

Photoactive nickel complexes in cross coupling catalysis

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Abstract: Transition metal catalyzed cross coupling reactions are important in chemical synthesis for the formation of C-C and C-heteroatom bonds. Suitable catalysts are frequently based on palladium or nickel, and lately the cheaper and more abundant first-row transition metal element has been much in focus. The combination of nickel catalysis with photoredox chemistry has opened new synthetic possibilities, and in some cases electronically excited states of nickel complexes play a key role. This is a remarkable finding, because photo-excited metal complexes are underexplored in the context of organic bond-forming reactions, and because the photophysics and the photochemistry of first-row transition metal complexes are underdeveloped in comparison to their precious metal-based congeners. Consequently, there is much potential for innovation at the interface of synthetic-organic and physical-inorganic chemistry. This minireview highlights recent key findings in light-driven nickel catalysis and identifies essential concepts for the exploitation of photoactive nickel complexes in organic synthesis.

1. Introduction

Metal catalyzed bond forming reactions in organic synthesis typically take place on the ground-state potential energy surface. Despite the renaissance of photoredox catalysis,^[1] electronically excited states of metal complexes are rarely directly involved. This is because many photoredox reactions rely on light-induced changes of metal oxidation states, but the actual bond-forming chemistry then occurs with the catalysts in their electronic ground states. Whilst this approach has been very successful in many combinations of photoredox and transition metal catalysis,^[2] the excited-state reactivity of metal catalysts in bond forming reactions in organic synthesis remains underexplored.^[3] Moreover, the photophysics and the photochemistry of first-row transition metal complexes are far less well developed than for precious metal-based coordination compounds.^[4] The ligand substitution-lability needed in catalysis often stands in conflict with favorable excited-state properties (in particular long lifetimes or photoluminescence behavior), and consequently inorganic photophysics and photochemistry long concentrated on substitution-inert second- or third-row transition metal complexes.^[5] Now, the focal points of two traditionally separate research communities, synthetic organic chemistry on the one hand and physical-inorganic chemistry on the other hand, begin to converge at two specific elements in the periodic table: nickel and copper.

The development of photodriven Ullmann coupling methodologies several years ago revived interest in the photochemistry of Cu^I complexes.^[6] Aside from C-N couplings, several other C-heteroatom as well as C-C coupling reactions became possible under photoirradiation.^[7] Among first-row transition metals, Cu^I arguably received most attention from photophysicists and photochemists,^[8] but up to that point mostly following traditional design principles, geared at minimizing molecular distortions and ligand dissociation upon excitation of the complexes. By contrast, the newly developed photodriven cross coupling reactions rely on comparatively labile Cu^I complexes with substrates as ligands, some of which were sufficiently inert for isolation and photophysical characterization.^[7b, 9] Just recently,

Since reductive elimination from Ni^{II} complexes is energetically uphill for many synthetically relevant reactions,^[17] nickel catalysis frequently relies on five-coordinate Ni^{III} complexes from which reductive elimination is considerably more facile. The recently reported [NiCl₃(dppe)] complex (dppe = bis(diphenylphosphino)ethane), which undergoes photoelimination of chlorine radicals, has a distorted square-pyramidal geometry,^[18] but for related five-coordinate Ni^{III} complexes trigonal-bipyramidal and square-pyramidal geometries often represent two allomers that are energetically close to one another.

3. Scope of light-driven nickel catalyzed cross coupling reactions

In order to recognize the importance and the synthetic value of combined photoredox and nickel catalysis, it is useful to provide a brief overview of the different types of cross coupling reactions that have been achieved so far. Table 1 serves this purpose, but is not meant to give a comprehensive summary.

Table 1. Some cross coupling reactions by combined photoredox and nickel catalysis.

entry	bond formed	starting materials	products	refs.
1	C-N	iodoacetanilides, alkenes	indolines	[19]
2	C-N	aryl halides, amines	anilines	[20]
3	C-N	aryl halides, sulfonamides	<i>N</i> -aryl / <i>N</i> -heteroaryl sulfonamides	[21]
4	C-O	aryl halides, carboxylic acids	<i>O</i> -aryl esters	[3]
5	C-O	aryl bromides, alcohols	aryl ethers	[22]
6	C-S	aryl iodides, thiols	thioethers	[23]
7	C-S	(hetero)aryl bromides, thiols, hypervalent alkyl silicates	thioethers	[24]
8	C-S	(hetero)aryl halides, sulfinate salts	aromatic sulfones	[25]
9	C-C	aryl bromides, alkoxyalkyl-/benzyltrifluoroborates	C(sp ³)-C(sp ²) cross-coupled products	[12a, 26]
10	C-C	aryl halides, α -heteroatom containing carboxylic acids	C(sp ³)-C(sp ²) cross-coupled products	[12b, 27]
11	C-C	(hetero)aryl bromides, secondary and primary ammonium alkylsilicates	C(sp ³)-C(sp ²) cross-coupled products	[28]
12	C-C	aryl halides, amines	benzylic amines	[29]
13	C-C	<i>p</i> -bromobenzonitrile, hypervalent bis(catecholato) silicon compounds	C(sp ³)-C(sp ²) cross-coupled products	[30]
14	C-C	indoles, α -oxo acids	3-acylindoles	[31]
15	C-C	(hetero)aryl halides, substrates with α -heterosubstituted or benzylic C(sp ³)-H bonds	C-H arylation products	[32]
16	C-C	aryl bromides, toluene derivatives	C-H arylation products	[33]
17	C-C	aryl halides, organozinc reagents	C(sp ³)-C(sp ²) cross-coupled products	[34]
18	C-C	amides, aliphatic C(sp ³)-H bonds	ketones	[35]

