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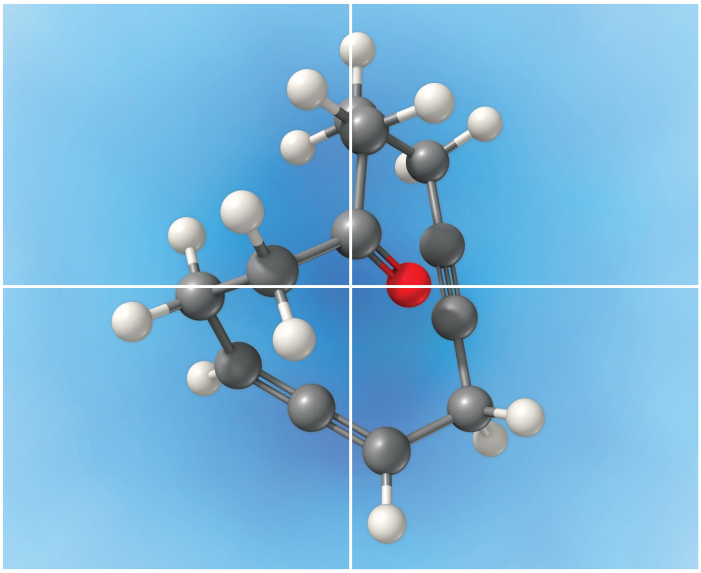

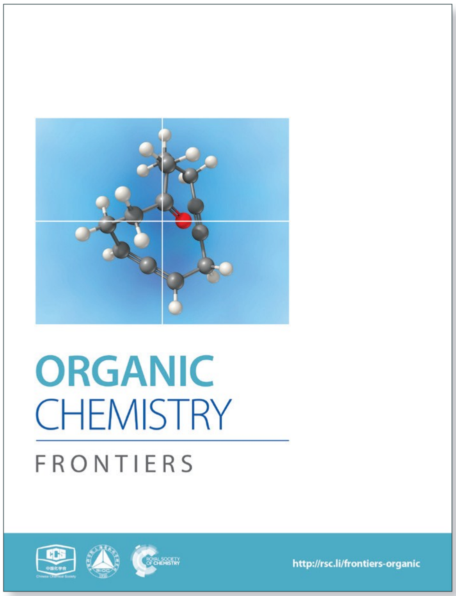

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ARTICLE

How easy is CO_2 fixation by M-C bond containing complexes (M = Cu, Ni, Co, Rh, Ir)?

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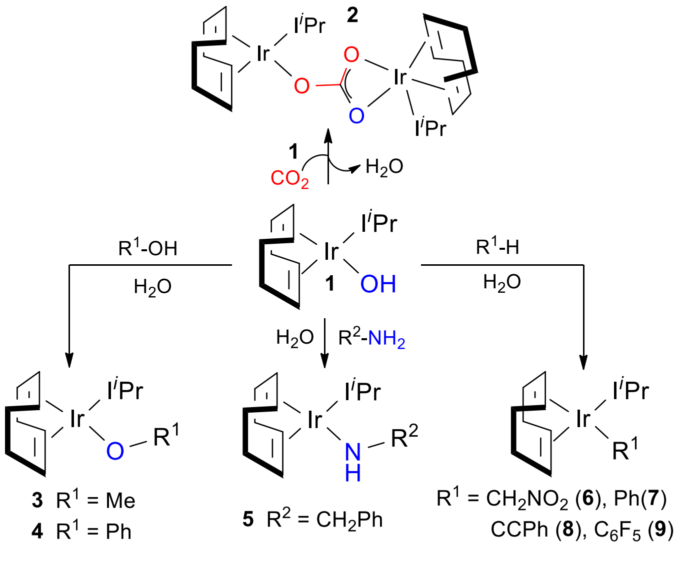
A comparison between different M-C bonds (M = Cu(I), Ni(II), Co(I), Rh(I) and Ir(I)) has been reported by using density functional theory (DFT) calculations to explore the role of the metal in the fixtion or incorporation of CO_2 into such complexes. The systems investigated are various metal based congeners of the Ir-complex **8** [(cod)(I^iPr)Ir-CCPh], with a ligand scaffold based on cod and IiPr ligands (cod=1,5-cyclooctadiene; I^iPr = 1,3-bis(isopropyl)imidazol-2-ylidene). Results of this study show that the calculated CO_2 insertion barriers follow the trend: Cu(I) (20.8 kcal/mol) < Rh(I) (30.0 kcal/mol) < Co(I) (31.3 kcal/mol) < Ir(I) (37.5 kcal/mol) < Ni(II) (45.4 kcal/mol), indicating that the Cu(I) based analogue is the best CO_2 *fixer*, while Ni(II) is the worst in the studied series.

