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Pyrazolylamidino Ligands from Coupling of Acetonitrile and Pyrazoles: A Systematic Study

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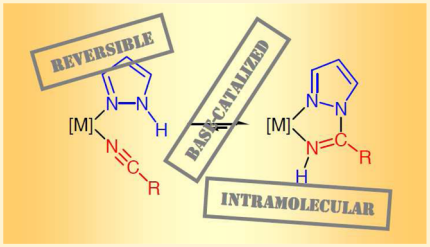
Supporting Information

ABSTRACT: Mixed pyrazole−acetonitrile complexes, both neutral *fac*-[ReBr(CO)$_3$(NCMe)(pz*H)] (pz*H = pzH, pyrazole; dmpzH, 3,5-dimethylpyrazole; or indzH, indazole) and cationic *fac*-[Re(CO)$_3$(NCMe)(pz*H)$_2$]A (A = BF_4, ClO_4, or OTf), are described. Their role as the only starting products to obtain final pyrazolylamidino complexes *fac*-[ReBr(CO)$_3$(NH=C(Me)pz*-κ^2*N,N*)] and *fac*-[Re(CO)$_3$(pz*H)(NH=C(Me)pz*-κ^2*N,N*)]A, respectively, is examined. Other products involved in the processes, such as *fac*-[ReBr(CO)$_3$(pz*H)$_2$], *fac*-[Re(CO)$_3$(NCMe)(NH=C(Me)pz*-κ^2*N,N*)]A, and *fac*-[Re(CO)$_3$(pz*H)$_2$(OTf)] are also described. Warming CD_3CN solutions of *fac*-[Re(CO)$_3$(NCMe)(pz*H)$_2$]A at 40 °C gives cleanly the pyrazolylamidino complexes [Re(CO)$_3$(pz*H)(NH=C(Me)pz*-κ^2*N,N*)]A as the only products, pointing to an intramolecular process. This is confirmed by carrying out reactions in the presence of one equivalent of a pyrazole different from that coordinated, which affords complexes where the pyrazolylamidino ligand contains only the pyrazole previously coordinated. When the reactions lead to an equilibrium mixture of the final and starting products, the reverse reaction gives the same equilibrium mixture, which indicates that the coupling reaction of pyrazoles and nitriles to obtain pyrazolylamidino ligands is a reversible intramolecular process. A systematic study of the possible factors which may affect the reaction gives the following results: (a) the yields of the direct reactions are higher for lower temperatures; (b) the tendency of the pyrazoles to give pyrazolylamidino complexes follows the sequence indzH > pzH > dmpzH; and (c) the reaction rates do not depend on the nature of the anion even when a large excess is added. The presence of a small amount of aqueous solution of NaOH catalyzes the reaction. Thus, addition of 0.5−1% of NaOH (aq) to solutions of *fac*-[ReBr(CO)$_3$(NCMe)(pz*H)] (in CD_3CN) or *fac*-[Re(CO)$_3$(NCMe)(pz*H)$_2$]A (in CD_3CN, CD_3NO_2 or $(CD_3)_2CO$) allowed the syntheses of the corresponding pyrazolylamidino complexes [ReBr(CO)$_3$(NH=C(Me)pz*-κ^2*N,N*)] or [Re(CO)$_3$(pz*H)(NH=C(Me)pz*-κ^2*N,N*)]A with better yields, more rapidly, and in milder conditions.



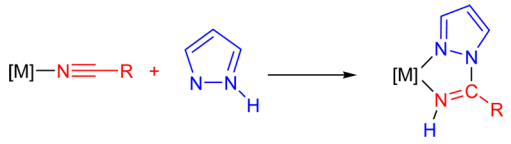
INTRODUCTION

The electrophilic character of nitriles is enhanced by coordination to a Lewis-acidic metal fragment, and therefore, coordinated nitriles react with different nucleophiles to obtain a wide variety of ligands.[1] When the nucleophile is a pyrazole, pyrazolylamidino complexes are obtained (Scheme 1).[2,3]

Pyrazolylamidino ligands belong to the family of pyrazole- or pyrazolyl-containing chelating ligands. Complexes containing these ligands are receiving the most attention because they are involved in different and interdisciplinary aspects, such as synthesis of supramolecular assemblies, design of molecules displaying physical properties of interest, or their role in catalysis or materials science.[4] In particular, pyrazolylamidino ligands present several appealing features: (a) their synthesis in situ (Scheme 1) allows one to obtain easily new bidentate chelating ligands of distinct electronic and steric properties just using different nitriles and pyrazoles, both readily available; (b) the different properties of the two donor atoms and the electron delocalization within the ligand makes them potentially interesting for electron transfer processes and related physical properties; and (c) the NH group may give rise to further reactivity, as it may be involved in noncovalent interactions or may be deprotonated.

Although the reaction displayed in Scheme 1 has been described for several metals, the mechanism of this process remains unclear. It is generally assumed to be an intramolecular nucleophilic attack of the pyrazole to the nitrile, once both are coordinated cis (Scheme 2).[2e,j] This suggestion is difficult to

Scheme 1. Coupling Reaction of a Coordinated Nitrile and a Pyrazole To Obtain a Pyrazolylamidino Ligand



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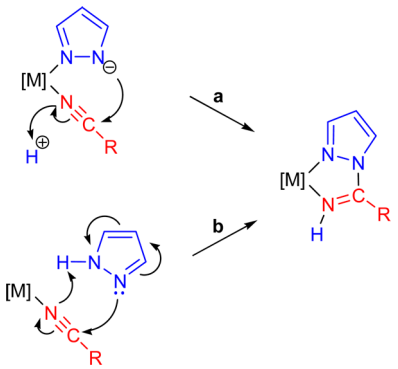
Scheme 2. Intramolecular (a) and Intermolecular (b) Mechanisms for the Coupling Reaction of a Pyrazole and a Coordinated Nitrile



reconcile with the lack of nucleophilicity of the uncoordinated nitrogen of the pyrazole, similar to a pyrrole. A possible solution to this problem has been proposed by considering the previous deprotonation of the NH group (Scheme 2, path a).[5]

The group of Kukushkin and Pombeiro reported both intramolecular or intermolecular paths depending on the electronic configuration of the metal center.[2b] The intermolecular mechanism, based on the attack of a uncoordinated pyrazole, is depicted in Scheme 2, path b. The more recent contribution to this problem is the report of a mechanism driven by anion-mediated/hydrogen-bonding proton transfer.[2a]

No direct evidence supporting either intra- or intermolecular coupling has been given so far. Path a in Scheme 2 shows that complexes containing both pyrazoles and nitriles can be considered as the only precursors of pyrazolylamidino complexes if the mechanism is intramolecular. There are very few reports of this type of complex.[2a,e,6] During the course of our studies on pyrazolylamidino rhenium complexes we were able to obtain mixed acetonitrile−pyrazole complexes such as *fac*-[ReBr(CO)$_3$(NCMe)(pzH)] (pzH = pyrazole), *fac*-[ReBr(CO)$_3$(NCMe)(dmpzH)] (dmpzH = 3,5-dimethylpyrazole), and cationic *fac*-[Re(CO)$_3$(NCMe)(dmpzH)$_2$]$^+$.[3c] Therefore, we decided to explore their reactivity as well as the processes where they are involved in order to support or discard the intramolecular mechanism. On the other hand, no previous research has been carried out on the ideal conditions to obtain pyrazolylamidino complexes. Herein, a systematic study of the factors which may affect the process is reported.

RESULTS AND DISCUSSION

All complexes involved in this study are collected in Table 1 and Chart 1. In addition to the mixed acetonitrile−pyrazole complexes *fac*-[ReBr(CO)$_3$(NCMe)(pz*H)] (**1**) (pz*H = pzH, pyrazole; dmpzH, 3,5-dimethylpyrazole; or indzH, indazole) and cationic *fac*-[Re(CO)$_3$(NCMe)(pz*H)$_2$]$^+$ (**4**), which play the leading role in this work as starting materials, we also describe herein other complexes which are either byproducts (**3**, **5**) or final products of the processes studied (**2**, **6**, and **7**). Most of the pzH and dmpzH complexes had been previously reported by the group of Ardizzoia and Masciocchi[7] or by us.[3c] We decided to synthesize a similar family of complexes with a third pyrazole, i.e., indazole, in order to have a wider range of complexes to carry out in the study. The syntheses and characterization of the species involved in these processes are described next, before discussing the coupling reaction.

Table 1. Complexes Used in This Study[a]

	pzH	dmpzH	indzH
fac-[ReBr(CO)$_3$(NCMe)(pz*H)]	**1a**[3c]	**1b**[3c]	**1c**
fac-[ReBr(CO)$_3$(NH=C(Me)pz*-κ^2*N,N*)]	**2a**[3c]	**2b**[3c]	**2c**
fac-[ReBr(CO)$_3$(pz*H)$_2$]	**3a**[7]	**3b**[7]	**3c**
fac-[Re(CO)$_3$(NCMe)(pz*H)$_2$]$^+$	**4a**	**4b**[3c] [b]	**4c**
fac-[Re(CO)$_3$(pz*H)$_2$(OTf)][c]	**5a**	**5b**	**5c**
fac-[Re(CO)$_3$(pz*H)(NH=C(Me)pz*-κ^2*N,N*)]$^+$	**6a**[3c]	**6b**[3c]	**6c**
fac-[Re(CO)$_3$(NCMe)(NH=C(Me)pz*-κ^2*N,N*)]$^+$	**7a**[3c]	**7b**[3c]	**7c**

[a]Complexes **4**, **6**, and **7** have been isolated as BF_4, ClO_4, or OTf salts. Only one of them is described for each complex in the Experimental Section, since the spectroscopic data are esentially the same. [b]Previously described with the anion BAr'_4 (Ar′ = 3,5-bis(trifluoromethyl)phenyl). [c]Complexes with coordinated perchlorate gave similar spectroscopic data.

