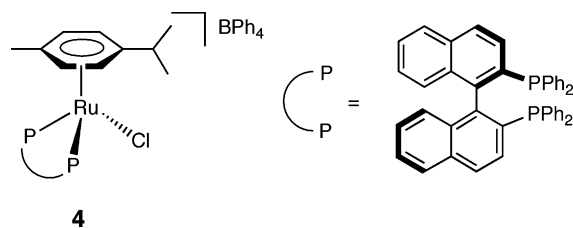
4	Cations (^1H)	8.16	6.6	10.55	6.9	6.03	6.9
	BPh_4 (^1H)	9.66	5.5	14.52	5.0	5.98	6.9



^a D is $\times 10^{-10} \text{ m}^2 \text{ s}^{-1}$; r_H is in Å; 2mM solutions. Estimated using the diffusion coefficient of HDO in D_2O as the reference. ^b Viscosity, η (299 K, $\text{kg s}^{-1} \text{ m}^{-1}$): CH_2Cl_2 , 0.414; acetone, 0.306; CDCl_3 , 0.534. ^c The size of BPh_4 was estimated using a 2mM solution of NaBPh_4 at 299 K in MeOD ($\eta = 0.523$): $D = 8.08$, $r_H = 5.1$ Å. For **3b** in MeOD: $D_{\text{cation}} = 9.58$, $r_H = 4.4$ Å; $D_{\text{anion}} = 7.75$, $r_H = 5.4$ Å. For **1a** in D_2O ($\eta = 0.894$): $D_{\text{cation}} = 7.04$, $r_H^c = 3.5$ Å. For **2a** in D_2O ($\eta = 0.894$): $D_{\text{cation}} = 7.68$, $r_H = 3.2$ Å.

show an r_H value of ca. 4.5 Å which we take to mean that (allowing for acetone rather than water solvation) there is little or no ion pairing. However, in **3c**, the larger value of 5.2 Å for the cation suggests significant but not complete ion pairing, and this is supported by a somewhat larger r_H value of 6.5 Å for the BArF anion. The r_H values in acetone for the BPh_4 anion are somewhat puzzling. For all three salts, **1b–3b**, the diffusion data suggest identical translation for both the cation and the anion. However, we believe this is simply a coincidence. The r_H values for the anion are consistent with an isolated BPh_4 anion so that it is possible that the cation is very strongly solvated by the acetone and thus appears to have the same radius as the anion.

Since there are not many PGSE data on BPh_4 salts available, we measured the $\text{RuCl}(\text{p-cymene})(\text{Binap})$ model salt, **4**, in the same three solvents.



There are a number of related diffusion measurements known for this type of cationic Binap complex.^{28b,e} The observed D and r_H values are also given in Table 3 and suggest strong ion pairing in chloroform, significant (but not complete) ion pairing for this salt in dichloromethane solution, and separated ions in acetone. Consequently, the diffusion results for our BPh_4 Mn complexes are somewhat unusual.

NOE Experiments. To support the diffusion data on the Mn complexes in dichloromethane, we have measured ^1H , ^1H NOESY spectra for the two tetraphenyl borate complexes, **1b** and **2b**, and show sections of these spectra in Figure 2. Clearly, for **1b** there are strong contacts from the ortho protons of the tetraphenyl borate anion to the complexed arene ring protons. In **1b**, there is also a strong contact to the methoxy methyl resonance. In **2b**, the strongest crosspeaks stem from the aromatic signals, but there is no contact to the methoxy group. One does observe a contact to the arene para proton, but this is rather weak when compared to the crosspeaks resulting from the ortho and meta signals. Perhaps the anion prefers to be remote from the halogen atom in **1b**. NOESY spectra for the salts **1b** and **3b** in acetone

