

RESEARCH ARTICLE

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Mechanochemical access to NDI-bridged Janus di-NHC complexes for light-driven redox-responsive catalysis

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We describe the mechanochemical synthesis of previously inaccessible NDI-bridged Janus di-N-heterocyclic carbene (di-NHC) rhodium and iridium binuclear complexes, overcoming oxidative degradation pathways associated with conventional solution-based methods. These systems exhibit strong electronic communication between the redox-active naphthalene diimide (NDI) core and the metal centers, enabling reversible access to three distinct electronic states, as supported by spectroscopic, electrochemical, and DFT studies. The rigid, electron-deficient NDI scaffold enforces well-defined metal–metal arrangements and imparts multistate electronic tunability, highlighting their potential as versatile platforms for redox-responsive catalysis and functional metallosupramolecular assemblies. The complexes undergo selective one-electron reduction either with cobaltocene or *via* visible-light irradiation in the presence of triethylamine, which acts as an efficient reductive quencher. Under these conditions, NEt_3 delivers catalytic performance comparable to that of cobaltocene in the activation of the NDI-di-NHC-di-iridium(III) system for the cycloisomerization of 4-pentynoic acid, while offering practical advantages such as lower cost, air stability, and milder, more controlled reactivity.

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Introduction

Over the past decade, Janus di-N-heterocyclic carbene (di-NHC) ligands¹ have emerged as powerful platforms for the development of unconventional supramolecular organometallic complexes² and homogeneous catalysts.³ Among these systems, Janus di-NHCs whose backbones are linked by polycyclic aromatic hydrocarbons (PAHs) are particularly relevant. Their planar and rigid architectures provide fixed and predictable metal–metal distances within the ditopic ligand, while the conjugated π systems of the polyaromatic scaffolds offer the potential for electronic communication between the coordinated metal centers.^{1c}

One of the most attractive features of Janus di-NHCs is the possibility of modulating their properties to suit specific applications. However, such modulation has largely relied on struc-

tural design, leading to ligand systems that are synthesized to be “task-specific” rather than inherently modulable or adjustable for a broader range of functions. The concept of ‘*in situ*’ adaptability is closely related to so-called SMART ligands, which can be switched, adapted, or tuned to meet the requirements of a given catalytic transformation.⁴ It also relates to the more recent concept of *adaptive* catalytic systems,⁵ a term that describes catalysts capable of adjusting their performance states in response to dynamic changes in the reaction environment.

NHCs fused to polycyclic aromatic hydrocarbons have already demonstrated a degree of adaptability, as their electronic properties can be subtly modulated through the addition of external π -stacking additives.⁶ Nevertheless, a major challenge in the field of Janus di-NHCs remains the development of systems that can be activated by multiple, orthogonal stimuli. Equally important is the design of complexes capable of modulating their properties across three or more discrete levels of electronic control, thereby enabling multi-tunable behavior tailored to the specific demands of a given application.

In this context, we have been particularly interested in merging the outstanding photophysical and electrochemical properties of naphthalene diimides (NDIs)⁷ with those of N-heterocyclic carbene (NHC) ligands. We initially developed a

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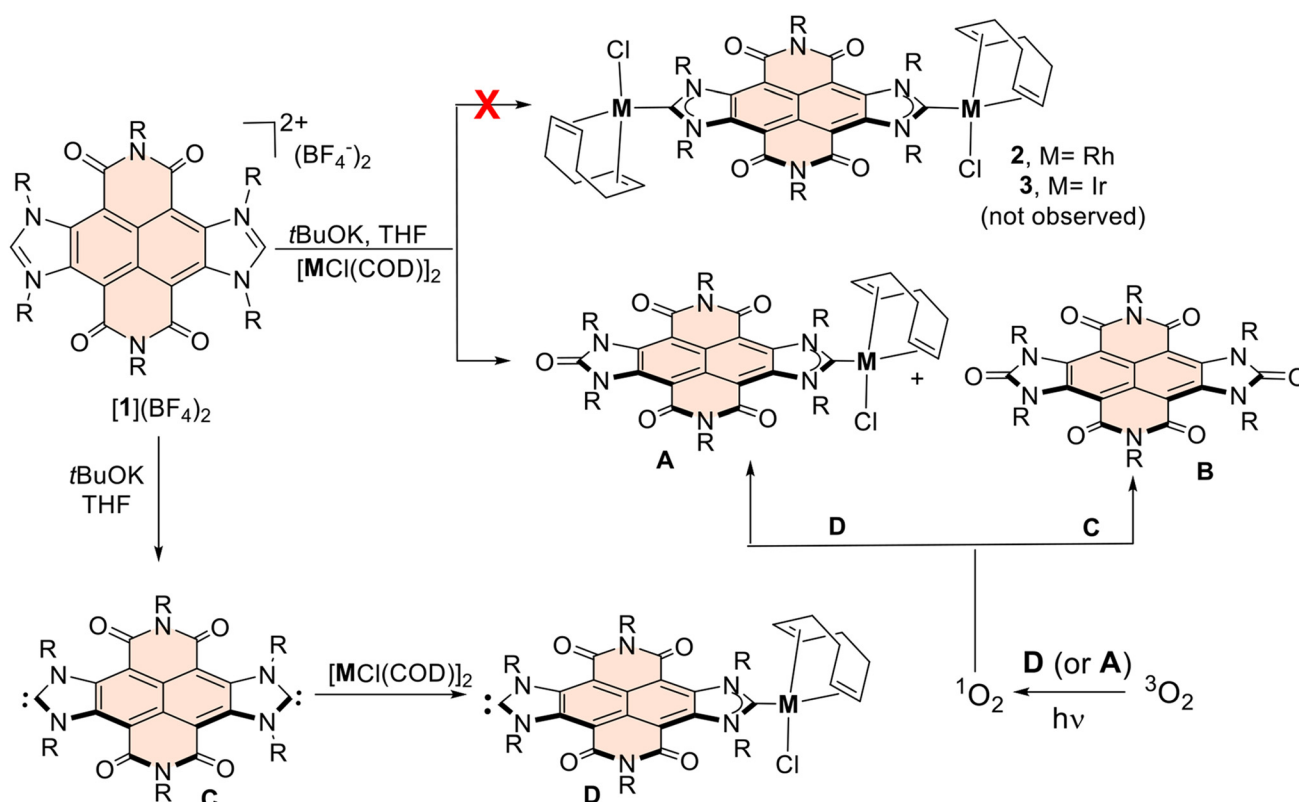
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family of NDI-NHC ligands and demonstrated that their metal complexes function as redox-switchable catalysts in several catalytic reactions.⁸ These studies showed that the redox activity of the NDI unit enables controlled and reversible modulation of the electron-donating properties of the NDI-NHC ligands. Notably, incorporation of the NDI core provides access to three distinct electronic states (neutral, one-electron reduced, and two-electron reduced), therefore constituting rare examples of multi-state redox-switchable catalysis.

