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Regioselective control of the nickel-mediated coupling of acetylene and carbon dioxide – A DFT study

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ABSTRACT

The nickel-mediated coupling of asymmetric alkynes with carbon dioxide is known to be highly regioselective with respect to the formation of nickelacycle intermediates and α,β-unsaturated carboxylic acid products. Using density functional theory (DFT), we have investigated the effect that parameters such as acetylene-substituent, ancillary ligand and solvent have on the potential energy surface of the nickelacycle coupling reaction. 3-R-substituted nickelacycles are the thermodynamically preferred product in all cases surveyed, however, the transition structure characterised by the attack of CO_2 on the alkyne carbon distal from the R-group is generally lower in energy, making the 2-R-substituted nickelacycle the kinetically favoured product. Ligating the zerovalent nickel species with the diazabicyclo[5.4.0]undec-7-ene (DBU) ancillary ligand in preference to 2,2′-bipyridine (BIPY) leads to lower activation energies for the coupling reaction and products that are less susceptible to steric bulk in the 2-position of the nickelacycle. Solvation with dimethylformamide (DMF) has the advantage of lowering the activation barrier for the coupling reaction when compared to tetrahydrofuran (THF).

1. Introduction

The use of carbon dioxide (CO_2) as an industrial C1 feedstock is attractive given its abundance and low cost. Not surprisingly then, the development of transition-metal-based system that can effect the coupling of CO_2 with other organic feedstocks to generate industrially relevant products represents a particularly active area of research [1–4].

Nickel-based compounds have shown to exhibit a high degree of activity for the coupling of CO_2 with unsaturated hydrocarbons [5–16]. The early work of Hoberg showed that saturated carboxylic acids could be afforded from alkenes and CO_2 via protonolysis of a nickelacycle intermediate (Scheme 1) [13]. The reaction proceeds using stoichiometric amounts of the zerovalent nickel complex with the catalytic applicability of the reaction likely to be hampered not by unfavourable side reactions as first reported, but by the overall thermodynamics of the coupling reaction [17].

The inherent thermodynamic stability of CO_2 highlights the need for a high-energy coupling partner in order to thermodynamically favour the formation of a coupled product. As a result of this, there has been much greater success in CO_2 coupling reactions when alkynes are used in preference to alkenes. The pioneering work in the nickel-mediated coupling of CO_2 with alkynes was performed in the groups of Inoue and Hoberg in the late 1970s and early 1980s [5,18,19]. Hoberg first reported [5] the synthesis of an unsaturated nickelacycle from the coupling of 2-butyne and CO_2 using a stoichiometric amount of nickel(0) complex with an ancillary TMEDA ligand (Scheme 2). The formation of unsaturated nickelacycles from alkyne/CO_2 coupling has the distinct advantage that protonolysis furnishes the more synthetically useful α,β-unsaturated carboxylic acids. The stoichiometric coupling reaction has proven useful for synthesis of a number of α,β-unsaturated carboxylic acids as well as carboxylation and cyclisation of enynes [20].

The stoichiometric reaction was later adapted to function catalytically via both electrochemical means and through the use of an alkylzinc reagent. Dunach reported [21–23] the catalytic synthesis of a number of α,β-unsaturated carboxylic acids using an electrochemical cell in which the catalytically active (BIPY)Ni^0 reagent could be regenerated at the anode. The proposed nickelacycle intermediate was isolated from the reaction. Using stoichiometric amounts of an alkylzinc reagent, Shimizu was able to use catalytic amounts of zerovalent nickel to synthesize a variety of α,β-unsaturated carboxylic acids [16]. Through a transmetallation reaction with the nickelacycle, the alkylzinc reagent effected the reductive elimination of the product from the nickel centre with concomitant regeneration of the active zerovalent catalyst. In addition to the synthesis of α,β-unsaturated carboxylic acids, the combined zerovalent nickel–alkylzinc route has been exploited for the preparation of a number of organic products [24], including pyrones, which may be synthesised via carboxylative cyclisation of both dienes [25,26] and diynes [27].

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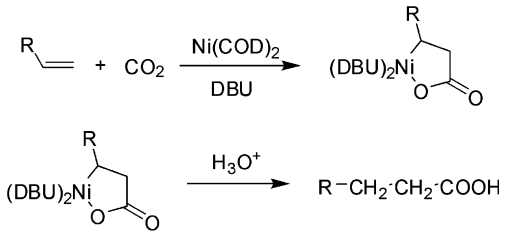
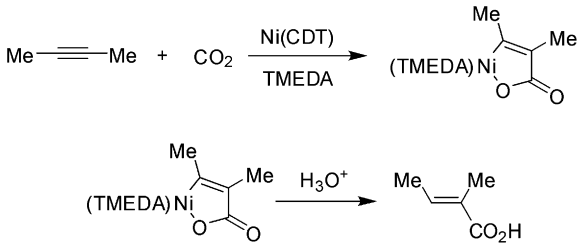
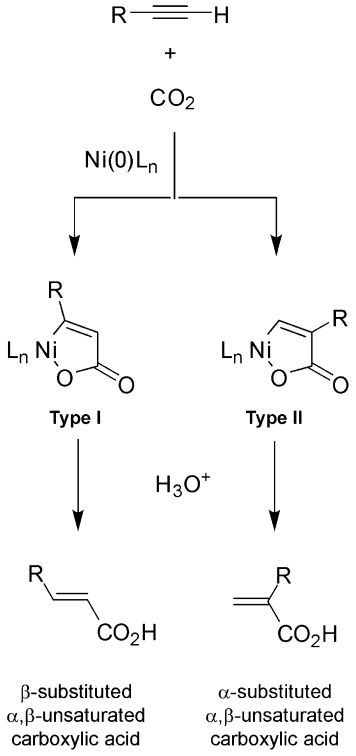


Scheme 1. Synthesis of a substituted carboxylic acid via protonolysis of a nickelacycle intermediate formed through the coupling of carbon dioxide with an alkene.



