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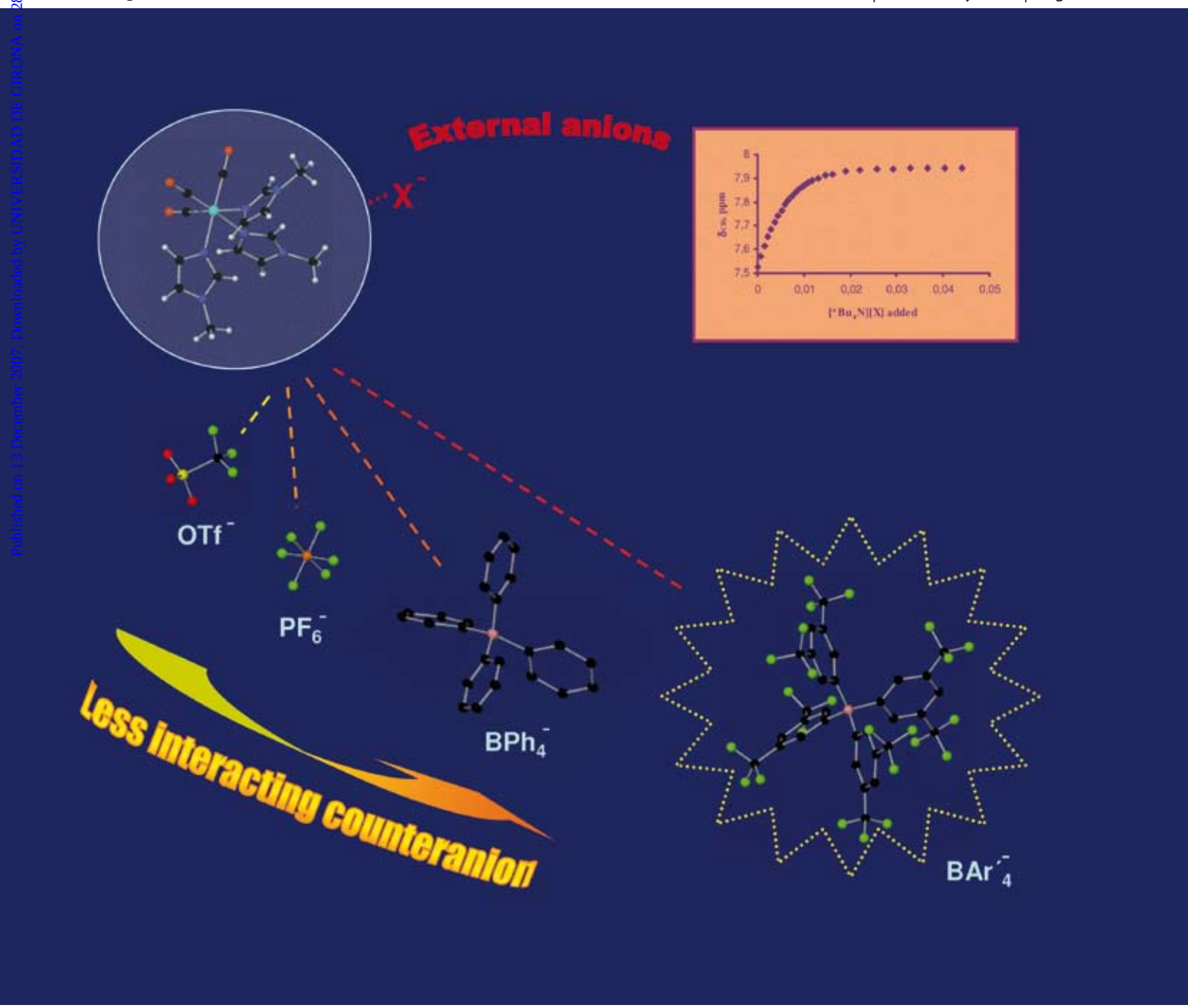

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Second-sphere interaction of anions with a weakly binding metal complex host: probing the effect of counteranions†‡

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The reaction of [Re(OTf)(CO)$_5$] with *N*-methylimidazole (MeIm) afforded [Re(CO)$_3$(MeIm)$_3$]OTf (**1**). The reactions of **1** with KPF$_6$, NaBPh$_4$ and NaBAr′$_4$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl) afforded [Re(CO)$_3$(MeIm)$_3$]PF$_6$ (**2**) [Re(CO)$_3$(MeIm)$_3$]BPh$_4$ (**3**) and [Re(CO)$_3$(MeIm)$_3$]BAr′$_4$ (**4**) respectively. An analogous reaction using *N*-phenylimidazole (PhIm) yielded [Re(CO)$_3$(PhIm)$_3$]BAr′$_4$ (**7**). These new compounds were characterized by IR and NMR, and the structures of **1** and **2** were determined by X-ray diffraction. Compounds [Re(CO)$_3$(MeIm)$_3$]$_2$[PtCl$_6$] (**5**), [Re(CO)$_3$(MeIm)$_3$][HSO$_4$] (**6**), [Re(CO)$_3$(PhIm)$_3$][Br] (**8**) and [Re(CO)$_3$(PhIm)$_3$][NO$_3$] (**9**) were crystallized from equimolar mixtures of either **4** or **7** and the tetrabutylammonium salt of the corresponding anion, and their structures were determined by X-ray diffraction. The solution behavior of **1–4**, **7** toward several anions was studied spectroscopically, including the quantitative determination of binding constants by ^{1}H NMR. The cationic tris(imidazole)complexes are stable against imidazole-by-anion substitution, and the main hydrogen bonding interactions involve the imidazole NC(H)N groups. The binding constants for compounds **1–4** with several external anions follow the order **1** < **2** < **3** < **4**, indicating that the strength of the cationic complex–counteranion interaction follows the order OTf$^-$ > PF$_6^-$ > BPh$_4^-$ > BAr′$_4^-$.

Introduction

Coordination of an *N*-alkylimidazole to a Lewis-acidic metal center could be envisaged as a way to increase the hydrogen-bond donor ability of the imidazole NC(H)N group. The combination of their σ-donor and π-acceptor properties makes imidazoles good ligands for a variety of transition metal centers, including organometallic fragments with the metal in a low oxidation state.[1] Coordination of the parent imidazole (or other N–H containing imidazole derivatives) to metal centers have been found to increase the acidity of the N–H group,[2] but the effect on the C–H group, a weaker hydrogen-bond donor, remains unexplored.

Imidazolium salts are most often prepared by means of the reaction of an *N*-alkylimidazole with a RX (*e.g.*, alkyl bromide or iodide) electrophile. The complex resulting from coordination of a *N*-alkylimidazole to a cationic, Lewis acidic metal center, could be regarded as an analog of an imidazolium cation. The NC(H)N group of imidazolium cations is a relatively strong hydrogen-bond donor. The importance of its interactions with anions within ionic liquids has been noted,[3] and organic molecules containing several imidazolium groups in a mutually convergent disposition have recently emerged as a new type of artificial host for anions.[4]

In addition to acting as a Lewis acid, a transition metal fragment can be used (as an alternative to organic scaffolds) as an element of geometric organization. Thus, the metal coordination of simple ditopic molecules featuring both heteroatoms bearing lone electron pairs (*i.e.*, hydrogen bond acceptors) and hydrogen-bond donor groups (such as N–H groups) have been used for the synthesis of new anion receptors.[5] In this context, we have recently studied the interactions of [Re(CO)$_3$(Hpz)$_3$]BAr′$_4$ compounds (Hpz = generic pyrazole, Ar′ = 3,5-bis(trifluoromethyl)phenyl) with anions.[6] In these species, N-coordination of the pyrazoles to the relatively inert Re center in a metal-enforced mutually *fac* geometry allows the simultaneous interaction of at least two of the N–H groups with external anionic guests (Chart 1a,) and, therefore, a significant overall interaction.