Beyond their electrochemical behavior, NDIs also exhibit attractive photochemical properties with significant catalytic potential.⁹ We exploited these features by developing an NDI-NHC-Au(I) catalyst for oxidative C–C coupling reactions, including the coupling of aryldiazonium salts with alkynylsilanes and mesitylene.¹⁰ In addition, the pronounced positive quadrupole moment of NDIs makes them ideal platforms for probing anion- π ¹¹ and lone pair- π interactions,¹² owing to their strong affinity for electron-rich species. Leveraging this property, we recently designed halide-sensitive catalysts that can be reversibly switched between three activity levels upon addition of fluoride¹³ or chloride,¹⁴ leading to the introduction of the concept of Halide-Induced Switchable Catalysis (HISC).¹⁵

To combine the exceptional multi-stimuli responsiveness of NDIs with the broad applicability of Janus di-NHCs in catalysis

and metallocupramolecular chemistry, we previously synthesized an NDI-linked bis-imidazolium salt as a precursor to the corresponding NDI-bridged di-NHC binuclear complexes (Scheme 1).^{8a} We anticipated that this NDI-connected di-NHC ligand would enable access to new materials with multifunctional structural, optical, electronic, and magnetic properties, arising from through-space electronic communication and the multiple accessible redox states of the NDI core. We also expected the NDI-bis-imidazolylidene framework to resemble pyrene-linked di-NHCs structurally, while displaying markedly different electronic properties due to the strongly electron-deficient nature of the NDI scaffold. Unfortunately, despite our expectations, all attempts to access binuclear complexes supported by the NDI-bridged di-NHC ligand were unsuccessful. Instead, we exclusively obtained NHC-based mononuclear complexes, as the second carbene site consistently underwent oxidation to form an NHC=O cyclic urea (complex **A**, Scheme 1). In addition to the NHC-based mononuclear complex, we also observed the formation of significant amounts of the bis-urea product resulting from the oxidation of both NHCs (**B**, Scheme 1). This oxidation occurred irrespective of the coordination strategy employed for the NDI-connected bis-imidazolium precursor, and even under rigorously anhydrous conditions, strict inert atmosphere, and the use of strong or weak oxygen-free bases. The formation of cyclic ureas



Scheme 1 Products obtained from the reactions of NDI-connected bis-imidazolium salts with $[\text{MCl}(\text{COD})]_2$ ($\text{M} = \text{Rh}$ or Ir) under basic conditions. The formation of the cyclic ureas in **A** and **B** could be partially explained by the oxidation of the free NHC carbenes by $^1\text{O}_2$, photochemically generated by the mononuclear NDI-NHC complexes **A** or **D**.

from NHCs has been attributed to factors such as steric effects, hydrophilicity, and strong binding of NHCs to O₂ or H₂O,¹⁶ as well as to reductive elimination processes involving metal-bound NHCs and oxygen-containing bases¹⁷ (mechanisms that are considered among the principal decomposition pathways of NHC-based catalysts under strongly basic conditions). However, these explanations do not satisfactorily account for the persistent formation of the azolone (cyclic urea) observed in our system. In our case, we initially considered that carbene oxidation might arise from the photochemical generation of singlet oxygen (¹O₂), facilitated by reaction intermediates formed along the reaction pathway. This hypothesis is supported by our recent findings, which demonstrate that NDI-NHC-M complexes are highly efficient photosensitizers for the production of ¹O₂.¹⁰ We therefore reasoned that the presence of ¹O₂ in the reaction medium could account for the formation of oxidized NDI-bridged di-NHCs and this might also explain the consistent failure to obtain dinuclear complexes.

Given that the oxidation of singlet carbenes by ¹O₂ is well established,^{16a,18} we envisioned that metalation of the NDI-bridged di-imidazolium salt in the presence of a strong base would initially generate an NDI-bridged dicarbene species (**C**, Scheme 1). Upon addition of the metal precursor, **C** would coordinate to a mononuclear complex **D**, in which one NHC ligand is bound to the metal center while the second remains uncoordinated. Under light and in the presence of trace oxygen, this intermediate should efficiently generate ¹O₂, thereby promoting oxidation of the free NHC moieties in both **D** and **C** to yield compounds **A** and **B**, respectively. Accordingly, we hypothesized that suppressing this photochemical pathway could enable access to the desired NDI-bridged di-NHC dinuclear complexes.

As we are certain that access to NDI-connected di-NHC binuclear complexes could open new avenues in the design of homogeneous catalysts and metallocsupramolecular assemblies, we continued to search for alternative strategies capable of preventing oxidation of the NHC into undesired cyclic ureas. As all conventional methods proved unsuccessful, we turned our attention to two unconventional approaches. First, we decided to perform the coordination of our NDI-bridged bis-imidazolium salt in the absence of light and in the presence of a ¹O₂ quencher. As a second alternative, we turned our attention to mechanochemical approaches. Mechanochemistry offers an attractive alternative to traditional solution-based syntheses by enabling chemical transformations in the absence of light and in the absence of solvents, thereby reducing solvent waste and eliminating time- and energy-intensive purification steps.¹⁹ Despite these advantages, mechanochemical methods have been scarcely explored for the preparation of NHC-based complexes.²⁰

On this basis, we now report an efficient synthesis of a series of NDI-connected di-NHC binuclear complexes. Additionally, we also provide a comprehensive experimental and computational investigation of the structural and electronic properties of these complexes, which reveals distinctive features arising from the electron-deficient NDI scaffold and