Scheme 2. Synthesis of a substituted unsaturated carboxylic acid via protonolysis of an unsaturated nickelacycle intermediate formed through the coupling of carbon dioxide with an alkyne.

Coupling reactions that involve terminal (asymmetric) alkyne precursors and carbon dioxide can generate α,β-unsaturated carboxylic acids substituted at either the 1-position (β-substituted) or the 2-position (α-substituted) of the alkyne. These reactions have been shown to be highly regioselective and depending on a number of parameters, either the α-substituted or β-substituted product may predominate (Scheme 3).



Scheme 3. Coupling of an asymmetric alkyne and carbon dioxide may result in one of two unsaturated carboxylic acid regioisomers via Type I or Type II nickelacycle.

Saito has reported [14] the synthesis of a variety of α,β-unsaturated carboxylic acids using the $Ni(DBU)_2$ complex (DBU = diazabicyclo[5.4.0]undec-7-ene) generated *in situ* at 0 °C in THF. The products were dominated by the β-substituted regioisomer suggesting the preference for initial formation of Type I nickelacycle intermediate (Scheme 3). Similar results were reported in the works by both Shimizu [16] and Takimoto [15] who – with the exception of effecting the nickelacycle cleavage with an alkylzinc reagent in preference to H_2SO_4 – used the same conditions as Saito, and observed similar product distributions for alkyl and aryl-substituted alkynes, again indicating the preference for Type I nickelacycle intermediate. In contrast, the coupling reactions carried out by Dunach and coworkers [21,23] mediated by the electrochemically generated (BIPY)Ni^0 complex showed product regioselectivity dominated by Type II nickelacycle intermediate. These reactions used a variety of R-substituents including Ph and *n*-hexyl, and took place in DMF at temperatures between 20 and 80 °C. Further work by both Dunach [22] and Aoki [28] reinforced the sensitivity of the regioselectivity of the reaction by showing how subtle variations in the ancillary ligand could shift the regioisomeric preference of the product.

Changes in the electronic and steric nature of the terminal alkyne have also led to a shift in the regioselectivity of the product. Using a variety of trimethylsilyl(TMS)-substituted terminal alkynes (RCC–$SiMe_3$), Shimizu unexpectedly observed the predominant formation of the α-substituted-α,β-unsaturated carboxylic acids indicating a preference for Type II intermediate, whereas *t*Bu and Ph substituted alkynes preferred the alternative regioisomer (via Type I) [16]. A shift from electron donating to electron withdrawing R-groups increased preference for Type II pathway.

The electron-donating abilities of the acetylenic substituents and ancillary ligands have also been observed to affect the rate of the coupling reaction. After comparing the reaction rates of both Ph- and MeO-*p*-C_6H_4-substituted alkynes with CO_2, Saito concluded that electron-donating groups resulted in an attenuation of the reaction rate [14], whereas Dunach noted that the reaction rate increased with the basicity of the ancillary ligand [22].

As a further step toward a better understanding of the zerovalent nickel-mediated coupling of alkynes and carbon dioxide, here we investigate the effect that a number of parameters have on the formation of the nickelacycle intermediate. Using density functional theory (DFT), we aim to establish and rationalise the effects that changes in solvent, spectator ligand and acetylene substituent have on the overall reaction energetics and regioselectivity.

2. Computational details

All geometry optimisations were carried out using the B3LYP [29–31] density functional and the LANL2DZ:6-31+G(d,p) compound basis set (consisting of the LANL2DZ basis-set [32,33] on nickel and 6-31+G(d,p) [34–37] on the remaining atoms), with pure d-functions (5D) used throughout.

In an effort to reduce the cost of calculations, a truncated model of the diazabicyclo[5.4.0]undec-7-ene (DBU) ligand was employed. The model ligand (denoted *m*DBU) has three carbon atoms removed from the seven-membered ring distal to the coordinating nitrogen (Fig. 1). The model ligand showed excellent agreement with the full ligand system in our previous study involving calculations on the nickel-mediated coupling of carbon dioxide with ethylene [17].

Harmonic vibrational frequencies were calculated on the optimised geometries to ascertain the nature of the stationary points, with zero point vibrational energy (ZPVE) and thermodynamic

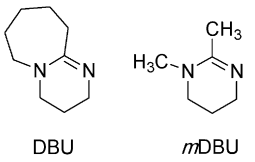


Fig. 1. Diazabicyclo[5.4.0]undec-7-ene (DBU) ligand (left) and the abbreviated model ligand (*m*DBU) used in this study (right).

corrections obtained using unscaled frequencies. For transition structures, the connection between reactants and products was verified by following the normal coordinate corresponding to the imaginary frequency using the Berny optimisation algorithm with a reduced maximum step size (pseudo-IRC calculation). Single-point energies on optimised geometries were performed using the B3LYP density functional and the 6-311+G(2d,p) basis set. Energy corrections due to solvation were applied to optimised geometries by means of the polarisable continuum model (IEF-PCM) [38–41] using radii based on the United Atom Topological Model (RADII = UAHF). For tetrahydrofuran (THF) calculations, the internal default for the dielectric constant (ε) was used (7.58). For dimethylformamide (DMF), values for DENSITY (0.0078) and EPS (ε, 38.25) were generated from tabulated data [42], while the value for RSOLV (2.52) was calculated via the Stearn–Eyring equation [43].

