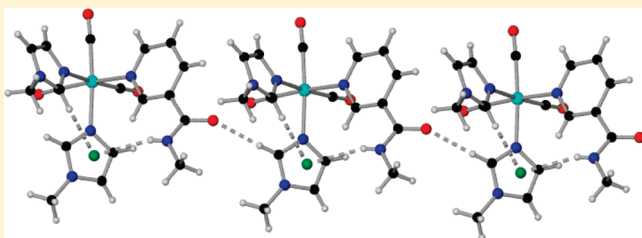


Two Different Hydrogen Bond Donor Ligands Together: A Selectivity Improvement in Organometallic $\{\text{Re}(\text{CO})_3\}$ Anion Hosts ∇ Laura Ion,[†] Sonia Nieto,[†] Julio Pérez,^{*,†} Lucía Riera,^{*,†} Víctor Riera,[†] Jesús Díaz,[§] Ramón López,^{||} Kirsty M. Anderson,[⊥] and Jonathan W. Steed[⊥][†]Departamento de Química Orgánica e Inorgánica-IUQOEM, Universidad de Oviedo-CSIC, C/Julián Clavería, 8. 33006 Oviedo, Spain[‡]Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Universidad de Zaragoza-CSIC, C/Pedro Cerbuna, 12. 50009 Zaragoza, Spain[§]Departamento de Química Orgánica e Inorgánica, Universidad de Extremadura, Facultad de Veterinaria, 10071 Cáceres, Spain^{||}Departamento de Química Física y Analítica, Universidad de Oviedo, C/Julián Clavería, 8. 33006 Oviedo, Spain[⊥]Department of Chemistry, University of Durham, DH1 3LE Durham, United Kingdom

S Supporting Information

ABSTRACT: Rhenium(I) compounds $[\text{Re}(\text{CO})_3(\text{Hdmpz})_2(\text{ampy})]\text{BAR}'_4$ and $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{ampy})]\text{BAR}'_4$ (Hdmpz = 3,5-dimethylpyrazole, N-MeIm = N-methylimidazole, ampy = 2-aminopyridine or 3-aminopyridine) have been prepared stepwise as the sole reaction products in good yields. The cationic complexes feature two different types of hydrogen bond donor ligands, and their anion binding behavior has been studied both in solution and in the solid state. Compounds with 2-ampy ligands are labile in the presence of nearly all of the anions tested. The X-ray structure of the complex $[\text{Re}(\text{CO})_3(\text{Hdmpz})_2(\text{ampy})]^+$ (**2**) shows that the 2-ampy ligand is metal-coordinated through the amino group, a fact that can be responsible for its labile character. The 3-ampy derivatives (coordinated through the pyridinic nitrogen atom) are stable toward the addition of several anions and are more selective anion hosts than their tris(pyrazole) or tris(imidazole) counterparts. This selectivity is higher for compound $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{MeNA})]\text{BAR}'_4$ (**5** · BAR'_4 , MeNA = N-methylnicotinamide) that features an amido moiety, which is a better hydrogen bond donor than the amino group. Some of the receptor-anion adducts have been characterized in the solid state by X-ray diffraction, showing that both types of hydrogen bond donor ligands of the cationic receptor participate in the interaction with the anion hosts. DFT calculations suggest that coordination of the ampy ligands is more favorable through the amino group only for the cationic complex **2**, as a consequence of the existence of a strong intramolecular hydrogen bond. In all other cases, the pyridinic coordination is clearly favored.



■ INTRODUCTION

The incorporation of metal fragments in the structure of anion receptors can be a useful tool.¹ While the synthesis of purely organic anion receptors can be a tedious task, often metal-based receptors are straightforwardly prepared, in good yields and as the only products of simple reactions. The role of the metal can be crucial for the behavior of the host toward an external anion guest, as (i) it can be a Lewis acidic center and therefore a key component of the anion binding site; (ii) it can bear positive charge so that the electrostatic attraction will contribute to the overall host–guest interaction; and (iii) it can act as part of a redox, luminescent, or colorimetric reporter group, etc. One of its multiple purposes is to preorganize hydrogen-bond donor functional groups for anion binding by coordination of the ligands bearing those groups to a metal center. This preorganization can be achieved in two different ways: (a) metal–ligand coordination can be used to enforce a particular conformation of a ligand that will result in an optimal organization of hydrogen-bond donor groups (as it occurs with bis(carbamoyl)-2,2'-bipyridines² or

biimidazole,³ for example), or (b) metal ligand coordination can be used to place simple moderate ligands in positions such that their hydrogen-bond donor groups can converge toward an external anion.⁴ Using the latter strategy, we have prepared rhenium(I) organometallic compounds bearing three azole ligands (Figure 1) in a facial disposition and studied their behavior as anion receptors.

The use of N-alkylimidazole ligands (N-RIm) allowed us to evaluate the effect of the counteranion present in the receptor.⁵ For compounds $[\text{Re}(\text{CO})_3(\text{N-RIm})_3]\text{X}$ (Figure 1b), the best hydrogen bond donor groups are the central C–H groups of the imidazole ligands. The host–guest interactions between the cationic metal complex and the external anions are intrinsically weak and therefore allowed the comparison of different counteranions X^- (OTf^- , PF_6^- , BF_4^- , etc.). The results showed that BAR'_4^- ($\text{Ar}' = 3,5\text{-bis(trifluoromethyl)phenyl}$), an anion that has been widely used in organometallic chemistry and catalysis as an

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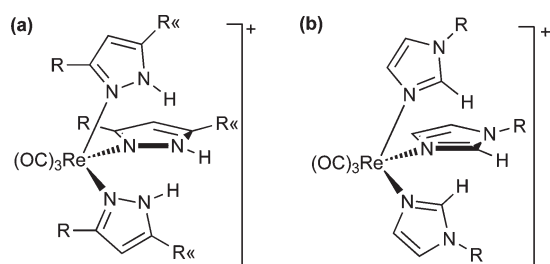


Figure 1. Tris(pyrazole) (a) and tris(imidazole) (b) rhenium compounds previously used by our group as anion receptors.

alternative to less innocent counteranions such as hexafluorophosphate, tetrafluoroborate, perchlorate, etc.,⁶ is advantageous over more conventional counteranions for cationic receptors. This fact is mainly due to the poorly coordinating character of this tetraarylborate, which minimizes its competition with the external anion for the cationic guest.

