Review

$Re^{I}(CO)_3$ complexes with diimine ligands synthesized *in situ*

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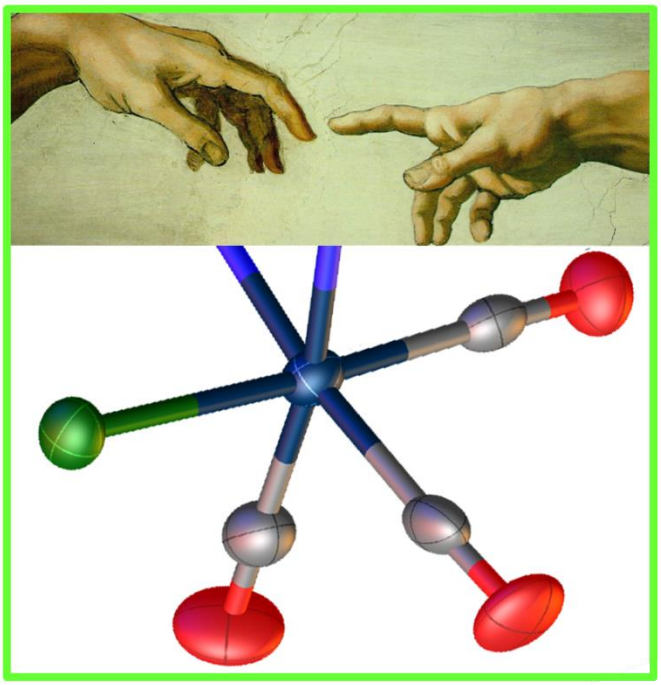
GRAPHICAL ABSTRACT



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ABSTRACT

This work covers the coupling reactions of monodentate ligands coordinated to the "$Re^{I}(CO)_3$" moiety to afford *in situ* new bidentate diimine ligands. Similar reactions leading to tridentate ligands are also included. The reactions reviewed present evident advantages respect to the usual synthetic methods of these ligands. Besides, choosing the appropriate substituents allows an easy tuning of the properties of the final complexes. Following an approximate chronological order, the formation of bidentate ligands by C-N coupling from a coordinated carbonyl group, from diiminoisoindoline, and the formation of amidino ligands from nitriles are reviewed first. This is followed by the formation of bidentate ligands by C-C coupling, and finally by the formation of tridentate ligands, either by C-C coupling, by B-N coupling, or by using "click" reactions.

Keywords

Coupling reactions; diimines; *in situ* synthesis; rhenium; tridentate ligands.

Contents

1. Introduction

2. *N*,*N*-chelating ligands obtained by C-N coupling

    2.1. Diimines from a *O*-coordinated carbonyl group

    2.2. *N*,*N*-chelating ligands from diiminoisoindoline

    2.3. Amidino ligands from nitriles

3. Diimines by C-C coupling

4. Formation of tridentate ligands

    4.1. By C-C coupling

    4.2. By B-N coupling

    4.3. "Click" chemistry and beyond

5. Conclusions and perspectives

References

1. Introduction

Reports on the photophysical properties of complexes of the type *fac*-[ReX(CO)$_3$(diimine)] (X is a halide or pseudo-halide in neutral complexes, or a neutral ligand in cationic complexes) started more than 40 years ago [1-3]. Since then, they have been profusely studied, mainly due to their luminescence, which is associated to their long-lived triplet metal-to-ligand charge transfer (^{3}MLCT) excited state [4-11]. These properties have allowed the development of many and diverse applications for these complexes [12], such as their photocatalytic activity for the reduction of CO_2 [13-15], their behavior as biomolecular agents [16-22], as molecular sensors or photoswitches [23-26], or as light-emitting devices [27].

Their photophysical properties may be adjusted by making changes at the diimine ligand, at the "sixth" ligand "X", or varying the solvent [23,28-30]. A wide diversity of diimine ligands, usually derived from bipy (2,2'-bipyridyl) or phen (1,10-phenantroline), may be found in the literature. However, the synthetic methods to obtain them are often difficult and/or tiresome, depending on the substituents required to reach the desired properties. Thus, one of the remaining challenges of the field would be finding alternatives for obtaining new *N,N*-chelating ligands by straightforward and accessible paths. The coupling of two monodentate ligands to afford a chelating diimine ligand is one of the immediate solutions for this problem. This process should be favored by the coordination of the monodentate ligands to a Lewis acidic metal center, which would enhance the electrophilic character of the donors designed to be coupled. In fact, important achievements have been recently reported on transition metal-mediated oxidative cross-coupling of heteroarenes to obtain heterobiaryls [31,32].

When the metallic fragment is a "$Re^{I}(CO)_3$" moiety, the photophysical or biomedical properties of the final complex may be tuned by choosing the monodentate ligands with the appropriate substituents. A main advantage of this tricarbonyl fragment is its rigid facial geometry, which is a consequence of the nonlability of the carbonyl units in the presence of ligands without significant back-bonding [33].

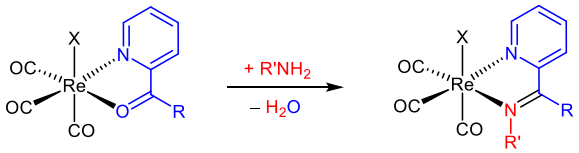
This review covers the different coupling processes leading to diimine (or tridentate ligands containing a diimine unit) so far reported in the literature.

2. *N,N*-chelating ligands obtained by C-N coupling

2.1. Diimines from a O-coordinated carbonyl group

The first report of a C-N coupling reaction mediated by the "$Re^{I}(CO)_3$" fragment was described by the group of Alberto in 2003 [34]. The reaction of aliphatic or aromatic amines with coordinated 2-acetyl-pyridine or 2-pyridylcarboxaldehyde (pyca) afforded the corresponding Schiff

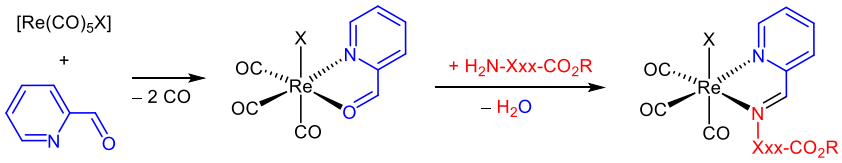
bases (Scheme 1). The process is favored by the coordination of the carbonyl group. The reactions are much faster than the similar reactions when the aldehyde or ketone are free, and occur exclusively in protic solvents or in water. Aprotic coordinating solvents such as MeCN are not suitable for the reaction, since deprotonation of coordinated 2-acetyl-pyridine yields a coordinated enolate, precluding the formation of the imine. Similar deprotonation at the pyca ligand gives a semiacetal complex which does also react with amines. A kinetic study shows that the reaction is several orders of magnitude faster than the similar reactions between the amine and free aldehyde or free ketone. Therefore, this method presents considerable advantages over traditional procedures where the iminopyridine ligand must be firstly synthesized, and then coordinated to the metal. The authors foresaw a wide applicability for this reaction, since the amine may be functionalized with biomolecules, what would allow direct labeling without deactivation of the metal complex. This work may be considered as seminal, as it was later applied and extended by further research carried out by the groups of Herrick and Miguel.



