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Pyrazole Complexes and Supramolecular Chemistry

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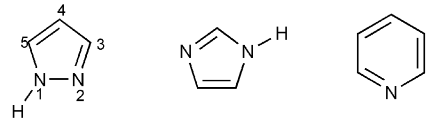
This Microreview deals with the supramolecular chemistry of pyrazole metal complexes, in particular, complexes of pyrazoles with a nonsubstituted N–H group, which are able to engage in hydrogen bonding. The most pertinent general features of pyrazoles, in comparison with other heterocycles that are also popular ligands, and some aspects of the supramolecular chemistry of free pyrazoles are also included. In addition to the general supramolecular chemistry of pyrazole complexes, sections of this Microreview are devoted to liquid crystals, self-assembled species, and hosts for anions.

Introduction

Azole heterocycles are interesting because of, among other reasons, their occurrence in natural and unnatural molecules with biological activity and the wide application of azole-derived ligands in all areas of coordination chemistry. Pyrazoles, while rarely found in naturally occurring molecules, are present in many pharmaceuticals with a wide range of biological activities.[1]

Aromatic N-heterocycles such as pyrazoles, imidazoles, and pyridines (Figure 1) contain, as part of the aromatic ring, a nitrogen atom with a localized lone electron pair on an in-plane orbital. They also feature low-energy empty orbitals, the antibonding π* orbitals of the aromatic system, perpendicular to the molecular plane. Therefore, electronically, these heterocycles are both σ-donor and π-acceptor ligands.[2] As per their steric characteristics, their planarity makes these aromatic molecules relatively unencumbered ligands. This is more so in the case of the azoles, with a CNC angle of 108° about the donor N atom, compared with 120° for pyridine. However, the exact steric profile is highly dependent on the presence of substituents, their size, and their position on the ring.



(a) (b) (c)

Figure 1. Pyrazole with numbering scheme (a), imidazole (b), and pyridine (c).

As ligands, pyrazoles have attracted considerable interest mainly because their conjugate bases, pyrazolates, have been found to bind metals in a variety of coordination modes and, in particular, are robust bridging ligands.[3] Among other properties, pyrazolato complexes have been used as precursors for chemical vapor deposition and they have luminescent properties.[4] Moreover, pyrazole and pyr-

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azolate moieties can be integrated as part of many polydentate ligands.[5] Among these, polypyrazolylborates are some of the most useful and widely employed ligands in several areas of coordination chemistry.[6]

As excellent reviews have dealt with pyrazolato complexes[3] and with the chemistry of polypyrazolylborate and related ligands,[5,6] in this Microreview we will focus mainly on metal complexes of simple N–H pyrazoles and those aspects of their chemistry in which noncovalent interactions, prominently hydrogen bonding, play a major role.

Pyrazoles, which can be used as ligands or as precursors of pyrazolate-based ligands, are, in general, accessible by well-established synthetic methods.[7] These methods are quite general, and this allows the preparation of pyrazoles with a variety of substitution patterns and with different functionalities as substituents of the pyrazole ring.

The parent azoles possess, besides a pyridine-like nitrogen atom bearing a lone electron pair, a pyrrole-like nitrogen atom, with its relatively acidic hydrogen atom. Therefore, the azoles are both basic and acidic according to the Brønsted-Lowry definition, that is, they are amphiprotic species. Their conjugate bases (their deprotonated forms), namely, the azolate anions, are well-known ligands. Due to the presence of two basic nitrogen sites the azolates often act as bridging ligands.

The conjugate acids (or protonated forms) of the azoles, namely, the azolium cations, are present in many salts. The behavior of azolium cations as supramolecular guests toward certain hosts has been studied.[8] While imidazolium cations have been the ones most extensively applied, pyrazolium cations have been found to play crucial roles in some cases. For instance, theoretical studies suggest that ionic pairing involving hydrogen bonds between the N–H groups of pyrazolium cations and chlorido ligands of tetrachloroplatinate anions (Figure 2) is important in the Shilov-like C–H activation catalyzed by $PtCl_2$ in concentrated H_2SO_4 and a pyrazole-based ionic liquid.[9]

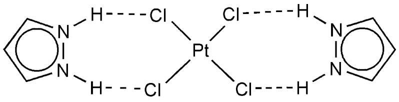


Figure 2. Neutral adduct formed between the tetrachloroplatinate(II) anion and two pyrazolium cations.

Supramolecular Behavior of Free Pyrazoles

Besides being able to fully accept or donate H^+, the basic site of azole molecules can act as a hydrogen-bond acceptor, and the N–H group can act as a hydrogen-bond donor. The ability of this N–H group to act as a hydrogen-bond donor is the main reason why azoles are important molecules in supramolecular chemistry. Since both hydrogen-bond-donor and -acceptor sites are present on the same molecule, relatively strong intermolecular N–H···N hydrogen bonding occurs in N–H azoles. This interaction is an important contribution to the melting point of imidazoles and pyrazoles: whereas at room temperature pyrazole and imidazole are solids, *N*-methylpyrazole and *N*-methylimidazole are, like pyridine, liquids.[10]

The two different nitrogen atoms are in the 1,2-positions (vicinal) in pyrazoles, and in the 1,3-positions (alternate) in imidazoles. An important consequence is that only open, chain-like structures, termed catemers, are possible for imidazoles. For pyrazoles, both catemers and cyclic oligomers have been found (Figure 3). The particular type of aggregation that occurs in the solid-state structure of N–H pyrazoles has been found to be largely dependent on the substitution pattern of the pyrazole ring. For instance, the known structures of N–H pyrazoles with only C–H or C–CH_3 ring carbon atoms are either catemers (pyrazole and 3,4,5-trimethylpyrazole) or trimers [4-methylpyrazole, 3(5),4-dimethylpyrazole, and 3,5-dimethylpyrazole]. For N–H pyrazoles with bulky substituents at the 3- and 5-positions, dimers, tetramers, or hexamers were found.[11] This secondary structure, in turn, explains some surprising trends in melting points: for instance, the melting points of 4-methylpyrazole and 4,5-dimethylpyrazole are lower than that of pyrazole. Now, unlike N–CH_3 pyrazoles, these three compounds possess N–H groups, and their molecules engage in N–H···N hydrogen bonding. 4-Methylpyrazole and 4,5-dimethylpyrazole have larger molecular weights than pyrazole. Hence, larger van der Waals forces are present, and, as a result, higher melting points would be expected. The fact that the opposite is observed is attributed to the inability of the trimeric structure of the methylpyrazoles to form extended hydrogen-bonded structures like the catemer formed by pyrazole.

In solution, the degree of aggregation of pyrazoles varies strongly, depending on the nature of the solvent: in relatively “inert” solvents such as chloroform or toluene, a high degree of intermolecular hydrogen bonding persists between pyrazole molecules. In solvents with a higher ability to act as hydrogen-bond acceptors, this hydrogen bonding is mostly broken and replaced by solvent–pyrazole interactions. This is reflected, for instance, in the shift to lower field observed for the N–H signals of pyrazoles upon changing the solvent from thf to toluene. The shift indicates that the hydrogen bonds between pyrazole molecules (the ones occurring predominantly in toluene) are stronger (thus giving rise to lower-field signals) than those between pyrazole and thf.[12]

The ability of pyrazoles to act both as hydrogen-bond donors and acceptors likens them to molecules such as carboxylic acids, which also self-associate. Because of this common feature, supramolecular adducts of carboxylic acids with pyrazoles (Figure 4) have been used as crystal engineering synthons.[13]

N–H pyrazoles undergo tautomeric prototropy (Figure 5).[14] For many pyrazoles, this has been found to be a fast process in solution at room temperature. However, with a combination of low temperature and aprotic solvents of high polarity, it can usually be slowed down to the point that separate signals for the two tautomers can be observed by NMR spectroscopy.[15] Of course, for the two tautomers

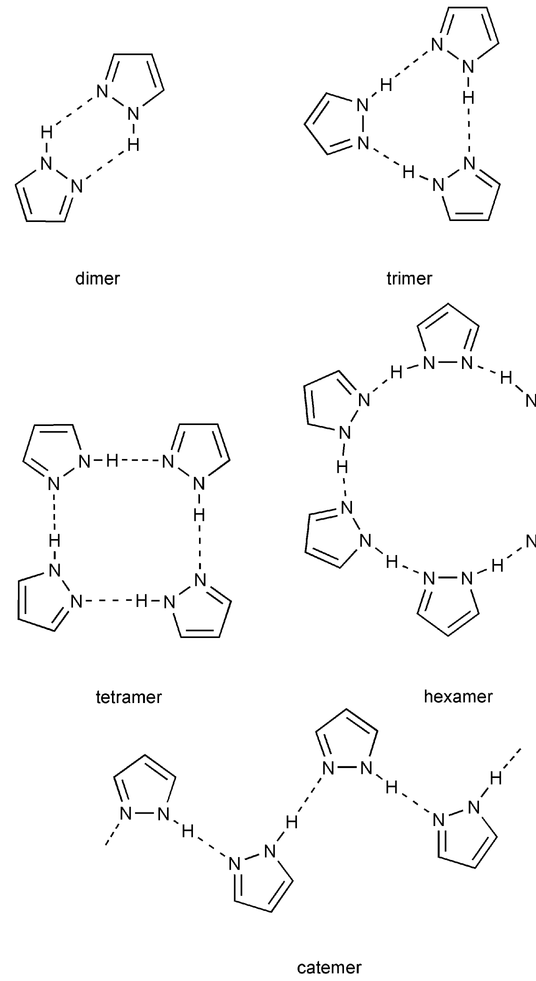


Figure 3. Oligomers formed by pyrazoles.