On the other hand, we have studied the interactions of $[\text{Re}(\text{CO})_3(\text{Rpz})_3]\text{BAR}'_4$ ($\text{Rpz} = 3(5\text{-}tert\text{-butylpyrazol}, 3,5\text{-dimethylpyrazole}; \text{Figure } 1\text{a})$) with anions, both in solution and in the solid state. These results have shown that there is a significant host–guest interaction in which at least two of the three pyrazole ligands interact simultaneously with the same external anion.⁷

Herein, we report the study of the behavior of “mixed” compounds of formula $[\text{Re}(\text{CO})_3(\text{Lz})_2(\text{Lz}')]\text{BAR}'_4$ ($\text{Lz} = 3,5\text{-dimethylpyrazole}$ or $N\text{-methylimidazole}$; $\text{Lz}' = 2\text{-aminopyridine}$, 3-aminopyridine , or $N\text{-methylnicotinamide}$) that bear more than one type of hydrogen bond donor group.⁸ We have chosen the *fac*- $\{\text{Re}(\text{CO})_3\}$ scaffold, as it has previously been shown to be a stable host, positively charged (so that Coulombic attraction enhances the overall host–guest interaction) and the presence of CO ligands allows the employment of IR spectroscopy to quickly and easily detect side reactions such as ligand substitution, deprotonation, etc. The new compounds feature two imidazole or pyrazole ligands (the same previously employed in *fac*- $[\text{Re}(\text{CO})_3(\text{Lz})_3]^+$ receptors) and one amino or amidopyridine. These pyridine derivatives display a binding site (usually the pyridinic nitrogen) and a functionality that possesses good hydrogen bonding donor groups, i.e., $N\text{-H}$ groups from amide or amine moieties.⁹ In fact, these ligands have been used previously for the design of metal-based anion receptors.⁴

The modular synthesis of these complexes allows the preparation of hosts of the same general geometrical type, but in which the ligands bearing the hydrogen bond donor groups and, in turn, the exact size and shape of the anion-recognizing molecular cleft can be varied. In this paper, it will be shown that complexes in which two different types of such ligands coexist in the coordination sphere of the same metal can be prepared. Apart from 2-aminopyridine derivatives, these complexes are stable against ligand redistribution reactions and against ligand substitution by the external anionic guest, a condition that plagues hosts based on metal complexes of monodentate ligands. In addition, it will be shown that these hosts display enhanced selectivity toward the smaller anions compared with their simpler counterparts with only one type of hydrogen bond donor ligand.

EXPERIMENTAL SECTION

General. All manipulations were carried out under a nitrogen atmosphere using Schlenk techniques. Compounds $[\text{ReBr}(\text{CO})_5]$,¹⁰

$[\text{Re}(\text{CO})_3(\text{Hdmpz})_2(2\text{-ampy})]\text{BAR}'_4$ ($2\cdot\text{BAR}'_4$),⁸ and $[\text{Re}(\text{CO})_3(\text{Hdmpz})_2(3\text{-ampy})]\text{BAR}'_4$ ($4\cdot\text{BAR}'_4$)⁸ were prepared as previously reported. Tetrabutylammonium salts were purchased from Fluka or Aldrich. Deuterated dichloromethane (Cambridge Isotope Laboratories, Inc.) was stored under nitrogen in a Young tube and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 300, DPX-300, or Advance 400 spectrometer. NMR spectra are referred to the internal residual solvent peak for ^1H and $^{13}\text{C}\{^1\text{H}\}$ 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 afterward. When the change in δ is small, 20 μL of salt solution was added from the beginning. Data were treated using the WinEQNMR program.¹¹

Computational Details. Quantum chemical computations were carried out with the Gaussian 03 series of programs.¹² Full geometry optimizations of stable species were performed in the gas phase by employing the hybrid density functional B3LYP¹³ with the 6-31G(d) basis set for nonmetal atoms¹⁴ together with the LANL2DZ for Re¹⁵ and by using the standard Schlegel’s algorithm.¹⁶ The B3LYP functional combines the Becke’s three-parameter nonlocal hybrid exchange potential with the nonlocal correlation functional of Lee, Yang, and Parr. The nature of the stationary points was verified by analytical computations of harmonic vibrational frequencies. H , ΔS , and ΔG were also calculated within the ideal gas, rigid rotor, and harmonic oscillator approximations.¹⁷ A pressure of 1 atm and a temperature of 298.15 K were assumed in the calculations. For interpretation purposes, a natural bond orbital (NBO) analysis was also performed.¹⁸

Crystal Structure Determination. General Description: For Compounds 1·ReO₄, 3·Cl, 3·Br, 3·NO₃ and 5·Br. For each structure determination, a single crystal was mounted on a Bruker diffractometer equipped with a SMART 1K or 6K CCD area detector and Oxford Cryostream N₂ cooling device, using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined with full-matrix least-squares technique on F^2 using the SHELXS and SHELXL programs. Information on the individual data collections and refinements can be found in the respective CIF files. CCDC-821877 (1·ReO₄), CCDC-821878 (3·Br), CCDC-821879 (3·Cl), CCDC-821880 (3·NO₃), and CCDC-821881 (5·Br) contain supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB2 1EZ, U. K.; fax: (+44) 1223–336033 or e-mail: deposit@ccdc.cam.ac.uk).

Synthesis of $[\text{Re}(\text{CO})_3(N\text{-MeIm})_2(2\text{-ampy})]\text{BAR}'_4$ (1·BAR'₄). *N*-MeIm (0.040 mL, 0.492 mmol) was added to a solution of $[\text{ReBr}(\text{CO})_5]$ (0.100 g, 0.246 mmol) in toluene (20 mL), and the mixture was refluxed for 30 min. The solvent was then evaporated to dryness under vacuum. The residue was redissolved in CH_2Cl_2 (20 mL). AgOTf (0.064 g, 0.246 mmol) was added, and the mixture was stirred in the dark for 1 h. The resulting solution was filtered from the white solid (AgBr) through Celite. NaBAR'_4 (0.209 g, 0.246 mmol) and 2-ampy (0.024 g, 0.246 mmol) were added, and the reaction mixture was allowed to stir at room temperature for 1 h. The solution was filtered off

(via canula) from the white solid (NaOTf) and concentrated to a volume of 5 mL; the addition of *n*-hexane (20 mL) caused the precipitation of $1 \cdot \text{BAR}'_4$ as a pale brown solid, which was washed with *n*-hexane (2×20 mL). Yield: 0.300 g, 88%. IR (CH_2Cl_2): 2032s, 1919s (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 7.76 [m, 8H, H_o , BAR'_4], 7.61 [s, 2H, CH, *N*-MeIm], 7.60 [m, 4H, H_p , BAR'_4], 7.55 [m, 1H, CH, 2-ampy], 7.28 [m, 1H, CH, 2-ampy], 7.00 [s, 2H, CH, *N*-MeIm], 6.93 [s, 2H, CH, *N*-MeIm], 6.79 [m, 1H, CH, 2-ampy], 6.51 [m, 1H, CH, 2-ampy], 5.41 [s, broad, 2H, NH_2 , 2-ampy], 3.71 [s, 6H, CH_3 , *N*-MeIm]. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 193.8 [CO], 193.5 [$2 \times \text{CO}$], 161.3 [q ($^1J_{\text{CB}} = 50.0$ Hz), C_i , BAR'_4], 160.1, 149.2 [2-ampy], 141.2 [*N*-MeIm], 140.0 [2-ampy], 134.8 [C_o , BAR'_4], 130.4 [*N*-MeIm], 128.8 [q ($^2J_{\text{CF}} = 31.6$ Hz), C_{mm} , BAR'_4], 124.6 [q ($^1J_{\text{CF}} = 272.4$ Hz), CF_3 , BAR'_4], 122.9 [*N*-MeIm], 117.5 [C_{pp} , BAR'_4], 114.6 [2-ampy], 112.0 [2-ampy], 34.7 [CH_3 , *N*-MeIm]. Anal. Calcd for $\text{C}_{48}\text{H}_{30}\text{BF}_2\text{N}_6\text{O}_3\text{Re}$: C, 41.42; H, 2.17; N, 6.04. Found: C, 41.54; H, 2.11; N, 6.06%.