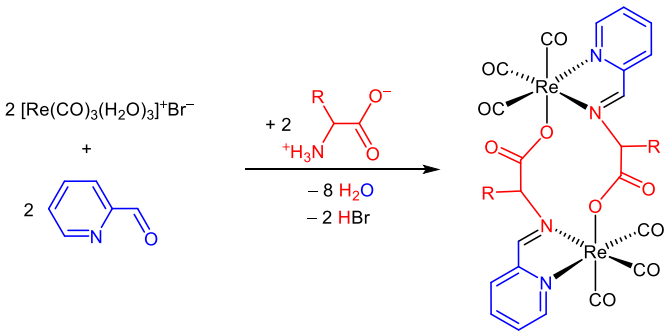
Scheme 1. Synthesis of iminopyridine complexes (X = Br; R = H, Me; R' = ^{i}Pr, Ph) [34]; (X = Cl, Br; R = H; R' = sulfanylamide or 4-aminofluorescein) [37]; (X = Cl, Br; R = H; R' = NH_2) [39].

As predicted, the use of biomolecules in this reaction was immediate, and Herrick's group described only one year later the one-pot reaction of $[Re(CO)_5Cl]$ with different ester protected amino acids in the presence of pyca, what yielded conjugated diimine ligands with pendant ester groups (Scheme 2) [35]. Their electronic spectra were the expected for complexes of the *fac*-$[ReX(CO)_3(diimine)]$ type, and photophysical experiments showed that *fac*-$[Re(CO)_3Cl(pyca\text{-}\beta\text{-}Ala\text{-}OEt)]$ is luminescent in different organic solvents in air at room temperature. The same group reported later the one-pot reaction between the cationic precursor *fac*-$[Re(CO)_3(H_2O)_3]^+$, pyca, and

amino acids such as glycine or alanine to form the corresponding diimine chelating complexes, this time as bridging carboxylate dimers (Scheme 3) [36]. Other biomedically interesting amines used to coordinate the corresponding imines to the "$Re^{I}(CO)_3$" moiety were sulfanylamide or 4-aminofluorescein (Scheme 1) [37].



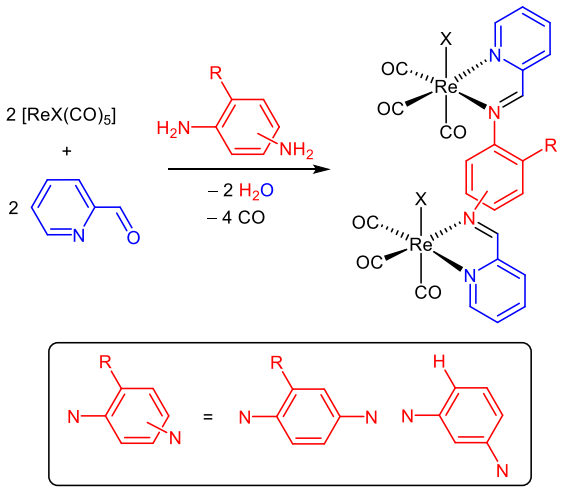
Scheme 2. Synthesis of iminopyridine complexes containing ester protected amino acids (X = Cl, H_2N-Xxx-CO_2R = H-L-Ala-OEt, H-β-Ala-OEt, H-L-Val-OMe, H-GABA-OMe (GABA = γ-aminobutyric acid), H-L-Asp(OMe)-OMe, H-L-Met-OMe) [35]; amino acids or peptides (X = Br; Xxx = $(CH_2)_2$, $(CH_2)_3$, *m*-C_6H_4, GlyGly, GlyVal, GlyGlyGly; R = H) [42,43].



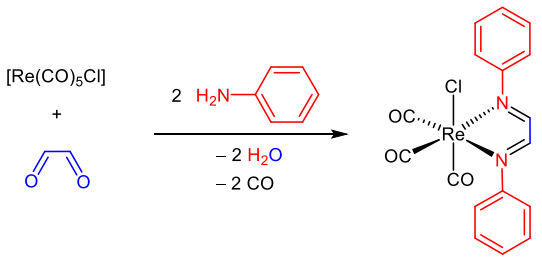
Scheme 3. One-pot reaction between *fac*-$[Re(CO)_3(H_2O)_3]^+$, pyca, and glycine or alanine [36].

In bimetallic complexes the MLCT interaction may be altered by intramolecular electron transfer, which is affected by the type, size, aromaticity, and conjugation of the bridging ligand. The coupling between the "$Re^{I}(CO)_3$" fragments bridged by phenylene groups depends on the substitution position in the ring. Bimetallic complexes were thus obtained by one-pot reaction of $[Re(CO)_5X]$ (X = Cl, Br), with pyca, and *o*-, *m*-, or *p*-phenylenediamine. A sulfonate derivative was also synthesized in order to improve solubility (Scheme 4) [38]. UV/Vis spectroscopy and cyclic voltammetry of the phenylenediimine bridged compounds revealed coupling between the metal

atoms. This work also includes the synthesis of a monometallic complex with coordinated diazabutadiene, obtained from the mediated rhenium reaction of aniline and glyoxal (Scheme 5) [38]. This complex does not contain any pyridyl group, as opposite to those previously mentioned. So far, the last work of Herrick's group on this topic describes the synthesis of the diimine complex resulting from the reaction of *fac*-[$Re(CO)_3X(pyca)$] (X = Cl, Br) with hydrazine (Scheme 1, R' = NH_2) [39].