Transition metal catalyzed C-C coupling reactions traditionally involve sp²-hybridized carbons of aryls or olefins, whereas sp³ alkyl carbons are trickier to couple. Seminal studies merging photoredox and nickel catalysis addressed this fundamental challenge by enabling C(sp³)-C(sp²) coupling via light-induced formation of alkyl radicals that entered the nickel catalysis cycle (Figure 2e).^[12] This concept has been adapted to a range of alkyl radicals sources,^[28, 30] and was furthermore extended to achieve enantioselective reactions.^[27] The activation of C(sp³)-H bonds remains a

continuous challenge in organic synthesis, and hence the photodriven coupling of (hetero)aryl halides with activated α -hetero-substituted or benzylic $C(sp^3)$ -H bonds represented another highlight in combined photoredox / nickel catalysis (Figure 2f).^[32] From a photochemical viewpoint, there are several mechanistically intriguing aspects in these C-C coupling reactions, as discussed in more detail below.

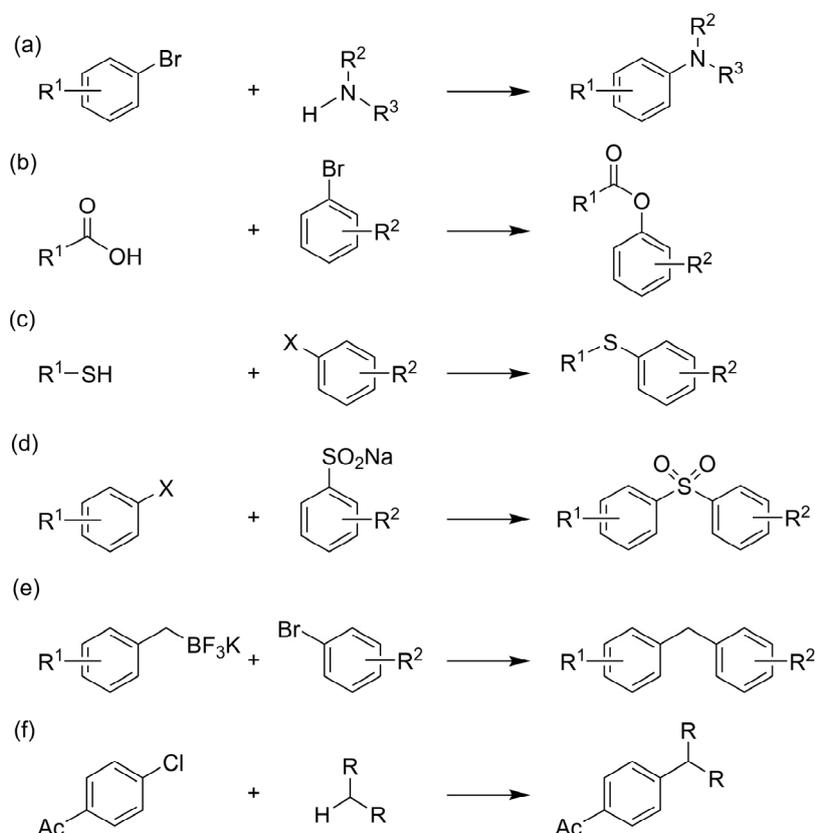


Figure 2. Examples of cross coupling reactions by combined nickel and photoredox catalysis. (a) C-N coupling (entry 2 in Table 1),^[20] (b) aryl esterification (entry 4),^[3] (c) C-S coupling via thiyl radicals (entry 6),^[23] (d) synthesis of aromatic sulfones (entry 8),^[25] (e) $C(sp^3)$ - $C(sp^2)$ coupling of benzylic trifluoroborates with aryl bromides (entry 9),^[12a, 26] (f) C-H arylation (entry 15).^[32b]

