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Rhenium-Mediated Coupling of Acetonitrile and Pyrazoles. New Molecular Clefts for Anion Binding§

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The reaction of *fac*-[ReBr(CO)$_3$(NCMe)$_2$] (**1**) with either pyrazole (Hpz) or 3,5-dimethylpyrazole (Hdmpz) in a 1:2 Re/pyrazole ratio affords the known complexes *fac*-[ReBr(CO)$_3$(Hpz)$_2$] (**2**) and [ReBr(CO)$_3$(Hdmpz)$_2$] (**3**). Using a 1:1 ratio, MeCN as solvent, and longer reaction times led to a mixture in which the major components are the pyrazolylamidino complexes *fac*-[ReBr(CO)$_3$(H*N*═C(CH$_3$)pz-κ^2*N*,*N*)] (**4**) and *fac*-[ReBr(CO)$_3$(H*N*═C(CH$_3$)dmpz-κ^2*N*,*N*)] (**5**). The complexes *fac*-[ReBr(CO)$_3$(Hpz)(NCMe)] (**6**) and *fac*-[ReBr(CO)$_3$(Hdmpz)(NCMe)] (**7**) (along with **2** and **3**) were found to be minor components of these reactions. Analogous reactions of *fac*-[Re(OClO$_3$)(CO)$_3$(NCMe)$_2$] yielded *fac*-[Re(NCCH$_3$)(CO)$_3$(H*N*═C(CH$_3$)pz-κ^2*N*,*N*)]ClO$_4$ (**8**), *fac*-[Re(NCCH$_3$)(CO)$_3$(H*N*═C(CH$_3$)dmpz-κ^2*N*,*N*)]ClO$_4$ (**9**), *fac*-[Re(Hpz)(CO)$_3$(H*N*═C(CH$_3$)pz-κ^2*N*,*N*)]ClO$_4$ (**10**), and *fac*-[Re(Hdmpz)(CO)$_3$(H*N*═C(CH$_3$)dmpz-κ^2*N*,*N*)]ClO$_4$ (**11**). The X-ray structure of **11** showed the perchlorate anion to be hydrogen-bonded by the N–H groups of the pyrazole and pyrazolylamidino ligands. The behavior of the compound *fac*-[Re(Hdmpz)(CO)$_3$(H*N*═C(CH$_3$)dmpz-κ^2*N*,*N*)]BAr′$_4$ (**13**) (synthesized by reaction of [ReBr(CO)$_3$(Hdmpz)$_2$] (**3**) with (i) AgOTf and (ii) NaBAr′$_4$/MeCN) as an anion receptor has been studied in CD$_3$CN solution. In addition, the structure of the supramolecular adduct *fac*-[Re(CO)$_3$(Hdmpz)(H*N*═C(CH$_3$)dmpz-κ^2*N*,*N*)]·Cl (**14**), featuring chloride binding by the two N–H groups, was determined by X-ray diffraction.

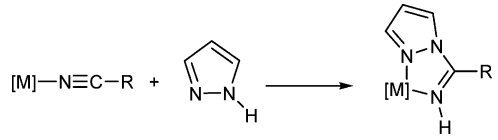
Introduction

The reaction of a pyrazole and a nitrile in the presence of a transition metal center to yield a metal-ligated pyrazolylamidino group was reported for the first time by McCleverty and co-workers in 1986.[1] Since then, only a few other examples of this reaction have been published.[2] The reaction, depicted in Scheme 1, can be described as an addition of the N−H bond of the pyrazole across the nitrile C≡N bond.[3]

Mechanistically, it is generally considered to be a nucleophilic addition to the nitrile,[4] which electrophilic character is enhanced by coordination to a Lewis-acidic metal fragment.

Some of us have recently reported such a reaction on a manganese tricarbonyl center,[5] and it seemed to us that it would be of interest to extend this chemistry to rhenium because its more kinetically inert character could allow the isolation of intermediates.

Scheme 1. Formation of a Metal-Ligated Pyrazolylamidino Group



In the course of our study, it was found that the amidino N−H group of the pyrazolylamidino products can act as a

§ This paper is dedicated to Professor Victor Riera on the occasion of his 70th birthday.

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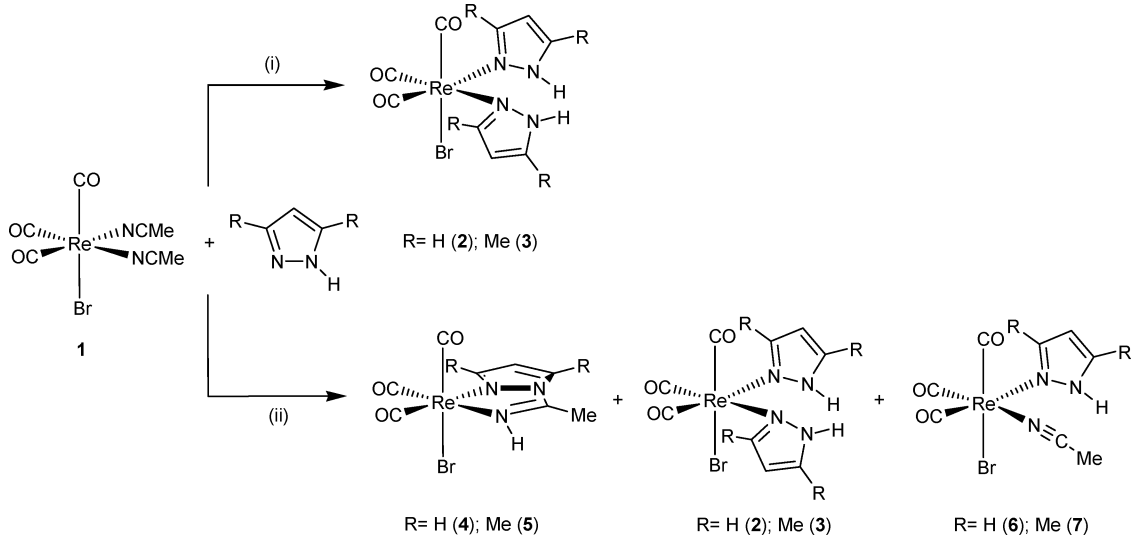
Scheme 2. Reactions of **1** with Pyrazoles in (i) 1:2 Ratio, Toluene, Reflux, 30 min and (ii) 1:1 Ratio, MeCN, Reflux, 14 h



hydrogen-bond donor toward external anions. Some of us have recently reported that the compounds *fac*-[Re(CO)$_3$(Hpz)$_3$]BAr′$_4$ (Hpz = generic pyrazole, Ar′ = 3,5-bis(trifluoromethyl)phenyl) interact with anions through a combination of electrostatic attraction and hydrogen bonds with two of the N−H pyrazole groups.[6] Individual hydrogen bonds are relatively weak, and the simultaneous occurrence of at least two of them (as, for instance, in ureas) is required for significant anion binding. It occurred to us that, in a rhenium tricarbonyl complex featuring both a pyrazolylamidino ligand and a pyrazole ligand, there would be two N−H groups in mutual cis disposition (there is a strong preference for a *fac* geometry in Re(CO)$_3$ derivatives, and therefore, the three rhenium-bonded nitrogen atoms in a pyrazolylamidino-pyrazole complex would be necessarily also in a mutual *fac* disposition). Then, those N−H groups would be able to simultaneously interact with an external anion. The present paper reports our efforts to delineate the conditions in which different, neutral and cationic, rhenium tricarbonyl pyrazolylamidino complexes can be synthesized, as well as the behavior of one of these complexes, namely, a cationic pyrazolylamidino-pyrazole derivative, as an anion receptor.