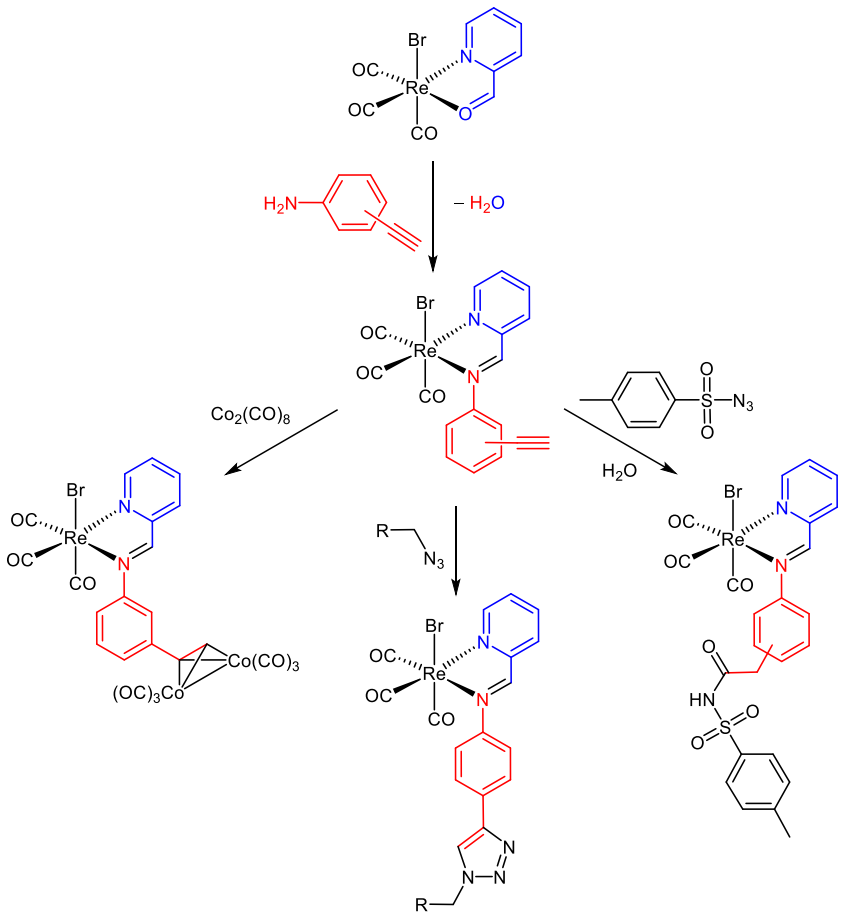
Scheme 4. Reaction of [$Re(CO)_5X$] with pyca, and *o*-, *m*-, or *p*-phenylenediamine to yield bimetallic complexes (X = Cl, Br; R = H, SO_3Na) [38].



Scheme 5. Reaction of [$Re(CO)_5Cl$] with aniline and glyoxal to yield a monometallic complex with coordinated diazabutadiene [38].

As indicated above, Miguel's group also expanded the work initiated by Alberto. In its first paper on this topic, the use of anilines functionalized with ethynyl groups in *meta* or *para* positions afforded the corresponding ethynyl functionalized iminopyridines (Scheme 6, above) [40]. These

complexes react with dicobalt octacarbonyl to afford the expected tetrahedrane species (Scheme 6, left). The reactivity of the ethynyl functionalized iminopyridine complexes towards organic azides to give the copper azide–alkyne (or "click") cycloaddition (CuAAC) was reported in a subsequent paper [41]. The Schiff condensation followed by CuAAC demonstrated to be completely compatible, since they were carried out either sequentially, either in a one-pot process using the three components (pyca complex, ethynylphenylamine, and azide). The result of the "click" reaction depends on the electronic features of the azide employed, since alkyl or benzyl azides lead to the expected triazole derivatives (Scheme 6, below center), whereas sulfonylazide affords the N-acylsulfonamide (Scheme 6, right).

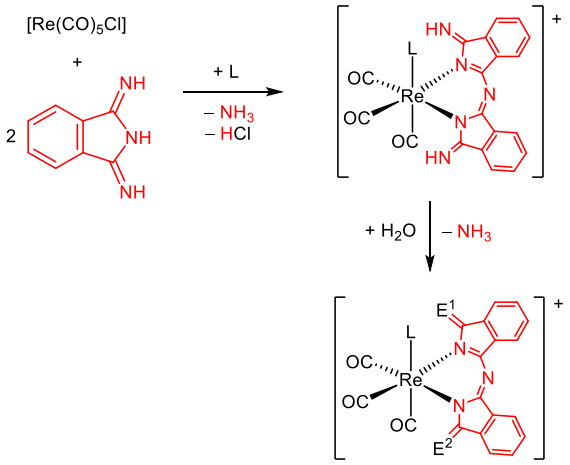


Scheme 6. Formation of coordinated 3-ethinyliminopyridine (above) and further reactions with $Co_2(CO)_8$ (left) [40], and "click" reaction with alkyl or benzyl azides (below center), and with p-toluenesulfonyl azide (right) [41].

Miguel's group also described the formation of iminopyridines containing amino acids (β-alanine, γ-aminobutyric acid, or 3-aminobenzoic acid) [42] or peptides (dipeptides Gly-Gly and Gly-L-Val, and the tripeptide Gly-Gly-Gly) [43] (Scheme 2). The crystal structures determinations revealed either the well-known centrosymmetric dimeric arrangement of H-bonding patterns in which the peptide chains show antiparallel arrangements with complementary disposition of the CO and NH bonds, either H-bonds with polar molecules of solvent.

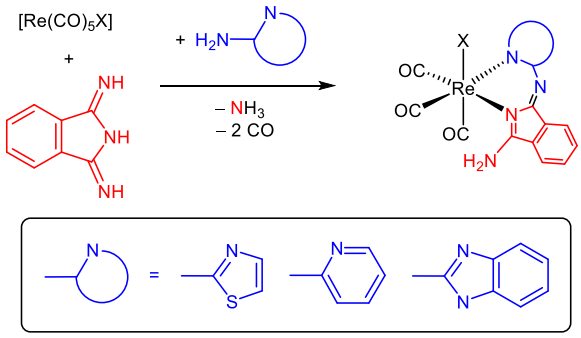
2.2. N,N-chelating ligands from diiminoisoindoline

The group of Herrick and Ziegler has recently extended its contribution to this field by describing the "$Re^{I}(CO)_3$" templated formation of *N,N*-chelating ligands starting from the phthalocyanine precursor diiminoisoindoline (DII). Thus, the condensation of two DII molecules with $[Re(CO)_5Cl]$ yielded a complex containing an aza(dibenzopyrro)methene (ADBM) chelating ligand (Scheme 7, above) [33], which can be considered as a half-phthalocyanine moiety. The reactions occurred in the presence of pyridine or N-methylimidazole, which coordinate to Re in the "sixth" position. The metal fragment seems to be responsible for the formation of the chelate, preventing the formation of the expected phthalocyanine. These complexes were obtained only when distilled and dried solvents were used, since the imino-terminated compounds were shown to be unstable to hydrolysis, what yielded bis(oxo)-, or mixed-imine/oxo chelates (Scheme 7, below). All the complexes show MLCT-type absorptions in their UV−visible spectra, and red shifts are detected when an oxo group replaces an imine group. The electrochemical studies show that the substitution of imine by oxo groups shifts the reduction potential to more negative values, what is in accordance with the destabilization of the LUMO occurring in these compounds.



