Mechanism of Reppe's Nickel-Catalyzed Ethyne Tetramerization to Cyclooctatetraene: A DFT Study

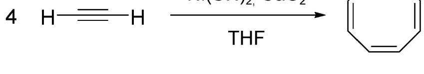
Bernd F. Straub* and Caroline Gollub[a]

Abstract: In this B3LYP model study, homoleptic nickel(0) ethyne complexes have been predicted as the catalyst resting state for the title reaction. Ethyne ligand coupling of $Ni(C_2H_2)_3$ yields monoethyne nickelacyclopentadiene in the rate-determining step. Ethyne coordination is followed by insertion of an ethyne ligand into the Ni–C σ bond. A highly strained monoethyne *trans*-nickelacycloheptatriene is formed. This *trans* intermediate is unable to reductively eliminate benzene without prior isomerization to a *cis*-structure. Instead, it rapidly collapses to a nickelacyclononatetraene. Ethyne coordination induces reductive elimination to the cyclooctatetraene complex $Ni(\eta^2\text{-}C_2H_2)(\eta^2\text{-}C_8H_8)$, followed by facile ligand exchange. Other ethyne coupling pathways have been computed to be less favored. The cyclooctatetraene ligand binds significantly weaker to nickel(0) than ethyne, both for mononuclear, and for dinuclear species. For this reason, C–C bond formation steps at $Ni_2(\mu\text{-cot})$ fragments have been predicted to feature prohibitively high overall reaction barriers.

Keywords: alkyne ligands • C–C coupling • density functional calculations • homogeneous catalysis • nickel

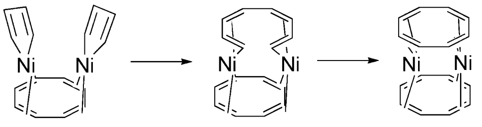
Introduction

Cyclooctatetraene (COT) is one of the most prominent compounds for chemists, both due to its historical role in aromaticity concepts,[1] and due to its fascinating organic[2] and organometallic chemistry.[3] The Willstätter group described the first cyclooctatetraene synthesis in 1911. They prepared COT in seven steps from pseudopelletierine.[4] In 1948, the Reppe group at BASF reported the synthesis of COT in a one-step procedure from easily available ethyne with a $Ni(CN)_2/CaC_2$ precatalyst in THF at 30–60 °C (Scheme 1).[5] This unsurpassed approach for eight-membered carbocycles nearly led to the rise of COT into the league of mass chemicals. However, ethene based on naphtha cracking substituted the expensive ethyne in the 1960's and 70's as the most important industrial C_2 building block.



Scheme 1. Reppe's cyclooctatetraene synthesis.

The mechanism of Reppe's COT synthesis has puzzled organic and organometallic chemists for more than half a century. Schrauzer postulated pseudo-octahedral nickel(II) complexes with four ethyne ligands as central intermediates that undergo either concerted or stepwise ethyne C–C coupling.[6] Colborn and Vollhardt investigated the mechanism of COT synthesis by an elegant ^{13}C labeling study, which shows that the dicarbon fragment of ethyne remains intact in the product.[7] Insertion of ethyne into benzene or cyclobutadiene complexes and carbyne complex intermediates can thus be ruled out. Wilke reported the high activity and selectivity of $Ni_2(cot)_2$, underlining the role of nickel(0) complexes as active species.[8] He proposed a dinuclear $Ni_2(cot)$ active catalyst fragment (Scheme 2), inspired by the reversible C–C bond formation and fission of the cyclooctatetraene ligand in $(CpCr)_2(C_8H_8)$.[9]



Scheme 2. Wilke's proposed COT formation mechanism.

Homogeneous Ni^0 catalysis in the ethyne coupling process was further substantiated by the characterization of nickelacyclopentadiene complexes[10] such as **A**.[10g,h] Coupling of

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Supporting information for this article, which includes cartesian coordinates and energy data, is available on the WWW under http://www.chemeurj.org or from the corresponding author.

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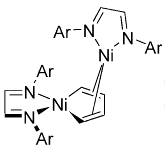
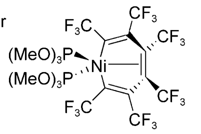


A



B

Ar = 2,6-$Me_2C_6H_3$

three $(CF_3)C{\equiv}C(CF_3)$ at a nickel(0) precursor even yielded a nickelacycloheptatriene (**B**) with *trans* alkenyl ligands at nickel [$\alpha_{CNiC} = 157.1(6)°$].[11]

However, a complete catalytic cycle has remained elusive. Here, we report on a quantum-chemical gas-phase model study, and we put forward a low-barrier mechanism for the nickel-catalyzed ethyne tetramerization to COT.[12]