Results and Discussion

The reactions of *fac*-[ReBr(CO)$_3$(NCMe)$_2$] (**1**) with either pyrazole (Hpz) or 3,5-dimethylpyrazole (Hdmpz) in a 1:2 rhenium/pyrazole ratio, in refluxing toluene, afford, in 30 min, the complexes *fac*-[ReBr(CO)$_3$(Hpz)$_2$] (**2**) or *fac*-[ReBr(CO)$_3$(Hdmpz)$_2$] (**3**), previously reported by Ardizzoia, Masciocchi, and co-workers.[7] The reactions are simple thermal substitutions of the two nitrile ligands, a well-known transformation. However, when the reactions are carried out using equimolar amounts of the reagents, acetonitrile as solvent, and a long refluxing time, the new complexes *fac*-[ReBr(CO)$_3$(H*N*=C(CH$_3$)pz-κ^2*N*,*N*)] (**4**) or *fac*-[ReBr(CO)$_3$(H*N*=C(CH$_3$)dmpz-κ^2*N*,*N*)] (**5**) are obtained as the major products (see Scheme 2 and Experimental Section). These reactions involve not only nitrile substitution but also the coupling of pyrazole and nitrile to afford the pyrazolylamidino ligand, coordinated as a bidentate chelate in **4** and **5**. The coupling requires excess of the nitrile reagent, employed as solvent, as otherwise the reaction of the nitrile complexes yields the bis(pyrazole) substitution products. This suggests that nitrile is, compared with pyrazole, a labile ligand, and without excess nitrile, formation of the bis(pyrazole) complexes occurs, which would be unreactive toward nitrile. This idea agrees with the general assumption that the coupling resulting in the amidino formation proceeds by nucleophilic attack of pyrazole on a coordinated, metal-activated nitrile.

The bis(pyrazole) complexes **2** and **3**, along with trace amounts of the new complexes *fac*-[ReBr(CO)$_3$(Hpz)(NCMe)] (**6**) and *fac*-[ReBr(CO)$_3$(Hdmpz)(NCMe)] (**7**), are obtained as minor products. Attempts to synthesize selectively the pyrazolylamidino complexes by varying solvents, temperature, and reaction time were unsuccessful. This behavior is similar to that observed for the syntheses of related pyrazolylamidino manganese complexes.[5]

The new compounds were characterized by IR, NMR, and microanalysis (see Experimental Section). In addition, the structures of **5** and **7** were determined by X-ray diffraction. Thermal ellipsoid plots are shown in Figure 1. These results establish the structures as the ones shown in Scheme 2 and are otherwise unremarkable.

(3) For a review of amidino ligands, see: Baker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219.

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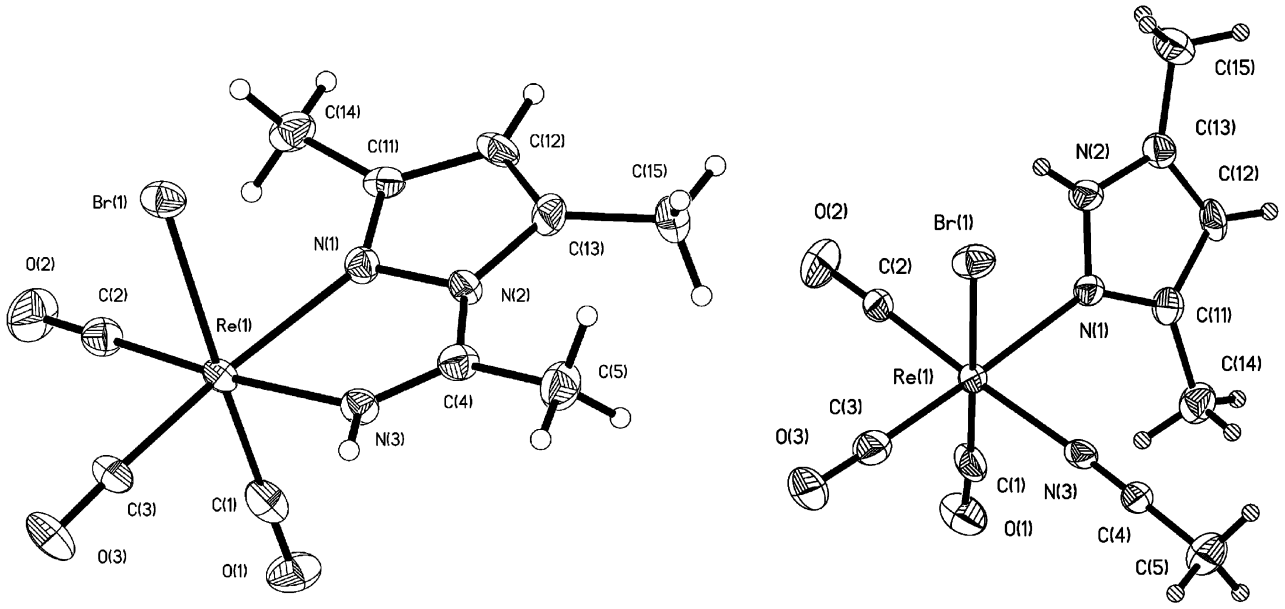
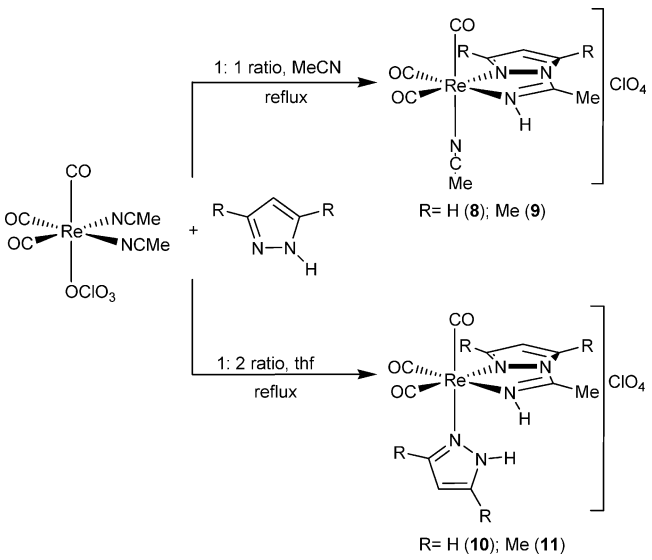


Figure 1. (a) Thermal ellipsoid (30%) plot of *fac*-[ReBr(CO)$_3$(H*N*=C(CH$_3$)dmpz-κ^2*N*,*N*)] (**5**). (b) Thermal ellipsoid (30%) plot of *fac*-[ReBr(CO)$_3$(Hdmpz)(NCMe)] (**7**). Selected distances [Å] and angles [deg] for **5**: Re(1)−N(1) 2.178(6), Re(1)−N(3) 2.131(6), N(1)−N(2) 1.397(10), N(2)−C(4) 1.396(10), N(3)−C(4) 1.274(10), N(3)−Re(1)−N(1) 72.1(2) and for **7**: Re(1)−N(1) 2.206(7), Re(1)−N(3) 2.139(7), N(1)−N(2) 1.350(9), N(3)−C(4) 1.155(10), N(3)−Re(1)−N(1) 85.7(2).

