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# Circumventing metallic intrinsic reactivity: radical generation with redox-active ligands

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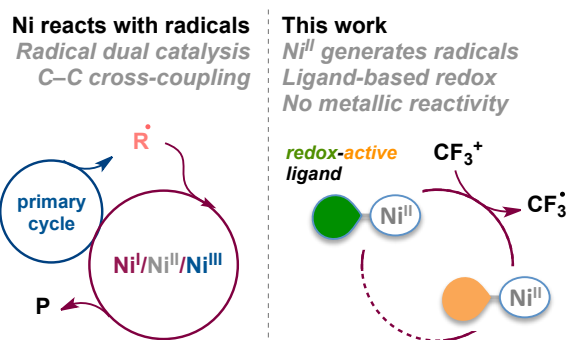
**Abstract:** Nickel complexes have gained sustained attention as efficient catalysts in cross-coupling reactions and co-catalysts in dual systems due to their ability to react with radical species. Central to this reactivity is nickel's propensity to shuttle through several accessible redox states from Ni<sup>0</sup> to Ni<sup>IV</sup>. Here, we report the catalytic generation of trifluoromethyl radicals from a nickel complex bearing redox-active iminosemiquinone ligands. This unprecedented reactivity is enabled through ligand-based oxidation performing electron transfer to an electrophilic CF<sub>3</sub><sup>+</sup> source while the nickel oxidation state is preserved. Additionally, extension of this reactivity to a copper complex bearing a single redox equivalent is reported, thus providing a unified reactivity scheme. These results open new pathways in radical chemistry with redox-active ligands.

The generation of radical species by organometallic catalytic manifolds is an area of intense investigation, largely sustained by the current interest in channeling their inherent high reactivity into productive catalytic systems. Among the leading methods for the generation of radicals are photoredox organometallic<sup>1</sup> and organic<sup>2</sup> manifolds. Both systems have garnered increasing attention due to the mild and easy-to-handle use of visible light as a cheap and waste-free activation source. Generation of radicals by these systems usually implies single-electron transfer (SET) between the photoinduced excited state of the catalyst and an organic substrate.<sup>3</sup>

Radical dual catalysis hinges on the productive merger of two sequential mono- and bis-electronic catalytic cycles. This field is at the forefront of task-performing systems for the synthetic integration of radicals generated by a primary cycle into a secondary catalytic cycle.<sup>4</sup> Regarding the secondary catalytic cycle, a number of radical dual strategies involve nickel complexes, capitalizing on this metal's intrinsic ability to react with radicals and adopt several oxidation states (from Ni<sup>0</sup> to

Ni<sup>IV</sup>).<sup>5</sup> This behavior has been a stepping stone in the development of efficient catalytic methods<sup>6</sup> and has provided a wealth of synthetic opportunities.<sup>7</sup>

Due to their unique electronic properties, redox-active ligands display an innate ability to promote ligand-centered redox events. This striking feature can be used to alleviate metal-centered redox events, thus providing promising opportunities to develop alternative catalytic systems based on earth-abundant metals and/or provide new reactivity profiles altogether.<sup>8</sup> Recent reports have established the possibility of fostering single-electron behavior with palladium complexes<sup>9</sup> bearing redox-active amidophenolate ligands.<sup>8h</sup> In the case of electrocatalytic C–C coupling reactions with Ni-diimine complexes, spectroscopic evidences point towards a mechanism involving in the most reduced form a ligand-centered reduction.<sup>10</sup> We have recently reported the use of a copper complex Cu(L<sub>SQ</sub>)<sub>2</sub> bearing non-innocent redox iminosemiquinone (SQ) ligands for the controlled generation of CF<sub>3</sub><sup>•</sup> radicals and their application to the trifluoromethylation of heteroaromatics and silyl enol ethers, and the hydrotrifluoromethylation of alkynes.<sup>11</sup> The redox iminosemiquinone ligand used in this system was shown to sustain the SET occurring between an electrophilic CF<sub>3</sub><sup>+</sup> source and the complex, thereby being oxidized to the iminobenzoquinone (BQ) form while the oxidation state of the metal center is preserved.