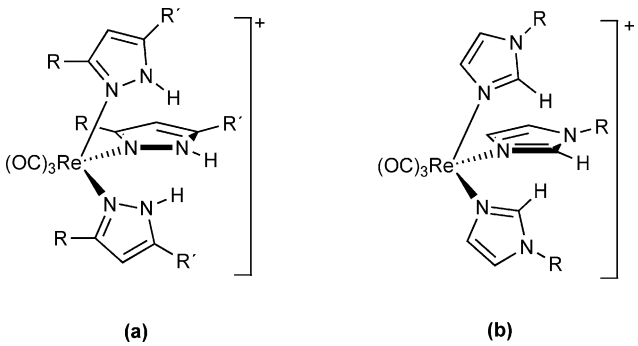

Chart 1 (a) Geometry of our recently reported tris(pyrazole) complexes,[6] and (b) the tris(*N*-alkylimidazole) complexes reported in this work.

A drawback of cationic receptors of anions is that the accompanying counteranion competes with the external anionic guest for

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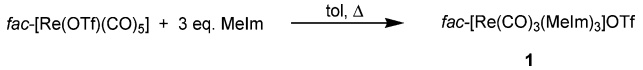
the receptor.[5c] We have proposed that the employment of the highly charge-delocalized $BAr'_4{}^-$ tetraarylborate anion should minimize such interference.[6] Whereas $BAr'_4{}^-$ has become quite popular in organometallic chemistry and catalysis as an alternative to less innocent counteranions such as perchlorate, triflate, tetrafluoroborate, hexafluorophosphate, tetraphenylborate, *etc.*,[7] our recent work is the first example of its use as counteranion of cationic anion hosts. Intrinsically weak host–guest interactions, such as those expected to occur between the C–H groups of imidazole ligands and external anions, appear as a good benchmark test for the magnitude of the effect of having a less coordinating counteranion. N-coordination of three *N*-alkylimidazoles to the *fac*-{$Re(CO)_3$} fragment could afford a geometry similar to that of the above mentioned tris(pyrazole) complexes,[6] the C–H groups being now the ones able to simultaneously interact with external anions (Chart 1b). Therefore, we sought to prepare cationic rhenium tricarbonyl tris(*N*-alkylimidazole) complexes with several different low-interacting counteranions, including $BAr'_4{}^-$, and compare the magnitudes of their interaction with external anions. Our results are discussed below.

Results and discussion

The reaction of $[Re(OTf)(CO)_5]$ with a three-fold molar amount of *N*-methylimidazole (MeIm) in refluxing toluene afforded $[Re(CO)_3(MeIm)_3]OTf$ (**1**) in high yield (Scheme 1). We have previously found that the similar reaction using pyrazoles (Hpz) affords a mixture of products, presumably the compounds $[Re(CO)_3(Hpz)_3]OTf$ and $[Re(OTf)(CO)_3(Hpz)_2]$.[6a] In contrast, **1** was obtained as the single product of the above mentioned reaction, the difference reflecting the fact that imidazoles are better ligands than pyrazoles.[1] Compound **1** was characterized by IR, NMR (^1H and ^{13}C) and single-crystal X-ray diffraction (see Fig. 1).



Scheme 1 Synthesis of compound **1**.

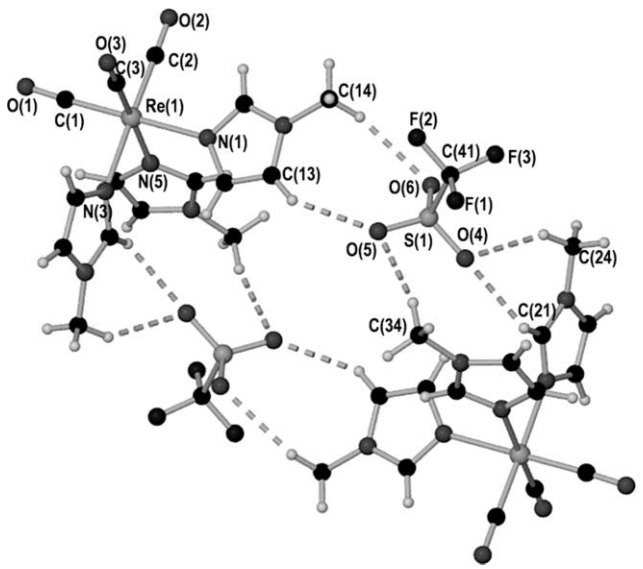


Fig. 1 Structure of **1** showing the main hydrogen bonds as dotted lines.

The IR ν_{CO} bands of **1**, indicative of a *fac*-$Re(CO)_3$ geometry, occur at wavenumber values (2025 and 1907 cm^{-1} in CH_2Cl_2) significantly lower than those of the structurally related tris(pyrazole) compounds (2039 and 1929 cm^{-1} for $[Re(CO)_3(Hdmpz)_3]BAr'_4$ (Hdmpz = 3,5-dimethylpyrazole) and 2038 and 1933 cm^{-1} for $[Re(CO)_3(H'Bupz)_3]BAr'_4$ (H'Bupz = 3(5)-*tert*-butylpyrazole) in CH_2Cl_2).[6] The difference reflects that *N*-methylimidazole is a ligand more electron-releasing than Hdmpz or H'Bupz.

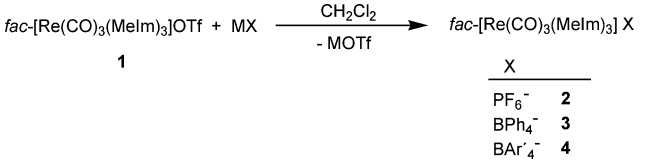
The structure of the cationic tris(imidazole) complex in **1** consists of a rhenium atom coordinated to three carbonyl ligands in a mutually facial disposition, in agreement with the solution data, and to the non-substituted nitrogen atoms of three molecules of *N*-methylimidazole. Despite the difference in the donor character of the heterocyclic ligands inferred from the differences in the IR spectra (see above), the Re–N and Re–C distances and the angles about Re in **1** (see Table 1) are closely similar to those found in the tris(pyrazole) complexes mentioned above.[6]

The crystalline structure of **1** features a network of weak hydrogen bonds between the C–H groups of the cationic tris(*N*-methylimidazole) complex and the oxygen atoms of the triflate anion. The stronger (but still very weak; note the angle, far from linear) among these hydrogen bonds are those involving the imidazole NC(H)N group ($C(21)\cdots O(4)$ = 3.24 Å and $C(21)\cdots H\cdots O(4)$ = 134°). Only one NC(H)N group of each cationic complex interacts with each triflate anion. At least in the solid state, thus, there is no convergence of several NC(H)N hydrogen-bond donor groups from a single rhenium complex toward a given anion. This is in contrast to the related tris(pyrazole) complexes, in which the N–H groups of two pyrazole ligands of each complex converge toward one oxygen atom of even weak hydrogen-bond acceptors such as acetone or the perchlorate anion.[6] The difference can be attributed to the weaker hydrogen bond donor ability of the imidazole C–H bonds compared with the pyrazole N–H bonds.