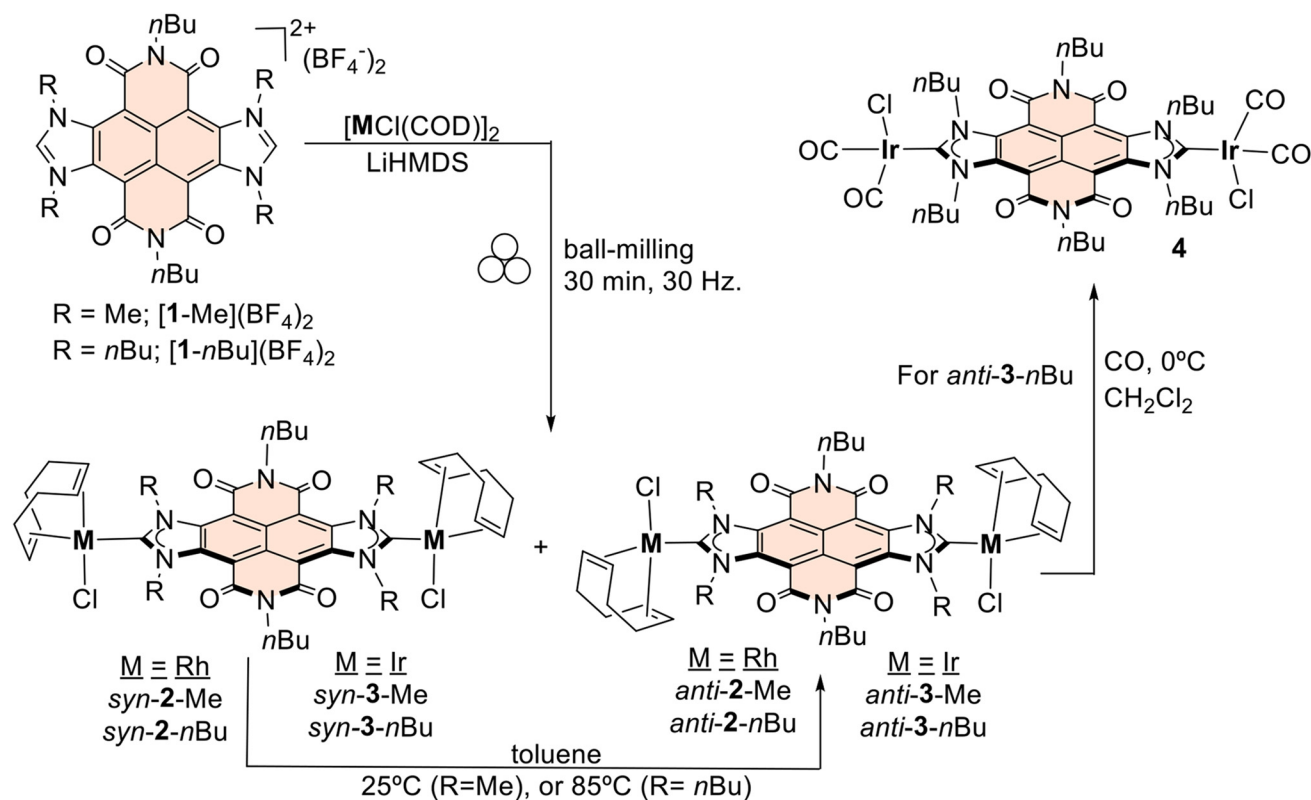
the enforced proximity of the two metal centers. As detailed in the following sections, these unprecedented characteristics establish a new platform for the development of advanced families of homogeneous catalysts and metallocsupramolecular assemblies with multi-responsive and tunable behavior.

Results and discussion

Our initial attempt to access the NDI-di-NHC-bridged dirhodium and diiridium complexes **2** and **3** involved reacting an equimolar solution of [1-*n*Bu](BF₄)₂ and [MCl(COD)]₂ (M = Rh, Ir) at 40 °C in the dark, in the presence of NaN₃, a known quencher of singlet oxygen.²¹ Under these conditions, the target complexes *anti*-2-*n*Bu and *anti*-3-*n*Bu (Scheme 2) were obtained, but only in very low yields (*ca.* 10%), along with significant amounts of byproducts arising from oxidation of the N-heterocyclic carbene (**A** and **B**, Scheme 1). Although this approach did not provide an efficient synthetic route to the desired dinuclear species, the partial suppression of oxidation supports the involvement of singlet oxygen, at least to some extent, in the degradation of the NHC ligands.

A much more efficient preparation of the NDI-di-NHC-bridged dirhodium and diiridium complexes **2** and **3** was achieved mechanochemically, by milling a mixture of [1-*n*Bu](BF₄)₂, [MCl(COD)]₂ (M = Rh, Ir) and lithium bis(trimethylsilyl) amide (LiHMDS) in a milling jar under argon atmosphere (Scheme 2). The reactions were carried out in the dark at room temperature for 30 minutes, and the resulting products were purified by column chromatography. The relative disposition of the [MCl(COD)] fragments with respect to the NDI plane is expected to give rise to two different atropisomers, namely, the *syn* isomer (in which the two chloride ligands are placed at the same side of the NDI plane), and the *anti* isomer (with the two chloride ligands on opposite sides of the NDI plane). In the reactions with [1-Me](BF₄)₂, only a single product was obtained: *anti*-2-Me (M = Rh; 74% yield) and *anti*-3-Me (M = Ir; 75% yield). In this case, the small size of the *N*-methyl substituents of the NDI fragment facilitates free rotation about the C-M bond, resulting in rapid interconversion in solution of the two rotamers (*syn* and *anti* atropisomers). In contrast, similar reactions with [1-*n*Bu](BF₄)₂ afforded the two atropisomers, as the bulkier *n*-butyl group exerts sufficient steric hindrance to restrict C-M bond rotation. Chromatographic separations provided the *syn* and *anti* isomers in 54% and 18% yields, respectively, for rhodium (*syn*-2-*n*Bu and *anti*-2-*n*Bu), and in 58% and 19% yields for iridium (*syn*-3-*n*Bu and *anti*-3-*n*Bu). These results indicate that formation of the *syn* atropisomers is kinetically favored over that of the *anti* counterparts.

Thermal treatment of the isolated *syn* rhodium and iridium complexes in toluene at 85 °C for 6 h led to quantitative conversion into the corresponding *anti* atropisomers, indicating that the *anti* form is thermodynamically favored. Consistently, when the crude reaction mixtures obtained from [1-*n*Bu](BF₄)₂ with [MCl(COD)]₂ were dissolved in toluene and heated at 85 °C for 6 hours, then only the *anti* complexes were isolated,



Scheme 2 Preparation of the NDI-di-NHC-connected dinuclear complexes **2** (Rh) and **3** (Ir).

in yields of 72% for rhodium (*anti-2-nBu*) and 77% for iridium (*anti-3-nBu*). This result is remarkable because, whereas solution-based protocols systematically led to exclusive formation of oxidized NHC-derived ureas, the mechanochemical approach selectively delivers the desired binuclear complexes, highlighting a profound change in reaction selectivity.

All complexes **2** and **3** were characterized by means of NMR spectroscopy and mass spectrometry. All details about the experimental characterization of these complexes can be found in the SI.

