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Pyrazole Complexes as Anion Receptors

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Dedicated to Dr. José Antonio Abad on the occasion of his regretted retirement

Abstract: The behavior of the receptors $[Re(CO)_3(Hdmpz)_3]BAr'_4$ (Hdmpz = 3,5-dimethylpyrazole) (**1**) and $[Re(CO)_3(HtBupz)_3]BAr'_4$ (H*t*Bupz = 3(5)-*tert*-butylpyrazole) (**2**; Ar′ = 3,5-bis(trifluoromethyl)phenyl) toward the anions fluoride, chloride, bromide, iodide, hydrogensulfate, dihydrogenphosphate, nitrate, and perrhenate was studied in CD_3CN solution. In most cases, the receptors were stable. Anion exchange was fast, and binding constants were calculated from the NMR titration profiles. The structure of the adduct $[Re(CO)_3(HtBupz)_3]\cdot NO_3$ (**3**) was determined by X-ray diffraction. Two pyrazole moieties are hydrogen-bonded to one nitrate oxygen atom, and the third pyrazole moiety is hydrogen-bonded to an oxygen atom of an adjacent nitrate, leading to infinite chains. The structure of the adduct $[Re(CO)_3(Hdmpz)_3]BAr'_4\cdot$acetone (**4**), also determined by X-ray diffraction, showed a similar interaction of two pyrazole N–H groups with the acetone oxygen atom. F^- and $H_2PO_4^-$ deprotonate the receptors, and HSO_4^- decomposed **1**. The structure of one of the decomposition products (**5**), determined by X-ray diffraction, is consistent with pyrazole protonation and substitution by sulfate.

Keywords: anion receptors · coordination complexes · hydrogen bonds · rhenium · supramolecular chemistry

Introduction

The design of supramolecular receptors of anions based on hydrogen-bond interactions is an area of much current interest.[1] The relatively small strength of individual hydrogen bonds and their directional character requires several hydrogen-bond donor groups to be arranged within the receptor in a geometry allowing their simultaneous binding of the anionic guest. This poses a considerable challenge to the synthesis of the receptors. Transition-metal fragments have been incorporated in the structure of anion receptors as carriers of positive charge or Lewis acid character.[2] In addition, those fragments can serve as scaffolds onto which the hydrogen-bond donor groups can be attached by means of simple ligand substitution reactions. This requires the employment of molecules containing both the hydrogen-bond donor group and a metal binding site. Such a strategy is elegantly exemplified in the synthesis by Beer and co-workers of ruthenium complexes of 5,5′-diamido-2,2′-bipyridines, which coordinate the metal center through the bipyridine moiety and bind anions through the amide groups.[3] Bondy, Gale, and Loeb demonstrated that simple monodentate nicotinamides could also be employed for the synthesis of receptors, leading to synthetic procedures considerably simpler than those used for the preparation of most purely organic receptors.[4] However, using monodentate ligands has two important consequences. First, the geometry of the receptor will be more entirely dictated by the metal fragment, the choice of which becomes more crucial; thus, simultaneous anion binding by at least two amide groups is made possible in the receptors designed by Bondy, Gale, and Loeb by the square-planar geometry of the nicotinamide complexes, in turn enforced by the orbital preference of the Pt^{II} center. Second, without the additional stability lent by the chelate effect (as in the bidentate 2,2′-bipyridine ligands), the synthesis of receptors stable toward metal-ligand dissociation requires the choice of kinetically inert transition-metal centers, such as Pt^{II}.

We have recently reported the synthesis of the new receptors $[Re(CO)_3(Hdmpz)_3]BAr'_4$ (Hdmpz = 3,5-dimethylpyrazole) (**1**) and $[Re(CO)_3(HtBupz)_3]BAr'_4$ (H*t*Bupz = 3(5)-*tert*-butylpyrazole) (**2**); Ar′ = 3,5-bis(trifluoromethyl)phenyl).[5]

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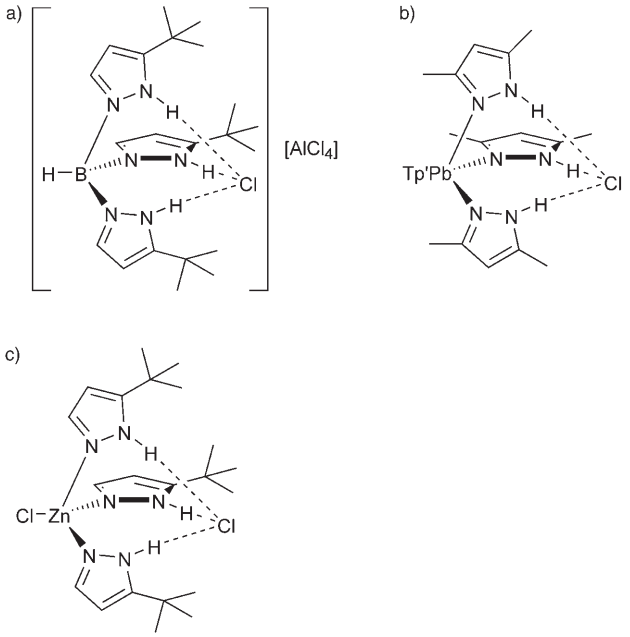
In these species, the geometry around the metal center in the cationic complex is octahedral, and we hypothesized that the *fac* disposition of the three pyrazole moieties could allow a convergent orientation of the three N–H bonds and, therefore, their simultaneous binding of an anionic guest.[6] Moreover, three previously known, structurally characterized compounds (Scheme 1) reported by the groups of Parkin,[7] Reger,[8] and Halcrow[9] can be considered as models of such a supramolecular adduct.[10,11]



Scheme 1. Structurally characterized tris(pyrazole)–anion adducts reported by a) Parkin et al,[7] b) Reger et al (Tp′ = HB(dmpz)$_3$),[8] and c) Halcrow et al.[9]

Cationic receptors of anions such as compounds **1** and **2** combine hydrogen bonding with coulombic attraction. In cationic receptors, the counteranion competes to some extent with the external anion. The tetraarylborate counteranion $BAr'_4{}^{-1}$ in our receptors was chosen with the aim to minimize this interference.