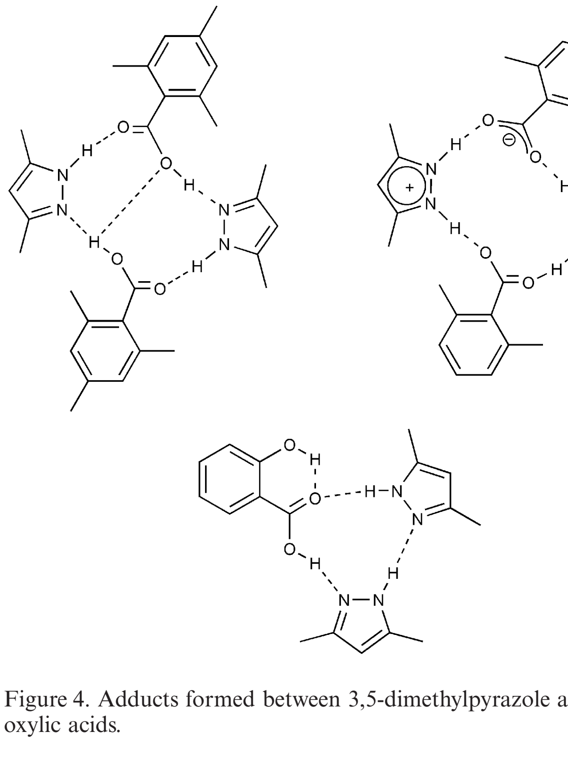


Figure 4. Adducts formed between 3,5-dimethylpyrazole and carboxylic acids.

to be observed by NMR spectroscopy, they must be different. In symmetric systems with the same substituents at the 3- and 5-positions, such as pyrazole or 3,5-dimethylpyrazole, the two tautomers are identical (this tautomerism is termed autotrope or degenerate),[14] and only one species is observed even at low temperature. However, when the tautomerism is slowed down, separate signals can be seen, for instance, for the carbon atoms C3 and C5.[15] Despite the fact that tautomerism in pyrazoles is relatively fast, it is an intermolecular process. Several theoretical studies have indicated that this intramolecular tautomerism has a relatively high energy barrier (around 50 kcal mol^{-1}).[16]

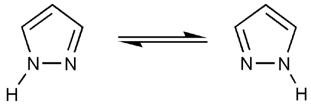


Figure 5. Prototropy in pyrazole.

Recent investigations have tackled the study of tautomerism in the solid state. It has been found that one of the requirements for it to occur is that the numbers of transferred protons must be small. As a consequence, it occurs in pyrazoles that crystallize by forming trimers, such as 3,5-dimethylpyrazole, but is not observed in catemers.[11]

Pyrazole Complexes: Synthesis and Stability

Azole complexes are almost invariably prepared by substitution reactions of the free azole with a suitable precursor containing a coordinative unsaturation or a ligand that can be displaced easily under the reaction conditions. In a few cases, pyrazole complexes were prepared by the substitution reaction of a preformed pyrazolate salt with a metal complex such as a halide complex.[17] The latter reaction affords a pyrazolato complex that is protonated in a subsequent step to yield the pyrazole complex.[17] Complexes containing pyrazolato ligands can be prepared by reaction of preformed alkaline pyrazolate salts with suitable metal complexes (e.g., halide complexes, so that the pyrazolate anion replaces the halide), but also by treating preformed pyrazole complexes with a base.[18] In many cases the employment of preformed pyrazolate salts or pyrazole complexes is not required for the synthesis of metal pyrazolato complexes. Rather, they can be directly formed from suitable metal precursors, the pyrazole, and a base.[19] However, the formation of pyrazolato complexes can also occur by the reaction of the metal precursor and the pyrazole without the purposeful addition of an external base. For instance, if the metal complex contains ligands (X) such as alkyl, hydrido, alkoxido, amido, etc., its reaction with relatively acidic N–H groups such as those of azoles can afford azolatometal complexes upon elimination of HX (HX = alkane, dihydrogen, alcohol, amine, etc).[20] A similar reactivity has been encountered for some η^5-cyclopentadienyl complexes.[21]

Even with less reactive ligands, such as chlorido, elimination of hydrogen chloride can occur, which is favored by its volatility.[22] Moreover, since azoles themselves are bases, part of the azole added as ligand can act as a base instead.[23] This feature is particularly important when the possible product of elimination is strongly acidic, such as HCl. Even when pyrazole complexes can be accessed under conditions of kinetic control, the simultaneous presence in the coordination sphere of the same metal center of the pyrazole and some basic ligand X, able to eliminate HX, should be seen as a possible source of thermal instability.

Some pyrazole complexes do not possess ligands X that are able to eliminate products HX, but are nevertheless thermodynamically unstable. One needs to keep in mind that electron-rich metal centers, if they are unsaturated or can lose some ligand to generate an unsaturation, can undergo oxidative addition of the N–H group of azoles.[24] If this reaction is kinetically viable and the products are not stable, then the metal complexes of, for instance, N–H azoles, will be unstable. Also, an N-donor ligand such as an azole, a relatively hard base, can be a poor ligand for a soft metal center, such as a low-oxidation-state, electron-rich metal complex. As a recent example, *cis*-[Mo(CO)$_4$(Hpz)$_2$] complexes were found to be isolable as crystals, yet they were thermally quite unstable in solution.[25]

Pyrazole Complexes: Supramolecular Chemistry

Coordination of azoles to metal centers has several effects. First, electron donation from the pyridine-like nitrogen atom of the azole to the Lewis acidic metal center increases the acidity of the azole N–H group. This can lead to the formation of pyrazolate rather than pyrazole complexes. Even when stable pyrazole complexes can be prepared, the increase in the acidity of the N–H group due to pyrazole coordination can result in the deprotonation of the complexes in the presence of even very weak bases. If full deprotonation does not occur, coordination of the azole increases the ability of the azole N–H group to act as a hydrogen-bond donor. This increase will be higher if the complex is positively charged. In this case, the electrostatic attraction between the cationic complex and the anionic host will add to the hydrogen-bond interaction between the two species.

A second effect of the coordination of the azole to a metal center is placing the azole in the proximity of other ligands. When a coordinated pyrazole is adjacent to a hydrogen-bond-acceptor ligand, intramolecular hydrogen bonding can occur. Note that this is not possible for an imidazole, in which the donor N and the N–H group are in alternate positions. Such hydrogen bonds have been deemed partly responsible for the difference in the behavior of pyrazole and imidazole as ligands toward nickel(II) chloride. Thus, even when using a large excess of pyrazole (Hpz), only [NiCl$_2$(Hpz)$_4$] could be isolated, and no further substitution of chlorido ligands could be achieved. In this species, intramolecular hydrogen bonds between each Cl ligand and the N–H groups of the two adjacent pyrazole ligands stabilize the metal-coordinated chloride anions (Figure 6).[26] In contrast, with imidazole (Him), [Ni(Him)$_6$]Cl$_2$ is isolated, in which the hydrogen bonds between the N–H groups and the chloride anions outside the first coordination sphere of the metal are intermolecular.

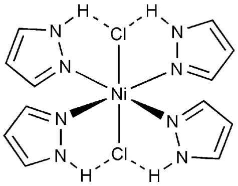


Figure 6. Structure of [NiCl$_2$(Hpz)$_4$] showing intramolecular hydrogen bonds as dashed lines.

Among pyrazoles, the number, positions, and size of the substituents contribute significantly to the nature of the product in the reaction with metal precursors. Guzei and Winter studied the reactions of titanium tetrachloride with two equivalents of different pyrazoles and found the results summarized in Scheme 1.[27]

With 3,5-dimethylpyrazole and 4-iodopyrazole, neutral complexes [TiCl$_4$(Hpz)$_2$] were obtained as the only products. The bulkier 3,5-dimethylpyrazole affords the *trans* isomer, whilst with 4-iodopyrazole the *cis* isomer is obtained. In contrast, the reaction with 3,5-bis(*tert*-butyl)pyrazole, which would be too bulky a ligand, yielded a mixture of the neutral [Ti{κ^2(*N*,*N'*)-pz}$_2$Cl$_2$] (in the κ^2-coordinated pyrazolates, the bulky *t*Bu groups are kept away from the metal, in contrast to the situation observed with a monodentate neutral pyrazole) and the salt [H$_2$pz][TiCl$_6$]. In the latter, a significant lengthening of one of the Ti–Cl distances is attributed to a strong N–H···Cl hydrogen bond.

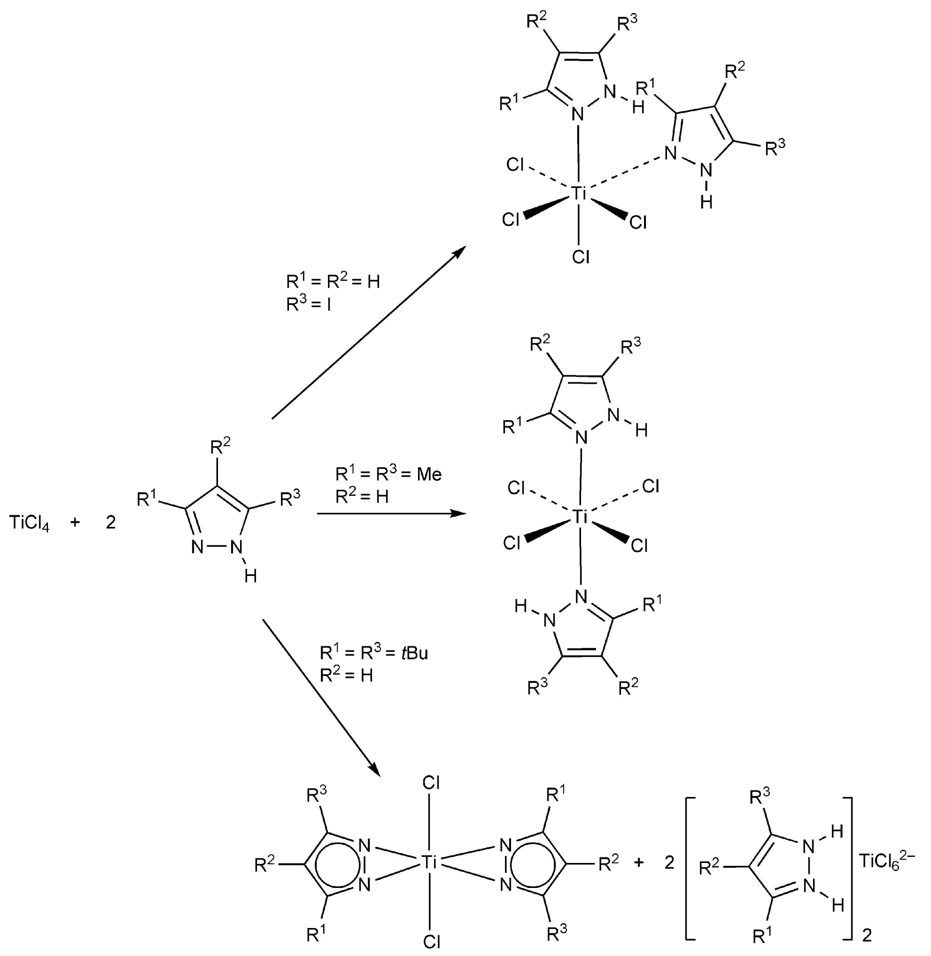
Pyrazolato ligands have a strong tendency to act as bridges between two metal centers. In fact, most pyrazolato complexes are binuclear species. Because the two nitrogen atoms in pyrazoles are directly bonded, the distance between the two metals in pyrazolato-bridged bimetallic complexes is small, being compatible with distances resulting from other small bridges, such as halido, hydroxido, etc.[28]