Scheme 3. Formation of the Cationic Pyrazolylamidino Complexes **8**−**11**



We decided to explore the syntheses of cationic pyrazolylamidino complexes. The reactions of *fac*-[Re(OClO$_3$)(CO)$_3$(NCMe)$_2$] (synthesized in situ from *fac*-[ReBr(CO)$_3$(NCMe)$_2$] and AgClO$_4$) with Hpz or Hdmpz in a 1:1 ratio in CH$_3$CN afforded *fac*-[Re(NCCH$_3$)(CO)$_3$(H*N*=C(CH$_3$)pz-κ^2*N*,*N*)]ClO$_4$ (**8**) or *fac*-[Re(NCCH$_3$)(CO)$_3$(H*N*=C(CH$_3$)dmpz-κ^2*N*,*N*)]ClO$_4$ (**9**) (Scheme 3).

The use of a 1:2 Re/pyrazole ratio and tetrahydrofuran (thf) as solvent leads to the formation of *fac*-[Re(Hpz)(CO)$_3$(H*N*=C(CH$_3$)pz-κ^2*N*,*N*)]ClO$_4$ (**10**) or *fac*-[Re(Hdmpz)(CO)$_3$(H*N*=C(CH$_3$)dmpz-κ^2*N*,*N*)]ClO$_4$ (**11**) (Scheme 3). Unlike for the neutral complexes, coupling to give the amidino ligand (instead of simple substitution) is observed even without excess nitrile. This can be rationalized taking into account that the activation toward nucleophilic attack should be higher when the nitrile is coordinated to the cationic metal fragment.

The formation of cationic complexes as perchlorate salts results from the lability of this anion when coordinated. These reactions turned out to be more selective than those leading to the neutral complexes **4** and **5**, as only traces of **8** or **9** (or **10** or **11**) could be detected in the mother liquors of the reactions to obtain **10** or **11** (or **8** or **9**).

Compounds **8**−**11** were analytically and spectroscopically characterized (see Experimental Section). The structures of **9** and **11** were determined by X-ray diffraction, and the results are shown in Figure 2.

In these structures, the perchlorate anion forms hydrogen bonds with the N−H groups of the cationic complexes. The shortest contacts correspond to H(3)···O(11), 1.92 Å; with N(3)···O(11) 2.935(7) Å (i.e., involving the pyrazolylamidino N−H group) in **9**, and H(5)···O(13), 2.01 Å; with N(5)···O(13) 2.947(7) Å (involving the pyrazole N−H group) in **11**. Additional contacts in the latter are represented by dotted lines in Figure 2.

The hydrogen bonding of perchlorate with both N−H groups of *fac*-[Re(Hdmpz)(CO)$_3$(H*N*=C(CH$_3$)dmpz-κ^2*N*,*N*)]$^+$ in **11** made us wonder if this cation could be used as a molecular cleft toward anions in solution.[8] This question includes the following. Is the complex *fac*-[Re(Hdmpz)(CO)$_3$(H*N*=C(CH$_3$)dmpz-κ^2*N*,*N*)]$^+$ stable toward anions, or would they substitute the monodentate, neutral pyrazole ligand? Such a substitution would be electrostatically favored for a cationic complex. Although rhenium d^6 fragments are kinetically quite inert and thus the *fac*-[Re(Hdmpz)$_3$(CO)$_3$]$^+$ complex and its 3(5)-*tert*-butyl analogue are substitutionally stable toward several anions, we have encountered several instances of fast substitution of neutral monodentate ligands by anions in cationic rhenium tricarbonyl complexes.[9]

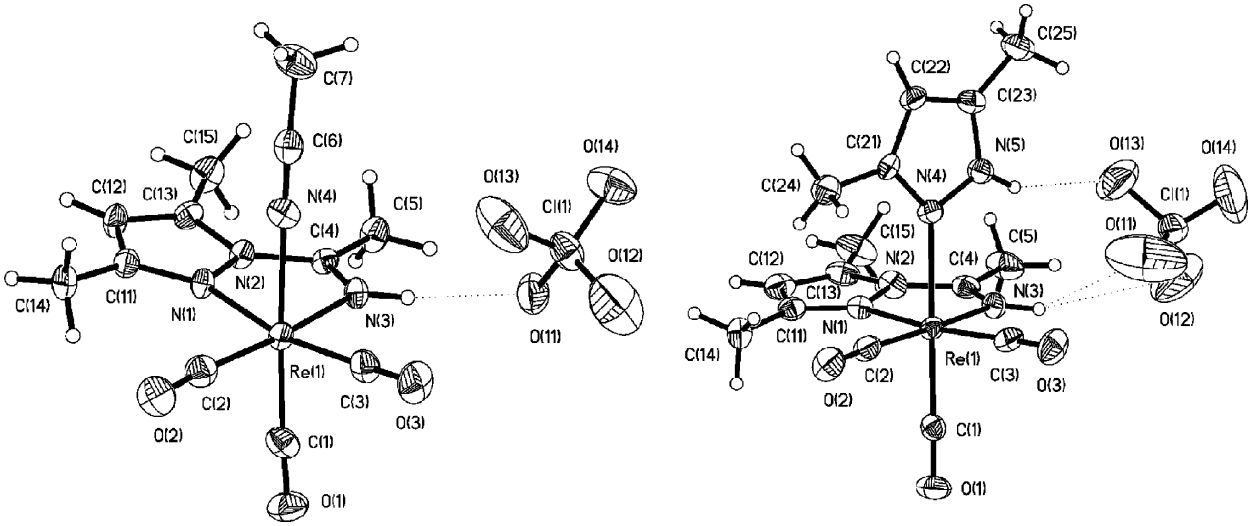
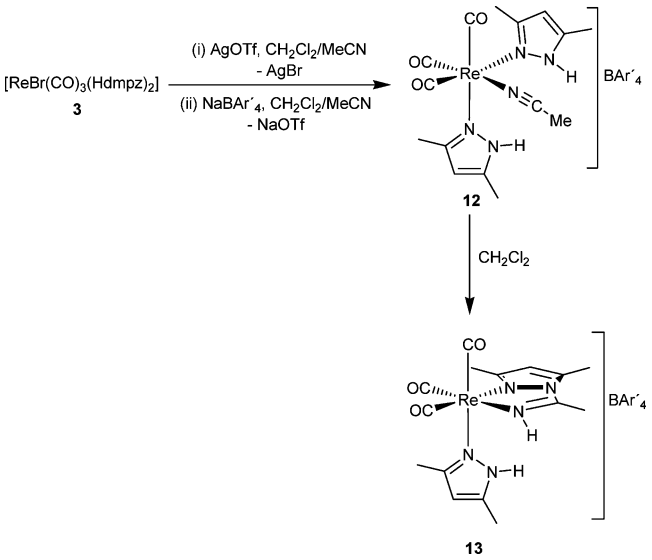


Figure 2. **(a)** Thermal ellipsoid (30%) plot of **9**. **(b)** Thermal ellipsoid (30%) plot of **11**. Selected distances [Å] and angles [deg] for **9**: Re(1)−N(1) 2.176(6), Re(1)−N(3) 2.139(6), Re(1)−N(4) 2.141(7), N(1)−N(2) 1.379(8), N(2)−C(4) 1.384(8), N(3)−C(4) 1.280(9), N(3)−Re(1)−N(1) 72.7(2) and for **11**: Re(1)−N(1) 2.181(5), Re(1)−N(3) 2.146(5), Re(1)−N(4) 2.226(4), N(1)−N(2) 1.396(6), N(2)−C(4) 1.390(8), N(3)−C(4) 1.263(7), N(3)−Re(1)−N(1) 72.12(2).