Here we report the detailed[12] study of the interaction between several anions and receptors **1** and **2**.

Results and Discussion

The behavior of receptors **1** and **2** toward chloride, bromide, iodide, hydrogensulfate, nitrate, and perrhenate was investigated by means of NMR titrations with the respective tetrabutylammonium salts in CD_3CN. Receptor **1** was found to undergo decomposition upon reaction with hydrogensulfate (see below). In every other case, the receptors were found to be stable against dissociation of the pyrazole ligands.[13]

Addition of the different anions to receptors **1** and **2** shifted the ^{1}H NMR signals of the N–H groups to higher frequencies.[14] Fast anion exchange was found, and the binding constants were calculated by using the WinEQNMR program.[15] The results are summarized in Figure 1 (titration profiles) and in Table 1.

For each receptor, the relative magnitudes of the association constants for the halide anions studied correlate with tendency to form strong H-bond interactions ($Cl^- > Br^- > I^-$; see below for F^-). This correlation extends to the anions nitrate and perrhenate. For each anion, the strength of anion binding is higher for receptor **1**, a fact that can be attributed to the hindrance imposed on the approach of the anion by the bulky *tert*-butyl substituent present in the pyrazole rings of receptor **2**.[16] The same factor can account for the somewhat selective (toward chloride) character displayed by **2**.

The treatment of receptors **1** or **2** with the anions mentioned above led to small shifts in the IR ν(CO) bands (3 cm^{-1} for the high energy band of **1** upon interaction with chloride in CH_2Cl_2) toward lower wavenumber values. In contrast, treatment of receptor **1** with tetrabutylammonium fluoride caused a large lowering in the ν(CO) values (21 cm^{-1} for the higher frequency band), suggesting deprotonation of the receptor to afford a neutral complex (see Scheme 2).

This was confirmed by the fact that identical IR ν(CO) bands were obtained when **1** was allowed to react with an equimolar amount of triethylamine. The IR and ^{1}H NMR spectra indicated that the product was the complex $[Re(CO)_3(Hdmpz)_2(dmpz)]$, previously synthesized by Ardizzoia, Masciocchi and co-workers by the reaction of $[ReBr(CO)_3(Hdmpz)_2]$ with 3,5-dimethylpyrazole and triethylamine.[17] A similar result was found when **1** was treated with tetrabutylammonium dihydrogenphosphate, although in this case only partial deprotonation took place, as indicated by the IR spectrum of the resulting mixture. Receptor **2** behaved similarly.

Attempts to grow single crystals of the adducts formed between **1** or **2** and the different anions were successful only for the combination **2**/NO_3^-. Slow diffusion of hexane into a solution of an equimolar mixture of **2** and tetrabutylammonium nitrate in CH_2Cl_2 at −30 °C afforded white crystals of what was found to be the neutral adduct $[Re(CO)_3(Ht\text{Bupz})_3]\cdot NO_3$ (**3**), whilst $[Bu_4N][BAr'_4]$ remained in solution. The structure of the supramolecular adduct **3** was determined by X-ray diffraction, and the results are summarized in Figure 2 and Table 2. Two pyrazole ligands of an octahedral cationic complex *fac*-$[Re(CO)_3(Ht\text{Bupz})_3]^+$ form hydrogen bonds with one of the oxygen atoms of a nitrate anion (N···O = 2.800(6) and 2.838(5) Å), and the third pyrazole is hydrogen-bonded to one of the oxygen atoms of an adjacent nitrate anion (N···O = 2.849(6) Å), resulting in a crystal structure consisting of infinite chains.[18]

It is instructive to compare the structures of **2**[12] and **3**. The N-Re-N angles in **2** are 85.75(16), 84.07(16), and 83.47(16)°. In **3**, the angles are 83.88(13), 83.48(13), and 92.15(13)°, the latter and wider angle corresponding to the two pyrazole ligands that are simultaneously binding nitrate.