Synthesis of $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(3\text{-ampy})]\text{BAR}'_4$ ($3 \cdot \text{BAR}'_4$).

The preparation was as described for $1 \cdot \text{BAR}'_4$, starting from $[\text{ReBr}(\text{CO})_5]$ (0.100 g, 0.246 mmol), *N*-MeIm (0.040 mL, 0.492 mmol), AgOTf (0.064 g, 0.246 mmol), NaBAR'_4 (0.209 g, 0.246 mmol), and 3-ampy (0.024 g, 0.246 mmol). Compound $3 \cdot \text{BAR}'_4$ was obtained as a white microcrystalline solid. Yield: 0.280 g, 82%. IR (CH_2Cl_2): 2031s, 1917s (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 7.89 [m, 1H, CH, 3-ampy], 7.75 [m, 8H, H_o , BAR'_4], 7.61 [m, 7H, CH + H_p and CH, 3-ampy + BAR'_4 and *N*-MeIm], 7.16 [m, 2H, CH, 3-ampy], 6.99 [s, 2H, CH, *N*-MeIm], 6.76 [s, 2H, CH, *N*-MeIm], 4.03 [s, broad, 2H, NH_2 , 3-ampy], 3.71 [s, 6H, CH_3 , *N*-MeIm]. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 197.1 [CO], 196.6 [$2 \times \text{CO}$], 164.1 [q ($^1J_{\text{CB}} = 49.5$ Hz), C_i , BAR'_4], 147.8, 144.5 [3-ampy], 143.5 [*N*-MeIm], 142.2 [3-ampy], 137.2 [C_o , BAR'_4], 132.5 [*N*-MeIm], 131.3 [q ($^2J_{\text{CF}} = 31.4$ Hz), C_{mm} , BAR'_4], 128.9 [3-ampy], 127.0 [q ($^1J_{\text{CF}} = 272.7$ Hz), CF_3 , BAR'_4], 126.6 [3-ampy], 125.2 [*N*-MeIm], 119.9 [C_{pp} , BAR'_4], 37.1 [CH_3 , *N*-MeIm]. Anal. Calcd for $\text{C}_{48}\text{H}_{30}\text{BF}_2\text{N}_6\text{O}_3\text{Re}$: C, 41.42; H, 2.17; N, 6.04. Found: C, 41.72; H, 2.16; N, 5.98%.

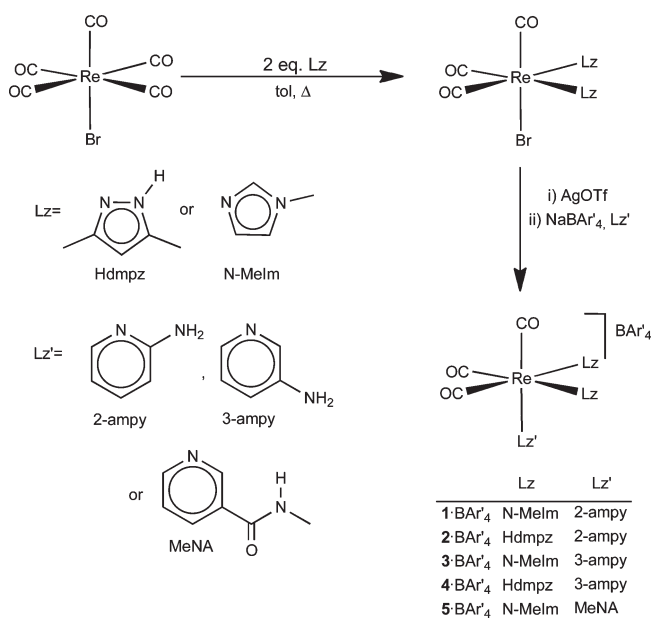
Synthesis of $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{MeNA})]\text{BAR}'_4$ ($5 \cdot \text{BAR}'_4$).

Compound $5 \cdot \text{BAR}'_4$ was prepared as described above for compound $1 \cdot \text{BAR}'_4$ starting from $[\text{ReBr}(\text{CO})_5]$ (0.100 g, 0.246 mmol), *N*-MeIm (0.040 mL, 0.492 mmol), AgOTf (0.064 g, 0.246 mmol), NaBAR'_4 (0.209 g, 0.246 mmol), and MeNA (0.035 g, 0.246 mmol). Yield: 0.251 g, 71%. IR (CH_2Cl_2): 2033s, 1919s (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 8.90 [m, 1H, CH, MeNA], 8.53 [m, 1H, CH, MeNA], 8.20 [m, 1H, CH, MeNA], 7.77 [m, 8H, H_o , BAR'_4], 7.65 [s, 2H, CH, *N*-MeIm], 7.60 [m, 4H, H_p , BAR'_4], 7.54 [m, 1H, CH, MeNA], 7.06 [s, 2H, CH, *N*-MeIm], 6.76 [s, 2H, CH, *N*-MeIm], 6.27 [s, broad, 1H, NH , MeNA], 3.77 [s, 6H, CH_3 , *N*-MeIm], 3.00 [d ($^3J_{\text{HH}} = 5.0$ Hz), CH_3 , MeNA]. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 194.3 [CO], 193.8 [$2 \times \text{CO}$], 163.2 [CO, MeNA], 161.7 [q ($^1J_{\text{CB}} = 49.9$ Hz), C_i , BAR'_4], 154.8, 153.1 [MeNA], 141.2 [*N*-MeIm], 136.8 [MeNA], 134.8 [C_o , BAR'_4], 133.3 [MeNA], 130.0 [*N*-MeIm], 128.9 [q ($^2J_{\text{CF}} = 32.7$ Hz), C_{mm} , BAR'_4], 126.2 [MeNA], 124.6 [q ($^1J_{\text{CF}} = 272.3$ Hz), CF_3 , BAR'_4], 123.1 [*N*-MeIm], 117.5 [C_{pp} , BAR'_4], 34.7 [CH_3 , *N*-MeIm], 26.7 [CH_3 , MeNA]. Anal. Calcd for $\text{C}_{50}\text{H}_{32}\text{BF}_2\text{N}_6\text{O}_4\text{Re}$: C, 41.88; H, 2.25; N, 5.86. Found: C, 41.97; H, 2.26; N, 5.99%.

