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N Ligands

C–C Coupling of N-Heterocycles at the *fac*-Re(CO)$_3$ Fragment: Synthesis of Pyridylimidazole and Bipyridine Ligands

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Abstract: A new family of cationic rhenium tricarbonyl complexes with either two N-alkylimidazole (N-RIm) and one pyridine (Py) ligand, or two pyridine and one N-RIm ligand, $[Re(CO)_3(N\text{-}RIm)_{(3-x)}(Py)_x]^+$, has been prepared. The reaction of these complexes with a strong base, followed by an oxidant, selectively afforded 2,2′-pyridylimidazole complexes as the result of intramolecular dehydrogenative C–C coupling reactions. For tris(pyridine) complexes $[Re(CO)_3(Py)_3]^+$ the reaction pattern upon a deprotonation/oxidation sequence is maintained, which allows the generation of complexes with 2,2′-bipyridine ligands. In the particular combination of two different types of pyridine ligand in the cationic *fac*-Re(CO)$_3$ complexes only the cross-coupling products with asymmetric 2,2′-bipyridine ligands were obtained; the homocoupling products were not observed.

Introduction

Aromatic heterobiaryls are ubiquitous motifs in many natural products and bioactive compounds, pharmaceutical agents, and functional materials.[1] Classical transition-metal-catalyzed methods for the synthesis of biaryls require functionalized substrates to link two heteroarenes with a C–C bond (Figure 1 A).[2]

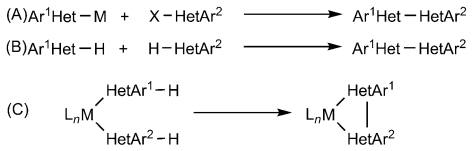

Figure 1. Synthesis of aromatic heterobiaryl compounds.

Oxidative cross-coupling between two heteroarenes by twofold C–H activation would be the ideal route to heterobiaryls because it would avoid tedious prefunctionalization (Figure 1 B).[3] In this context some important achievements have been reported in recent years;[4] however, the heteroarylation of pyridine and related azines still remains a challenge.[5] Whereas significant progress in the arylation of pyridines by C–H/C–X coupling reactions has been achieved,[6] examples of heteroarylation of pyridines are scarce, and only very recently You et al.[7] have reported, for the first time, a selective methodology for the direct C2 heteroarylation of pyridines with a wide range of heteroarenes.

On the other hand, despite the significant progress made, the transition-metal-catalyzed oxidative cross-coupling between two partners with similar structure and electronic characteristics faces significant hurdles because homocoupled products are frequently found along with the desired products of heterocoupling.[8]

We have found that coordination to a transition organometallic fragment can suffice as the only prefunctionalization required to selectively obtain cross-coupled heterobiaryl ligands from precursors that contain monodentate heteroarenes.[9] Coordination of two different aromatic N-heterocycles to the same metal fragment can result in enhancement of the nucleophilicity of one (the α-CH groups become more acidic)[10] and the electrophilicity of the other,[11,12] which generates the appropriate counterparts to undergo a intramolecular cross-coupling reaction (Figure 1 C).

By this strategy we have accomplished the cross-coupling of pyridine (Py) and N-alkylimidazole (N-RIm) ligands to afford 2,2′-pyridylimidazole (Pyim) complexes and, in a similar way, even more interestingly, 2,2′-bipyridines by oxidative coupling of two pyridyl ligands. For the latter the selective cross-coupling of two different pyridyl ligands to afford asymmetric 2,2′-bipyridine complexes has been achieved and the homocoupling products were not observed.

Synthetic routes to aromatic N,N′-chelating ligands remain a challenge and often lead to low yields, thus limiting access to metal derivatives of interest. Among such complexes, *fac*-Re(CO)$_3$ derivatives are widely employed in several areas of chemical research. Currently available synthetic routes invariably rely on substitution reactions from precursors such as

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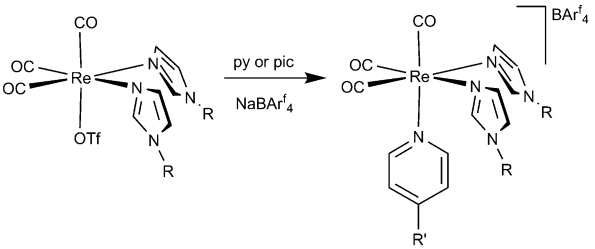
$[ReX(CO)_5]$ (X = Cl, Br), which employ preformed chelates. Herein, we propose an alternative based on at-the-metal modular synthesis of the chelate. Our route begins with the synthesis of a complex with the monodentate building blocks (readily available compounds), followed by a deprotonation/oxidation sequence in which a C–C bond is created between two of the monodentate ligands and results in the formation of the metal-bonded chelate. A clear advantage of this method is that it allows access to derivatives that contain difficult-to-synthesize chelates, such as asymmetric 2,2′-bipyridines.

Results and Discussion

Compounds $[Re(CO)_3(N\text{-}RIm)_2(Py\text{-}R')]BAr^f_4$ (**1a–d**; R = Me, mesityl (Mes); R′ = H, Me; Ar^f = 3,5-bis(trifluoromethyl)phenyl) with both pyridyl and imidazole ligands were prepared by reaction of the triflato bis(imidazole) complexes $[Re(CO)_3(N\text{-}RIm)_2(OTf)]$ (in turn, synthesized from $[Re(CO)_5(OTf)]$ and N-alkylimidazoles)[10e] with a slight excess of pyridine or γ-picoline (pic) in the presence of $NaBAr^f_4$ (Scheme 1). The new cationic complexes were obtained in good yields and characterized by IR



	R	R'	Yield
1a	Me	H	87 %
1b	Me	Me	80 %
1c	Mes	H	88 %
1d	Mes	Me	83 %

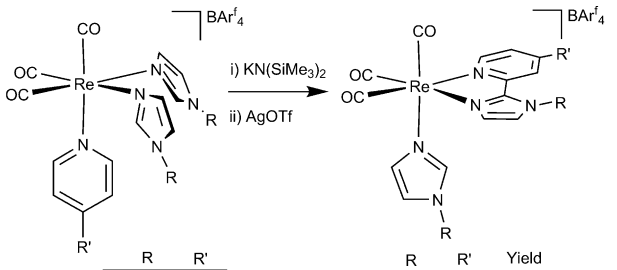
Scheme 1. Synthesis of complexes $[Re(CO)_3(N\text{-}RIm)_2(Py\text{-}R')]BAr^f_4$ (**1a–d**).

and NMR spectroscopy in solution. The IR $\tilde{\nu}_{CO}$ bands of **1a–d** showed the typical pattern for cationic Re^I *fac*-tricarbonyl complexes and the ^1H and ^{13}C NMR spectra were in agreement with the stoichiometry and geometry shown in Scheme 1.

In contrast to traditional prefunctionalized N-heterocycles,[13] compounds **1a–d** are easy to prepare on a half-gram scale, are relatively stable, and can be kept for weeks under nitrogen atmosphere at room temperature.

The reaction of compounds **1a–d** with $KN(SiMe_3)_2$ (1 equiv) in THF at −78 °C led immediately to neutral species (evidenced by large shifts of the $\tilde{\nu}_{CO}$ bands in the IR spectra to lower wavenumbers) that were unstable for isolation. Addition of silver trifluoromethanesulfonate as an oxidant afforded the formation of cationic compounds **2a–d** (Scheme 2).

