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Activation Barriers of Co(IV)-centered Reductive-Elimination Correlate with Quantified Interatomic Noncovalent Interactions.

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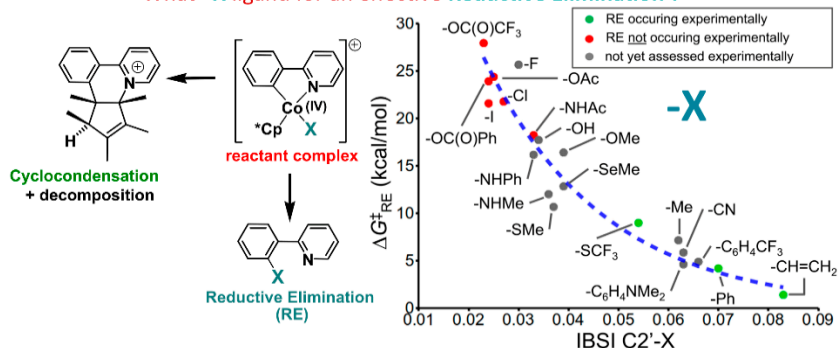
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What -X ligand for an effective Reductive Elimination ?



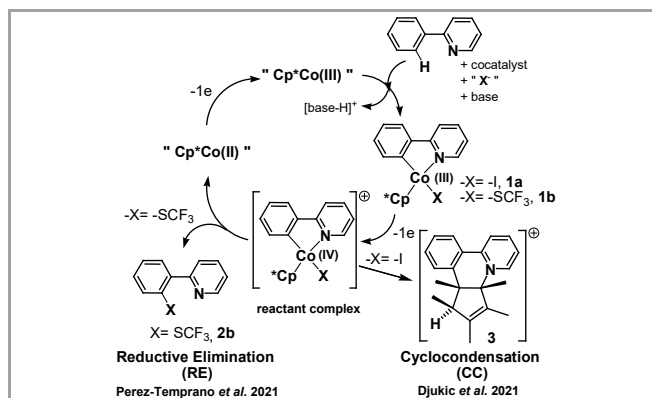
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Abstract In this joint theoretical and experimental study, the analysis of weak interligand noncovalent interactions within Co(IV) [Cp*Co(*phpy*)X]⁺ cobaltacycles (*phpy* = 2-phenylenepyridine, κ^{C,N}) was carried out using the the Independent Gradient Model/Intrinsic Bond Strength Index (IGM/IBSI) method to evaluate the dependency of the catalytically desired reductive elimination pathway (RE) on the nature of the -X ligand. It is shown that the barrier of activation of the RE pathway correlates directly with the IBSI of the X-to-carbanionic chelate's carbon. This correlation suggests that the *in silico* prediction of which -X ligand is more prone to operate an efficient Cp*Co-catalyzed directed X-functionalization of aromatic C-H bond is at reach. A set of experiments staging various sources of -X ligands supports the theoretical conclusions.

Key words Metallacycle; Cobalt; Density Functional Theory, Noncovalent Interactions.

Analyzing the role of the dispersion force and noncovalent interactions (abbr. NCI) in a broader sense is crucial in understanding the roots of molecular cohesion but also in apprehending the chemical reactivity of organometallic molecules.¹ Recently, a few reports² have indeed illustrated in depth this issue by establishing the existence of a favorable “NCI coding” in agostic reactant complexes as a prerequisite for effective C-H bond activation by a metal center in the Concerted Metalation Deprotonation mechanism (CMD³ also formulated as Ambiphilic Metal Ligand Activation -AMLA⁴-), i.e. one variant of the existing C-H bond activation mechanisms⁵ such as the Base-Assisted Intramolecular Electrophilic Substitution (BIES⁶). The upsurge of interest for 3d metal complexes⁷ and particularly for Co-containing ones as catalysts of C-H bond functionalization⁸ poses a wider mechanistic challenge: the engineering of new catalysts requires a control of both the chemoselectivity and the durability of the catalytically active species. Indeed, in two recent studies⁹ the central role of highly reactive transient Co(IV) metallacycles in C-H bond functionalization was outlined