Thus, at least in the solid state, where the distance between ions is small, the multitude of other non-covalent interactions at play overcomes the formation of two or three hydrogen bonds between one given anion and the NC(H)N groups of one given cationic complex. For instance, in the structure of **1**, weak hydrogen bonds occur between the triflate oxygens and the other C–H groups, including those of the methyl groups, as displayed in Fig. 1.

Rhenium(I) tris(*N*-alkylimidazole) compounds were previously unknown; however, analogs containing the parent imidazole were reported by Alberto *et al.*[8]

Compounds $[Re(CO)_3(MeIm)_3]PF_6$ (**2**), $[Re(CO)_3(MeIm)_3]BPh_4$ (**3**) and $[Re(CO)_3(MeIm)_3]BAr'_4$ (**4**) were cleanly obtained by the anion exchange reactions of **1** with the salts KPF_6, $NaBPh_4$ and $NaBAr'_4$ respectively in CH_2Cl_2 (see Scheme 2).



Scheme 2 Synthesis of compounds **2–4**.

Compounds **2–4** were spectroscopically characterized (see Experimental); in addition, the structure of **2** was determined by

Table 1 Selected bond distances (Å) and angles (°) for compound $[Re(CO)_3(MeIm)_3]OTf$ (**1**) and the tris(pyrazole) complexes $[Re(CO)_3(Hpz)_3]BAr'_4$ (Hpz = Hdmpz, H′Bupz)

	Bond Distances/Å		
	1	$[Re(CO)_3(Hdmpz)_3]^+$	$[Re(CO)_3(H'Bupz)_3]^+$
Re(1)–N(1)	2.202(2)	2.204(6)	2.191(4)
Re(1)–N(3)	2.204(2)	2.186(8)	2.187(4)
Re(1)–N(5)	2.182(2)	2.195(7)	2.193(4)
Re(1)–C(1)	1.914(3)	1.938(11)	1.936(6)
Re(1)–C(2)	1.906(3)	1.946(11)	1.918(6)
Re(1)–C(3)	1.912(3)	1.926(11)	1.910(7)
	Bond Angles/°		
C(1)–Re(1)–C(2)	87.01(13)	85.8(5)	89.0(2)
C(2)–Re(1)–N(1)	93.14(11)	91.2(3)	92.0(2)
N(1)–Re(1)–N(3)	86.63(9)	87.2(2)	85.75(16)
C(1)–Re(1)–N(3)	93.24(11)	95.9(4)	93.19(19)
C(3)–Re(1)–N(5)	174.61(10)	176.4(4)	176.3(2)
C(1)–Re(1)–C(3)	89.26(12)	86.4(4)	87.8(2)
C(1)–Re(1)–N(5)	93.80(11)	92.6(3)	94.8(2)
N(1)–Re(1)–C(3)	90.30(10)	97.0(3)	93.8(2)
N(1)–Re(1)–N(5)	86.63(9)	84.1(2)	83.47(16)

X-ray diffraction (Fig. 2). Because the only difference within the **1–4** family of compounds is the counteranion, and the four complexes feature low interacting counteranions, the IR and NMR spectroscopic data of the cationic complexes are very similar in **1–4**.

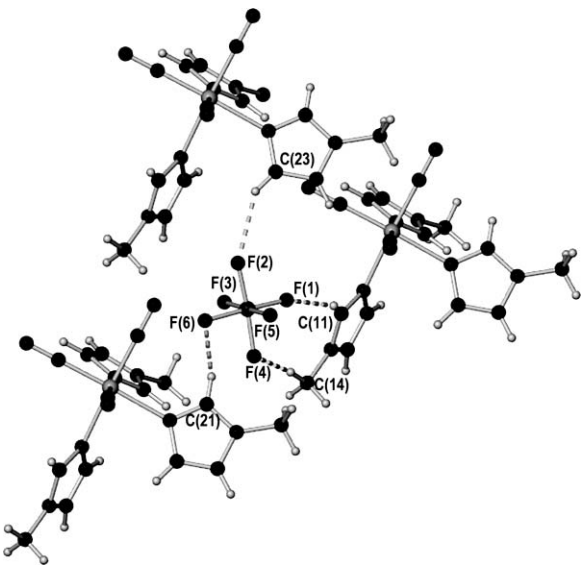


Fig. 2 Structure of compound **2** showing the main hydrogen bond interactions.

The structure of **2** consists of a cation virtually identical to the one described for **1**, with weak hydrogen bonds to PF_6^-. The shorter of these hydrogen bonds involves the NC(H)N group of a ligated imidazole, with C(11)···F(1) = 3.32 Å and C(11)···H···F(1) = 155° (Fig. 2). As in the structure of **1**, only one of the *N*-methylimidazole ligands of each complex interacts with a given hexafluorophosphate anion, and the other C–H bonds of the imidazole ligands are involved in weaker hydrogen bonds.

In principle, one could imagine that the C_3 symmetry of the tris(*N*-methylimidazole) complexes could allow them to interact in a three-point fashion with a C_3-symmetric anion such as a triflate or with an O_h-symmetric anion such as hexafluorophosphate (Chart 2).

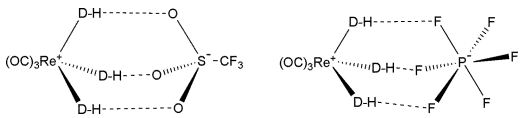


Chart 2 Possible three-point contact structures in **1** and **2**.

The fact that this interaction is not found in the solid state could be attributed to the low hydrogen-bond acceptor capability of these anions. However, neither the octahedral, dianionic complex $PtCl_6^{2-}$ in compound $[Re(CO)_3(MeIm)_3]_2[PtCl_6]$ (**5**), presumably a much better hydrogen-bond acceptor (besides being dianionic, metal–chloride bonds have been found to be good hydrogen-bond acceptors),[9] nor the hydrogensulfate anion in $[Re(CO)_3(MeIm)_3][HSO_4]$ (**6**) (see Experimental for the synthesis and characterization, and Fig. 3 and 4 for plots of the structures) were found to establish three-point hydrogen bond connections with the $[Re(CO)_3(MeIm)_3]^+$ cation.

In **5**, the hydrogen bond between the NC(H)N group of one of the imidazole ligands and one of the chlorides is characterized by C(11)···Cl(1) = 3.76 Å and C(11)···H···Cl(1) = 148°. Again, only one of such interactions exists within a given ion pair. Hydrogen bonds involving the other types of C–H groups have shorter distances and similar angles in this structure; thus C(24)···Cl(3) = 3.55 Å and C(24)···H···Cl(3) = 141° for a hydrogen bond involving a methyl C–H group, and C(33)···Cl(1) = 3.69 Å and C(33)···H···Cl(1) = 151° (not shown in Fig. 3) for one of the other C–H bonds of the imidazole ring. However, this feature of the solid state structure does not extend to the solution phase. Rather, as it will be discussed below, the NC(H)N group is by large the C–H group that more significantly takes part in the formation in hydrogen bonds in solution.