Development of catalysts capable of utilising CO_2 as feedstock,[1-4] possibly in large volume transformations,[5-7] is considered to be one of the key challenges in modern chemistry. However, the wide spread use of CO_2 in chemical transformations is limited due to its chemical inertness.[8] In recent past, despite some attempts with metal-free processes,[9,10] even organocatalyzed trapping of CO_2 through C-C and C-O bond formation,[11] progress has been made in exploring the CO_2 reactivity with a large number of its reactions being insertion into transition metal-X bond (where X = C, O, N) supported with appropriate ligands.[12-17] These reactions are believed to be one of the most challenging organometallic reactions as CO_2 is thermodynamically stable and kinetically inert.[18-24] To this end, a novel organometallic complex as well as chemical mechanism able to perform or explain the capture of CO_2 would be extremely interesting and valuable in directing catalyst design efforts.[25-46] Therefore, a thorough understanding of the mechanism of CO_2 insertion into the M-X bonds is of fundamental importance and could guide advances in the development of this important reaction.

Despite the very recent large number of experimental[47-52] and theoretical[53-59] studies focusing on CO_2 insertion, reports on direct comparison between theoretical and experimental results remain very limited.[53,60,61] To partially fill this gap, we have recently reported density functional theory based investigations of CO_2 fixation mechanism as proposed by Nolan *et al* for a new Ir(I) complex,[61-63] [Ir(cod)I^iPr)(OH)] (**1**) (cod=1,5-cyclooctadiene; I^iPr = 1,3-bis(isopropyl)imidazol-2-ylidene) and its derivatives containing Ir-O (complexes **3** and **4**), Ir-N (complex **5**), and Ir-C bonds (complexes **6**, **7**, **8** and **9**; see Scheme 1).[64] According to the experiments, complexes containing Ir-heteroatom bonds (**1**, **3-5**) display high reactivity towards CO_2, while complexes with Ir-C bonds (**6-9**) are completely unreactive towards the green house gas.



Scheme 1.

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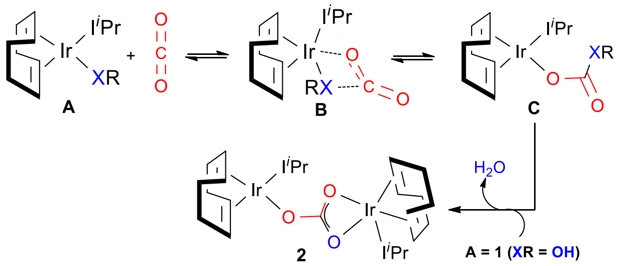
Based on the experimental findings, a plausible mechanism for CO_2 insertion into the M-X bonds (X = O or N) proposed by Nolan *et al* is outlined in Scheme 2. Considering complex **A**, the nucleophilic attack of the heteroatom X onto CO_2 does not proceed via the oxygen atoms but through the carbon atom, involving a four-membered cyclic center, hypothetically structure **B**, i.e. most probably **B** is the transition state itself. The particular structural nature of **1** allows for a second molecule of **1** to react yielding a dimeric structural product **2**; this occurs once a water molecule has been released from intermediate **C**.



Scheme 2.