Computational Methods

All model structures were geometry optimized at the B3LYP level of theory[13] with the SDD ECP and basis set on Ni,[14] and the 6-31G(d) basis set on C and H[15] with the Gaussian 98 program package.[16] Stationary points were characterized as equilibrium structures (NIMAG = 0) or transition states (NIMAG = 1). Single-point energy calculations were performed with the 6-311+G(2d,p) basis set on C and H. For Gibbs free energies discussed in this study, the single-point energies were combined with the Gibbs correction data for 298.15 K and 1 atm obtained from the frequency analyses. We have not discussed weak dipole or multipole aggregates of nickel complexes and ligands, nor have we searched for ligand exchange transition states, which result from the existence of such aggregates. We consider such structures as artifacts of the missing solvation in our model study and they should be meaningless for the real catalysis in for example, tetrahydrofurane (THF) solvent.

Preliminary scans and geometry preoptimizations were performed with the fast Jaguar 4.1 and 4.2 quantum chemistry program package[17] at the B3LYP/LACVP* level of theory.[13,15,18] Due to some geometry optimization convergence problems, particularly for dinuclear nickel complexes, and due to the need for a flexible nickel basis set, we here report only the calculations performed by using the Gaussian 98 program.

The ball-and-stick model images were rendered by the ray-tracing program POV-Ray (version 3.1).[19]

By definition, overall free activation energy means the Gibbs energy difference between the catalyst resting state, and the transition state of the rate-determining step. According to the Curtin–Hammett principle,[20] rapid pre-equilibria (conformational or in this case ligand exchange equilibria with constant substrate and metal concentration) have no impact on the reaction rate or selectivities.

Abstract in German: In dieser B3LYP-Studie werden homoleptische Nickel(0)-Ethinkomplexe als Katalysatorruhezustand von Reppes Cyclooctatetraensynthese vorhergesagt. Kupplung zweier Ethinliganden in $Ni(C_2H_2)_3$ ergibt Monoethin-Nickelacyclopentadien im geschwindigkeitsbestimmenden Schritt. Der Koordination von Ethin folgt die Insertion eines Ethinliganden in die Ni−C σ-Bindung. Ein hoch gespanntes Monoethin-*trans*-Nickelacycloheptatrien wird gebildet. Dieses *trans*-Intermediat ist nicht in der Lage, Benzol reduktiv zu eliminieren, ohne vorher in eine *cis*-Struktur zu isomerisieren. Stattdessen kollabiert es schnell zu Nickelacyclononatetraen. Koordination von Ethin induziert eine barrierefreie reduktive Eliminierung zum Cyclooctatetraen Komplex $Ni(\eta^2\text{-}C_2H_2)(\eta^2\text{-}C_8H_8)$, gefolgt von einem einfach verlaufenden Ligandenaustausch. Andere Ethinkupplungspfade wurden als weniger begünstigt berechnet. Der COT-Ligand bindet sowohl für mononukleare als auch für dinukleare Spezies deutlich schwächer an Nickel(0) als Ethin. Aus diesem Grund werden für C−C-Bindungsbildungsschritte am $Ni_2(\mu\text{-cot})$-Fragment prohibitiv hohe freie Aktivierungsenthalpien vorhergesagt.

Results and Discussion

First, we present a complete COT formation mechanism, which we consider to be the most preferable catalytic pathway. Then, we present other reasonable candidates for C−C bond coupling pathways. These have higher computed Gibbs free activation energies than the species in our proposed mechanism and are thus unlikely for the real catalytic cycle.

Proposed mechanism: We identified the model structure $Ni(C_2H_2)_2$ (**1**) (Figure 1) as the most stable Ni^0 species with the accessible ligands ethyne and COT. Gibbs free energies of all other model complexes in this study will be given relative to the Gibbs free energy of structure **1**. Addition of ethyne to complex **1** via transition state **2** yields $Ni(C_2H_2)_3$ (**3**).[21] The origin of the intrinsic barrier in the ethyne coordination is the rehybridization in the D_{2d}-symmetric complex **1** with its orthogonal ethyne ligands to the D_3-symmetric structure **3**. The electronic structures of model complexes **1** and **3** have already been reported.[22,23] Within the accuracy of the used methodology, and considering its gas-phase restriction, either complex **1** or complex **3** can be the resting state of the catalyst. Both entropic and enthalpic contributions influence the relative stability of the nickel species in solution. For association reactions, Cooper and Ziegler estimated a solvation contribution to the activation entropy of about 50% of the gas-phase value.[24] In a recent DFT study on the nickel-catalyzed butadiene and ethene co-oligomerization, Tobisch deduced a decrease in entropical costs by 6.0 $kcal\,mol^{-1}$ (25.1 $kJ\,mol^{-1}$) for butadiene association at a nickel center in solution relative to the gas phase.[25] Thus, entropic considerations are in favor of a tris(ethyne)nickel resting state, while enthalpic estimations would have to take the hydrogen bonds of ethyne in THF into account. To the best of our knowledge, neither one of the homoleptic nickel ethyne complexes **1** or **3** have ever been experimentally characterized or even isolated, which leaves the question of their relative stabilities unanswered.