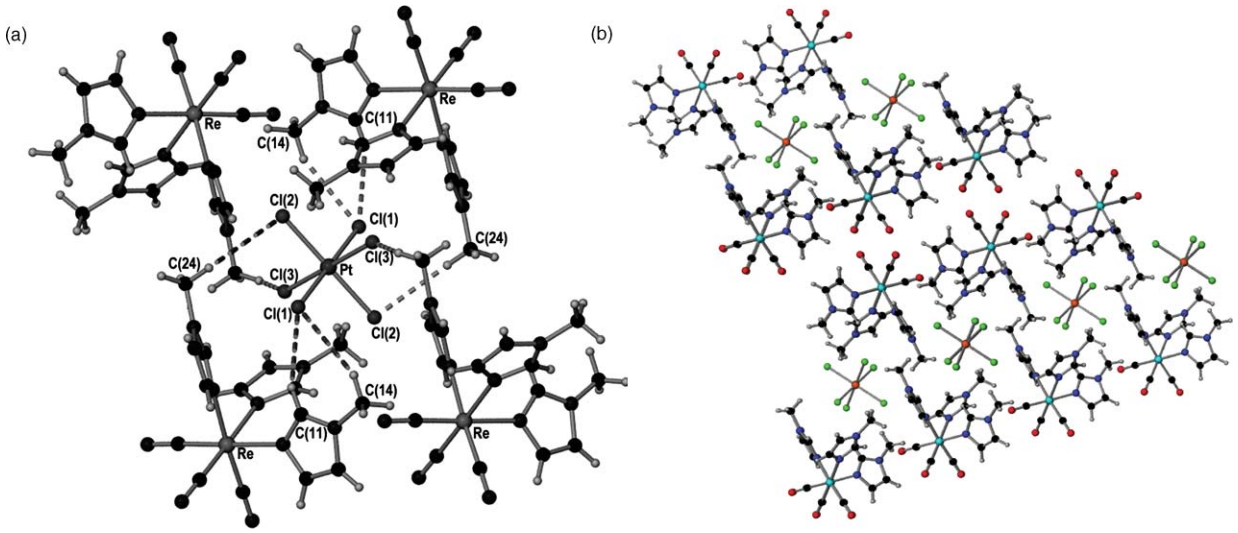


Fig. 3 (a) Molecular structure of $[Re(CO)_3(MeIm)_3]_2[PtCl_6]$ (**5**) adduct. (b) View of the ribbons (see text) in the structure of **5**.

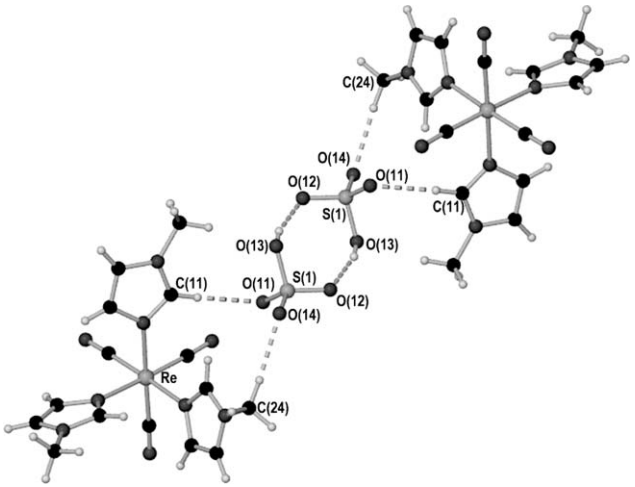


Fig. 4 View of the molecular structure of a $\{[Re(CO)_3(MeIm)_3][HSO_4]\}_2$ pair in **6**.

The view in Fig. 3b shows that the solid state structure of **5** can be described as neutral ribbons each consisting of a row of hexachloroplatinate dianions sandwiched between two rows of cationic rhenium complexes. Within each ribbon, the rhenium complexes orient their hydrogen-bond donor $Re(MeIm)_3$ side toward the inner row of anions, whereas their outward $Re(CO)_3$ sides face the $Re(CO)_3$ periphery of another ribbon. Within each ribbon, the main interactions are charge-assisted C–H···Cl–Pt hydrogen bonds, whereas the ribbons are linked mainly by van der Waals forces. Obviously, this is only an approximation, as some C···H···OC–Re interactions exist between ribbons.

In the structure of **6** (Fig. 4a), the hydrogensulfate anions are paired *via* self-complementary hydrogen bonds forming pseudo-chair-like rings. Both "free" oxygens of each sulfate unit form a hydrogen bond, one with the NC(H)N group of an imidazole ligand (C(11)···O(11) = 3.12 Å and C(11)···H···O(11) = 134°) and the other with a CH_3 group of a different imidazole ligand of the same rhenium complex (C(24)···O(14) = 3.29 Å and C(24)···H···O(14) = 175°). Like in the structure of the hexachloroplatinate adduct **5**, the (dianionic) hydrogensulfate dimers in **6** occupy the space in between rows of cationic complexes (with which they interact through charge-assisted C···H···O hydrogen bonds), and the latter present their $Re(CO)_3$ faces to each other. In **6**, in between these Re-dianion–Re ribbons, "hydrophobic" voids are occupied by molecules of dichloromethane (see ESI‡).

Attempts to crystallize adducts of the $[Re(CO)_3(MeIm)_3]^+$ cation with other anions were unsuccessful. Better crystallinity was found for the adducts obtained *via* anion exchange from the tris(*N*-phenylimidazole) compound $[Re(CO)_3(PhIm)_3]BAr'_4$ (**7**), synthesized in a manner analogous to that described above for **4**. Thus, single crystals of $[Re(CO)_3(PhIm)_3][Br]$ (**8**) and $[Re(CO)_3(PhIm)_3][NO_3]$ (**9**), grown by slow diffusion of hexane into concentrate dichloromethane solutions of the equimolar mixtures of **7** and either $[Bu_4N][Br]$ or $[Bu_4N][NO_3]$ at room temperature, were employed to determine the crystalline structures of these two compounds by X-ray diffraction. The results, displayed in Fig. 5a showed the presence of $[Re(CO)_3(PhIm)_3]^+$ cations with a rhenium first coordination sphere like the one described above for the *N*-methylimidazole derivatives, involved in a complex network of hydrogen bonds to the anions. In addition to the imidazole NC(H)N group, the phenyl substituents were found to act as additional sources of hydrogen-bond donor groups. Thus, as depicted in Fig. 5a, the stronger hydrogen bonds to a given bromide in **8** are those to the NC(H)N groups of two of the imidazole ligands of a cationic complex (C(11)···Br = 3.66 Å, C(11)···H···Br = 167°), but there are also two hydrogen bonds to the C–H groups of the *ortho* carbons of the phenyl substituents on these same imidazoles (C(19)···Br = 3.66 Å, C(19)···H···Br = 139°). This bromide forms two weaker hydrogen bonds to the NC(H)N (C(21)···Br = 3.90 Å, C(21)···H···Br = 179°) and *ortho* CH phenyl (C(25)···Br = 3.94 Å, C(25)···H···Br = 174°) groups of the "third" imidazole ligand of a neighbor cationic complex. When viewed along the plane of that "third" phenylimidazole, the structure consists of chains in which anion and cation occupy alternating positions, and adjacent chains run in an anti-parallel fashion (see ESI‡). Fig. 5b shows that each of the two imidazoles