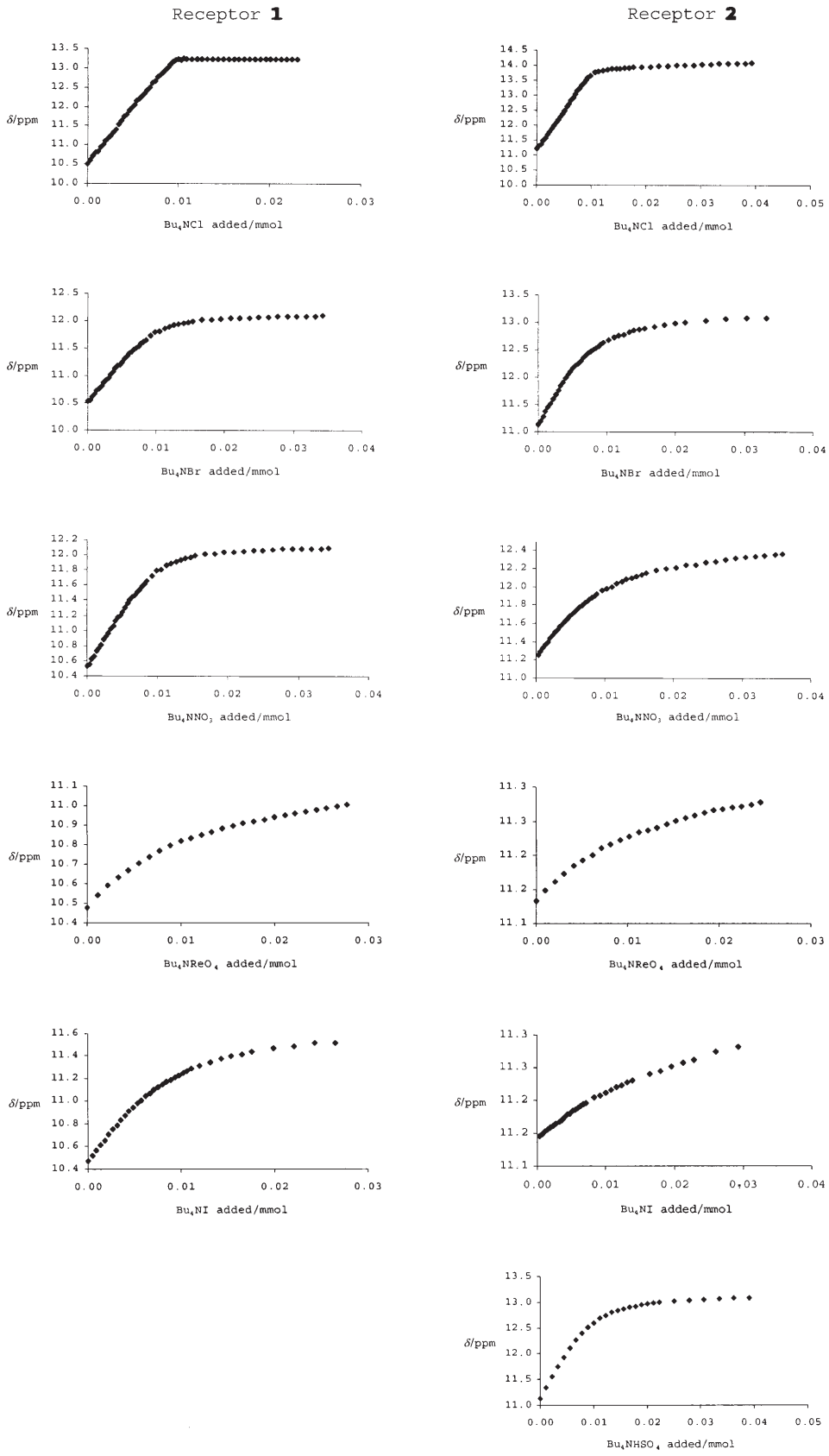


Figure 1. ^{1}H NMR titration plots of receptors **1** and **2** with different anions.

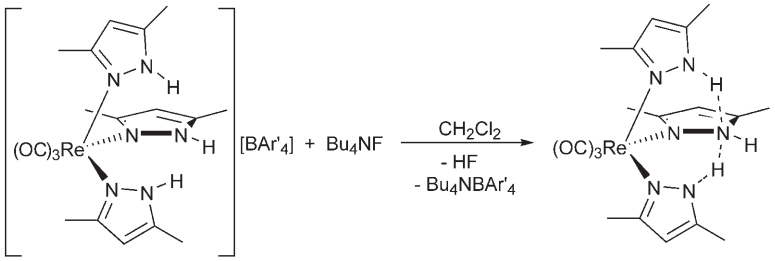
It is also pertinent to consider a similar comparison between the structures of the compound $[Re(CO)_3(Hdmpz)_3]BAr'_4$ (**1**)[5] and its acetone adduct, **4**, crystals of which were obtained by slow diffusion of hexane into a concentrated solution of **1** in dichloromethane containing a trace of acetone. The structure of **4** was determined by single-crystal X-ray diffraction, and the results are displayed in Figure 3 and Table 3.

The structure is reminiscent of that of $[Re(CO)_3(H\textit{t}Bupz)_3]\cdot NO_3$ (**3**) in that the N−H groups of two of the pyrazole ligands form hydrogen bonds with the acetone oxygen atom (N···O = 2.877(6) and 2.925(7) Å). These distances are slightly longer than those found for the nitrate adduct (see above), reflecting that the hydrogen bonds with the neutral acetone molecule are weaker than those with the nitrate anion.[19] The N-Re-N angles in **1** are 84.0(3), 87.28(2), and 84.1(2). In the adduct $[Re(CO)_3(Hdmpz)_3]BAr'_4\cdot$acetone (**4**), these angles are 84.08(15), 85.71(17), and 90.26(15)°, again the latter and wider angle corresponding to the two pyrazole ligands that are simultaneously binding the hydrogen-bond acceptor, now the molecule of acetone. Given the differences between the structures of the two adducts **3** and **4** (the former consisting of chains, whereas in the latter the ions $[Re(CO)_3(Hdmpz)_3]^+\cdot$acetone and $BAr'_4{}^{-1}$ are essentially unassociated), the mentioned differences in the angles can be attributed to the binding of the nitrate or acetone guest by two pyrazole ligands of the *fac*-$[Re(CO)_3(Hpz)_3]^+$ host. Thus, the binding of even a small oxygen atom of either nitrate or acetone causes a significant structural distortion

Table 1. Binding constants for receptors **1** and **2** toward different anions.