Structure **3** acts as the starting complex for a stepwise ethyne coupling sequence. A partial C−C bond formation in transition structure **4** results in high-energy intermediate **5**. The energy surface in this area is very shallow. Nevertheless, on the total electronic energy hypersurface, intermediate **5** is clearly characterized as a local minimum. The C−C distance between the two ethyne fragments amounts to 1.623 Å, which is clearly more than that for a typical $C(sp^2)-C(sp^2)$ bond. The ancillary ethyne ligand is in plane

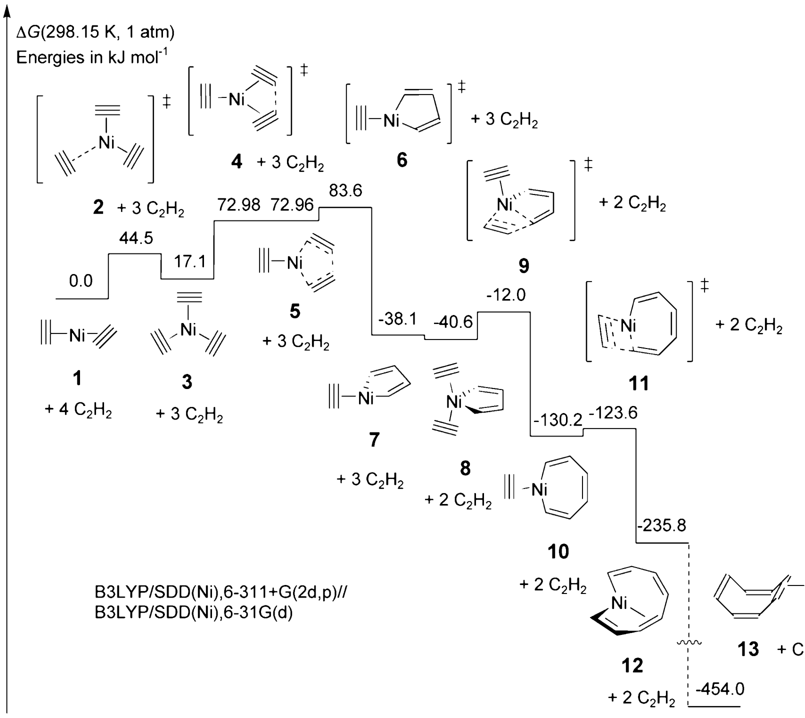


Figure 1. Proposed lowest-barrier pathway with four C–C bond-coupling steps at a nickel center. Dotted lines (between **7** and **8**, **12** and **13**) indicate a ligand association or a rearrangement with no intrinsic barrier.

with the residual NiC_4 fragment, which reflects the overall C_{2v} symmetry of this electronically highly delocalized complex. The rate-determining step **6** completes the C–C bond forming process; this involves rotation of the ethyne spectator ligand. The ancillary ethyne ligand in structures **3** to **5** withdraws electron density from the same nickel d orbital that donates its electron occupation to the two coupling ethyne ligands in the overall formal oxidative addition step. By rotation of the ethyne ancillary ligand in transition state **6**, the competing electronic pull of the ancillary ligand and the ethyne coupling is lifted; this leads to structure **7**. The d^8-ML_3 character of this ethyne nickelacyclopentadiene complex **7** is the origin of the T-shape coordination geometry of the nickel(II) center.[26]

Without an intrinsic barrier, ethyne coordination produces *cyclo*-$NiC_4H_4(C_2H_2)_2$ (**8**). This d^8-ML_4-type complex features an unusual pseudotetrahedral nickel(II) environment. Due to the high π-acidity and low σ-donation capability of the ethyne ligands, the pseudo-square-planar coordination geometry of the phosphane and imine analogues such as **A** is unstable for structure **8**.

With amine and phosphane ligands, several nickelacyclopentadienes (nickeloles) have been characterized and isolated.[10c,f,g,h] Due to their intrinsic stability and the labeling results of Colborn and Vollhardt,[7] a possible role of cyclobutadiene complexes was not further investigated.