**Figure 1.** Classical nickel reactivity with radicals (left) and radical generation for nickel complexes enabled by redox-active ligands (right).

Here, we show that the use of such ligands can allow unprecedented nickel-catalyzed generation of trifluoromethyl radicals (Fig. 1). The redox transfer occurring between the electrophilic source and the nickel complex **1** is sustained by the redox-active ligand, thus overriding metal-based redox reactivity. We also report that the copper-catalyzed SET reactivity can be extended to another family of redox ligands bearing a single

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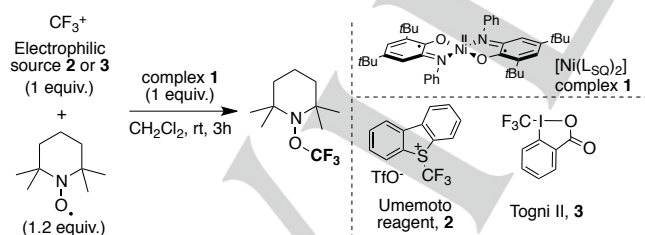
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“redox equivalent”, thus aiming towards the generalization of this approach.

In contrast with nickel's well-known affinity towards radicals, generation of radical species by nickel complexes is less documented but has been implicated in nickel-catalyzed cross-coupling reactions.<sup>6c,f,g</sup> Metal-centered redox transfers are involved in these examples but possible implication of a bipyridine ligand by delocalization of electronic density was reported in the nickel-based formation of carbon-centered radicals from an alkyl halide.<sup>12</sup> Stepping away from alkyl radicals, generation of  $\text{CF}_3^\bullet$  radicals from nickel complexes has been reported by Vicic through homolytic splitting of Ni– $\text{CF}_3$  bond in BOXAM<sup>13</sup> and terpyridine<sup>14</sup> nickel complexes. Interestingly, in the former case, study of the singly oxidized radical complex before dissociation showed a high extent of ligand-based oxidation at the BOXAM ligand. Although stoichiometric and occurring from preformed Ni– $\text{CF}_3$  complexes, these examples provide insights into the possible role of ligands in the generation of  $\text{CF}_3^\bullet$  radical species from nickel complexes.

We were curious to explore the possibility of using redox ligands as a chemical handle towards the production of radical species by a nickel complex through ligand-based electronic transfer. The nickel complex used in this work is  $\text{Ni}(\text{L}_{\text{SQ}})_2$  (complex **1**, see SI for preparation, Figure S1, tables S1 and S2 for X-Ray structure determination), a  $\text{Ni}^{\text{II}}$  complex bearing two redox-active iminosemiquinone ligands. Its electronic structure was reported as a singlet diradical with a diamagnetic  $d^8$  central metal ion and two strongly antiferromagnetically coupled SQ radical ligands (see SI Figures S2-4 and Table S3 for theoretical data).<sup>15</sup> No catalytic activity has been reported to date with this complex but related complexes with coordination spheres featuring iminosemiquinone-based motifs have been prepared,<sup>16</sup> and more recently studied in heterobimetallic Au/Ni complexes.<sup>17</sup> The initial assessment of our working hypothesis was carried out through TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl radical) trapping experiments (Table 1). Indeed, upon reacting complex **1** with an electrophilic  $\text{CF}_3^+$  source (**2** or **3**), the corresponding TEMPO– $\text{CF}_3$  adduct was observed by <sup>19</sup>F NMR spectroscopy, thus suggesting the formation of a  $\text{CF}_3^\bullet$  radical in the reaction medium.