Syntheses and Characterization of the Complexes. Reactions between *fac*-[ReBr(CO)$_3$(MeCN)$_2$] and indzH occur similarly to those previously reported for pzH or dmpzH,[3c,7] giving the substitution (**1c**, **3c**) or the insertion (**2c**) products depending on the ratio and temperature used (eqs 1−3). Thus, 0 °C and a 1/1 ratio allow one to obtain the mixed acetonitrile−indazole complex *fac*-[ReBr(CO)$_3$(NCMe)(indzH)] (**1c**), whereas a 1/2 ratio at room temperature gives the disubstituted product, *fac*-[ReBr(CO)$_3$(indzH)$_2$], **3c**. A 1/1 ratio, but at 80 °C, leads to the pyrazolylamidino ligand resulting from the coupling of indazole and acetonitrile, that is, *fac*-[ReBr(CO)$_3$(NH=C(Me)indz-κ^2*N,N*)], **2c**.

$$fac\text{-}[ReBr(CO)_3(MeCN)_2] + indzH \xrightarrow[-MeCN]{1/1,0\,^\circ C} fac\text{-}[ReBr(CO)_3(NCMe)(indzH)]\,(\mathbf{1c}) \quad (1)$$

$$fac\text{-}[ReBr(CO)_3(MeCN)_2] + indzH \xrightarrow[-MeCN]{1/1,80\,^\circ C} fac\text{-}[ReBr(CO)_3(NH{=}C(Me)(indz\text{-}\kappa^2N, N)]\,(\mathbf{2c}) \quad (2)$$

$$fac\text{-}[ReBr(CO)_3(MeCN)_2] + 2indzH \xrightarrow[-2MeCN]{1/2,r.t.} fac\text{-}[ReBr(CO)_3(indzH)_2]\,(\mathbf{3c}) \quad (3)$$

Their spectroscopic data are collected in the Experimental Section. **2c**, **3b**,[8] and **3c** were subjected to crystallographic studies, shown in Figure 1 (**2c**), 2 (**3c**), and S1 (**3b**), Supporting Information. The distances and angles (available from the CIF in the Supporting Information) are similar to those found in other pyrazolylamidino- and bis(pyrazole)rhenium complexes.[3,7] As observed in the structures of similar manganese complexes,[3d] dimethylpyrazole ligands in **3b** are tilted in the same sense around the Re−N bonds in order to reduce the steric hindrance of the methyl groups, in this case 34° and 39° with respect to the "ideal" orientation, perpendicular to the ReN_2 plane. This is not observed in the structure of **3c**, where less hindered indazoles are coordinated perpendicular to the ReN_2 plane.

Cationic acetonitrile−pyrazole mixed complexes *fac*-[Re(CO)$_3$(NCMe)(pz*H)$_2$]$^+$, **4**, are easily obtained from complexes **3** by extracting the bromido ligand with the appropriate silver salt in THF and ulterior addition of an excess of MeCN (eq 4). Synthesis and characterization of the pyrazole and indazole complexes **4a** and **4c** are herein described, whereas the

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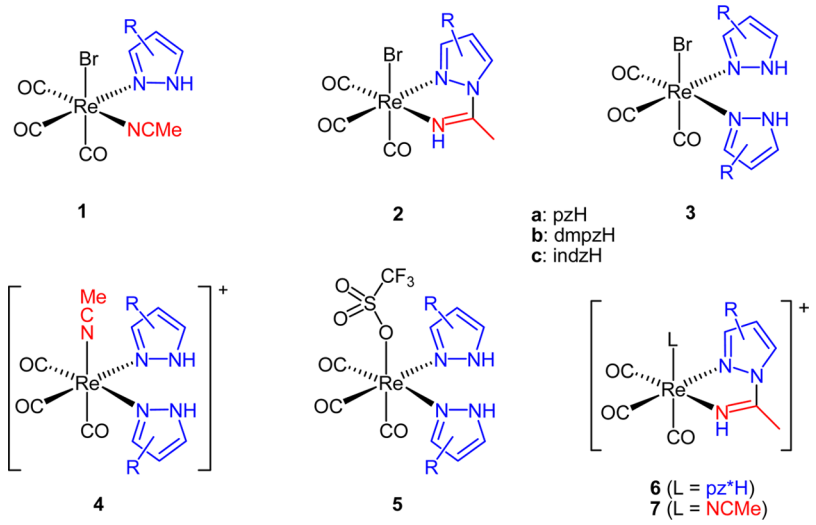
Chart 1. Complexes Used in This Study



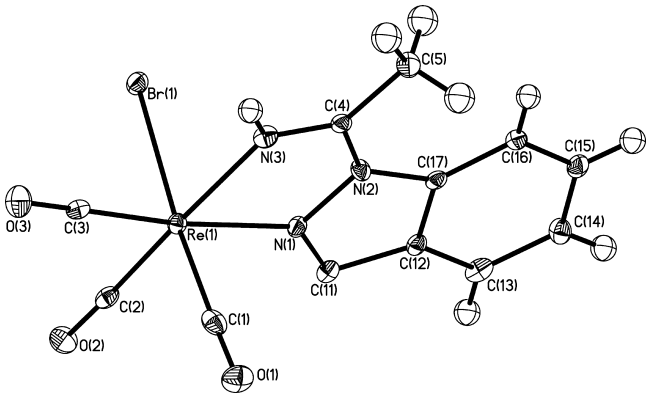


Figure 1. Perspective view of *fac*-[ReBr(CO)$_3$(NH=C(Me)indz-κ^2N,N)], **2c**, showing the atom numbering. Ellipsoids are drawn at 30% probability.

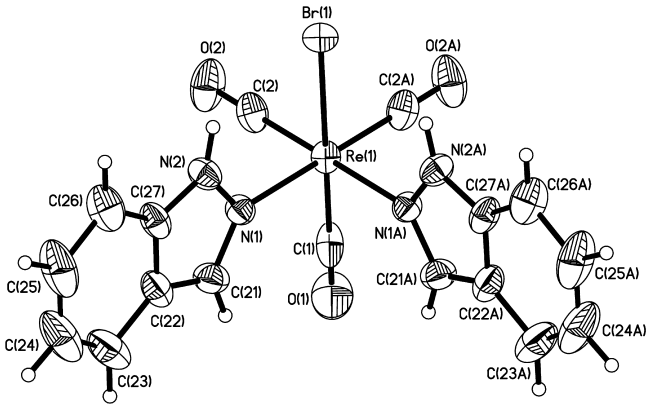


Figure 2. Perspective view of *fac*-[ReBr(CO)$_3$(indzH)$_2$], **3c**, showing the atom numbering. Ellipsoids are drawn at 30% probability.

dimethylpyrazole complex **4b** has been previously reported.[3c] As indicated in Table 1, they can be isolated as BF_4, ClO_4, or OTf salts, although only one of them (BF_4 salts) is described in the Experimental Section, since the spectroscopic data are esentially the same. Their spectroscopic and analytical data support the proposed structure, which was confirmed by an X-ray diffraction study for **4a**-ClO_4. Figure 3 shows a perspective view of the

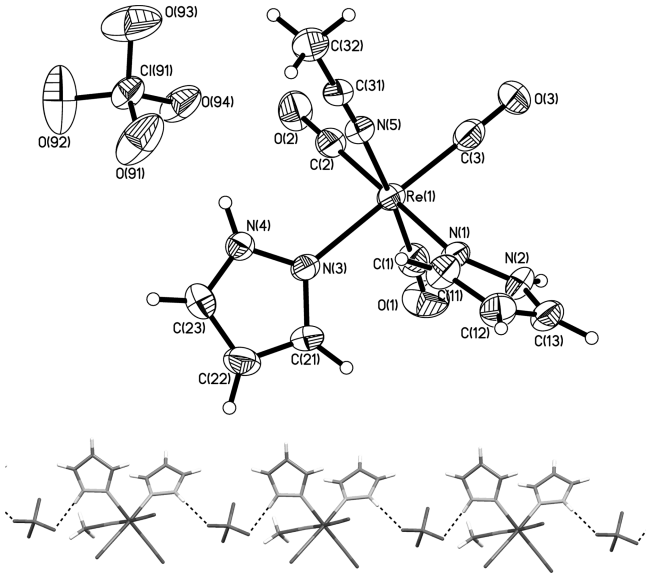


Figure 3. Perspective view showing the atom numbering (top, ellipsoids are drawn at 30% probability) and hydrogen bonds (bottom) of *fac*-[Re(CO)$_3$(NCMe)(pzH)$_2$]$^+$, **4a**-ClO_4.

molecule as well as the hydrogen bonds detected in the solid state structure: the N-bound hydrogens of each pyrazole and the oxygens of the perchlorate form a chain structure. The distances and angles detected (H(2)···O(92) 1.974(10) Å, N(2)···O(92) 2.953(12) Å, N(2)−H(2)···O(92) 157.9(5)°, and H(4)···O(94), 1.869(7) Å; N(4)···O(94) 2.893(10) Å, N(4)−H(4)···O(94) 171.9(5)°) may be considered as "moderate" hydrogen bonds.[9]

$$fac\text{-}[ReBr(CO)_3(pz^*H)_2]\,(\mathbf{3}) \xrightarrow[(2)+MeCN]{(1)+Ag^+A^-,AgBr} fac\text{-}[Re(CO)_3(NCMe)(pz^*H)_2]^+A^-\,(\mathbf{4}) \quad (4)$$

Substitution of the acetonitrile ligand present in complexes **4** by the corresponding counterion was observed during their reactivity studies. Therefore, we decided to isolate and characterize the neutral complexes containing the coordinated anion. Their synthesis was carried out by extracting the bromido

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ligand of complexes **3** with the appropriate silver salt in the absence of MeCN (see eq 5 for OTf complexes). As expected, tetrafluoroborate complexes were shown to be very unstable, which precluded their characterization. Both perchlorate and triflate could be isolated, giving almost coincident spectroscopic data, and again only one of them (containing coordinated OTf) is described in the Experimental Section. The crystal structure of the dimethylpyrazole complex **5b** containing either triflato or perchlorato ligands could be obtained. They are shown in Figures 4 and S2, Supporting Information, respectively. Distances and