Anion	**1**, K_a [M^{-1}]	**2**, K_a [M^{-1}]
Cl^-	6385 ± 362	4692 ± 570
Br^-	5593 ± 198	543 ± 67
I^-	26 ± 2	27 ± 1
NO_3^-	1126 ± 28	97 ± 6
ReO_4^-	253 ± 4	28 ± 1
HSO_4^-	–	425 ± 5

consisting of an opening of the N-Re-N angles formed by the metal and the two involved pyrazole ligands.



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Scheme 2. Deprotonation reaction of $[Re(CO)_3(Hdmpz)_3]BAr'_4$ (**1**) by fluoride.

Table 2. Selected bonds lengths [Å] and angles [°] for **3**.

bond lengths			
Re(1)–N(1)	2.190(3)	C(1)–O(1)	1.163(5)
Re(1)–N(3)	2.234(3)	C(2)–O(2)	1.134(5)
Re(1)–N(5)	2.199(4)	C(3)–O(3)	1.156(6)
Re(1)–C(1)	1.909(5)	N(4)···O(4)	2.800(6)
Re(1)–C(2)	1.915(5)	N(6)···O(4)	2.838(5)
Re(1)–C(3)	1.905(6)	N(2)···O(6)	2.849(6)
bond angles			
N(1)-Re(1)-N(3)	83.48(13)	C(2)-Re(1)-C(3)	88.9(2)
N(1)-Re(1)-N(5)	83.88(13)	N(4)-H(4)···O(4)	150(5)
N(3)-Re(1)-N(5)	92.15(13)	N(6)-H(6)···O(4)	168(4)
C(1)-Re(1)-C(2)	86.3(2)	N(2)-H(2)···O(6)	165(4)
C(1)-Re(1)-C(3)	87.71(19)		

A comparison between the Re–N distances of $[Re(CO)_3(Hdmpz)_3]BAr'_4$ (**1**; 2.186(8), 2.195(7), and 2.204(6) Å) and those of the acetone adduct **4** (2.195(4), 2.234(4), and 2.239(4) Å) shows a lengthening of the distances (second and third) for the pyrazole ligands involved in the hydrogen-bonding of the substrate. This suggests that the opening

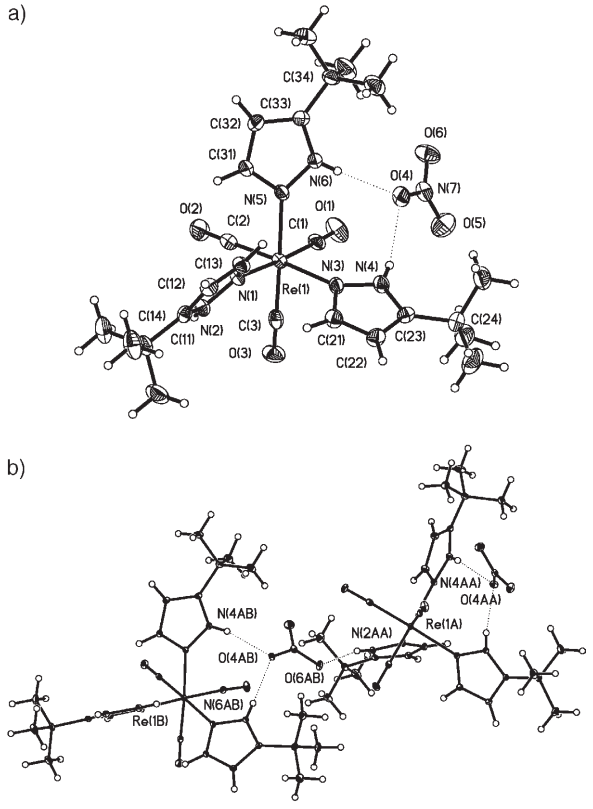


Figure 2. a) Structure of $[Re(CO)_3(HtBupz)_3]\cdot NO_3$ (**3**); thermal ellipsoid (30%) plot. b) View of the intermolecular interactions in **3,** which lead to infinite chains.

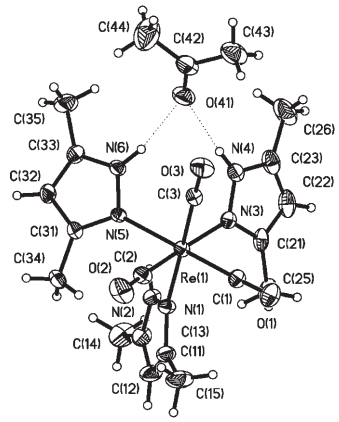


Figure 3. Structure of $[Re(CO)_3(Hdmpz)_3]BAr'_4\cdot$acetone (**4**); thermal ellipsoid (30%) plot.

Table 3. Selected bonds lengths [Å] and angles [°] for **4**.

bond lengths			
Re(1)–N(1)	2.195(4)	C(1)–O(1)	1.137(7)
Re(1)–N(3)	2.239(4)	C(2)–O(2)	1.134(7)
Re(1)–N(5)	2.234(4)	C(3)–O(3)	1.135(7)
Re(1)–C(1)	1.928(6)	N(4)···O(41)	2.925(7)
Re(1)–C(2)	1.948(6)	N(6)···O(41)	2.877(6)
Re(1)–C(3)	1.942(6)		
bond angles			
N(1)-Re(1)-N(3)	85.71(17)	C(1)-Re(1)-C(3)	86.8(2)
N(1)-Re(1)-N(5)	84.08(15)	C(2)-Re(1)-C(3)	86.6(2)
N(3)-Re(1)-N(5)	90.26(15)	N(4)-H(4)···O(41)	174.0(4)
C(1)-Re(1)-C(2)	90.0(2)	N(6)-H(6)···O(41)	162.7(3)

of the N-Re-N angles needed to accommodate the guest results, probably through a loss of orbital overlap, in weaker Re–N bonds and therefore longer Re–N distances. This effect is only slightly perceptible when the Re–N distances of $[Re(CO)_3(HtBupz)_3]BAr'_4$ (**2**) (2.178(4), 2.191(4), and 2.193(4) Å) and those of $[Re(CO)_3(HtBupz)_3]\cdot NO_3$ (**3**) (2.190(3), 2.199(4), and 2.234(3) Å) are compared, probably because in the latter structure the third pyrazole ligand is also involved in relatively strong hydrogen-bonding of an adjacent nitrate.