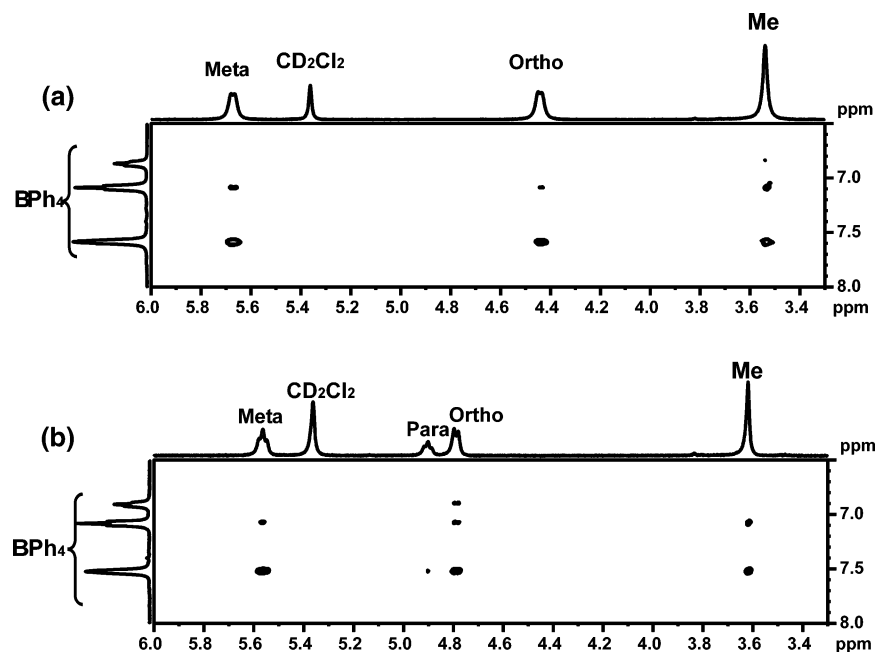


Figure 2. Sections of the $^1\text{H}, ^1\text{H}$ NOESY spectra of (a) **1b** and (b) **2b** revealing the strong inter-ion NOE's from the BPh_4^- ions.

solution show no inter-ion contacts, in keeping with our interpretation of their diffusion data.

The corresponding $^1\text{H}, ^1\text{H}$ NOESY spectrum for BArF salt **2c** contains no crosspeak which stems from the BArF^- anion (Figure 3). Obviously, this anion occupies a relatively remote position with respect to the cation, in keeping with the results from the PGSE measurements.

In Tables 4 and 5 we show ^1H and ^{13}C data for **1** and **2**. In dichloromethane solution, we note marked low frequency changes in the proton resonance positions of the arene of **2b**, relative to an acetone solution, and assign these differences to the anisotropic effects from the proximate tetraphenyl borate anion. The analogous ^{13}C changes are rather modest and consistent with a solvent effect (i.e., the carbonyl resonances and the arene resonances are all shifted in the same direction by a modest 1–3 ppm).

We conclude that both the diffusion and NOE results point to a somewhat unexpected ion pairing selectivity for the two tetraphenyl borate complexes. The IR data reflect these differences, although the actual source of the change in the ν_{CO} shifts is not clear.⁵⁰ In any case, the PGSE methodology has once again proven to be one of the most useful tools for elucidating how ions interact in solution.

Experimental Section

We have used the viscosities for the nondeuterated solvent, given in the on-line version of the Chemical Properties Handbook (McGraw-Hill, 1999, <http://www.knovel.com>).

(49) Martinez-Viviente, E.; Pregosin, P. S.; Vial, L.; Herse, C.; Lacour, J. *Chem. Eur. J.* **2004**, *10*, 2912–2918.

(50) The interaction between the anion and the cation and the resulting changes in the IR data may well involve changes in the arene bonding (the ^{13}C data do reveal a ca. 3 ppm shift for the complexed arene), rather than a direct interaction with the Mn center. This subject remains open.