Using mononuclear pyrazolato complexes as metalloligands for a second metal center (which can be different from the first) or reacting mononuclear pyrazole complexes with a suitable metal precursor in the presence of a base can serve as a rational synthetic procedure for the stepwise synthesis of binuclear (including heterobinuclear) complexes.[28–30]

Pyrazolato ligands can abstract protons from carboxylic acids without cleavage of the N–metal bonds; the resulting cationic pyrazole complexes form strong, charge-assisted, N–H···O hydrogen bonds with the carboxylato anions (Figure 7).[31]

A few complexes are known in which both a bridging pyrazolato ligand and a monodentate pyrazolato or pyrazole ligand coexist, and the dynamic processes interconverting the two ligands have been studied.[32]

It has been mentioned above that prototropic tautomerism in pyrazoles is usually fast at room temperature, and that the steric profile of pyrazoles as ligands depends of



Scheme 1. Influence of the substitution pattern of pyrazoles on the nature of the product of the reaction of $TiCl_4$ and pyrazoles.

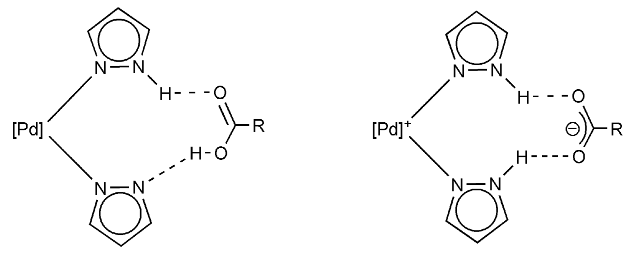


Figure 7. Intermolecular hydrogen bonds formed between pyrazolato ligands and carboxylic acids. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Adapted from ref.[31] with permission.

the position of the substituents on the ring. 3-Substituted pyrazoles are usually in a dynamic equilibrium with their 5-substituted tautomers. Sometimes, such an equilibrium also occurs in metal-complexed pyrazoles, and it involves metallotropy in addition to prototropy; that is, the proton and the metal exchange sites (Figure 8). Often, coordination of the pyrazole to a metal center leads to the formation of a complex with the 5-substituted tautomer of the pyrazole as the only product, because it is the one with the lower steric hindrance.[33,34] Accordingly, the presence of a bulky substituent in the 5-position of a pyrazole ligand usually prevents metallotropy. A few examples have been reported in which the presence of linkage isomerism for pyrazole ligands has been demonstrated.[34,35] In the Pt^{II} complexes investigated by Bokach et al., the presence of the 3-methylpyrazole or 5-methylpyrazole isomers was attributed by the authors, in part, to the hydrogen bonding between the N–H group of the pyrazole ligands and the Cl or O atoms of the $PtCl_4^-$ or picrate counteranions.

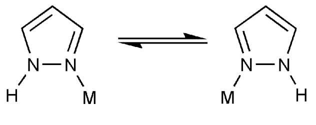


Figure 8. Simultaneous prototropy and metallotropy.

Compared with prototropy in free pyrazoles, metallotropy in N–H pyrazoles involves not only proton scrambling, but also simultaneous metal scrambling between the two nitrogen atoms. As a result, metallotropy is a kinetically more difficult process.[18] Thus, in solution most pyrazoles display prototropy, but only some of their metal complexes display metallotropy. The occurrence of metallotropy is sensitive to the strength of the M–N(pyrazole) bond, which, for a given metal, usually correlates with the basicity of pyrazole. Thus, stronger M–N(pyrazole) bonds can suppress metallotropy. However, it must be noted that the deprotonation of a pyrazole to generate a (more basic) pyrazolato ligand makes metallotropy a more facile process, because it now involves only metal (not H^+) scrambling.

Dixon and co-workers, in the first study of the dynamic behavior of pyrazole complexes, noted the occurrence of metallotropy for palladium complexes, whilst the platinum analogues were found to be static, in accord with the more inert M–N bond for the third-row metal.[36] The same effect was found by Villafañe and co-workers in a study of Ag pyrazole complexes as compared with their Au analogues.[37]

Grotjahn and co-workers prepared chelating ligands containing an N–H pyrazole and either a phosphane or a thioether, and their dichlorido-*cis*-palladium(II) complexes are depicted in Figure 9. The authors found that prototropy occurs in the free ligands, but not in the complexes.[38] In this case, dissociation of the pyrazole donor from the metal would be more difficult than it would be in monodentate pyrazoles because of the chelate effect. Moreover, metal bonding by the phosphane or thioether, along with the rigidity of the pyrazole ring donor would make the alternative arrangement resulting from metallotropy highly unstable. In addition, pyrazole dissociation can be hampered by the presence of an intramolecular N–H···Cl hydrogen bond.

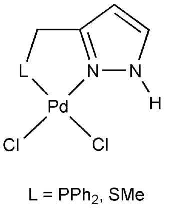


Figure 9. Dichloridopalladium(II) complexes of a chelating pyrazole prepared by Grotjahn and co-workers (see text).

Several complexes contain pyrazole and pyrazolato ligands coordinated to the same metal center.[17,18,39,40] For these species, another dynamic process has been noted: H^+ scrambling between the different noncoordinated nitrogen atoms. In these species, proton scrambling does not require a concomitant metallotropy and is therefore kinetically more facile than prototropy in complexes with only pyrazole ligands. In addition, intra- and intermolecular N–H···N hydrogen bonds have been found in such complexes.

Hydrogen bonds involving the N–H groups of coordinated pyrazoles as donors have been found to be important in determining the structures and properties of extended networks, but also of some molecular species.[41] Rocha and co-workers attributed the enhanced basicity of the pyrazolato ligand in [RuCl(dmpz)(bipy)$_2$][PF$_6$] to the formation of an intramolecular N–H···Cl hydrogen bond in its protonation product (Figure 10).[42]

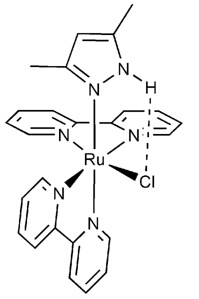


Figure 10. The product of protonation of a pyrazolato complex reported by Rocha and co-workers (see text).

Pyrazole complexes of low-valent organometallic fragments offer opportunities to observe important effects of even weak hydrogen bonds. For instance, Villafañe et al. proposed that the rotational (about the Mn–N bond) orientation of the pyrazole ligands in [MnBr(CO)$_3$(Hpz)$_2$] complexes is in part due to the intramolecular N–H···Br hydrogen bonds.[43]

In some of these low-valent organometallic species, the lack of good hydrogen-bond donors allows the detection of, for instance, intermolecular hydrogen bonds in which the acceptor is the oxygen atom of a carbonyl ligand. For instance, Villafañe et al. reported that [Mo(CO)$_4$(Hdmpz)$_2$] complexes are dimers formed by two such complementary hydrogen bonds (see Figure 11).[25] The structural consequences of the latter distort significantly the first coordination sphere: to allow the formation of the hydrogen bonds, the Mo–N bonds of the involved pyrazoles are tilted out of the pyrazole plane by 16.0(4)°.

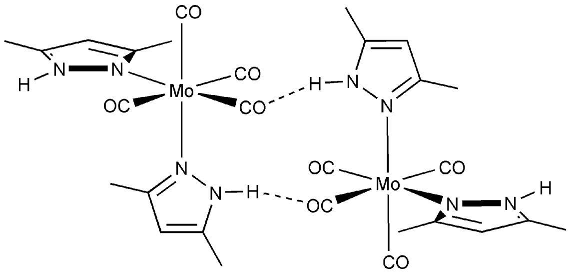


Figure 11. Dimerization by N–H···OC–M hydrogen bond formation in a complex reported by Villafañe and co-workers (see text).

In the [Mo(η^3-C$_3$H$_5$)(CO)$_2$(Hpz)$_2$] complexes, the same research group notes a dramatic effect in the IR spectrum that could be attributed to hydrogen bonding.[30] When comparing the IR spectra of the nonsubstituted pyrazole and the 3,5-dimethylpyrazole complexes, the authors found that, in thf, slightly higher ν(CO) values are found for the former, as expected, because Hdmpz is a stronger donor. Solid-state structures of the two complexes showed them to be isostructural and are consistent with the stronger donor character of Hdmpz. However, in the solid state (where hydrogen bonds are not broken by the solvent), the bands of the Hdmpz complex occur at considerably higher wavenumber values than those of the parent pyrazole complex. The authors note that in the pyrazole complex (but not in the 3,5-dimethylpyrazole complex) there are intermolecular

N–H···O hydrogen bonds. The absence of the intermolecular hydrogen bonds in the Hdmpz complex could be due to the higher steric hindrance resulting from the presence of the Me groups.