The insertion process of one of the ethyne ligands in **8** via transition state **9** leads to the nickelacycloheptatriene derivative **10**. Therein, the two alkenyl fragments are in a strained *trans* position at the nickel center ($\alpha_{CNiC} = 140.7°$). The deviation from the ideal 180° angle originates from the small number of only seven ring atoms. Due to the ring strain, complex **10** represents a labile species with a negligible rearrangement barrier of 6.6 kJ mol^{-1} for the insertion of the residual ethyne ligand into a Ni–C σ-bond via transition state **11**. Though structure **10** appears to have a free coordination site, the intramolecular rearrangement via transition state **11** will be orders of magnitude faster than any entropy- or diffusion-controlled intermolecular ligand association or cycloaddition reaction. Reppe et al. have already discussed the rearrangement product, *cis*-nickelacyclononatetraene (**12**), as a possible catalytic intermediate.[5] Due to the intramolecular η^2-coordination of the π-system, nickel(II) complex **12** is a 14 valence electron d^8-ML_3 structure.

The last coupling step in the C–C bond formation cascade occurs after ethyne coordination at the unsaturated nickelacyclononatetraene **12**. A cyclooctatetraene ligand reductively eliminates without an intrinsic barrier, and forms $Ni(\eta^2$-$cot)(C_2H_2)$ (**13**). The coordination of nickel to the C_8 π-system prevents high-energy transition structures with only 12 valence electrons.[27] Overall, the stepwise ethyne coupling and insertion steps can be classified as a "zipper mechanism".[7] Ball-and-stick models of structures **1** to **13**, including Ni–C and C–C bond lengths are displayed in Figure 2.

Coordination of a second ethyne ligand to structure **13** proceeds easily, producing $Ni(\eta^2$-$cot)(C_2H_2)_2$ (**14**) (Figure 3). Dissociation of the final product COT via transition state **15** regenerates resting state **1**, thereby closing the catalytic cycle.

From complex **13**, a reversible low-barrier intramolecular rearrangement pathway via transition state **16** leads to the more stable isomer $Ni(\eta^2{:}\eta^2$-$cot)(C_2H_2)$ (**17**) (Figure 4). The latter, however, is by far less stable than the catalyst resting state plus COT. Thus, it can only be formed in an unproductive equilibrium in minor amounts.

Nickelacycloheptatriene isomers: The *trans* coordination pattern of the formally T-shaped[28] seven-membered metallacycle **10** is the determining factor for product selectivity of the catalytic cycle. Only from a *cis*-complex, highly stable benzene can be reductively eliminated. If instead of ethyne another ligand such as a phosphane or pyridine was attached to the *trans*-nickelacycloheptatriene fragment, no further ethyne insertion would be possible. Instead, an isomerization to a more stable, less strained *cis*-complex such as **18** could take place (Figure 5). The *cis* nature of the vinylic ligands at the nickel center is characterized by a C-Ni-C angle of 93.6°. However, the rearrangement of structure **10**