RESULTS AND DISCUSSION

The mixed compounds were prepared in a stepwise manner by sequential substitution reactions from $[\text{ReBr}(\text{CO})_5]$ (see Scheme 1). The reaction of $[\text{ReBr}(\text{CO})_5]$ with two equivalents of the azole (*N*-methylimidazole, *N*-MeIm, or 3,5-dimethylpyrazole, Hdmpz) in refluxing toluene afforded after 30 min the corresponding *fac*-tricarbonyl complexes $[\text{ReBr}(\text{CO})_3(\text{Lz})_2]$ ($\text{Lz} = \text{Hdmpz}$ or *N*-MeIm). The reactions of these neutral complexes with AgOTf led to the substitution of the bromide by the labile triflate ligand, which was subsequently replaced by the 2- or 3-aminopyridine (2-ampy or 3-ampy) moiety in the presence of the NaBAR'_4 salt

Scheme 1. Synthesis of the “Mixed” Organometallic Compounds $[1-5] \cdot \text{BAR}'_4$



(used as a triflate abstractor, taking advantage of the low solubility of sodium triflate in dichloromethane, and as the way to introduce the noncoordinating BAR'_4 counteranion) to afford the cationic compounds $[\text{Re}(\text{CO})_3(\text{Lz})_2(\text{ampy})]\text{BAR}'_4$ (see Scheme 1).

Compounds $[1-4] \cdot \text{BAR}'_4$ were spectroscopically characterized in solution by IR and NMR spectroscopies (see the Experimental Section). The IR spectra showed the typical pattern for cationic complexes of the *fac*- $\{\text{Re}(\text{CO})_3\}$ fragment, whose ν_{CO} values are similar to those of the $[\text{Re}(\text{CO})_3(\text{Lz})_3]^+$ complexes previously reported.^{5,7} ^1H and ^{13}C NMR spectra showed the equivalence of the two Hdmpz or *N*-MeIm ligands present in each complex and only two signals for the three CO ligands indicating the existence of a molecular mirror plane in each compound. For compounds $1 \cdot \text{BAR}'_4$ and $4 \cdot \text{BAR}'_4$, the presence in the ^1H NMR spectra of two different signals for the two methyl groups indicated that a fast dissociation-recoordination process of the pyrazole ligands does not take place.

All of the new compounds $[1-4] \cdot \text{BAR}'_4$ were found to be stable in solution for at least two days at room temperature, and no product of intermolecular ligand redistribution could be spectroscopically detected. The behavior of $[1-4] \cdot \text{BAR}'_4$ toward several anions, as their tetrabutylammonium salts, were investigated by means of IR and NMR spectroscopy. Compounds $1 \cdot \text{BAR}'_4$ and $2 \cdot \text{BAR}'_4$, with the 2-ampy ligand, were found to be labile in the presence of chloride, bromide, or nitrate anions in solution, as was clearly evidenced by a $10\text{--}15\text{ cm}^{-1}$ shift to lower wavenumber values in the IR spectra. In the case of the bromide, the addition of an equimolar amount of $[\text{Bu}_4\text{N}][\text{Br}]$ to the solution of compound $1 \cdot \text{BAR}'_4$ or $2 \cdot \text{BAR}'_4$ led to the formation of the previously known neutral products $[\text{ReBr}(\text{CO})_3(\text{Hdmpz})_2]$ ¹⁹ or $[\text{ReBr}(\text{CO})_3(\text{N-MeIm})_2]$,²⁰ respectively, indicating that the 2-ampy ligand is displaced by the bromide anion. Compounds $1 \cdot \text{BAR}'_4$ and $2 \cdot \text{BAR}'_4$ were found to be stable only in the presence of the weakly basic anions ReO_4^- and ClO_4^- . Slow diffusion of hexane into a concentrated solution of an equimolar mixture of $1 \cdot \text{BAR}'_4$ and $[\text{Bu}_4\text{N}][\text{ReO}_4]$ at -20°C

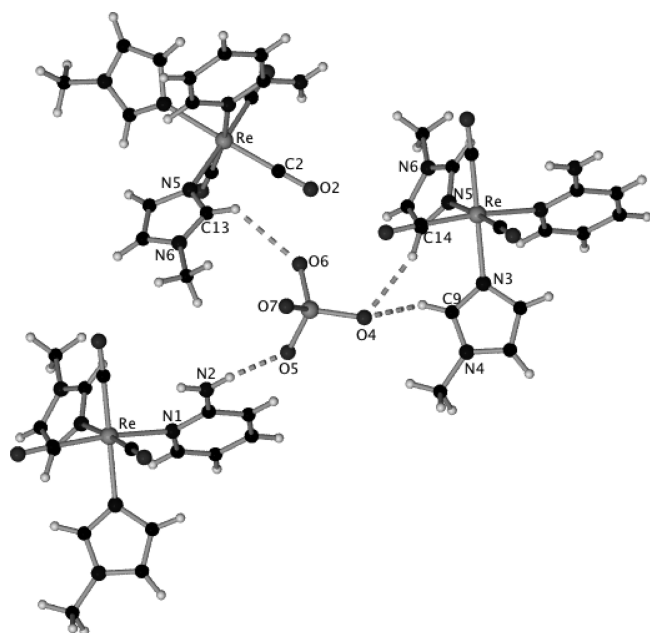


Figure 2. Molecular structure of $1 \cdot \text{ReO}_4$ showing the main hydrogen bonds as dashed lines.

afforded crystals of the $1 \cdot \text{ReO}_4$ adduct,²¹ while the salt $[\text{Bu}_4\text{N}][\text{BAR}'_4]$ remained in solution.

As shown in Figure 2, the cation of $1 \cdot \text{ReO}_4$ is a *fac*- $\{\text{Re}(\text{CO})_3\}$ pseudooctahedral complex, with a 2-ampy and two N-MeIm ligands bonded to the metal center. 2-Aminopyridine is coordinated in its most usual mode through the pyridinic nitrogen. One N–H group of the amino moiety forms a hydrogen bond with one oxygen atom of the perchlorate anion ($d(\text{N}2 \cdots \text{O}5) = 2.940 \text{ \AA}$, $\angle(\text{N}2-\text{H} \cdots \text{O}5) = 174.0^\circ$), while O4 and O6 atoms form weaker hydrogen bonds with imidazole central CH groups of other cationic complexes (see Figure 2). Therefore, the oxoanion interacts with at least three rhenium complexes, through hydrogen bonds with NH and central CH groups, but there is no evidence in the solid state of simultaneous interaction of NH and NC(H)N groups of the same metal cation with the oxygen atoms of a given external anionic guest.