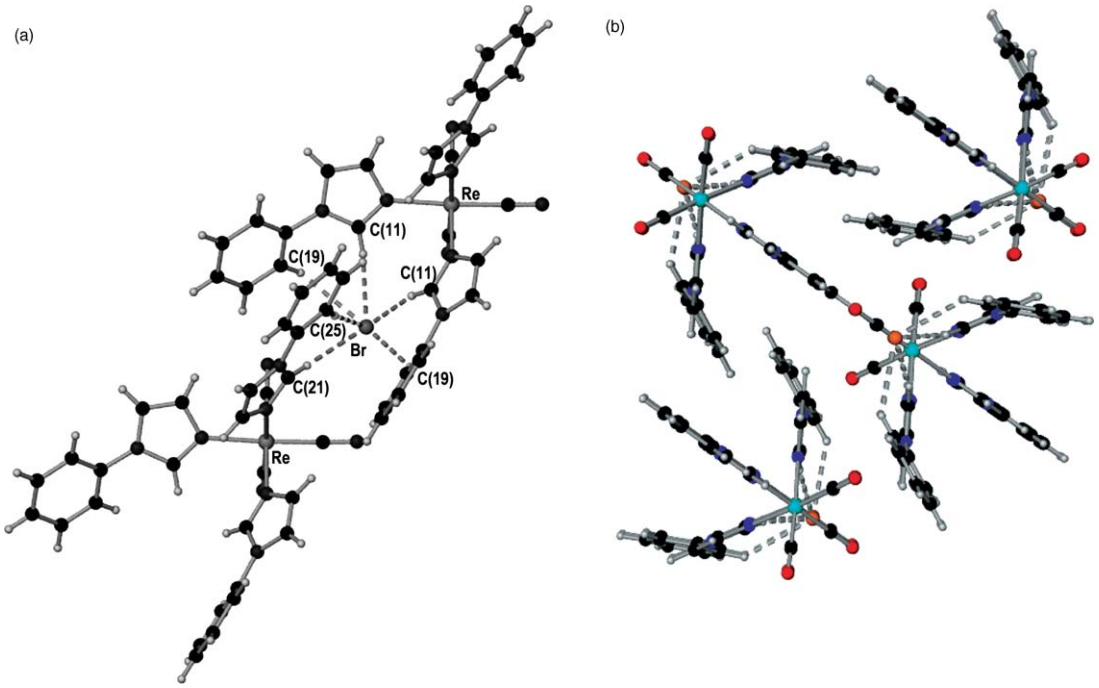


Fig. 5 (a) Molecular structure of $[Re(CO)_3(PhIm)_3][Br]$ (**8**). (b) View of the inter-chain ring stacking present in the molecular structure of **8**.

of a given complex that converge toward a bromide anion inserts parallel to two consecutive imidazoles of the same type of an adjacent, anti-parallel chain, suggesting some degree of inter-chain π-stacking.

The structure of the nitrate adduct **9** is considerably more complex than the ones previously discussed, with an asymmetric unit containing two non-equivalent cationic complexes and two non-equivalent nitrate anions. In contrast with the structure of **8**, now the phenyl and imidazole rings within each phenylimidazole ligand are not coplanar. The main hydrogen bonds occur between nitrate oxygens and NC(H)N and *ortho* CH phenyl groups. As depicted in Fig. 6, each nitrate anion (only one of the two non-equivalent nitrate anions is displayed, but the environment of the other is qualitatively similar) interacts mainly with four CH groups of three cationic complexes.

The cationic tricarbonyltris(imidazole) complexes in **1–4**, **7** were found to be stable (*i.e.*, not to undergo substitution or deprotonation) toward the anions fluoride, chloride, bromide, iodide, nitrate, hydrogensulfate, dihydrogenphosphate and acetate both in dichloromethane and in acetonitrile. ^{1}H NMR studies of the interaction of compounds **1–4**, **7** with the tetrabutylammonium salts of the anions mentioned above showed that the signals of the complex that undergo larger shifts upon anion addition are those due to the NC(H)N groups of the ligated imidazoles. When CD_3CN was used as solvent, this anion-induced change in chemical shift was much smaller than the one found when tris(pyrazole) compounds $[Re(CO)_3(Hpz)_3]BAr'_4$ were used as hosts in the same solvent.[6] For some anions, such as chloride, nitrate or hydrogensulfate the magnitude of this change in chemical shift in CD_3CN solution was sufficient to allow the construction of Job plots, that showed the formation of 1 : 1 adducts between the anions and the cationic rhenium complex. Binding constants were calculated for **3** (see ESI‡) by ^{1}H NMR titrations (fast

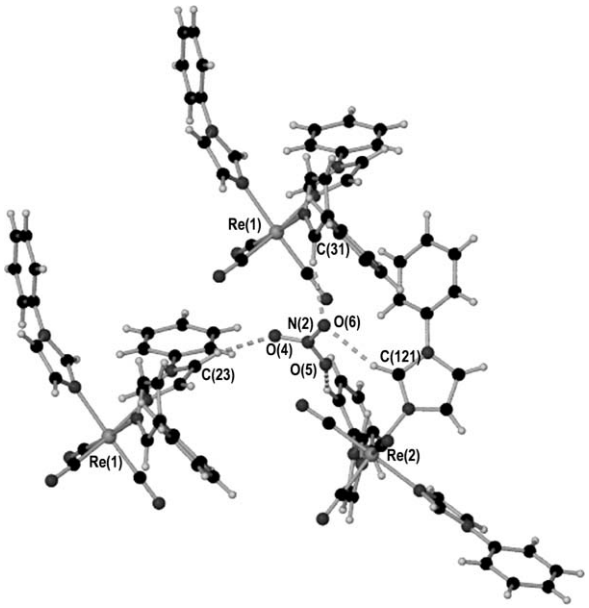


Fig. 6 Molecular structure of one of the two non-equivalent $[Re(CO)_3(PhIm)_3][NO_3]$ pair present in the structure of **9**.

anion exchange was found).[10] Again, the values of these constants were much smaller than those found for the tris(pyrazole) hosts mentioned above,[6] indicating that the interaction between the tris(imidazole) complexes and the anions is much weaker, as expected because, in general, CH groups are weaker hydrogen bond donors than N–H groups. The weakness of these interactions in solution agrees with the presence of only weak hydrogen bonds in the crystalline structures discussed above. In this regard, we note that on the tris(imidazole) complexes reported here, C–H groups

are the only hydrogen bond donors (*i.e.*, they are not assisted by simultaneous formation of stronger (*e.g.*, those involving N–H or O–H groups) hydrogen bonds. Moreover, unlike in purely organic tris(imidazolium) receptors, the complexes reported here carry a single positive charge.