The binuclear compound prepared by Palma and co-workers (Figure 12) possesses a pyrazolate bridge and a 3,5-dimethylpyrazole coordinated to one of the nickel atoms.[32] Despite being a bromide salt, it is soluble in toluene, and its acetone solution shows low conductivity, suggesting a strong N–H···Br hydrogen bond. In accordance, no ν(NH) band was visible in its IR spectrum, and an N–H···Br hydrogen bond was found in its solid-state structure. The analogue with tetraphenylborate (a weaker hydrogen-bond acceptor than bromide) as counteranion turned out to be insoluble in toluene, displayed a much higher conductivity in acetone, and a ν(NH) band was visible in its IR spectrum. Furthermore, the proposed mechanism of a dynamic process operative on the bromide derivative includes dissociation of the pyrazole ligand assisted by metal-coordinated bromide.

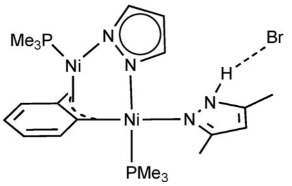


Figure 12. Strong N–H···Br hydrogen bonding in the Ni compound reported by Palma and co-workers has important consequences (see text).

Pyrazole Complexes and Liquid Crystals

Some *cis*-[MCl(CO)$_2$L] {M = Rh, Ir; L = nitrogen donor, calamitic (rodlike) premesogenic ligand} complexes have been found to display mesogenic behavior. Mesogenic behavior was observed in some calamitic pyrazoles synthesized by Oro, Serrano, and co-workers, who synthesized [RhCl(CO)$_2$(pyrazole)] complexes. The the pyrazole complex shown in Figure 13 formed a monotropic nematic phase.[44]

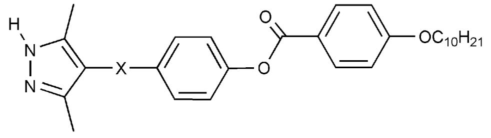


Figure 13. A calamitic pyrazole for which mesogenic behavior was found.

The same group viewed the planar supramolecular trimers formed by pyrazole aggregation as potential discotic mesogens that could be used to prepare columnar phases. This idea failed, but it was observed that geometrically analogous pyrazolate-bridged gold trimers shown in Figure 14 formed columnar mesophases at room temperature.[45]

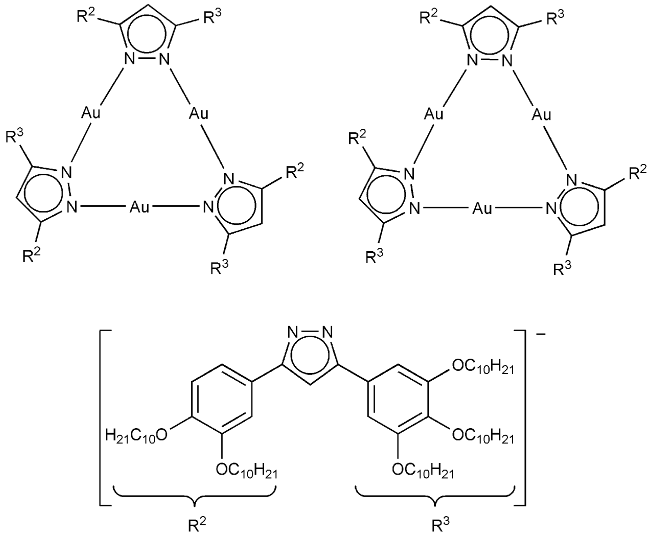


Figure 14. Mesogenic pyrazolate-bridged gold trimers.

In similar complexes, Cano et al. noted the presence of an intramolecular hydrogen bond between the *cis*-chloro and 3-substituted pyrazole ligands.[46] Perhaps this hydrogen bond helps to restrict the rotation about the Rh–pyrazole bond and therefore to maintain the observed stacking of the square-planar units in the solid state (Figure 15). The intermolecular separation is short, so that some degree of metal–metal bonding along the stacking axis is proposed. In addition, there is some interdigitation between consecutive layers. The importance of interdigitation in the formation of metallomesogens has been stressed in a recent review by Noveron and co-workers.[47]

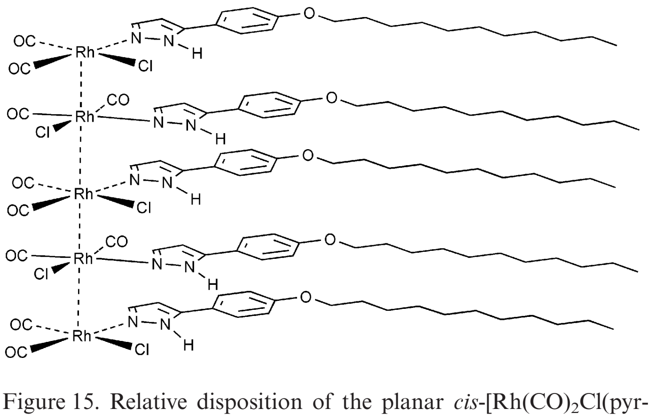


Figure 15. Relative disposition of the planar *cis*-[Rh(CO)$_2$Cl(pyrazole)] complexes reported by Cano et al. (see text).

Attempts by Cano and co-workers to synthesize [RhCl(CO)$_2$(pyrazole)] complexes with a range of new mesogenic, 3,5-disubstituted pyrazoles led to the isolation of the nonmesogenic pyrazolato complexes shown in Figure 16 via HCl elimination, despite the fact that a basic medium was not used.[48]

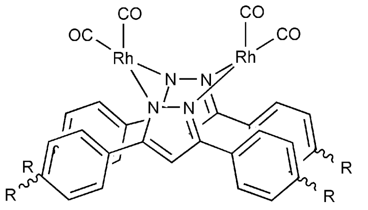


Figure 16. Pyrazolate-bridged rhodium dimers reported by Cano and co-workers (see text).

Giménez, Elduque et al. studied the preparation of columnar mesophases by using $[RhCl(CO)_2(pyrazole)]$ complexes of nonmesogenic 3,5-disubstituted pyrazoles.[49] The pyrazoles employed in this study bear highly alkoxy-substituted aryl groups, and only with a pyrazole having six decyloxy chains could mesomorphism be achieved (Figure 17). The authors noted the importance of the N–H···Cl hydrogen bonds in the adoption of the columnar mesophase. Using the same type of 3,5-disubstituted pyrazoles, Giménez et al. prepared $[ZnCl_2(pyrazole)_2]$ complexes.[50] Unlike all the species mentioned above, these are tetrahedral complexes, as expected for Zn coordination compounds. This is a major difference from most mesogens, which typically have either calamitic or discotic (disc-like) molecules. In solution, the bis(pyrazole) molecules display metallotropy. In the solid state, $[ZnCl_2(pyrazole)_2]$ molecules aggregate into dimers through intermolecular N–H···Cl hydrogen bonds. The mesomorphic behavior of the complexes depends on the number of decyloxy substituents of the pyrazoles, columnar mesomorphism being reached for the higher substitution (Figure 18). The new compounds were found to display luminescence both in solution and in the mesophase.[51]

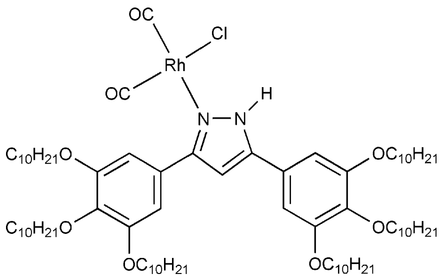


Figure 17. A mesomorphic complex reported by Giménez, Elduque et al. (see text).

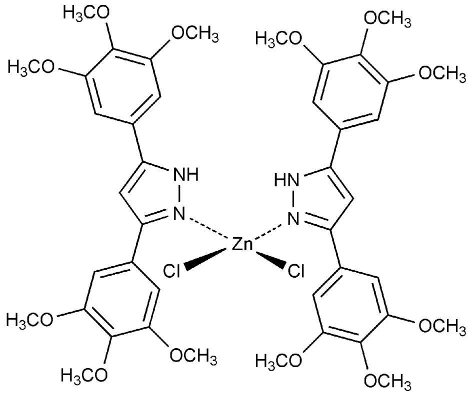


Figure 18. A tetrahedral, mesomorphic complex reported by Giménez et al. (see text).

Lodeiro, Cano et al. prepared a number of $[M(pyrazole)_2]$-X (M = Ag, Au; X = anion) salts and observed hydrogen bonding between the ligated pyrazoles and the anion in the solid state (Figure 19), metallotropy in solution, mesomorphism, and luminescent behavior in solution and, for some compounds, in the mesophase.[51]

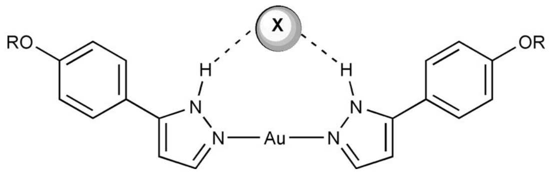


Figure 19. Gold compound reported by Lodeiro, Cano et al., showing anion–cation hydrogen bonding.

Self-Assembled Supramolecular Entities

The mixture of a labile metal precursor and a pyrazole (and perhaps additional components) in the appropriate medium has been used to synthesize self-assembled solid networks.[52] In 1991, Looney, Parkin, and Rheingold reported that the reaction of thallium tris(3-*tert*-butylpyrazolyl)hydroborate with HCl, followed by addition of $AlCl_3$, yielded the compound shown in Figure 20a.[53] This species can be considered as a supramolecular adduct formed between the protonated form of a tris(pyrazolyl)borate and a chloride anion, which would be held together by a combination of electrostatic attraction and hydrogen bonds. The chloride ion forms strong hydrogen bonds with the three N–H groups. The authors noted that, unlike in previous examples in supramolecular adducts of chloride anions, in which the anion was encapsulated by the receptor, in this case, the three N–H groups interact with only one face of the chloride anion.