In contrast, the structure of $2 \cdot \text{ClO}_4$, determined by X-ray diffraction (Figure 3), shows that, in this case, the 2-ampy ligand is bonded to the Re atom through the amino group. The participation of the amino group in the coordination of 2-aminopyridine to a metal center is rare, and only a few examples of complexes with neutral 2-ampy ligands acting as bridges are known.²² $\text{N}(\kappa^1)$ -bonding via the exocyclic amino group is rather exceptional and may occur only if coordination at the pyridine N-donor site is not feasible for steric reasons.²³ In $2 \cdot \text{ClO}_4$, this feature is attributed to the presence of an intramolecular hydrogen bond between the N–H group of one of the pyrazole ligands and the pyridine nitrogen atom, characterized by $\text{N}4 \cdots \text{N}6 = 2.893(7) \text{ \AA}$ and $\text{N}4-\text{H} \cdots \text{N}6 = 162.3(6)^\circ$. In addition, the ClO_4^- anion forms weak hydrogen bonds with N–H groups of pyrazole and 2-ampy ligands. Hydrogen bonds between the perchlorate anion and one cationic host are shown in Figure 3, as dotted lines (for a more complete view, see the Supporting Information).

Compound $3 \cdot \text{BAR}'_4$, with a 3-ampy ligand, was found to be stable toward the addition of external anionic substrates

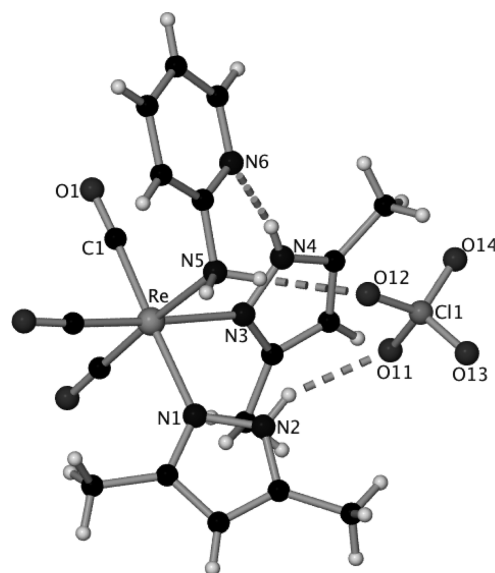


Figure 3. Molecular structure of $2 \cdot \text{ClO}_4$ showing the main hydrogen bond interactions.

resembling the behavior found for $4 \cdot \text{BAR}'_4$, which features the same pyridinic ligand.⁸ For pyrazole compounds $2 \cdot \text{BAR}'_4$ and $4 \cdot \text{BAR}'_4$, the dramatically different stability toward the substitution reactions by external anions can be attributed to the different coordination mode of the aminopyridine ligand: the amino bonded 2-ampy in $2 \cdot \text{BAR}'_4$ is labile, whereas the pyridine-ligated 3-ampy in $4 \cdot \text{BAR}'_4$ is stable. For N-methylimidazole derivatives $1 \cdot \text{BAR}'_4$ and $3 \cdot \text{BAR}'_4$, in which the ampy ligands are in the same coordination mode, steric hindrance should be responsible for the different stability found: the amino group *ortho* to the pyridinic nitrogen makes the ligand bulkier and therefore more labile than in $3 \cdot \text{BAR}'_4$, in which the amino group is in a *meta* position.

Density functional theory (DFT) computations at the B3LYP/6-31G(d) (LANL2DZ for Re) level of theory were employed to fully optimize the structures of complexes 1–4 (see the Supporting Information for computational details). Given the different species determined by X-ray diffraction, two isomeric forms were considered in our calculations for each complex that is identified by the corresponding Roman numeral. This is followed by either the letter **a** for the amino-bonded isomer or letter **b** for the pyridine-bonded one. In Figure 4, ball-and-stick representations of the optimized structures for both idealized isomers are shown for complexes 2 and 4. Figure S1 and Table S1 in the Supporting Information collect the optimized structures for complexes 1 and 3 and all the energy data, respectively.

Consistent with the experimental observations, on the basis of the Gibbs energy difference between the two optimized isomers, **IIa** is more stable than **IIb** by 2.8 kcal/mol (Figure 4). This unusual coordination of the 2-ampy ligand can be attributed to the formation of a strong intramolecular hydrogen bond between the pyridinic nitrogen and a NH-pyrazole group. In effect, a NBO (natural bond orbital) analysis indicates that complex **IIa** shows a strong interaction between the electron lone pair of the pyridine nitrogen and the σ antibonding N–H of the pyrazole group with a second order perturbation energy of 19.6 kcal/mol. Therefore, the formation of the hydrogen bond between the pyridinic nitrogen and pyrazole N–H group is the main delocalization of

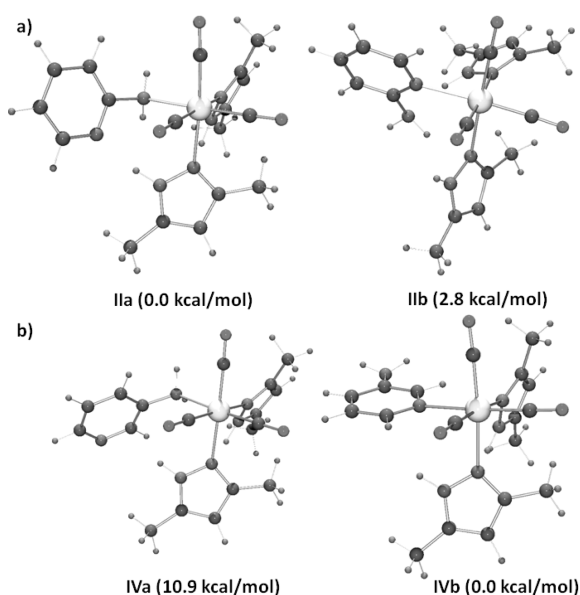


Figure 4. B3LYP/6-31G* optimized structures for cationic complexes 2 (a) and 4 (b).

the lone pair of the pyridine nitrogen. In contrast, for **IIb**, the formation of a hydrogen bond between the N–H of pyrazole and the amino group ($N_{\text{pyrazole}}-\text{H}\cdots N_{\text{amino}}$) implies a second-order perturbation energy of only 4.5 kcal/mol, the principal delocation of the lone pair of the amino nitrogen being into the pyridinic ring (32.5 kcal/mol).