Relative energies quoted throughout the text are in kJ mol^{-1} and refer to THF solvation-corrected Gibbs free energies at 298 °C unless otherwise specified.

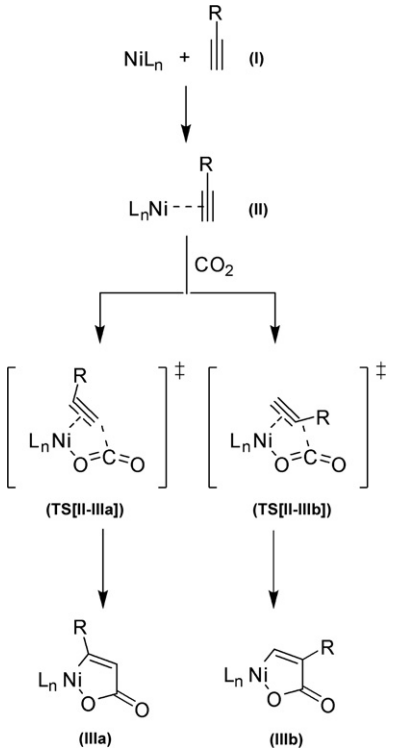
All calculations were carried out using the GAUSSIAN03 suite of programs [44].

3. Results and discussion

The general pathway under investigation is shown in Scheme 4. As a first step, it is of interest to compare the potential energy surfaces for the simplest case, *i.e.* acetylene/CO_2 coupling with the coupling of ethylene and CO_2. While a number of researchers have performed theoretical calculations on the ethylene/CO_2 coupling reaction [17,45,46], there has been comparatively less investigation of the analogous acetylene/CO_2 coupling reaction [47,48], and no direct comparison of the two surfaces has been undertaken. Fig. 2 shows the potential energy surfaces for coupling of carbon dioxide with ethylene and acetylene, respectively, mediated by zerovalent Ni(*m*DBU)$_2$.

The encounter complex formed between Ni(*m*DBU)$_2$ and acetylene (**II**) lies at −68.5 kJ mol^{-1}, which is 31.9 kJ mol^{-1} more stable than the analogous ethylene complex (−36.6 kJ mol^{-1}). The activation barrier required to negotiate the transition structure (**TS[II–III]**) is 99.7 kJ mol^{-1} in the case of the acetylene pathway (114.2 kJ mol^{-1} for ethylene) and results in a thermodynamically favourable nickelacycle product (**III**) lying 125.1 kJ mol^{-1} below the energy of the reactants. The analogous saturated nickelacycle resulting from the coupling of ethylene and CO_2 is still thermodynamically favourable, but much less so, lying at −42.1 kJ mol^{-1} relative to reactants.

The geometry of the transition structure located for the coupling of acetylene and CO_2 was found to be quite similar to those located previously [17,46] for the ethylene/CO_2 coupling reaction. Much like the ethylene reaction, the acetylene reaction pathway proceeds first through the η^2-coordination of the acetylene to zerovalent nickel, with subsequent attack of the CO_2 carbon on one of the carbons of the coordinated alkyne. The located transition



Scheme 4. The alkyne/CO_2 coupling pathways under consideration. R = *t*Bu, TMS, Ph, 4-MeOPh; Ln = (*m*DBU)$_2$, BIPY.

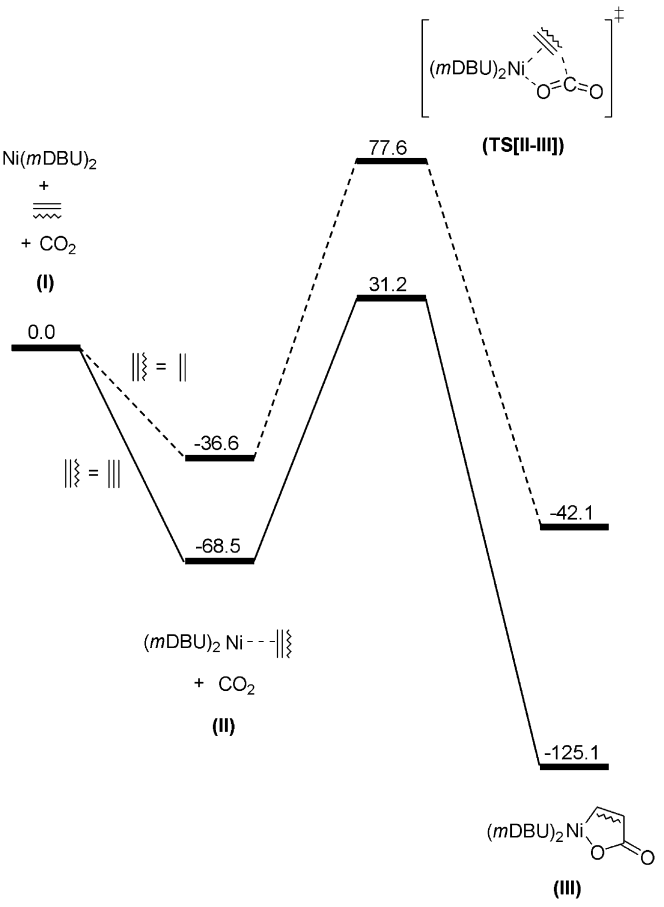


Fig. 2. Gibbs free energy surfaces for the coupling of carbon dioxide with ethylene (dashed-line) or acetylene (solid-line) to form saturated and unsaturated nickelacycles, respectively. Energies are in kJ mol^{-1}.