Scheme 4. Syntheses of Compounds **12** and **13**



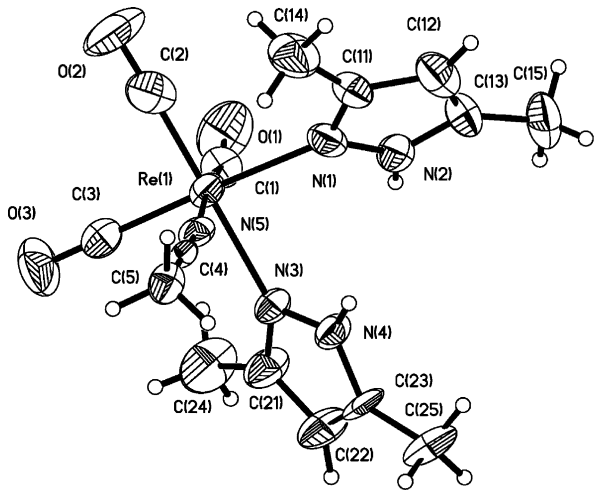


Figure 3. Thermal ellipsoid (30%) plot of the cation *fac*-[Re(NCMe)(Hdmpz)$_2$(CO)$_3$]$^+$ of compound **12**. Selected distances [Å] and angles [deg] for **12**: Re(1)−N(1) 2.192(13), Re(1)−N(3) 2.178(11), N(3)−Re(1)−N(1) 85.9(5).

The competition of the counteranion with the external, target anion is a limitation of cationic anion receptors. Indeed, the structure of **11** shows hydrogen bonding between the cationic complex and perchlorate, one of the more "innocent" anions. Thus, we set out to synthesize the cationic complex *fac*-[Re(Hdmpz)(CO)$_3$(H*N*═C(CH$_3$)dmpz-κ^2*N*,*N*)]$^+$ as its BAr′$_4^-$ salt. The presence of two strongly electron-withdrawing CF_3 groups on each of its aryl groups make this bulky borate a very low interacting counteranion.[6,10]

As depicted in Scheme 4 and detailed in the Experimental Section, **3** was allowed to react with AgOTf and then with NaBAr′$_4$ in a dichloromethane/acetonitrile mixture. Crystallization afforded (72%) the white solid *fac*-[Re(NCMe)(Hdmpz)$_2$(CO)$_3$][BAr′$_4$] (**12**). After standing at room-temperature for several hours, an in situ generated colorless CH_2Cl_2 solution of the nitrile bis(pyrazole) compound **12** becomes yellow and the IR indicates its transformation to another compound, *fac*-[Re(CO)$_3$(Hdmpz)(H*N*═C(CH$_3$)-dmpz-κ^2*N*,*N*)][BAr′$_4$] (**13**), isolated by crystallization in 78% yield (Scheme 4).

Compounds **12** and **13** were characterized spectroscopically (see Experimental Section) and, in the case of **12**, also by X-ray diffraction (Figure 3). Compound **13** was found to be an isomer of **12** containing both a pyrazole ligand and a chelating pyrazolylamidino ligand. It would be naïve to take

(8) For an overview of supramolecular anion binding, see: (a) *Supramolecular Chemistry of Anions*; Bianchi, A., Bowman-James, K., García-España, E., Eds.; Wiley-VCH: New York, 1997. (b) Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609. (c) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486. (d) Gale, P. A., Ed. *Coord. Chem. Rev.* **2003**, 240. (e) Bowman-James, K. *Acc. Chem. Res.* **2005**, *38*, 671. (f) *Anion Receptor Chemistry*; Sessler, J. L., Gale, P. A., Cho, W.-S., Eds.; RSC Publishing: Cambridge, U.K., 2006. An overview of anion receptors that consist of transition metal complexes of ligands featuring nitrogen-bond donor groups is included in: (g) Steed, J. W. *Chem. Commun.* **2006**, 2637.

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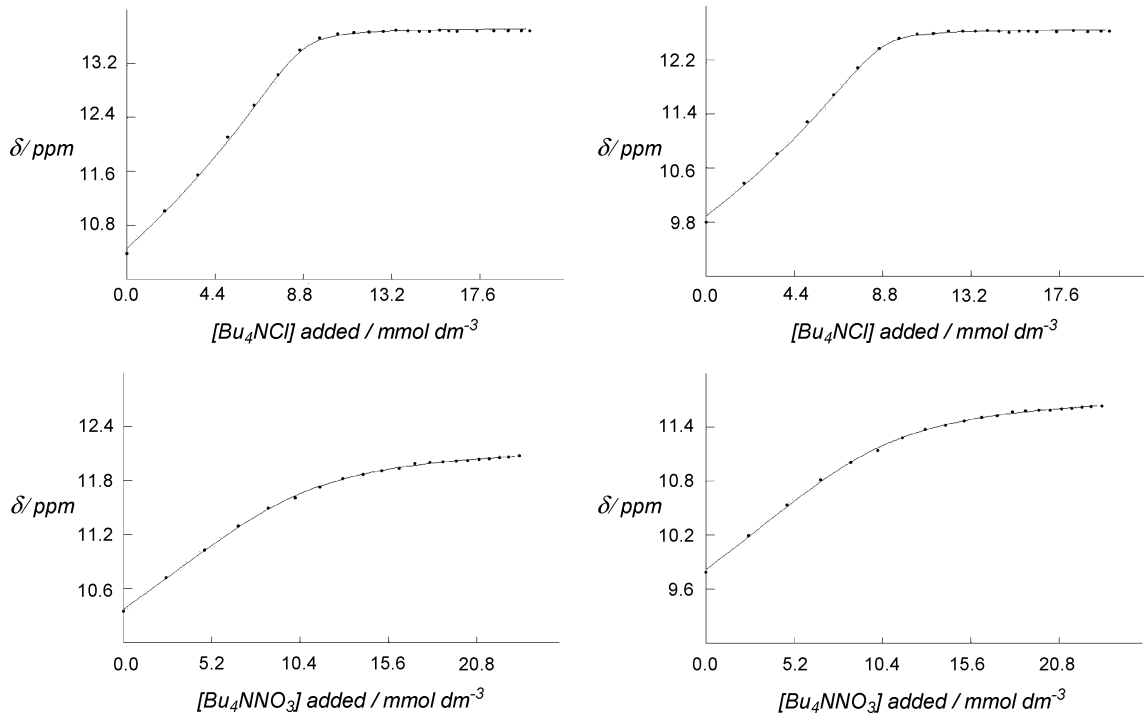

Figure 4. ^{1}H NMR titration plots of receptor **13** with chloride and nitrate anions for the two different N−H groups (pyrazole and pyrazolylamidino). Points are experimental data, while the curves were calculated from the fitting program.

the transformation of **12** into **13** as implying that the pyrazole−nitrile coupling requires the coordination of both ligands to the metal fragment. Rather, it is perfectly conceivable that, under the reaction conditions, slow dissociation of pyrazole occurs followed by attack of this pyrazole to the coordinated nitrile, in agreement with the commonly accepted mechanism. We wish to stress that in the absence of kinetic studies, which we have not carried out, no conclusions regarding the mechanism can be drawn.