Regarding C-N coupling reactions, aryl amination via combined photoredox / nickel catalysis is a key discovery that attracted considerable attention (Figure 2a),^[20a] because this represents a complementary method to analogous palladium catalyzed reactions.^[36] In particular, the reductive elimination step resulting in C-N bond formation was much in focus. Partly based on early studies, which indicated that Ni^{II} amido complexes tend to not undergo reductive elimination at room temperature,^[17] photo-driven oxidation of Ni^{II} to Ni^{III} was considered essential.^[19-20] Some investigators noted early on that electronically excited Ni^{II} intermediates could play a more important role than Ni^{III} ,^[20a] and recent systematic studies support that view.^[3, 10, 20b, 20c, 21] This photochemical key aspect will be considered in further detail below. Whilst aryl aminations yielding anilines received particular attention,^[20, 37] C-N bond forming reactions by combined photoredox and nickel catalysis further include the synthesis of indolines^[19] and sulfonamides.^[21] Selected photodriven C-N coupling reactions have been performed on the kilogram scale.^[38] C-O and C-S coupling reactions using aryl halides and alcohols or thiols leading to aryl esters (Figure 2b)^[3] and thioethers (Figure 2c)^[23] have been reported to proceed with broad substrate scope, yet very disparate reaction

pathways have been proposed by different investigators. In one case, thioetherification was discovered serendipitously when using hypervalent alkylsilicates for the photochemical formation of alkyl radicals.^[24] In the presence of thiols, hydrogen atom transfer leads to thiyl radicals which then act as reaction partners with (hetero)aryl bromides, yielding thioethers rather than the initially targeted C(sp³)-C(sp²) coupling products.

4. Prototypical catalytic cycles

The mechanisms of nickel catalyzed cross coupling reactions have been reviewed,^[11b] and there exists also a prior review specifically focusing on dual photoredox and nickel-catalyzed *cascade* reactions.^[39] Here, it is meaningful to give a brief survey of some of the most commonly encountered mechanistic features, in order to recognize photochemically relevant key steps. Traditionally, cross coupling reactions with C(sp²) electrophiles proceed via a sequence of oxidative addition to the Pd⁰ or Ni⁰ catalyst, subsequent transmetalation of an organometallic nucleophile, and finally reductive elimination from a diorganopalladium(II) or diorganonickel(II) intermediate, liberating the cross coupled product and regenerating the catalyst in its initial (zero-valent) form. In the case of nickel, the +I and +III oxidation states are more readily accessible than for palladium,^[11] and consequently different modes of reactivity become possible. This includes Ni^I/Ni^{III} cycles in addition to the traditional Ni⁰/Ni^{II} (or Pd⁰/Pd^{II}) cycles, as well as radical mechanisms involving single-electron transfer pathways that become particularly relevant in combined photoredox / nickel catalysis.

The mechanism in Figure 3a is prototypical for many nickel catalysis cycles that have been brought into play in combination with a photoredox catalytic cycle.^[12] Starting from a Ni⁰ species (A), oxidative addition of an aryl halide (Ar-X) yields a square-planar Ni^{II} complex (B) to which a photo-generated radical (R•) can add to form a Ni^{III} intermediate (C). Reductive elimination (liberating the cross-coupled reaction product Ar-R) gives a Ni^I compound (D), which is then reduced to the initial Ni⁰ species (A) by the photoredox catalyst (liberating a halogenide ligand X⁻). Solvent molecules (solv) can complement the coordination sphere of the Ni⁰ species (A). In a separate photoredox cycle (not shown), R• is typically generated from a closed-shell precursor R by an excited iridium complex acting as photo-oxidant. The reduced iridium complex subsequently provides the necessary electron (e⁻) for the reduction of Ni^I to Ni⁰ (step D→A). In the cross coupling cycle of Figure 3a, there are no photoactive nickel species; all nickel intermediates involved are in their electronic ground states. However, in a variant of the cycle of Figure 3a, photoexcitation of the Ni^{III} intermediate C seemed necessary to induce halogen atom release,^[32b] in analogy to a prior report of halogen photo-elimination from a pentacoordinate Ni^{III} complex.^[18] A closely related study instead considered halogen atom elimination from photoexcited Ni^{II} species B.^[32a] Thus, two very disparate mechanisms have been proposed for closely related C(sp³)-H arylation reactions,^[32] and from a photochemical viewpoint this difference is very important even though the final reaction outcome is similar in both cases.