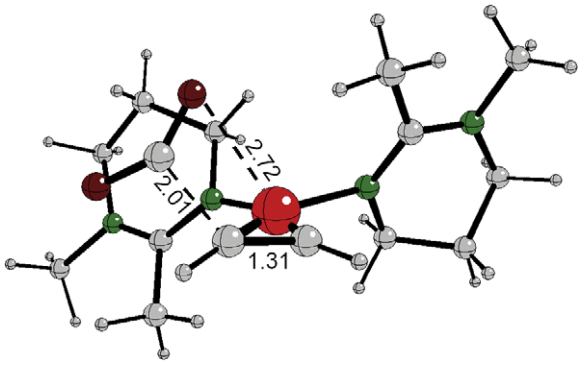


Fig. 3. Transition structure geometry for the coupling of acetylene and carbon dioxide mediated by Ni(*m*DBU)$_2$ (bond lengths are in Å).

structure (Fig. 3) is characterised by a transition vector corresponding to the formation of a new carbon–carbon bond with concomitant formation of a nickel–oxygen bond. Much like our previous investigation involving the coupling of ethylene and CO_2 [17], no evidence was found for a transition structure corresponding to attack of acetylene on a nickel–CO_2 complex, and a more facile route via an alternative dissociative mechanism was not observed.

3.1. Effect of the alkyne R-substituent

To gauge the effect that any variation of the alkyne R-substituent has on the reaction thermodynamics, calculation of potential energy surfaces for the coupling reaction were performed with alkynes bearing four different substituents: trimethylsilyl (TMS), *tert*-butyl (*t*Bu), 4-methoxyphenyl (MeOPh), and phenyl (Ph). The four PESs for the coupling reaction that proceed to Type I nickelacycle (*i.e.* the 2-substituted nickelacycle) are shown in Fig. 4. The initial stabilising interaction between the alkyne and the zerovalent nickel to form the precursor complex (**II–R–DBU**) is favourable, occurring with solvation-corrected free energy changes between −17 to −41 kJ mol^{-1}. Including the electron-donating methoxy group on the phenyl ring of the encounter complex (**II–MeOPH–DBU**) equates to a destabilisation with reference to the phenyl-substituted alkyne of 5.2 kJ mol^{-1}. The activation energies for Type I transition structures are similar at 95.9, 98.1, 102.8 and 104.5 kJ mol^{-1} for *t*Bu, MeOPh, Ph, and TMS, respectively. The difference in activation barrier between the sterically similar MeOPh and Ph substituents must be electronic in nature, with the electron-donating MeOPh substituted pathway subject to a lower activation energy due primarily to the destabilisation of the encounter complex relative to the analogous Ph-substituted species. The Gibbs free energies for all the reactions are favourable ranging between −50 and −100 kJ mol^{-1}. Due to the close proximity of the R-substituent to the ancillary ligand in Type I nickelacycle, the large TMS and *t*Bu-substituted alkynes show overall reaction free energies that are much less favourable than those for the less sterically imposing MeOPh and Ph substituted alkynes.

The analogous four potential energy surfaces for the coupling reaction that proceeds to Type II nickelacycle (*i.e.* the 3-substituted nickelacycle) are shown in Fig. 5. With the exception of the TMS-substituted alkyne there is an increase in activation energy of approximately 15–20 kJ mol^{-1} over Type I transition structures

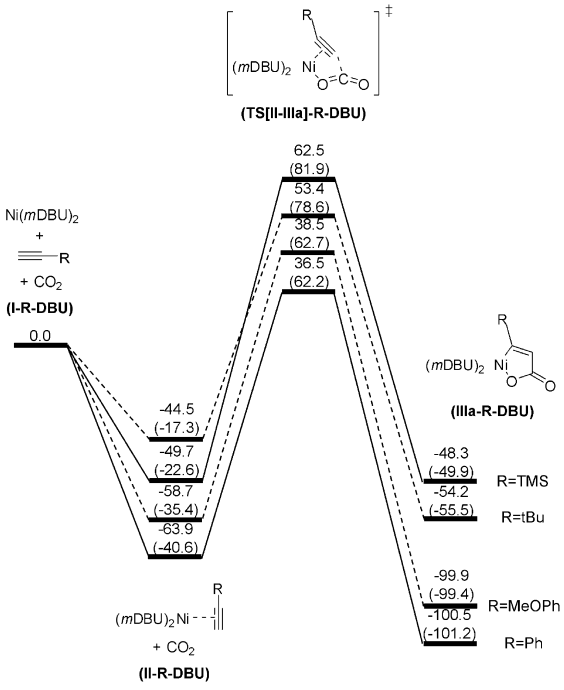


Fig. 4. Gibbs free energy surfaces for the coupling of various substituted acetylenes with carbon dioxide via a Type I pathway to form 2-substituted nickelacycles. Gibbs free energies are in kJ mol^{-1}, with solvation-corrected (THF) free energies in parentheses.