Single crystals of *anti-2-nBu* suitable for X-ray diffraction studies were obtained by slow diffusion of hexane into a chloroform solution of the complex (Fig. 1). The molecular

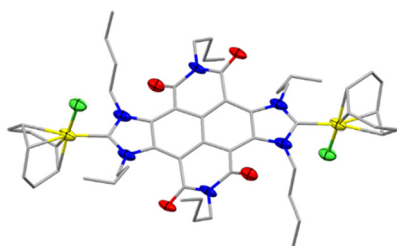


Fig. 1 Molecular structure of complex *anti-2-nBu* obtained from a single crystal X-ray diffraction study. Rhodium atoms are in yellow, nitrogen atoms in blue, oxygen atoms in red and carbons in grey. Ellipsoids shown at 50% probability level.

structure consists of an NDI-connected-di-NHC ligand bridging two rhodium atoms, which complete their coordination spheres with a 1,5-cyclooctadiene (COD) ligand and a chloride ligand. The hexacyclic NHC ligand consists of an NDI core flanked by two imidazolydene rings. All six nitrogen atoms of the NDI-di-NHC ligand are functionalized with *n*-butyl chains. The relative disposition of the chloride ligands relative to the NDI plane is *anti*, as the two ligands are pointing in opposite directions. The Rh–C(carbene) distance is 1.979 Å and the distance between the two metal atoms measures 13.00 Å. The two imide-functionalized six-membered rings deviate from the plane formed by the naphthalene moiety by an angle of 27.25°, measured as the dihedral angle between the plane formed by the four oxygen atoms of the imide rings and the naphthalene plane.

To assess the electron-donating properties of the NDI-di-NHC ligand, we synthesized the diiridium tetracarbonyl derivative **4** by bubbling CO into a dichloromethane solution of *anti-3-nBu* at 0 °C, as shown in Scheme 2. Complex **4** was characterized by NMR and infrared (IR) spectroscopy. The IR spectrum (CH_2Cl_2) displays two $\nu(\text{CO})$ stretching bands at 2074 and 1994 cm^{-1} . These values are slightly higher than those observed for the mono-iridium complex bearing the NDI-NHC ligand **A** (Scheme 1), which exhibits $\nu(\text{CO})$ absorptions at 2072 and 1991 cm^{-1} . The upshift in the CO stretching frequencies indicates that the ligand in **4** is less electron-donating than the NDI-NHC ligand in **A**. This behavior is most likely due to the

ditopic nature of the NDI-di-NHC ligand, whose electron-donating capacity is shared between two metal centers.

Cyclic voltammetry (CV) experiments for complexes *anti*-2-*n*Bu and *anti*-3-*n*Bu reveal two well-separated, reversible one-electron reduction processes (Fig. 2). For the rhodium complex *anti*-2-*n*Bu, these events occur at $E_{1/2} = -0.91$ and -1.31 V (vs. Fc^+/Fc), while for the iridium analogue *anti*-3-*n*Bu they are observed at -0.96 and -1.35 V (vs. Fc^+/Fc), respectively. In both complexes, the first reduction corresponds to one-electron reduction of the NDI core to the monoanionic radical species, whereas the second reduction is assigned to formation of the doubly reduced dianionic NDI unit.

Density functional theory calculations were performed to obtain a more detailed understanding of these two reduction processes and confirm that both reductions are ligand-centered, with no contribution from the metals. To ensure computational efficiency, all the calculations were performed with ethyl derivatives; the simplified models are referred to as *anti*-2 (Rh-complex) and *anti*-3 (Ir-complex). A comparative study was performed to confirm that their photophysical properties remain unaffected within this approximation (Fig. S42). The electronic spin-density plot of the mono-reduced species of *anti*-2 ($[\text{anti-2}]^{\cdot-}$ in Fig. S43) reveals strong delocalization of the unpaired electron over the entire NDI-di-NHC framework, rather than localization at a specific position on the naphthalene core.

In all cases, the peak potentials are independent of scan rate, consistent with electrochemically reversible processes. In addition, the CV traces of both complexes display a further redox feature at positive potentials, at 0.64 V for *anti*-2-*n*Bu and 0.62 V for *anti*-3-*n*Bu (vs. Fc^+/Fc), which is attributed to the quasireversible metal-centered oxidation between the +I and +II oxidation states. This is further confirmed by looking at the molecular electrostatic potential (MEP) maps reported in Fig. S45. The MEPs clearly reveal the electron-poor nature of

the NDI core and highlight a net depletion of electron density on the naphthalene core upon ligand substitution (bluer regions in the MEPs), which consistently accounts for the more positive reduction potentials observed for complex **4** compared to *anti*-3.

To elucidate the electronic consequence of the redox events, we investigated the structural and energetic evolution of the complexes upon reduction, at DFT level and employing the Absolutely Localized Molecular Orbital Energy Decomposition Analysis (ALMO-EDA) (see SI for more details, Fig. S46–S48). The inspection of the main geometrical parameters reported in Table S3, interestingly reveals the progressive elongation of the $\text{Rh-C}_{\text{carbene}}$ bond length from 2.013 Å (neutral) to 2.046 Å (dianion). The ALMO-EDA analysis provides an explanation of this geometrical effect, since it dissects the total interaction energy (ΔE_{INT}) between the metal centers and the carbene carbons of the di-NHC-NDI-ligand into three contributions: frozen interaction (ΔE_{FRZ}), polarization (ΔE_{POL}), and charge transfer (ΔE_{CT}).²² As shown in Fig. S46, the metal-ligand interface is characterized by a predominant CT (ΔE_{CT}) component, which indicates a high degree of covalency of the bond. Concerning the frozen interaction (ΔE_{FRZ}) which accounts for permanent electrostatics, Pauli repulsion, and dispersion, it remains positive across all redox states. This indicates that the assembly of the complex would be sterically and electrostatically repulsive in the absence of orbital relaxation. Consequently, the stability of the system is strictly dictated by charge transfer and, in less extent, by polarization, confirming the dominant covalent character of the Rh-NHC interaction. The covalency is further confirmed by the perturbative charge transfer (PCT) analysis reported in Fig. S47 which clearly indicates that the bond is governed by a robust σ -donation from the di-NHC lone pairs to the d_{π} -orbitals of the metal centers, with nearly symmetrical contributions to both sides of the bridge. This is accompanied by a modest π -backdonation, consistent with the low π -acidity typically reported for NHC ligands. The specific donor and acceptor orbitals involved in these interactions were identified through Complementary Occupied-Virtual Pairs (COVP)s analysis (Fig. S48). Upon reduction, the ALMO-EDA analysis reveals a decreasing of E_{PAULI} from 1752.7 to 1657.8 kJ mol^{-1} , indicating reduced steric/electronic repulsion, which drives geometrical relaxation as the metal fragments shift outward in response to the increased electron density of the NDI core. The polarization term, which accounts for the energy gain from the internal redistribution of electron density within fragments, increases from -154.9 kJ mol^{-1} (neutral) to -200.8 kJ mol^{-1} (dianion). This trend highlights the increased electronic “softness” or deformability of the reduced di-NHC-NDI framework, which enables the core to better accommodate the electric field of the metal centers, providing a significant secondary stabilization mechanism for the dianionic state (Fig. S46). Moreover, the PCT reveals that the π -backdonation drops significantly from ~ -65.5 kJ mol^{-1} (neutral) to ~ -39.5 kJ mol^{-1} (dianion). The resulting loss of partial double-bond character directly correlates with the observed $\text{Rh-C}_{\text{carbene}}$ bond