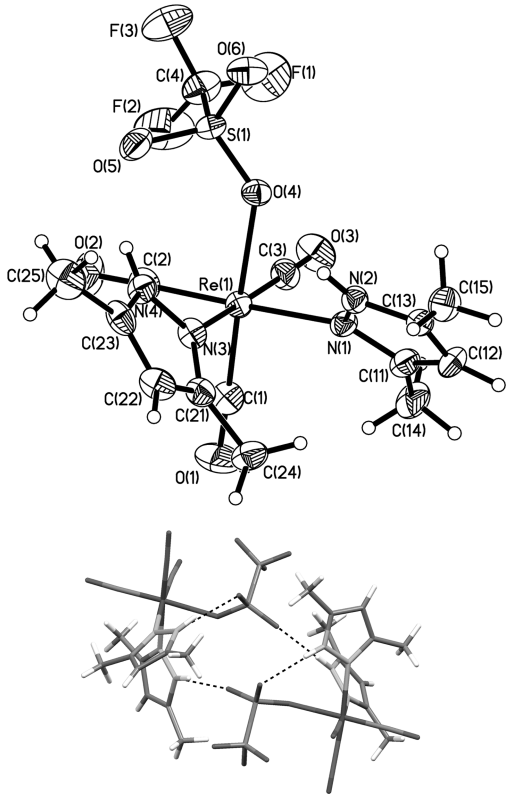

Figure 4. Perspective view of *fac*-[Re(CO)$_3$(dmpzH)$_2$(OTf)], **5b**-OTf (above), and hydrogen bonds (below), showing atom numbering. Ellipsoids are drawn at 30% probability.

angles, which are available from the CIF in the Supporting Information, show the analogy between these structures and that of **3b**.

$$fac\text{-}[ReBr(CO)_3(pz^*H)_2]\ (\mathbf{3}) \xrightarrow[-AgBr]{+AgOTf} fac\text{-}[Re(CO)_3(pz^*H)_2(OTf)](\ \mathbf{5}\text{-OTf}) \quad (5)$$

Opposite to **4a**, which forms anion−cations hydrogen-bonded chains (Figure 3, below), the solid crystal structure of **5b** indicates that in these cases hydrogen bonds generate discrete dimer ionic pairs (Figure 4, below). Uncoordinated oxygen atoms of the coordinated triflate are hydrogen bonded with N-bound hydrogens of dimethylpyrazoles. The distances and angles detected (H(2)···O(56) 1.938(6) Å, N(2)···O(56) 2.933(9) Å, N(2)−H(2)···O(56) 161.5(4)°, and H(4)···O(5) 1.903(5) Å; N(4)···O(5) 2.862(8) Å; N(4)−H(4)···O(5) 153.4(5)° for **5b**-OTf) indicate that these may be considered again as "moderate" hydrogen bonds.[9]

Cationic pyrazolylamidino complexes *fac*-[Re(CO)$_3$(indzH)(NH=C(Me)indz-κ^2*N,N*)]$^+$, **6c**, and *fac*-[Re(CO)$_3$(NCMe)(NH=C(Me)indz-κ^2*N,N*)]$^+$, **7c**, were obtained as previously described for similar pyrazolilamidino complexes with pyrazole or dimethylpyrazole. Alternatively, **6c** could also be obtained by substituting the coordinated anion in **5** by MeCN and subsequent coupling (eqs 6−8). Their spectroscopic and analytic data (Experimental Section) are as expected given this analogy.[3c] As discussed below, the reaction conditions are milder for pyrazolilamidino complexes derived from indazole with respect to pyrazole or dimethylpyrazole. The crystal structure of **7c**-ClO$_4$

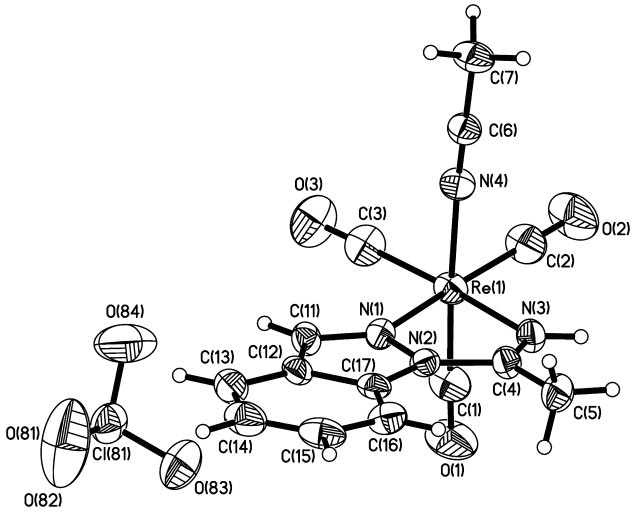

Figure 5. Perspective view of *fac*-[Re(CO)$_3$(NCMe)(NH=C(Me)-indz-κ^2*N,N*)]ClO$_4$, **7c**-ClO$_4$, showing the atom numbering. Ellipsoids are drawn at 30% probability.

is depicted in Figure 5, and distances and angles are available from the CIF in the Supporting Information.

$$fac\text{-}[Re(CO)_3(NCMe)(indzH)_2]OTf\ (\mathbf{4c}\text{-OTf}) \rightarrow fac\text{-}[Re(CO)_3(indzH)(NH{=}C(Me)indz\text{-}\kappa^2N,N)]OTf\ (\mathbf{6c}\text{-OTf}) \quad (6)$$

$$fac\text{-}[Re(CO)_3(indzH_2](OTf)\ (\mathbf{5c}\text{-OTf}) \xrightarrow{+MeCN} fac\text{-}[Re(CO)_3(indzH)(NH{=}C(Me)indz\text{-}\kappa^2N,N)]OTf\ (\mathbf{6c}\text{-OTf}) \quad (7)$$

$$fac\text{-}[ReBr(CO)_3(NH{=}C(Me)indz\text{-}\kappa^2N,N)]\ (\mathbf{2c}) \xrightarrow[(2)+MeCN]{(1)+AgOTf,-AgBr} fac\text{-}[Re(CO)_3(NCMe)(NH{=}C(Me)indz\text{-}\kappa^2N,N)]OTf\ (\mathbf{7c}\text{-OTf}) \quad (8)$$

Kinetic Studies of the Coupling Processes. The first attempt to obtain pyrazolylamidino complexes from mixed acetonitrile−pyrazole complexes as the only starting material was carried out using neutral bromido complexes **1b** or **1c** in CD$_3$CN solution.[10] Heating any of these complexes at 80 °C leads to a mixture of complexes **2** and **3**, unreacted **1**, as well as other very minor products, which were identified mainly as a mixture of **6** and **7**. Figure 6 shows the concentrations of the species present in solution when **1b** is heated in CD$_3$CN at 80 °C. Similar mixtures were obtained when using **1c** as starting material or solutions of different concentrations. When the processes were attempted at lower temperatures, the reactions were too slow. On the other hand, the reactions were repeated with a noncoordinating solvent, but heating **1** at 80 °C in CD$_3$NO$_2$ led to residual amounts of the pyrazolylamidino complexes **2b** or **2c**, with bis(pyrazole) complexes **3** being the main products (ca. 50%). This expected result shows that conditions favoring uncoordination of acetonitrile preclude the coupling process.

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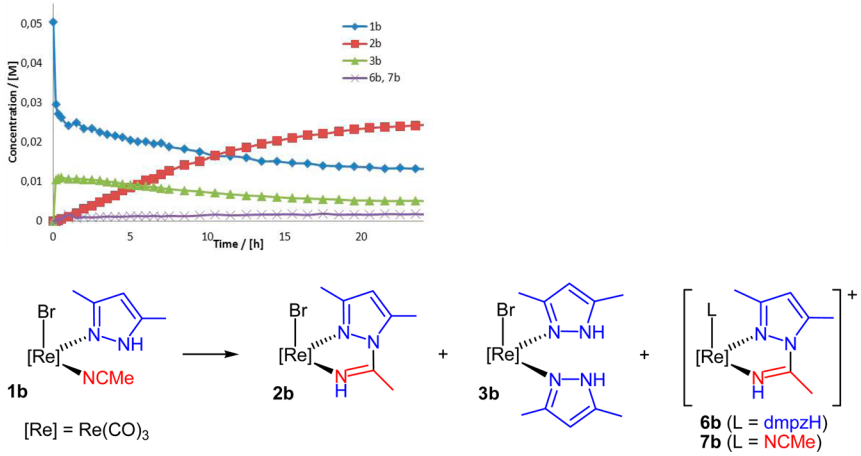
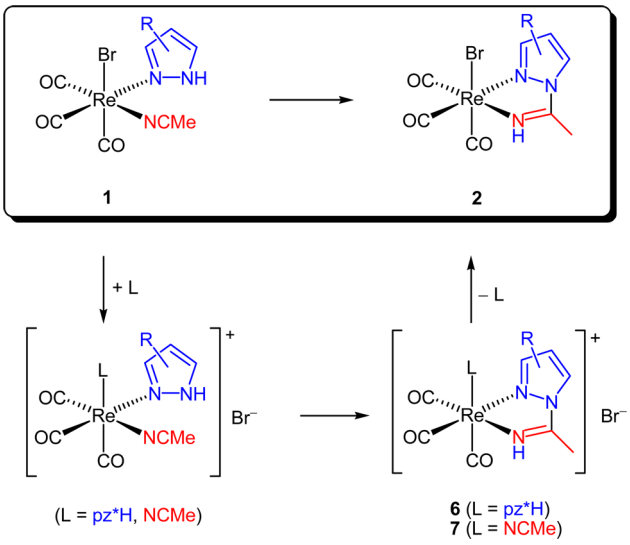


Figure 6. Representation of the concentrations of **1b**, **2b**, **3b**, and the mixture **6b** + **7b** vs time when **1b** is heated in CD_3CN at 80 °C. Final ratio: **1b**/**2b**/**3b**/(**6b** + **7b**) = 25/50/10/5.[13]

The most striking feature about the processes carried out in CD_3CN at 80 °C was the presence of small amounts of the cationic complexes **6** and **7**. In a cationic complex, the coordinated acetonitrile should be more activated than when coordinated to a neutral complex, and therefore, the coupling process to form the pyrazolylamidino ligand should be easier. This led us to consider the possibility of the presence of cationic complexes as intermediates for the process, as depicted in Scheme 3. It is well known that MeCN may coordinate to Mn and Re complexes by substituting the halide ligand.[11] This process would give rise to cationic complexes, where the electrophilic character of the nitrile should be enhanced, and thus, the coupling process should be favored. Therefore, we decided to focus our work on the cationic acetonitrile−pyrazole complexes and investigate whether they could be intermediates in the coupling process to obtain cationic pyrazolylamidino complexes.