For complex **4**, analogous to **2** with a 3-ampy ligand, the orientation of the amino moiety precludes the formation of the mentioned hydrogen bond. Accordingly, the theoretical calculations have shown that the pyridine-bonded isomer, **IVb**, is 10.9 kcal/mol more stable than **IVa** (Figure 4b). This situation is virtually identical to that of complex **3**, $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(3\text{-ampy})]^+$, isomer **IIIb** (pyridine-bonded) being 10.2 kcal/mol more stable than **IIIa** (amino-bonded isomer).²⁴ Finally, geometry optimizations were undertaken for complex **1**, $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(2\text{-ampy})]^+$, which contains a 2-ampy ligand but does not feature pyrazole NH groups able to form strong hydrogen bonds. In this case, the pyridinic isomer (**1b**) is preferred over the amino-bonded one (**1a**) by 3.2 kcal/mol.²⁴ The smaller energy difference in the latter with respect to **IIIa** and **IIIb** and **IVa** and **IVb** isomers is probably due to the more steric hindrance of the amino group being in an *ortho* instead of a *meta* position. This fact is in complete concordance with the experimental finding of the 2-ampy ligand being much more labile than 3-ampy in **1**· BAR'_4 and **3**· BAR'_4 receptors (see above).

The addition of $\text{Bu}_4\text{N}\cdot\text{X}$ salts ($\text{X} = \text{F}^-$, Cl^- , Br^- , I^- , CH_3COO^- , NO_3^- , and ReO_4^-) to **3**· BAR'_4 solutions in CD_2Cl_2 caused noticeable shifts in the ^1H NMR spectroscopic signals of the amine N–H and imidazole NC(H)N groups. Anion exchange was found to be fast, and 1:1 binding constants (Job plots for chloride and nitrate anions, indicating formation of 1:1 adducts, are shown in Figure 5) were obtained from ^1H NMR titrations in CD_2Cl_2 .¹¹ The magnitudes of these binding constants were found to be on the same order when they were calculated either from the amino N–H or from the imidazole C–H downfield shifts in the ^1H NMR spectra. The relative magnitude of the binding constants (Table 1) showed that the

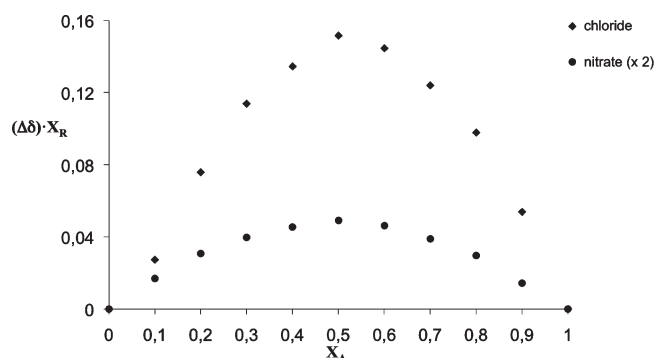


Figure 5. Job plot of receptor **3**· BAR'_4 toward chloride and nitrate anions.

Table 1. Binding Constant Values for Compound **3**· BAR'_4 in CD_2Cl_2

anion	K_a/M^{-1}	anion	K_a/M^{-1}
F^-	2129 (± 323)	NO_3^-	490 (± 39)
Cl^-	1220 (± 56)	ReO_4^-	246 (± 29)
Br^-	1405 (± 204)	CH_3COO^-	547 (± 4)
I^-	799 (± 68)		

substitution of one *N*-MeIm by a 3-ampy ligand increases the strength of the anion binding by the complex. More interestingly, the K_a value for acetate, one of the more basic anions employed, is quite low, a fact that can be attributed to a preference of the receptor for small, spherical anions.

Single crystals of the chloride, bromide, and nitrate adducts were obtained by the slow diffusion of hexane into saturated CH_2Cl_2 solutions at -20°C . The solid state structures were determined by X-ray diffraction, and it was found that in every case the $\text{Bu}_4\text{N}\cdot\text{BAR}'_4$ salt crystallized separately. The metallic cationic complex was found to be virtually identical in the three adducts: a pseudooctahedral rhenium atom bearing three carbonyl ligands in a facial disposition, two *N*-MeIm and one 3-ampy ligand coordinated to the metal through the pyridine nitrogen. The solid state structures of both halide adducts (Cl^- and Br^-)^{25,26} are quite complex, resulting in tridimensional networks of hydrogen bonds between the halides and amino N–H and imidazole central C–H groups of the cationic rhenium complexes (Figure 6). Each halide anion participates in several hydrogen bonds, the stronger interactions being those that involve the N–H groups of the amino moieties of 3-ampy ligands.

The solid state structure of the **3**· NO_3 adduct (shown in Figure 7)²⁷ can be described as antiparallel ribbons of cationic rhenium complexes, the nitrate anions being encapsulated between them. Within each ribbon, the rhenium complexes orient their $\{\text{Re}(\text{CO})_3\}$ fragments toward the outside and their hydrogen bond donor side toward the nitrate anions. Each nitrate anion interacts at least with three metal cations, and it was found that the stronger hydrogen bonds are those of the amino group [$d(\text{N}6\cdots\text{O}7) = 2.919\text{ \AA}$, $\angle(\text{N}6-\text{H}\cdots\text{O}7) = 173^\circ$, $d(\text{N}6\cdots\text{O}8) = 3.116\text{ \AA}$, $\angle(\text{N}6-\text{H}\cdots\text{O}8) = 158^\circ$].

The N–H groups of amides are considerably stronger hydrogen bond donors than those of amines. Therefore, a compound with methylnicotinamide as a ligand instead of 3-ampy should bind anions more effectively than the 3-ampy analogue.

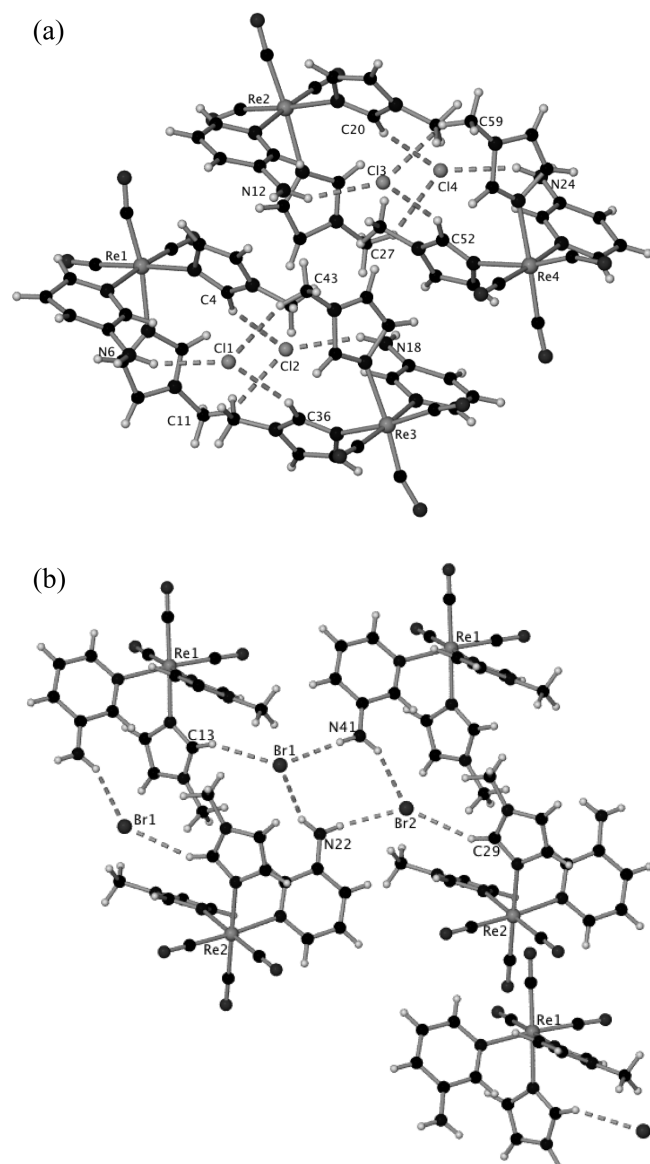


Figure 6. Molecular structure of (a) $3 \cdot \text{Cl}$ and (b) $3 \cdot \text{Br}$ adducts, showing the main hydrogen bonds as dotted lines.