Scheme 7. Condensation of two DII molecules with $[Re(CO)_5Cl]$ to yield the ADBM complex (above), and the result of their hydrolysis (below) (L = py, MeIm; E^1, E^2 = NH, O) [33].

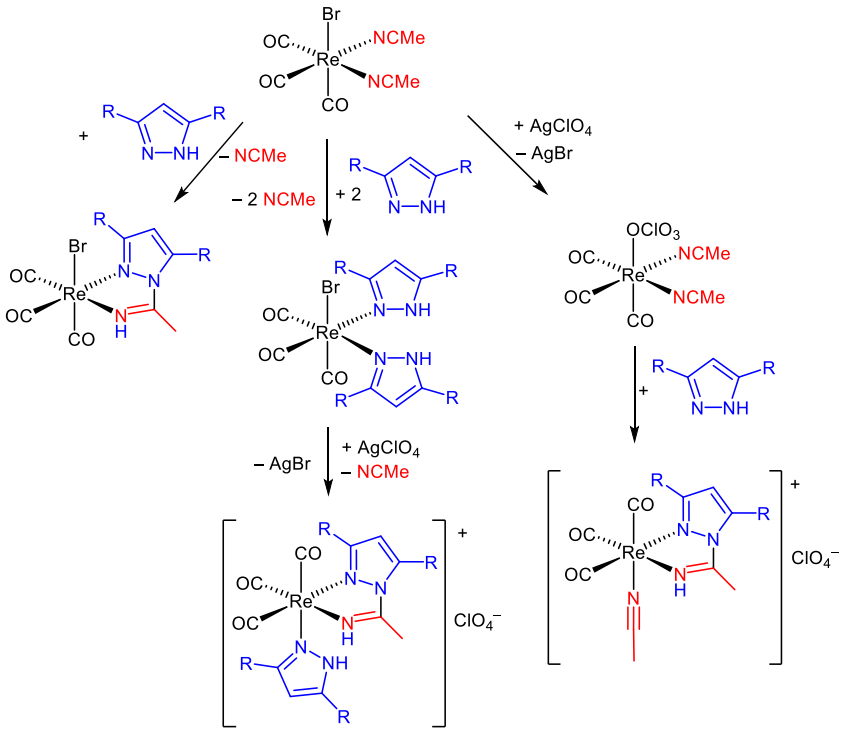
DII may also be used to coordinate half-hemiporphyrazine macrocycles. They were obtained when $[Re(CO)_5Cl]$ reacted with heterocycles with an amino group in α position (Scheme 8) [44]. As in the previous work, the "$Re^I(CO)_3$" fragment induces the formation of the chelate, and plays an essential role in preventing the otherwise expected macrocycle. MLCT-type absorptions are again observed in the UV−visible absorption spectra of the complexes obtained, and the experimental observations were supported by density functional theory methods (TD-DFT).



Scheme 8. Reaction of DII, $[Re(CO)_5Cl]$, with heterocycles containing an amino group in α position to give half-hemiporphyrazine macrocycles (X = Cl, Br) [44].

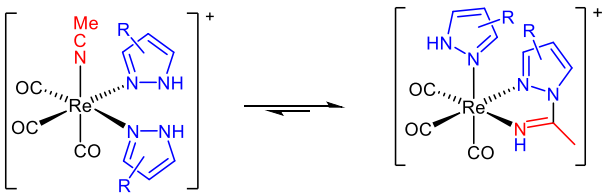
2.3. Amidino ligands from nitriles

Our group reported in 2006 the "$Re^{I}(CO)_3$" mediated coupling of acetonitrile and pyrazoles (pz*H = pzH, pyrazole, or dmpzH, 3,5-dimethylpyrazole) to give pyrazolylamidino ligands (Scheme 9) [45]. The processes yielded neutral (with Br as the "sixth" ligand, Scheme 9, left) or cationic complexes (with MeCN or pyrazoles as the "sixth" ligand, Scheme 9, right and center, respectively). The starting materials could be either acetonitrile (*fac*-$[Re(CO)_3X(NCMe)_2]$; X = Br, $OClO_3$) or pyrazole complexes (*fac*-$[Re(CO)_3Br(pz*H)_2]$). The work, done in collaboration with Pérez's group, included a study on the properties of the complexes as anion receptors. Thus, the cationic complex containing 3,5-dimethylpyrazolylamidino and dmpzH ligands showed a strong preference for chloride through a combination of electrostatic attraction and hydrogen bonding, and the structure of the supramolecular adduct showing chloride binding by the two N-H groups could be determined by X-ray diffraction.



Scheme 9. Coupling of MeCN and pyrazoles [R = H (pzH), Me (dmpzH)] to give neutral (left) or cationic (right and center) pyrazolylamidino complexes [45].

During this work, several neutral and cationic mixed acetonitrile−pyrazole complexes such as *fac*-[ReBr(CO)$_3$(NCMe)(dmpzH)] or *fac*-[Re(CO)$_3$(NCMe)(dmpzH)$_2$]$^+$ could be obtained. These were appropriate species to be used as starting materials for supporting or discarding an intramolecular mechanism for the formation of the pyrazolylamidino ligand. The study, carried out on cationic complexes where the coordinated nitrile is more activated and thus more electrophilic than in neutral complexes, supports that the coupling reaction occurs by a reversible intramolecular mechanism (Scheme 10) [46]. A systematic study on the reaction revealed that the coupling process is base-catalyzed, and more favored at moderate temperatures, and with the increasing acidity of the pyrazole.