The solid-state structures of **2a** and **2b**, derived from bis(*N*-methylimidazole) complexes, were determined by X-ray diffraction and confirmed the reactivity pattern depicted in Scheme 2.[9] The spectroscopic data of compounds **2c** and **2d** in solution were in accordance with the formation of 2,2′-pyri-



	R	R'
1a	Me	H
1b	Me	Me
1c	Mes	H
1d	Mes	Me

	R	R'	Yield
2a	Me	H	47 %
2b	Me	Me	56 %
2c	Mes	H	69 %
2d	Mes	Me	56 %

Scheme 2. Synthesis of 2,2′-pyridylimidazole complexes **2a–d**.

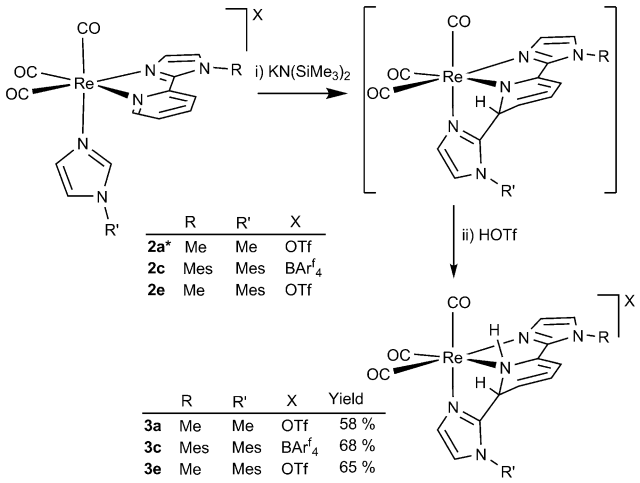
dylimidazole ligands, and showed the presence of an intact *N*-MesIm ligand coordinated to the *fac*-$Re(CO)_3$ unit, which indicates that in this reaction the imidazole substituent is not crucial to determine the reaction product.[14] No side reactions were detected, not even of the methyl group of the γ-picoline ligand, despite its acidic character.

Pyridylimidazoles are usually synthesized by the de novo construction of the imidazole ring[15] and a growing number of pyridylimidazole complexes are known. There is no precedent for their metal-templated synthesis; in fact, the synthesis of bidentate ligands by C–C coupling of monodentate ligands remains rare.[16]

It is interesting to note that the presence of an intact imidazole ligand (which, because of the positive charge of the complex, could be deprotonated) in compounds **2a–d** *cis* to the pyridylimidazole chelate (the potential electrophile) could permit a second, base-triggered C–C-coupling reaction. Unlike in the first reaction (see above), the *fac* disposition of the ligands would prevent planarity and, hence, rearomatization. Therefore, we decided to further study the deprotonation reaction of the imidazole-pyridylimidazole species.

The treatment of compound **2a***[17] with the strong base $KN(SiMe_3)_2$ instantaneously produced a neutral species, evidenced by shifts of the bands in the IR spectra to lower wavenumbers ($\tilde{\nu}_{CO}$ = 2026, 1915 to 2004, 1885 cm^{-1}), which was too unstable for isolation. The addition of HOTf (1 equiv) afforded compound **3a**, in which the nitrogen atom adjacent to the attacked carbon atom (on the pyridine ring) is protonated, as the only product of the reaction (Scheme 3).

Compound **3a** was fully characterized and the X-ray structure was determined (Figure 2a).[18] The cationic complex consists of a *fac*-$Re^I(CO)_3$ fragment bonded to a tridentate N-donor ligand. The latter results from C–C coupling between the central carbon atom of the *N*-MeIm ligand and the *ortho*-carbon atom of the pyridyl ring of the bidentate ligand. As a consequence of the formation of this new single C2–C6 bond, the pyridyl group is dearomatized, evidenced by the bond lengths C6–C7 = 1.53(2) Å, C6–N2 = 1.49(1) Å, and N2–C10 = 1.49(1) Å, which are clearly longer than those expected for an aromatic ring. The C6 atom is, therefore, sp^3 hybridized, and shows angles consistent with an approximately tetrahedral geometry (C2-C6-N2 = 105.5(10)°, C2-C6-C7 = 109.2(9)°, C7-C6-



Scheme 3. Reactivity of 2,2′-pyridylimidazole complexes.

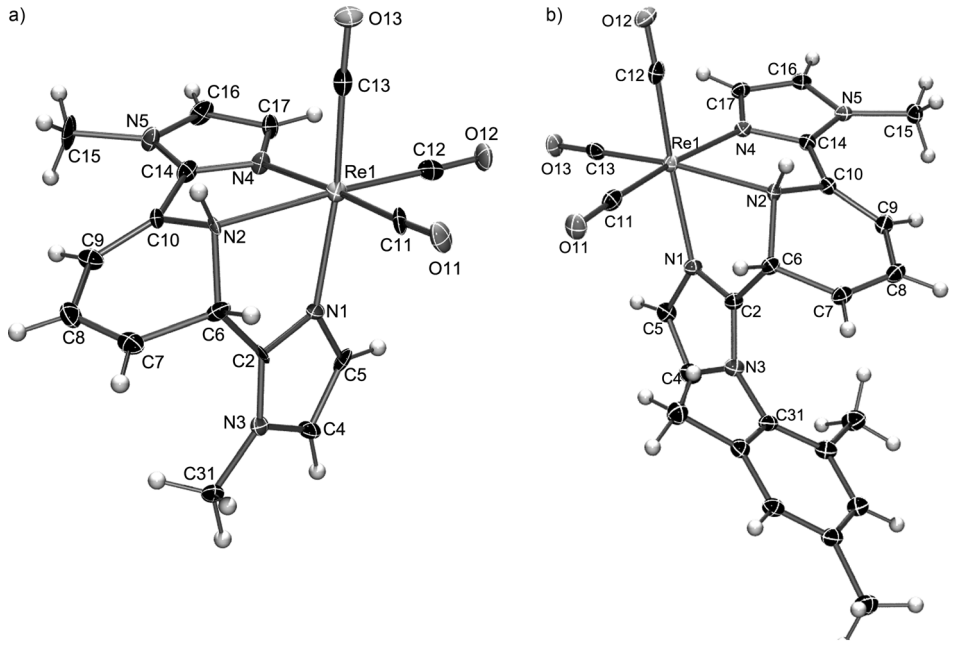


Figure 2. a) Molecular structure of the cation of complex **3a**. b) Molecular structure of the cation complex of **3e**.

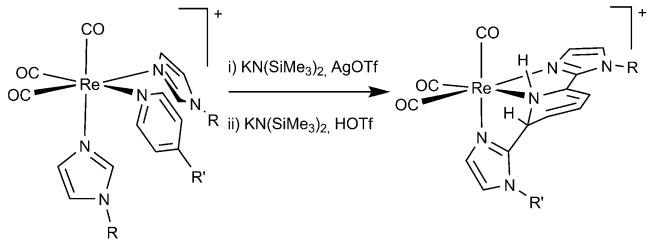
N2 = 114.9(11)°). The angles around the N2 nitrogen atom (107.8(6), 110.1(6), and 110.6(9)°) are also in agreement with an almost tetrahedral geometry. In solution, evidence of dearomatization is provided by the presence of a multiplet at δ5.42 ppm in the ^{1}H NMR spectrum and a signal at δ56.4 ppm in the ^{13}C NMR spectrum for the pyridine CH group that underwent the nucleophilic attack to give an sp^3 center.