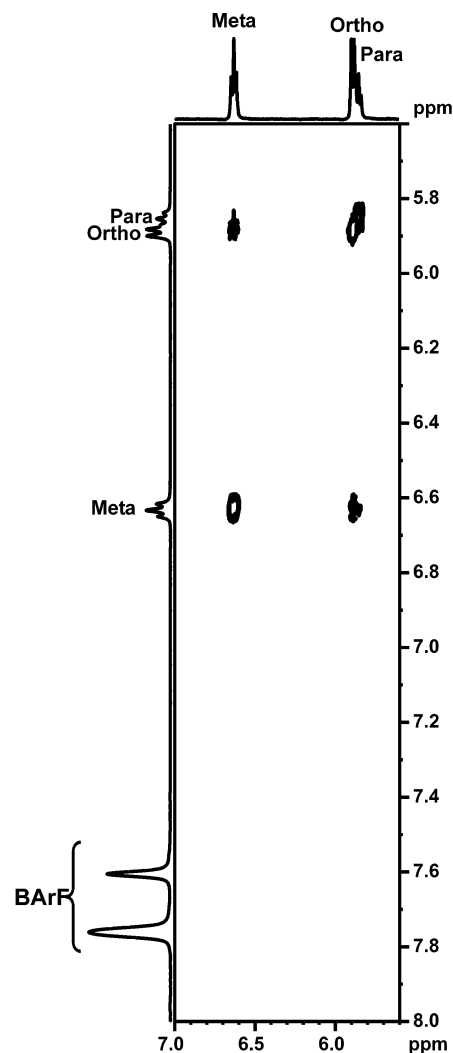


Figure 3. Section of the $^1\text{H}, ^1\text{H}$ NOESY spectrum of **2c**. There are no contacts from the BArF^- to the cation.

Table 4. ^1H and ^{13}C NMR Data for the Salts^a

1b				1c			
	δ	assignment		δ	assignment		
^1H	7.38	<i>ortho</i> -BPh ₄		7.80	<i>ortho</i> -BArF		
		<i>meta</i> -arom Mn		7.55	<i>meta</i> -arom Mn		
	6.95	<i>meta</i> -BPh ₄		—	—		
	6.79	<i>para</i> -BPh ₄		7.69	<i>para</i> -BArF		
	6.50	<i>ortho</i> -arom. Mn		6.69	<i>ortho</i> -arom. Mn		
^{13}C	4.16	Me—O		4.24	Me—O		
	58.4	Me—O		60.1	Me—O		
	82.7	<i>ortho</i> -arom Mn		84.8	<i>ortho</i> -arom Mn		
	103.3	<i>meta</i> -arom Mn		105.2	<i>meta</i> -arom Mn		
	106.5	quaternary-Cl-arom Mn		108.5	quaternary-Cl-arom Mn		
	121.6	<i>para</i> -BPh ₄		119.1	<i>para</i> -BArF		
	125.4	<i>meta</i> -BPh ₄		136.2	<i>ortho</i> -BArF		
	136.1	<i>ortho</i> -BPh ₄		130.8	<i>meta</i> -BArF		
	147.1	quaternary-MeO-arom Mn		149.1	quaternary-MeO-arom Mn		
	164.1	quaternary-BPh ₄		163.3	quaternary-BArF		
	214.7	CO		216.3	CO		
	—	—		126.1	CF ₃		

2b				2c			
	δ	assignment		δ	assignment		
^1H	7.37	<i>ortho</i> -BPh ₄		7.80	<i>ortho</i> -BArF		
	6.94	<i>meta</i> -BPh ₄		—	—		
	6.79	<i>para</i> -BPh ₄		7.69	<i>para</i> -BArF		
	7.09	<i>meta</i> -arom Mn		6.52	<i>meta</i> -arom Mn		
	6.38	<i>ortho</i> -arom Mn		6.52	<i>ortho</i> -arom Mn		
^{13}C	6.23	<i>para</i> -arom Mn		6.38	<i>para</i> -arom Mn		
	4.17	Me—O		4.24	Me—O		
	59.5	Me—O		59.6	Me—O		
	84.4	<i>ortho</i> -arom Mn		84.8	<i>ortho</i> -arom Mn		
	106.7	<i>meta</i> -arom Mn		107.0	<i>meta</i> -arom Mn		
	91.1	<i>para</i> -arom Mn		91.5	<i>para</i> -arom Mn		
	123.1	<i>para</i> -BPh ₄		119.2	<i>para</i> -BArF		
	127.0	<i>meta</i> -BPh ₄		136.3	<i>ortho</i> -BArF		
	137.7	<i>ortho</i> -BPh ₄		130.8	<i>meta</i> -BArF		
	151.4	quaternary-MeO-arom Mn		151.8	quaternary-MeO-arom Mn		
	165.7	quaternary-BPh ₄		151.8	quaternary-BArF		
	217.3	CO		217.3	CO		
	—	—		123.5	CF ₃		

^a ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded in d_6 -acetone at 299 K.