Our detailed investigation of the proposed mechanism in Scheme 2 for complex **1** revealed that the CO_2 insertion step is the rate determining step rather than the subsequent dimerization step, **C→2**, (15.8 kcal/mol vs 9.4 kcal/mol, respectively).[62] This finding contradicts the recent study by Truscott et al.[61] as they argued that dimerization is probably the rate-limiting step for complex **1**. In fact, we pointed out that the facile dimerization step is due to the cooperative nature of the iridium centers. Additionally, in agreement with experiments, the calculated low CO_2 insertion barriers for complex **1** and its derivatives **3**-**5** (**3** (11.8 kcal/mol) < **4** (22.5 kcal/mol) < **5** (17.7 kcal/mol)) indicated that the CO_2 insertion into Ir-O and Ir-N bonds is kinetically facile. On the other hand, significantly higher barrier values were estimated for complexes **6**-**9** (ranges from 35.0-50.0 kcal/mol), suggesting that CO_2 insertion into Ir-C bonds is kinetically more challenging and supports the experimental observation that the Ir-C bond are unreactive towards CO_2.

Having rationalized the behaviour of the systems proposed in the literature (**1**, **3**-**9**), in the present study we turn our attention to the effect of changing the metal (but keeping the same ligand scaffold; cod and I^{i}Pr ligands) with the aim of finding one metal that can induce CO_2 insertion into M-C bonds. It is well documented in the literature that CO_2 can be inserted into the M-C bonds of Rh and other transition metals such as Cu and Ni.[65-67] To this end, we studied the CO_2 insertion step for different metal (Cu(I), Rh(I) and Ni(II)) based congeners of **8** [(cod)(I^{i}Pr)Rh-CCPh],[68] which presented the lowest CO_2 insertion barrier (37.5 kcal/mol) among the investigated Ir-C bond containing complex in the series **6**-**9**.

To clarify the role of the metal in the CO_2 insertion DFT calculations were carried out. All DFT static calculations have been performed at the GGA level with the Gaussian09 set of programs,[69] using the BP86 functional of Becke and Perdew.[70,71] The electronic configuration of the molecular systems was described with the standard split-valence basis set with a polarization function of Ahlrichs and co-workers for H, C, N, and O (TZVP keyword in Gaussian).[72] For Cu, Ni, Rh and Ir, the quasi-relativistic Stuttgart/Dresden effective core potential was used, with the associated valence basis set (standard SDD keywords in Gaussian09).[73-75] The geometry optimizations were carried out without symmetry constraints, and the characterization of the stationary points was performed by analytical frequency calculations. Single point calculations on the BP86 optimized geometries were performed using the M06 functional[76] with the triple-ζ basis set of Ahlrichs for main-group atoms (TZVP keyword in Gaussian),[77] while for Ir the SDD basis set has been employed. These single point calculations also used the polarizable continuous model PCM to address solvent effects, using benzene as a solvent.[78,79] The reported free energies in this work include energies obtained at the M06/TZVP level corrected with zero-point energies, thermal corrections and entropy effects evaluated at 298 K with the BP86/SVP method in the gas phase.[80,81]

Figure 1 presents the computed energy profile for the CO_2 insertion into M-C bond of different metal analogues of **8**. The reference point is the energy of complex **8** analogues plus free CO_2. For the selected metals, the calculated CO_2 insertion barriers (for simplicity named **TS_8**, in analogy with our Ir(I)-complexes of Scheme 1) follows the trend: Cu(I) (20.8 kcal/mol) < Rh(I) (30.0 kcal/mol) < Co(I) (31.3 kcal/mol) < Ir(I) (37.5 kcal/mol) < Ni(II) (45.4 kcal/mol), indicating that the Cu(I) based analogue is the best CO_2 *fixer*, while Ni(II) is the worst of the studied metal series. However, from a thermodynamic stand point, the overall CO_2 insertion reaction is endergonic in nature for all examined metals (see the energy values for **II_8** in Figure 1), being less endergonic in the case of Cu(I) (5.0 kcal/mol) than Ni(II) (22.3 kcal/mol). It is worth mentioning here that we calculated the CO_2 insertion barrier for high spin Co(II) complex and is predicted to be 32.9 kcal/mol, which is slightly higher in energy (by 1.6 kcal/mol) than the calculated barrier for low spin Co complex (31.3 kcal/mol).