These observations suggest that guest binding through the N–H groups of the three pyrazole ligands in our rhenium receptors could be unfavorable as a result of the severe structural distortion (from the pseudooctahedral geometry) needed. Conversely, guest binding through the N–H groups of the three pyrazole ligands in the adducts $[HB(HtBupz)_3\cdot Cl]^+$[7] and $[ClZn(HtBupz)_3\cdot Cl]$[9] referred to in the Introduction would be allowed by the pseudotetrahedral geometry (and therefore wider N-E-N angles) about E = B or Zn in these species. Moreover, in the hexacoordinate adduct $[Pb(Tp')(Hdmpz)_3\cdot Cl]$ ($Tp' = HB(dmpz)_3$), the N-Pb-N angles subtended by the Hdmpz ligands are 111.8(3)°.[8]

To investigate whether anion binding by two (out of the three) ligated pyrazoles occurs in solution, low-temperature ^{1}H NMR spectra of both a) an equimolar mixture of **1** and tetrabutylammonium chloride and b) compound **1** were recorded. CD_2Cl_2 was chosen as solvent to provide a temperature range wider than that available for CD_3CN. At 178 K, the C–H signal of the 3,5-dimethylpyrazole ligands in sample a, a singlet in the room temperature spectrum, decoalesced into two singlets displaying a 1:2 integral ratio, whilst the same signal remained unchanged in sample b at the same temperature. These results are consistent with chloride exchange over pairs of pyrazole ligands, which is fast at room temperature, being frozen. The low temperature at which this occurs is in accordance with a kinetically facile ($\Delta G^{\neq} = 34\ kJ\,mol^{-1}$) dynamic process in which no covalent bonds need to be broken. Therefore, the two-pyrazole anion binding found in the solid state (see above) is maintained in the instantaneous solution structure.

As mentioned above, receptor **1** decomposed when treated with tetrabutylammonium hydrogensulfate. The ^{1}H NMR spectrum of the resulting crude reaction mixture was complex, suggesting the presence of several species, and no conclusions could be drawn as to the nature of the decomposition process. Fortunately, slow diffusion of hexane into a concentrated solution of the crude mixture in CH_2Cl_2 afforded single crystals that were used for a structural determination. The results, shown in Figure 4 and Table 4, indicate

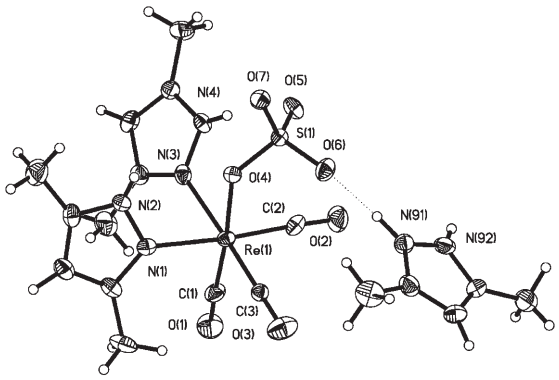
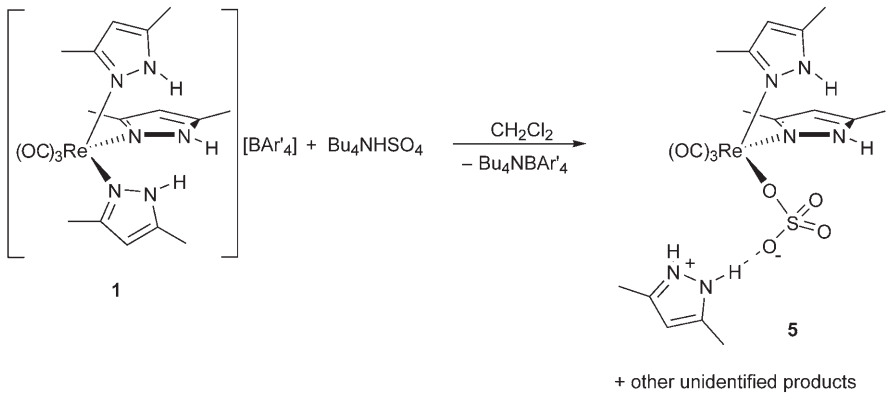


Figure 4. Structure of $[Re(OSO_3)(CO)_3(Hdmpz)_2]\cdot H_2dmpz$ (**5**); thermal ellipsoid (30%) plot.