In 1994, Reger and co-workers reported a similar structural motif in the lead compound shown in Figure 20b, obtained as a low-yield decomposition product by the reaction of $Pb(NO_3)_2$, $P(O)(3,5\text{-}Me_2pz)_3$, potassium tris(3,5-dimethylpyrazolyl)borate, and HCl.[54] This decomposition reaction is an example of cleavage of the B–N bond of a polypyrazolylborate ligand on protonation,[55] a quite general transformation that would complicate attempts of using triprotonated forms of such ligands as receptors of anions.[56] Halcrow and co-workers reported the synthesis and structural characterization of the self-assembled compound shown in Figure 20c by reaction of zinc halide and three equivalents of 3(5)-*tert*-butyl pyrazole.[57] The pyrazoles can, therefore, be considered ditopic ligands, which are able to interact simultaneously with the metal (as a Lewis base) and with the anion (through the hydrogen-bond-donor N–H groups). Alternatively, the supramolecular product can

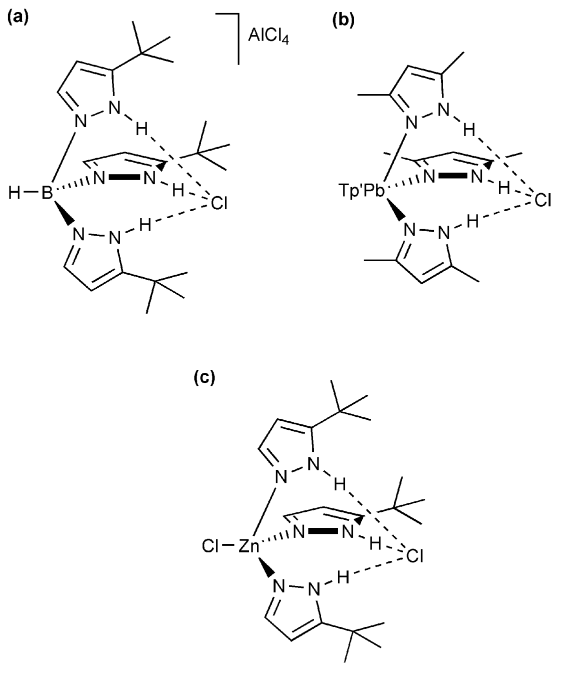


Figure 20. Self-assembled adducts reported by the groups of Parkin (a), Reger (b), and Halcrow (c), showing hydrogen bonds between the anion and the N–H groups of three pyrazole ligands. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Adapted from ref.[68] with permission.

be viewed as an adduct of anion X^- with "host" $[XZn(pzH)_3]^+$. However, it should be noted that the formation of the product is an example of self-assembly rather than host–guest chemistry. The neutral supramolecular adduct is soluble in solvents of low polarity, including chloroform and benzene, and it is even sparingly soluble in pentane. The authors pointed out that, in addition to the hydrogen bonds to the N–H groups, the chloride anion lies in the hydrophobic cavity created by the bulky *tert*-butyl groups.

In benzene, chloroform, and dichloromethane solution, NMR spectroscopy indicated the integrity of the supramolecular adducts. In contrast, in acetone, the pyrazole ligands are in rapid chemical exchange. Moreover, even in less polar solvents, an excess (1.5 equiv.) of halide also promotes pyrazole exchange, presumably through nucleophilic attack to the Zn center. Besides showing the lability of the supramolecular adducts, this behavior precludes the use of NMR spectroscopic titrations to determine binding constants. When a BF_4^- salt is added instead, the labilizing effect, as expected (BF_4^- is less nucleophilic than the halides), is less perceptible, but δ_{N-H} is lowered, indicating that BF_4^- competes to an appreciable degree with the halides for the complex anion-binding site. Further work with other anions of relatively low nucleophilicity such as nitrate, triflate, and hexafluorophosphate, reinforces this view. The authors showed that the reaction of $[ZnCl(HpztBu)_3]Cl$ with silver or thallium salts of different anions (X) affords $[ZnCl(HpztBu)_3]X$.[58] When very large, weakly nucleophilic carbaborane anions are used, only one of the three pyrazole ligands orients its N–H group towards the anion, whereas the other two form hydrogen bonds with the chlorido ligand of the other complex, thus leading to the formation of dimers.[59]

Pyrazole Complexes as Hosts for Anions

Several receptors for anions to be used in the aqueous phase contain pyrazole moieties in their structure.[60] In many cases the function of the pyrazole units is to act as a rigid spacer, a ligand (often for Cu^{II}), or both. N–H pyrazoles are often deprotonated under the conditions used. Here we will focus on the metal complexes containing simple pyrazoles as ligands and that are used in organic media, where the only possible base is the anionic guest.

One of the roles that metals can play in the construction of supramolecular hosts for anions is to serve as geometry-organizing elements. Beer and co-workers used metals to impart rigidity to 2,2′-bipyridines (Figure 21a), thus enforcing the convergence of the amido groups on their backbone towards external anions.[61] Our own group used a similar strategy with 2,2′-biimidazole (Figure 21b).[62] With the right choice of metal fragment, even monodentate ligands featuring hydrogen-bond-donor groups can be used for the synthesis of metal-based hosts.[63] Our group employed pseudo-octahedral metal complexes with three pyrazole ligands.[64] To be able to converge towards an external guest, the three pyrazole groups must be in a *fac* geometry. CO groups and other strongly π-accepting ligands tend to adopt *cis* (two ligands) or *fac* (three ligands) geometries to minimize the competition of the ligands for the metal back-donation of electron density. Therefore, we explored their tris(pyrazole) complexes. We chose cationic fragments so that coulombic attraction between host and guest would add to hydrogen bonding. Mid transition metals in low oxidation states provide carbonyl complexes with pseudo-octahedral geometries and sufficient stability. We prepared the molyb-

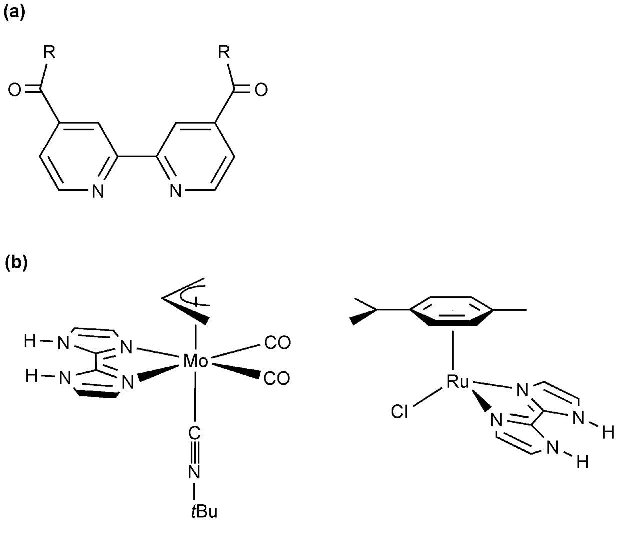


Figure 21. The 4,4′-bis(carbamoyl)-2,2′-bipyridine ligand employed by Beer (a) and 2,2′-biimidazole complexes used as anion receptors by our group (b).

denum, manganese, and rhenium complexes shown in Figure 22.[65] When cationic complexes are to be used as anion hosts, the nature of the counteranion is particularly important. The tetraarylborate BAr′$_4$ [Ar′ = 3,5-bis(trifluoromethyl)phenyl] counteranion, with a high degree of charge delocalization, was chosen because it is more inert toward B–C bond cleavage and group transfer, less coordinating, and interacts less with the cationic hosts than other more frequently used anions. In addition, as a result of the presence of the CF_3 substituents, it imparts to its salts large solubility in organic solvents of moderate polarity.[66]

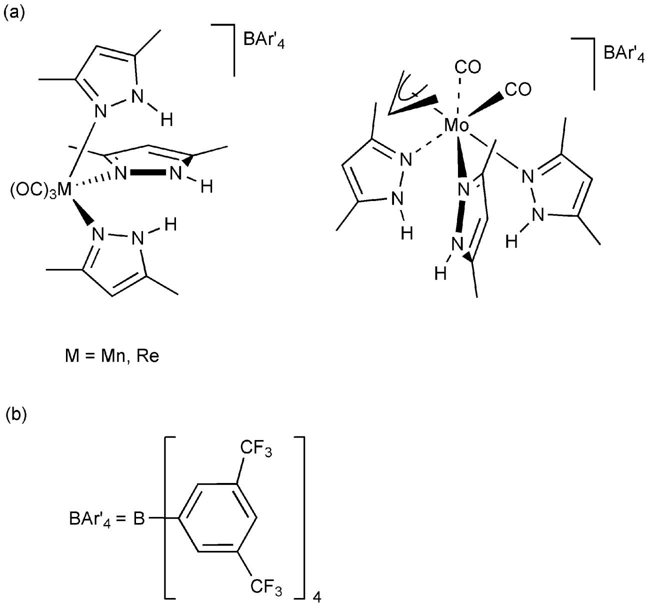
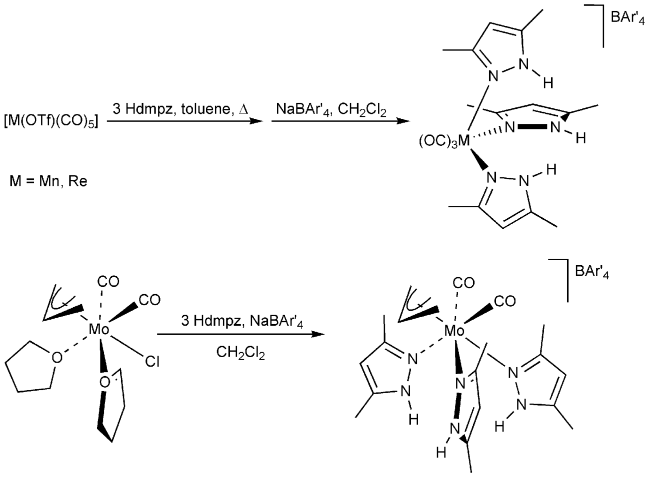


Figure 22. Tris(pyrazole) complexes reported by our group (a) and the BAr′$_4^-$ anion (b).