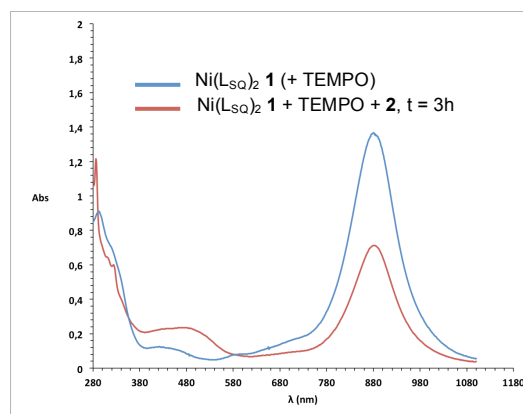
**Table 1.** TEMPO trapping experiments for the generation of radicals by complex **1**.

entry	complex	$\text{CF}_3^+$ source	Time	TEMPO– $\text{CF}_3$ Yield <sup>[a]</sup> (Conv.) <sup>[b]</sup>
1	$\text{Ni}(\text{L}_{\text{SQ}})_2$ <b>1</b>	<b>2</b>	3h	66 % (100 %)
2	$\text{Ni}(\text{L}_{\text{SQ}})_2$ <b>1</b>	<b>3</b>	3h	70 % (100 %)

3	$\text{Ni}(\text{L}_{\text{SQ}})_2$ <b>1</b>	<b>2</b> (2 equiv.) <sup>[b]</sup>	24h	57 % (75 %)
4	$\text{Ni}(\text{L}_{\text{SQ}})_2$ <b>1</b>	<b>3</b> (2 equiv.) <sup>[b]</sup>	24h	46 % (100 %)

[a] Yields were determined by <sup>19</sup>F NMR spectroscopy with fluorobenzene as an internal standard and calculated considering the trifluoromethylating agent as limiting reactant. [b] 2.4 equiv. of TEMPO were used.

UV-vis spectroscopy is an efficient tool for the monitoring of such electron transfer reactions as the original complex **1** displays an intense intervalence charge transfer band (IVCT) at  $\lambda = 880$  nm, due to the presence of two redox active iminosemiquinone ligands (Figure 2, blue trace). Similarly to earlier findings,<sup>11</sup> no reaction was found to occur between **1** and TEMPO. Upon reaction of complex **1** with the  $\text{CF}_3^+$  source, one would expect the formation of  $\text{Ni}(\text{L}_{\text{SQ}})(\text{L}_{\text{BQ}})^+$  complex **4** where one of the SQ ligands has been oxidized upon ligand-based SET to a BQ ligand, as is observed in the case of the copper complex.<sup>11</sup> However, the recorded UV-vis spectrum for the TEMPO-trapping experiments with complex **1** and  $\text{CF}_3^+$  source **2** (Figure 2 red trace) shows a decrease of only 50% of the IVCT band at 880 nm, with an additional band growing around 480 nm similar to the electronic absorption signature of  $\text{Ni}(\text{L}_{\text{BQ}})_2^{2+}$  **5** (SI Figure S5). This spectrum displays the same profile as an equimolar mixture of complexes  $\text{Ni}(\text{L}_{\text{SQ}})_2$  **1** and fully oxidized  $\text{Ni}(\text{L}_{\text{BQ}})_2^{2+}$  **5** (see SI for preparation and Figure S5 green trace). Monitoring the reaction by UV-vis at 25°C under argon atmosphere, shows a slow direct conversion of **1** to **5** which was illustrated by the presence of two isosbestic points at 360 nm and 590 nm (SI, Figures S6 and S7). These results are however not surprising and in agreement with the electrochemical studies reported by Wieghardt et al.,<sup>15</sup> which have shown a 2e-reversible oxidation wave for the  $\text{Ni}(\text{L}_{\text{BQ}})_2^{2+}/\text{Ni}(\text{L}_{\text{SQ}})_2$  redox couple (see Figure S8 and table S4). The latter proceeds via an ECE (Electrochemical Chemical Event) mechanism with two successive SET.