However, the strongly electron-withdrawing alkoxy carbonyl substituent should make the pyridine ligand a weaker donor than the 3-ampy, and therefore one would need to worry about the stability of the rhenium complex. Compound $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{MeNA})]\text{BAR}'_4$ ($5 \cdot \text{BAR}'_4$, MeNA = methylnicotinamide) was prepared following the same procedure used before for the synthesis of compounds $[1-4] \cdot \text{BAR}'_4$, using methylnicotinamide instead of an ampy ligand. Compound $5 \cdot \text{BAR}'_4$ was obtained in good yield (71%), as the only product of the reaction, as a yellow analytically pure solid (see the Experimental Section). The complex was found to be stable against ligand dissociation and redistribution. The ability of $5 \cdot \text{BAR}'_4$ to act as an anion receptor was determined in solution by measuring the association constants (K_a) in CD_2Cl_2 . The results for several anions are summarized in Table 2, and Job plots showed that the adducts have a 1:1 receptor/anion ratio (the Job Plots are given as Supporting Information).

The binding constants are higher than those of *N*-methylimidazole rhenium receptors, discussed above, showing the higher

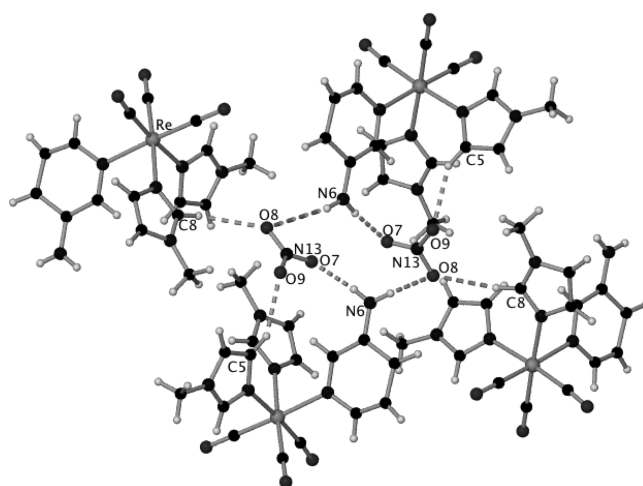


Figure 7. Molecular structure of $3 \cdot \text{NO}_3$ host-guest adduct, showing the main hydrogen bond interactions as dashed lines.

Table 2. Binding Constant Values for Compound $5 \cdot \text{BAR}'_4$ in CD_2Cl_2

anion	K_a/M^{-1}	anion	K_a/M^{-1}
F^-	11802 (± 1981)	I^-	2294 (± 247)
Cl^-	13550 (± 1520)	NO_3^-	1738 (± 149)
Br^-	2358 (± 203)	NO_3^-	2060 (± 340)

ability of the amido N–H group to act as a hydrogen bond donor group. In addition, there is a significant preference for fluoride and chloride anions over other anions tested. Unfortunately, crystals of these halide adducts ($5 \cdot \text{F}$ or $5 \cdot \text{Cl}$) could not be grown despite numerous attempts using different conditions. The solid state structure of the bromide adduct, which crystallized separately to the $\text{Bu}_4\text{N} \cdot \text{BAR}'_4$ salt, was determined by X-ray diffraction.²⁸ As shown in Figure 8a, the rhenium primary coordination sphere is in agreement with the one deduced from spectroscopic data in solution, the Re–N(MeNA) distance being noticeably longer [$d(\text{Re}–\text{N5}) = 2.242(2)$ Å] than the Re–N(ampy) bond distances found [$2.189(4)$ Å for $3 \cdot \text{Br}$, for example]. This fact can be attributed to the higher electronic withdrawing ability of the carbamoyl group present in the nicotinamide ligand. As shown in Figure 8a, the bromide anion interacts simultaneously through hydrogen bonds with the amido N–H group [$d(\text{N6} \cdots \text{Br1}) = 3.263$ Å, $\angle(\text{N6}–\text{H} \cdots \text{Br1}) = 158.6^\circ$], and with the central C–H group of one N–MeIm ligand [$d(\text{C4} \cdots \text{Br1}) = 3.601$ Å, $\angle(\text{C4}–\text{H} \cdots \text{Br1}) = 155.9^\circ$]. The remaining imidazole NC(H)N group of the rhenium cation forms a hydrogen bond with the CO group of the amido-pyridine ligand of a neighbor complex [$d(\text{C8} \cdots \text{O4}) = 3.254$ Å, $\angle(\text{C8}–\text{H} \cdots \text{O4}) = 170.71^\circ$], so the structure results in chains (see Figure 8b).

In view of the solid state structure of the bromide adduct, it can be suggested that the smaller size of fluoride and chloride should allow them to approach closer to the hydrogen bond donor groups. This would produce stronger hydrogen bonds and a higher electrostatic attraction and therefore a stronger overall receptor–anion interaction, in agreement with the behavior found in solution for fluoride and chloride anions.