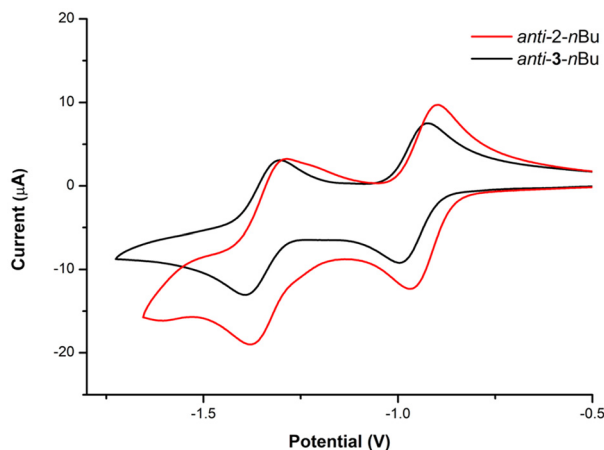


Fig. 2 Negative-potential region of the cyclic voltammogram of complexes *anti*-2-*n*Bu (red) and *anti*-3-*n*Bu (black) in dry CH_2Cl_2 (0.25 M $[(\text{nBu})_4][\text{PF}_6]$). Measurements were performed at 100 mV s^{-1} and referenced against ferrocene/ferrocenium.

lengthening. However, the σ -donation rises from ~ -203.7 kJ mol $^{-1}$ (neutral) to (~ -231.2 kJ mol $^{-1}$ (dianion)), ensuring that the complex remains highly stable in its reduced states, and is an indication of the stronger electron-donating ability of the di-NHC-NDI ligand upon reduction (Fig. S47).

The carbonyl complex **4** exhibits two reversible reduction waves at -0.67 and -1.10 V (vs. Fc^+/Fc), again corresponding to the stepwise one-electron reduction of the NDI moiety to the monoanionic radical and the doubly reduced dianionic species, respectively. Notably, these reduction potentials are significantly shifted to less negative values compared to those of the COD-containing complex *anti-3-nBu*, indicating that the decreased electron density at the metal centers upon substitution of COD by π -accepting carbonyl ligands substantially influences the redox behavior of the NDI ligand. This observation provides clear evidence for strong electronic communication between the NDI core and the metal centers.

The photophysical properties of the novel binuclear complexes were investigated using UV-Vis absorption and TDDFT calculations to gain deeper insights into their interaction with light (Fig. 3). The experimental absorption spectra of these complexes, shown in Fig. 3a, display broad low-energy absorption bands at 531 nm for *anti-2* and 565 nm for *anti-3*, along

with an additional intense absorption below 300 nm. The introduction of a second metal center within the backbone of the complex induces a bathochromic shift of the lowest-energy absorption bands relative to the corresponding monometallic complexes (**A**, Scheme 1),^{8a} amounting to 16 nm for Rh and 51 nm for Ir.

Computational studies are in agreement with the experimental values, especially for the iridium complex *anti-3*, predicting for it the lowest energy absorption band at 578 nm (vs. 565 exp), while a larger discrepancy was found for the rhodium complex *anti-2* (571 vs. 531 nm exp), as can be observed in Fig. 3b. Despite this difference, the bathochromic shift due to the change of metal was correctly reproduced. The excited state configurations were determined by computing the corresponding natural transition orbitals (NTOs) and by computing charge-transfer descriptors through fragment-based analyses.²³ The bright state is dominated by metal-to-ligand charge transfer (MLCT, $\sim 55\%$) from both metal centers to the NHC-NDI core, accompanied by an absorption of intraligand character ($\text{IL}_{\text{NHC-NDI}}$, $\sim 20\%$) and a further ligand-to-ligand charge transfer component from Cl/COD toward the NHC-NDI unit (LLCT, $\sim 20\%$). The highest energy band observed experimentally at 472 and 467 nm, for *anti-2-nBu* and *anti-3-nBu*, respectively, was characterized to have an $\text{IL}_{\text{NHC-NDI}}$ nature, while a further mixed $\text{IL}_{\text{NHC-NDI}}/\text{LLCT}$ transition was also computed at shorter wavelengths for both complexes, reproducing the very small intense band experimentally found at 390 and 420 nm, for *anti-2-nBu* and *anti-3-nBu*, respectively. The corresponding NTOs for all relevant transitions, Mos plots and further details on the electronic spectra are reported in the SI (Fig. S49–S52 and Tables S4–S6).

To complement the electrochemical data and characterize the electronic nature of the complexes, UV-Vis spectroelectrochemical (SEC) experiments were performed. As an example, the spectral evolution of the reduction of the di-iridium complex *anti-3-nBu* is shown in Fig. 4. The UV-vis spectrum of this complex in CH_2Cl_2 displays a vibronically resolved strong band centered at 550 nm, which is assigned to ligand-based transitions centered at the NDI unit. Upon applying a negative potential, the intensity of this band decreased, while a new band due to the one-electron reduced species [*anti-3-nBu*] $^{\cdot-}$ appears at 818 nm. Further reduction produced the disappearance of the bands due to the mono-reduced complex and the appearance of new broad bands at 667 and 615 nm, which are attributed to the formation of the two-electron reduced complex [*anti-3-nBu*] $^{2-}$. The transition between these three species occurred without the detection of reaction intermediates, as indicated by the presence of isosbestic points at 615 and 720 nm for the first and second reduction steps, respectively. This observation also indicates that the three species involved in the reduction process are fairly stable under the conditions used for the experiments. The UV-Vis-SEC experiment performed for the rhodium complex *anti-3-nBu* showed very similar behavior (see Fig. S35 in SI for full details).