Scheme 3. Proposal of the Coupling Process of Neutral Complexes through Cationic Intermediates



Heating cationic complexes **4** in the same conditions, CD_3CN at 80 °C, gave a mixture of the pyrazolylamidino cationic complexes **6** and **7** as well as unreacted **4** and free pyrazole. Figure 7 shows the concentrations of the species detected in solution for reaction of **4b**-BF_4. Although this result may seem disappointing, close study of the first minutes of the process reveals that conversion of **4b** to **6b** is clean (Scheme 4, framed reaction). Only after ca. 30 min, the concentration of **6b** reaches a maximum and starts to decrease whereas the concentations of equimolar amounts of **7b** and free pyrazole increase. This indicates that the pyrazole coordinated in **6b** is being substituted by acetonitrile from the solvent to give **7b** and free pyrazole (Scheme 4, right). This is a somehow surprising result, because pyrazoles are better ligands than nitriles, but in this case the high temperature might favor this entropy-driven process. As this secondary process is favored by higher temperatures and the coupling process should be easier for cationic complexes, the reaction was repeated at 40 °C.

In these conditions, conversion of **4** into **6** is clean (Scheme 4, framed reaction), as shown in Figure 8 for **4b**-OTf (see Figure S3, Supporting Information, for **4a**-ClO_4 and **4c**-ClO_4), which supports that the coupling reaction of pyrazoles and nitriles to obtain pyrazolylamidino ligands is an intramolecular process. However, mild temperatures are crucial to obtain this result, as at 60 °C or higher temperatures substitution of the coordinated pyrazole in **6** by CD_3CN from the solvent to get **7** and free pyrazole is favored (Scheme 4, right). Another process observed when the reaction is carried out above 40 °C is the scrambling of the coordinated CH_3CN with the solvent, CD_3CN. This scrambling process is detected by examining the methyl group signal in the ^1H NMR spectra, which integrates at lower values than expected. In fact, the framed reaction leads to a mixture of **6b** and "deuterated" **6b** in a ca. 40/60 ratio when the reaction was carried out at 80 °C but to neat **6b** when the reaction ocurs at 40 °C. However, this scrambling at higher temperatures should occur before the coupling process and does not affect the intramolecular nature of the reaction. Therefore, all data support that the methyl group in the pyrazolylamidino ligand, either deuterated or not, is present in the coordinated acetonitrile.

When the same reaction was attempted using CD_3NO_2 as solvent, conversion of **4** into **6** was not so clean as in CD_3CN, because the final pyrazolylamidino complexes **6** were usually mixed with neutral complexes **5** (Scheme 4, left, and Figure S4, Supporting Information). However, addition of a slight excess of MeCN to complexes **5** did not afford back **4** in the reaction conditions.

Clean conversion of **4** into **6** (Figure 8 and Scheme 4, framed reaction) clearly demonstates that the coupling reaction occurs

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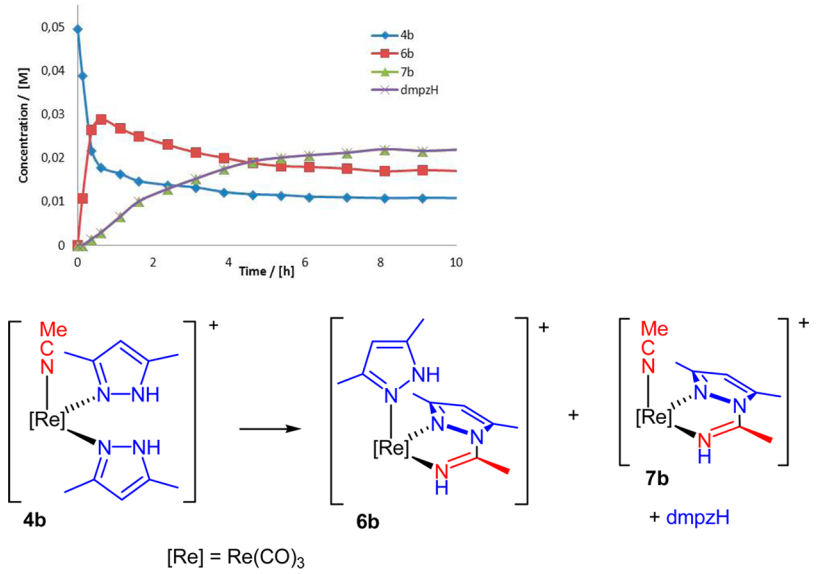
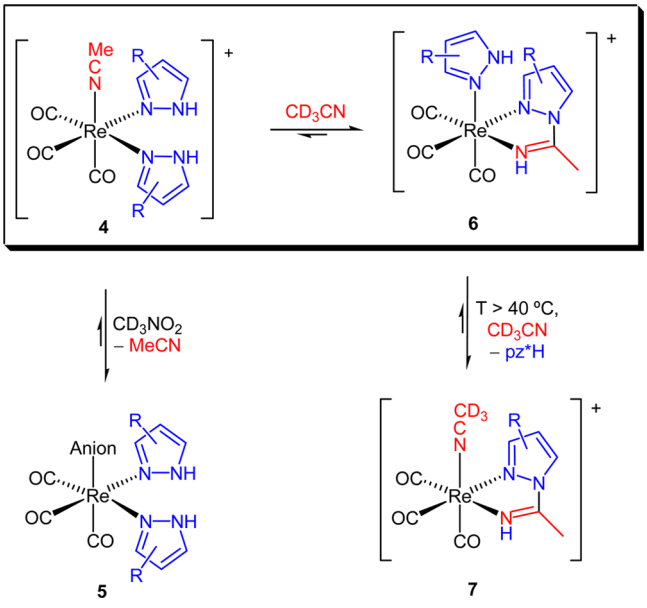


Figure 7. Representation of the observed concentrations of **4b**-BF_4, **6b**-BF_4, **7b**-BF_4, and dmpzH vs time when **4b** is heated in CD_3CN at 80 °C. Final ratio **4b**-BF_4/**6b**-BF_4/**7b**-BF_4 = 22/34/44.

Scheme 4. Conversions of 4 Into 6 in CD_3CN (framed reaction) and Byproducts Detected When the Process Is Carried out at Higher Temperatures (right) and in CD_3NO_2 (left)



when both the nitrile and the pyrazole are coordinated, and therefore, it is an intramolecular process. In order to confirm this proposal, the coupling process was carried out in the presence of a pyrazole different from that coordinated. Thus, a solution of **4b**-OTf and an equimolar amount of indzH in CD_3CN was heated at 40 °C, giving only **6b**-OTf and unreacted indzH (Scheme 5, above). The results were the same after exchanging the role of the pyrazoles, and reaction of **4c**-ClO_4 and a equimolar amount of dmpzH in CD_3CN at room temperature again gave only **6c**-ClO_4 and unreacted dmpzH (Scheme 5, below). These results confirm that the pyrazole which undergoes the coupling process is that previously coordinated, thus supporting definitively a intramolecular mechanism for this reaction.

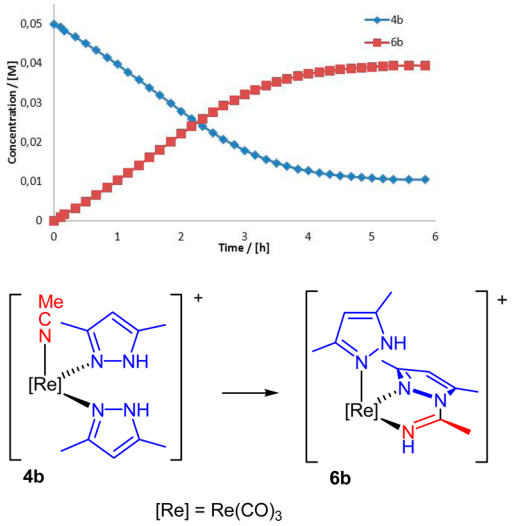


Figure 8. Representation of the observed concentrations of **4b**-OTf and **6b**-OTf when **4b**-OTf is heated in CD_3CN at 40 °C. Final ratio: **4b**-OTf/**6b**-OTf = 21/79.

A 100% conversion is not usually achieved in all these processes where mixed acetonitrile−pyrazole cationic complexes convert into the corresponding pyrazolylamidino ligands; instead, a constant ratio mixture of species is commonly obtained (for example, 79/21 for the process depicted in Figure 8, although 100/0 for that shown in Figure S3, Supporting Information). According to the principle of microscopic reversibility, if the reaction were reversible the same mixture should be obtained by the reverse reaction, which is using the final product as starting material. In order to confirm this, different experiments were designed in order to carry out the inverse experiments to those described in the framed reaction of Scheme 4. Thus, heating **6b**-OTf at 40 °C in CD_3CN afforded a mixture of **6b**-OTf and **4b**-OTf in a 80/20 ratio, that is, similar to that obtained in the direct process described in Figure 8.

On the other hand, in a separate experiment, reaction of **4b**-OTf in CD_3CN at 40 °C was allowed to reach to the final

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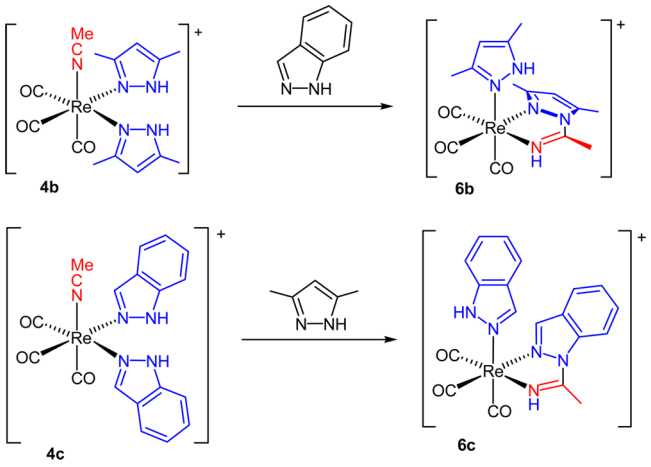
Scheme 5. Reactions Supporting That the Coupling Process Proceeds via an Intramolecular Mechanism



equilibrium, giving the expected mixture of 79/21 of **6b**-OTf/**4b**-OTf (Figure 8), and then 5 mg of **4b**-OTf was added. When the reaction was heated again to 40 °C, the final ratio was the same (Figure S5, Supporting Information), thus supporting that the coupling reaction of pyrazoles and nitriles to obtain pyrazolylamidino ligands is a reversible intramolecular process.