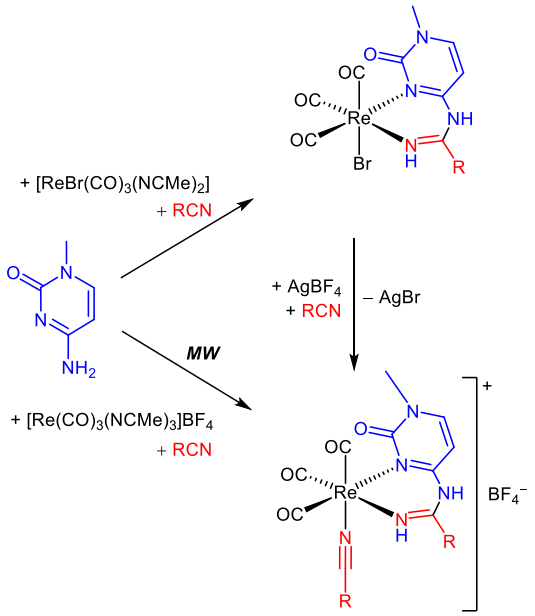


Scheme 10. Reversible intramolecular mechanism for the formation of pyrazolylamidino ligands (pz*H = pzH, dmpzH, indzH) [46].

These results opened a broad range of synthetic possibilities to obtain new pyrazolylamidino complexes, and thus new neutral and cationic "Re^I(CO)$_3$" derivatives from different pyrazoles and nitriles were next obtained. Photophysical, electrochemical and computational studies were carried out in order to determine the influence of both the substituents at the pyrazolylamidino and the "sixth" ligand [47]. As expected, all complexes exhibit phosphorescent decays from a prevalently ^{3}MLCT excited state, with long lifetimes. TD-DFT calculations were consistent with the experimental values.

Coordinated nitriles also can react with other amines, so this work was extended to nucleobases, what constitutes a new method to attach biomolecules to the "Re^I(CO)$_3$" moiety. Neutral or cationic complexes containing amidino chelating ligands were obtained from the

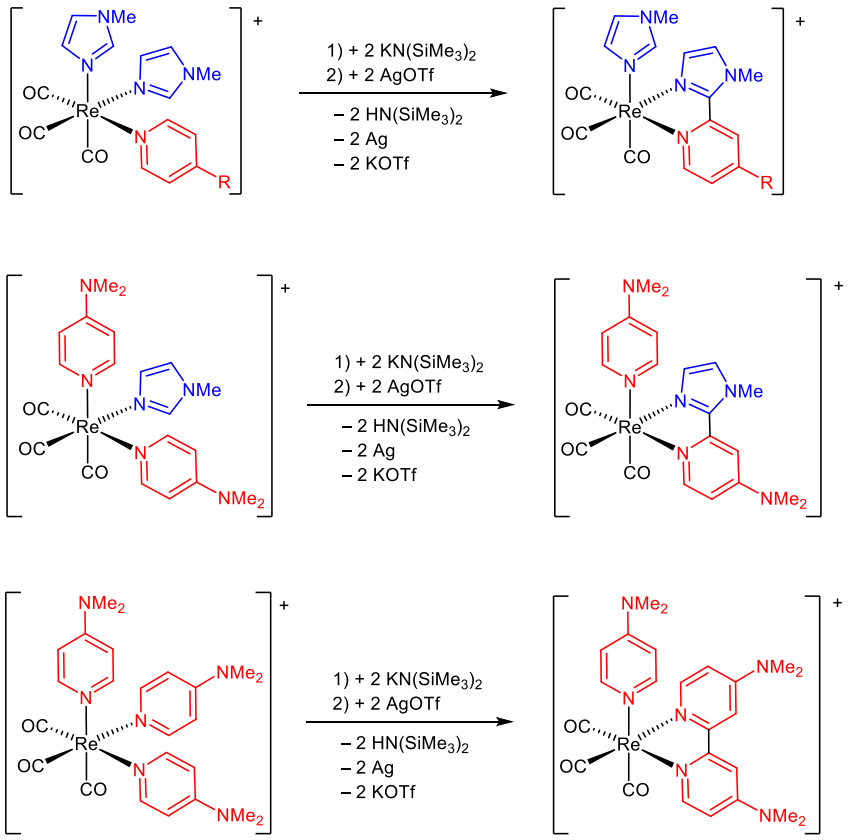
coupling reaction of 1-methylcytosine and nitriles (Scheme 11). The reactions were carried out thermally or were microwave assisted, and afforded again luminescent complexes [48].



Scheme 11. Amidino complexes obtained from the reactions of 1-methylcytosine with nitriles and the appropriate "$Re^{I}(CO)_3$" precursors (R = Me, Ph) [48].

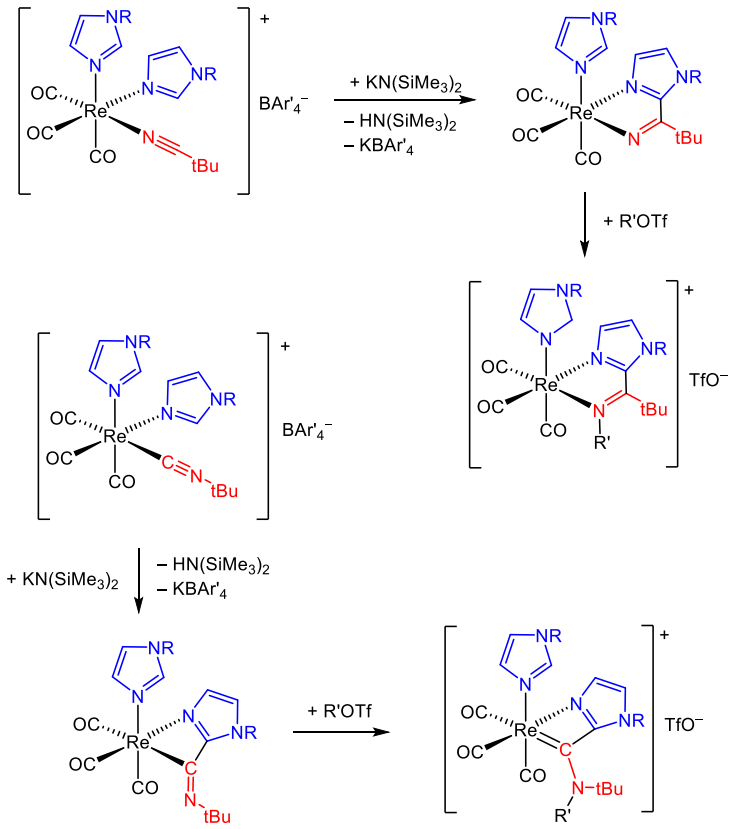
3. Diimines by C-C coupling

In situ C-C coupling leading to diimines coordinated to the "$Re^{I}(CO)_3$" fragment have been reported by the group of Pérez [49]. Thus, pyridylimidazole or bipyridine bidentate ligands were obtained from deprotonation with $KN(SiMe_3)_2$ and the subsequent oxidation with AgOTf of the complexes containing coordinated N-alkylimidazoles and/or pyridines (Scheme 12) [49]. When the monodentate ligands are different, N-methylimidazole showed a higher preference to give the C-C coupling respect to pyridines.