To amplify the magnitude of the binding constants and compare their values for the hosts having different counteranions, the ^{1}H NMR titration experiments of **1–4**, **7** with tetrabutylammonium salts were carried out in CD_2Cl_2, a less competitive solvent. In this solvent, the anion-induced shift is also much higher for the imidazole NC(H)N groups (several tenths of ppm); albeit detectable, shifts in the CH_3 (in **1–4**) or *o*-C_6H_5 (in **7**) groups are generally an order of magnitude lower. In contrast with the deprotonation of the $[Re(CO)_3(Hpz)_3]BAr'_4$ compounds effected by fluoride,[6] and with the vanishing of the N–H signals observed upon fluoride addition to many anion receptors containing N–H groups, the signals of the C–H groups of hosts **1–4**, **7** remained sharp when these complexes were titrated with $[Bu_4N][F]$. Again fast exchange was found in every instance, Job plots indicated the presence of 1 : 1 adducts, and binding constants in CD_2Cl_2 for the anions listed above were obtained for **1–4**, **7** using ^{1}H NMR titrations (Job plots and titration curves are given as ESI‡). The results are shown in Table 2. For comparison, binding constants were also obtained for the tris(*N*-phenylimidazole) compound **7**.

First, the comparison between $[Re(CO)_3(MeIm)_3]BAr'_4$ (**4**) and $[Re(CO)_3(PhIm)_3]BAr'_4$ (**7**) shows that the interactions of the latter with anions in solution are weaker, in spite of the involvement of some of the phenyl C–H groups in hydrogen bonding. Interestingly, the IR ν_{CO} bands of **7** (2032 and 1917 cm^{-1}) occur at wavenumber values slightly higher than those of **4** (2029 and 1912 cm^{-1}), so the phenyl substituents act as electron withdrawing groups compared with the methyl groups. That should make the C–H groups of **7** better hydrogen-bond donors. Therefore, given that this is not what is actually observed, the predominant effect of the phenyl substituents on **7** must be to sterically hinder the approach of anions.

Second, a comparison of compounds **1–4** indicates that the magnitude of the interaction of the cationic complex with external anions varies in the order of **1** < **2** < **3** < **4**. In as much as the only difference between these compounds is the counteranion, the strength of the cationic complex–counteranion interaction must follow the opposite order, *i.e.*, $OTf^- > PF_6^- > BPh_4^- > BAr'_4{}^-$. Triflate, and specially hexafluorophosphate, are often used as counteranions of cationic receptors of anions. In part, this is due to the fact that their silver salts are commercially available, providing an easy route to anion exchange driven by precipitation of insoluble silver halides. Tetraphenylborate interacts with the cationic complexes less than triflate or hexafluorophosphate. However, the interactions between hydrogen-bond donor groups and the π electron density of the BPh_4^- rings are well known. For instance, Kiviniemi *et al.* have studied the behavior of BPh_4^- toward azolium cations.[11] Finally, the strongly electron-withdrawing effect of the trifluoromethyl groups on the aryl rings of the $BAr'_4{}^-$ counteranion make it the more innocent; *i.e.*, the one that interacts less with the cationic complexes. The magnitude of the effect revealed by Table 2 is small, so that when strong interactions between a cationic receptor and an anionic guest are at play, having $BAr'_4{}^-$ as counteranion instead of, for instance, PF_6^-, does not offer a significant advantage in the sense of affording higher binding constants. This being true, it should be kept in mind that the $BAr'_4{}^-$ salts are endowed with other often desirable properties: (a) $BAr'_4{}^-$ salts are much more soluble in organic solvents, the difference becoming particularly important in those of moderate polarity (*e.g.* CH_2Cl_2), and (b) $BAr'_4{}^-$ does not undergo hydrolysis (it even resists sulfuric acid!),[12] in contrast with the documented hydrolysis of PF_6^- to difluorophosphate in the presence of, for instance, electrophilic metal centers,[5c,13] or with the relatively easy cleavage of the B–C bonds of BPh_4^- in the presence of strong acids or electrophiles.[7a] More generally, our results suggest that, in those instances in which host–guest interactions are intrinsically weak (such as hydrogen bonds or other non-covalent interactions between a catalyst and its substrate), the $BAr'_4{}^-$ anion, already widely used in other fields of chemistry, can be a better choice than other more conventional counteranions.

Conclusions

A comparative study of the behavior of $[Re(CO)_3(MeIm)_3]OTf$ (**1**), $[Re(CO)_3(MeIm)_3]PF_6$ (**2**) $[Re(CO)_3(MeIm)_3]BPh_4$ (**3**) and $[Re(CO)_3(MeIm)_3]BAr'_4$ (**4**) toward several anions showed that the cationic tris(imidazole) rhenium complex forms 1 : 1 adducts with the anions, that the main hydrogen bond interactions within these adducts are those between the anion and the imidazole NC(H)N groups, and that the tetraarylborate $BAr'_4{}^-$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl) is the anion that interacts less with the cationic complex, thus leading to larger complex–anion binding constants. These results suggest that $BAr'_4{}^-$, so far used in organometallic chemistry and catalysis, but not in supramolecular chemistry, would be advantageous over more conventional counteranions for cationic supramolecular receptors, and that, in general, its use would enhance hydrogen bonding between polar substrates and cationic complexes.

Table 2 Binding constant values for compounds **1–4**, **7** in CD_2Cl_2

Anion	**1**, K_a/M^{-1}	**2**, K_a/M^{-1}	**3**, K_a/M^{-1}	**4**, K_a/M^{-1}	**7**, K_a/M^{-1}
F^-	81 ± 8	107 ± 2	400 ± 7	1002 ± 112	830 ± 152
Cl^-	77 ± 9	100 ± 2	176 ± 16	291 ± 19	144 ± 14
Br^-	79 ± 1	62 ± 5	174 ± 1	261 ± 18	101 ± 5
I^-	60 ± 1	57 ± 5	151 ± 1	292 ± 20	78 ± 6
NO_3^-	38 ± 1	38 ± 3	132 ± 11	234 ± 16	168 ± 21
HSO_4^-	61 ± 3	78 ± 2	373 ± 43	[a]	78 ± 7
$COOCH_3^-$	65 ± 6	105 ± 16	243 ± 4	290 ± 19	200 ± 18

[a] ^{1}H NMR signals of interest were obscured by those of the $BAr'_4{}^-$ anion, precluding calculation of binding constants.

Experimental

General

All manipulations were carried out under a nitrogen atmosphere using Schlenk techniques. Compound $[Re(OTf)(CO)_5]$[14] was prepared as previously reported. Tetrabutylammonium salts were purchased from Fluka or Aldrich. Deuterated acetonitrile and dichloromethane (Cambridge Isotope Laboratories, Inc.) were stored under nitrogen in Young tubes and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300, DPX-300 or Avance 400 spectrometer. NMR spectra are referred to the internal residual solvent peak for ^{1}H and $^{13}C\{^1H\}$ NMR. IR solution spectra were obtained in a Perkin-Elmer FT 1720-X spectrometer using 0.2 mm CaF_2 cells. NMR samples were prepared under nitrogen using Kontes manifolds purchased from Aldrich. Oven-dried 5 mm NMR tubes were subjected to several vacuum-nitrogen cycles, filled with the solution of the receptor (prepared separately in a Schlenk tube, typically in a 10^{-2} M concentration in CD_2Cl_2) by means of a 1 mL syringe, and stoppered with rubber septa. After the NMR spectrum of the receptor was recorded, the successive aliquots of the tetrabutylammonium salt (typically 4×10^{-2} M in CD_2Cl_2, separately prepared and kept in a septum-stoppered vial during the titration) were injected through the septum using Hamilton microsyringes (10–100 μL). The volume of each addition was 10 μL before reaching the saturation zone (nearly horizontal line of the titration profile), and 20 or 40 μL afterwards. When the change in δ is small, 20 μL of salt solution were added from the beginning. Data were treated using the WinEQNMR program.[10]

Crystal structure determination. General description

For compounds 5 and 6. Data collection was performed at 150(2) K on a Nonius KappaCCD single crystal diffractometer, using Cu-Kα radiation ($\lambda = 1.5418$ Å). Images were collected up to $2\theta = 140°$ at a 29 mm fixed crystal-detector distance, using the oscillation method. Data collection strategy was calculated with the program Collect.[15] Data reduction and cell refinement were performed with the program HKL Denzo and Scalepack.[16] A semi-empirical absorption correction was applied using the program SORTAV.[17]

For compound 2. A crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite monochromatized Mo-Kα X-radiation and a CCD area detector. A hemisphere of the reciprocal space was collected up to $2\theta = 48.6°$. Raw frame data were integrated with the SAINT[18] program. An empirical absorption correction was applied with the program SADABS.[19]

For compounds 1, 8 and 9. A single crystal was mounted on a Bruker diffractometer equipped with a SMART 1 K CCD area detector and Oxford Cryostream N_2 cooling device, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). .