The behavior of **13** toward chloride, bromide, iodide, nitrate, and perchlorate anions (as tetrabutylammonium salts) in CD_3CN solution was investigated by IR and ^{1}H NMR spectroscopies. Compound **13** was found to be substitutionally stable toward the mentioned anions, and no products of the substitution of pyrazole by anion could be spectroscopically (IR and NMR) detected over a period of several hours. Fast anion exchange was found, and the binding constants were calculated from the response of both (pyrazole and pyrazolylamidino) N−H signals of **13** to the addition of successive amounts of the Bu_4N^+ salts. For every anion, the observed behavior was consistent with the formation of 1:1 adducts (in Figure 4 the calculated NMR curves from the fitting program for Cl^- and NO_3^- are shown), and in Table 1 the binding constant values for several anions are summarized.

This was confirmed by the X-ray characterization of the adduct *fac*-[Re(CO)$_3$(Hdmpz)(H*N*═C(CH$_3$)dmpz-κ^2*N*,*N*)]·Cl (**14**), crystallized from a CH_2Cl_2 solution containing equimolar amounts of Bu_4NCl and **13**. As it was recently found in other works of one of our groups,[6,10] the adduct crystallized separately from the salt $[Bu_4N][BAr'_4]$, in contrast with the commonly observed behavior, i.e., the presence of the four ions in the solid lattice. The results of the structure

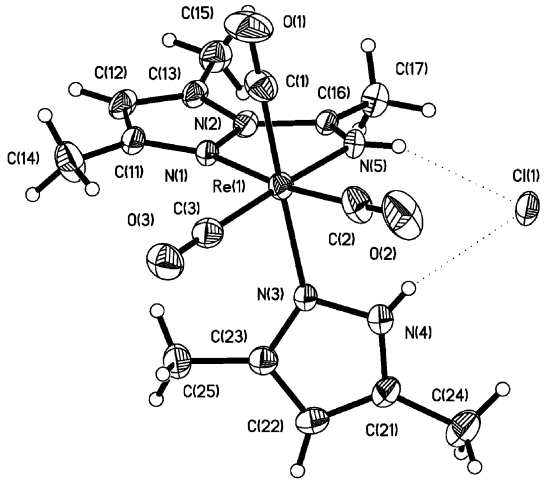

Figure 5. Thermal ellipsoid (30%) plot of the *fac*-[Re(CO)$_3$(Hdmpz)(H*N*═C(CH$_3$)dmpz-κ^2*N*,*N*)]·Cl (**14**) adduct. Selected distances [Å] and angles [deg] for **14**: Re(1)−N(1) 2.174(6), Re(1)−N(3) 2.205(6), Re(1)−N(5) 2.138(6), N(1)−N(2) 1.368(8), N(2)−C(16) 1.405(8), N(5)−C(16) 1.252(9), N(3)−Re(1)−N(1) 72.3(2).

Table 1. Binding Constant Values for Compound **13** in CD_3CN

anion	K (M^{-1})	anion	K (M^{-1})
Cl^-	8725 (±280)	NO_3^-	521 (±26)
Br^-	1505 (±17)	ClO_4^-	9 (±0.4)
I^-	373 (±37)		

determination, shown in Figure 5, indicate that both N−H groups of the cationic complex can simultaneously bind even a monoanionic, relatively small anion such as chloride. Indeed, the relative magnitude of the binding constants display a marked bias toward chloride while, as expected, perchlorate is the less interacting anion. In line with the relatively large binding constant for chloride, the N(4)···Cl

(3.183(7) Å) and N(5)···Cl (3.184(6) Å) distances are rather short.[11]

In summary, we have shown that neutral and cationic rhenium tricarbonyl fragments promote the coupling of acetonitrile and either pyrazole or 3,5-dimethylpyrazole to afford complexes of the chelating pyrazolylamidino ligand. By carefully choosing the reaction conditions, either these coupling products or the uncoupled pyrazole nitrile complexes can be obtained. The compound *fac*-[Re(CO)$_3$(Hdmpz)(H*N*═C(CH$_3$)dmpz-κ^2*N*,*N*)][BAr′$_4$], one of the coupling products, binds anions through a combination of electrostatic attraction and hydrogen bonding with the N−H groups of the pyrazole and pyrazolylamidino ligands.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere using conventional Schlenk techniques. Solvents were purified according to standard procedures.[12] **1**,[13] **2**,[7] and **3**[7] were prepared according to literature procedures. Other reagents were purchased and used as received. ***CAUTION!*** *Although no difficulties were experienced with the perchlorate complexes described herein, all perchlorate species should be treated as potentially explosive and should be handled with care.* Deuterated solvents were stored under nitrogen in Young tubes. ^{1}H NMR (300 or 400 MHz) and ^{13}C NMR spectra were recorded on a Bruker AC-300, ARX-300, Advance 300, DPX-300, or Advance 400 spectrometers. NMR spectra are referred to the internal residual solvent peak for ^{1}H and ^{13}C{^{1}H} NMR. IR solution spectra were obtained in a Perkin-Elmer FT 1720-X or RX I FT-IR spectrometer using 0.2 mm. CaF_2 cells. Elemental analyses were performed on a Perkin-Elmer 2400B microanalyzer.

***fac*-[ReBr(CO)$_3$(H*N*═C(CH$_3$)pz-κ^2*N*,*N*)] (4).** Hpz (0.034 g, 0.5 mmol) was added to a solution of *fac*-[ReBr(CO)$_3$(NCMe)$_2$] (0.216 g, 0.5 mmol) in CH_3CN (20 mL), and the solution was refluxed for 14 h. The solvent was removed in vacuo, and the yellow residue was extracted with thf (20 mL) and filtered. Hexane was added (10 mL), and the solution was concentrated and cooled to −20 °C, giving a yellow-orange microcrystalline solid, which was decanted, washed with hexane (3 × 3 mL), and dried in vacuo, yielding 0.131 g (57%) of **4**. **2**[7] and **6** were detected in the mother liquor. IR (thf, cm^{-1}): 2022 vs, 1921 vs, 1892 vs (ν_{CO}). ^{1}H NMR ((CD$_3$)$_2$CO): δ 2.96 (s, N═C(C*H*$_3$), 3H), 6.86 (t, J = 2.6 Hz, *H*^{4} pz, 1H), 8.35 (d, J = 1.8 Hz, *H*^{3} pz, 1H), 8.66 (d, J = 2.9 Hz, *H*^{5} pz, 1H), 11.31 (br, N*H*, 1H). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO): δ 18.9 (HN═C(*C*H$_3$)), 112.3 (*C*^{4} pz), 134.1 (*C*^{3,5} pz), 147.7 (*C*^{5,3} pz), 163.8 (HN═*C*(CH$_3$)), 188.7 (CO), 197.3 (CO), 197.5 (CO). Anal. Calcd for $C_8H_7BrN_3O_3Re$: C, 20.92; H, 1.54; N, 9.15. Found: C, 21.28; H, 1.42; N, 8.91.