Scheme 12. Pyridylimidazole or bipy bidentate ligands obtained by reaction with $KN(SiMe_3)_2$ followed by oxidation with AgOTf to complexes containing N-alkylimidazoles and/or pyridines (R = H, Me) [49].

The coupling reactions were extended to cationic complexes containing N-alkylimidazole and either nitrile or isonitrile ligands. Their reactions with $KN(SiMe_3)_2$ are regioselective, and occur with deprotonation of the central CH imidazole group, affording either alkylideneamido or iminoacyl neutral products. Hence, new C-C bonds with either the central carbon atom of the nitrile or with the donor carbon atom of the isonitrile have been formed (Scheme 13) [50]. The reactions are regioselective, since the possible products resulting from attack of the base to the coordinated carbonyl groups were never detected. These neutral complexes react with HOTf or MeOTf to afford cationic complexes containing either imine or aminocarbene chelating ligands. The reaction involving the isonitrile coupling (Scheme 13, below) does not afford a diimine ligand, which is the topic of this review, but "$Re^{I}(CO)_3$" complexes containing aminocarbene chelating ligands also display interesting photophysical properties, and show a wide range of applications [51-55].



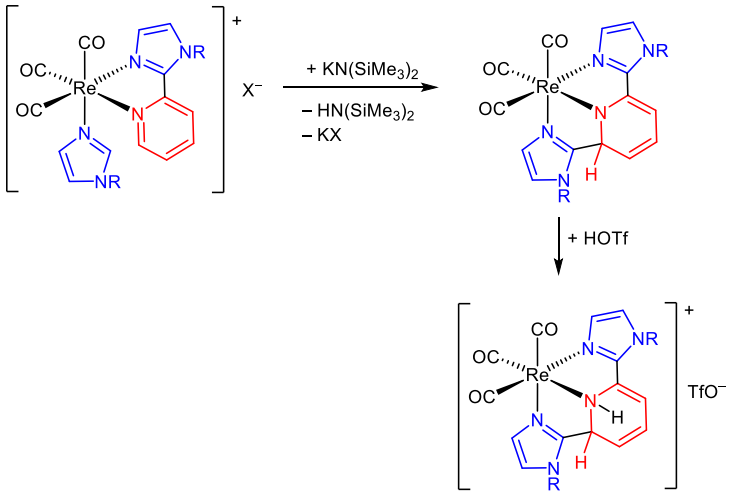
Scheme 13. Imine or aminocarbene chelating ligands obtained after reaction of HOTf or MeOTf with alkylideneamido or iminoacyl complexes, which result from deprotonation of cationic complexes containing N-alkylimidazole and either nitrile or isonitrile ligands [Ar' = 3,5-bis(trifluoromethyl)phenyl); R = Me, Mes; R' = H, Me] [50].

4. Formation of tridentate ligands

The diimine and the "sixth" ligands coordinated to the "$Re^{I}(CO)_3$" moiety may be part of a tridentate ligand. Examples of this type of complexes are scarce compared to the extensive studies carried out on the typical *fac*-[$ReX(CO)_3(N–N)$] species where X and N–N are distinct ligands. This may be related to the difficult synthesis of the tridentate ligands. Again, the advantages of *in situ* synthesis is based on the easy formation of tridentate ligands, otherwise unreachable or difficult to obtain.

4.1. By C-C coupling

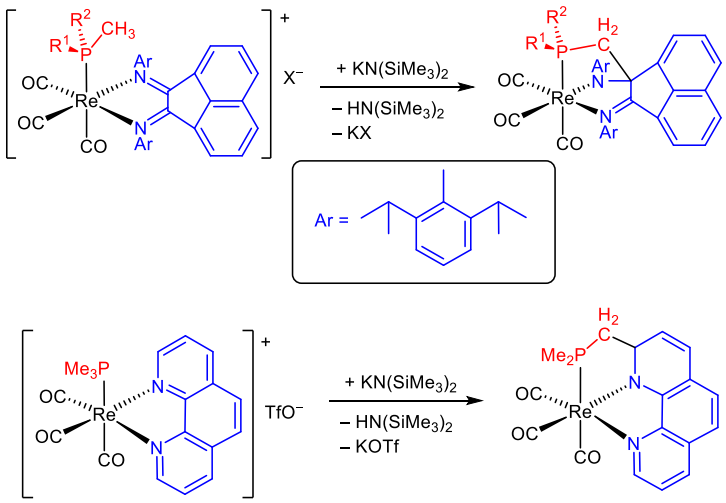
The reaction of the "$Re^{I}(CO)_3$" cationic complex containing a monodentate imidazole and a pyridylimidazole chelate ligand (Scheme 12, above) [49] with $KN(SiMe_3)_2$ afforded a neutral species, which was too unstable to be isolated. However, its spectroscopic data supported the formation of a new tridentate ligand by deprotonation of the central CH group of the imidazole, and further attack of the deprotonated N-coordinated imidazol-2-yl to the *ortho* CH group of the pyridyl ring (Scheme 14, above) [56]. The reaction occurs with dearomatization of the pyridyl group, now formally an anionic ligand, and it is selective, since the imidazole fragment of the pyridylimidazole chelate ligand remains unchanged. This neutral species is then protonated on the nitrogen donor atom of the former pyridyl group, affording a new tridentate neutral ligand coordinated to a cationic complex (Scheme 14, below). Considering that the pyridylimidazole chelate ligand of the starting compound came from a monodentate coordinated pyridine (Scheme 12, first reaction), then both *ortho* CH groups of the pyridine ligand have been finally activated.



Scheme 14. Deprotonation of the imidazole-pyridylimidazole cationic complex, and further protonation to give a new tridentate ligand [X = OTf, BAr^{F}_4, where Ar^{F} = 3,5-bis(trifluoromethyl)phenyl; R = Me, Mes] [56].