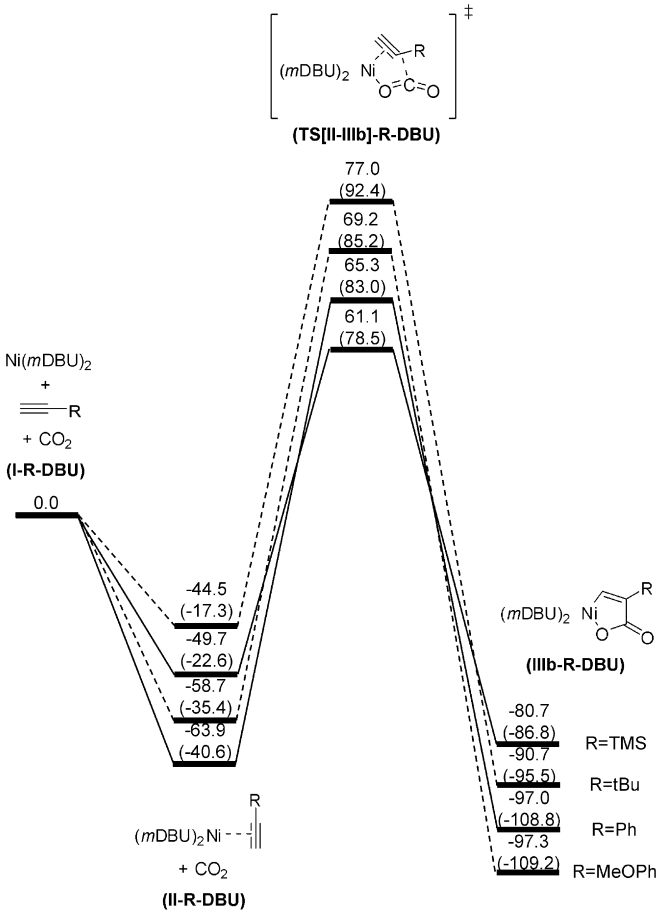


Fig. 5. Gibbs free energy surfaces for the coupling of various substituted acetylenes with carbon dioxide via a Type II pathway to form 3-substituted nickelacycles. Gibbs free energies are in kJ mol^{-1}, with solvation-corrected (THF) free energies in parentheses.

(101.1, 109.7, 120.6 and 123.6 kJ mol^{-1} for TMS, *t*Bu, MeOPh and Ph, respectively). This is due to the location of the R-substituent which now hinders the approach of the incoming CO_2 moiety. In contrast, the activation barrier for the TMS-substituted alkyne is similar for Type I and Type II pathways (104.5 vs. 101.1 kJ mol^{-1}, respectively) and this is a consequence of the sheer size of the TMS substituent which is more affected by the interaction between itself and the large DBU ligands in Type I transition structure than it is by the interaction between itself and the smaller CO_2 molecule in Type II transition structure. The Gibbs free energy for the reaction is more favourable across all R-substituents for formation of Type II nickelacycle. Compared to Type I products, the free energy of reaction is slightly more negative for Type II Ph and MeOPh substituted products (−108.8 and −109.2 kJ mol^{-1}, respectively, *cf.* −101.2 and −99.4 kJ mol^{-1}) and is substantially more negative for the TMS and *t*Bu substituted products (−86.8 and −95.5 kJ mol^{-1}, respectively, *cf.* −49.9 and −55.5 kJ mol^{-1}). This favourable increase in magnitude of the free energy of reaction (approximately 40 kJ mol^{-1}) is expected as the unfavourable interaction between these large substituents and the ancillary ligand is avoided when the substituent is attached to the 3- rather than the 2-position of the nickelacycle.

3.2. Effect of the ancillary ligand

The potential energy surfaces for the coupling of the simplest alkyne (acetylene) with carbon dioxide mediated by a zerovalent nickel complex bearing either two *m*DBU or a 2,2-bipyridine (BIPY) ligand(s) are shown in Fig. 6. When compared to the DBU surface, the BIPY-based surface exhibits a more favourable Gibbs free energy across all species. This is due to the high energy of the Ni(BIPY) fragment which is destabilised by the L-shaped configuration of its coordination sphere when compared to the linear arrangement of the corresponding Ni(*m*DBU)$_2$ species. However, the change in free energy on proceeding from the encounter complex to the product is much less pronounced for the BIPY species compared to the *m*DBU species. Progress from **II–DBU** to **III–DBU** represents a change in free energy of −86.3 kJ mol^{-1} compared to −62.5 kJ mol^{-1} for the analogous **II–BIPY** to **III–BIPY** transition. There is a significant increase in activation energy on exchanging the *m*DBU ligand to the BIPY ligand. The activation energy for the BIPY pathway (117.4 kJ mol^{-1}) is approximately 20 kJ mol^{-1} higher than the analogous *m*DBU-based pathway (97.7 kJ mol^{-1}).

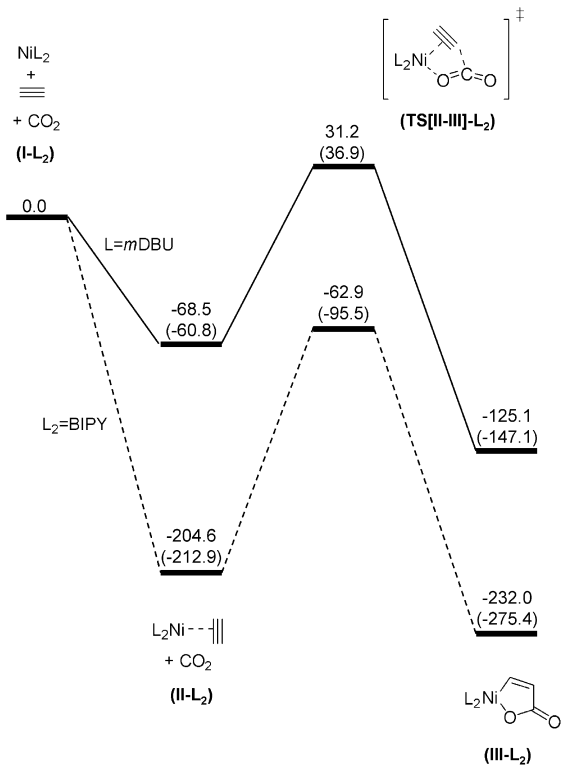


Fig. 6. Gibbs free energy surfaces for determining the effect of the ligand on the coupling of acetylene with carbon dioxide. Gibbs free energies are in kJ mol^{-1}, with solvation-corrected (THF) free energies in parentheses.