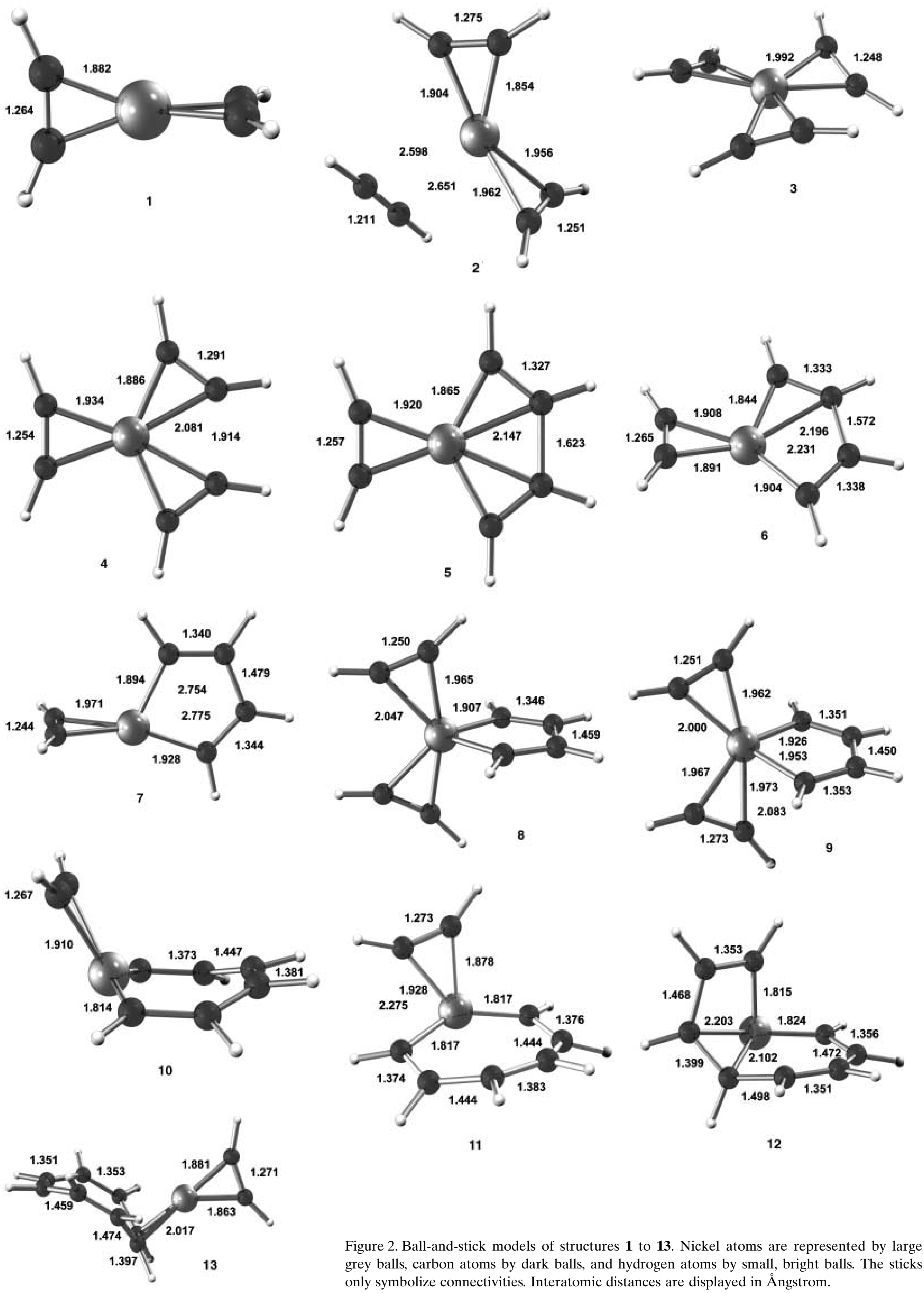


Figure 2. Ball-and-stick models of structures **1** to **13**. Nickel atoms are represented by large grey balls, carbon atoms by dark balls, and hydrogen atoms by small, bright balls. The sticks only symbolize connectivities. Interatomic distances are displayed in Ångstrom.

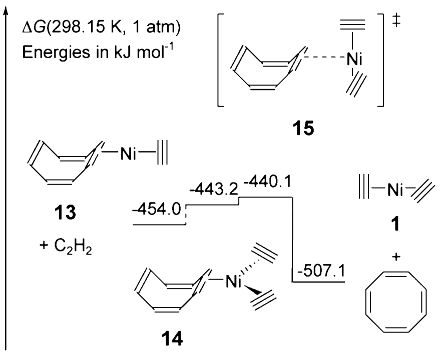


Figure 3. Final COT/ethyne ligand exchange.

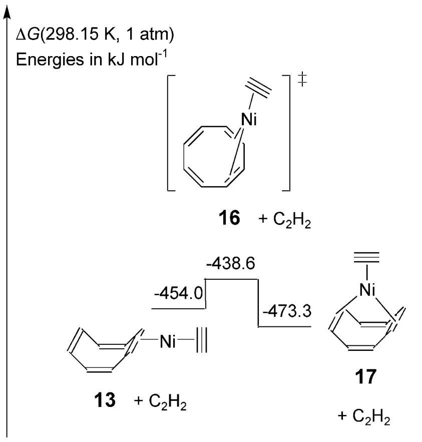


Figure 4. Isomeric Ni(cot)(C_2H_2) complexes.

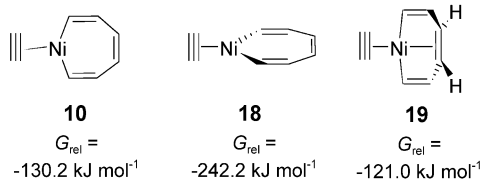


Figure 5. Structures and energies of isomeric nickelacycloheptatriene ethyne complexes.

(C_s) to isomer **18** (C_{2v}) is symmetry-forbidden, therefore our attempts to find a transition state failed. Preliminary scans indicate a high interconversion barrier with ethyne ligand dissociation.

Isomer **19** possesses the same structural backbone as compound **B** (vide supra). However, it is even less stable than the catalytic intermediate **10**. Due to the coordination of the central *E* double bond to the nickel atom in complex **19**, the C-Ni-C angle of 154.8° is closer to the ideal 180° *trans* angle than the C-Ni-C angle of metallacycle **10** (Figure 6).