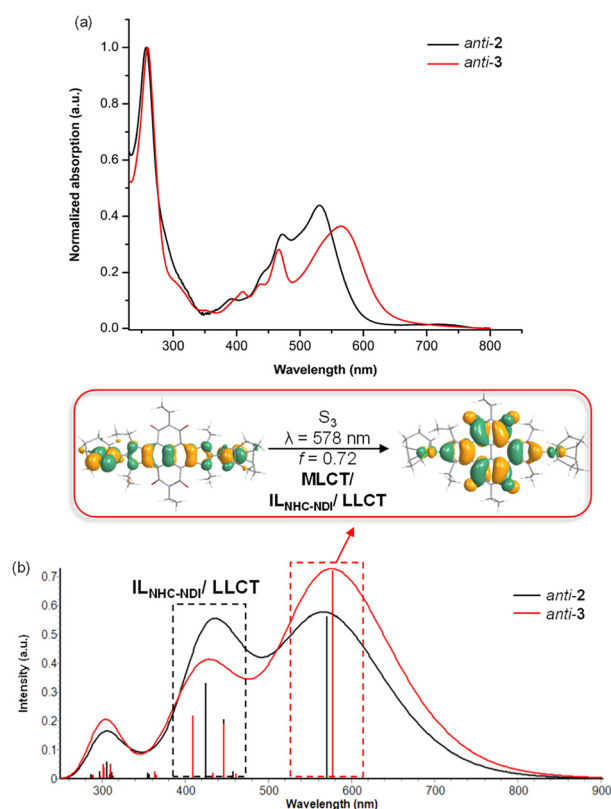


Fig. 3 (a) Experimental UV-Vis absorption spectra of *anti-2-nBu* (black) and *anti-3-nBu* (red) in dry CH_2Cl_2 . (b) Computed UV-Vis absorption spectra of *anti-2* (black) and *anti-3* (red) in CH_2Cl_2 at the M06/6-31+G(d,p)/SDD level of theory. Picture inset: Natural transition orbitals (NTOs) describing the bright absorption band for complex *anti-3*. MLCT refers to $\text{M} (\text{Rh}, \text{Ir}) \rightarrow \text{NHC-NDI}$, LLCT to $\text{Cl/COD} \rightarrow \text{NHC-NDI}$.

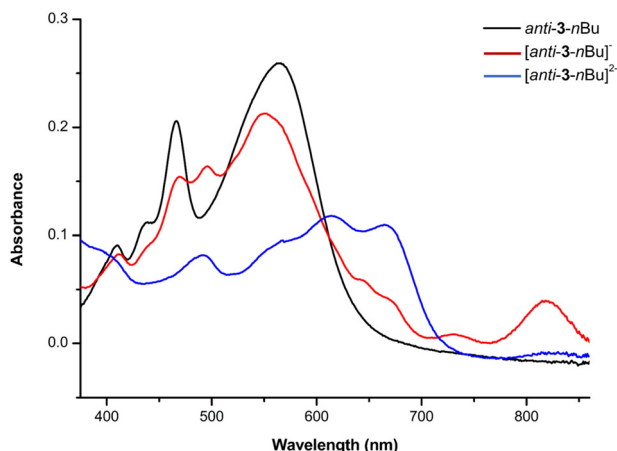


Fig. 4 UV-Vis SEC monitoring reduction of *anti*-3-*n*Bu in dry CH₂Cl₂ (0.1 M [N(*n*Bu)₄][PF₆]). The electrochemical reduction was performed applying progressively lower potentials with an Au working electrode, a Pt counter-electrode, and Ag wire pseudo-reference electrode. The solid lines represent the spectra of the starting (black), singly-reduced (red) and doubly-reduced (blue) species.

In order to get a deeper understanding about the nature of the reduced bands, we computed the spectra for the reduced forms of both complexes *anti*-2 and *anti*-3 (Fig. S53). Fig. 5 shows the computed spectra for neutral, mono-reduced and doubly reduced species of complex *anti*-3. Analysis of the spectra of the radical anion species [anti-3-*n*Bu]^{•-}, revealed a D₀ → D₁ transition, computed at 771 nm, with an IL_{NHC-NDI} character that reproduces the experimental band observed in the NIR at 820 nm. The bands observed experimentally at 565 and 496 nm for [anti-3]^{•-} were associated with two computed transitions at 514 (D₆) and 502 (D₇) nm for [anti-3]^{•-} (Fig. S56), with mainly an IL_{NHC-NDI} nature and a small MLCT and LLCT₂ (from Cl to NHC-NDI) character in D₆. The double-reduced species shows transitions computed at 674 (S₅) and 620 (S₈) nm for [anti-3]²⁻ characterized by a mixed IL_{NHC-NDI}/LMCT/LLCT' nature, associated with the bands experimentally observed at 667 and 615 nm, respectively. Here, the ligand-to-ligand charge transfer (LLCT) from the NHC-NDI core to Cl-COD can be explained considering the increased electron

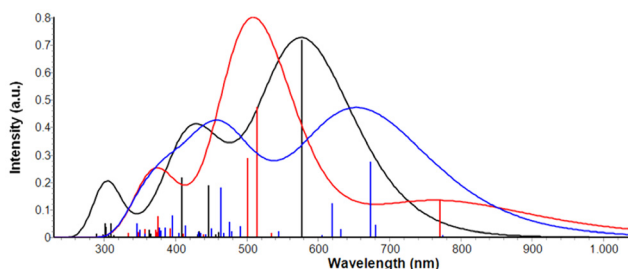


Fig. 5 Computed absorption spectra of neutral *anti*-3 (black), singly reduced (red) and doubly reduced (blue) species in CH₂Cl₂ at the M06/6-31+G(d,p)/SDD level of theory.

density on that moiety resulting from the reduction process. Further details are given in Fig. S54–S57.

To evaluate the effect of the reduction of the NDI unit on the electron density at the metal centers, we performed an infrared spectroelectrochemical (IR-SEC) study using the diiridium tetracarbonyl complex **4**. Fig. 6 displays the series of IR spectra recorded upon stepwise electrochemical reduction of the complex. Reduction of neutral complex **4** is accompanied by a decrease in intensity of the two $\nu(\text{CO})$ bands at 2074 and 1994 cm⁻¹, with the simultaneous emergence of two new bands at 2063 and 1984 cm⁻¹, which are assigned to the one-electron-reduced species [4]^{•-}. Further reduction at more negative potentials leads to the disappearance of these bands and the appearance of two additional $\nu(\text{CO})$ absorptions at 2055 and 1975 cm⁻¹, corresponding to the doubly reduced species [4]²⁻. Reapplication of a positive potential fully regenerates the neutral complex, demonstrating that both reduction processes are reversible.

Quantitatively, the first reduction induces an average shift in $\nu(\text{CO})$ of -11 cm⁻¹, while the second reduction produces an additional shift of -9 cm⁻¹. These stepwise shifts indicate that the electron density at the iridium centers can be increased in a tunable and fully reversible two-step manner through reduction of the NDI unit.