(scheme 1) revealing that the nature of the X ligand, often introduced to functionalize the aromatic C-H bond,¹⁰ was crucial^{9b}: such Co(IV) reactant complexes may indeed potentially evolve by at least two main pathways, i.e. 1) the reductive elimination^{9a} (abbr. RE) desired in catalysis¹⁰ or 2) the undesired mere collapse^{9b} of the key Cp*Co motif by a cyclocondensation (abbr. CC) of the carbanionic chelating ligand with the Cp* ligand (scheme 1).



Scheme 1 Proposed C-H bond functionalization catalytic cycle staging Cp*Co complexes with a cyclocondensation (CC) quenching step, the extent of which depends on the nature of -X. Note that for -X = -Cl in **1a** cation **3** is also the dominant product, similarly to **1a**^{9b}. Cp* = η⁵-pentamethylcyclopentadienyl.

We showed that quantitatively evaluating the strength of noncovalent interactions existing between reactive centers in those pseudo-tetrahedral Co(IV) intermediates with the help of the Independent Gradient Model (IGM)¹¹/Intrinsic Bond Strength Index (IBSI)¹² analytical methods revealed propensities^{1a, 9b} towards either RE or CC. In the present letter, we disclose a theoretical & experimental joint study covering a choice of X ligands on the RE pathway using the IGM/IBSI analysis,

correlating its output to computed activation barriers, and evaluating those trends by experimental assessment.

A series of $[\text{Co(III)Cp}^*(\text{phpy})\text{X}]^+ \text{I}^+$ complexes, as well as their $[\text{Co(IV)Cp}^*(\text{phpy})\text{X}]^+ \text{[I]}^+$ counterparts, has been optimized at the DFT ZORA-PBE-D4(EEQ)/all electron TZP level of theory using COSMO(CH_2Cl_2) as a standard for implicit solvation (cf. SI for computational details and references). The transition states corresponding to the first and limiting step of the RE, i.e. the formation of the C-X bond, and to the suggested first and limiting step of one of most favorable mechanism of CC,^{9b} i.e. the one the prior formation of the C-C bond between *phpy* and Cp^* , have also been searched for and optimized at the same level of theory (Tables S1). Previous studies suggested that the oxidation of the Co(III) **I** complex to a Co(IV) **[I]**⁺ was required to trigger the RE.^{9a} To clarify whether or not this oxidation is mandatory, the RE activation energies at the Co(III) and Co(IV) states were compared. Note that, while the Co(IV) transition states were readily located using a simple linear transit procedure, the Co(III) ones required a more careful exploration of the potential energy surface. Even though in some cases the theoretical RE energy barrier in the Co(III) state suggests that the reaction is feasible at room temperature (e.g. $\Delta G^\ddagger = 14$ kcal/mol for $-\text{X} = -\text{CH}=\text{CH}_2$ in **Ih**), the activation energy barrier drastically drops in the Co(IV) state (e.g. $\Delta G^\ddagger < 2$ kcal/mol for $-\text{X} = -\text{CH}=\text{CH}_2$ in **Ih**). The Co(IV) complex, e.g. **[Ih]**⁺, could then be considered as a reactant complex for the RE since the configuration of the system allows a lower energy barrier. The CC activation energy in the Co(IV) state is obviously weakly sensitive to the nature of the $-\text{X}$ ligand. Indeed, all activation barriers lie around +20 kcal/mol. In contrast, the RE activation energy in the Co(IV) state varies from $\Delta G^\ddagger < +2$ kcal/mol ($-\text{X} = -\text{CH}=\text{CH}_2$, **Ih**) to $\Delta G^\ddagger = +28$ kcal/mol ($-\text{X} = -\text{OC}(\text{O})\text{CF}_3$, **Ie**).