Increased benzene formation is observed upon pyridine, amine or PPh_3 addition to nickel(0) ethyne reaction mixtures.[6a,b,7,29] In contrast to the ethyne ligand, pyridine, amines, and phosphanes are unable to insert into Ni–C σ-bonds. Thus, only a *trans*/*cis* rearrangement can lead to a more stable complex if the *trans*-nickelacycloheptatriene fragment is attached to a nitrogen or phosphorus donor ligand. Subsequent reductive elimination of benzene from the pyridine, amine or phosphane analogue of complex **18** gives a rationale for the higher benzene yield (Scheme 3).

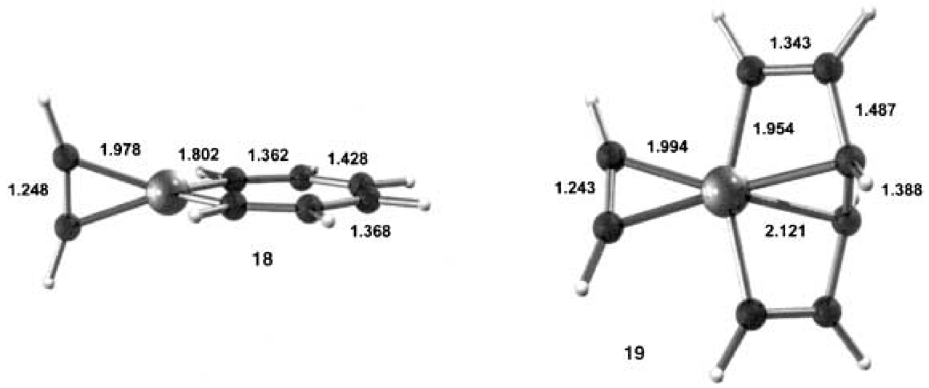
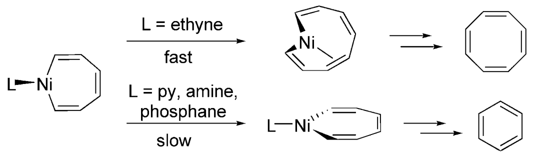
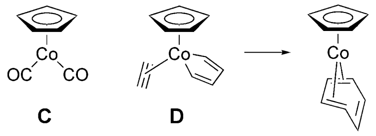


Figure 6. Ball-and-stick models of the nickelacycloheptatriene ethyne complexes **18** and **19**. Nickel atoms are represented by large grey balls, carbon atoms by dark balls, and hydrogen atoms by small, bright balls. The sticks only symbolize connectivities. Interatomic distances are displayed in Ångstrom.



Scheme 3. Postulated insertion versus rearrangement pathways from *trans*-nickelacycloheptatriene complexes.

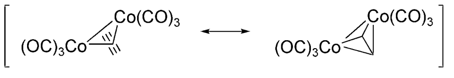
CpCo(CO)$_2$-catalyzed alkyne trimerization: Benzene derivatives are the product in Vollhardt's trimerization of alkynes by $CpCo^I$ catalysts such as $CpCo(CO)_2$ (**C**), or the Jonas reagent $CpCo(C_2H_4)_2$.[30] The different product selectivity of Ni^0 and $CpCo^I$ catalysts can be rationalized based on their electronic structure and ligation pattern. In a DFT study, the Albright group concluded that the final benzene formation step for CpCo catalysts involves structure **D**.[31] Therein, the Cp^- ligand facially binds to three coordination sites of the d^6-ML_6-type complex, rendering a *trans*-cobaltacycloheptatriene fragment impossible, and thus enforcing benzene formation.



Dinuclear complexes: So far, we have proposed a complete mechanism for nickel-catalyzed ethyne tetramerization.

Subsequently, we present alternative pathways composed of dinuclear intermediates. The higher overall activation barriers of these routes increase the credibility of the proposed mononuclear COT formation mechanism (Figures 1 and 3).

Dinuclear nickel(0) μ-ethyne complexes are d^{10}–d^{10} species. Derivatives of the structurally similar dicobalt(0) μ-ethyne complex **E** are key intermediates in the Pauson–Khand reaction.[32]



E

However, these d^9–d^9 complexes possess a classical Co–Co σ bond, while the Ni–Ni interaction would be considered as an important or even predominant van der Waals part.[33] Isoelectronic monovalent coinage metal dimers are known to interact through induced dipoles ("aurophilic interactions").[34]

Since the B3LYP functionals do not reproduce van der Waals interactions,[35] the complexes **20**, **21,** and **26** might well be somewhat more stable than computed. Pyykkö et al. estimated attractive Cu^I–Cu^I interaction energies of about 10—15 kJ mol^{-1} for dinuclear copper(I) complexes.[34] We expect similar or weaker metal–metal interactions in dinuclear nickel(0) species. Thus, C–C coupling steps in (μ-ethyne)-bridged dinickel species appear to have somewhat higher activation energies than the corresponding mononuclear pathway (Figures 7 and 8). However, it cannot be ruled out that a dinuclear pathway is favorable for a high Ni^0 concentration.

