Cationic *fac*-tris(pyrazole) complexes as anion receptors†

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New receptors *fac*-[Re(CO)$_3$(pz)$_3$]BAr′$_4$ (pz = 3,5-dimethylpyrazole or 3(5)-*tert*-butylpyrazole, Ar′ = 3,5-(CF$_3$)$_2$C$_6$H$_3$), synthesized from [Re(OTf)(CO)$_5$] and the pyrazoles, have been found to show a high affinity for chloride.

The self-assembly of supramolecular adducts between chloride and *fac*-tris(pyrazole) receptors (LnM(pz)$_3$) was reported in 1991 by Parkin and co-workers (LnM = HB, obtained by treatment of a thallium(I) hydrotris(pyrazolyl)borate with HCl and AlCl$_3$)[1a] and in 2002 by Halcrow and co-workers (LnM = ClZn, by reaction of ZnCl$_2$ with three equivalent of a pyrazole).[2] These findings suggest that a cationic complex [LnM(pz)$_3$]$^+$ (pz = generic pyrazole) could act as a receptor for anions,[2b] with which it would interact through a combination of electrostatic attraction and hydrogen bonds.[3] Such a receptor (which could be though of as an "anti-scorpionate"[4] for it would show an opposite complexation behavior; *i.e.*; it would bind anions), in its uncomplexed form, remains unknown since the two mentioned examples are directly obtained as the supramolecular chloride adducts. Recently, Bondy, Gale and Loeb synthesized anion receptors by assembling relatively simple organic molecules containing both a Lewis basic site (L) and a hydrogen-bond donor group (HD) around a metal fragment.[5] This approach offers a preparative procedure simpler than those needed to synthesize most purely organic receptors. In this kind of receptor, in addition to provide the positive charge and to enhance the polarization of the HD groups, the metal plays a major structural role, since the proper orientation of the HD groups is achieved by means of the coordination of the organic molecules to a metal fragment with a well defined geometric preference. On the other hand, the stability of the receptor requires inert metal-L bonds. Pyrazoles possess both a pyridine-type nitrogen that can serve as the L group, and a pyrrole-type nitrogen for the HD group; thus we targeted [Re(CO)$_3$(pz)$_3$]BAr′$_4$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl) compounds, chosen because of the strong preference for a *fac* geometry in [Re(CO)$_3$L$_3$] derivatives. A drawback of cationic receptors is that their accompanying counteranion interferes with binding of the external target anion. To minimize this interference, BF$_4^-$ or PF$_6^-$ are often the counteranions of choice due to their effective charge delocalization and resulting weaker interaction with the HD groups. Even more effective charge delocalization resulted in the widespread employment of the BAr′$_4$ counteranion in organometallic chemistry and catalysis, and thus we have incorporated it in our receptors.[6] Compounds [Re(CO)$_3$(pz)$_3$]BAr′$_4$ (**1**, pz = 3,5-dimethylpyrazole, **2**, pz = 3(5)-*tert*-butylpyrazole) were synthesized in a straightforward manner by reaction of [Re(OTf)(CO)$_5$][7] with the corresponding pyrazole in a 1:3 ratio in refluxing toluene, followed by anion metathesis with NaBAr′$_4$ in dichloromethane and crystallization from CH$_2$Cl$_2$–hexane. The salts **1** and **2** were fully characterized by IR and NMR (^{1}H and ^{13}C) spectroscopies in solution, and by single-crystal X-ray diffraction in the solid state (see Fig. 1 and ESI†).[8,9]

As expected, in the structure of **2**, the pyrazoles bind the rhenium atom through the nitrogen non-adjacent to the bulky *tert*-butyl group. In solution, the *fac* geometry of the cationic complexes was shown by the IR pattern in the *ν*(CO) region and by the single set of pyrazole signals, indicative of the equivalence of the three pz ligands, in the NMR spectra. The presence of two low-frequency singlets in the ^{1}H NMR of **1** indicates the non-equivalence of the two methyl groups in the 3 and 5 positions on the pz rings and therefore the absence of intermolecular pz exchange. This non-labile character of the pz ligands, necessary for the compounds to serve as receptors,[10] is also indicated by the observation of sharp singlets for all the carbon atoms of the pyrazole rings in the NMR spectrum of **2**.[2]