Structure solution and refinement (all). The structures were solved by direct methods with SHELXTL.[20] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. Calculations were made with SHELXTL and PARST.[21] Crystal and refinement details are collected in Table 3

Synthesis of $[Re(CO)_3(MeIm)_3]OTf$ (1)

A mixture of $[Re(OTf)(CO)_5]$ (0.200 g, 0.420 mmol) and MeIm (0.100 mL, 1.260 mmol) in toluene (25 mL) was refluxed for 3 h. The resulting solution was slowly cooled to room temperature affording colorless crystals of **1**, one of which was employed for an X-ray structure determination. Yield: 0.261 g, 93%; IR (CH_2Cl_2, cm^{-1}): 2025, 1907 (ν_{CO}); ^{1}H NMR (CD_2Cl_2): $\delta = 7.54$ (s, 3H, C*H* MeIm), 7.05 (s, 3H, C*H* MeIm), 7.02 (s, 3H, C*H* MeIm), 3.79 (s, 9H, CH_3 MeIm). ^{13}C NMR (CD_2Cl_2): $\delta = 195.5$ (CO), 141.0, 131.4, 122.5 (*C*H MeIm), 34.7 (*C*H$_3$ MeIm); ^{19}F NMR (CD_2Cl_2): $\delta = -79.0$; elemental analysis calcd (%) for $C_{16}H_{18}F_3N_6O_6ReS$: C 28.87, H 2.73, N 12.63; found: C 28.85, H 2.63, N 12.51.

Synthesis of $[Re(CO)_3(MeIm)_3]PF_6$ (2)

To a solution of $[Re(CO)_3(MeIm)_3]OTf$ (**1**) (0.100 g, 0.150 mmol) in CH_2Cl_2 (20 mL) and MeCN (2 mL), KPF_6 (0.028 g, 0.150 mmol) was added and the mixture was stirred at room temperature for 3 h. The resulting solution was filtered *via* canula and concentrated under reduced pressure to a volume of 10 mL. Addition of hexane (30 mL) caused the precipitation of a white solid which was washed with hexane (2×20 mL). Yield: 0.080 g, 87%; IR (CH_2Cl_2, cm^{-1}): 2025, 1908 (ν_{CO}); ^{1}H NMR (CD_2Cl_2): $\delta = 7.48$ (s, 3H, C*H* MeIm), 7.06 (s, 3H, C*H* MeIm), 7.10 (s, 3H, C*H* MeIm), 3.78 (s, 9H, CH_3 MeIm). ^{13}C NMR (CD_2Cl_2): $\delta = 195.5$ [CO], 140.9, 131.4, 122.6 [*C*H MeIm], 34.6 [*C*H$_3$ MeIm]; ^{31}P NMR (CD_2Cl_2): −144.6 [sep ($^1J_{PF} = 711.7$ Hz) *P*F$_6$]; ^{19}F NMR (CD_2Cl_2): −73.13 [d ($^1J_{PF} = 711.7$ Hz), P*F*$_6$]; elemental analysis calcd (%) for $C_{15}H_{18}F_6N_6O_3PRe$: C 27.24, H 2.74, N 12.70; found: C 27.55, H 2.52, N 12.65. Slow diffusion of hexane into a concentrated solution in CH_2Cl_2 at room temperature afforded colorless crystals of compound **2**, one of which was employed for an X-ray analysis.

Synthesis of $[Re(CO)_3(MeIm)_3]BPh_4$ (3)

To a solution of $[Re(CO)_3(MeIm)_3]OTf$ (**1**) (0.200 g, 0.301 mmol) in CH_2Cl_2 (20 mL), $NaBPh_4$ (0.103 g, 0.301 mmol) was added and the mixture was stirred at room temperature for 1 h. The resulting solution was filtered off the white solid (NaOTf) *via* canula and concentrated under reduced pressure to a volume of 5 mL. Addition of hexane caused the precipitation of a white solid which was washed with hexane (2×20 mL). Yield: 0.240 g, 96%; IR (CH_2Cl_2, cm^{-1}): 2027, 1911 (ν_{CO}); ^{1}H NMR (CD_2Cl_2): $\delta = 7.36$ (m, 11H, C*H* MeIm and BPh_4), 7.02 (m, 8H, BPh_4), 6.90 (m, 4H, BPh_4), 6.80 (s, 3H, C*H* MeIm),6.72 (s, 3H, C*H* MeIm), 3.41 (s, 9H, CH_3 MeIm). ^{13}C NMR (CD_2Cl_2): $\delta = 195.0$ (CO), 164.1 [q ($^1J_{CB} = 49.4$ Hz), C^i BPh_4], 140.7, [*C*H MeIm], 135.9 [C^o BPh_4], 130.2 [*C*H MeIm], 125.7 [C^m BPh_4], 122.8 [*C*H MeIm], 121.8 [C^p BPh_4], 34.5 [*C*H$_3$ MeIm]; elemental analysis calcd (%) for $C_{39}H_{38}BN_6O_3Re$: C 56.05, H 4.58, N 10.06; found: C 55.80, H 4.49, N 9.72.

Synthesis of $[Re(CO)_3(MeIm)_3]BAr'_4$ (4)

Compound **4** was prepared as described above for compound **3** from $[Re(CO)_3(MeIm)_3]OTf$ (**1**) (0.070 g, 0.105 mmol) and

Table 3 Crystal data and refinement details for compounds **1**, **2**, **5**, **6**, **8** and **9**