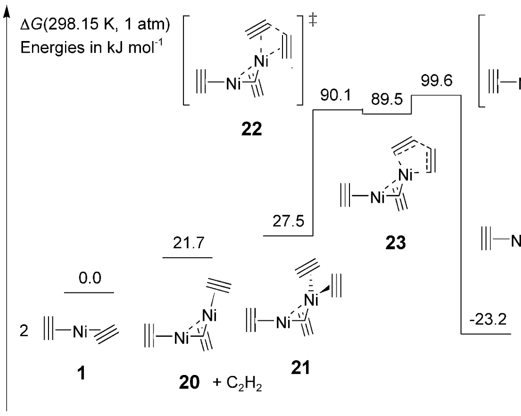


Figure 7. Ethyne coupling at dinuclear nickel complexes: $(C_2H_2)Ni(\mu\text{-}C_2H_2)$ as a spectator ligand.

COT is an alternative ligand for nickel. Thus, pathways involving cyclooctatetraene complexes have to be considered as alternative catalytic routes. However, ethyne coupling at Ni(cot) fragments generally suffers from the inferior Ni–COT bond strength relative to homoleptic nickel ethyne complexes (Figure 9).

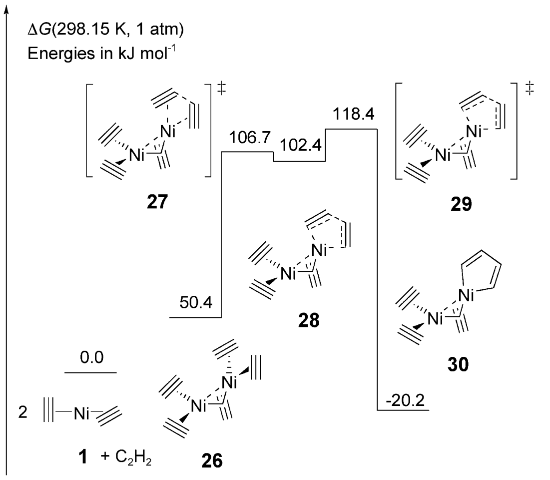


Figure 8. Ethyne coupling at dinuclear nickel complexes: $(C_2H_2)_2Ni(\mu\text{-}C_2H_2)$ as a spectator ligand.

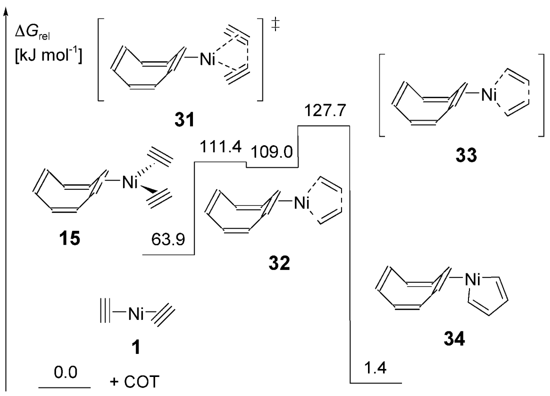


Figure 9. Ethyne coupling at a Ni(cot) fragment.

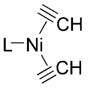
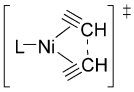
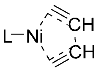
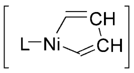
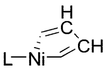
So far, we have presented a mechanism for four mononuclear ethyne coupling pathways (Figures 1, 7, 8 and 9, and Table 1). All four nickelacyclopentadiene formation sequences are formal oxidative addition reactions that proceed stepwise with similar intrinsic barriers between 63 and 72 kJ mol^{-1}. The larger differences in the overall barriers are determined by the bond strengths of the respective spectator ligand.

Dinuclear C–C coupling mechanisms: The μ-ethyne dinickel-mediated ethyne coupling displayed in Figure 5 has a barrier only slightly higher than that of the mononuclear pathway (Figure 1). The further domino-ethyne insertion mechanism from the dinuclear complex **35** via structures **37** and **39,** and transition states **36**, **38,** and **40** yields the dinickel cyclooctatetraene complexes **41** and **42**. The latter are thermodynamically unstable towards regeneration of the catalyst resting state **1** (Figure 10). Mutual intermediates for the final ligand exchange are the (μ-η^2:η^2-cot) complexes **43** and **44**.

This most favored dinuclear pathway (Figures 5 and 8) strongly resembles the mononuclear pathway (Figure 1).