Receptors **1** and **2** were titrated with Bu$_4$NCl in CD$_3$CN. The complex *fac*-[ReCl(CO)$_3$(Me$_2$pz)$_2$] (Me$_2$pz = 3,5- dimethylpyrazole, **3**), which would be the product of the displacement of Me$_2$pz from **1** by chloride, was independently synthesized by reaction of [ReCl(CO)$_5$] with two equivalents of Me$_2$pz in refluxing toluene, and characterized spectroscopically and by X-ray diffraction (see

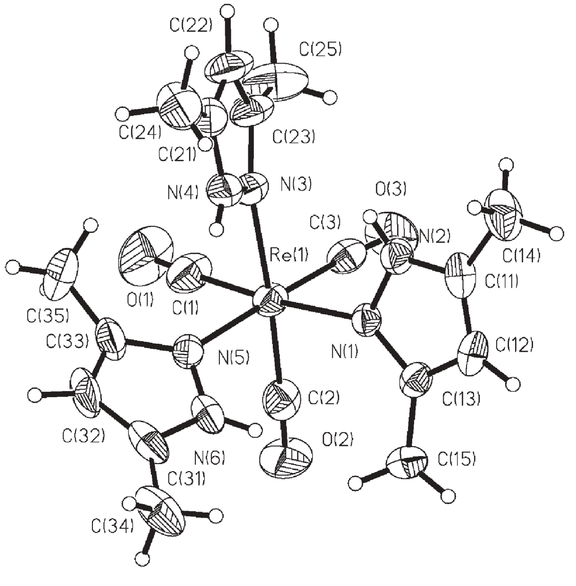

Fig. 1 Thermal ellipsoid (30%) plot of the cation of **1**.

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† Electronic supplementary information (ESI) available: Complete details for the synthesis of compound **3**, thermal ellipsoid plots of the cation of **2** and the molecule of **3**, and ^{1}H NMR titration plot of **2** with Bu$_4$NCl in MeCN. See http://www.rsc.org/suppdata/cc/b4/b414407d/

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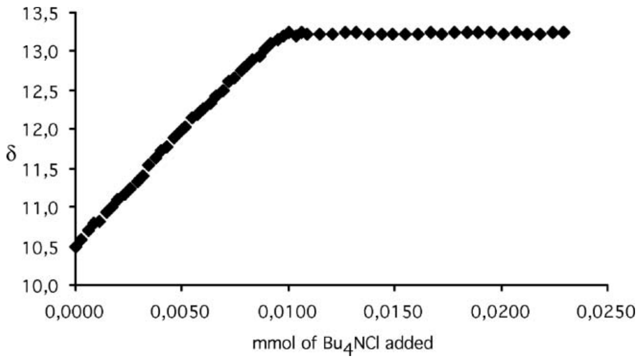

Fig. 2 ^1H NMR titration of **1** with Bu_4NCl in MeCN.

ESI†). It was assessed that when amounts of 0.25, 0.50 and 0.75 equivalents of Bu_4NCl were added to solutions containing an equimolar mixture of **1** and **3**, separate sets of signals could be observed for the **1**-Cl and **3**-Cl species. Thus, displacement of Me_2pz by chloride during the titration could be unambiguously ruled out because only the signals of **1**-Cl could be observed throughout it. The large shift to higher frequencies of the N–H signals in the ^1H NMR spectra of **1** or **2** upon addition of Bu_4NCl suggested a strong hydrogen-bond interaction (see Fig. 2). As expected, the shift was much lower for the neutral bis(pyrazole) complex **3**. The presence of a single set of signals during the course of these titrations was consistent with the fast exchange of chloride. When the data obtained from the titrations of **1** and **2** with Bu_4NCl were treated with the WinEQNMR computer program,[11] values of 6385(362) and 4692(570) M^{-1} respectively, quite high for acyclic receptors, were obtained for the 1:1 binding constants.

The interaction of receptor **1** with Bu_4NCl in CH_2Cl_2 solution lowers the IR *ν*(CO) values from to 2039 and 1929 (broad) to 2036, 1935 and 1911 cm^{-1} (for **1**:Cl^- = 1:1). Although small, this change suggests that IR spectroscopy could be used for anion sensing. Anion receptors containing optically or electrochemically-active transition metal fragments have been used as anions sensors.[3c,d,12] Changes in the IR spectrum as a signal has not been employed for anion sensing, and rarely for cation sensing,[13] despite the high sensitivity of FT-IR and the fact that metal carbonyls display intense bands in a region of the spectrum free from other absorptions.[14]

In summary, we have demonstrated the easy availability of cationic *fac*-tris(pyrazole) complexes as their salts with the BAr′$_4$ anion, their coordinative stability toward chloride, and their strong binding of this anion. Further studies on the behavior of these new receptors, and the extensions of these studies to other anions, and to receptors based in other metals, are in progress in our laboratory and will be reported in due course.