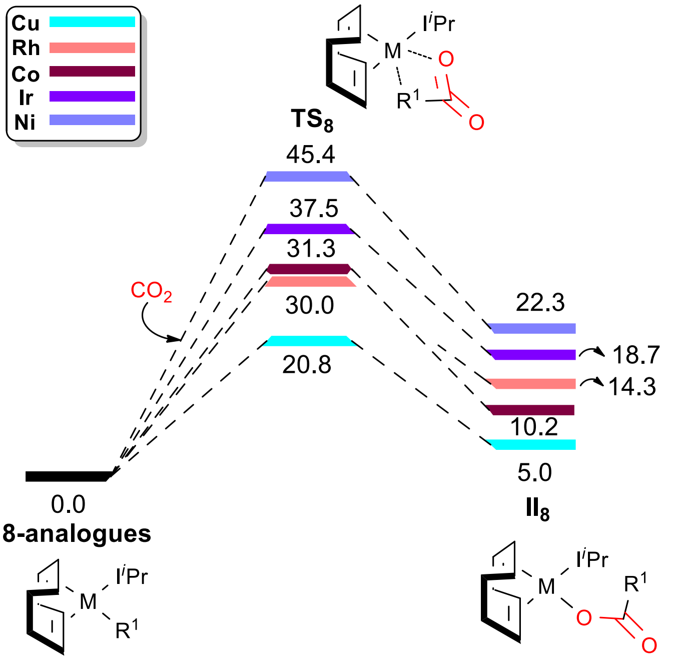


Figure 1. Computed free energy profile for the CO_2 insertion into M-C bond of different metal analogues of Ir(I)-complex **8** (where R^1 = CCPh). Free energies are given in kcal/mol. Ni(II) is a cationic complex (overall charge +1).