Investigating the geometries of the different complexes in both Co(III) **I** and Co(IV) **[I]**⁺ states reveals slight variations in the distances between the three ligands (Table S2). On one hand, for all studied systems, oxidation brings the *phpy* and Cp^* ligands closer to each other, as evidenced by the decrease of either or both of the distances between the carbanionic C_2 or/and the N of *phpy* and the respective closest C of the Cp^* ligand (C_4 and C_3 , respectively, Figure 1), suggesting a favorable rearrangement towards the CC reaction. On the other hand, the distance between C_2 of *phpy* and the atom of the X ligand bound to Co decreases or increases, depending on the nature of the X ligand. This variation in the C_2 -X distance correlates with the $\Delta G^\ddagger(\text{RE})$ in the Co(IV) state: the closer the atoms move to each other, the lower the energy barrier (Figure S1).

The IGM- δg^{inter} descriptor,¹¹ quantifying the gain in electron density gradient between two user-defined fragments in the real system compared to a corresponding non-interacting reference, gives a measure of the electron sharing between fragments: in this study it was used to investigate the interactions between different ligands (Table S3). The integrated value of this descriptor, the Δg^{inter} score, gives a quantification of the interaction. The derived IBSI descriptor measures any interatomic pairwise interaction against the covalent bond in H_2 that is used as a reference.¹² Even though multicenter interactions cannot be properly analyzed using IBSI,^{12b} the comparison of pairwise interactions between adjacent atoms bound to a common metal centre + ligand retinue in a series of

related species differing only by one variation in the structure (here $-\text{X}$) was not yet attempted. We speculated, assuming the electron density variations at the metal would not be significant, that IBSI could be used to quantify interactions in atom pairs involved in processes occurring at the Co-centered reactive site (Table S4) and help predicting reactivity. Here, from the variation of the Δg^{inter} values between *phpy* and X ligands upon Co(III)-to-Co(IV) oxidation no clear feature could be inferred; identical conclusion was drawn for the variation of the Δg^{inter} values between *phpy* and Cp^* (Figure S2).