Notably, the magnitude of the $\nu(\text{CO})$ shifts closely matches that observed for the mononuclear NDI-NHC complex **A** (Scheme 1),^{8a} suggesting that the influence of NDI reduction on the electronic properties of the metal centers is largely independent of the number of metals coordinated to the NDI core. The lower electron-donating ability of the NDI-di-NHC ligand in *anti*-3-*n*Bu compared to the NDI-NHC ligand in Ir-**A** is further supported by inspection of the backdonation from Ir-d_π to the π*(CO) orbitals. The ALMO-EDA results for complex **4** provide that the back-donation energies associated with each -Ir(CO)₂ fragment amount to -374.8 kJ mol⁻¹ for one metal and -374.7 kJ mol⁻¹ for the other one, both of which are lower

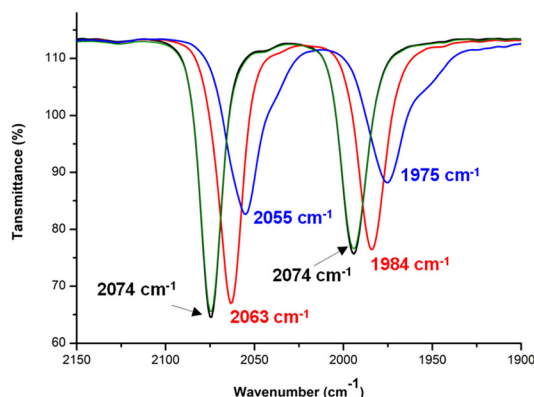


Fig. 6 IR-SEC monitoring reduction of **4** in CH₂Cl₂ (0.1 M [N(*n*Bu)₄][PF₆]). The lines represent the spectra of the starting (black), singly reduced (red) and doubly reduced (blue) species. Green line represents the spectrum of the species formed after applying positive potential to the doubly reduced species.

than the value calculated for the monometallic complex Ir-A(CO) ($-378.7 \text{ kJ mol}^{-1}$) (Table S7). Accordingly, slightly higher π -backdonation is predicted for Ir-A(CO), in agreement with the lower $\nu(\text{CO})$ observed experimentally.^{8a} These results also indicate that **4** features two nearly equivalent and electronically independent metal centers. COVP plots of the main donor and acceptor orbitals are reported in Fig. S58.

After thoroughly investigating the spectroscopic and electrochemical properties of our complexes, we turned our attention to achieving their reversible chemical reduction, as this underpins their potential application as redox-switchable catalysts. We selected *anti*-3-*n*Bu as the model complex for these studies. As shown by the UV-Vis spectra in Fig. 7a, treatment of *anti*-3-*n*Bu with one equivalent of cobaltocene in THF generates a new species whose spectrum matches that of the one-electron reduced complex [*anti*-3-*n*Bu]^{•−} (see Fig. 4 for the electrochemically generated analogue). The addition of further equivalents of cobaltocene does not lead to formation of the two-electron reduced species [*anti*-3-*n*Bu]^{2−}, indicating that cobaltocene enables selective one-electron reduction. Upon exposure of the solution to air for one minute, the UV-Vis spectrum confirms complete regeneration of the neutral *anti*-3-*n*Bu complex, demonstrating that the redox process is fully reversible under these chemical conditions.

We also explored whether reduction of the complex could be achieved photochemically. Given that NDIs have recently

been employed as efficient electro-photocatalysts,²⁴ we investigated whether the photoexcited species (*anti*-3-*n*Bu*) could undergo reductive quenching by triethylamine. NEt₃ is typically used in photochemistry, due to its ability to act as sacrificial electron donor (SED) or a reductive quencher of excited-state photosensitizers. As illustrated by the UV-Vis spectra in Fig. 7b, the addition of three equivalents of NEt₃ to a THF solution of *anti*-3-*n*Bu results in one-electron reduction of the iridium complex after a few minutes of visible-light irradiation. As before, bubbling air through the solution for a short period restores the neutral *anti*-3-*n*Bu complex quantitatively, confirming the reversibility of the process.

We also sought to determine whether this photochemically induced reduction could be extended to the tetracarbonyl complex **4**, as monitoring changes in the $\nu(\text{CO})$ stretching frequencies would provide direct insight into how the reduction influences the electron richness of the iridium center. As shown in Fig. 7c, irradiation of a solution of **4** with NEt₃ in DMSO results in an IR spectrum in which the two original C–O stretching bands of **4** are shifted to lower wavenumbers by 11 cm^{-1} . This shift is in strong agreement with the electrochemical reduction observed for the same complex (Fig. 6), thereby supporting the formation of [**4**]^{•−}.

Finally, we investigated whether reduction of the NDI moiety in our complexes influences their catalytic performance. To this end, we examined the cycloisomerization of 4-pentynoic acid to the corresponding exocyclic enol lactone, a reaction we have previously shown to be highly sensitive to the

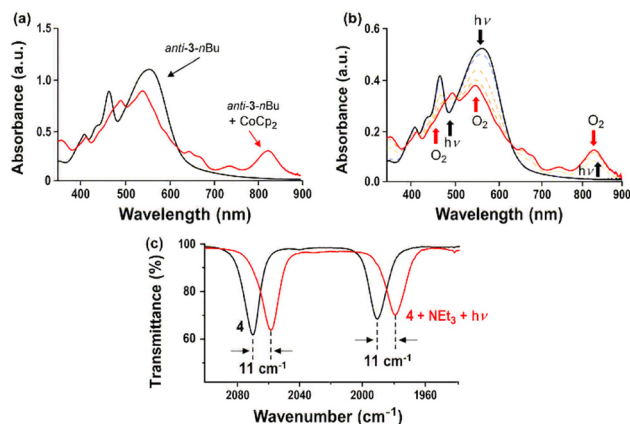


Fig. 7 (a) Chemical reduction of the *anti*-3-*n*Bu complex with cobaltocene in THF. The black line represents the UV-Vis spectrum of *anti*-3-*n*Bu, and the red line represents the spectrum of the compound after addition of 1 equivalent of CoCp₂. (b) Photochemically-induced reduction of *anti*-3-*n*Bu with NEt₃. The black line represents the UV-Vis spectrum of *anti*-3-*n*Bu with 3 equivalents of NEt₃ prior to irradiation. The three dotted lines correspond to the subsequent spectra recorded after irradiating with a white household lamp for 3, 5 and 10 minutes. The red line corresponds to the spectrum of the mixture after 15 minutes of irradiation. Black arrows indicate the evolution of the spectra during irradiation, while red arrows indicate the changes observed upon reoxidation of the sample with O₂ (air). (c) Photochemically-induced reduction of **4** with NEt₃. The black line represents the IR spectrum (THF) of **4** with 3 equivalents of NEt₃ prior to irradiation. The red line corresponds to the spectrum of the mixture after 5 minutes of irradiation.