***fac*-[ReBr(CO)$_3$(H*N*═C(CH$_3$)dmpz-κ^2*N*,*N*)] (5).** Hdmpz (0.048 g, 0.5 mmol) was added to a solution of *fac*-[ReBr(CO)$_3$(NCMe)$_2$] (0.216 g, 0.5 mmol) in CH_3CN (20 mL), and the solution was refluxed for 18 h. The solvent was removed in vacuo, and the yellow residue was extracted with thf (20 mL) and filtered. Workup as for **4** yielded 0.052 g (21%) of **5**. Variable amounts of **3** and **7** were detected in the mother liquor. IR (thf, cm^{-1}): 2019 vs, 1918 vs, 1890 vs (ν_{CO}). ^{1}H NMR ((CD$_3$)$_2$CO): δ 2.50 (s, C*H*$_3$ dmpz, 3H), 2.76 (s, C*H*$_3$ dmpz, 3H), 2.97 (s, N═C(C*H*$_3$), 3H), 6.46 (s, *H*^{4} dmpz, 1H), 10.91 (br, N*H*, 1H). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO): δ 14.2 (*C*H$_3$ dmpz), 16.1 (*C*H$_3$ dmpz), 21.4 (HN═C(*C*H$_3$)), 113.7 (*C*^{4} dmpz), 146.8 (*C*^{5,3} dmpz), 156.6 (*C*^{3,5} dmpz), 165.1 (HN═*C*(CH$_3$)), 188.9 (CO), 197.8 (CO), 198.2 (CO). Anal. Calcd for $C_{10}H_{11}BrN_3O_3Re$: C, 24.64; H, 2.27; N, 8.62. Found: C, 24.98; H, 2.28; N, 8.33.

***fac*-[ReBr(CO)$_3$(NCCH$_3$)(pzH)] (6).** To a solution of *fac*-[ReBr(CO)$_3$(NCMe)$_2$] (0.086 g, 0.2 mmol) in thf (20 mL) Hpz (0.014 g, 0.2 mmol) was added, and the mixture was refluxed for 2 h. The resulting solution was concentrated under reduced pressure to a volume of 5 mL. Addition of hexane (20 mL) and cooling at −20 °C caused the precipitation of a white solid. Complex **6** could not be isolated analytically pure, as it was always contaminated with *fac*-[ReBr(CO)$_3$(dmpzH)$_2$][7] and other minor products. IR (thf, cm^{-1}): 2028 vs, 1920 vs, 1896 vs (ν_{CO}). ^{1}H NMR ((CD$_3$)$_2$CO): δ 2.57 (s, C*H*$_3$ NCC*H*$_3$, 3H), 6.52 (s, *H*^{4} Hpz, 1H), 8.00 (m, *H*^{3} Hpz, 1H), 8.05 (m, *H*^{5} Hpz, 1H), 12.59 (br, N*H*, 1H).

***fac*-[ReBr(CO)$_3$(NCCH$_3$)(dmpzH)] (7).** Hdmpz (0.029 g, 0.3 mmol) was added to a solution of *fac*-[ReBr(CO)$_3$(NCMe)$_2$] (0.130 g, 0.3 mmol) in thf (20 mL), and the solution was refluxed for 2 h. The resulting solution was then concentrated in vacuo to a volume of 5 mL, and slow diffusion of hexane at −20 °C afforded crystals of **7** (0.079 g, 54%). Variable amounts of *fac*-[ReBr(CO)$_3$(dmpzH)$_2$][7] were detected in the mother liquor. IR (thf, cm^{-1}): 2026 vs, 1915 vs, 1891 vs (ν_{CO}). ^{1}H NMR ((CD$_3$)$_2$CO): δ 2.31 (s, C*H*$_3$ NCC*H*$_3$, 3H), 2.41 (s, C*H*$_3$ dmpzH, 3H), 2.60 (s, C*H*$_3$ dmpzH, 3H), 6.07 (s, *H*^{4} dmpzH, 1H), 11.57 (br, N*H*, 1H). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO): δ 3.3 (*C*H$_3$CN), 10.6 (*C*H$_3$ dmpzH), 15.6 (*C*H$_3$ dmpzH), 107.2 (*C*^{4} dmpz), 123.3 (CH$_3$*C*N), 143.3 (*C*^{3,5} dmpzH), 153.5 (*C*^{5,3} dmpzH), 190.3 (CO), 194.7 (CO), 196.9 (CO). Anal. Calcd for $C_{10}H_{11}BrN_3O_3Re$: C, 24.64; H, 2.27; N, 8.62. Found: C, 24.89; H, 2.06; N, 8.29.

***fac*-[Re(NCCH$_3$)(CO)$_3$(H*N*═C(CH$_3$)pz-κ^2*N*,*N*)]ClO$_4$ (8).** AgClO$_4$ (0.068 g, 0.33 mmol) was added to a solution of *fac*-[ReBr(CO)$_3$(NCMe)$_2$] (0.130 g, 0.2 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred at 40 °C for 1 h. The solution was filtered, and the solvent was removed in vacuo. The white residue was then dissolved in CH_3CN (10 mL), Hpz (0.020 g, 0.3 mmol) was added, and the solution was refluxed for 72 h. The solvent was removed in vacuo, and the white residue was extracted with CH_2Cl_2 (20 mL) and filtered. Workup as for **4** yielded 0.068 g (44%) of **8**. Small amounts of **10** were detected in the mother liquor. IR (thf, cm^{-1}): 2036 vs, 1932 vs (ν_{CO}). ^{1}H NMR ((CD$_3$)$_2$CO): δ 2.42 (s, NCC*H*$_3$, 3H), 3.00 (s, N═C(C*H*$_3$), 3H), 6.97 (pst, J = 2.6 Hz, *H*^{4} pz, 1H), 8.55 (d, J = 2.3 Hz, *H*^{3} pz, 1H), 8.83 (d, J = 3.5 Hz, *H*^{5} pz, 1H), 11.20 (br, N*H*, 1H). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO): δ 3.1 (*C*H$_3$CN), 19.2 (HN═C(*C*H$_3$)), 112.9 (*C*^{4} dmpz), 123.5 (CH$_3$*C*N), 135.9 (*C*^{3,5} pz), 149.5 (*C*^{5,3} pz), 167.3 (HN═*C*(CH$_3$)), 190.1 (CO), 193.9 (CO), 196.8 (CO). Anal. Calcd for $C_{10}H_{10}ClN_4O_7Re$: C, 23.10; H, 1.94; N, 10.78. Found: C, 22.79; H, 2.14; N, 10.49.

***fac*-[Re(NCCH$_3$)(CO)$_3$(H*N*═C(CH$_3$)dmpz-κ^2*N*,*N*)]ClO$_4$ (9).** AgClO$_4$ (0.045 g, 0.22 mmol) was added to a solution of *fac*-[ReBr(CO)$_3$(NCMe)$_2$] (0.086 g, 0.2 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred at 40 °C for 1 h. The solution was filtered, and the solvent was removed in vacuo. The white residue was then dissolved in CH_3CN (10 mL), Hdmpz (0.019 g, 0.2 mmol) was added, and the solution was refluxed for 72 h. The solvent was

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(12) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, 1988.

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removed in vacuo, and the white residue was extracted with CH_2Cl_2 (20 mL) and filtered. Workup as for **4** yielded 0.056 g (51%) of **9**. Small amounts of **11** were detected in the mother liquor. IR (thf, cm^{-1}): 2039 vs, 1934 vs (ν_{CO}). ^1H NMR ($(CD_3)_2CO$): δ 2.42 (s, NCCH_3, 3H), 2.56 (s, CH_3 dmpz, 3H), 2.98 (s, CH_3 dmpz, 3H), 3.00 (s, N=C(CH_3), 3H), 6.50 (s, H^4 dmpz, 1H), 10.74 (br, NH, 1H). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 3.2 (*C*H_3CN), 14.5 (*C*H_3 dmpz), 16.1 (*C*H_3 dmpz), 21.7 (HN=C(*C*H_3)), 114.5 (C^4 dmpz), 123.3 (CH$_3$*C*N), 148.9 ($C^{3,5}$ dmpz), 153.8 ($C^{5,3}$ dmpz), 168.9 (HN=*C*(CH$_3$)), 190.3 (CO), 194.2 (CO), 195.1 (CO). Anal. Calcd for $C_{12}H_{14}ClN_4O_7Re$: C, 26.30; H, 2.57; N, 10.22. Found: C, 26.54; H, 2.34; N, 10.36.