In an attempt to isolate the neutral intermediate species produced by deprotonation of the pyridylimidazole compound **2a***, we synthesized the analogous *N*-MesIm compound (**2e**) because we have found previously that the products derived from this imidazole are often noticeably more stable than the *N*-MeIm derivatives.[10c] The deprotonation of [Re(CO)$_3$(*N*-MesIm)(Pyim-Me)]OTf (**2e**) afforded complex ***II*e** (between brackets in Scheme 3), which was not stable enough for isolation, but could be characterized spectroscopically in solution. The IR data for ***II*e** ($\tilde{\nu}_{CO}$ = 2004, 1885 cm^{-1}) agree with its neutral nature and the ^{1}H NMR spectrum in [D$_8$]THF is consistent with dearomatization of the pyridine ring (two multiplets at δ = 4.18 and 5.77 ppm and two doublets at δ = 5.23 and 5.30 ppm for this group). The addition of HOTf (1 equiv) to a solution of ***II*e** in CH_2Cl_2 led to the formation of the protonated compound **3e** (Scheme 3). The solid-state structure of **3e** was determined by X-ray diffraction (Figure 2b)[19] and, like that of the *N*-MeIm derivative **3a** (Figure 2a), shows the formation of a C–C bond between the central imidazole carbon atom and the *ortho*-carbon atom of the pyridyl group, and the subsequent dearomatization of the pyridyl group.[20] The isolation of ***II*e** allows us to propose that the addition of a strong base to [Re(CO)$_3$(N-RIm)(Pyim-Me)]OTf compounds deprotonates the central CH group of the N-RIm ligand to generate a nucleophilic N-coordinated imidazol-2-yl ligand that attacks the *ortho* CH group of the pyridyl ring and results in dearomatization. The reaction is selective and attack onto the imidazole backbone of the pyridylimidazole ligand is not observed.

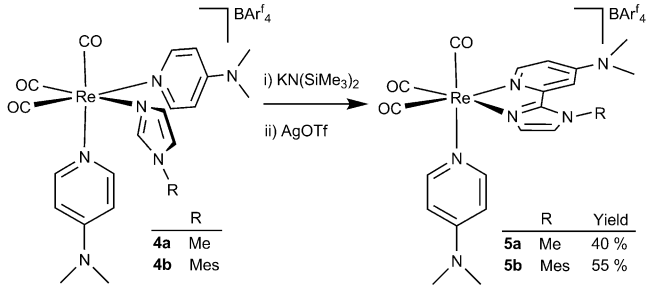
Finally, we studied the deprotonation/protonation reaction sequence of [Re(CO)$_3$(*N*-MesIm)(Pyim-Mes)]BAr$^f_4$ (**2c**)[21] and found the same reactivity pattern discussed above for the Pyim-Me derivatives. It is interesting to note that the synthesis of [Re(CO)$_3$(N-RIm)(Pyim-R)]$^+$ complexes from the corresponding bis(imidazole) compounds (Scheme 2) implies the activation of an *ortho*-CH group of a monodentate pyridyl ligand, and the formation of the dearomatized products from the pyridylimidazole complexes implies the activation of the remaining *ortho*-CH group of the same pyridine ligand (Scheme 3). Overall, the two *ortho* C–H groups of a monodentate pyridine ligand have been easily activated (Scheme 4), a reaction that, as far as we know, lacks any precedent.

To continue with our initial study of oxidative coupling of monodentate N-heterocyclic ligands to afford bis(heteroaromatic) ligands, we extended our results from complexes with two imidazole and one pyridine ligand to compounds with one imidazole and two pyridine ligands, [Re(CO)$_3$(dmap)$_2$(N-RIm)]BAr$^f_4$ (**4a**, R = Me; **4b**, R = Mes; dmap = 4-dimethylaminopyridine).[22] Treatment of **4a** or **4b** with KN(SiMe$_3$)$_2$ (1 equiv) in THF at −78 °C followed by reaction with AgOTf yielded the cationic pyridylimidazole complexes **5a** and **5b**, respectively (Scheme 5).

The NMR spectroscopic data of **5a** and **5b** in solution in CD_2Cl_2 show the asymmetry of the rhenium complexes. We ob-



Scheme 4. Activation of the two *ortho*-CH groups of a pyridine ligand.



Scheme 5. Reactivity of compounds **4a** and **4b**.

served three signals for the three carbonyl ligands in the ^{13}C NMR spectra and two sets of signals for the two different dmap groups (coupled and intact) in the ^{1}H NMR spectra. Significantly, the ^{1}H NMR spectra show only two signals for the imidazole ring CH groups, which indicated that the deprotonation occurred at this ligand. The molecular structure of the cation of compound **5b**, determined by X-ray diffraction,[23] is depicted in Figure 3 and is in agreement with the spectroscopic data in solution. The *fac*-$Re(CO)_3$ fragment displays a dmap ligand and a pyridylimidazole chelate formed by coupling of the *N*-MesIm central carbon atom (C2) and a C_{ortho} atom of the other dmap ligand (C6). The bidentate ligand formed is aromatic, evidenced by the angles and bond lengths found for both rings, which are virtually in the same plane.

This reaction shows that employment of the more electron-rich dmap ligand does not prevent the proposed (see below)

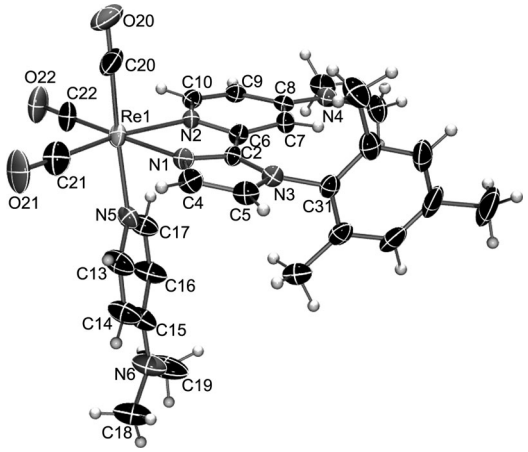


Figure 3. Molecular structure of the cation of **5b**.

nucleophilic attack of the imidazol-2-yl group, and the formation of the pyridylimidazole ligand.

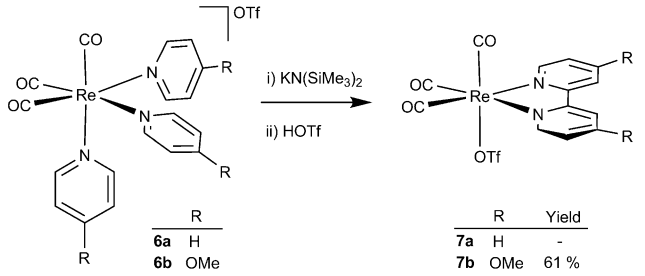
Note that, regardless of the particular composition of the cationic complex (two imidazole and one pyridine ligand, as in **1a–d**, or one imidazole and two pyridine ligands, as in **4a** and **4b**), no homocoupling products (with 2,2′-biimidazole or 2,2′-bipyridine chelates) have been detected, which suggests a clear-cut difference between the two types of ligands, in that N-alkylimidazoles are significantly more acidic and pyridines are more electrophilic.