Table 4. Selected bonds lengths [Å] and angles [°] for **5**.

	bond lengths		
Re(1)–N(1)	2.181(9)	Re(1)–C(3)	1.902(17)
Re(1)–N(3)	2.209(17)	C(1)–O(1)	1.158(13)
Re(1)–O(4)	2.145(6)	C(2)–O(2)	1.145(14)
Re(1)–C(1)	1.880(10)	C(3)–O(3)	1.17(2)
Re(1)–C(2)	1.904(11)	O(6)···N(91)	2.68(1)
	bond angles		
N(1)-Re(1)-N(3)	82.4(4)	C(1)-Re(1)-C(3)	88.2(5)
N(1)-Re(1)-O(4)	80.4(3)	C(2)-Re(1)-C(3)	88.5(6)
N(3)-Re(1)-O(4)	82.1(3)	N(91)-H(91)···O(6)	171(14)
C(1)-Re(1)-C(2)	87.8(5)		

that one of the pyrazole ligands has been protonated by HSO_4^- and dissociated from the first coordination sphere of rhenium, on which it has been substituted by a sulfate anion (see Scheme 3).[20] The product is the adduct $[Re(OSO_3)(CO)_3(Hdmpz)_2]\cdot H_2dmpz$ (**5**). Each pyrazolium cation bridges two $[Re(OSO_3)(CO)_3(Hdmpz)_2]$ complex anions through strong hydrogen bonds between pyrazolium N–H groups and sulfate oxygen atoms (only one shown, N···O distances of 2.680(1) and 2.687(1) Å). Adventitious water (not shown) is hydrogen-bonded to one of the ligated pyrazoles and one of the sulfate oxygen atoms.



Scheme 3. Reaction of $[Re(CO)_3(Hdmpz)_3]BAr'_4$ (**1**) with a hydrogensulfate anion.

Table 5. Crystal data and refinement details for compounds **3**–**5**.

	3	**4**	**5**
formula	$C_{24}H_{36}N_7O_6Re{\cdot}CH_2Cl_2$	$C_{53}H_{42}BF_{24}N_6O_4Re$	$C_{36}H_{54}N_{12}O_{16}Re_2S_2$
M_r	789.72	1479.94	1347.43
cryst. system	monoclinic	triclinic	monoclinic
space group	$P2(1)/n$	$P\bar{1}$	C_c
a [Å]	11.658(7)	12.911(7)	8.400(10)
b [Å]	19.172(12)	13.089(7)	24.64(3)
c [Å]	14.832(9)	18.448(10)	12.246(14)
α [°]	90	87.144(10)	90
β [°]	92.221(13)	82.542(9)	99.25(2)
γ [°]	90	88.635(10)	90
V [Å^3]	3312(4)	3087(3)	2501(5)
Z	4	2	2
T [K]	293(2)	296(2)	296(2)
ρ_{calcd} [g cm^{-3}]	1.584	1.592	1.789
$F(000)$	1576	1460	1328
$\lambda(Mo_{K\alpha})$ [Å]	0.71073	0.71073	0.71073
crystal size [mm]	$0.06\times0.15\times0.27$	$0.20\times0.28\times0.39$	$0.10\times0.25\times0.39$
μ [mm^{-1}]	3.876	2.088	4.995
scan range [°]	$1.74\leq\theta\leq23.30$	$1.11\leq\theta\leq23.29$	$1.65\leq\theta\leq23.45$
refl. measured	14529	13827	5543
independent refl.	4732	8743	3176
data/restraints/parameters	4732/0/391	8743/0/811	3176/2/332
goodness-of-fit on F^2	0.952	1.061	1.062
R_1/R_{w2} [$I>2\sigma(I)$]	0.0249/0.0561	0.0377/0.1003	0.0307/0.0826
R_1/R_{w2} (all data)	0.0362/0.0594	0.0427/0.1070	0.0313/0.0831

The fact that **2** is stable toward HSO_4^-, whereas this anion caused the decomposition of **1**, can be attributed to the better protection of the metal first coordination sphere imparted by the bulky *t*Bu groups.[16]

In summary, we have reported a new class of transition-metal-based receptors for anions; namely, the compounds $[Re(CO)_3(Hdmpz)_3]BAr'_4$ (**1**) and $[Re(CO)_3(HtBupz)_3]BAr'_4$ (**2**). Monodeprotonation by dihydrogenphosphate or fluoride, or pyrazole protonation coupled to pyrazole substitution by anion upon reaction with hydrogensulfate have been found to delineate the stability boundaries of **1** and **2**. Guest binding has been found to occur through two of the three N–H groups, and to require an opening of the N-Re-N angle for the involved pyrazole ligands. The more severe hindrance opposed to anion approach by the bulky *t*Bu substituents in **2** makes this receptor more stable, although it leads also to less strong binding.

Experimental Section

General: All manipulations were carried out under a nitrogen atmosphere using Schlenk techniques or a MBraun drybox. Receptors **1** and **2** were prepared as previously reported.[5] Tetrabutylammonium salts were purchased from Fluka or Aldrich. Deuterated acetonitrile (Cambridge Isotope Laboratories, Inc.) was stored under nitrogen in Young tubes. NMR spectra were recorded on Bruker AC-300 and DPX-300 instruments. IR solution spectra were obtained with 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 concentration of 10^{-2} M in CD_3CN) 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_3CN, separately prepared and kept in a septum-stoppered vial during the titration) were injected through the septum using Hamilton mycrosyringes (10–100 μL). The volume of each addition was 10 μL before reaching the saturation zone (a nearly horizontal line in the titration profile), and 20 or 40 μL afterwards. When the change in δ is small (as for ReO_4^-), 20 μL of salt solution was added from the beginning. Data were treated by using the WinEQNMR program.[15]

Crystal structure determination for compounds 3, 4 and 5: A suitable crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite-monochromatized $Mo_{K\alpha}$ radiation and a CCD area detector. One hemisphere of the reciprocal space was collected in each case. Raw frame data were integrated with the SAINT[21] program. The structures were solved by direct methods with SHELXTL.[22] An empirical absorption correction was applied with the program SADABS.[23] In every structure all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms. Drawings and other calculations were made with SHELXTL, PLATON,[24] and PARST[25] under WINGX.[26] Crystal and refinement details are collected in Table 5.