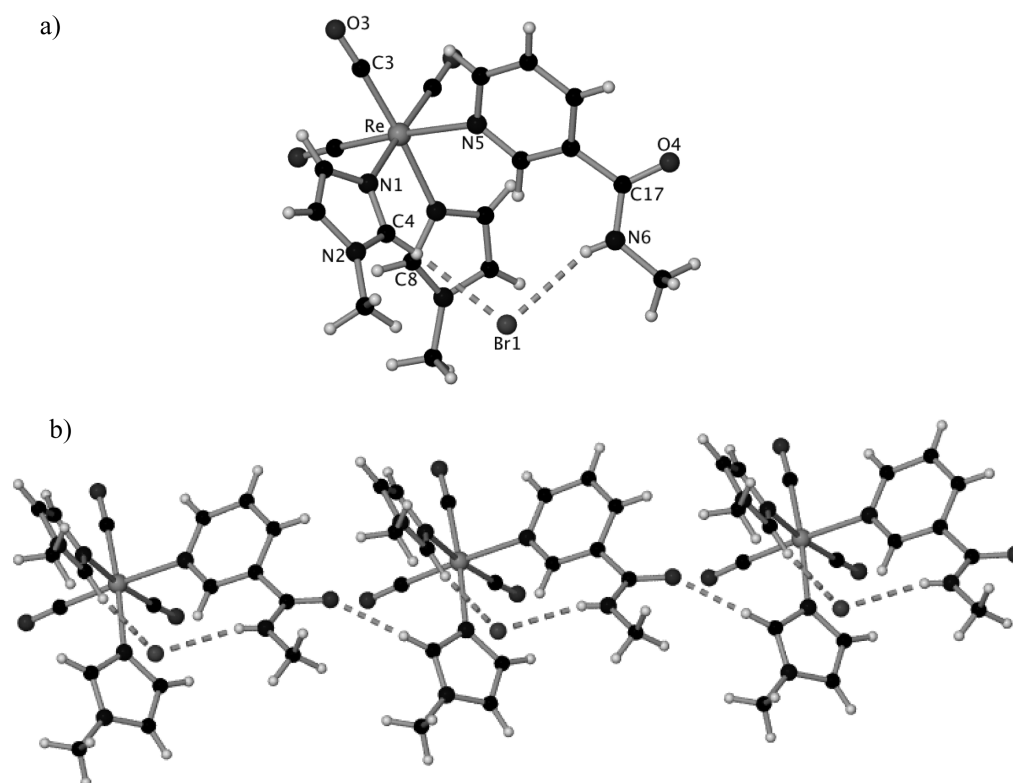


Figure 8. (a) Molecular structure of the $5 \cdot \text{Br}$ adduct, showing the main intramolecular hydrogen bonds as dashed lines. (b) View of the intermolecular interactions in $5 \cdot \text{Br}$, which lead to infinite chains.

CONCLUSIONS

Organometallic anion receptors derived from the $\{\text{Re}(\text{CO})_3\}$ fragment combining more than one class of hydrogen bond donor ligands can be easily prepared. The substitution of an azole by an amino or amido pyridine ligand in tris(imidazole) or tris(pyrazole) $[\text{Re}(\text{CO})_3(\text{Lz})_3]\text{BAR}'_4$ compounds leads to more selective anion receptors. The situation of the amino group in ampy ligands is crucial for determining the stability of its compounds. While $3 \cdot \text{BAR}'_4$ and $4 \cdot \text{BAR}'_4$, featuring a 3-ampy ligand, were found to be stable toward the addition of external anions, compounds with the 2-ampy ligand, $1 \cdot \text{BAR}'_4$ and $2 \cdot \text{BAR}'_4$, are labile in the presence of external anions. The solid state structure of $2 \cdot \text{ClO}_4$ revealed that the 2-ampy ligand is bonded to the rhenium atom through the amino moiety, a very rare coordination mode. DFT calculations along with an NBO analysis have shown that, for complex **2**, the amino-bonded isomer is preferred over the pyridine-bonded isomer by 2.83 kcal/mol, due to the formation of a strong intramolecular hydrogen bond between the pyridine nitrogen and the pyrazole N–H group. In the other complexes studied herein, the pyridinic coordination of ampy ligands is favored, both experimentally and theoretically. Compound $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{MeNA})]\text{BAR}'_4$ ($5 \cdot \text{BAR}'_4$) featuring a methylnicotinamide ligand showed a high preference for fluoride and chloride anions.

ASSOCIATED CONTENT

S Supporting Information. X-ray crystallographic data for compounds $1 \cdot \text{ReO}_4$, $3 \cdot \text{Br}$, $3 \cdot \text{Cl}$, $3 \cdot \text{NO}_3$, and $5 \cdot \text{Br}$ in CIF format; absolute and relative energies of complexes **1–4** and their optimized structures; ^1H NMR titration profiles; and Job

plots. This material is available free of charge via the Internet at <http://pubs.acs.org>

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DEDICATION

[▽]This paper is dedicated to the memory of Professor F. Gordon A. Stone.

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(21) Selected crystallographic data for **1**·ReO₄: C₁₆H₁₈N₆O₇Re₂, *M* = 778.78, monoclinic, *P*2₁/*c*, *a* = 11.563(3) Å, *b* = 14.051(4) Å, *c* = 14.491(4) Å, α = 90.0°, β = 112.798(5)°, γ = 90.0°, 120(2) K, *V* = 2170.5(10) Å³, *Z* = 4, 14 140 reflections measured, 3128 independent (*R*_{int} = 0.046). *R*₁ = 0.0305, *wR*₂ = 0.0659 (all data).

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(25) Selected crystallographic data for **3**·Cl: C₁₆H₁₈ClN₆O₃Re, *M* = 564.01, monoclinic, *P*2₁, *a* = 10.645(3) Å, *b* = 32.016(8) Å, *c* = 13.969(3) Å, α = 90.0°, β = 106.057(4)°, γ = 90.0°, 120(2) K, *V* = 4575(2) Å³, *Z* = 8, 47708 reflections measured, 20434 independent (*R*_{int} = 0.071). *R*₁ = 0.0981, *wR*₂ = 0.2866 (all data).

(26) Selected crystallographic data for **3**·Br: C_{34.5}H₄₁Br₂Cl₅N₁₂O₆Re₂, *M* = 1429.26, triclinic, *P* $\bar{1}$, *a* = 10.9770(18) Å, *b* = 14.000(2) Å, *c* = 16.027(3) Å, α = 83.475(3)°, β = 88.023(3)°, γ = 74.495(3)°, 120(2) K, *V* = 2358.0(6) Å³, *Z* = 2, 21 004 reflections measured, 6782 independent (*R*_{int} = 0.0469). *R*₁ = 0.0295, *wR*₂ = 0.0547 (all data).

(27) Selected crystallographic data for **3**·NO₃: C₁₆H₁₈N₇O₉Re, *M* = 590.57, monoclinic, *P*2₁/*c*, *a* = 31.69(3) Å, *b* = 7.200(6) Å, *c* = 18.848(17) Å, α = 90.0°, β = 105.62(3)°, γ = 90.0°, 120(2) K, *V* = 4142(6) Å³, *Z* = 8, 35 168 reflections measured, 11 042 independent (*R*_{int} = 0.109). *R*₁ = 0.2185, *wR*₂ = 0.4849 (all data).

(28) Selected crystallographic data for **5**·Br: C₁₈H₂₀BrN₆O₄Re, *M* = 650.51, monoclinic, *P*2₁/*c*, *a* = 17.646(4) Å, *b* = 9.6410(19) Å, *c* = 12.888(3) Å, α = 90.0°, β = 103.27(3)°, γ = 90.0°, 120(2) K, *V* = 2134.0(7) Å³, *Z* = 4, 37 286 reflections measured, 7323 independent (*R*_{int} = 0.0319). *R*₁ = 0.0271, *wR*₂ = 0.0648 (all data).