Moving to the Ph-substituted alkyne has only a minor effect on the difference between the *m*DBU and BIPY surfaces when compared to the acetylene surface (Fig. 7). The calculated potential energy surfaces for both the *m*DBU and BIPY ligand systems similarly predict pathways that go through Type I transition structures to be the lowest in energy, with the activation energy through the *m*DBU ligated TS (**TS[II–IIIa]–Ph–DBU**) calculated to be 8.8 kJ mol^{-1} lower in energy than that through the analogous BIPY ligated TS (**TS[II–IIIa]–Ph–BIPY**). Thermodynamically, for both the BIPY and *m*DBU ligated systems, Type II (*i.e.* the 3-substituted) nickelacycle is predicted to be more stable than Type I (2-substituted) product, although the energy difference is typically less than 10 kJ mol^{-1}. Thus it seems that for phenylacetylene at least, Type I pathway is kinetically favoured over Type II pathway for both the *m*DBU and BIPY ligands (by 20.8 and 30.6 kJ mol^{-1}, respectively) while Type II product is preferred thermodynamically – albeit only slightly. As was observed with the acetylene potential energy surface, the driving force for the product with reference to the encounter complex is greater for the *m*DBU ligated species.

Moving to a more sterically demanding R-substituent (*tert*-butyl) precipitates some considerable differences between the two ancillary ligand systems (Fig. 8). As was seen for the Ph-substituted alkyne, the kinetically favoured pathway for both ligand systems is still via Type I transition structure, with the activation energy for the *m*DBU ligated pathway (95.9 kJ mol^{-1}) considerably less than the alternate BIPY pathway (114.4 kJ mol^{-1}). Whereas there was little difference in the energies of the 2- and 3-Ph substituted nickelacycle products, the *t*Bu-substituted alkyne shows a distinct preference for the 3-substituted (Type II) nickelacycle product for both ligand systems. For the *m*DBU free energy surface Type I nickelacycle (**IIIa–tBu–DBU**) is destabilised by +40 kJ mol^{-1} compared to Type II nickelacycle (**IIIb–tBu–DBU**), however both products are still formed favourably with respect to the encounter complex (**II–tBu–DBU**). In contrast, while there is still a driving force for formation of Type II nickelacycle for the BIPY system from the encounter complex (**II–tBu–BIPY**), the free energy change for formation of Type I nickelacycle is positive (+0.7 kJ mol^{-1}) suggesting an equilibrium that would lie slightly to the left for the kinetically preferred pathway. The reason for the large observed differences between the phenyl- and *tert*-butyl-substituted alkyne comes down to the steric demands of the latter. The 2-*t*Bu-substituted (Type I) nickelacycle is destabilised compared to the analogous 2-Ph-substituted structures due to the interaction between the R-group and the ancillary ligand. This interaction is more pronounced for the BIPY ligated product as the BIPY ligand encroaches on the R-group to a much greater degree than does the *m*DBU ligand which is more flexible with regard to the position it can adopt within the coordination sphere (Fig. 9).

3.3. Effect of the solvent

Although most of the experimental work on nickel-mediated alkyne/CO_2 coupling has been performed in THF, the work using the