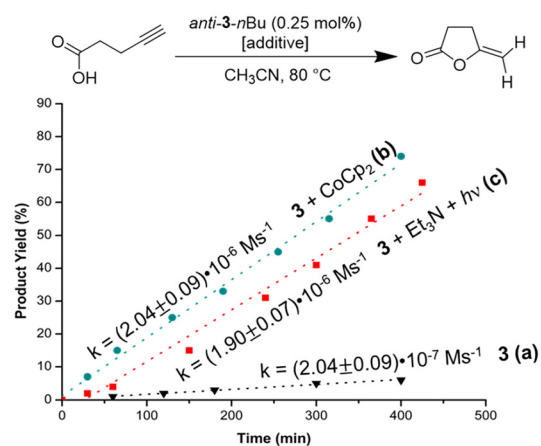


Fig. 8 Time-dependent reaction profiles for the cyclization of 4-pentynoic acid using (a) catalyst *anti*-3-*n*Bu, (b) catalyst *anti*-3-*n*Bu + cobaltocene, and (c) catalyst *anti*-3-*n*Bu + NEt₃ after 10 minutes of irradiation with visible light. The reactions were performed in CH₃CN and 80 °C, with an initial substrate concentration of 0.066 M and a catalyst loading of 0.25 mol%. The reaction carried out in the presence of cobaltocene was performed with a 0.25 mol% loading of CoCp₂ with respect to the substrate. The reaction performed with NEt₃ was carried out with a 2.5 mol% of the amine with respect to the substrate, and the solution was pre-irradiated for 10 minutes (no irradiation performed during the reaction course). Yields were determined by ¹H NMR spectroscopy, using 1,3,5-trimethoxybenzene as integration standard. Kinetic constants are also shown in the figure. **3** refers to *anti*-3-*n*Bu in the graphic.

electron-donating properties of ligands in Rh(I) and Ir(I) systems, making it an excellent model for redox-switchable catalysis.^{6d,8a,b,13} Reactions were conducted in acetonitrile at 80 °C using *anti*-3-*n*Bu (0.25 mol% catalyst, 0.5 mol% metal considering its dinuclear nature), and monitored by ¹H NMR spectroscopy. As can be observed from the time-dependent reaction profiles shown in Fig. 8, the reaction exhibits a zeroth order dependence on the substrate, in accordance with the reaction mechanism,^{6d} in which the substrate is coordinated to the coordination sphere of the metal in the resting state of the catalytic cycle. Under the reaction conditions used, *anti*-3-*n*Bu showed very low activity, affording only 6% product after 7 h (Fig. 8). In contrast, addition of one equivalent of cobaltocene (relative to the catalyst) increased the reaction rate by an order of magnitude, reaching ~90% yield after 7 h. A nearly identical catalytic profile was obtained when the reaction was performed with *anti*-3-*n*Bu in the presence of NEt₃, provided that the solution was pre-irradiated for 10 minutes to generate the singly reduced catalyst. As shown in Fig. 8, both systems exhibit essentially overlapping reaction profiles, demonstrating that reductive quenching of the photoexcited catalyst with triethylamine is a viable alternative to cobaltocene in organometallic redox-switchable homogeneous catalysis.

Conclusions

In summary, we now report the first successful synthesis of NDI-bridged Janus di-NHC dinuclear complexes, enabled by a mechanochemical strategy that overcomes the persistent limitations of conventional solution-based methods, which consistently led to oxidative degradation of the carbene sites. This solvent-free approach provides efficient and selective access to a family of rhodium and iridium complexes that had previously remained synthetically inaccessible, highlighting mechanochemistry as a powerful tool for the preparation of sensitive NHC-based organometallic architectures. We further demonstrate that oxidation of the NHC ligand to the corresponding cyclic urea can be attributed, at least in part, to singlet oxygen, likely generated by an intermediate NDI-NHC-M species.

A comprehensive combination of structural, spectroscopic, electrochemical, and spectroelectrochemical studies has revealed that the electron-deficient NDI scaffold plays a central role in dictating the electronic properties of these systems. The complexes exhibit two well-defined, reversible, ligand-centered reduction events, granting access to three discrete and stable redox states. Infrared spectroelectrochemical analysis of the corresponding carbonyl derivatives has shown that each reduction step induces a quantifiable and reversible increase in electron density at the metal centers, confirming that the NDI core functions as an efficient and tunable electronic reservoir capable of modulating metal-based reactivity in a stepwise manner.

Density functional theory calculations have provided a consistent framework for interpreting these observations, indicat-

ing that the two metal centers behave as electronically independent yet communication-enabled sites across all redox states. These findings underscore the importance of both through-space and through-ligand electronic communication in governing the optical and redox behavior of the complexes, and establish DFT as a valuable predictive tool for the rational design of future multi-responsive Janus di-NHC systems.

Importantly, these dinuclear complexes undergo selective one-electron reduction of the NDI moiety either *via* cobaltocene or through visible-light irradiation in the presence of triethylamine. The latter approach highlights the role of NEt₃ as an effective reductive quencher in photoactive organometallic systems, offering a practical alternative to cobaltocene for the design of redox-switchable catalysts. Notably, triethylamine provides clear advantages, including lower cost, air stability, ease of handling, and milder, more controlled reactivity with fewer side reactions. Consistent with this, NEt₃ delivers a catalytic performance comparable to that of cobaltocene in the activation of the dinuclear NDI-di-NHC-di-iridium(I) system for the cycloisomerization of 4-pentynoic acid.

Overall, this work expands the scope of Janus di-NHC chemistry by introducing a multifunctional, redox-active ditopic ligand that supports robust and electronically tunable binuclear architectures. By integrating mechanochemical synthesis with detailed experimental and computational analysis, this study establishes a versatile platform for the development of advanced homogeneous catalysts and metallosupramolecular systems whose structure and function can be reversibly modulated by external stimuli. Future efforts will focus on leveraging these properties to construct higher-order assemblies and cooperative systems with adaptive, multistate, and stimuli-responsive behavior.

Author contributions

F. Sangineto performed the characterization, catalytic studies and contributed to the computational studies. M. E. Alberto designed and performed the DFT studies. J. A. Cabeza designed the mechanochemical synthesis of the complexes. J. F. Reynes prepared the metal complexes through mechanochemical procedures. M. Poyatos and E. Peris designed and supervised all studies and wrote the preliminary draft of the manuscript. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

All data are included in the supplementary information (SI). Supplementary information: all the experimental details dealing with the synthesis, characterization, electrochemical

and spectroelectrochemical measurements, reactivity studies and catalytic experiments. The file also contains the data related to the crystallographic studies as well as the Cartesian coordinates of the optimized geometries. See DOI: <https://doi.org/10.1039/d6qi01077f>.

CCDC 2533065 contains the supplementary crystallographic data for this paper.²⁵

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