The compounds of choice were prepared in high yield by the routes outlined in Scheme 2 and isolated as pure solids that can be handled in the air. The presence of carbonyl ligands allows easy monitoring of the solution behavior of these species by IR spectroscopy in the ν(CO) region. In addition, the behavior of these diamagnetic compounds can be studied by means of NMR spectroscopy.

The new compounds were found to be stable and nonfluxional in solution, that is, the pyrazole ligands were not undergoing fast dynamic processes. However, for the molybdenum and manganese compounds, in the presence of most anions, one of the pyrazoles was rapidly displaced. In contrast, the rhenium complexes were found to be stable in solution even in the presence of several equivalents of anions. This is not surprising, since the high kinetic stability of rhenium tricarbonyl complexes, due to the d^6 electronic configuration and the third row metal, has been taken advantage of in, for instance, bioinorganic and medicinal chemistry.[67]

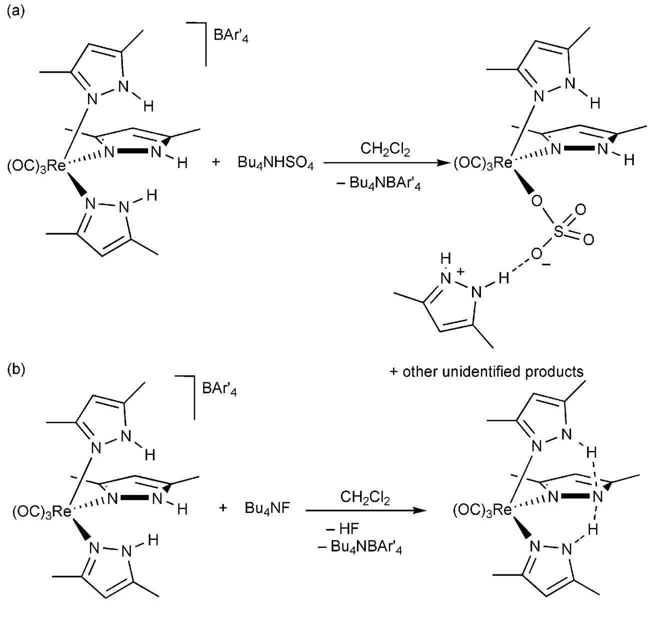
In the solid state, our investigation on the behavior of the new receptors towards anions has relied on the characterization by single-crystal X-ray diffraction of the anion–receptor adducts. In solution, IR and NMR spectroscopy were used. In ^{1}H NMR spectroscopy, successive additions of the chosen anion (as the tetrabutylammoniun salt) gave rise to the displacement of the signals of the N–H groups to higher frequencies rather than to the appearance of new signals. This demonstrated that the anion exchange was fast in the NMR timescale. This variation of the chemical shift was used to calculate the binding constants, in other words, the thermodynamic stability of the anion–receptor adducts.



Scheme 2. Synthesis of the compounds shown in Figure 22.

When the behavior of the new receptors towards the tetrabutylammonium salts of several anions (X^-) was investigated, two reactions appeared in addition to the formation of N–H···X hydrogen bonds.[68] With HSO_4^-, one of the pyrazole ligands was protonated, leading to the coordination of sulfate, to which the resulting pyrazolium cation, outside the first coordination sphere of the metal, is strongly hydrogen-bonded (Scheme 3a). With the fluoride anion, deprotonation of the NH group took place (Scheme 3b). Deprotonation of N–H groups of different receptors by the basic fluoride anion is a well-known reaction, which, in many instances, proves to be difficult to distinguish from hydrogen bond formation.[69] In our case, the neutral pyrazole/pyrazolate product is a complex previously prepared by another route by Masciocchi, Ardizzoia, and co-workers.[18] Its formation from the cationic tris(pyrazole) complex was accompanied by a large decrease in ν(CO) values. The straightforward detection of eventual deprotonation reactions is, therefore, an advantage of using carbonyl complexes as hosts. In addition, in the timescale of IR spectroscopy, all dynamic processes are slow; therefore, bands corresponding to the interconversion of individual species are visible in the IR spectrum.

The solid-state structures of the anion–host adducts show a difference from those of the self-assembled structures discussed in the preceding section: now only two out of the three pyrazole groups form hydrogen bonds with the anion (Figure 23). The comparison of the structural parameters of the free “receptor” {the $[Re(CO)_3(Hpz)_3]^+$ complex as BAr′$_4$ salt} with those of the X adducts revealed that the formation of the latter involves a perceptible degree of



Scheme 3. Protonation (a) and deprotonation (b) of pyrazole ligands in rhenium complexes. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Adapted from ref.[68] with permission.

deformation.[68] Thus, the N–Re–N angles need to open somewhat to form the hydrogen bonds with the anionic guest. The difference from the compounds studied by the groups of Parkin and Halcrow (see above) can be attributed to the different geometries of these adducts: octahedral (rhenium complexes) vs. tetrahedral (B or Zn). Such distortion would make hydrogen bonding to the three pyrazoles unfavorable. In contrast, the wider N–M–N angles about the pseudo-tetrahedral B or Zn centers would not need to distort to form three hydrogen bonds to the anion. In solution, variable-temperature studies showed that fast anion exchange occurs between pairs of pyrazoles.

The possibilities offered by the transition metal center allowed us to synthesize anion hosts featuring pyrazoles cooperating with other ligands. Thus, pyrazole–nitrile coupling, a reaction of which a few precedents were reported, was used to synthesize a bidentate pyrazolylamidino li-

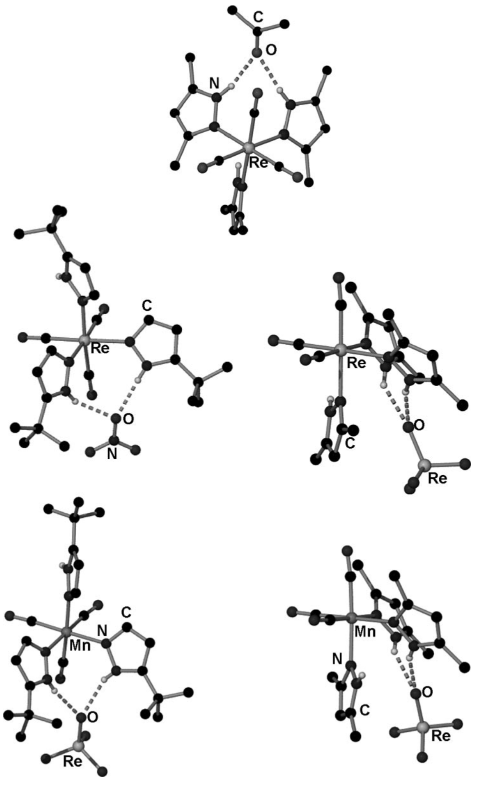
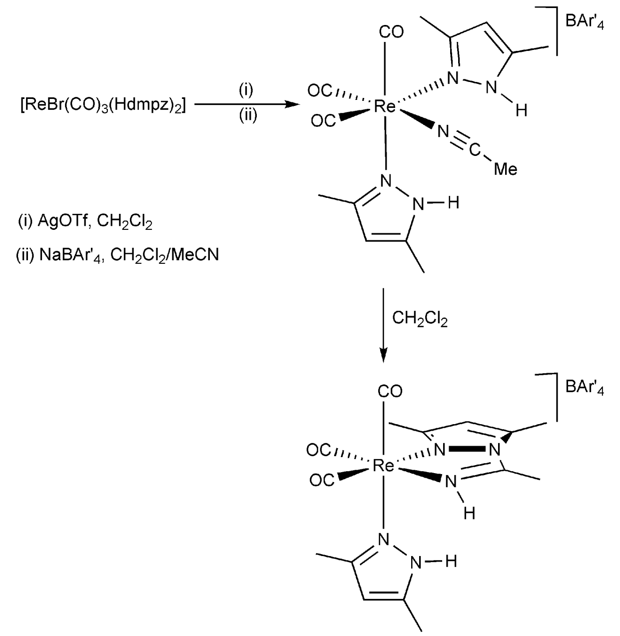
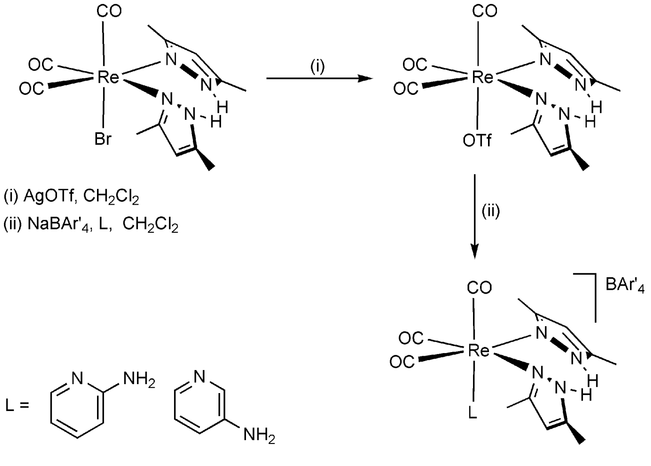


Figure 23. X-ray structures of the supramolecular adducts formed between several anions and $[M(CO)_3(Hpz)_3]BAr'_4$ (M = Mn or Re) receptors prepared by our group. The dashed lines represent the main hydrogen bonds between the anions and the N–H groups of the coordinated pyrazoles (see refs.[64,65,68]).