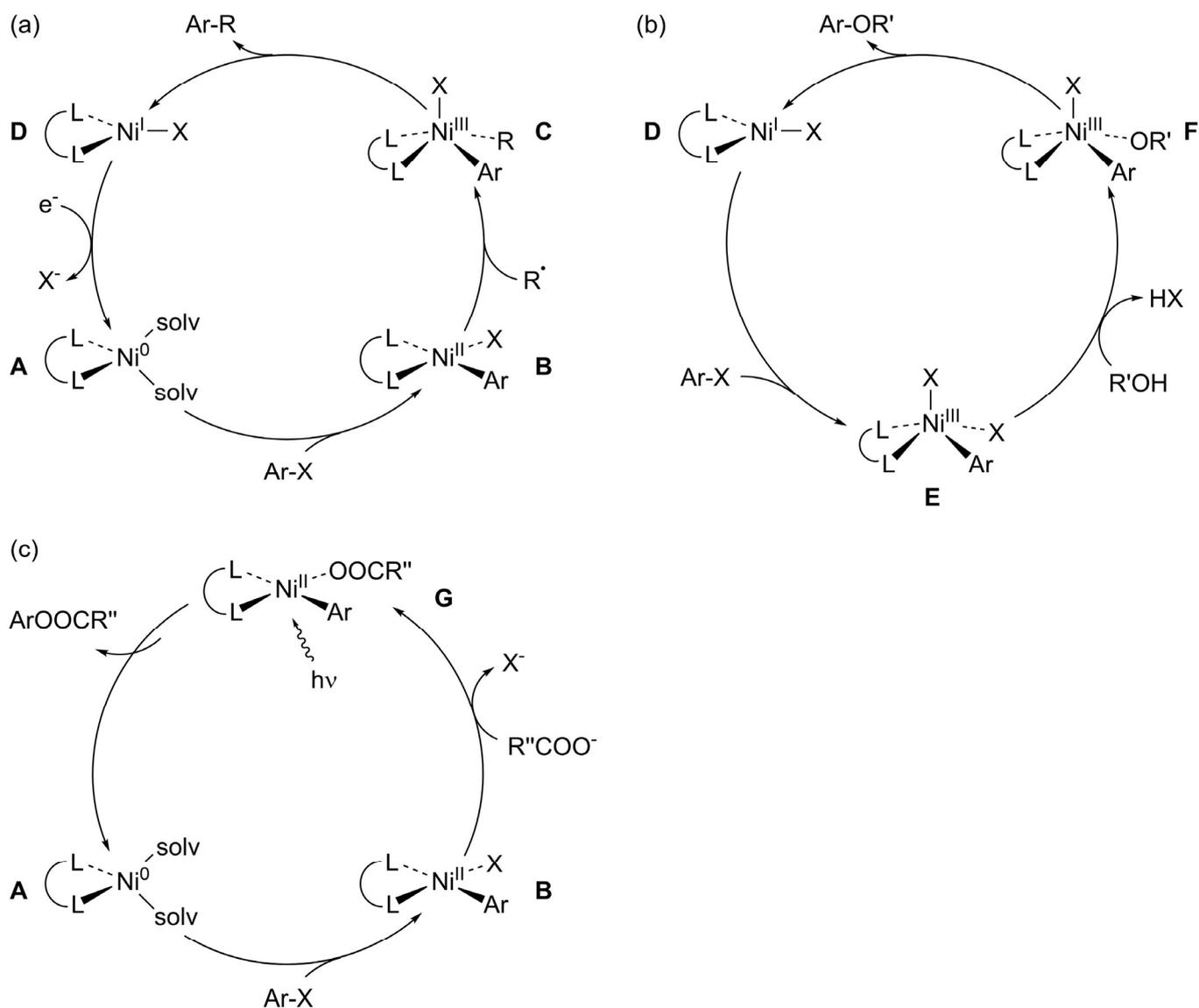


Figure 3. Prototypical nickel cycles relevant for light-driven cross coupling reactions. The term “solv” stands for solvent molecules.

The cycle of Figure 3a has been reconsidered later from a combined computational and experimental perspective, and it has been noted that depending on the relative Ni⁰ and Ni^{II} concentrations, an alternative cycle with a Ni^I key intermediate might play an important role.^[26] Regardless of that, both proposed nickel cycles converge at the common Ni^{III} species C, but the calculations suggest that radical dissociation (leading to a Ni^{II} species not shown in Figure 3a) is faster than reductive elimination (step C→D).

Leaving the subtleties of the cycle in Figure 3a behind, it is interesting to note that a recent mechanistically oriented cross coupling study came to the conclusion that a self-sustained Ni^I/Ni^{III} cycle (Figure 3b) is operative in aryl etherification.^[22c] Moreover, a subsequent study by other investigators reached a similar conclusion for C-N coupling reactions, considering the initially proposed Ni⁰/Ni^{II}/Ni^{III}/Ni^I mechanism of Figure 3a unlikely.^[40] In the case of aryl etherification, oxidative aryl halide addition occurs to Ni^I (instead of Ni⁰), yielding a pentacoordinate Ni^{III} intermediate (E) with two halogenide ligands, one of which needs to be exchanged by the cross coupling partner (here an alcoholate) to give the Ni^{III} species (F), from which reductive elimination to give the cross-coupled product (Ar-OR') can occur. The resulting three-coordinate Ni^I species (D) then restarts the cycle. The Ni^I and Ni^{III} complexes are

essentially identical in the mechanisms of Figure 3a (D, C) and Figure 3b (D, F), and the main difference is the lack of Ni⁰ and Ni^{II} intermediates in Figure 3b, as well as the argument that the Ni^I/Ni^{III} cycle is in principle self-sustainable. In Figure 3b, counterproductive comproportionation reactions (for example reaction between D and F) have been omitted for simplicity. The authors of the mechanistic aryl etherification study argued that photoredox steps are only necessary to rejuvenate the cycle in Figure 3b when such off-pathway reactions deplete the concentrations of the catalytically relevant Ni^I/Ni^{III} species.^[22c] Moreover, they identified and characterized a mixed-valent Ni^I/Ni^{II} dimer complex, which apparently forms by trapping of Ni^I intermediate D by excess Ni^{II} present in solution. Dissociation of that dimer therefore has an important influence on the concentration of catalytically competent Ni^I. A low concentration of Ni^I can help prevent dimerization and further aggregation to form so-called nickel-black,^[40] which can be detrimental for cross coupling activity.^[41] On the other hand, due to the vanishingly low levels of Ni^I, the Ni^I/Ni^{III} cycle is not self-perpetuating and continuous irradiation of an iridium photosensitizer is necessary to drive C-N cross coupling reactions to completion,^[40] particularly because the reduction of Ni^{II} to Ni^I (by a one-electron reduced iridium complex) was found to be inefficient and rate-determining.