In order to obtain more information about the mechanism of the coupling process, a systematic study was carried out considering the possible factors which may affect the reaction, that is, temperature, pyrazole, anion, and solvent. As shown below, this study allowed us to find a catalyst for this reaction.

All of the following experiments were carried out with cationic complexes **4**, since conversion of neutral bromido complexes **1** to the corresponding pyrazolylamidino complexes **2** is not clean nor reversible. The proposal suggested in Scheme 3 for the neutral bromido complexes is confirmed by the experiments just described, carried out with cationic complexes **4**. Removal of the bromido ligand in **1** and substitution by acetonitrile would afford cationic complexes of the type *fac*-$[Re(CO)_3(NCMe)_2(pz*H)]^+$,[12] which would give the pyrazolylamidino complexes **7** by the reversible intramolecular process explained above. Substitution of the labile acetonitrile in **7** by the bromide present in solution would afford the neutral pyrazolylamidino complexes **2** (Scheme 3). However, the high temperatures needed to remove the bromido ligand and thus to start the coupling process may give rise to other secondary reactions, such as substitution of nitriles by pyrazoles to afford bis(pyrazole) complexes **3**.[13] However, the proposed path through cationic complexes might not be the only way to obtain pyrazolylamidino neutral ligands, because they are also formed, although in lower yield, when the process is carried out with an excess of $^nBu_4NBr$, which should prevent formation of cationic complexes. Nevertheless, drawing conclusions from the latter experiment is difficult, since new species (probably polybromide anionic complexes) are present and contaminate the whole process.

(a) Temperature. As indicated above, clean conversion of **4** to **6** occurs at 40 °C in CD_3CN, whereas at 80 °C substitution of the pyrazole by CD_3CN is observed (Scheme 4). In order to know the optimal temperature for this process, we determined the yields for the synthesis of **6c**-OTf from **4c**-OTf at different temperatures (from 20 to 60 °C) in CD_3CN. In this range of temperatures the results (Table S1, Supporting Information) demonstrate that yields are higher for low temperatures, indicating that the reverse reaction (formation of the pyrazole−nitrile mixed complex from the pyrazolylamidino complex) is more favorable at higher temperatures. This result might be explained considering that the presence of a chelating ligand in the pyrazolylamidino complexes **6** represents a decrease in the entropy, and therefore, increasing temperatures prevents its formation.

(b) Pyrazole. Considering the temperatures and the time needed to achieve the reaction, the tendency of the pyrazoles used in this study to give pyrazolylamidino complexes follow the sequence indzH > pzH > dmpzH (Figure 9, Table S2, Supporting Information). This is in accordance with the acidity of the pyrazoles used, which has been experimentally demonstrated to be that theorically expected, indzH > pzH > dmpzH.[14] Therefore, the more acidic pyrazoles facilitate proton transfer from the pyrazole to the donor nitrogen atom of the pyrazolylamidino ligand. This is in accordance with a coupling process with concomitant deprotonation of the pyrazole, as mentioned in the Introduction (Scheme 2, path a).

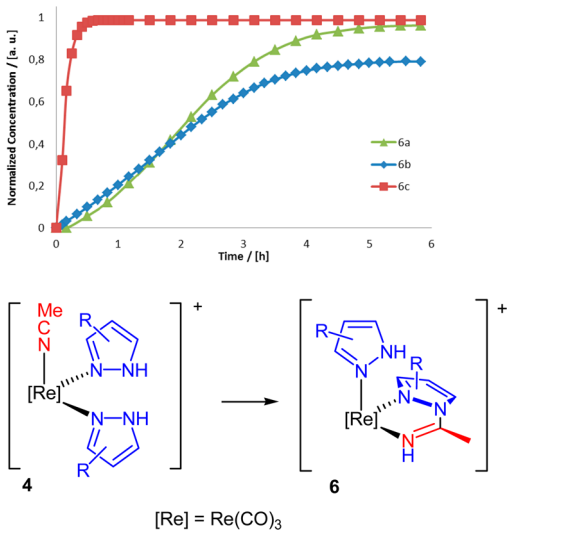


Figure 9. Representation of the observed concentrations vs time of complexes **6** when **4** are heated in CD_3CN at 40 °C.

(c) Anion. As indicated also in the Introduction, the influence of the anion in the coupling process of a coordinated nitrile and pyrazole to give pyrazolylamidino complexes has been already reported, and a transition state for the metal-activated pyrazole−nitrile coupling reaction was then proposed.[2a] However, in our case, use of different anions (BF_4^-, ClO_4^-, OTf^-) did not allow us to establish clear differences between them. Therefore, conversion reactions of **4** to **6** were repeated using an excess of sodium salts (usually 3/1, as a larger excess causes precipitation of the salts). Surprisingly, addition of a sodium salt of the anion present in the complex has two effects on the process: reducing both the reaction time and the temperature needed to observe the coupling process. On the other hand, the product/substrate final ratio does not change compared to that obtained without an excess of anion. These experiments allowed us to propose the following sequence for the accelerating role of the anions used in this reaction: OTf^- > ClO_4^- > BF_4^-. However, this sequence does not coincide with the strength of the acids involved, neither in the gas phase nor in MeCN.[15] Therefore, there must be *something else* accelerating the reaction, and it might be an

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impurity present in the sodium salts used, which points to a catalyst, given the small amount present and its decisive effect on the reaction.

The review of Kukushkin and Pombeiro on additions to metal-activated organonitriles described that some of them are base catalyzed,[1c] although this had not been previously reported for additions of pyrazoles to metal-activated organonitriles. This led us to conclude that the sodium salts used might be mixed with small amounts of a base. Then we measured the pH of 1 M solutions in H_2O of the sodium salts used, and the amount of impure base is directly related to the observed sequence (pH of 1 M solutions in H_2O): OTf^- (11.1) > ClO_4^- (9.3) > BF_4^- (2.6)). When the experiment was repeated with pure salts (pH of 1 M solutions in H_2O = 7) the excess of anions did not have any evident effect on the reaction time nor on the reaction yield (Figure S6, Supporting Information).

(d) Catalyst for the reaction. Therefore, we decided to repeat the coupling process in the presence of a small amount of aqueous solution of NaOH. Formation of pyrazolylamidino complexes **6** after addition of a 0.5% NaOH (as ca. 0.02 M aqueous solution) to CD_3CN solutions of **4** was immediate, occurring at room temperature and quantitatively (for pzH or indzH) or with very high yield (for dmpzH),

As described above, formation of pyrazolylamidino neutral bromo complexes **2** from **1** was not clean (Figure 6). However, when these processes were repeated in the presence of 1% of NaOH (again as ca. 0.02 M aqueous solution), formation of **2** occurred in milder conditions and with higher yields with respect to those reactions carried out without base (see the synthesis of **2c** in the Experimental Section, carried out by both methods, and Table S3, Supporting Information). As indicated above, reactions are not so favored for neutral complexes as for cationic complexes, since the nitrile is less activated. These experiments lead us to conclude that the coupling reaction of pyrazoles and acetonitrile to give pyrazolylamidino ligands is base catalyzed.

As we are using an aqueous solution of NaOH, we decided to explore the role in the reaction of (a) water and (b) acids (since the $NaBF_4$ first used was contaminated with acid). Figure 10 shows the concentration vs time of **6a**, when the parent complex **4a** was heated at 40 °C in dry CD_3CN or treated with either 0.5% of NaOH (aq), 0.5% of HBF_4 (aq), or the same amount of neutral H_2O in CD_3CN at room temperature. Figure 10 shows that the reaction is immediate when NaOH (aq) is added (the reaction had already concluded when the first NMR spectrum is obtained), whereas the reaction carried out in the presence of the same amount of H_2O is slower. The reaction rate of the latter is almost identical to that carried out when of 0.5% of HBF_4 is added; therefore, strong acids have no effect on the reaction rate. The concentration of the final product when the reaction is carried out in dry CD_3CN is shown at the bottom, but these data correspond to the reaction at 40 °C, because it is too slow in dry CD_3CN at room temperature.

We also explored the behavior of weaker bases than NaOH. Figure S7, Supporting Information, shows how addition of weaker bases than NaOH (aq), such as acetate or fluoride, produces the expected results considering their pH, which is a faster process than those with neutral or acid water but slower than those with the same amount of NaOH (aq). Surprisingly, addition of cyanide gives rise to an even slower process. Unfortunately, so far we have no explanation for this surprising behavior of the cyanide ion.

As indicated in the Introduction, intramolecular nucleophilic attack of the pyrazole to the coordinated nitrile coordinated cis is

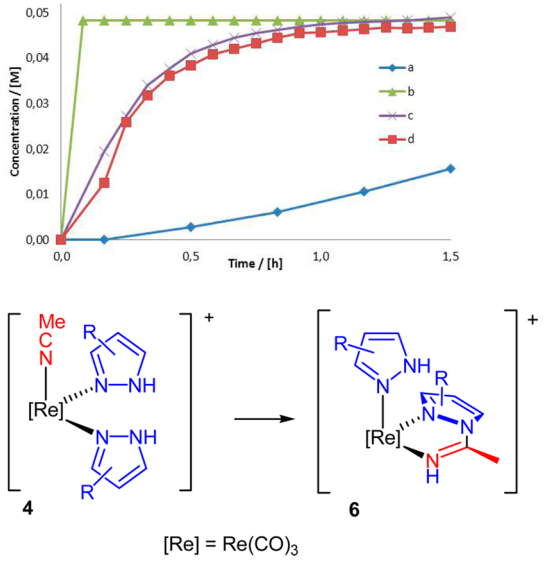

Figure 10. Representation of the observed concentrations of **6a** when (a) **4a**−ClO_4 is heated at 40 °C and when **4a**−BF_4, is stirred at room temperature with (b) 6.2 μL of 0.5% of NaOH (aq), (c) 6.2 μL of 0.5% of HBF_4 (aq), or (d) 6.2 μL of H_2O are added. All reactions are carried out in CD_3CN; 0.05 M is 100% yield.

only possible by considering the previous deprotonation of the NH group (Scheme 2, path a). Therefore, the actual role of the base as catalyst for this process may be facilitating this deprotonation. The fact that small amounts of water (either neutral or acidic) also accelerate the process (although less efectively compared to the aqueous base solution, Figure 10) might indicate that autoprotolysis occurring in aqueous media may also help this deprotonation and therefore the coupling process. Furthermore, a clear dependence of the basicity is established, as the effect of weaker bases is feebler than that of NaOH.