In the absence of mechanistic studies, we speculate that the formation of the pyridylimidazole complexes occurs by deprotonation of the imidazole C2–H, nucleophilic attack of the deprotonated carbon atom onto a pyridine *ortho*-carbon atom to afford a dearomatized intermediate, which then would be oxidized by Ag^{+},[24,25] the latter step encouraged by restoration of aromaticity and conjugation between the two adjacent aromatic rings.[26] We have encountered that two equivalents of AgOTf are required for the reactions to reach completion. This could be an indication of two consecutive one-electron oxidations: the neutral C–C coupled product would undergo a one-electron oxidation to give a radical cation, followed by deprotonation to give a radical, then oxidation to the observed product. The base for the second deprotonation (only one equivalent of $KN(SiMe_3)_2$ is used) would be $HN(SiMe_3)_2$ formed in the first deprotonation step.[27]

We extended this reactivity to tris(2-pyridyl) derivatives in an attempt to obtain 2,2′-bipyridine (bipy) ligands after the dehydrogenative C–C coupling reaction. A more difficult deprotonation was anticipated because pyridines are less acidic than N-alkylimidazoles.[28] 2,2′-Bipyridines are one of the most versatile and widely used type of bidentate ligand in organometallic and inorganic chemistry.[29] Heterogeneous catalytic pyridine homocoupling is not applicable to 4-substituted pyridines,[30] and the other major method to prepare the bipy moiety—transition-metal catalyzed cross-coupling reactions—requires prefunctionalization of the substrates.[31]

The reaction of $[Re(CO)_3(dmap)_3]OTf$, first with $KN(SiMe_3)_2$, then with AgOTf, afforded the coupling product $[Re(2,2'\text{-bipy-}4,4'\text{-}NMe_2)(CO)_3(dmap)]OTf$, which was fully characterized, including a solid-state X-ray structure determination.[9] Tris(2-pyridyl) compounds $[Re(CO)_3(Py\text{-}R)_3]OTf$ (**6a**, R = H; **6b**, OMe) were prepared by thermal substitution of the DMSO ligands of the known compound $[Re(CO)_3(dmso)_3]OTf$[32] by pyridine or 4-methoxypyridine, respectively.[22] The reaction of **6a** with $KN(SiMe_3)_2$ in THF at −78 °C, followed by oxidation with HOTf, led to the formation of **7a** (Scheme 6). The known bipy complex $[Re(2,2'\text{-bipy})(CO)_3(OTf)]$[33] was prepared independently from $[Re(CO)_5(OTf)]$ and 2,2′-bipy heated at reflux in toluene. Its spectroscopic data in solution are identical to those of **7a**, which confirms the composition of the latter.

The analogous deprotonation of **6b**, followed by addition of HOTf (1 equiv), afforded the triflato complex $[Re(2,2'\text{-bipy-}4,4'\text{-}OMe)(CO)_3(OTf)]$ (**7b**). The reaction was followed by IR spectroscopy, which showed that the addition of the base afforded a neutral species ($\tilde{\nu}_{CO}$ = 2029, 1917 cm^{-1} replaced by $\tilde{\nu}_{CO}$ = 1993, 1882, 1865 cm^{-1}) and that, upon HOTf addition, oxidative



Scheme 6. Reactivity of tris(pyridyl) compounds **6a** and **6b**.

rearomatization occurred (upfield shift to $\tilde{\nu}_{CO}=2032$, 1931, 1909 cm^{-1}). In accordance, the ^1H NMR spectrum of **7b** showed the typical pattern for a symmetric 4,4′-disubstituted-2,2′-bipyridine ligand and in the ^{13}C NMR spectrum only two signals, one twice the intensity of the other, are found for the three carbonyl ligands, which indicates the presence of a molecular mirror plane. The molecular structure of compound **7b**, determined by X-ray diffraction[34] (Figure 4) confirmed the

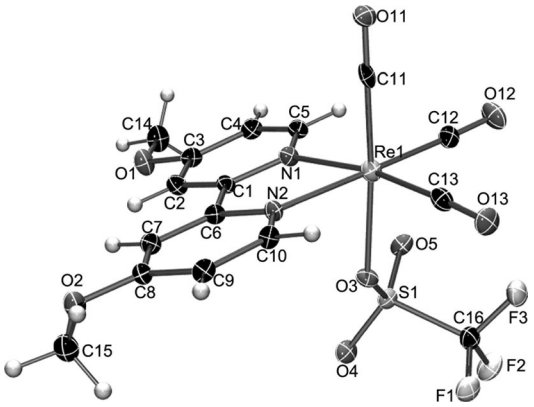
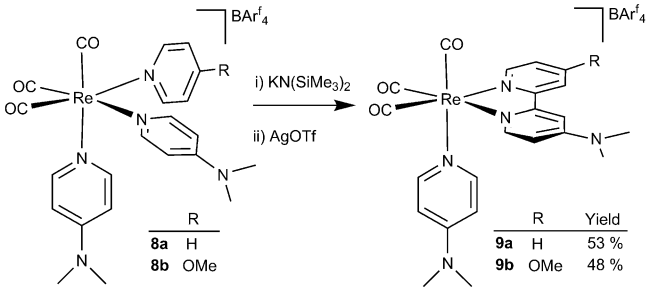


Figure 4. Molecular structure of complex **7b**.

presence of the 4,4′-dimethoxy-2,2′-bipyridine ligand coordinated to a *fac*-$Re(CO)_3$ fragment. The remaining coordination site (to complete the rhenium pseudo-octahedral geometry) is occupied by a triflato ligand.

For compounds **6a** and **6b**, we found that employment of HOTf as the oxidant afforded better results than AgOTf or other conventional oxidants (such as I_2, $FeCp_2^+$, or 2,2,6,6-tetramethylpiperidine *N*-oxide). In addition, we found that the uncoupled pyridine ligand is substituted by triflate. The formation of complexes **7a** and **7b** that contain 2,2′-bipyridine ligands shows that the deprotonation of an *ortho* C–H group of a pyridyl ligand has been achieved, a reaction that, to our knowledge, has no precedent.[9] In fact, there are just a few examples of metal-mediated coupling of pyridines, restricted to alkali metals or very reactive early transition metals.[16a,35]

Finally, going one step further, we synthesized mixed tris(pyridyl) complexes, that is, they simultaneously display two different types of pyridyl ligands coordinated to the rhenium tricarbonyl fragment. Compounds $[Re(CO)_3(dmap)_2(Py\text{-}R)]BAr^f_4$ (**8a**, R = H; **8b**, OMe) were synthesized by addition of pyridine or 4-methoxypyridine to $[Re(CO)_3(dmap)_2(OTf)]$ in the presence of $NaBAr^f_4$. The treatment of compounds **8a** and **8b** with $KN(SiMe_3)_2$ and AgOTf afforded compounds **9a** and **9b**, respectively, in good yields, as the only reaction products (Scheme 7).



Scheme 7. Reactivity of tris(pyridyl) compounds **8a** and **8b**.

The ^1H NMR spectrum of **9a** in CD_2Cl_2 shows the loss of the molecular mirror plane (present in **8a**) and displayed signals that correspond to an asymmetric complex. This is indicative of a cross-coupling product (the homocoupling reaction would lead to a symmetric derivative). Thus, in the ^1H NMR spectrum three signals are observed at $\delta=8.54$, 7.19, and 6.73 ppm, which integrate for one hydrogen atom each and correspond to the dmap ligand coupled to the pyridyl ring to form the asymmetric bipy unit. In accordance, three signals at $\delta=9.10$, 8.08, and 7.60 ppm that correspond to one, two, and one hydrogen atom, respectively, are observed for this pyridyl group. The spectrum also shows the *AA′BB′* system that corresponds to the dmap ligand and the two, now inequivalent, dimethylamino groups. The ^{13}C NMR spectrum of **9a** is in agreement with the asymmetry of the molecule, for example, one signal is observed for each bipy carbon atom. Analogously, compound **9b** features an asymmetric 4,4′-disubstituted-2,2′-bipyridine ligand, evidenced by its spectroscopic data in solution. The selectivity of these reactions is remarkable because the employment of very similar heteroaromatic ligands (different types of pyridines) leads only to the cross-coupling products, and the homocoupling products are not observed.