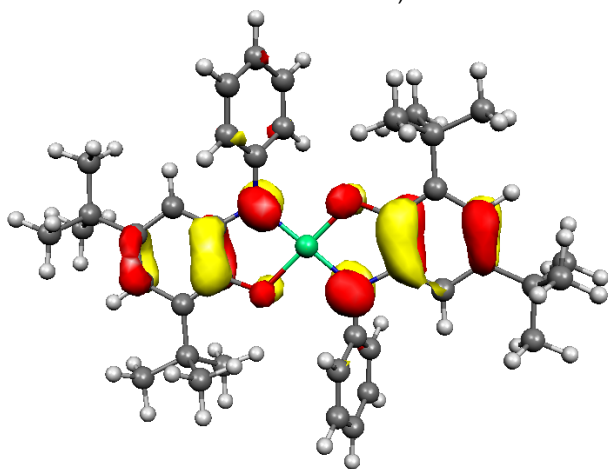


**Figure 2.** UV-vis studies for TEMPO-trapping experiments with complex **1** and  $\text{CF}_3^+$  source **2**.

To get insight into the nature of the intermediate resulting from SET from complex **1** to the  $\text{CF}_3^+$  source we have undertaken DFT calculations. The structure of the putative species was subjected to geometry optimization (Figure S9) and its electronic structure was investigated. Our results indicate that the Singly

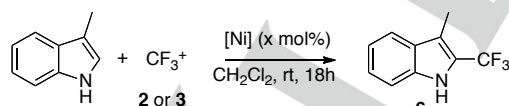
Occupied Molecular Orbital (SOMO, Figure 3) is a delocalized  $\pi$ -orbital essentially distributed over the iminosemiquinone moieties of the system (Figure S10). The intermediate is best described as a ligand-based radical species with a doublet  $S=1/2$  ground spin state, consistent with the formation of a  $\text{Ni}^{\text{II}}(\text{L}_{\text{SQ}})(\text{L}_{\text{BQ}})^+$  species (Table S5), which would support path A (see SI scheme S1).

On a related note, the observation of a redox-induced coordinative rearrangement from an hemilabile bis-SQ-derived nickel complex upon single-electron oxidation has been reported, which supports this transient instability.<sup>16c</sup> Nevertheless, the observation of the signature of  $\text{Ni}(\text{L}_{\text{BQ}})_2^{2+}$  **5** in these UV-vis experiments clearly indicates that, in the SET transfer to  $\text{CF}_3^+$ , the resulting oxidation of **1** is *ligand* centered (see SI Figures S10-11 and Table S4 for theoretical data).



**Figure 3.** Localized SOMO for putative species  $[\text{Ni}(\text{L}_{\text{SQ}})(\text{L}_{\text{BQ}})]^+$  **4** resulting from SET between complex  $\text{Ni}(\text{L}_{\text{SQ}})_2$  **1** with  $\text{CF}_3^+$  source.

Investigation of the synthetic applicability of these observations was implemented by reacting a catalytic amount of complex **1** with the electrophilic  $\text{CF}_3^+$  source and an organic substrate (Table 2). The isolation of trifluoromethylated product **6** from the reaction with 3-methylindole as the substrate shows that this reactivity can be useful synthetically.



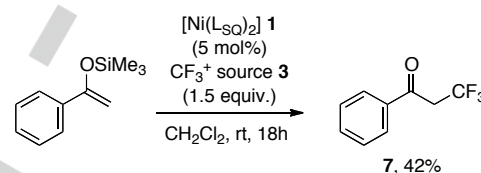
**Table 2.** Optimization studies for the transfer of generated  $\text{CF}_3^+$  radicals to 3-methylindole.

entry	[Ni] source	x (mol%)	Substrate equiv.	$\text{CF}_3^+$ source (equiv.)	Yield <sup>[a]</sup>
1	$\text{Ni}(\text{L}_{\text{SQ}})_2$ <b>1</b>	20	4	<b>2</b> (1 equiv.)	12%
2	$\text{Ni}(\text{L}_{\text{SQ}})_2$ <b>1</b>	20	4	<b>3</b> (1 equiv.)	69%
3	$\text{Ni}(\text{L}_{\text{SQ}})_2$ <b>1</b>	20	1	<b>3</b> (1.5 equiv.)	73% 78% <sup>[b]</sup>