(e). Solvent. As indicated above, all kinetic studies were carried out in CD_3CN because the attempts to carry out the reactions in CD_3NO_2 led to total or partial substitution of the acetonitrile ligand. However, as the reactions base catalyzed are immediate (starting from cationic complexes **4**) or very fast (for neutral complexes **1**), we decided to explore the use of other solvents in this case. For the latter, the processes could be carried out only in CD_3CN, since use of other solvents led again to mixtures of products. However, for cationic complexes **4**, the results of the base-catalyzed coupling processes in CD_3NO_2 or $(CD_3)_2CO$ are similar to those obtained in CD_3CN, that is, the reactions are quantitative and immediate and occurred at room temperature.

■ CONCLUSIONS

Synthesis of different rhenium complexes containing both pyrazole and nitrile ligands has allowed us to study the mechanism of the coupling reaction between these two ligands to afford pyrazolylamidino complexes. The study was carried out on cationic complexes because the nitrile is more electrophilic than in neutral complexes, and thus, for the latter higher temperatures are needed, which facilitates formation of different byproducts. All of the data obtained starting from pyrazole−nitrile mixed cationic complexes support that the coupling process to give pyrazolylamidino ligands occurs by a reversible intramolecular mechanism. The systematic study carried out on this process revealed that the coupling process is favored: (a) at

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moderate temperatures (and unfavored as the temperature increases), opposite to what was commonly accepted, since pyrazolylamidino complexes had been traditionally synthesized by refluxing or heating pyrazole complexes in nitriles as solvents, and (b) with the acidity of the pyrazole. We found that the coupling process is base catalyzed, and the reactions to obtain cationic pyrazolylamidino complexes are quantitative and immediate and occurred at room temperature for different solvents when ≤1% of NaOH (aq) is added to the parent complex solution. Neutral bromido pyrazolylamidino complexes are obtained rapidly and at room temperature when 1% of NaOH (aq) is added to the parent complex CD_3CN solution. We believe that these results open a broad range of synthetic possibilities to obtain new pyrazolylamidino complexes in the future.

EXPERIMENTAL SECTION

General Remarks. All manipulations were performed under N_2 atmosphere following conventional Schlenk techniques. Solvents were purified according to standard procedures.[16] *fac*-[$ReBr(CO)_3(NCMe)_2$] was obtained as previously described.[17] Table 1 collects references for the preparation and characterization of some of the complexes herein used. All other reagents were obtained from the usual commercial suppliers 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 handled with care.* Infrared spectra were recorded in a PerkinElmer FT-IR spectrum BX apparatus using 0.2 mm CaF_2 cells for solutions or on KBr pellets for solid samples. NMR spectra were recorded in Bruker AV-400 or Varian MR500 instruments at room temperature and are referred to the internal residual solvent peak for ^1H and $^{13}C\{^1H\}$ NMR. Assignment of the $^{13}C\{^1H\}$ NMR data was supported by 2D heteronuclear experiments and relative intensities of the resonance signals. Elemental analyses were performed on a PerkinElmer 2400B microanalyzer.

fac-[ReBr(CO)$_3$(NCMe)(indzH)], ***1c.*** Indazole (0.059 g, 0.50 mmol) was added to a solution of *fac*-[$ReBr(CO)_3(NCMe)_2$] (0.216 g, 0.50 mmol) in THF (15 mL). The solution was stirred at 0 °C for 10 min. Hexane (ca. 25 mL) was added, and the solution was concentrated in vacuo and cooled to −20 °C, giving a colorless microcrystalline solid, which was decanted, washed with hexane (3 × 3 mL approximately), and dried in vacuo, yielding 0.154 g (61%). IR (THF, cm^{-1}): 2030 vs, 1930 vs, 1900 vs. IR (KBr, cm^{-1}): 3378 m, 2028 vs, 1903 vs br, 1628 w, 1560 w, 1508 w, 1438 w, 1358 m, 1273 w, 1246 w, 1150 w, 1096 m, 1029 w, 964 w, 749 m, 640 w, 529 w, 487 w. ^1H NMR (399.8 MHz, Me_2CO-d_6): 2.58 (s, NCCH_3, 3 H), 7.30 (t, J = 7.5 Hz, H^6 indzH, 1 H), 7.56 (t, J = 7.5 Hz, H^5 indzH, 1 H), 7.76 (d, J = 8.5 Hz, H^4 indzH, 1 H), 7.91 (d, J = 8.0 Hz, H^7 indzH, 1 H), 8.68 (s, H^3 indzH, 1 H), 12.64 (s, NH, 1 H). $^{13}C\{^1H\}$ NMR (100.5 MHz, Me_2CO-d_6): 112.1 (s, C^4 indzH), 122.1 (s, $NCCH_3$), 122.4 (s, C^7H indzH), 123.9 (s, C^6 indzH), 124.5 (s, C^{3a} indzH), 130.6 (s, C^5 indzH), 141.2 (s, C^3 indzH), 142.4 (s, C^{7a} indzH), 163.6 (s, $NCCH_3$), CO not observed. Anal. Calcd for $C_{12}H_9BrN_3O_3Re$: C, 28.30; H, 1.78; N, 8.25. Found: C, 27.98; H, 2.00; N, 8.58.

fac-[ReBr(CO)$_3$(NH═C(Me)indz-κ^{2}N,N)], ***2c.*** *Method A.* Indazole (0.059 g, 0.50 mmol) was added to a solution of *fac*-[$ReBr(CO)_3(NCMe)_2$] (0.216 g, 0.50 mmol) in CH_3CN (15 mL). The solution was stirred at 80 °C for 17 h. Volatiles were removed in vacuo, and the yellow residue was crystallized in acetone/hexane at −20 °C, giving a yellow microcrystalline solid, which was decanted, washed with hexane (3 × 3 mL approximately), and dried in vacuo, yielding 0.172g (67%). *Method B.* Indazole (0.035 g, 0.30 mmol) was added to a solution of *fac*-[$ReBr(CO)_3(NCMe)_2$] (0.130 g, 0.30 mmol) in CH_3CN (15 mL), and the solution was stirred for 20 min at 40 °C. Then 0.17 mL of NaOH aqueous solution (0.018 M, 0.003 mmol) was added, and the solution was stirred for another 30 min at 40 °C. Volatiles were removed in vacuo, and the residue was crystallized in acetone/hexane at −20 °C, yielding 135 mg (89%). IR (THF, cm^{-1}): 2021 vs, 1923 vs, 1894 vs. IR (KBr, cm^{-1}): 3183 s, 2020 vs, 1925 vs, 1889 vs, 1632 m, 1509 m, 1474 m, 1449 m, 1355 m, 1280 m, 1218 w, 1201 m, 1160 w, 1102 w, 1063 m, 1016 w, 984 w, 913 w, 883 w, 839 w, 788 w, 768 m, 646 w, 623 w, 532m, 506 w, 492 w, 471 m. ^1H NMR (399.8 MHz, Me_2CO-d_6): 3.28 (s, NCCH_3, 3 H), 7.59 (t, J = 7.5 Hz, H^6 indz, 1 H), 7.82 (t, J = 8.0 Hz, H^5 indz, 1 H), 8.11 (d, J = 8.0 Hz, H^7 indz, 1 H), 8.19 (d, J = 9.0 Hz, H^4 indz, 1 H), 9.07 (s, H^3 indz, 1 H), 10.92 (s, NH, 1 H). $^{13}C\{^1H\}$ NMR (100.5 MHz, Me_2CO-d_6): 20.3 (s, $NCCH_3$), 112.2 (s, C^4 indz), 122.6 (s, C^7 indz), 125.1 (s, C^6 indz), 131.3 (s, C^5 indz), 143.8 (s, C^3 indz), 163.6 (s, $NCCH_3$), C^{3a} (indz), C^{7a} (indz) and CO were not observed due to the low solubility of the compound. Anal. Calcd for $C_{12}H_9BrN_3O_3Re$: C, 28.30; H, 1.78; N, 8.25. Found: C, 28.36; H, 1.73; N, 8.28.

fac-[ReBr(CO)$_3$(indzH)$_2$], ***3c.*** Indazole (0.071 g, 0.60 mmol) was added to a solution of *fac*-[$ReBr(CO)_3(MeCN)_2$] (0.130 g, 0.30 mmol) in THF (20 mL). The solution was stirred for 1 h at room temperature. Hexane (ca. 20 mL) was added, and the solution was concentrated and cooled to −20 °C, giving a colorless microcrystalline solid, which was decanted, washed with hexane (3 × 3 mL approximately), and dried in vacuo, yielding 0.143 g (81%). IR (THF, cm^{-1}): 2026 vs, 1924 vs, 1895 vs. IR (KBr, cm^{-1}): 3311 s, 2020 vs, 1910 vs, 1891 vs, 1629 m, 1511 w, 1356 m, 1244 m, 1002 w, 961 w, 832 m, 752 m, 744 m, 673 w, 660 m, 648 m, 542 m, 430 w. ^1H NMR (399.8 MHz, Me_2CO-d_6): 7.26 (t, J = 7.5 Hz, H^6 indzH, 2 H), 7.52 (t, J = 7.5 Hz, H^5 indzH, 2 H), 7.69 (d, J = 8.5 Hz, H^4 indzH, 2 H), 7.85 (d, J = 8.0 Hz, H^7 indzH, 2 H), 8.56 (s, H^3 indzH, 2 H), 12.63 (s, NH, 2 H). $^{13}C\{^1H\}$ NMR (100.5 MHz, Me_2CO-d_6): 112.3 (s, C^4 indzH), 122.7 (s, C^7 indzH), 124.2 (s, C^6 indzH), 124.8 (s, C^{3a} indzH), 130.8 (s, C^5 indzH), 141.6 (s, C^3 indzH), 142.7 (s, C^{7a} indzH), 191.9 (br, 1 CO), 197.4 (br, 2 CO). Anal. Calcd for $C_{17}H_{12}BrN_4O_3Re$: C, 34.82; H, 2.06; N, 9.55. Found: C, 34.75; H, 1.86; N, 9.09.