Conclusion

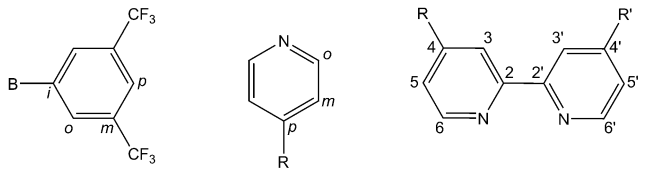
Unprecedented intramolecular oxidative C–H coupling to link either two pyridine or a pyridine and an imidazole ligand allowed the synthesis of 2,2′-heterobiaryl chelate ligands in the coordination sphere of rhenium tricarbonyl complexes. No functionalization of the imidazole or pyridine is needed other than their coordination to the same metal center, which increases the acidity of the C2–H imidazole group and the electrophilic character of the pyridine ligand. Pyridylimidazole complexes are selectively obtained, without any homocoupling (imidazole–imidazole or pyridine–pyridine) products. The extension of this reactivity to tris(pyridyl) complexes led to the synthesis of 2,2′-bipyridine ligands, which implies the deprotonation of an *ortho*-CH group of a pyridine ligand, a reaction without precedent.[9] The coordination of two different pyridyl

ligands to the same metal center selectively affords the cross-coupling products, asymmetric 4,4′-disubstituted-2,2′-bipyridines, and no homocoupling products are observed.

Experimental Section

General

All manipulations were carried out under a nitrogen atmosphere by using Schlenk techniques. Solvents were distilled from Na (toluene and hexanes), Na/benzophenone (THF), and CaH_2 (CH_2Cl_2). Compounds $[Re(CO)_3(N\text{-}RIm)_2(OTf)]$ (R = Me, Mes),[10e] $[Re(CO)_3(dmso)_3]OTf$,[32] *N*-MesIm,[36] and $NaBAr^f_4$[37] were prepared as previously reported. Deuterated dichloromethane (Cambridge Isotope Laboratories, Inc.) was stored under nitrogen in a Young tube and used without further purification. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 300, DPX-300 or Avance 400 spectrometer. Samples for NMR spectroscopy were prepared under nitrogen by using Kontes manifolds purchased from Aldrich. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the internal residual-solvent peak. IR spectra of samples in solution in 0.2 mm CaF_2 cells were measure with a PerkinElmer FT 1720-X spectrometer Full experimental details for all compounds are given in the Supporting Information, representative compounds are reported below. Labeling scheme for BAr^f_4, pyridine, and 2,2′-bipyridine ligands:



Crystal-structure determination for 3a, 3e, 5b, and 7b

Data collection was performed with an Oxford Diffraction Xcalibur Nova single-crystal diffractometer, by using $Cu_{K\alpha}$ radiation (λ = 1.5418 Å). Images were collected at a 65 mm fixed crystal–detector distance, by using the oscillation method, with 1° oscillation and variable exposure time per image (4–16 s). The data-collection strategy was calculated with the program CrysAlis^{Pro} CCD.[38] Data reduction and cell refinement was performed with the program CrysAlis^{Pro} RED.[38] An empirical absorption correction was applied by using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis^{Pro} RED.[38] In all cases, the structures were solved with SIR92[39] and finally refined by the full-matrix least-squares method based on F^2 by SHELXL.[40] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed riding on their parent atoms with isotropic displacement parameters set to ×1.2 the U_{eq} of the atoms to which they are attached (× 1.5 for methyl groups). Molecular graphics were constructed with ORTEP3.[41] CCDC-981228 (**5b**), 981229 (**7b**), 981230 (**3b**), and 981231 (**3a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Complex 1c

$NaBAr^f_4$ (0.124 g, 0.140 mmol) and pyridine (0.011 mL, 0.140 mmol) were added to a solution of $[Re(CO)_3(N\text{-MesIm})_2(OTf)]$ (0.100 g, 0.126 mmol) in CH_2Cl_2 (20 mL) and the mixture was stirred for 2 h at rt. The solution was filtered from \the white solid via cannula and concentrated under reduced pressure to a volume of 5 mL. Hexane (15 mL) was added and caused the precipitation of a white solid, which was washed with hexane (3×15 mL) and dried under vacuum to give **1c** (181 mg, 88%). ^1H NMR (300 MHz, CD_2Cl_2): δ = 8.49 (m, 2H; H_o py), 8.01 (m, 1H; H_p py), 7.74 (br s, 8H; H_o BAr^f_4), 7.65 (m, 2H; NC*H*N *N*-MesIm), 7.58 (s, 4H; H_p BAr^f_4), 7.51 (m, 2H; H_m py), 7.14 (m, 2H; C*H* *N*-MesIm), 7.07 (m, 2H; C*H* *N*-MesIm), 7.03 (s, 4H; H_m *N*-MesIm), 2.34 (s, 6H; CH_3 *N*-MesIm), 1.97 ppm (s, 12H; CH_3 *N*-MesIm); ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 194.7 (2×*C*O), 194.4 (*C*O), 162.2 (q, J = 49.8 Hz; C_i BAr^f_4), 153.5, 141.6, 141.3, 140.6, 134.7, 131.6, 130.6, 129.9, 127.3, 124.0 (*N*-MesIm and py), 135.2 (C_o BAr^f_4), 129.3 (q, J = 31.5 Hz; C_m BAr^f_4), 125.0 (q, J = 272.3 Hz; CF_3), 117.9 (C_p BAr^f_4), 21.0 (2×CH_3 *N*-MesIm), 17.4 ppm (4×CH_3 *N*-MesIm); IR (THF): $\tilde{\nu}_{CO}$ = 2031, 1918 cm^{-1}; elemental analysis calcd (%) for $C_{64}H_{45}BF_{24}N_5O_3Re$: C 48.50, H 2.86, N 4.42; found: C 48.72, H 3.07, N 4.50.

Complex 2c

$KN(SiMe_3)_2$ (0.120 mL, 0.5 M in toluene, 0.060 mmol) was added to a solution of **1c** (0.080 g, 0.050 mmol) in THF (20 mL) previously cooled to −78 °C. The color of the solution changed immediately from colorless to bright yellow. The mixture was allowed to reach rt, then AgOTf (0.027 g, 0.105 mmol) was added and the mixture was stirred for 5 min. The solvent was evaporated to dryness under reduced pressure, diethyl ether (25 mL) was added, and the suspension was decanted for 12 h at −20 °C. The crude reaction mixture was filtered via canula and the solvent was evaporated under vacuum. The residue was extracted with CH_2Cl_2 (20 mL), filtered through silica gel, the solvent was evaporated under reduced pressure, and the residue was washed with hexane (3×15 mL). Compound **2c** (55 mg, 69%) was obtained as a yellow oil. ^1H NMR (300 MHz, CD_2Cl_2): δ = 9.11 (m, 1H; *py*imMes), 7.75 (m, 1H; *py*imMes), 7.83 (s, 1H; C*H* py*imMes*), 7.77 (br s, 8H; H_o BAr^f_4), 7.59 (br s, 4H; H_p BAr^f_4), 7.51 (m, 2H; NC*H*N *N*-MesIm and *py*imMes), 7.30 (s, 1H; C*H* py*imMes*), 7.19 (s, 1H; H_m py*imMes*), 7.11 (s, 1H; H_m py*imMes*), 6.99 (s, 1H; H_m *N*-MesIm), 6.95 (s, 1H; H_m *N*-MesIm), 6.88 (s, 1H; C*H* *N*-MesIm), 6.73 (s, 1H; *py*imMes), 6.60 (s, 1H; C*H* *N*-MesIm), 2.40 (s, 3H; CH_3 py*imMes*), 2.30 (s, 3H; CH_3 *N*-MesIm), 2.01 (s, 3H; CH_3 py*imMes*), 1.68 (s, 3H; CH_3 py*imMes*), 1.85 (s, 3H; CH_3 *N*-MesIm), 1.63 ppm (s, 3H; CH_3 *N*-MesIm); ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 196.3, 195.3, 191.3 (*C*O), 162.2 (q, J = 49.8 Hz; C_i BAr^f_4), 154.5, 147.6, 147.0, 142.8, 141.5, 141.2, 140.4, 134.9, 134.8, 134.6, 134.1, 131.9, 131.5, 131.2, 130.9, 130.8, 129.8, 128.9, 127.8, 127.7, 123.2, 121.6 (*N*-MesIm and pyimMes), 135.2 (C_o BAr^f_4), 129.3 (q, J = 31.5 Hz; C_m BAr^f_4), 125.0 (q, J = 272.9 Hz; CF_3), 117.9 (C_p BAr^f_4), 21.2, 21.0, 17.4, 17.3 (CH_3 *N*-MesIm and py*imMes*), 17.0 ppm (2×CH_3 *N*-MesIm); IR (THF): $\tilde{\nu}_{CO}$ = 2031, 1922 cm^{-1}; elemental analysis calcd (%) for $C_{64}H_{43}BF_{24}N_5O_3Re$: C 48.56, H 2.74, N 4.42; found: C 48.78, H 2.89, N 4.17.