Table 5. ^1H and ^{13}C NMR Data for the Salts^a

2b (50mM)				2b (2mM)			
	δ	assignment		δ	assignment		
^1H	7.53	<i>ortho</i> -BPh ₄		7.50	<i>ortho</i> -BPh ₄		
	7.07	<i>meta</i> -BPh ₄		7.08	<i>meta</i> -BPh ₄		
	6.90	<i>para</i> -BPh ₄		6.90	<i>para</i> -BPh ₄		
	5.36	<i>meta</i> -arom Mn		5.73	<i>meta</i> -arom Mn		
	4.58	<i>ortho</i> -arom Mn		4.94	<i>ortho</i> -arom Mn		
^{13}C	4.69	<i>para</i> -arom Mn		5.05	<i>para</i> -arom Mn		
	3.52	Me—O		3.68	Me—O		
	58.7	Me—O					
	81.4	<i>ortho</i> -arom Mn					
	104.2	<i>meta</i> -arom Mn					
	88.0	<i>para</i> -arom Mn					
	122.6	<i>para</i> -BPh ₄					
	136.3	<i>ortho</i> -BPh ₄					
	126.6	<i>meta</i> -BPh ₄					
	149.3	quaternary-MeO-arom Mn					
	164.5	quaternary-BPh ₄					
	214.8	CO					

^a ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded in CD_2Cl_2 at 299 K. The ^1H spectra were recorded at two concentrations, but the ^{13}C at the higher concentration only.

General Procedures. $\text{Mn}_2(\text{CO})_{10}$ was purchased from Aldrich; AgBF_4 , anisole, and 1-chloro-4-methoxybenzene were purchased from Acros Organics, and 1,3,5-trimethoxybenzene was purchased from Avocado. Anisole and 1-chloro-4-methoxybenzene were distilled over CaH_2 prior to use. $\text{BrMn}(\text{CO})_5$ was prepared according

to a described procedure.^{38c} CH_2Cl_2 was dried and distilled over CaH_2 , and all of the complexation reactions were carried out in the dark under an inert atmosphere. For the anion metathesis, NaBPh_4 was purchased from Avocado, and NaBArF was prepared according to the procedure described by Reger.³⁹ These anion exchanges were performed in air. NMR spectra of complexes **1a–3a** were recorded on a Bruker ARX 200 MHz or Avance 400 MHz spectrometer. ^1H and ^{13}C signals of residual acetone were used as internal standard at $\delta = 2.09$ and 30.60, respectively. Deuterated solvents used in the PGSE experiments were dried by distillation over molecular sieves and stored over molecular sieves under N_2 . MS/HRMS were obtained from the University of Lille on an Applied Biosystems Voyager DE-STR MALDI-TOF MS. Infrared spectra were measured on a Bruker Tensor 27 spectrometer via the “single reflection horizontal ATR” method, which allows one to deposit the pure product on a crystalline diamond surface. Consequently, the samples are “neat” in that they are not mixed with a support material.

Diffusion Measurements. All of the measurements were performed on a Bruker Avance spectrometer, 400 MHz, equipped with a microprocessor-controlled gradient unit and a multinuclear inverse probe with an actively shielded Z-gradient coil.