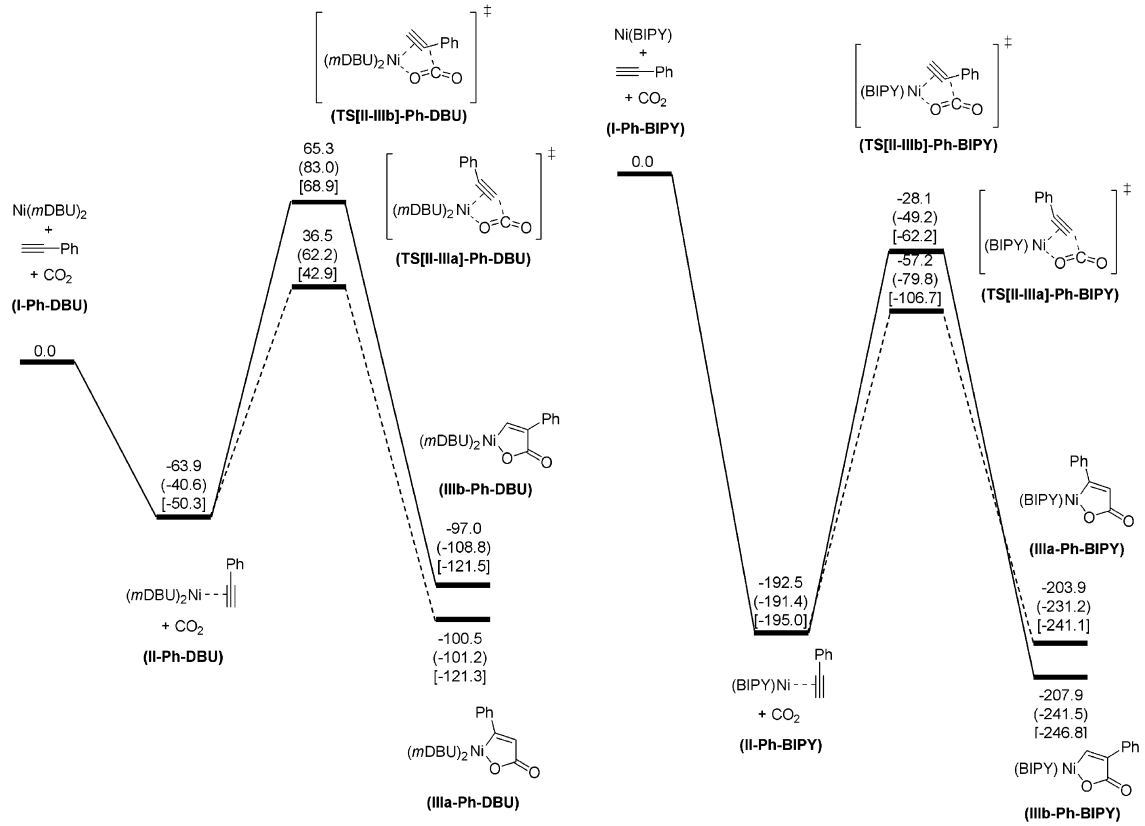


Fig. 7. Gibbs free energy surfaces for the coupling of phenylacetylene with carbon dioxide mediated by either a Ni(*m*DBU)$_2$ complex (left) or a Ni(BIPY) complex (right). Solid lines represent Type II pathways with dashed lines representing Type I pathways. Gibbs free energies are in kJ mol^{-1} with solvation-corrected energies in parentheses (THF) and brackets (DMF).

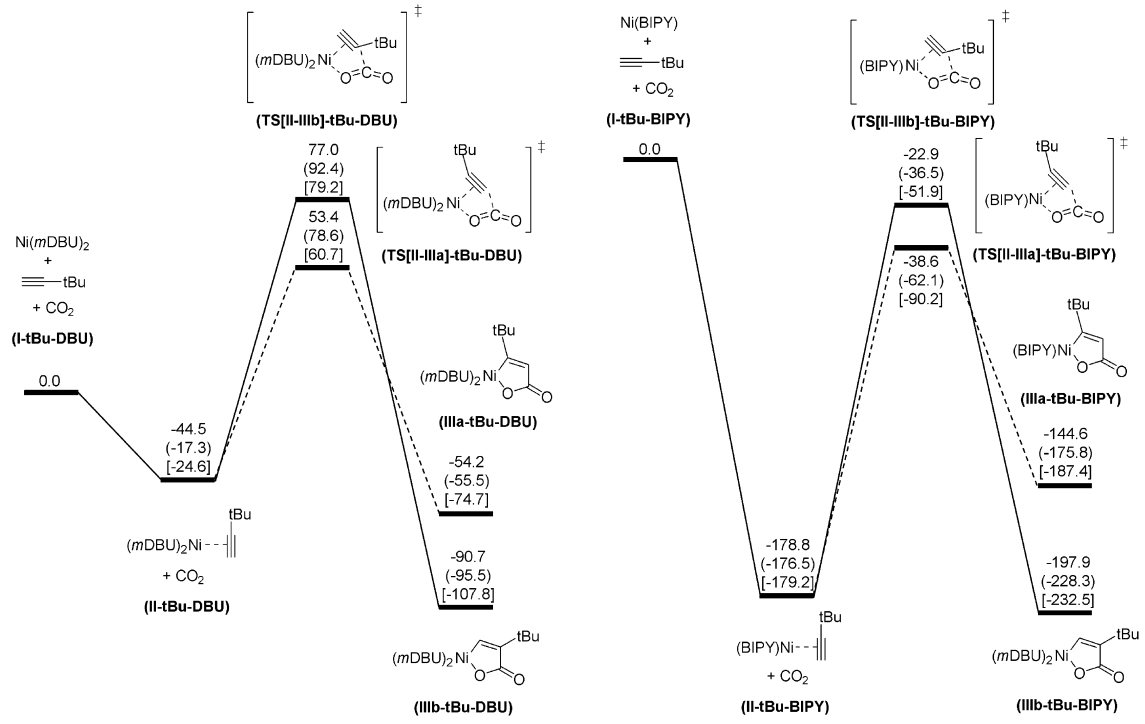


Fig. 8. Gibbs free energy surfaces for the coupling of *tert*-butyl-acetylene with carbon dioxide mediated by either a Ni(mDBU)2 complex (left) or a Ni(BIPY) complex (right). Solid lines represent Type II pathways with dashed lines representing Type I pathways. Gibbs free energies are in kJ mol^{-1} with solvation-corrected energies in parentheses (THF) and brackets (DMF).