fac-[Re(CO)$_3$(NCMe)(pzH)$_2$]BF$_4$, ***4a-BF$_4$.*** Silver tetrafluoroborate (0.054 g, 0.28 mmol) was added to a solution of **3a** (0.122 g, 0.25 mmol) in THF (20 mL), and the mixture was stirred for 1 h at 40 °C in the absence of light. The reaction mixture was dried in vacuo, and the residue was extracted with CH_2Cl_2 (20 mL), filtered, and dried in vacuo. The white residue was dissolved in $CHCl_3$/MeCN (5 mL/5 mL), and the solution was stirred for 4 h at 0 °C. The solvent was then removed in vacuo to give a white solid, which was recrystallized from $CHCl_3$/hexane at −20 °C, giving a colorless microcrystalline solid, which was decanted, washed with hexane (3 × 3 mL approximately), and dried in vacuo, yielding 87 mg (60%). IR (THF, cm^{-1}): 2034 vs, 1934 vs, 1922 vs. IR (KBr, cm^{-1}): 3222 m, 3160 m, 2040 vs, 1950 vs, 1918 vs, 1290 s, 1257 s, 1244 s, 1224 m, 1182 s, 1131 m, 1070 w, 1055 m, 1026 s, 950 w, 878 w, 777 m, 652 w, 637 m, 606 w, 575 w, 519 w, 494 w, 411w. ^1H NMR (399.8 MHz, $CDCl_3$): 2.67 (s, NCCH_3, 3 H), 6.39 (s, H^4 pzH, 2 H), 7.71 (s, $H^{3,5}$ pzH, 2 H), 7.77 (s, $H^{5,3}$ pzH, 2 H), 12.19 (s, NH, 2 H). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): 5.8 (s, NCCH3), 107.7 (s, C^4 pzH), 125.3 (s, NCCH3), 133.5 (s, $C^{5,3}$ pzH), 145.3 (s, $C^{3,5}$ pzH), 191.7 (s, 3 CO). ^{19}F NMR (376.2 MHz, $CDCl_3$): −149.8 (s, $^{10}BF_4$, 4 F), −149,9 (s, $^{11}BF_4$, 4 F). Anal. Calcd for $C_{11}H_{11}BF_4N_5O_3Re$: C, 24.67; H, 2.07; N, 13.08. Found: C, 24.44; H, 1.71; N, 12.78.

fac-[Re(CO)$_3$(NCMe)(indzH)$_2$]BF$_4$, ***4c-BF$_4$.*** Silver tetrafluoroborate (0.107 g, 0.55 mmol) was added to a solution of **3c** (0.293 g, 0.50 mmol) in THF (30 mL). Working up as for **4a**-BF_4 gave 173 mg (53%) of **4c**-BF_4 as a colorless microcrystalline solid. IR (THF, cm^{-1}): 2036 vs, 1929 vs. IR (KBr cm^{-1}): 3338 m, 3138 m, 2291 w, 2041 vs, 1943 vs, 1925 vs, 1630 m, 1515 m, 1388 m, 1377 m, 1360 m, 1285 w, 1247 w, 1226 w, 1084 vs, 1062 vs, 1031 s, 902 w, 840 w, 782 w, 753 m, 647 w, 534 w, 482 w, 432 w. ^1H NMR (499.7 MHz, $CDCl_3$): 2.82 (s, NCCH_3, 3 H), 7.24 (partially overlapped by the solvent signal, H^6 indzH, 2 H), 7.51 (t, J = 8.0 Hz, H^5 indzH, 2 H), 7.69 (d, J = 7.5 Hz, H^7 indzH, 2 H), 7.82 (d, J = 8.5 Hz, H^4 indzH, 2 H), 8.32 (s, H^3 indzH, 2 H), 11.74 (s, br, NH, 2 H). $^{13}C\{^1H\}$ NMR (499.7 MHz, $CDCl_3$): 5.9 (s, $NCCH_3$), 112.1 (s, C^4 indzH), 120.4 (s, C^7 indzH), 122.8 (s, C^{3a} indzH), 123.5 (s, C^6 indzH), 126.4 (s, $NCCH_3$), 130.2 (s, C^5 indzH), 141.0 (s, C^3 indzH), 141.8 (s, C^{7a} indzH), 191.3 (s, 2 CO), 192.0 (s, CO). ^{19}F NMR (470.2 MHz, $CDCl_3$): −149.97 (s, $^{10}BF_4$, 4 F), −150.2 (s, $^{11}BF_4$, 4 F). Anal. Calcd for $C_{19}H_{15}BF_4N_5O_3Re$: C, 35.90; H, 2.38; N, 11.02. Found: C, 35.62 ; H, 2.11 ; N, 10.77.

fac-[Re(CO)$_3$(pzH)$_2$(OTf)], ***5a.*** Silver triflate (0.084 g, 0.33 mmol) was added to a solution of **3a** (0.146 g, 0.3 mmol) in THF (15 mL), and the mixture was stirred for 1 h at room temperature in the absence of light. The reaction mixture was filtered, and hexane was added to the filtrate. The solution was concentrated and cooled to −20 °C, giving a colorless

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microcrystalline solid, which was decanted, washed with hexane (3 × 3 mL approximately), and dried in vacuo, yielding 0.145 g (87%). IR (THF, cm^{-1}): 2037 vs, 1932 vs, 1905 vs. IR (KBr, cm^{-1}): 3291 s, 3270 s, 2036 vs, 1930 vs, 1917 vs, 1654 w,1560 w, 1540 w, 1491 w, 1412 w, 1364 w, 1314 s, 1236 s, 1212 s, 1191 m, 1139 m, 1070 w, 1057 m, 1031 m, 952 w, 912 w, 863 w, 777 m, 659 w, 633 m, 606 w, 573 w, 537 w. ^{1}H NMR (399.8 MHz, $CDCl_3$): 6.45 (s, H^4 pzH, 1 H), 7.58 (s, $H^{3,5}$ pzH, 1 H), 7.71 (s, $H^{5,3}$ pzH, 1 H), 11,42 (s, NH, 1 H). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$): 107.8 (s, C^4 pzH), 119.1 (s, CF_3SO_3), 131.5 (s, $C^{5,3}$ pzH), 143.1 (s, $C^{3,5}$ pzH), 192.3 (s, 1 CO), 193.0 (s, 2 CO). ^{19}F NMR (376.2 MHz, $CDCl_3$): −75.5 (s, CF_3SO_3). Anal. Calcd for $C_{10}H_8F_3N_4O_6ReS$: C, 21.58; H, 1.45; N, 10.07. Found: C, 21.77; H, 1.36 ; N, 9.90.

fac-[Re(CO)$_3$(dmpzH)$_2$(OTf)], ***5b***. Silver triflate (0.056 g, 0.22 mmol) was added to a solution of **3b** (0.108 g, 0.2 mmol) in THF (15 mL), and the mixture was stirred for 2 h at room temperature in the absence of light. Working up as for **5a** gave 0.103 g (84%) of **5b** as a colorless solid. IR (THF, cm^{-1}): 2034 s, 1928 vs, 1901 vs. IR (KBr, cm^{-1}): 3446 m, 3349 m, 3288 m, 2036 vs, 1923 vs, 1917 vs, 1654 w, 1636 w, 1578 w, 1419 w, 1379 w, 1316 m, 1294 m, 1261 m, 1233 m, 1205 m, 1186 m, 1053 w, 1026 m, 819 w, 800 w, 661 w, 636 m, 518 w, 458 w, 419 w. ^{1}H NMR (399.8 MHz, $CDCl_3$): 2.11 (s, C^3H_3 dmpzH, 6 H), 2.21 (s, C^5H_3 dmpzH, 6 H), 5.93 (s, H^4 dmpzH, 2 H), 10.63 (s, NH, 2 H). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$): 10.9 (s, C^5H_3 dmpzH), 14.5 (s, C^3H_3 dmpzH), 106.7 (s, C^4H dmpzH), 119.2 (q, J = 318.5 Hz, $CF_3SO_3^-$), 143.2 (s, CCH_3 dmpzH), 153.7 (s, CCH_3 dmpzH), 193.4 (s, CO), 193.5 (s, 2 CO). ^{19}F NMR (376.2 MHz, $CDCl_3$): −75.6 (s, CF_3SO_3). Anal. Calcd for $C_{14}H_{16}F_3N_4O_6ReS$: C, 27.49; H, 2.64; N, 9.16. Found: C, 27.24 ; H, 2.36 ; N, 8.99.

fac-[Re(CO)$_3$(indzH)$_2$(OTf)], ***5c***. Silver triflate (0.056 g, 0.22 mmol) was added to a solution of **3c** (0.117 g, 0.2 mmol) in THF (15 mL), and the mixture was stirred for 2 h at room temperature in the absence of light. Working up as for **5a** gave 0.123 g (94%) of **5c** as a colorless solid. IR (THF, cm^{-1}): 2038 vs, 1937 vs, 1910 vs. IR (KBr, cm^{-1}): 3415 m, 3134 m, 3055 m, 2974 m, 2880 m, 2036 vs, 1924 vs, 1906 vs, 1630m, 1516 w, 1360m, 1338m, 1234 s, 1199 s, 1174 s, 1150 m, 1084 w, 1050 m, 1014 s, 886 w, 839 w, 751 m, 658 w, 631 m, 572 w, 526 w, 482 w, 433 w. ^{1}H NMR (399.8 MHz, $CDCl_3$): 7.26 (m, H^6 indzH 2 H), 7.51−7.53 (m, H^5 and H^7 indzH, 4 H), 7.71 (d, J = 8.5 Hz, H^4 indzH, 2H), 8.15 (s, H^3 indzH, 2 H), 11.39 (s, NH indzH, 2 H). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$): 110.5 (s, C^7 indzH), 119.1 (q, J = 314.0 Hz, $CF_3SO_3^-$), 120.1 (s, C^4 indzH), 122.6 (s, C^{3a} indzH), 123.2 (s, C^6 indzH), 129.9 (s, C^5 indzH), 138.8 (s, C^3 indzH), 140.6 (s, C^{7a} indzH), 192.4 (br, 1 CO), 192.9 (br, 2 CO). ^{19}F NMR (376.2 MHz, $CDCl_3$): −75.4 (s, CF_3SO_3). Anal. Calcd for $C_{18}H_{12}F_3N_4O_6ReS$: C, 32.98; H, 1.84; N, 8.55. Found: C, 32.68; H, 1.76; N, 8.49.