The gradient shape was rectangular and its length was of 1.75 ms. Its strength was increased by steps of 4% during the course of the experiment. The time between midpoints of the gradients was 167.75 ms for all experiments. The experiments were carried out at a set temperature of 299 K within the NMR probe. Cation diffusion rates were measured using the ^1H signal from the MeO group, and anion diffusion was obtained from the ^1H signal of the *ortho* proton of the aromatic ring attached to boron. In the case of **3c** in CD_2Cl_2 , the anion diffusion was also measured using the ^{19}F signal for comparison. The error coefficient for the D values is ± 0.06 .

Preparation of $[(\eta^6\text{-Arene})\text{Mn}(\text{CO})_3][\text{BF}_4]$ (1a–3a**).** Complexes **1a–3a** were prepared following previously described complexation procedures^{38a,b} by reaction of the arene with a mixture of $\text{BrMn}(\text{CO})_5$ and AgBF_4 in dichloromethane.

$[(\eta^6\text{-1-Chloro-4-methoxybenzene})\text{Mn}(\text{CO})_3][\text{BF}_4]$ (1a**).** Yield: 55%. ^1H NMR (200 MHz, acetone- d_6): δ 4.23 (s, 3H, OMe), 6.67 (d, $^3J = 7.6$ Hz, 2H, $\text{H}^{3,5}$), 7.53 (d, $^3J = 7.6$ Hz, 2H, $\text{H}^{2,6}$). ^{13}C NMR (100 MHz, acetone- d_6): δ 60.1 (OMe), 84.8 ($\text{C}^{3,5}$), 105.4 ($\text{C}^{2,6}$), 108.2 (C^1), 149.2 (C^4), 216.2 ($\text{Mn}(\text{CO})_3^+$). IR (ATR Diamant, cm^{-1}): ν 2021 ($\text{Mn}(\text{CO})_3^+$), 2077 ($\text{Mn}(\text{CO})_3^+$).

$[(\eta^6\text{-Anisole})\text{Mn}(\text{CO})_3][\text{BF}_4]$ (2a**).** Yield: 77%. ^1H NMR (200 MHz, acetone- d_6): δ 4.24 (s, 3H, OMe), 6.36 (t, $^3J = 6.7$ Hz, 1H, H^4), 6.51 (d, $^3J = 6.7$ Hz, 2H, $\text{H}^{2,6}$), 7.22 (t, $^3J = 6.7$ Hz, 2H, $\text{H}^{3,5}$). ^{13}C NMR (100 MHz, acetone- d_6): δ 59.5 (OMe), 84.7 ($\text{C}^{2,6}$), 91.4 (C^4), 107.0 ($\text{C}^{3,5}$), 151.7 (C^1), 217.3 ($\text{Mn}(\text{CO})_3^+$). IR (ATR Diamant, cm^{-1}): ν 2004 ($\text{Mn}(\text{CO})_3^+$), 2071 ($\text{Mn}(\text{CO})_3^+$).

$[(\eta^6\text{-1,3,5-Trimethoxybenzene})\text{Mn}(\text{CO})_3][\text{BF}_4]$ (3a**).** Yield: 70%. ^1H NMR (200 MHz, acetone- d_6): δ 4.25 (s, 9H, OMe), 6.20 (s, 3H, H^2). ^{13}C NMR (100 MHz, acetone- d_6): δ 59.8 (OMe), 66.2 (C^2), 151.6 (C^1), 218.4 ($\text{Mn}(\text{CO})_3^+$). IR (ATR Diamant, cm^{-1}): ν 2013 ($\text{Mn}(\text{CO})_3^+$), 2067 ($\text{Mn}(\text{CO})_3^+$).

Anion Metathesis. Complexes **1b–3b** and **1c–3c** were prepared from **1a–3a** and either NaBPh_4 or NaBArF (NaX) according to the following general procedure. In a 100 mL Erlenmeyer flask equipped with a magnetic stirring bar, the $[(\eta^6\text{-arene})\text{Mn}(\text{CO})_3][\text{BF}_4]$ complex (0.5 mmol) was dissolved in the minimum amount of water (50 mL). A concentrated solution of NaX (1.0 equiv) in methanol (2 mL) was then added. The resulting mixture was stirred for 15 min. The reaction mixture was extracted twice with dichloromethane (30 mL). The combined organic phases were washed with water

(30 mL), dried over magnesium sulfate, and filtered. Evaporation of the solvent under reduced pressure produced the $[(\eta^6\text{-arene})\text{-Mn}(\text{CO})_3][\text{X}]$ complex as a light yellow powder.