	1	**2**	**5**	**6**	**8**	**9**
Formula	$C_{16}H_{18}F_3N_6O_6ReS$	$C_{15}H_{18}F_6N_6O_3PRe$	$C_{30}H_{36}Cl_6N_{12}O_6PtRe_2{\cdot}2CH_2Cl_2$	$C_{16}H_{21}Cl_2N_6O_7ReS$	$C_{30}H_{24}BrN_6O_3Re$	$C_{30}H_{24}N_7O_6Re$
M_r	665.62	661.52	1610.75	698.55	782.66	764.76
Cryst. system	Triclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	*P*-1	$P2_1$	$P2_1/c$	*P*-1	*Pnma*	$P2_1$
a/Å	7.0294(8)	8.336(5)	18.384(4)	7.1111(14)	19.1346(17)	10.5765(14)
b/Å	12.1099(14)	13.146(8)	9.2341(18)	10.866(2)	14.3590(13)	24.603(3)
c/Å	13.4786(16)	10.254(6)	15.713(3)	16.743(3)	10.2350(9)	11.3361(14)
α/°	95.450(2)	90	90	97.15(3)	90	90
β/°	98.829(2)	96.923(11)	111.20(3)	96.72(3)	90	90.570(3)
γ/°	90.805(2)	90	90	107.55(3)	90	90
V/Å^3	1128(2)	1115.6(12)	2486.9(9)	1207.5(4)	2812.1(4)	2949.6(6)
Z	2	2	2	2	4	4
T_c/K	120(2)	293(2)	120(2)	293(2)	120(2)	120(2)
ρ_{calcd}/g cm^{-3}	1.959	1.969	2.151	1.921	1.849	1.722
F(000)	644	636	1524	680	1520	1504
λ/Å	0.71073	0.71073	1.54184	1.54184	0.71073	0.71073
Crystal size/mm	0.20 × 0.20 × 0.10	0.24 × 0.17 × 0.11	0.10 × 0.10 × 0.02	0.25 × 0.10 × 0.07	0.20 × 0.10 × 0.10	0.30 × 0.10 × 0.10
μ/mm^{-1}	5.548	5.597	19.864	13.129	5.786	4.176
Scan range/°	1.54 to 29.17	2.00 to 23.30	2.58 to 68.48	2.70 to 68.87	2.13 to 29.16	1.66 to 29.16
Refl. measured	15709	5003	4547	6292	31396	34367
Independent refl.	6034	2999	4547	4407	3931	15746
Data/restraints/parameters	6034/0/301	2999/1/293	4547/0/289	4407/0/305	1931/0/208	15746/1/793
Goodness-of-fit on F^2	1.010	1.004	1.064	1.122	1.024	0.918
R_1/R_{w2} [$I > 2\sigma(I)$]	0.0234/0.0467	0.0223/0.0541	0.0573/0.1516	0.0696/0.1879	0.0200/0.0392	0.0467/0.0733
R_1/R_{w2} (all data)	0.0307/0.0484	0.0239/0.0547	0.0655/0.1651	0.0850/0.2308	0.0273/0.0412	0.0707/0.0801
R_{int}	0.0337	0.0202	0.0713	0.0966	0.040	0.0670

$NaBAr'_4$ (0.093 g, 0.105 mmol). Yield: 0.090 g, 62%; IR (CH_2Cl_2, cm^{-1}): 2029, 1912 (ν_{CO}); ^1H NMR (CD_2Cl_2): $\delta = 7.74$ (s, 8H, H_o BAr'_4), 7.58 (s, 4H, H_p BAr'_4), 7.54 (s, 3H, C*H* MeIm), 7.00 (s, 3H, C*H* MeIm),6.72 (s, 3H, C*H* MeIm), 3.74 (s, 9H, CH_3 MeIm). ^{13}C NMR (CD_2Cl_2): $\delta = 194.8$ (CO), 161.7 [q ($^1J_{CB} = 49.8$ Hz), C^i BAr'_4], 140.9, [*C*H MeIm], 134.8 [C^o BAr'_4], 130.2 [*C*H MeIm], 128.9 [q ($^2J_{CF} = 31.4$ Hz), C^m BAr'_4], 124.6 [q ($^1J_{CF} = 272.4$ Hz), CF_3 BAr'_4], 122.6 [*C*H MeIm], 117.5 [C^p BAr'_4], 34.6 [CH_3 MeIm]; elemental analysis calcd (%) for $C_{47}H_{30}BF_{24}N_6O_3Re$: C 40.91, H 2.19, N 6.09; found: C 40.92, H 2.19, N 6.06.

Synthesis of $[Re(CO)_3(MeIm)_3]_2[PtCl_6]$ (5)

To a solution of $[Re(CO)_3(MeIm)_3]BPh_4$ (**3**) (0.027 g, 0.030 mmol) in CH_2Cl_2 (15 mL), $[^nBu_4N]_2[PtCl_6]$ (0.050 g, 0.060 mmol) was added and the mixture was stirred at room temperature for 15 min. The resulting yellow solution was filtered *via* canula and concentrated under reduced pressure to a volume of 5 mL. Addition of hexane caused the precipitation of a yellow solid which was washed with hexane (2 × 20 mL). Slow diffusion of hexane into a concentrated solution of **5** in CH_2Cl_2 at room temperature afforded yellow crystals, one of which was employed for an X-ray structure determination. Yield: 0.040 g, 93%; IR (CH_2Cl_2, cm^{-1}): 2024, 1906 (ν_{CO}); ^1H NMR (CD_2Cl_2): $\delta = 7.59$ (s, 3H, C*H* MeIm), 7.05 (m, 6H, C*H* MeIm), 3.88 (s, 9H, CH_3 MeIm). ^{13}C NMR (CD_2Cl_2): $\delta =$ 198.1 (CO), 143.4, 133.9, 125.2 [*C*H MeIm], 38.3 [CH_3 MeIm]; elemental analysis calcd (%) for $C_{30}H_{36}Cl_6N_{12}O_6PtRe_2$: C 25.01, H 2.52, N 11.66; found: C 25.36, H 2.56, N 11.32.

Synthesis of $[Re(CO)_3(PhIm)_3]BAr'_4$ (7)

A mixture of $[Re(OTf)(CO)_5]$ (0.150 g, 0.316 mmol) and PhIm (0.120 mL, 0.948 mmol) in toluene (25 mL) was refluxed for 3 h. The solvent was evaporated to dryness. The residue was redissolved in CH_2Cl_2 (20 mL), $NaBAr'_4$ (0.280 g, 0.316 mmol) was added and the reaction mixture was stirred for 1 h at room temperature. The resulting colorless solution was filtered off the white solid (NaOTf) and concentrated under reduced pressure to a volume of 5 mL. Addition of hexane (20 mL) caused the precipitation of a microcrystalline solid that was washed with hexane (2 × 10 mL). Yield: 0.310 g, 63%; IR (CH_2Cl_2, cm^{-1}): 2032, 1919 (ν_{CO}); ^1H NMR (CD_2Cl_2): $\delta = 8.11$ (s, 3H, C*H* PhIm), 7.77 (s, 8H, H_o BAr'_4), 7.56 (m, 13H, H_p BAr'_4 and C_6H_5 PhIm), 7.46 (m, 9H, PhIm), 7.06 (s, 3H, C*H* PhIm). ^{13}C NMR CD_2Cl_2): $\delta =$ 194.2 (CO), 161.7 [q ($^1J_{CB} = 49.8$ Hz), C^i BAr'_4], 139.4, [*C*H PhIm], 135.3 [PhIm], 134.8 [C^o BAr'_4], 130.8 [*C*H PhIm], 130.4 [PhIm], 129.7 [*C*H PhIm], 128.9 [q ($^2J_{CF} = 31.0$ Hz), C^m BAr'_4], 124.5 [q ($^1J_{CF} = 272.0$ Hz), CF_3 BAr'_4], 122.0 [PhIm], 121.3 [PhIm], 117.5 [C^p BAr'_4]; elemental analysis calcd (%) for $C_{62}H_{36}BF_{24}N_6O_3Re$: C 47.55, H 2.32, N 5.37; found: C 47.69, H 2.15, N 5.37.

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