fac-[Re(CO)$_3$(indzH)(NH=C(Me)indz-κ^{2}N,N)]OTf, ***6c***-OTf.[18] A solution of **5c**-OTf (0.197 g, 0.3 mmol) in MeCN (15 mL) was stirred for 10 h at room temperature. Volatiles were removed in vacuo to give a yellow solid, which was recrystallized from THF/hexane at −20 °C, giving a yellow microcrystalline solid, which was decanted, washed with hexane (3 × 3 mL approximately), and dried in vacuo, yielding 0.186 g (89%). IR (THF, cm^{-1}): 2035 vs, 1939 vs, 1924 vs. IR (KBr, cm^{-1}): 3434 m, 3125 m, 2976 m, 2874 w, 2031 vs, 1916 vs br, 1631 m, 1514 w, 1480 m, 1463 w, 1425 m, 1356 m, 1281 w, 1194 w, 1117 s, 1086 s, 1044 m, 915 w, 884 w, 845 w, 795 w, 753 m, 624 m, 535 w, 521 w, 475w. ^{1}H NMR (399.8 MHz, Me_2CO-d_6): 3.32 (s, NH=CCH_3, 3 H), 7.19 (t, J = 7.5 Hz, H^5 indzH, 1 H), 7.47 (t, J = 7.5 Hz, H^6 indzH, 1 H), 7.55 (d, J = 8.5 Hz, H^7 indzH, 1 H), 7.59 (t, J = 7.5 Hz, H^5 indz, 1 H), 7.71 (d, J = 8.5 Hz, H^4 indzH, 1 H), 7.82 (t, J = 8.0, H^6 indz 1 H), 8.11 (d, J = 9.0 Hz, H^7 indz, 1 H), 8.14 (d, J = 9.0 Hz, H^4 indz, 1 H), 8.36 (s, H^3 indzH, 1 H), 9.47 (s, H^3 indz, 1 H), 10.86 (s, NH=CCH$_3$, 1 H), 12.81 (s, NH indH, 1 H). ^{13}C{^{1}H} NMR (100.5 MHz, Me_2CO-d_6): 21.6 (s, NH=CCH_3), 111.2 (s, C^7 indzH), 113.7 (s, C^7 indz), 121.8 (s, C^4 indzH), 123.5 (s, C^5 indzH), 124.4 (s, C^4 indz), 126.6 (s, C^5 indz), 127.2 (C^{3a}, the other C^{3a} was not observed), 130.3 (s, C^6 indzH), 133.4 (s, C^3 indzH), 140.6 (C^{7a}), 142.1 (C^{7a}), 148.0 (s, C^3 indz), 168.3 (s, NH=CCH_3), 191.6 (s, CO), 195.2 (s, CO), 195.4 (s, CO). ^{19}F NMR (376.2 MHz, Me_2CO-d_6): −73.7 (s, CF_3SO_3). Anal. Calcd for $C_{20}H_{15}F_3N_5O_6ReS$: C, 34.43; H, 2.17; N, 10.04. Found: C, 34.79; H, 2.29; N, 9.86.

fac-[Re(CO)$_3$(NCMe)(NH=C(Me)indz-κ^{2}N,N)]OTf, ***7c***-OTf. Silver triflate (0.085 g, 0.33 mmol) was added to a solution of **2c** (0.152 mg, 0.30 mmol) in MeCN (30 mL). The mixture was refluxed for 2 h in the absence of light. The reaction mixture was then filtered and dried in vacuo. The yellow residue was crystallized in acetone/hexane at −20 °C, giving a yellow microcrystalline solid, which was decanted, washed with hexane (3 × 3 mL approximately), and dried in vacuo, yielding 0.158 g (85%). IR (THF, cm^{-1}): 2035 vs, 1939 vs, 1924 vs. IR (KBr, cm^{-1}): 3194 w, 2027 vs, 1902 vs br, 1638 m, 1512 w, 1484w, 1424 m, 1355 m, 1276 s, 1253s, 1222s, 1149 s, 1091 w, 1030 w, 876 w, 800 w, 758 s, 668 w, 637 s, 572 w, 517 m, 485 m, 431 w. ^{1}H NMR (376.2 MHz, Me_2CO-d_6): 2.38 (s, NCCH_3, 3 H), 3.30 (s, NH=CCH_3, 3 H), 7.64 (t, J = 8.0 Hz, H^6 indz, 1 H), 7.91 (t, J = 8.0 Hz, H^5 indz, 1 H), 8.17 (d, J = 8.0 Hz, H^7 indz, 1 H), 8.22 (d, J = 9.0 Hz, H^4 indz, 1 H), 9.29 (s, H^3 indz, 1 H), 10.87 (s, br, NH, 1 H). ^{13}C{^{1}H} NMR (125.7 MHz, Me_2CO-d_6): 3.2 (s, NCCH_3), 21.4 (s, NH=CCH_3), 113.7 (s, C^4 indz), 123.41 (s, C^7 indz), 126.5 (s, C^6 indz), 127.2 (s, C^{3a} indz), 133.4 (s, C^5 indz), 140.5 (s, C^{7a} indz), 147.4 (s, C^3 indz), 167.8 (s, $NCCH_3$), 190.2 (s, CO), 194.1 (s, 2 CO). ^{19}F NMR (470.2 MHz, Me_2CO-d_6): −73.69 (s, CF_3SO_3). Anal. Calcd for $C_{15}H_{12}F_3N_4O_6ReS$: C, 29.03; H, 1.95; N, 9.03. Found: C, 28.74; H, 1.71; N, 8.88.

Kinetic Studies. Reactions were monitored by ^{1}H NMR using 0.05 M solutions prepared under Ar atmosphere. Pure $NaBF_4$, $NaClO_4$, and NaOTf were prepared by adding NaOH solutions to the corresponding acid solutions until pH = 7 (measured with a pH meter) and drying to dryness. Studies with excess of NaOH (aq) were carried out by mixing 0.025 M solutions of the complex and a recently prepared 0.02 M aqueous solution of NaOH. The NMR probe temperature was calibrated using an ethylene glycol standard before and after the experiment.

Crystal Structure Determination for Compounds 2c, 3b, 3c, 4a-ClO$_4$, 5b-OTf, 5b-ClO$_4$, and 7c-ClO$_4$. Crystals were grown by slow diffusion of hexane into concentrated solutions of the complexes in chloroform (for **3b**, **3c**, **4a**-ClO_4, **5b**-OTf) or acetone (for **2c**, **7c**-ClO_4) at −20 °C. Relevant crystallographic details can be found in the CIF. For all complexes except **2c**, a crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite monochromatized Mo Kα X-radiation and a CCD area detector. Raw frame data were integrated with the SAINT program.[19] The structure was solved by direct methods with SHELXTL.[20] A semiempirical absorption correction was applied with the program SADABS.[21] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All calculations and graphics were made with SHELXTL. Distances and angles of hydrogen bonds were calculated with PARST[22] (normalized values).[23] For **2c**, crystal structure determination was accomplished on an Oxford Diffraction Xcalibur S diffractometer: data collection, CrysAlis CCD;[24] cell refinement, CrysAlis RED;[24] data reduction, CrysAlis RED; absorption correction, multiscan.[24] Crystal structure determinations were effected at −100 °C (Mo Kα radiation, α = 0.71073 Å). The structure was solved by applying direct and Fourier methods using SHELXS97 and SHELXL-97.[20] All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions, and each was assigned a fixed isotropic displacement parameter based on a riding model.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data for compounds **2c**, **3b**, **3c**, **4a**-ClO_4, **5b**-OTf, **5b**-ClO_4, and **7c**-ClO_4 in CIF format; figures of the crystal structures of *fac*-[$ReBr(CO)_3(dmpzH)_2$], **3b**, [$Re(CO)_3(dmpzH)_2(OClO_3)$], **5b**-$ClO_4$, representations and tables of kinetic experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(12) These complexes could not be isolated. For the pzH complex, its logical precursors is complex **1a**, which could not be isolated pure (ref 3c). The dmpzH complex could be detected and identified in solution IR (THF, cm^{-1}): 2045 vs, 1939 vs br. ^1H NMR (Me_2CO-d_6): 2.35 (s, C^5H_3 dmpzH, 3 H), 2.43 (s, C^3CH_3 dmpzH, 3 H), 2.65 (s, NCC*H*3, 6 H), 6.19 (s, H^4 dmpzH, 1 H), 11.73 (br, N*H* dmpzH, 1 H). All attempts to obtain the indzH complex were unsuccessful and gave the inserted product **7c** because removal of bromido by a silver salt needs a long time or mild heating, conditions where the coupling process occurs.

(13) Formation of **3** from **1** should occur with concomitant formation of $[ReBr(CO)_3(NCMe)_2]$, but this complex or other nitrile complexes which might also be present in solution such as $[Re(CO)_3(NCMe)_3]^+$ cannot be detected by ^1H NMR in CD_3CN due to rapid exchange of the MeCN ligands with the solvent at temperatures higher than 40 °C.

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(18) Alternative synthesis of **6c**-BF_4: 0.028 mL of a NaOH aqueous solution (0.018 M, 0.0005 mmol) was added to a solution of **4c**-BF_4 (0.070 g, 0.10 mmol) in CH_3CN (10 mL). After stirring for 15 min at room temperature, the volatiles were removed in vacuo and the yellow residue was crystallized from acetone/hexane at −20 °C, yielding 61 mg (96% of **6c**-BF_4).

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