4	$\text{Ni}(\text{L}_{\text{SQ}})_2$ <b>1</b>	5	4	<b>3</b> (1 equiv.)	38%
5	$\text{Ni}(\text{acac})_2$	20	1	<b>3</b> (1.5 equiv.)	20%
6	$\text{NiCl}_2(\text{dme})$	20	1	<b>3</b> (1.5 equiv.)	2%
7	none	-	4	<b>3</b> (1 equiv.)	traces

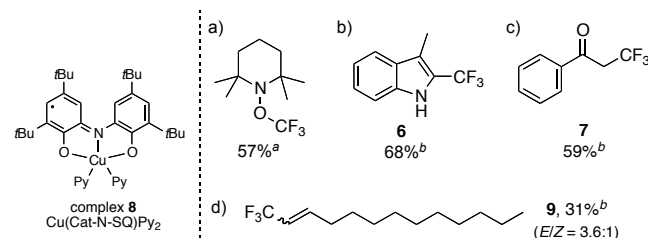
[a] Yields were determined by  $^{19}\text{F}$  NMR spectroscopy with fluorobenzene as an internal standard. [b] Isolated yield.

Optimal conditions were found to involve 20 mol% of complex **1** and 1.5 equiv. of  $\text{CF}_3^+$  source **3**. Under these conditions, expected trifluoromethylated adduct **6** was obtained in 78% yield (entry 3). Interestingly, substituting isolated complex **1** with  $\text{Ni}(\text{acac})_2$  or  $\text{NiCl}_2(\text{dme})$  (entries 5 and 6) proved detrimental to the reaction, thus underscoring the central role of the redox-active ligand. Also, control experiments confirm that the reaction does not work without catalyst. The reactivity observed towards the indole-based structure was successfully extended to the formation of  $\alpha$ -trifluoromethylated ketone **7** in 42% yield (from starting trimethylsilyl enol ether) (Scheme 1).



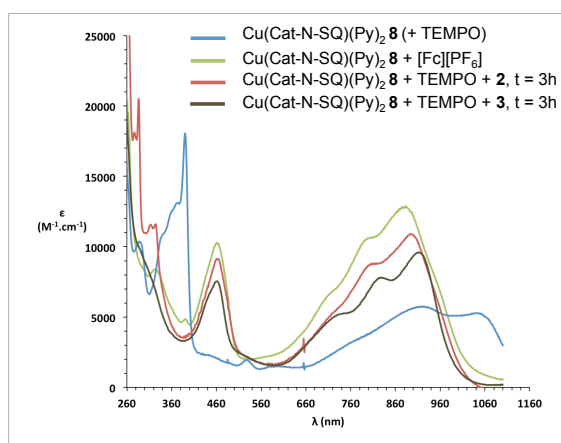
**Scheme 1.** Trifluoromethylation of a silyl enol ether by complex **1**.  $^{19}\text{F}$  NMR yield was determined using fluorobenzene as internal standard.

Since the generation of radicals by SET between a redox-active complex and an oxidative source should inherently require only one electron from the ligand, it occurred to us that the use of two redox ligands was superfluous and that this reactivity should be feasible with complexes having only one "redox-equivalent" ligand. We selected the redox O,N,O ligand Cat-N-SQ (Cat=catechol, scheme 2)<sup>18</sup> and the reasons for this choice are three-fold (i) structural proximity with the original SQ ligand, (ii) distinct tridentate coordination sphere and (iii) only one oxidized state available. The nickel complex bearing one Cat-N-SQ ligand cannot be isolated as only the  $(\text{Cat-N-SQ})_2\text{Ni}$  complex is recovered.<sup>18a</sup> However,  $[\text{Cu}^{\text{II}}(\text{Cat-N-SQ})(\text{Py})_2]$  complex **8** is readily available<sup>18b</sup> and, considering our previous results on SET performed by copper complex  $\text{Cu}(\text{L}_{\text{SQ}})_2$  **1**,<sup>11</sup> its reactivity was investigated. Interestingly, complex **8** exhibits a similar behavior and TEMPO- $\text{CF}_3$  adduct was isolated in 57% yield (Scheme 2). Furthermore, complex **8** performs trifluoromethylation to provide compounds **6** and **7** in 68% and 59% yield respectively, and hydrotrifluoromethylation of 1-dodecyne in 31% yield.