Scheme 4. Synthesis of a rhenium pyrazole pyrazolylamidino compound.



Scheme 5. Synthesis of mixed receptors featuring both pyrazole and aminopyridine ligands.

gand.[70] A cationic complex (with $BAr'_4{}^-$ as counteranion) with both the pyrazolylamidino and a pyrazole ligands was prepared as shown in Scheme 4.

As a different example, complexes featuring two different types of monodentate ligands, namely, pyrazoles and aminopyridines, were synthesized by using the sequence depicted in Scheme 5.[71]

Both types of mixed complexes showed higher selectivity for the chloride anion than the tris(pyrazole) hosts.

Conclusions

The presence of pyrazoles containing N–H groups as ligands in metal complexes presents both difficulties and opportunities. The facile deprotonation of the N–H groups, which opens a way for the synthesis of pyrazolato complexes, can hamper attempts to synthesize the pyrazole complexes. Prototropy and metallotropy can occur in pyrazole complexes. The occurrence of intra- or intermolecular hydrogen bonding, in which the N–H groups of coordinated pyrazoles act as donors, is a major feature in pyrazole complexes. These hydrogen bonds can contribute to the determination of the molecular structure of the metal complexes, including their stoichiometry, geometry, and solid-state structures. They can also have a dramatic effect on reactivity, solubility, and spectroscopic properties. Metal complexes with pyrazole ligands can display mesomorphic properties, can serve as synthons for crystal engineering, can afford self-assembled supramolecular adducts, and can be used as supramolecular hosts for anions.

Acknowledgments

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[1] R. Blomstrand, H. Östling-Wintzell, A. Löf, K. McMartin, B.-R. Tolf, K.-G. Hedström, *Proc. Natl. Acad. Sci. USA* **1979**, *76*, 3499–3503; J. Elguero, P. Goya, N. Jagerovic, A. M. S. Silva, "Pyrazoles as Drugs: Facts and Fantasies" in *Targets in Heteroyclic Systems* (Eds.: O. A. Attanasi, D. Spinelli), Italian Society of Chemistry, Roma, **2002**, vol. 6, pp. 52–98; D. R. Sliskovic, B. D. Roth, M. W. Wilson, M. L. Hoefle, R. S. Newton, *J. Med. Chem.* **1990**, *33*, 31–38; T. D. Penning, J. J. Talley, S. R. Bertenshaw, J. S. Carter, P. W. Collins, S. Docter, M. J. Graneto, L. F. Lee, J. W. Malecha, J. M. Miyashiro, R. S. Rogers, D. J. Rogier, S. S. Yu, G. D. Anderson, E. G. Burton, J. N. Cogburn, S. A. Gregory, C. M. Koboldt, W. E. Perkins, K. Seibert, A. W. Veenhuizen, Y. Y. Zhang, P. C. Isakson, *J. Med. Chem.* **1997**, *40*, 1347–1365; K. W. Moore, K. Bonner, E. A. Jones, F. Emms, P. D. Leeson, R. Marwood, S. Patel, S. Patel, M. Rowley, S. Thomas, R. W. Carling, *Bioorg. Med. Chem. Lett.* **1999**, *9*, 1285–1290; S. R. Stauffer, J. A. Katzenellenbogen, *J. Comb. Chem.* **2000**, *2*, 318–329.

[2] J. Reedijk in *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, Oxford, **1987**, vol. 2.

[3] G. LaMonica, G. A. Ardizzoia, *Prog. Inorg. Chem.* **1997**, *46*, 151–238; F. Meyer, *Eur. J. Inorg. Chem.* **2006**, 3789–3800; M. A. Halcrow, *Dalton Trans.* **2009**, 2059–2073.

[4] A. A. Mohamed, A. Burini, J. P. Fackler Jr., *J. Am. Chem. Soc.* **2005**, *127*, 5012–5013; M. A. Omary, M. A. Rawashdeh-Omary, M. W. A. Gonser, O. Elbjeirami, T. Grimes, T. R. Cundari, H. V. K. Diyabalanage, C. S. P. Gamage, H. V. R. Dias, *Inorg. Chem.* **2005**, *44*, 8200–8210; H. V. R. Dias, H. V. K. Diyabalanage, M. G. Eldabaja, O. Elbjeirami, M. A. Rawashdeh-Omary, M. A. Omary, *J. Am. Chem. Soc.* **2005**, *127*, 7489–7501; B. Hu, G. Gahungu, J. Zhang, *J. Phys. Chem. A* **2007**, *111*, 4965–4973.

[5] R. Mukherjee, *Coord. Chem. Rev.* **2000**, *203*, 151–218; A. Otero, J. Fernández-Baeza, A. Lara-Sánchez, J. Tejeda, L. F. Sánchez-Barba, *Eur. J. Inorg. Chem.* **2008**, *34*, 5309–5326; J. Klingele, S. Dechert, F. Meyer, *Coord. Chem. Rev.* **2009**, *253*, 2698–2741.

[6] S. Trofimenko, *Polyhedron* **2004**, *23*, 197–203 and references cited therein.

[7] R. Goikhman, T. L. Jacques, D. Sames, *J. Am. Chem. Soc.* **2009**, *131*, 3042–3048 and references cited therein.

[8] S. Kiviniemi, A. Sillampää, M. Nissinen, K. Rissanen, M. T. Lämsä, J. Pursiainen, *Chem. Commun.* **1999**, 897–898; S. Kiviniemi, M. Nissinen, M. T. Lämsä, J. Jalonen, K. Rissanen, J. Pursiainen, *New J. Chem.* **2000**, *24*, 47–52; S. Kiviniemi, M. Nissinen, T. Alaviuhkola, K. Rissanen, J. Pursiainen, *J. Chem. Soc. Perkin Trans. 2* **2001**, 2364–2369.

[9] Z. Xu, J. Oxgaard, W. Goddard, *Organometallics* **2008**, *27*, 3770–3773.

[10] R. Goddard, R. M. Claramunt, C. Escolástico, J. Elguero, *New J. Chem.* **1999**, 237–240.

[11] R. M. Claramunt, P. Cornago, V. Torres, E. Pinilla, M. R. Torres, A. Samat, V. Lokshin, M. Valdés, J. Elguero, *J. Org. Chem.* **2006**, *71*, 6881–6891.

[12] F. Aguilar-Padilla, C. Cativiela, M. D. Diaz de Villegas, J. Elguero, C. Foces-Foces, J. I. García Laureiro, F. H. Cano, H.-H. Limbach, J. A. S. Smith, C. Toiron, *J. Chem. Soc. Perkin Trans. 2* **1992**, 1737–1742.

[13] C. López, R. M. Claramunt, M. A. García, E. Pinillla, M. R. Torres, I. Alkorta, J. Elguero, *Cryst. Growth Des.* **2007**, *7*, 1176–1184.

[14] E. D. Raczynska, W. Kosinska, B. Osmialowski, R. Gawinecki, *Chem. Rev.* **2005**, *105*, 3561–3612; I. Alkorta, P. Goya, J. Elguero, S. P. Singh, *Natl. Acad. Sci. Lett.* **2007**, *30*, 139–159.

[15] M. T. Chenon, C. Coupry, D. M. Grant, R. J. Pugmire, *J. Org. Chem.* **1977**, *42*, 659–661; R. M. Claramunt, C. López, M. A. García, M. Pierrot, M. Giorgi, J. Elguero, *J. Chem. Soc. Perkin Trans. 2* **2000**, 2049–2053.

[16] I. Alkorta, J. Elguero, *J. Chem. Soc. Perkin Trans. 2* **1998**, 2497–2503.

[17] For an example, see: A. L. Bandini, G. Banditelli, B. Bovio, *Polyhedron* **2001**, *20*, 2869–2875.

[18] For an example, see: G. A. Ardizzoia, G. LaMonica, A. Maspero, M. Moret, N. Masciocchi, *Eur. J. Inorg. Chem.* **1998**, 1503–1512.

[19] L. R. Falvello, J. Forniés, A. Martín, V. Sicilia, P. Villarroya, *Organometallics* **2002**, *21*, 4604–4610.

[20] G. López, J. Ruiz, G. García, C. Vicente, J. Casabó, E. Molins, C. Miravitlles, *Inorg. Chem.* **1991**, *30*, 2605–2610; E. Sebe, I. A. Guzei, M. J. Heeg, L. M. Liable-Sands, A. L. Rheingold, C. H. Winter, *Eur. J. Inorg. Chem.* **2005**, 3955–3961.

[21] W. Tan, Z. Yu, B. Liu, K. Wu, Z. Liu, J. Chen, *J. Organomet. Chem.* **2009**, *694*, 199–206.

[22] B. Machura, J. O. Dziegielewski, R. Kruszynski, T. J. Bartczak, J. Kusz, *Inorg. Chim. Acta* **2004**, *357*, 1011–1022.

[23] Y. Chi, H.-L. Yu, W.-L. Ching, C.-S. Liu, Y.-L. Chen, T.-Y. Chou, S.-M. Peng, G.-H. Lee, *J. Mater. Chem.* **2002**, *12*, 1363–1369.

[24] G. A. Ardizzoia, S. Brenna, G. LaMonica, A. Maspero, N. Masciocchi, M. Moret, *Inorg. Chem.* **2002**, *41*,610–614; J. T. Chantson, S. Lotz, *J. Organomet. Chem.* **2004**, *689*, 1315–1324.

[25] P. Paredes, M. Arroyo, D. Miguel, F. Villafañe, *J. Organomet. Chem.* **2003**, *667*, 120–125.

[26] J. Reedijk, *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1451–1470; C. W. Reimann, A. D. Mighell, F. Mauer, *Acta Crystallogr.* **1967**, *23*, 135–141.

[27] I. A. Guzei, C. H. Winter, *Inorg. Chem.* **1997**, *36*, 4415–4420.