Like the mechanism in Figure 3a, the cycle in Figure 3b does not involve any electronically excited nickel complexes. This is different for the mechanism in Figure 3c, which starts analogously to the cycle in Figure 3a with a Ni⁰ species (A) to which the aryl halide substrate (Ar-X) adds oxidatively to form Ni^{II} complex B.^[3] After exchange of the halide ligand by the coupling partner (here a carboxylate, R''COO⁻), the resulting Ni^{II} complex G is promoted to an electronically excited state (wavy arrow labeled with “hv”) from which the reductive elimination of the product (ArOOCR'') occurs. Excitation of Ni^{II} complex G occurred indirectly, via Dexter-type energy transfer from an electronically excited photosensitizer, both for esterification^[3] and sulfonamidation reactions.^[21] Conceptually related studies identified Förster energy transfer as key step for the activation of Ni^{II} intermediates towards reductive elimination of cross-coupled products.^[20b, 20c] The main point in Figure 3c is the occurrence of photoexcited nickel complexes, which is in strong contrast to the cycles of Figures 3a/3b where only ground-state nickel complexes are involved.

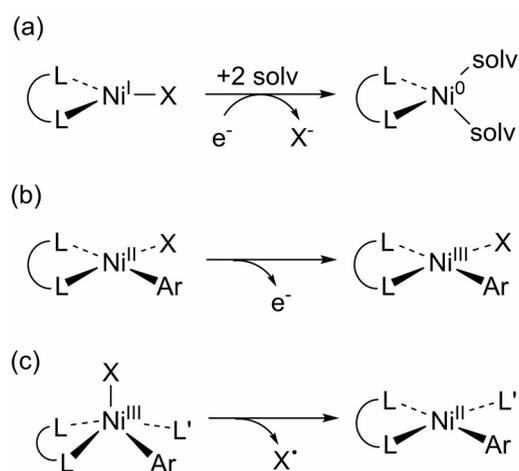


Figure 4. Some elementary reaction steps in light-driven cross coupling reactions catalyzed by nickel. The term “solv” stands for solvent molecules.

5. Activation of nickel complexes by photoinduced electron transfer

As has emerged from the preceding section, the reduction of Ni^{I} to Ni^{0} is a key step for which photoredox and nickel catalysis cycles are coupled to one another, for example in the mechanism of Figure 3a (step D→A). In most cases, that redox process (Figure 4a) is not photochemical, but instead involves the reaction between two complexes in their electronic ground states. In particular, thermal electron transfer from the one-electron reduced form of the photocatalyst, typically an iridium complex, to the Ni^{I} species was often considered relevant for this purpose.^[12, 20a, 22a, 28, 32b] This Ni^{I} to Ni^{0} reduction activates the catalyst for oxidative addition,^[15] although this does not seem necessary in all cases (Figure 3b).^[22c, 40] In some examples of C-N and C-S coupling, the reduced photocatalyst was thought to reduce a Ni^{II} intermediate to a Ni^{I} species,^[23, 37] yet this remains a thermal (non-photochemical) reaction step. For the $[\text{NiBr}(\text{bpy})(\text{tol})]$ model complex (bpy = 2,2'-bipyridine, tol = *ortho*-tolyl), a $\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}$ reduction potential of ca. -1.7 V vs. SCE has been reported.^[42] Consequently, a one-electron reduced photocatalyst must provide at least that potential when comparable σ -organonickel(II) intermediates need to be reduced. The two-electron reduction of $[\text{Ni}^{\text{II}}\text{Br}_2(\text{bpy})]$ in DMF is less demanding as it occurs already ca. -1.1 V vs. SCE,^[43] further implying that reduction of $[\text{Ni}^{\text{I}}\text{Br}(\text{bpy})]$ to $[\text{Ni}^{\text{0}}(\text{bpy})]$ (presumably with solvent molecules complementing the coordination sphere of four-coordinate tetrahedral Ni^{0} , Figure 1) occurs at even less negative potential.^[12a] Many different types of photocatalysts are therefore suitable for the reduction of dihalo(bipyridine)nickel(II) complexes, particularly in their one-electron reduced ground states. Photochemical Ni^{II} to Ni^{III} oxidation to activate the nickel catalyst for reductive elimination has been reported with photoexcited ruthenium and iridium complexes (Figure 4b).^[19-20, 22a, 32b] In other cases, however, the oxidation to Ni^{III} occurs via addition of (neutral) radicals to Ni^{II} intermediates,^[12] and the photochemical step is needed instead to generate these neutral organic radicals. Photoexcited nickel species are not involved in these cases, and merely the photocatalyst undergoes electronic excitation. Thermodynamically, the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ oxidation step of σ -organonickel(II) species is not particularly demanding. For instance, the representative $[\text{Ni}^{\text{II}}(\text{Mes})(\text{OMe})\text{bpy}]$ compound (Mes = mesityl), is oxidized at a potential of ca. 0.7 V vs. SCE.^[44]