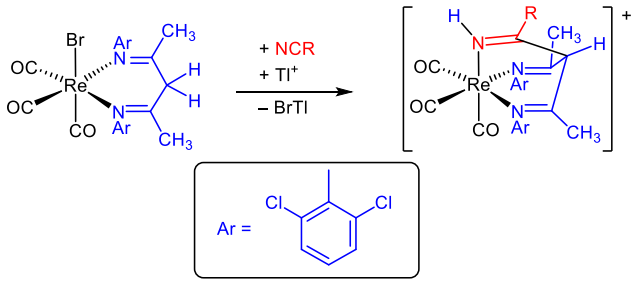
Neutral species similar to those unstable in the previous reactions could be isolated and characterized when cationic *fac*-$[Re(CO)_3(^{i}Pr_2BIAN)(PR_2Me)]^{+}$ (R = Me, Ph; $^{i}Pr_2BIAN$ = 1,2-

bis[(2,6-diisopropylphenyl)imino]acenaphthene) complexes were treated with $KN(SiMe_3)_2$. Deprotonation of the methylphosphane ligand yielded neutral complexes where a new C-C bond linking the phosphane and the diimine had been formed, giving a new tridentate ligand (Scheme 15, above) [57]. The planarity of the nitrogen donor atom bonded to the attacked carbon supports its coordination as an amido ligand. When the reaction was carried out with the analogous bipy complex, the main product was *cis,trans*-$[Re(bipy)(CO)_2(CN)(PMe_3)]$, as a result of the nucleophilic attack of the base to one of the carbonyl ligands, with concomitant elimination of hexamethyldisiloxane. In this case the minor coupled complex containing a new C-C bond between the methylene group from PMe_3 and the CH group in *ortho* position of bipy is a subproduct, which resulted to be thermally unstable. However, C-C coupling is the only process ocurring when $KN(SiMe_3)_2$ is reversibly added to phen in *fac*-$[Re(CO)_3(phen)(PMe_3)]OTf$, what yields a stable product which is the result of PMe_3 deprotonation by free amide, followed by intramolecular addition of the P-CH_2 moiety to phen (Scheme 15, below) [58]. Two intermediates could be detected by low-temperature NMR, in both PMe_3 is intact and one of the pyridine ring is dearomatized. These intermediates are the first steps of the amide attack to phen, and differ in the relative orientation of the $N(SiMe_3)_2$ group.



Scheme 15. Reaction of $KN(SiMe_3)_2$ with *fac*-$[Re(CO)_3(^iPr_2BIAN)(PR_2Me)]^+$ (R=Me, Ph; $^iPr_2BIAN$ = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) (above) [57], and with *fac*-$[Re(CO)_3(phen)(PMe_3)]^+$ (below) complexes (R^1, R^2 = Me, Ph; X = OTf, BAr^F_4) [58].

The chemistry of the "$Re^I(CO)_3$" complexes with 1,3- (or β-) diimines is relatively unexplored compared to that of complexes containing 1,2- (or α-) diimines. The group of Arndtsen and Bengali studied the chemistry of Mn(I) and Re(I) tricarbonyl complexes containing $(2,6\text{-}Cl_2C_6H_3NCMe)_2CH_2$ (L^{Ar}), a β-diketimine ligand of the Hnacnac type. The reaction of *fac*-$[Re(CO)_3Br(L^{Ar})]$ with RCN (R = Me, Ph) resulted in the C−C coupling of the nitrile with the methylene carbon of the diimine ligand, yielding a new triimine ligand (Scheme 16) [59]. The authors propose the coordination of the nitrile in a cationic complex, which is then attacked by the β-carbon of the diimine, either after its deprotonation-coupling and further protonation of the nitrogen donor atom, either after rearrangement of the β-diketimine to its enamine-imine tautomer, where the nucleophilic attack occurs.

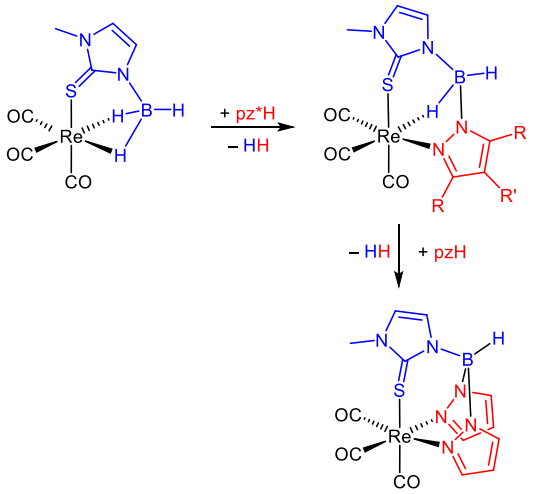


Scheme 16. Reaction of *fac*-$[Re(CO)_3Br(L^{Ar})]$ [L^{Ar} = $(2,6\text{-}Cl_2C_6H_3NCMe)_2CH_2$] with RCN (R = Me, Ph) with nitrile to yield a new tridentate triimine ligand (R = Me, Ph) [59].

4.2. By B-N coupling

Poly(azolyl)borates generated in situ by B-N coupling were described by the group of Santos. The reactions of *fac*-$[Re\{(\mu\text{-}H)_2(tim^{Me})BH\text{-}\kappa^3\text{-}H,H,S\}(CO)_3]$ ($tim^{Me}H$ = 2-mercapto-1-

methylimidazole) with pyrazoles afforded new κ^3-*H,S,N* or κ^3-*S,N,N* tris(azolyl)borate complexes (Scheme 17) [60]. Cleavage of the Re-H bonds, release of H_2, and formation of B-N bonds occurred during the process. Although no kinetic experiments were made, the authors propose a [2 + 1] intermediate, considering their previous results. This would reflect the better ability of pyrazole to cleave the Re-H-B bond, which would be the limiting step in the process. An adequate tuning of the conditions allowed the selective addition of one or two pyrazolates. The complexes were easily purified and remarkably stable both in the presence of air and wet solvents. The use of a functionalized pyrazole in C-4 shows how biomolecules may be also introduced in the system.



Scheme 17. Stepwise reactions of *fac*-[Re{(μ-H)$_2$(tim^{Me})BH-κ^3-*H,H,S*}(CO)$_3$] (tim^{Me}H = 2-mercapto-1-methylimidazole) with pyrazoles to afford complexes containing κ^3-*H,S,N* (above) or κ^3-*S,N,N* (below) tris(azolyl)borates (R = R' = H (pzH); R = Me, R' = $CH_2C(O)OEt$) [60].