Complex 2a*

N-Methylimidazole (0.015 mL, 0.188 mmol) was added to a solution of [Re (CO)$_3$(OTf)(Pyim-Me)] (0.100 g, 0.173 mmol)[22] in CH_2Cl_2 (20 mL) and the mixture was stirred overnight. The resultant solution was concentrated to a volume of 5 mL. Hexane (15 mL) was added and the precipitate was washed with hexane (2×15 mL) to give **2a*** (89 mg, 78%) as a yellow solid. ^1H NMR (300 MHz, CD_2Cl_2): δ = 9.03 (m, 1H; *py*imMe), 8.25 (m, 2H; *py*imMe), 7.56 (m, 1H; *py*imMe), 7.44 (s, 1H; C*H* py*imMe*), 7.36 (s, 1H; NC*H*N *N*-MeIm), 7.18 (s, 1H; C*H* py*imMe*), 6.82 (m, 1H; C*H* *N*-MeIm), 6.75 (m, 1H;

C*H* *N*-MeIm), 4.27 (s, 3H; C*H*$_3$ py*imMe*), 3.56 ppm (s, 3H; C*H*$_3$ N-MeIm); ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 197.1, 196.0, 192.2 (*C*O), 154.4, 148.4, 147.5, 141.3, 139.8, 130.5, 130.1, 129.1, 127.0, 123.7, 122.7 (pyimMe and *N*-MeIm), 37.7, 34.9 ppm (*C*H$_3$ py*imMe* and *N*-MeIm); IR (CH_2Cl_2): $\tilde{\nu}_{CO}$ = 2029, 1917 cm^{-1}; elemental analysis calcd (%) for $C_{17}H_{15}F_3N_5O_6ReS$: C 30.91, H 2.29, N 10.60; found: C 30.80, H 2.15, N 10.69.

Complex 2e

Complex **2e** was prepared as described above for **2a*** from *N*-MesIm (0.035 g, 0.188 mmol) and [Re (CO)$_3$(OTf)(Pyim-Me)] (0.100 g, 0.173 mmol). Complex **2e** (112 mg, 85%) was obtained as a yellow solid. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.08 (m, 1H; *py*imMe), 8.35 (m, 2H; *py*imMe), 7.61 (m, 1H; *py*imMe), 7.48 (m, 1H; NC*H*N *N*-MesIm), 7.39 (s, 1H; C*H* py*imMe*), 7.32 (s, 1H; C*H* py*imMe*), 6.97 (s, 2H; *N*-MesIm), 6.83 (m, 1H; C*H* *N*-MesIm), 6.64 (m, 1H; C*H* *N*-MesIm), 4.27 (s, 3H; C*H*$_3$ py*imMe*), 2.36 (s, 3H; C*H*$_3$, *N*-MeIm), 1.77 (s, 3H, C*H*$_3$ *N*-MesIm), 1.74 ppm (s, 3H; C*H*$_3$ *N*-MesIm); ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 196.9, 195.8, 191.8 (*C*O), 154.3, 148.4, 147.3, 141.9, 140.8, 140.0, 134.9, 131.7, 130.3, 129.7, 129.5, 129.2, 127.2, 123.8, 123.2 (pyimMe and *N*-MesIm), 37.9 (*C*H$_3$ py*imMe*), 21.1 (*C*H$_3$ *N*-MesIm), 17.1 ppm (2×*C*H$_3$ *N*-MesIm); IR (CH_2Cl_2): $\tilde{\nu}_{CO}$ = 2032, 1927, 1917 cm^{-1}; elemental analysis calcd (%) for $C_{25}H_{23}F_3N_5O_6ReS$: C 39.27, H 3.03, N 9.16; found: C 39.51, H 3.22, N 9.37.

Complex 3a

$KN(SiMe_3)_2$ (0.260 mL, 0.5 M in toluene, 0.130 mmol) was added to a solution of **2a*** (0.080 g, 0.121 mmol) in THF (20 mL) previously cooled to −78 °C; an immediate color change of the solution from yellow to red was observed. The solvent was evaporated to dryness, the residue extracted with CH_2Cl_2 (20 mL), and HOTf (12 μL, 0.136 mmol) was added. After 15 min stirring at rt, the reaction mixture was filtered via canula and the resultant orange solution was concentrated under reduced pressure to a volume of 5 mL. Addition of hexane (20 mL) caused precipitation. The precipitate was washed with hexane (2×15 mL) to give **3a** (46 mg, 58%) as a dark-yellow solid. Slow diffusion of hexane (25 mL) into a concentrated solution of **3a** in CH_2Cl_2 at −20 °C afforded yellow crystals suitable for X-ray structure determination. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.33, 7.09, 7.03, and 6.90 (m, 1H each; C*H* py*imMe* and *N*-MeIm), 6.67 (m, 3H; *py*imMe), 5.42 (m, 1H; *py*imMe), 3.85 and 3.71 ppm (s, 3H each; C*H*$_3$ py*imMe* and *N*-MeIm); ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 195.4, 194.7, 194.5 (*C*O), 147.6, 146.9, 130.1, 128.7, 128.3, 126.4, 126.1, 125.6, 124.7, 121.1 (pyimMe and *N*-MeIm), 56.4 (C_{sp3} pyimMe), 35.8, 35.1 ppm (*C*H$_3$ py*imMe* and *N*-MeIm); IR (CH_2Cl_2): $\tilde{\nu}_{CO}$ = 2032, 1925, 1915 cm^{-1}; elemental analysis calcd (%) for $C_{17}H_{15}F_3N_5O_6ReS$: C 30.91, H 2.29, N 10.60; found: C 31.14, H 2.45, N 10.86.