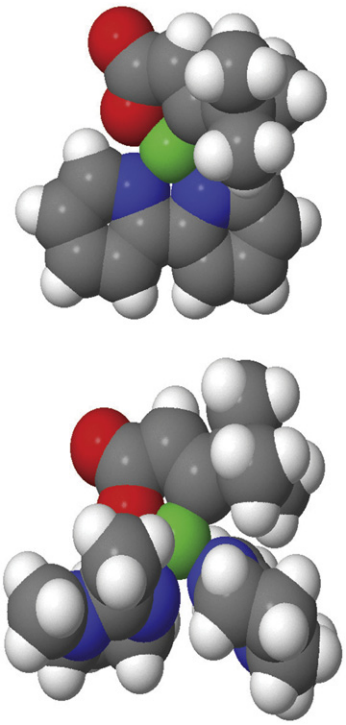


Fig. 9. Space-filling representation of the transition structure geometry for the coupling of acetylene and carbon dioxide mediated by Ni(BIPY) (top) and Ni(*m*DBU)$_2$ (bottom).

electrochemically generated Ni(BIPY) catalyst was undertaken in dimethylformamide (DMF). The DMF solvent-corrected energies are included in Figs. 7 and 8 (in square brackets). In general, compared to the THF-corrected energies, DMF has a stabilising effect on all of the structures on the potential energy surface. For the coupling pathways involving the phenyl-substituted alkyne (Fig. 7), all the structures are stabilised, however the transition structures are stabilised more so than the encounter complexes leading to an overall reduction in the reaction activation barrier. For the Ph–DBU system, the activation energy for Type I pathway reduces from 102.8 (THF) to 93.2 kJ mol^{-1} (DMF), with Type II pathway reducing from 123.9 (THF) to 119.2 kJ mol^{-1}. The trend is similar for the Ph–BIPY system with a reduction in the activation barrier from 111.6 (THF) to 88.3 kJ mol^{-1} (DMF) for Type I pathway and 142.2 (THF) to 132.8 kJ mol^{-1} (DMF) for Type II pathway. The observed difference in the stabilising effect of the two solvents on the reaction barrier can be traced to the change in polarity of the species on going from the reactant to the transition structure. Interaction of the weak dipole alkyne and CO_2 species with the nickel centre acts to increase the polarity of the transition structure compared to the reactants and thus the barrier is more effectively lowered by the higher-polarity solvent (*i.e.* DMF). A similar result is seen for the *tert*-butyl substituted alkyne pathway (Fig. 8). For the DBU system, a reduction in the activation barrier from 95.9 (THF) to 85.3 kJ mol^{-1} (DMF) is calculated for Type I reaction, with a reduction from 109.7 (THF) to 103.8 kJ mol^{-1} (DMF) for Type II system. Analogously, for the BIPY system a reduction from 114.4 (THF) to 89.0 kJ mol^{-1} (DMF) is calculated for the activation barrier in Type I reaction, with a reduction from 140.0 (THF) to 127.3 kJ mol^{-1} (DMF) for Type II reaction. An additional noteworthy change for the BIPY system is the difference in Gibbs free energy between the encounter complex (**II**–*t***Bu**–**BIPY**) and Type I nickelacycle product (**IIIa**–*t***Bu**–**BIPY**) which goes from an unfavourable 0.7 kJ mol^{-1} (as described earlier) to a slightly more favourable −8.2 kJ mol^{-1} moving from THF to DMF as a solvent.

4. Conclusions

The nickel-mediated coupling of acetylene with CO_2 was found to proceed via the same mechanism as the analogous ethylene/CO_2 coupling. The use of acetylene in preference to ethylene results in a coupling reaction that is preferred both kinetically (E_{act} = 99.7 *cf.* 114.2 kJ mol^{-1}) and thermodynamically (ΔG = −125.1 *cf.* −42.1 kJ mol^{-1}).

Asymmetric substitution of the acetylene substrate shows a thermodynamic preference for Type II (3-substituted) nickelacycle due to the steric interaction between the alkyne-substituent and the ancillary ligand. In the Ni(DBU)$_2$ system, Type I pathway is kinetically favoured with activation energies generally 15–20 kJ mol^{-1} below those of the analogous Type II reaction, suggesting that reactions where Type I product is experimentally observed are kinetically controlled. An exception to this is the TMS-substituted alkyne where the Type II nickelacycle is calculated to be both kinetically and thermodynamically preferred – paralleling experimental observations. The kinetic preference for Type II TMS species is due to the sheer size of the substituent, with the steric interaction between the incoming CO_2 moiety and the TMS group in Type II TS energetically preferred over the steric hindrance between the TMS group and the ancillary ligand in Type I TS. Only a minor difference in the reaction energetics was observed when the electron-donating ability of phenylacetylene was enhanced by adding a methoxy group. The activation barrier decreased from 102.8 to 98.1 kJ mol^{-1} – due primarily to a relative destabilisation of the encounter complex – with the Gibbs free energy of reaction becoming slightly less favourable going from −101.2 to −99.4 kJ mol^{-1}.

Replacing the DBU ancillary ligand with BIPY results in a larger overall free energy of reaction due to the high energy of the Ni(BIPY) fragment. However, in the BIPY system there is less driving force for the product relative to the encounter complex. Activation energies are higher by approximately 20 kJ mol^{-1} for reactions mediated by the more basic BIPY-ligated nickel species, with a Type I mechanism again kinetically preferred. For a sterically less-demanding alkyne such as phenylacetylene, the affect of the auxiliary ligand on the thermodynamically preferred regioisomer is relatively minor, with a Type II pathway preferred. However, the combination of sterically demanding alkynes such as *tert*-butyl-acetylene with the BIPY ligand system exhibits no driving force for formation of the kinetically preferred Type I product and thus the thermodynamically preferred (Type II) product would likely result.

A change in solvent from THF to DMF shows a decrease of all activation barriers independent of the other parameters, with no preference observed for either Type I or Type II pathway. Therefore, the dominance of Type II products observed by Dunach [21,23] is more likely related to the BIPY–ligand system which disfavours the formation of sterically hindered Type I products more than the DBU system. However, the explanation may be even simpler than this, with the higher reaction temperatures used by Dunach helping to favour the thermodynamically preferred Type II product over the kinetically preferred Type I product.

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