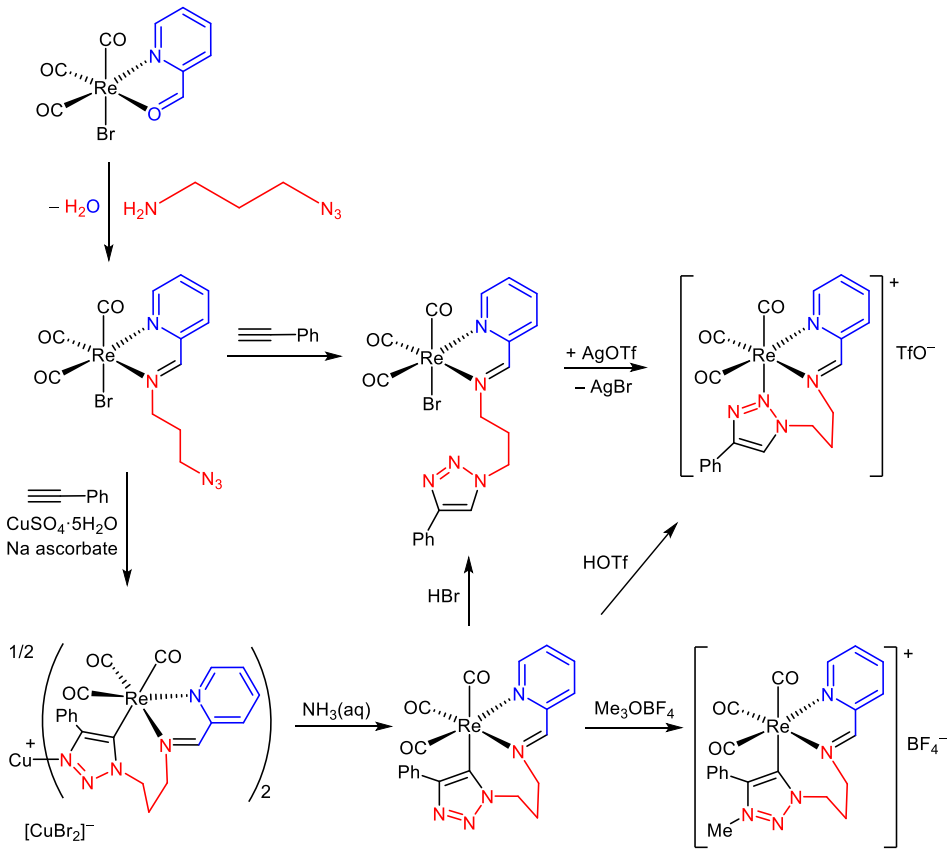
4.3. "Click" chemistry and beyond

The group of Miguel also reported the "click" reaction of a pendant azide in a iminopyridine bonded to the "Re^I(CO)$_3$" fragment, and the coordination of the triazolyl obtained, either as *N*- or as *C*-donor. The target was an iminopyridine functionalized with a triazolyl group which would

coordinate as a κ^3-*N,N,N*-tridentate ligand. However, an unexpected transmetalation led to its transformation to *C*-triazolyl, and finally to a triazolylidene mesoionic carbene [61].

The reaction of phenyl acetylene with the complex containing the azide functionality in the presence of catalytic amounts of $CuSO_4 \cdot 5H_2O$ and sodium ascorbate led to the expected complex containing a triazole, as a result of the cycloaddition of azide and acetylene (Scheme 18, center, left). This triazole was coordinated, after bromide abstraction with AgOTf, to afford the corresponding cationic complex (Scheme 18, center, right). However, when stoichiometric amounts of the copper reagent were used, an unexpected polymetallic complex with the triazolyl ring bridging Re and Cu (as *C*- and *N*-bonded respectively), was obtained (Scheme 18, center). Therefore, *C*- or *N*-coordination of the triazole ring are obtained by choosing either stoichiometric or catalytic conditions. The unprecedent process leading to this polymetallic species is rationalized by the authors considering that the initial copper *C*-bonded triazolyl group resulting from the cycloaddition would be transferred to the rhenium atom with exchange of the bromido ligand, whereas the nitrogen donor atom of triazolyl is coordinated to copper.

The rhenium fragment was liberated from copper by treating the polymetallic complex with an aqueous solution of ammonia, affording the expected mononuclear "$Re^{I}(CO)_3$" complex containing a tridentate κ^3-*N,N,C*-triazolylpropyliminopyridine (Scheme 18, below, center). The treatment of this compound with acids led to either uncoordinated triazole (Br is coordinated when using HBr) or to a κ^3-*N,N,N*-coordinated triazole with HOTf (Scheme 18, above, center and right, respectively). Finally, the reaction of the tridentate κ^3-*N,N,C*-triazolylpropyliminopyridine complex with Me_3OBF_4 afforded a cationic complex where the triazolyl ring was converted into a triazolylidene. This is a mesoionic carbene, since the heterocyclic ring formally contains a positive and a negative formal charges (Scheme 18, below, right).



Scheme 18. Reactions of a pendant azide group in a coordinated iminopyridine, coordination of the triazolyl, as *N*- or *C*-donor, and further transformation of the *C*-triazolyl into a triazolylidene mesoionic carbene [61].

5. Conclusions and Perspectives

In situ coupling of monodentate ligands is an alternative method to obtain new *N*,*N*-chelating (and also tridentate) ligands coordinated to the "$Re^{I}(CO)_3$" moiety. The most evident advantages of this approach are not only avoiding the often tedious synthesis of the chelating ligand previous to its coordination, but also the adequate tuning of the photophysical or biomedical properties of the final complex, by choosing the appropriate substituents.

So far, new diimines have been obtained in situ by C-N or C-C couplings. Tridentate ligands coordinated to the "$Re^{I}(CO)_3$" moiety have also been synthesized in situ by C-C or B-N coupling, or by coordination of a triazolyl obtained, either as *N*- or as *C*-donor.

In summary, new polydentate ligands are readily accessible by the coupling of coordinated monodentate ligands. Reports on the use of this method are yet relatively scarce, and they are mainly focused on the reactions and mechanisms, more than on the photophysical or biomedical properties of the final complexes. This review might encourage and help researchers to extend or improve the interesting features of "$Re^{I}(CO)_3$" complexes by coupling of coordinated ligands.

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