Complex 3e

Compound **3e** was prepared as described above for **3a**, from $KN(SiMe_3)_2$ (0.240 mL, 0.5 M in toluene, 0.120 mmol), **2e** (0.080 g, 0.105 mmol), and HOTf (10 μL, 0.113 mmol). Slow diffusion of hexane (25 mL) into a concentrated solution of **3e** in CH_2Cl_2 at −20 °C afforded crystals of **3e** (52 mg, 65%) suitable for X-ray structure determination. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.98 (br s, 1H; N*H*), 7.38, 7.26, 7.14, and 6.95 (m, 1H each; C*H* py*imMe* and *N*-MesIm), 7.09 (s, 1H; *N*-MesIm), 7.01 (s, 1H; *N*-MesIm), 6.54 (m, 1H; *py*imMe), 6.19 (m, 1H; *py*imMe), 5.25 (m, 2H; *py*imMe), 3.86 (s, 3H; C*H*$_3$ pyimMe), 2.40 (s, 3H; C*H*$_3$, *N*-MesIm), 1.98 (s, 3H; C*H*$_3$, *N*-MesIm), 1.80 ppm (s, 3H; C*H*$_3$, *N*-MesIm); ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 195.7, 195.0, 194.6 (*C*O), 149.1, 148.2, 141.5, 135.2, 131.1, 130.6, 130.3, 129.9, 129.8, 128.7, 126.8, 125.7, 124.3, 124.0, 121.0 (pyimMe and *N*-MesIm), 56.8 (C_{sp3} pyimMe), 36.2 (*C*H$_3$ py*imMe*), 21.2 (*C*H$_3$ *N*-MesIm), 18.0, 17.1 ppm (*C*H$_3$ *N*-MesIm); IR (CH_2Cl_2): $\tilde{\nu}_{CO}$ = 2032, 1923 cm^{-1}; elemental analysis calcd (%) for $C_{25}H_{23}F_3N_5O_6ReS$: C 39.27, H 3.03, N 9.16; found: C 39.11, H 3.30, N 9.47.

Compound 4a

A mixture of [$ReBr(CO)_5$] (0.069 g, 0.170 mmol) and DMAP (0.044 g, 0.357 mmol) were heated at reflux in toluene for 2 h. The solvent was evaporated to dryness, the white residue was dissolved in CH_2Cl_2 (20 mL), AgOTf (0.053 g, 0.206 mmol) was added, and the mixture was stirred in the dark for 2 h. The solution was filtered to separate the white solid (AgBr), the filtrate was evaporated to dryness, and the residue was washed with hexane (2×15 mL) and diethylether (2×15 mL). [$Re(CO)_3(dmap)_2(OTf)$] was obtained as a white microcrystalline solid. $NaBAr^f_4$ (0.147 g, 0.166 mmol) and *N*-MeIm (0.013 mL, 0.166 mmol) were added to a solution of [$Re(CO)_3(dmap)_2(OTf)$] (0.100 g, 0.151 mmol) in CH_2Cl_2 (25 mL) and the reaction mixture was stirred for 3 h at rt. The solution was filtered via canula and concentrated under reduced pressure to a volume of 5 mL. Hexane (15 mL) was added and caused a white solid to precipitate. The precipitate was separated, washed with hexane (2×15 mL), and dried under vacuum to give **4a** (198 mg, 90%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.87 (d, *J* = 5.9 Hz, 4H; dmap), 7.80 (br s, 8H; H$_o$ BAr^f_4), 7.62 (br s, 4H; H$_p$ BAr^f_4), 7.60 (s, 1H; NC*H*N *N*-MeIm), 6.98 (m, 1H; C*H* *N*-MeIm), 6.90 (m, 1H; C*H* *N*-MeIm), 6.49 (d, *J* = 5.9 Hz, 2H; dmap), 3.69 (s, 3H; C*H*$_3$ *N*-MeIm), 3.01 ppm (s, 12H; C*H*$_3$ dmap); ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 195.8 (br s; *C*O), 162.2 (q, *J* = 50.4 Hz; C$_i$ BAr^f_4), 155.2 (C$_p$ dmap), 152.2 (C$_o$ dmap), 141.2 (NCHN, *N*-MeIm), 135.2 (C$_o$ BAr^f_4), 130.5 (*C*H, *N*-MeIm), 129.3 (q, *J* = 31.0 Hz; C$_m$ BAr^f_4), 125.0 (q, *J* = 272.0 Hz; CF_3), 122.9 (*C*H, *N*-MeIm), 117.9 (C$_p$ BAr^f_4), 108.5 (C$_m$ dmap), 39.2 (4×*C*H$_3$ dmap), 34.9 ppm (*C*H$_3$ *N*-MeIm); IR (THF): $\tilde{\nu}_{CO}$ = 2024, 1909 cm^{-1}; elemental analysis calcd (%) for $C_{53}H_{38}BF_{24}N_6O_3Re$: C 43.60, H 2.62, N 5.76; found: C 43.81, H 2.69, N 5.61.

Complex 5a

Compound **5a** was prepared as described above for **2a**, from **4a** (0.088 g, 0.060 mmol), $KN(SiMe_3)_2$ (0.150 mL, 0.5 M solution in toluene, 0.075 mmol), and AgOTf (0.032 g, 0.124 mmol). Compound **5a** (35 mg, 40%) was obtained as a yellow microcrystalline solid. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.55 (d, *J* = 6.9 Hz, 1H; *dmap*imMe), 7.78 (br s, 8H; H$_o$ BAr^f_4), 7.67 (d, *J* = 6.1 Hz, 2H; dmap), 7.60 (br s, 4H; H$_p$ BAr^f_4), 7.46 (d, *J* = 1.2 Hz, 1H; C*H* dmap*imMe*), 7.11 (d, *J* = 1.2 Hz, 1H; C*H* dmap*imMe*), 6.90 (d, *J* = 2.6 Hz, 1H; *dmap*imMe), 6.64 (dd, *J* = 6.9, 2.6 Hz, 1H; *dmap*imMe), 6.29 (d, *J* = 6.1 Hz, 2H; dmap), 4.00 (s, 3H; C*H*$_3$ dmap*imMe*), 3.10 and 2.87 ppm (s, 6H each; C*H*$_3$ *dmap*imMe and dmap); ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 197.6, 196.5, 192.9 (*C*O), 162.2 (q, *J* = 50.4 Hz; C$_i$ BAr^f_4), 155.4, 154.8, 153.0, 150.7, 149.2, 147.0, 129.7, 128.0, 108.5, 108.1, 104.6 (dmap and dmapimMe), 135.2 (C$_o$ BAr^f_4), 129.3 (q, *J* = 31.4 Hz; C$_m$ BAr^f_4), 125.0 (q, *J* = 272.5 Hz; CF_3), 117.9 (C$_p$ BAr^f_4), 39.8, 39.1 (2×*C*H$_3$; *dmap*imMe and dmap), 37.1 ppm (*C*H$_3$ dmap*imMe*); IR (THF): $\tilde{\nu}_{CO}$ = 2024, 1913 cm^{-1}); elemental analysis calcd (%) for $C_{53}H_{36}BF_{24}N_6O_3Re$: C 43.66, H 2.49, N 5.76; found: C 43.97, H 2.62, N 5.45.

Complex 6a

The synthesis of compound **6a** is an adaptation of those previously reported.[32,42] A mixture of $[Re(CO)_3(dmso)_3]OTf$ (0.200 g, 0.306 mmol) and pyridine (0.74 mL, 9.18 mmol) was heated at reflux in acetone (40 mL) for 30 h. The solvent was evaporated to dryness and the sticky residue was washed with Et_2O (3×20 mL) and dried under vacuum to afford compound **6a** (149 mg, 73%) as a white solid. ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 8.53$ (m, 6H; H_o py), 8.10 (m, 3H; H_p py), 7.63 ppm (m, 6H; H_m py); ^{13}C NMR (300 MHz, CD_2Cl_2): $\delta = 194.3$ (CO), 153.7 (C_o py), 140.9 (C_p py), 128.0 ppm (C_m py); IR (THF): $\tilde{\nu}_{CO} = 2033$, 1924 cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{15}F_3N_3O_6ReS$: C 34.76, H 2.30, N 6.40; found: C 34.55, H 2.24, N 6.12.