$[(\eta^6\text{-1-Chloro-4-methoxybenzene})\text{Mn}(\text{CO})_3][\text{BPh}_4]$ (1b). Yield: 81%. MALDI TOF MS positive mode (m/z): 280.93 $[(\eta^6\text{-1-chloro-4-methoxybenzene})\text{Mn}(\text{CO})_3]^+$. MALDI TOF MS negative mode (m/z): 319.1 (BPh_4^-).

$[(\eta^6\text{-1-Chloro-4-methoxybenzene})\text{Mn}(\text{CO})_3][\text{BArF}]$ (1c). Yield: 78%. MALDI TOF MS positive mode (m/z): 280.9 $[(\eta^6\text{-1-chloro-4-methoxybenzene})\text{Mn}(\text{CO})_3]^+$, 224.9 $[(\eta^6\text{-1-chloro-4-methoxybenzene})\text{Mn}(\text{CO})]^+$. MALDI TOF MS negative mode (m/z): 863.1 (BArF^-).

$[(\eta^6\text{-Anisole})\text{Mn}(\text{CO})_3][\text{BPh}_4]$ (2b). Yield: 86%. MALDI TOF MS positive mode (m/z): 246.99 $[(\eta^6\text{-anisole})\text{Mn}(\text{CO})_3]^+$. MALDI TOF MS negative mode (m/z): 319.2 (BPh_4^-).

$[(\eta^6\text{-Anisole})\text{Mn}(\text{CO})_3][\text{BArF}]$ (2c). Yield: 87%. MALDI TOF MS positive mode (m/z): 246.9 $[(\eta^6\text{-anisole})\text{Mn}(\text{CO})_3]^+$, 191.0 $[(\eta^6\text{-anisole})\text{Mn}(\text{CO})]^+$. MALDI TOF MS negative mode (m/z): 863.1 (BArF^-).

$[(\eta^6\text{-1,3,5-Trimethoxybenzene})\text{Mn}(\text{CO})_3][\text{BPh}_4]$ (3b). Yield: 93%. ^{13}C NMR (100 MHz, acetone- d_6): δ 59.7 (OMe), 66.2 (C^2), 122.9 (C *para*- BPh_4), 137.7 (bs, C *ortho*- BPh_4), 126.7 (C *meta*- BPh_4), 151.3 (C^1), 165.6 (q, $^1J^{\text{CB}} = 49$ Hz, C–B), 218.3 ($\text{Mn}(\text{CO})_3^+$). MALDI TOF MS positive mode (m/z): 307.02 $[(\eta^6\text{-1,3,5-trimethoxybenzene})\text{Mn}(\text{CO})_3]^+$. MALDI TOF MS negative mode (m/z): 319.2 (BPh_4^-).

$[(\eta^6\text{-1,3,5-Trimethoxybenzene})\text{Mn}(\text{CO})_3][\text{BArF}]$ (3c). Yield: 92%. ^{13}C NMR (100 MHz, acetone- d_6): δ 59.9 (OMe), 66.3 (C^2),

119.2 (C *para*- BArF), 126.1 (q, $^1J^{\text{CF}} = 270$ Hz, CF_3), 130.8 (q, $^2J^{\text{CF}} = 31$ Hz, C *meta*- BArF), 136.3 (C *ortho*- BArF), 151.5 (C^1), 163.3 (q, $^1J^{\text{CB}} = 50$ Hz, C–B), 218.4 ($\text{Mn}(\text{CO})_3^+$). MALDI TOF MS positive mode (m/z): 307.01 $[(\eta^6\text{-1,3,5-trimethoxybenzene})\text{Mn}(\text{CO})_3]^+$. MALDI TOF MS negative mode (m/z): 863.3 (BArF^-).

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Supporting Information Available: One X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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