***fac*-[Re(pzH)(CO)$_3$(H*N*=C(CH$_3$)pz-κ^2*N,N*)]ClO$_4$ (10).** $AgClO_4$ (0.045 g, 0.22 mmol) was added to a solution of *fac*-[ReBr(CO)$_3$(NCMe)$_2$] (0.086 g, 0.2 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred at 40 °C for 1 h. The solution was filtered, and the solvent was removed in vacuo. The white residue was then dissolved in thf (10 mL), and Hpz (0.027 g, 0.4 mmol) was added to the solution, which was refluxed for 24 h. The solvent was removed in vacuo, and the white residue was extracted with thf (20 mL) and filtered. Workup as for **4** yielded 0.056 g (51%) of **10**. Small amounts of **8** were detected in the mother liquor. IR (thf, cm^{-1}): 2034 s, 1924 vs (ν_{CO}). ^1H NMR ($(CD_3)_2CO$): δ 3.02 (s, N=C(CH_3), 3H), 6.43 (s, H^4 pzH, 1H), 6.96 (t, J = 2.6 Hz, H^4 pz, 1H), 7.59 (s, H^3 pzH, 1H), 7.93 (d, J = 2.3 Hz, H^5 pzH, 1H), 8.68 (d, J = 2.3 Hz, H^3 pz, 1H), 8.79 (d, J = 2.9 Hz, H^5 pz, 1H), 11.25 (br, MeCNH, 1H), 12.88 (br, NH pzH, 1H). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 19.2 (HN=C(*C*H$_3$)), 108.0 (C^4 pzH), 113.1 (C^4 pz), 133.7 ($C^{3,5}$ pzH), 136.1 ($C^{3,5}$ pz), 143.8 ($C^{5,3}$ pzH), 149.8 ($C^{5,3}$ pz), 167.4 (HN=*C*(CH$_3$)), 191.6 (CO), 195.2 (CO). Anal. Calcd for $C_{11}H_{11}ClN_5O_7Re$: C, 24.16; H, 2.03; N, 12.81. Found: C, 23.90; H, 2.10; N, 12.80.

***fac*-[Re(dmpzH)(CO)$_3$(H*N*=C(CH$_3$)dmpz-κ^2*N,N*)]ClO$_4$ (11).** $AgClO_4$ (0.091 g, 0.44 mmol) was added to a solution of *fac*-[ReBr(CO)$_3$(NCMe)$_2$] (0.173 g, 0.4 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred at 40 °C for 1 h. The solution was filtered, and the solvent was removed in vacuo. The white residue was then dissolved in thf (10 mL), and Hdmpz (0.077 g, 0.8 mmol) was added to the solution, which was refluxed for 14 h. The solvent was removed in vacuo, and the white residue was extracted with thf (ca. 20 mL) and filtered. Workup as for **4** yielded 0.092 g (38%) of **11**. Small amounts of **9** were detected in the mother liquor. IR (thf, cm^{-1}): 2031 s, 1928 s sh, 1916 vs (ν_{CO}). ^1H NMR ($(CD_3)_2CO$): δ 2.20 (s, CH_3 dmpzH, 3H), 2.22 (s, CH_3 dmpzH, 3H), 2.69 (s, CH_3 dmpz, 3H), 2.71 (s, CH_3 dmpz, 3H), 3.00 (s, N=C(CH_3), 3H), 6.03 (s, H^4 dmpzH, 1H), 6.61 (s, H^4 dmpz, 1H), 10.68 (br, MeCNH, 1H), 11.47 (br, NH dmpzH, 1H). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 10.6 (*C*H$_3$ dmpzH), 14.5 (*C*H$_3$ dmpz), 15.0 (*C*H$_3$ dmpzH), 16.7 (*C*H$_3$ dmpz), 21.7 (HN=C(*C*H$_3$)), 107.5 (C^4 dmpzH), 114.6 (C^4 dmpz), 144.7 ($C^{3,5}$ dmpzH), 149.2 ($C^{3,5}$ dmpz), 153.8 ($C^{5,3}$ dmpzH), 159.5 ($C^{5,3}$ dmpz), 168.9 (HN=*C*(CH$_3$)), 191.5 (CO), 194.9 (CO), 196.7 (CO). Anal. Calcd for $C_{15}H_{19}ClN_5O_7Re$: C, 29.88; H, 3.17; N, 11.61. Found: C, 30.13; H, 3.04; N, 11.85.

***fac*-[Re(NCMe)(Hdmpz)$_2$(CO)$_3$][BAr′$_4$] (12).** To a solution of **3** (0.067 g, 0.123 mmol) in CH_2Cl_2 (20 mL), AgOTf (0.032 g, 0.123 mmol) and a drop of MeCN were added. The mixture was stirred in the dark for 30 min, filtered by cannula, and evaporated to dryness. The white residue was redissolved in CH_2Cl_2, NaBAr′$_4$ (0.109 g, 0.123 mmol) was added, and the mixture was stirred at room temperature for 30 min. Filtration followed by concentration and precipitation by addition of hexane afforded compound **12** as a white microcrystalline solid (0.121 g, 72%). Slow diffusion of Et_2O into a solution of **12** in CH_2Cl_2 at room temperature produced colorless crystals of **12**, one of which was used for the X-ray analysis. IR(thf, cm^{-1}): 2030 s, 1923 vs (ν_{CO}). ^1H NMR ($(CD_3)_2CO$): δ 2.24 (s, CH_3 dmpzH, 6H), 2.27 (s, CH_3 dmpzH, 6H), 2.73 (s, CH_3 NCCH_3, 3H), 6.21 (s, H^4 dmpzH, 2H), 7.69 (m, H$_p$ BAr′$_4$, 4H), 7.80 (m, H$_o$ BAr′$_4$, 8H), 12.03 (br, NH, 2H). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 3.3 (*C*H$_3$CN), 9.8 (*C*H$_3$ dmpzH), 13.9 (*C*H$_3$ dmpzH), 107.0 (C^4 dmpzH), 117.6 (C^p BAr′$_4$), 125.2 (CH$_3$*C*N), 124.4 (c($^1J_{CF}$ = 271.0 Hz), *C*F$_3$ BAr′$_4$), 129.1 (c($^2J_{CF}$ = 30.5 Hz), C^m BAr′$_4$), 134.6 (C^o BAr′$_4$), 144.3 ($C^{3,5}$), 154.2 ($C^{5,3}$), 161.7 (c($^1J_{CB}$ = 49.9 Hz), C^i BAr′$_4$), 192.2 (br, *C*O). Anal. Calcd for $C_{47}H_{31}BF_{24}N_5O_3Re$: C,41.30; H, 2.29; 5.12. Found: C,41.48; H, 2.12; 5.36.