**Scheme 2.** Generalization to a copper complex bearing a single redox equivalent.<sup>a</sup> CF<sub>3</sub><sup>+</sup> source **2**, <sup>b</sup> CF<sub>3</sub><sup>+</sup> source **3**. Reaction conditions for TEMPO–CF<sub>3</sub> and compounds **6** and **7** are identical to optimized conditions from Tables 1 and 2, and scheme 1 respectively. Catalyst loading: 20 mol%.

The UV-vis profiles of the TEMPO-trapping reactions (Figure 4, red and black spectra) were a close match to the UV-vis spectrum recorded upon independent oxidation of complex **8** with one equivalent of [Fc][PF<sub>6</sub>] (ferrocenium hexafluorophosphate, green spectrum) thus evidencing ligand-based SET from complex **8** for the formation of CF<sub>3</sub><sup>+</sup> radicals. The EPR spectra of complex **8** before and after oxidation were recorded (SI, figure S12). As could be expected from the antiferromagnetic coupling between the ligand radical and the Cu<sup>II</sup> center (S=0 ground state), complex **8** is EPR silent (Figure S12 red trace).<sup>19</sup> After reaction with the CF<sub>3</sub><sup>+</sup> source in the presence of TEMPO, a strong axial signal with a *g*<sub>||</sub> of 2.26 and *A*<sub>||</sub> of 152G (Figure S12 black trace), typical of a Cu-centered S=1/2 spin (ie Cu<sup>II</sup>) center is obtained, presumably resulting from the one electron oxidation of the ligand to the diamagnetic L<sub>BQ</sub> form. These results show that a “single redox-equivalent” ligand is enough to promote the reactivity.



**Figure 4.** UV-vis spectra for TEMPO-trapping experiments of CF<sub>3</sub><sup>+</sup> source with complex **8**.

In conclusion, we have demonstrated that the use of redox-active ligands can outmanoeuvre nickel's intrinsic reactivity by promoting radical generation through single-electron transfer with an electrophilic CF<sub>3</sub><sup>+</sup> source, thus enabling previously unreported catalytic reactivity. The extension to another family of redox ligands provides an outlook towards a unified reactivity scheme and the generalization of SET reactivity from redox ligands. Collectively, these results pave the way for future developments in the controlled generation of highly reactive species by redox organometallic systems.

## Experimental Section

CCDC 1561909 (**1**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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**Keywords:** nickel • redox-active ligand • CF<sub>3</sub><sup>+</sup> radicals • single electron transfer

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- [19] As EPR is a very sensitive technique, traces of a Cu<sup>II</sup> species and of an organic radical have been detected, with an intensity more than 100 times lower than the final Cu<sup>II</sup> complex.

## Entry for the Table of Contents

## COMMUNICATION

**Electro[Ni]c.** Electronic transfer from a nickel complex bearing redox-active ligands to form radical species is studied. Combined UV-vis and DFT experiments suggest that the redox-active ligands in the complex sustains this reactivity, while metal-based reactivity is outmaneuvered. This reactivity can be extended to a complex bearing a single "redox-equivalent".

Nickel reacts with radicals  
Nickel reacts with radicals  
Nickel  radicals  
Nickel reacts with radicals  
Nickel reacts with radicals  
Nickel **generates** radicals

*Jérémy Jacquet, Khaled Cheaib, Yufeng Ren, Hervé Vezin, Maylis Orio, Sébastien Blanchard, Louis Fensterbank and Marine Desage-El Murr\**

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**Circumventing metallic intrinsic reactivity: radical generation with redox-active ligands**