CCDC-279519 (**3**), CCDC-279520 (**4**), and CCDC-279521 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] Reviews: a) *Supramolecular Chemistry of Anions* (Eds: A. Bianchi, K. Bowman-James, E. García-España), Wiley-VCH, Weinheim,

1997; b) F. P. Schmidtchen, M. Berger, *Chem. Rev.* **1997**, *97*, 1609–1646; c) for a special volume dedicated to this topic, see: *Coord. Chem. Rev.* **2003**, *240*.

[2] a) P. D. Beer, *Chem. Commun.* **1996**, 689–696; b) P. D. Beer, D. K. Smith, *Prog. Inorg. Chem.* **1997**, *46*, 1–96; c) P. D. Beer, P. A. Gale, *Angew. Chem.* **2001**, *113*, 502–532; *Angew. Chem. Int. Ed.* **2001**, *40*, 486–516.

[3] a) L. H. Uppadine, M. G. B. Drew, P. D. Beer, *Chem. Commun.* **2001**, 291–292. For other examples of this concept using bidentate ligands, see: b) I. Prévot-Halter, T. J. Smith, J. Weiss, *J. Org. Chem.* **1997**, *62*, 2186–2192; c) L. P. Harding, J. C. Jeffery, T. Riis-Johannessen, C. R. Rice, Z. Zeng, *Dalton Trans.* **2004**, 2396–2397.

[4] C. R. Bondy, P. A. Gale, S. J. Loeb, *Chem. Commun.* **2001**, 729–730. For an extension of this work with four 8-(*n*-butylurea)isoquinoline ligands coordinated to Pt^{II}, and BF_4 as counteranion, see: C. R. Bondy, P. A. Gale, S. J. Loeb, *J. Am. Chem. Soc.* **2004**, *126*, 5030–5031.

[5] S. Nieto, J. Pérez, V. Riera, D. Miguel, C. Alvarez, *Chem. Commun.* **2005**, 546–548.

[6] A few examples of macrocyclic receptors of anions incorporating pyrazole moieties have been reported, see: Miranda, F. Escartí, L. Lamarque, E. García-España, P. Navarro, J. Latorre, F. Lloret, H. R. Jiménez, M. J. R. Yunta, *Eur. J. Inorg. Chem.* **2005**, 189–208, and references therein.

[7] a) A. Looney, G. Parkin, A. L Rheingold, *Inorg. Chem.* **1991**, *30*, 3099–3101; b) G. Parkin, *Adv. Inorg. Chem.* **1995**, *42*, 291 (see in particular pp. 370–372). For a different example of host–guest chemistry based on a tris(pyrazolyl)borate scaffold, see: B. S. Hammes, X. Luo, M. W. Carrano, C. J. Carrano, *Angew. Chem.* **2002**, *114*, 3393–3395; *Angew. Chem. Int. Ed.* **2002**, *41*, 3259–3261.

[8] D. L. Reger, Y. Ding, A. L. Rheingold, R. L. Ostrander, *Inorg. Chem.* **1994**, *33*, 4226–4230.

[9] a) X. Liu, C. A. Kilner, M. A. Halcrow, *Chem. Commun.* **2002**, 704–705; b) S. L. Renard, C. A. Kilner, J. Fisher, M. A. Halcrow, *Dalton Trans.* **2002**, 4206–4212. For related chemistry, see: c) S. L. Renard, A. Franken, C. A. Kilner, J. D. Kennedy, M. A. Halcrow, *New J. Chem.* **2002**, *26*, 1634–1637.

[10] A similar motif involving the two pyrazole ligands of the *cis*-$[Pt(dppe)(Hpz)_2](BF_4)_2$ (dppe = 1,2-bis(diphenylphosphino)etane; Hpz = pyrazole) complex has been crystallographically characterized; see: A. L. Bandini, G. Banditelli, B. Bovio, *Polyhedron*, **2001**, *20*, 2869–2875.

[11] The supramolecular adducts reported in references [7–10] were serendipitously obtained, and the corresponding anion-free receptors are not known. On the other hand, many metal–pyrazole complexes are known, and the significance of hydrogen bonding involving their coordinated pyrazole ligands has been noted. Nevertheless, to the best of our knowledge, their solution behavior as anion receptors was never studied. See also: a) I. A. Guzei, C. H. Winter, *Inorg. Chem.* **1997**, *36*, 4415–4420; b) M. Cano, J. V. Veras, M. L. Gallego, J. Perles, C. Ruiz-Valero, E. Pinilla, M. R. Torres, *Helv. Chim. Acta* **2003**, *86*, 3194–3203; c) M. L. Gallego, P. Ovejero, M. Cano, J. V. Veras, J. A. Campo, E. Pinilla, M. R. Torres, *Eur. J. Inorg. Chem.* **2004**, 3089–3098; d) S. Tanase, E. Bouwman, G. J. Long, A. M. Shahin, A. M. Mills, A. L. Spek, J. Reedijk, *Eur. J. Inorg. Chem.* **2004**, 4572–4578.

[12] Synthetic, spectroscopic, and structural details of compounds **1** and **2** were given in our preliminary communication[5] and will not be repeated here.