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Notes and references

1 (*a*) A. Looney, G. Parkin and A. L. Rheingold, *Inorg. Chem.*, 1991, **30**, 3099–3101; (*b*) G. Parkin, *Adv. Inorg. Chem.*, 1995, **42**, 291–393.

2 (*a*) X. Liu, C. A. Kilner and M. A. Halcrow, *Chem. Commun.*, 2002, 704–705; (*b*) S. L. Renard, C. A. Kilner, J. Fisher and M. A. Halcrow, *J. Chem. Soc., Dalton Trans.*, 2002, 4206–4212.

3 For overviews of anion-binding receptors, see: (*a*) *Supramolecular Chemistry of Anions*, ed. A. Bianchi, K. Bowman-James and E. García-España, Wiley-VCH, New York, 1997; (*b*) *Coord. Chem. Rev.*, 2003, **240**, thematic issue; (*c*) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486–516; (*d*) P. D. Beer and D. K. Smith, *Prog. Inorg. Chem.*, 1997, **46**, 1–96; (*e*) F. P. Schmidtchen and M. Berger, *Chem. Rev.*, 1997, **97**, 1609–1646.

4 For recent overviews on scorpionate ligands in coordination chemistry, see: (*a*) S. Trofimenko, *The Coordination Chemistry of Polypyrazolylborate Ligands*, University College Press, London, 1999; (*b*) S. Trofimenko, *Polyhedron*, 2004, **23**, 193–203.

5 (*a*) C. R. Bondy, P. A. Gale and S. J. Loeb, *Chem. Commun.*, 2001, 729–730; (*b*) C. R. Bondy, P. A. Gale and S. J. Loeb, *J. Am. Chem. Soc.*, 2004, **126**, 5030–5031; (*c*) For other examples of this concept see: K. J. Wallace, R. Daari, W. J. Belcher, L. O. Abouderbala, M. G. Boutelle and J. W. Steed, *J. Organomet. Chem.*, 2003, **666**, 63–74.

6 For reviews of low-coordinating anions, see: (*a*) S. H. Strauss, *Chem. Rev.*, 1993, **93**, 927–942; (*b*) I. Krossing and I. Raabe, *Angew. Chem., Int. Ed.*, 2004, **43**, 2066–2090.

7 S. P. Schmidt, J. Nitschke and W. C. Trogler, *Inorg. Synth.*, 1989, **26**, 113–116.

8 *Synthesis* of $[Re(CO)_3(3,5\text{-dimethylpyrazole})_3]BAr'_4$ (**1**): A mixture of $[Re(OTf)(CO)_5]$ (0.250 g, 0.564 mmol) and 3,5-dimethylpyrazole (0.163 g, 1.692 mmol) in toluene (20 mL) was refluxed for 2 h and the solvent was evaporated to dryness. The residue was dissolved in CH_2Cl_2 (20 mL), $NaBAr_4'$ (0.500 g, 0.564 mmol) was added and, after stirring for 5 min., the mixture was filtered through diatomaceous earth. The solution was concentrated *in vacuo*, layered with hexane and stored at −20 °C for 12 h affording colorless crystals of **1**, one of which was used for the X-ray structure determination. Yield: 0.557 g, 81%. IR (CH_2Cl_2): 2039s, 1929vs. ^1H NMR (CD_2Cl_2): δ 8.98 [s br, 3H, NH of pz], 7.72 [m, 8H, H_o of Ar′$_4$], 7.57 [m, 4H, H_p of Ar′$_4$], 6.25 [s, 3H, pz], 2.38 [s, 9H, Ch_3 of pz], 2.25 [s, 9H, CH_3 of pz]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 192.9 [s, CO], 162.1 [q ($^1J_{CB}$ = 49.8 Hz), C^I of Ar′$_4$], 157.5, 145.9 [s, pz], 135.2 [s, C^o of Ar′$_4$], 129.3 [q ($^2J_{CF}$ = 30.5 Hz), C^m of Ar′$_4$], 124.9 [q ($^1J_{CF}$ = 272.3 Hz), CF_3 of Ar′$_4$], 117.9 [s, C^p of Ar′$_4$], 109.7 [s, pz], 15.7 [s, CH_3 of pz], 11.3 [s, CH_3 of pz]; *Synthesis* of $[Re(CO)_3(3(5)\text{-}tert\text{-butylpyrazole})_3]BAr'_4$ (**2**): This was prepared in a similar way, starting from $[Re(OTf)(CO)_5]$ (0.250 g, 0.564 mmol), 3(5)-*tert*-butylpyrazole (0.203 g, 1.638 mmol) and $NaBAr_4'$ (0.500 g, 0.564 mmol). Yield: 0.550 g, 65%. IR (CH_2Cl_2): 2038s, 1933vs. ^1H NMR (CD_2Cl_2): δ 9.33 [s br, 3H, N-H of pz], 7.70 [m, 8H, H_o of Ar′$_4$], 7.57 [m, 4H, H_p of Ar′$_4$], 7.24 [t ($^3J_{HH}$ = 2,08 Hz), 3H, pz], 6.35 [t ($^3J_{HH}$ = 2.08 Hz), 3H, pz], 1.27 [s, 27H, CH_3 of pz]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 193.3 [s, CO], 162.1 [q ($^1J_{CB}$ = 49.8 Hz), C^i of Ar′$_4$], 159.2, 145.1 [s, pz], 135.2 [s, C^o of Ar′$_4$], 129.2 [q ($^2J_{CF}$ = 32.3 Hz), C^m of Ar′$_4$], 124.9 [q ($^1J_{CF}$ = 272.6 Hz), CF_3 of Ar′$_4$], 117.9 [s, C^p of Ar′$_4$], 105.9 [s, pz], 31.8 [s, pz], 29.7 [s, CH_3 of pz].