Compound 7a

$KN(SiMe_3)_2$ (0.340 mL, 0.5 M solution in toluene, 0.170 mmol) was added to a solution of **6a** (0.100 g, 0.152 mmol) in THF (20 mL) at −78 °C. The mixture was allowed to stir for 15 min, then the solvent was evaporated to dryness under reduced pressure. A solution of HOTf (15 μL, 0.170 mmol) in toluene (20 mL) was added to the residue and the resultant yellow solution was filtered via canula. The solvent was evaporated under reduced pressure to a volume of 3 mL. Addition of hexane (15 mL) caused the precipitation of **7a** as a yellow solid, determined by comparison of the spectral data with the literature data.[33]

Compound 8a

A mixture of $[Re(CO)_3(dmap)_2(OTf)]$ (0.105 g, 0.158 mmol), prepared as described above for **4a**, $NaBAr^f_4$ (0.151 g, 0.170 mmol), and pyridine (14 μL, 0.173 mmol) in CH_2Cl_2 (20 mL) was stirred for 3 h at rt. The colorless solution was separated from the white solid (NaOTf) via canula and concentrated under reduced pressure to a volume of 4 mL. Addition of hexane (20 mL) caused the precipitation of a white solid, which was washed with hexane (2×15 mL) to give **8a** (399 mg, 74%). ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 8.47$ (m, 2H; H_o py), 7.97 (m, 1H; H_p py), 7.83 (d, $J = 7.4$ Hz, 4H; H_o dmap), 7.74 (br s, 8H; H_o BAr^f_4), 7.57 (br s, 4H; H_p BAr^f_4), 7.47 (m, 2H; H_m py), 6.50 (d, $J = 7.4$ Hz, 4H; H_m dmap), 3.03 ppm (s, 12H; CH_3 dmap); ^{13}C NMR (300 MHz, CD_2Cl_2): $\delta = 195.4$ (br s; CO), 162.1 (q, $J = 52.8$ Hz; C_i BAr^f_4), 155.2 (C_p dmap), 153.4 (C_o py), 152.0 (C_o dmap), 140.2 (C_p py), 135.2 (C_o BAr^f_4), 129.3 (q, $J = 29.9$ Hz; C_m BAr^f_4), 127.2 (C_m py), 124.9 (q, $J = 272.7$ Hz; CF_3), 117.8 (C_p BAr^f_4), 108.8 (C_m dmap), 39.4 ppm (4×CH_3 dmap); IR (THF): $\tilde{\nu}_{CO} = 2028$, 1916 cm^{-1}; elemental analysis calcd (%) for $C_{54}H_{37}BF_{24}N_5O_3Re$: C 44.52, H 2.56, N 4.81; found: C 44.79, H 2.50, N 5.11.

Compound 9a

$KN(SiMe_3)_2$ (0.150 mL, 0.5 M solution in toluene, 0.075 mmol) was added to a solution of **8a** (0.100 g, 0.069 mmol) in THF (20 mL) that was previously cooled to −78 °C. The color of the solution changed immediately form colorless to bright yellow. The mixture was allowed to reach room temperature and stirred for 15 min, then AgOTf (38 mg, 0.150 mmol) was added. The solvent was evaporated to dryness, Et_2O (25 mL) was added, and the reaction mixture was allowed to settle down for 12 h at −20 °C. The yellow solution was filtered via canula and the solvent evaporated under vacuum. The residue was extracted with CH_2Cl_2 and filtered through silica gel. The filtrate was evaporated to dryness to give a yellow oil, which was washed with hexane (2×15 mL) to give **9a** (54 mg, 53%). ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 9.10$ (m, 1H; H_6 bipy-4-NMe_2), 8.54 (d, $J = 6.7$ Hz, 1H; H_6 bipy-4-NMe_2), 8.08 (m, 2H H_3 and H_4 bipy-4-NMe_2), 7.74 (br s, 8H; H_o BAr^f_4), 7.61 (m, 1H; H_5 bipy-4-NMe_2), 7.55 (m, 6H; H_p BAr^f_4 and H_o dmap), 7.19 (d, $J = 2.6$ Hz, 1H; H_3 bipy-4-NMe_2), 6.73 (dd, $J = 6.7$, 2.6 Hz, 1H; H_5 bipy-4-NMe_2), 6.25 (d, $J = 6.2$ Hz, 2H; H_m dmap), 3.15 (s, 6H; CH_3 bipy-4-NMe_2), 2.87 ppm (s, 6H; CH_3 bipy-4-NMe_2); ^{13}C NMR (300 MHz, CD_2Cl_2): $\delta =$ 197.2 (2×CO), 193.0 (CO), 162.1 (q, $J = 52.8$ Hz, C_i BAr^f_4), 157.3, 155.6, 155.1, 154.9, 153.4, 153.2, 152.1, 152.0, 150.4 (dmap and bipy-4-NMe_2), 135.2 (C_o BAr^f_4), 129.3 (q, $J = 29.9$ Hz; C_m BAr^f_4), 128.0, 127.2 (dmap and bipy-4-NMe_2), 124.9 (q, $J = 272.2$ Hz; CF_3), 117.8 (C_p BAr^f_4), 123.4, 110.1, 108.8, 108.3, 39.9 (dmap and bipy-4-NMe_2), 39.2 ppm (CH_3 dmap and bipy-4-NMe_2); IR (THF): $\tilde{\nu}_{CO} = 2026$, 1916 cm^{-1}; elemental analysis calcd (%) for $C_{54}H_{35}BF_{24}N_5O_3Re$: C 44.58, H 2.42, N 4.81; found: C 44.67, H 2.51, N 4.69.

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[18] Selected crystallographic data for **3a**: $C_{34}H_{30}F_6N_{10}O_{12}Re_2S_2$; M = 1321.20; monoclinic; $P21$; a = 11.447(5) Å; b = 16.617(5) Å; c = 11.665(5) Å; α = 90°; β = 105.613(5)°; γ = 90°; 123.0(1) K; V = 2137.0(15) Å^3; Z = 2; 8384 reflections measured; 5665 independent reflns; R_{int} = 0.0380; R_1 = 0.0356; wR_2 = 0.0858 (all data). The results of the structural determination showed the presence of two independent molecules of **3a** in the asymmetric unit, the cation of one molecule is represented in Figure 2a.

[19] Selected crystallographic data for **3b**: $C_{25}H_{23}F_3N_5O_6ReS$; M_r = 764.76; monoclinic; $P21/c$; a = 14.9383(2) Å; b = 8.9059(1) Å; c = 20.7025(2) Å; α = 90°; β = 100.451(1)°; γ = 90°; 100.0(1) K; V = 2708.55(5) Å^3; Z = 4; 29469 reflections measured, 5433 independent reflns; R_{int} = 0.0229; R_1 = 0.0511; wR_2 = 0.0531 (all data).

[20] This reaction pattern is reminiscent of that found for the deprotonation of $[Re(CO)_3(N\text{-}N)(N\text{-}RIm)]OTf$ (N-N = bipy, phenanthroline) complexes, which afforded the C–C coupling and dearomatized products; see ref. [10c].

[21] Notably, compound **2c** is not easy to prepare by an alternative method because the pyridyl-mesitylimidazole ligand is not known.

[22] For further experimental details see the Supporting Information.

[23] Selected crystallographic data for **5b**: $C_{61}H_{44}BF_{24}N_5O_3Re$; M_r = 1562.03; monoclinic; $P21/c$; a = 19.1379(2) Å; b = 18.1429(2) Å; c = 20.2252(2) Å; α = 90°; β = 114.260(1)°; γ = 90°; 149.9 K; V = 6402.4(1) Å^3; Z = 4; 35956 reflections measured; 12603 independent reflns; R_{int} = 0.0453; R_1 = 0.0535; wR_2 = 0.1544 (all data).

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