As noted above, certain combined photoredox / nickel catalysis cycles involve the photoelimination of halogen atoms (X^{\bullet}) from Ni^{III} complexes (Figure 4c).^[32b, 33] Such reactions are furthermore of interest in the context of splitting HX to H_2 and X_2 for (solar) energy storage. For Ni^{II} complexes the photoelimination of halogens typically requires UV irradiation,^[45] but in Ni^{III} complexes the relevant LMCT (ligand-to-metal charge transfer) absorption bands can be shifted into the visible spectral range.^[18]

In one case of C-N coupling between aryl halides and aryl amines, the authors claimed that visible-light excitation of a Ni^{I} amido complex should produce a long-lived and highly reducing excited state, but there was no experimental evidence to support this claim.^[37]

To summarize this section, it is noted that photoexcited nickel species are so far rarely directly involved in electron transfer events of combined photoredox / nickel catalysis. Thermodynamic restrictions regarding the reducing ability of the photocatalyst are more demanding than concerning their oxidizing properties, because Ni^{II} reduction may require potentials between -1.1 to -1.7 V vs. SCE, whereas $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ oxidation can occur already at potentials near +0.7 V vs. SCE (in the pertinent coordination environments).

6. Activation of nickel complexes by energy transfer or by direct excitation

Reductive elimination from Ni^{II} complexes is often thermodynamically disfavored,^[17] and further activation is frequently necessary to liberate the cross coupled reaction products. Oxidation of Ni^{II} to Ni^{III} is a viable option that has been proposed from the very beginning of combined photoredox / nickel catalysis, but some investigators early on considered the possibility that photoexcitation of Ni^{II} (Figure 5a) via energy transfer from a triplet excited photosensitizer (^{3*}PS) might be sufficient for that purpose.^[20a] Furthermore, the possibility of photo-elimination of bromine radicals from an excited Ni^{II} complex in the course of C-H arylation reactions was considered,^[32a] contrasting a related study in which photo-elimination of chlorine radicals seemed to occur from an excited Ni^{III} complex.^[32b] More recent work provides further evidence for the formation of electronically excited Ni^{II} complexes.^[3, 20b, 20c, 21] Two of these studies use a range of different photosensitizers to activate the Ni^{II} intermediates via Dexter energy transfer, and they both find a correlation of product yields with photosensitizer triplet energies, whilst at the same time an anti-correlation with the oxidizing power of the photosensitizer is detectable.^[3, 21] This observation clearly points towards the importance of electronically excited Ni^{II} complexes and speaks against photo-oxidation of Ni^{II} to Ni^{III} in the investigated cases. The respective photoreactions (coupling of aryl halides with carboxylic acids and sulfonamidation), proceeded well with photosensitizers with triplet energies on the order of 40-45 kcal/mol or greater, whereas only poor product yields were obtainable below that threshold.^[3, 21] A more recent study employing UV-Vis transient absorption spectroscopy strongly supports the mechanism in Figure 5a for C-O coupling, in which the reductive elimination occurs from a triplet-excited nickel species.^[46] However, it was also noted that depending on substrate, the electronic structure of the relevant Ni^{II} intermediate could change to the extent that triplet-triplet energy transfer is no longer the preferred photochemical reaction path, and that the photoexcited iridium sensitizer instead oxidizes the Ni^{II} intermediate, followed by reductive elimination from ground-state Ni^{III}. The energy transfer pathway is also amenable with purely organic photosensitizers instead of iridium complexes.^[47]

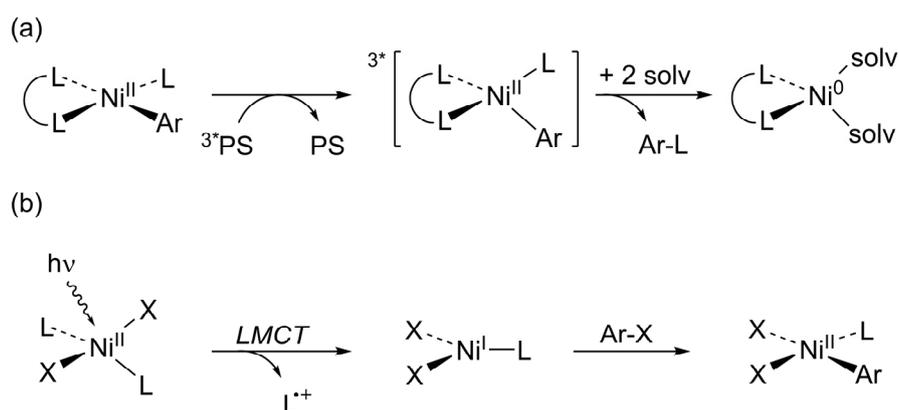


Figure 5. (a) Excitation of Ni^{II} complexes via triplet energy transfer from triplet-excited photosensitizers (^{3*}PS) followed by reductive elimination to yield the cross-coupling product (Ar-L); solv = solvent molecules. (b) Excitation into a ligand-to-metal charge transfer (LMCT) excited state leading to a Ni^I intermediate that is activated for oxidative addition of the aryl halide (Ar-X) substrate.