9 *Crystal data*: for compound **1**, $C_{50}H_{36}BF_{24}N_6O_3Re$: crystal dimensions 0.20 × 0.22 × 0.38 mm, monoclinic, space group $P2_1/n$, a = 14.756(7), b = 26.143(12), c = 15.501(7) Å, β = 105.642(9)°, V = 5758(5) Å^3, Z = 4, T = 296(2) K, D_c = 1.640 g cm^{-3}, Mo-Kα radiation (λ = 0.71073 Å), 26020 reflections collected, 8406 independent reflections ($1.56 \leqslant \theta \leqslant 23.49°$), R_1 = 0.0546, $wR2$ = 0.1257, GOF on F^2 = 1.032. For compound **2**, $C_{56}H_{48}BF_{24}N_6O_3Re$: crystal dimensions 0.10 × 0.10 × 0.25 mm, triclinic, space group $P\bar{1}$, a = 10.819(6), b = 15.760(8), c = 19.839(10) Å, α = 74.846(11), β = 76.806(9), γ = 82.664(10)°, V = 3170(3) Å^3, Z = 2, T = 296(2) K, D_c = 1.578 g cm^{-3}, Mo-Kα radiation (λ = 0.71073 Å), 14258 reflections collected, 8980 independent reflections ($1.09 \leqslant \theta \leqslant 23.32°$), R_1 = 0.0408, $wR2$ = 0.0904, GOF on F^2 = 1.004. For compound **3**, $C_{26}H_{32}Cl_2N_8O_6Re_2$: crystal dimensions 0.13 × 0.17 × 0.28 mm, monoclinic, space group $P2_1/c$, a = 13.765(3), b = 18.596(4), c = 13.707(3) Å, β = 97.329(4)°, V = 3479.8(13) Å^3, Z = 4, T = 296(2) K, D_c = 1.901 g cm^{-3}, Mo-Kα radiation (λ = 0.71073 Å), 15207 reflections collected, 4993 independent reflections ($1.49 \leqslant \theta \leqslant 23.28°$), R_1 = 0.0262, $wR2$ = 0.0608, GOF

on F^2 = 1.004. CCDC 246231–246233. See http://www.rsc.org/cc/b4/b414407d/ for crystallographic data in .cif or other electronic format.

10 However, for a different concept (involving labile, self-assembled complexes) see: D. R. Turner, E. C. Spencer, J. A. K. Howard, D. A. Tocher and J. W. Steed, *Chem. Commun.*, 2004, 1352–1353.

11 M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, 311–312.

12 For a review of anion sensors, see: R. Martínez-Máñez and F. Sancenón, *Chem. Rev.*, 2003, **103**, 4419–4476.

13 C. E. Anson, C. S. Creaser and G. R. Stephenson, *J. Chem. Soc., Chem. Commun.*, 1994, 2175–2176.

14 G. Jaouen, A. Vessières and I. S. Butler, *Acc. Chem. Res.*, 1993, **26**, 361–369.