[28] D. Carmona, F. J. Lahoz, R. Atencio, A. J. Edwards, L. A. Oro, M. P. Lamata, M. Esteban, S. Trofimenko, *Inorg. Chem.* **1996**, *35*, 2549–2557.

[29] D. Carmona, J. Ferrer, L. A. Oro, M. C. Apreda, C. Foces-Foces, F. H. Cano, J. Elguero, M. L. Gimeno, *J. Chem. Soc., Dalton Trans.* **1990**, 1463–1476; M. P. García, A. M. López, M. A. Esteruelas, F. J. Lahoz, L. A. Oro, *J. Chem. Soc., Dalton Trans.* **1990**, 3465–3472; G. A. Ardizzoia, G. La Monica, A. Maspero, N. Masciocchi, M. Moret, *Eur. J. Inorg. Chem.* **1999**, 1301–1307; G. A. Ardizzoia, G. La Monica, A. Maspero, M. Moret, N. Masciocchi, *Eur. J. Inorg. Chem.* **2000**, 181–187.

[30] P. Paredes, D. Miguel, F. Villafañe, *Eur. J. Inorg. Chem.* **2003**, 995–1004.

[31] I. Ara, J. Forniés, R. Lasheras, A. Martín, V. Sicilia, *Eur. J. Inorg. Chem.* **2006**, 948–957.

[32] J. Cámpora, J. A. López, C. M. Maya, P. Palma, E. Carmona, C. Ruiz, *Organometallics* **2000**, *19*, 2707–2715.

[33] C. S. Hong, J. Koo, S.-K. Son, Y. S. Lee, Y.-S. Kim, Y. Do, *Chem. Eur. J.* **2001**, *7*, 4243–4252.

[34] D. H. Choi, J. H. Yoon, J. H. Lim, H. C. Kim, C. S. Hong, *Inorg. Chem.* **2006**, *45*, 5947–5952.

[35] A. V. Khripun, N. A. Bokach, S. I. Selivanov, M. Haukka, M. D. Revenco, V. Y. Kukushkin, *Inorg. Chem. Commun.* **2008**, *11*, 1352–1355.

[36] G. W. Bushnell, K. R. Dixon, D. T. Eadie, S. R. Stobart, *Inorg. Chem.* **1981**, *20*, 1545–1552.

[37] V. García-Pacios, M. Arroyo, N. Antón, F. Villafañe, *Dalton Trans.* **2009**, 2135–2141.

[38] 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.

[39] D. Carmona, L. A. Oro, M. Pilar Lamata, J. Elguero, M. C. Apreda, C. Foces-Foces, F. H. Cano, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1114–1115.

[40] G. Albertin, S. Antoniutti, A. Bacchi, G. Pelizzi, M. Tollon, *J. Organomet. Chem.* **2005**, *690*, 4573–4582.

[41] X. Liu, J. A. McAllister, M. P. de Miranda, B. J. Whitaker, C. A. Kilner, M. Thornton-Pett, M. A. Halcrow, *Angew. Chem. Int. Ed.* **2002**, *41*, 756–758; A. V. G. Netto, R. G. C. Frem, A. E. Mauro, E. T. de Almeida, A. M. Santana, J. de Souza Jr., R. H. A. Santos, *Inorg. Chim. Acta* **2003**, *350*, 252–258; M. Cano, J. V. Heras, M. Luz Gallego, J. Perles, C. Ruiz-Valero, E. Pinilla, M. R. Torres, *Helv. Chim. Acta* **2003**, *86*, 3194–3203; S. Tanase, E. Bouwman, G. J. Long, A. Shahin, A. M. Mills, A. L. Spek, J. Reedijk, *Eur. J. Inorg. Chem.* **2004**, 4572–4578.

[42] H. Jude, F. N. Rein, W. Chen, B. L. Scott, D. M. Dattelbaum, R. Rocha, *Eur. J. Inorg. Chem.* **2009**, 683–690.

[43] M. Arroyo, A. López-Sanvicente, D. Miguel, F. Villafañe, *Eur. J. Inorg. Chem.* **2005**, 4430–4437.

[44] J. Barberá, A. Elduque, R. Giménez, F. J. Lahoz, J. A. López, L. A. Oro, J. L. Serrano, B. Villacampa, J. Villalba, *Inorg. Chem.* **1999**, *38*, 3085–3092.

[45] J. Barberá, A. Elduque, R. Giménez, L. A. Oro, J. L. Serano, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2832–2835.

[46] M. C. Torralba, M. Cano, J. A. Campo, J. V. Heras, E. Pinilla, M. R. Torres, *J. Organomet. Chem.* **2001**, *633*, 91–104.

[47] B. Porta, J. Khamsi, J. C. Noveron, *Curr. Org. Chem.* **2008**, *12*, 1298–1321.

[48] M. C. Torralba, M. Cano, J. A. Campo, J. V. Heras, E. Pinilla, M. R. Torres, *J. Organomet. Chem.* **2002**, *654*, 150–161.

[49] R. Giménez, A. Elduque, J. A. López, J. Barberá, E. Cavero, I. Lantero, L. A. Oro, J. L. Serrano, *Inorg. Chem.* **2006**, *45*, 10363–10370.

[50] E. Cavero, S. Uriel, P. Romero, J. L. Serrano, R. Giménez, *J. Am. Chem. Soc.* **2007**, *129*, 11608–11618.

[51] M. J. Mayoral, P. Ovejero, J. A. Campo, J. V. Heras, E. Pinilla, M. R. Torres, C. Lodeiro, M. Cano, *Dalton Trans.* **2008**, 6912–6924.

[52] For an example, see: J. Thomas, A. Ramanan, *Cryst. Growth Des.* **2007**, *7*, 966–971.

[53] A. Looney, G. Parkin, A. L. Rheingold, *Inorg. Chem.* **1991**, *30*, 3099–3101.

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

[55] W. Kläui, M. Berghahn, G. Rheinwald, H. Lang, *Angew. Chem. Int. Ed.* **2000**, *39*, 2464–2466.

[56] G. Parkin, *Adv. Inorg. Chem.* **1995**, *42*, 291–393.

[57] X. Liu, C. A. Kilner, M. A. Halcrow, *Chem. Commun.* **2002**, 704–705.

[58] S. L. Renard, C. A. Kilner, J. Fisher, M. A. Halcrow, *J. Chem. Soc., Dalton Trans.* **2002**, 4206–4212.

[59] S. L. Renard, A. Franken, C. A. Kilner, J. D. Kennedy, M. A. Halcrow, *New J. Chem.* **2002**, *26*, 1634–1637.

[60] C. 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.

[61] P. D. Beer, F. Szemes, V. Balzani, C. M. Sala, M. G. B. Drew, S. W. Dent, M. Maestri, *J. Am. Chem. Soc.* **1997**, *119*, 11864–11875.

[62] L. Ion, D. Morales, J. Pérez, L. Riera, V. Riera, D. Miguel, *Chem. Commun.* **2006**, 91–93; L. Ion, D. Morales, S. Nieto, J. Pérez, L. Riera, V. Riera, D. Miguel, R. A. Kowenicki, M. McPartlin, *Inorg. Chem.* **2007**, *46*, 2846–2853.

[63] C. R. Bondy, P. A. Gale, S. J. Loeb, *Chem. Commun.* **2001**, 729–730; C. R. Bondy, P. A. Gale, S. J. Loeb, *J. Am. Chem. Soc.* **2004**, *126*, 5030–5031; I. El Drubi Vega, P. A. Gale, M. E. Light, S. J. Loeb, *Chem. Commun.* **2005**, 4913–4915; M. Fisher, P. A. Gale, M. E. Light, S. J. Loeb, *Chem. Commun.* **2008**, 5695–5697; K. J. Wallace, R. Daari, W. J. Belcher, L. O. Abouderbala, M. G. Boutelle, J. W. Steed, *J. Organomet. Chem.* **2003**, *666*, 63–74; S. J. Dickson, S. C. G. Biagini, J. W. Steed, *Chem. Commun.* **2007**, 4955–4957; S. J. Dickson, M. J. Paterson, C. E. Willans, K. M. Anderson, J. W. Steed, *Chem. Eur. J.* **2008**, *14*, 7296–7305.

[64] S. Nieto, J. Pérez, V. Riera, D. Miguel, C. Álvarez, *Chem. Commun.* **2005**, 546–548; J. Pérez, L. Riera, *Chem. Commun.* **2008**, 533–543; J. Pérez, L. Riera, *Chem. Soc. Rev.* **2008**, *37*, 2658–2667.

[65] J. Pérez, D. Morales, S. Nieto, L. Riera, V. Riera, D. Miguel, *Dalton Trans.* **2005**, 884–888; S. Nieto, J. Pérez, L. Riera, V. Riera, D. Miguel, J. A. Golen, A. L. Rheingold, *Inorg. Chem.* **2007**, *46*, 33407–33418.

[66] I. Krossing, I. Raabe, *Angew. Chem. Int. Ed.* **2004**, *43*, 2066–2090.

[67] F. Zobi, B. Spingler, R. Alberto, *Dalton Trans.* **2005**, 2859–2865; P. C. Kunz, N. E. Brueckmann, B. Spingler, *Eur. J. Inorg. Chem.* **2007**, 394–399.

[68] S. Nieto, J. Pérez, L. Riera, V. Riera, D. Miguel, *Chem. Eur. J.* **2006**, *12*, 2244–2251.

[69] V. Amendola, D. Esteban-Gómez, L. Fabbrizzi, M. Licchelli, *Acc. Chem. Res.* **2006**, *39*, 343–353.

[70] M. Arroyo, D. Miguel, F. Villafañe, S. Nieto, J. Pérez, L. Riera, *Inorg. Chem.* **2006**, *45*, 7018–7026.

[71] S. Nieto, J. Pérez, L. Riera, V. Riera, D. Miguel, *Chem. Commun.* **2009**, 3279–3281.

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