Direct excitation of nickel(II) complexes has been reported for [NiBr₂(morph)₂] and [NiBr₂(morph)₃] (morph = morpholine),^[20c] which form in roughly 1:3 ratio under the pertinent reaction conditions for C-N coupling between

morpholine and aryl halides.^[20b] Under 365 nm irradiation, LMCT excitation was thought to yield a morpholine radical cation ($L^{\bullet+}$) and Ni^I (Figure 5b), which would correspond to an activation for subsequent oxidative addition of the aryl halide ($Ar-X$).^[20c] Indirect excitation of these nickel(II)-amine complexes using photosensitizers and Förster energy transfer is also possible and has been investigated in considerable detail.^[20b] The UV irradiation of $NiCl_2$ to form catalytically competent Ni^I species seems conceptually related.^[33]

7. Photoactive excited states of relevant nickel complexes: 3MLCT versus ^3d-d

The nickel(II) complex in Figure 6a is an isolable representative of catalytically relevant reaction intermediates in aryl esterification.^[3, 46] Whilst this complex is thermally stable, its direct photo-irradiation with blue light yields the reductive elimination product 2,6-bis(trifluoromethyl)phenyl acetate. Similarly, when an iridium photosensitizer with sufficiently high triplet energy (> 42 kcal/mol) is present, photo-irradiation of that photosensitizer induces reductive elimination of the same product from the nickel(II) complex in Figure 6a, implying (triplet-triplet) energy transfer from the photosensitizer to the nickel(II) complex.^[3] Furthermore, the yield for C-O coupling between methyl 4-bromobenzoate and benzoic acid correlates with the triplet energy of the photosensitizer and anti-correlates with the oxidizing power of the photosensitizer. Transient absorption studies with the complex in Figure 6a corroborate that view,^[46] as noted above. In the experimentally accessible range, the excited-state lifetime of that complex is insensitive to its concentration, signaling that photoinduced disproportionation^[22b] is relatively unimportant in this case and reductive elimination is a unimolecular process.^[46] These combined observations led to the conclusion that the aryl esterification occurs via energy transfer-mediated catalysis involving triplet-excited nickel(II) complexes,^[3] although it was noted that depending on substrate and the exact electronic structure of the nickel(II) intermediate, oxidation to Ni^{III} could instead occur.^[46]

Nickel(II) complexes of the type in Figure 6b with $R = tBu$, $R' = Me$, and $X = Cl$ or Br were initially explored in the context of $C(sp^3)-H$ cross-coupling reactions involving the photoinduced generation of chlorine or bromine radicals.^[32] In the case with $X = Br$, the authors considered an energy transfer mechanism most relevant,^[32a] similar to what the abovementioned later study for the complex in Figure 6a found. For the case with $X = Cl$ a mechanism based on electron transfer between the photosensitizer and the Ni^{II} complex was postulated, leading to a Ni^{III} intermediate, which, after further excitation, is followed by the liberation of a chlorine radical from the complex.^[32b]

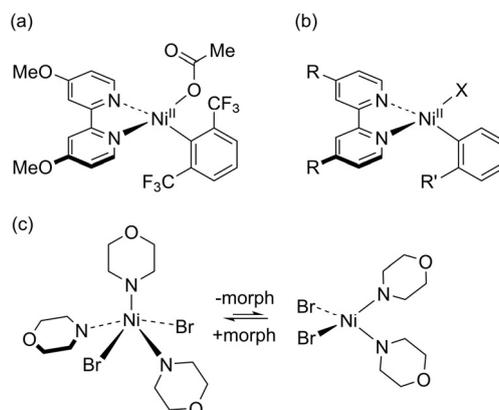


Figure 6. Complexes for which in-depth photophysical and photochemical studies have been performed.^[3, 10, 20b, 46] $R = OMe, CF_3, H$; $R' = OMe, tBu, H, Ph, CO_2Et$; $X = Cl, Br$; morph = morpholine.

Subsequent photophysical and photochemical studies of analogous types of complexes came to the conclusion that they have a long-lived (ca. 4 ns) $^3\text{MLCT}$ (metal-to-ligand charge transfer) excited state,^[22b, 48] but this interpretation was revised later when studying a fairly broad range of structurally closely related Ni^{II} complexes.^[10] Specifically, complexes of the type in Figure 6b with $\text{R} = \text{OMe}, \text{CF}_3, \text{H}$ and $\text{R}' = \text{OMe}, \text{tBu}, \text{H}, \text{Ph}, \text{CO}_2\text{Et}$ and $\text{X} = \text{Cl}$ or Br were investigated. Most revealing is a time-resolved infrared absorption experiment (in combination with UV-Vis transient absorption spectroscopy), which makes it quite clear that the long-lived (ca. 4 ns) excited state is in fact a metal-centered ($^3\text{d-d}$) state rather than a $^3\text{MLCT}$ state. Thus, at this point there is much compelling evidence that complexes of the types in Figure 6a/b react through metal-centered ($^3\text{d-d}$) excited states, which are populated either via (triplet) energy transfer from suitable photosensitizers or via direct excitation of the Ni^{II} complexes into $^1\text{MLCT}$ states that subsequently relax (within ca. 5-10 ps) to $^3\text{d-d}$ states (Figure 7).^[10] In the respective long-lived (ca. 4 ns) $^3\text{d-d}$ excited state, the Ni^{II} complexes are tetrahedral and thermal Ni-aryl bond homolysis becomes feasible from that state (right part of Figure 7).