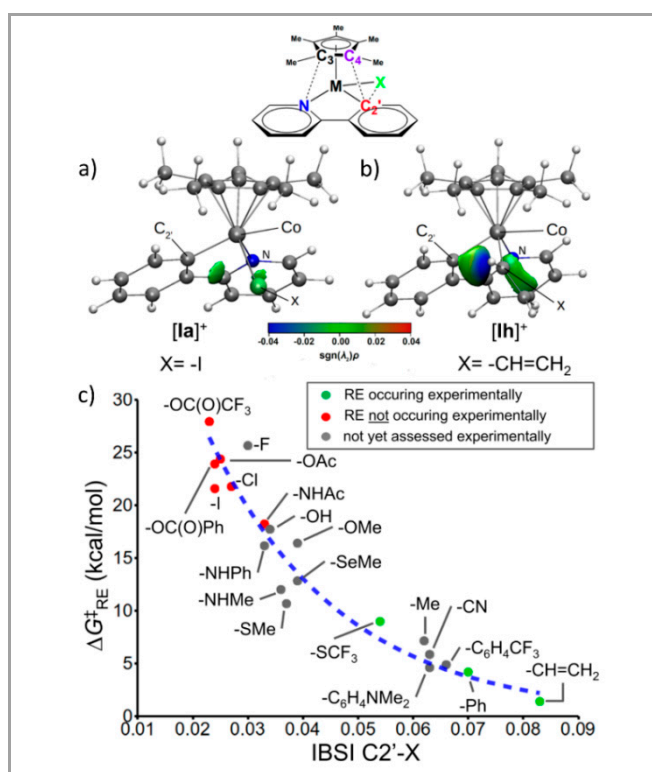


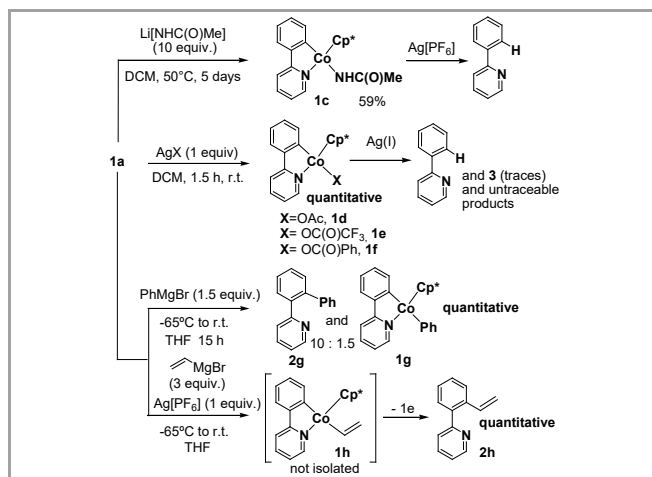
Figure 1 a) and b) are IGM- δg^{inter} isosurface plots (cutoff: $\delta g^{\text{inter}} = 0.01 \text{ a.u.}$) of the interaction between the *phpy* and $-\text{X}$ ligands: a) $-\text{X} = -\text{I}$, b) $-\text{X} = -\text{CH}=\text{CH}_2$. (color code: blue = attractive interaction, green = nonbonding interactions, red = repulsive interactions). c) Correlation plot between the RE Gibbs free energy of activation (ΔG^\ddagger) and the C_2 -X Intrinsic Bond Strength Index (IBSI) for a series of different X ligands in **[I]**⁺ species. The blue dashed line represents a trend curve of equation $\Delta G^\ddagger = a \cdot \exp(-b \cdot \text{IBSI})$ ($a = 69$ kcal/mol; $b = 42$; $r^2 = 0.94$). Red and Green dots outline the cases for which experimental results are reported in this work ($-\text{X} = -\text{NHAc}$, $-\text{OAc}$, $-\text{OC}(\text{O})\text{Ph}$, $-\text{OC}(\text{O})\text{CF}_3$, $-\text{Ph}$, $-\text{CH}=\text{CH}_2$) and in the literature⁹ ($-\text{X} = -\text{I}$, $-\text{Cl}$, $-\text{SCF}_3$).

However, for all considered complexes, the Co(III)-to-Co(IV) oxidation led to a stronger C_2 - C_4 interaction, as evidenced by the increase of the IBSI. This suggests that the C_2 - C_4 bond formation between *phpy* and Cp^* is eased in the Co(IV) state compared to the Co(III) state. Furthermore, systems for which the RE activation barrier is $\Delta G^\ddagger < 10$ kcal/mol in the Co(IV) state undergo an increase in the C_2 -X interaction strength. Conversely, systems for which the RE activation barrier in the Co(IV) state is $\Delta G^\ddagger > 10$ kcal/mol undergo a decrease of the same interaction (Figure S3). If we focus only on the Co(IV) reactant complexes **[I]**⁺, a first qualitative investigation was carried out looking at the IGM- δg^{inter} isosurfaces (Figure 1a-b and S8-S35), which materialize attractive, repulsive and nonbonding interaction areas between two user-defined fragments. A slight attractive isosurface can be observed between C_2 and C_4