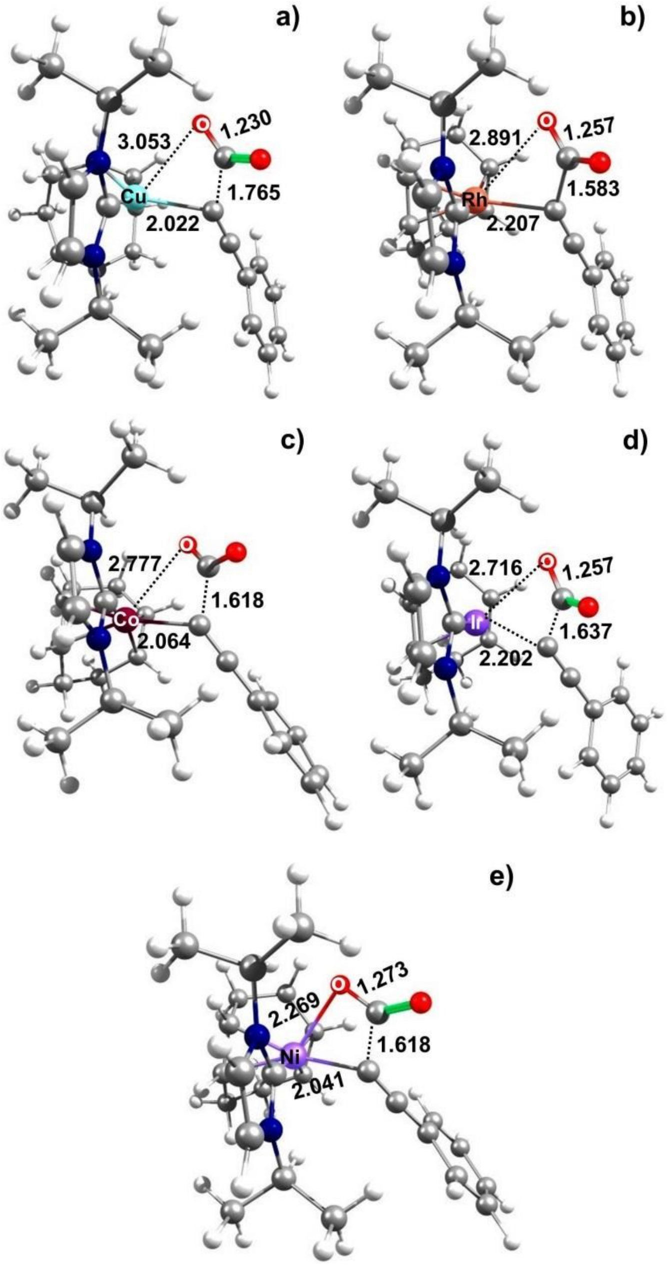


Figure 2. Calculated transition states of CO_2 fixation mechanism promoted by different metals analogues of Ir(I)-complex **8**: (a) Cu(I); (b) Rh(I); (c) Co(I); (d) Ir(I); and (e) Ni(II). The most notable distances are given in Å.

A plausible explanation for the remarkable metal effect on the calculated CO_2 insertion barriers can be drawn from the geometries of the TS structures (see Figure 2) and by considering the Hammond postulate. In detail, the calculated high energy TS for Ni(II) can be considered as a textbook example of a "late TS" closer to product (r(Ni-O) = 2.269 Å; see Figure 2e). By changing the metal from Ni(II) to Cu(I), the transition state moves towards the reactants as the reaction becomes less endothermic. Thus, the calculated low energy TS for Cu(I) can be considered as an "early TS" closer to the reactants (r(Cu-O) = 3.053 Å; see Figure 2a). Intermediate situations are reported for Rh and Ir (r(Rh-O) = 2.891 Å and r(Ir-O) = 2.716 Å; Figure 2b and c, respectively).

Having these results at hand, we then calculated the CO_2 insertion barrier for the experimentally known Cu(I) complex, [Cu(IPr)(CCPh)],[82] and further, to be compared with other group 11 metals Ag(I) and Au(I). The calculated CO_2 insertion barrier follows the trend: Ag(I) (30.9 kcal/mol) < Cu(I) (34.6 kcal/mol) < Au(I) (37.0 kcal/mol), indicating that the Ag(I) based analogue is the best CO_2 *fixer*, followed by Cu(I) and Au(I) based analogues. However, the calculated CO_2 insertion barriers are still above 30.0 kcal/mol, suggesting that the CO_2 fixation is kinetically challenging in the considered group 11 metal series. Calculations attempting to screen a longer series of ligands to characterize in detail how the CO_2 insertion barrier is affected by the nature of the ligand are ongoing.[82,83]

Last but not least, eventhough the energy data include the correction for dispersion implicitly, the geometry optimization is not included, as previously reported,[62,79,80] however new tests performed on the transition states for Ni and Cu displayed in Figure 2 reveal an increase in the energy barrier of +0.4 kcal/mol for Ni and a decrease of 0.8 kcal/mol for Cu, which suggest that in absolute value the difference is small to negligeable and that there is no obvious trend concerning the effect of dispersion on the CO_2 insertion barriers.

Conclusions

We have explored the role of metal in the CO_2 insertion into M-C bond by considering various metal (M = Cu(I), Co(I), Rh(I) and Ni(II)) analogues of Ir(I)-complex **8**. Results show that among the considered metals, Cu(I) was the best CO_2 *fixer* with an estimated barrier of 20.8 kcal/mol, while Ni(II) was found to be the least reactive with a barrier of 45.4 kcal/mol. As a final note, the large spread in the activation energies estimated by changing the metal but with the same ligand scaffold (cod and ^{i}Pr ligands) strongly suggests that there is a large space to explore for a suitable combination of ligand and metal to add important components to improve/affect the thermodynamics of this fascinating reaction.

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