By contrast, the $[\text{NiBr}_2(\text{morph})_2]$ and $[\text{NiBr}_2(\text{morph})_3]$ complexes (Figure 6c) involve LMCT excitation (with UV light) to react along the pathway in Figure 5b, as discussed above.

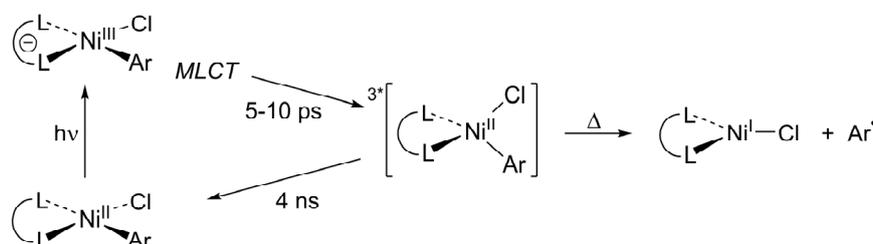


Figure 7. Photoexcitation of σ -organonickel(II) complexes initially populates a short-lived MLCT state that relaxes to a longer-lived metal-centered ($^3\text{d-d}$) excited state, from which Ni-aryl bond homolysis can occur under further (thermal) activation.

8. Conclusions and outlook

Important progress has been made in recent years concerning the elucidation of photochemical reaction pathways and photophysically relevant species in nickel based cross coupling catalysis. Latest in-depth photochemical studies by several independent research groups point toward the importance of dark, more or less self-sustained $\text{Ni}^{\text{I}}/\text{Ni}^{\text{III}}$ cycles (Figure 3b), rather than initially proposed $\text{Ni}^{\text{0}}/\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}/\text{Ni}^{\text{I}}$ cycles (Figure 3a).^[22c, 40] Moreover, it seems that energy transfer catalysis^[49] could play a more important role than photoredox catalysis in many cases. Key intermediates such as G in Figure 3c have triplet excited states from which reductive elimination to yield cross coupled products can readily occur in unimolecular fashion.^[3, 46] Another widely relevant key intermediate is species B in Figure 3a/c (with a halogenide ligand X), which has now been demonstrated to have an energetically low-lying metal-centered ($^3\text{d-d}$) excited state (ca. 0.5 eV above the electronic ground state) with tetrahedral geometry, from which Ni-aryl bond homolysis can occur.^[10] Furthermore, the population of LMCT excited states in Ni^{II} -substrate complexes can initiate catalysis via the light-driven formation of Ni^{I} intermediates.^[20b, 20c]

These insights are fundamentally important and should facilitate the rational design of chemical reactivity from electronically excited states. This research avenue has great potential for the future, because bond-forming reactions in

organic synthesis traditionally rely on ground-state species whereas the excited states of metal complexes have remained largely unexploited in that context.

Compared to complexes of other first-row transition metals such as chromium,^[50] copper^[8c, 8d] or iron,^[51] the photophysical and photochemical properties of nickel complexes are still underexplored. Very recently, new ligands have been developed to engage Ni^{II} complexes in other types of photoredox catalysis^[52] or to obtain luminescent Ni⁰ or Ni^{II} complexes.^[13, 53] The insights gained in the course of mechanistic investigations of combined photoredox and nickel catalysis are very encouraging for further development and exploration of photoactive nickel complexes, in order to access unusual photochemistry that goes beyond the traditional single-electron transfer reactivity. Research along these lines will likely be of interest to physical-inorganic and organic-synthetic chemists alike, and consequently this field holds much promise for the future.

Acknowledgments

Funding by the Swiss National Science Foundation through grant number 200021_178760 and through the NCCR Molecular Systems Engineering is gratefully acknowledged.

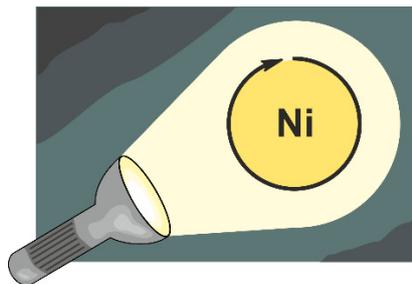
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Table of contents



Photophysically and photochemically relevant aspects of light-driven cross coupling reactions by nickel catalysis are reviewed. The importance of energetically low-lying triplet excited states is highlighted.

Keywords: cross-coupling, photocatalysis, energy transfer, electron transfer, photophysics