for all systems. The attractive feature between C_2' and X however only appears for systems that present a lower activation barrier, the extent of the attractive area seemingly varying with the barrier height. This observation might be regarded as a qualitative evidence of the propensity of the Co(IV) reactant complex to undergo the RE: the larger the area, the more likely the reactant complex is to evolve towards RE. In all studied cases, the ΔG^{inter} score for the *phpy*-Cp* interaction exceeds the value for the *phpy*-X interaction. This might be attributed to the size of the contact area between the ligands; indeed, Cp* could approach *phpy* to bind with two sites in the CC scenario, while -X would only interact significantly with one site in the RE one (Table S3). In an attempt to check the reliability of the IBSI as a reactivity descriptor, the correlation between the activation energies towards RE and CC in the Co(IV) state and the IBSI values for the interactions between atoms involved in the respective reaction site was studied. Even if systems with smaller CC energy barriers tend to present higher C_2' - C_4 IBSI values, no clear correlation could be drawn between the IBSI and the reactivity towards CC (Figure S6). The only information that could be extracted is that systems for which $\text{IBSI}(C_2'-C_4) > 0.05$ tend to present CC activation energies $\Delta G^\ddagger(\text{CC}) > 20$ kcal/mol. This lack of correlation might be attributed to the potential involvement of the N atom of *phpy* in the first step of the CC process as some doubts still remain regarding its actual mechanism. IBSI, as a pairwise interaction strength descriptor is irrelevant for multicentre delocalized interactions.^{12b} For this reason, its use for the CC process even in the mechanistic scenario considered here is subject to caution. In the case of the RE process, IBSI values of C_2' -X correlate remarkably well with RE activation barriers; the RE activation barriers decreasing with increasing C_2' -X interaction strength (IBSI), coming close to zero for the strongest IBSI values (Figure 1c). From a mathematical point of view, such a behavior was best reproduced using a decreasing exponential formula. We thus considered the possibility to correlate the ΔG^\ddagger to the IBSI via a decreasing exponential relation, (i.e. $\Delta G^\ddagger = a \cdot \exp(-b \cdot \text{IBSI})$ ($r^2 = 0.94$), (Figure 1c). The IBSI therefore appears to be a decent predictive descriptor of the reactivity of $[\text{I}]^+$ towards RE. From Figure 1c, another trend can be drawn: the weaker the interaction (i.e. low $\text{IBSI}(C_2'-X)$ value) the likelier any other opportunistic pathway may supplant the RE like suggested by experimental data (vide infra). A frontier emerges at around $\text{IBSI}(C_2'-X) = 0.05$: those Co(IV) $[\text{I}]^+$ systems with higher IBSI values tend to have $\Delta G^\ddagger(\text{RE}) < 10$ kcal/mol and are thus more likely to undergo RE. Comparing the C_2' -X and C_2' - C_4 IBSI values, the general trend seems to be that the two interactions vary oppositely: $[\text{I}]^+$ systems with stronger C_2' -X interactions tend to have a weaker C_2' - C_4 interaction compared to other systems, and vice versa (cf. SI). Especially, systems with $\text{IBSI}(C_2'-X) < 0.03$, all show $\text{IBSI}(C_2'-C_4) > 0.05$. These systems possess a RE activation barrier of $\Delta G^\ddagger(\text{RE}) > 20$ kcal/mol and CC activation barrier of $\Delta G^\ddagger(\text{CC}) < 20$ kcal/mol. They are therefore more likely to undergo CC than RE in the Co(IV) state.

To verify the trends suggested by the IGM/IBSI study, a limited series of Cp*Co(III) metallacycles derived from 2-phenylpyridine containing different -X ligands were synthesized with the aim of figuring out which pathway is favored once submitted to oxidizing conditions (Scheme 2). A first set of compounds was synthesized by displacement of the

iodo ligand by treatment of complex **1a** with either alkali salts or silver salts. Co(III) compounds **1c-f** were all isolated pure and submitted to oxidative conditions using Ag(I) salts to initiate the formation of the key Co(IV). In all cases the potential products of RE were absent. The dominating product was that of the hydro-de-metalation of *phpy*, i.e. 2-phenylpyridine. The formation of cation **3** was detected only in the case of the carboxylato complexes **1d-f**.



Scheme 2 Experimental assessment of the theoretical predictive approach for -X= -NHC(O)Me, -OAc, -OC(O)CF₃, -OC(O)Ph, -Ph and -CH=CH₂.