***fac*-[Re(dmpzH)(CO)$_3$(H*N*=C(CH$_3$)dmpz-κ^2*N,N*)]BAr′$_4$ (13).** A solution of **12** (0.158 g, 0.116 mmol) in CH_2Cl_2 (20 mL) and MeCN (1 mL) was stirred at room temperature for 4 h. The solution was then concentrated in vacuo to a volume of 5 mL, and slow diffusion of hexane at −20 °C afforded light yellow crystals of **13** (0.124 g, 78%). IR(thf, cm^{-1}): 2030 s, 1922 vs (ν_{CO}).^1H NMR ($(CD_3)_2CO$): δ 2.23 (s, CH_3 dmpzH, 3H), 2.29 (s, CH_3 dmpzH, 3H), 2.74 (s, CH_3 dmpz, 3H), 2.78 (s, CH_3 dmpz, 3H), 3.06 (s, N=C(CH_3), 3H), 6.09 (s, H^4 dmpzH, 1H), 6.67 (s, H^4 dmpz, 1H), 7.71 (m, H$_p$ BAr′$_4$, 4H), 7.82 (m, H$_o$ BAr′$_4$, 8H), 10.82 (br, NH, 1H), 11.66 (br, NH, 1H). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 11.4 (s, *C*H$_3$ dmpzH), 15.3 (s, *C*H$_3$ dmpz), 15.8 (s, *C*H$_3$ dmpzH), 17.5 (s, *C*H$_3$ dmpz), 22.7 (s, HN=C(*C*H$_3$)), 108.5 (s, C^4 dmpzH), 115.4 (s, C^4 dmpz), 119.2 (C^p BAr′$_4$), 126.1 (c($^1J_{CF}$ = 273.0 Hz), *C*F$_3$ BAr′$_4$), 130.8 (c($^2J_{CF}$ = 30.8 Hz), C^m BAr′$_4$), 134.3 (C^o BAr′$_4$), 145.5 ($C^{3,5}$ dmpzH), 150.1 ($C^{3,5}$ dmpz), 154.9 ($C^{5,3}$ dmpzH), 155.9 ($C^{5,3}$ dmpz), 163.3 (c($^1J_{CB}$ = 50.8 Hz), C^i BAr′$_4$), 163.3 (s, HN=*C*(CH$_3$)), 192.1 (CO), 195.8 (CO), 197.1 (CO). Anal. Calcd for $C_{47}H_{31}BF_{24}N_5O_3Re$: C,41.30; H, 2.29; 5.12. Found: C,41.12; H, 2.41; 4.98.

General Procedure for Titration Experiments. 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 by dissolving compound 13 (10 mg, 7.32×10^{-3} mmol) in 0.4 mL of CD_3CN) by means of a 1 mL syringe, and stoppered with rubber septa. After the NMR spectrum of the receptor was recorded, the succesive 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). Data were treated using the WinEQNMR program.[14] The constants given in Table 1 are the average of the values obtained from the signals of the two N−H groups. Deuterated acetonitrile was purchased from Cambridge Isotopes and used without furter purification. The percent of water was estimated to be 0.015%.

Crystal Structure Determination for Compounds 5, 7, 9, 11, 12, and 14. General Description. A suitable crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite-monochromatized Mo Kα X-ray 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[15] program. The structures were solved by direct methods with SHELXTL.[16] An empirical absorption correction was applied with the program SADABS.[17] All non-hydrogen atoms were

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(15) *SAINT+. SAX area detector integration program*, Version 6.02; Bruker AXS, Inc.: Madison, WI, 1999.
(16) Sheldrick, G. M. *SHELXTL, An integrated system for solving, refining, and displaying crystal structures from diffraction data*, Version 5.1; Bruker AXS, Inc.: Madison, WI, 1998.
(17) Sheldrick, G. M. *SADABS, Empirical Absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1997.

Table 2. Selected Crystal, Measurement, and Refinement Data for Compounds **5**, **7**, **9**, **11**, **12**, and **14**

	5	**7**	**9**	**11**	**12**	**14**
formula	$C_{10}H_{11}BrN_3O_3Re$	$C_{10}H_{11}BrN_3O_3Re$	$C_{12}H_{14}ClN_4O_7Re$	$C_{15}H_{19}ClN_5O_7Re$	$C_{47}H_{31}BF_{24}N_5O_3Re.0.5CH_2Cl_2$	$C_{16}H_{21}Cl_3N_5O_3Re$
fw	487.33	487.33	547.92	603.00	1409.24	623.93
color	pale yellow	colorless	colorless	pale yellow	colorless	colorless
cryst syst	triclinic	triclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$C2/c$
a, Å	7.691(4)	7.829(2)	8.2464(16)	13.347(4)	10.804(3)	31.835(8)
b, Å	9.301(5)	8.585(3)	9.2149(18)	11.803(4)	14.493(4)	10.994(3)
c, Å	10.775(6)	12.186(5)	12.074(2)	13.944(4)	19.198(5)	14.058(4)
α, deg	103.747(10)	99.709(7)	84.399(4)	90	106.726(6)	90
β, deg	109.936(9)	107.179(8)	87.253(4)	107.567(6)	96.428(5)	110.459(5)
γ, deg	101.172(9)	108.596(5)	77.109(4)	90	98.093(4)	90
V, Å^3	671.1(6)	709.7(4)	889.8(3)	2094.4(12)	2813.1(12)	4610(2)
Z	2	2	2	4	2	8
F(000)	452	452	524	1168	1378	2416
D_{calcd}, g cm^{-3}	2.412	2.280	2.045	1.912	1.664	1.798
radiation (λ, Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
μ, mm^{-1}	12.033	11.378	7.020	5.976	2.331	5.645
cryst size, mm^3	0.33 × 0.13 × 0.10	0.23 × 0.21 × 0.15	0.30 × 0.29 × 0.10	0.23 × 0.14 × 0.09	0.23 × 0.10 × 0.06	0.42 × 0.17 × 0.13
T, K	296(2)	293(2)	296(2)	296(2)	293(2)	296(2)
θ limits, deg	2.13−23.36	2.62−23.34	1.70−23.29‘	1.60−23.29	1.12−23.34	1.97−23.26
min/max h, k, l	−7/8, −10/10, −11/7	−8/8, −9/8, −11/13	−7/9, −8/10, −13/13	−14/14, −13/6, −14/15	−11/11, −15/16, −19/21	−27/35, −12/12, −15/12
collected reflns	3035	3253	3981	9049	12 825	9956
unique reflns	1934	2029	2531	3017	8043	3303
reflns with $I > 2\sigma(I)$	1804	1841	2409	2538	3627	2881
absorption correction	SADABS	SADABS	SADABS	SADABS	SADABS	SADABS
params/restraints	167/0	167/0	231/1	268/0	741/0	266/1
GOF on F^2	1.003	1.029	1.066	1.046	1.050	1.046
R1 (on F, $I > 2\sigma(I)$)	0.0321	0.0314	0.0369	0.0284	0.0789	0.0336
wR2 (on F^2, all data)	0.0882	0.0824	0.1007	0.0800	0.1518	0.0950
max/min $\Delta\rho$, e Å^{-3}	1.752 and −1.511	1.906 and −1.048	1.456 and −1.994	1.027 and −0.784	0.710 and −2.706	1.287 and −1.228

refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms. Drawings and other calculations were made with SHELXTL. Crystal and refinement details are collected in Table 2.

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Supporting Information Available: ^{1}H NMR titration plots of receptor **13** with Cl^-, Br^-, I^-, NO_3^-, and ClO_4^- anions. X-ray crystallographic data for compounds **5**, **7**, **9**, **11**, **12**, and **14** as CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

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