[13] In CD_2Cl_2 or CD_3CN solution, the ^1H NMR spectra of compounds **1** and **2** display a single set of pyrazole signals, indicating the equivalence of the three pyrazole ligands, as expected for a *fac* geometry (in turn indicated by the ν(CO) pattern in the IR spectra). The ^1H NMR spectra of **1** feature two low-frequency CH_3 singlets with a 1:1 integral ratio, indicating the non-equivalence of the two methyl groups in the 3 and 5 positions on the pyrazole rings. This implies that, even in the CD_3CN donor solvent, the dimethylpyrazole and the solvent are not in rapid chemical exchange. Such a rapid exchange would give rise to a single methyl signal, due to tautomeric H exchange over the two N sites in the uncoordinated 3,5-dimethylpyrazole. In compound **2**, the absence of the mentioned fast exchange is shown by the observation of sharp singlets for all the carbon atoms of the pyrazole rings in the ^{13}C NMR spectrum.[9] Regarding the stability of the receptors in the presence of the anions investigated, the complex *fac*-$[ReCl(CO)_3(Hdmpz)_2]$, which would be the product of the displacement of Hdmpz from **1** by chloride (the more nucleophilic of the anions for which NMR titrations could be carried out), was independently synthesized by reaction of $[ReCl(CO)_5]$ with two equivalents of Hdmpz in refluxing toluene, and characterized both spectroscopically and by means of single-crystal X-ray diffraction (see Supporting Information for reference [5]). The ν(CO) IR bands of the neutral chlorobis(pyrazole) complex were not observed in the solution mixture of **1** and Bu_4NCl. In addition, it was found that when 0.25, 0.50, and 0.75 equivalents of Bu_4NCl were added to solutions containing an equimolar mixture of **1** and $[ReCl(CO)_3(Hdmpz)_2]$, separate sets of signals could be observed for the **1**·Cl and $[ReCl(CO)_3(Hdmpz)_2]$·Cl species in the ^1H NMR spectra. Thus, displacement of Hdmpz by chloride during the titration could be unambiguously ruled out because only the signals of **1**·Cl could be observed throughout it. Similar results were found for compound **2**.

[14] This is the normal behavior for anion receptors based on hydrogen bonding (and indeed the normal response of a hydrogen-bond donor to the interaction with an anion, a hydrogen-bond acceptor); however, it deserves to be noted here since we have found that, in contrast, the addition of tetrabutylammonium chloride to a dichloromethane solution of 3,5-dimethylpyrazole shifts the N–H signal to lower frequencies. We attribute this apparently abnormal fact to the existence of intermolecular interactions in the solution of Hdmpz in the low competing solvent dichloromethane. Self-association of pyrazoles is well documented in the solid state (see: O. Klein, F. Aguilar-Parrilla, J. M. López, N. Jagerovic, J. Elguero, H.-H. Limbach, *J. Am. Chem. Soc.* **2004**, *126*, 11718–11732, and references therein) and results from the presence of a basic nitrogen (a hydrogen-bond acceptor) and a N–H group (a hydrogen bond donor) in their molecules. Addition of anions would then weaken these strong intermolecular interactions and therefore would give rise to a shift toward lower frequencies in the N–H ^1H NMR signals. Hence, one of the roles that the metal center plays in receptors **1** and **2** is to prevent, by blocking the basic, pyridine-like nitrogen (which is used for metal complexation) self-association of the pyrazole molecules. In the more competitive solvent CD_3CN we have found normal behavior (i.e., shift to higher frequencies upon addition of chloride) for Hdmpz, and a binding constant of $11(\pm1)\ M^{-1}$ was calculated from the NMR titration.

[15] M. J. Hynes, *J. Chem. Soc. Dalton Trans.* **1993**, 311–312.

[16] For a precedent of this idea applied to a pyrazole-containing ligand, see: D. B. Grotjahn, S. Van, D. Combs, D. A. Lev, C. Schneider, C. D. Incarvito, K.-C. Lam, G. Rossi, A. L. Rheingold, M. Rideout, C. Meyer, G. Hernández, L. Mejorado, *Inorg. Chem.* **2003**, *42*, 3347–3355.

[17] G. A. Ardizzoia, G. LaMonica, A. Maspero, M. Moret, N. Masciocchi, *Eur. J. Inorg. Chem.* **1998**, 1503–1512.

[18] In contrast with the inequivalence of the pyrazole ligands in the solid state, each room temperature ^1H NMR spectrum along the titration of **1** or **2** with the $[Bu_4N]X$ salts displays a single set of pyrazole signals and therefore indicates magnetic equivalence of the three pyrazole ligands, in accord with fast anion exchange in solution.

[19] Addition of a few equivalents of acetone to CD_3CN solutions of **1** or **2** did not cause any visible shift of the N–H signals of the ligated pyrazoles, indicating that, in these solutions, the interaction is negligible. This illustrates that crystallographic data may be of little relevance with regard to anion–receptor interactions in solution.

[20] On the basis of crystallographic results alone, an alternative description as a hydrogensulfate ligand hydrogen-bonded to a molecule of Hdmpz is equally valid. Rhenium carbonyl complexes with sulfate (or hydrogensulfate) ligands are very rare; see: E. Fritsch, J. Hei-

drich, K. Polborn, W. Beck, *J. Organomet. Chem.* **1992**, *441*, 203–213.
[21] SAINT+. SAX area detector integration program. Version 6.02. Bruker AXS, Inc. Madison, WI, **1999**.
[22] G. M. Sheldrick, SHELXTL, An integrated system for solving, refining, and displaying crystal structures from diffraction data. Version 5.1. Bruker AXS, Inc. Madison, WI, **1998**.
[23] G. M. Sheldrick, SADABS, Empirical Absorption Correction Program, University of Göttingen, Göttingen, Germany, **1997**.
[24] a) PLUTON: A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34. b) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, A. L. Spek, **1998**.
[25] a) M. Nardelli, *Comput. Chem.* **1983**, *7*, 95–97; b) M. Nardelli, *J. Appl. Crystallogr.* **1995**, *28*, 659.
[26] WINGX 1.70.00: L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

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