The introduction of carbanionic -X ligands was also attempted with Grignard reagents such as PhMgBr and CH₂=CHMgBr. Quite intriguing was the reaction of **1a** with PhMgBr, which produced a large amount of 2-(2'-phenylphenyl)pyridine **2g**¹³ and minute amounts of **1g** after ca. 15 h of reaction. Attempts to isolate **1g** by flash chromatography resulted in tiny amounts of material that was characterized by ¹H and ¹³C NMR, and electropray (positive mode)-MS spectroscopies. Monitoring a solution of **1g** in CD₂Cl₂ kept at room temperature for over 1 month did not reveal any sign of spontaneous conversion to **2g**, thus ruling out the mere decomposition of **1g** by RE as the origin of **2g**. Therefore the *in situ* formation of **2g** necessarily implies the interference of an occasional oxidant: two hypotheses may be put forward i.e. either 1) unreacted **1a** acts somehow as an oxidant of **1g** and/or 2) in the conditions of the reaction, the Schlenk equilibrium¹⁴ established for PhMgBr in THF¹⁵ produces an electrolyte¹⁶ capable of oxidizing **1g** as it forms to give **2g**. These conjectures, which require further investigations, are reminiscent of the reports by Nakamura *et al.*^{13, 17} and by Ackermann, Neidig *et al.*¹⁸ on the Fe(II)-mediated C-H bond arylation with organo-magnesium and zinc reagents that require all an oxidative step. Worthy to note, mixing **1a** with CH₂=CHMgBr (even in slight excess) gave no reaction. Suspecting a difficult nucleophilic displacement of the Co-bound iodo ligand by CH₂=CHMgBr, the same experiment carried out in the presence of 1 equivalent of Ag[PF₆] led quantitatively to 2-(2'-vinylphenyl)pyridine **2h**¹⁹. This suggests that the iodo ligand replacement at **1a** and the presence of a one electron oxidant are both required for the formation of **2h**.

The experimental data disclosed here match the theoretical features displayed in Figure 1c. Indeed, $[\text{I}]^+$ systems close to the asymptote, with $\text{IBSI}(C_2'-X) > 0.05$ and thus $\Delta G^\ddagger(\text{RE}) < 10$

kcal/mol (**1b** and **1g-h**), do actually yield the RE product upon oxidation. On the other end of the graph, $[I]^+$ systems with $IBSI(C2'-X) < 0.03$ and thus $\Delta G^\ddagger(RE) > 20$ kcal/mol (**1a**, **1d-f** and **1j**) do not undergo RE upon oxidation, but instead tend to undergo the hydro-de-metalation of the *phpy* ligand and to a lesser extent CC like confirmed by experiment. What may happen to systems for which $0.03 < IBSI(C2'-X) < 0.05$ remains to be addressed.

In summary, this study discloses an exponential correlation existing between RE activation barriers and IBSI, validated by a preliminary experimental assessment carried out on a limited number of cases that belong to complexes with -X ligands expected to give either effective RE process with low activation barriers in the Co(IV) state or no RE process at all. This correlation, even though qualitatively meaningful and of fundamental importance, remains to be fully rationalized and validated with different molecular systems from which reactant complexes related to RE can be readily made. The $C2'-X$ IBSI emerges as a reliable reactivity descriptor of the propensity of Co(IV) $[CoCp^*(phpy)X]^+$ systems $[I]^+$ to undergo RE: this trend remains yet to be assessed when structural changes at peripheral ligands of Co are considered. This study also confirms that the Co(III)-to-Co(IV) oxidation lowers the barrier of activation of the RE pathway. It appears that when the RE pathway is not favored with $[I]^+$, other processes requiring lower activation barriers may take over, impacting catalytic efficiency: the most evident are the hydro-de-metalation of the *phpy* ligand and the CC pathway that causes the irreversible collapse of the catalytically relevant "Cp*Co" motif.^{9b}

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Supporting Information

YES

Primary Data

NO.

Conflict of Interest

The authors declare no conflict of interest.

References and Notes

† Note that computed structures are noted with roman numerals and experimentally probed compounds with Arabic ones throughout this article.

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