Ethyne inserts more readily into Ni–C bonds than a μ-ethyne ligand. As a consequence, ethyne inserts into the nickelacyclopentadiene Ni–C bond first (transition state **36**). Subsequently, the bridging ethyne ligand inserts into nickel-

Table 1. C–C distances and free activation energies for ethyne coupling reactions in nickel(0) complexes, obtained at the B3LYP/SDD(Ni),6–31G(d) level of theory.

[d(C–C)] [Å] L = /(complex)	η^2-C_2H_2	(η^2-C_2H_2)Ni (η^2:η^2-C_2H_2)	(η^2-C_2H_2)$_2$Ni (η^2:η^2-C_2H_2)	η^2-cot
	2.701 (**3**)	2.686 (**21**)	2.706 (**26**)	2.653 (**15**)
	1.914 (**4**)	1.972 (**22**)	1.929 (**27**)	1.935 (**31**)
	1.623 (**5**)	1.626 (**23**)	1.596 (**28**)	1.599 (**32**)
	1.572 (**6**)	1.623 (**24**)	1.566 (**29**)	1.561 (**33**)
	1.479 (**7**)	1.478 (**25**)	1.478 (**30**)	1.477 (**34**)
free rearrangement activation energy [kJ mol^{-1}]	66.5	72.1	68.0	63.8
overall free activation energy [kJ mol^{-1}]	83.6	99.6	118.4	127.7

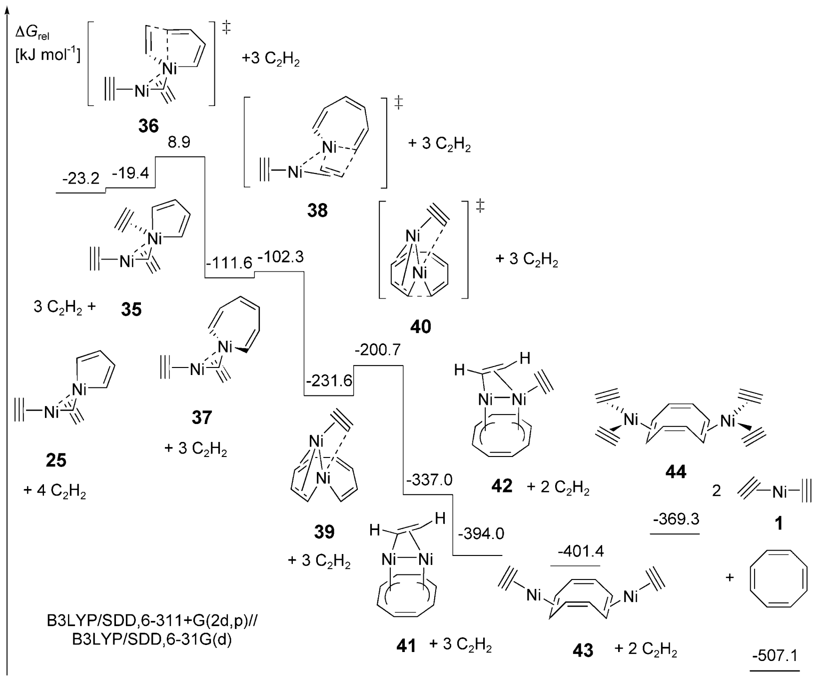


Figure 10. Most favorable dinuclear COT formation pathway.

acycloheptatriene (transition state **38**). An inverted order of the insertion steps starting from complex **35** leads to a higher free activation energy in the decisive first step (transition state **36** versus **46**) (Figures 10 and 11).

We have not investigated the ethyne insertion cascade originating from dinickel complex **45**. The electronic influence of the additional ethyne ligand at the "spectator nickel" is presumably negligible, while the energetic influence for the corresponding intermediates appears to be a constant energetic increase by about 15 kJ mol^{-1}.

Ni_2(cot)$_2$: In our study, Wilke's highly effective precatalyst Ni_2(cot)$_2$ (**49**) is predicted to be a high-energy precursor for catalyst **1** (Figure 12). The nickel centers in complex **49** are electronically saturated, and attempts to locate an ethyne association structure failed. The excellent precatalyst property of **49** might thus be attributed to the release of active Ni^0 species over a prolonged period of time, thus preventing very low catalyst concentrations.

C–C-coupling of two ethyne ligands across two nickel centers is highly disfavored, both due to the high relative free energy of complex **42**, and to the high free activation energy via transition state **50** to the dinickelacyclohexa-1,3-diene derivative **51**.

The Wilke mechanism: Though we have not computed all steps of Wilke's proposed mechanism (Scheme 2), our model calculation data is sufficient to predict that a (μ-cot) bis(nickelacyclopentadiene) will neither be formed at a Ni_2(cot) fragment nor be produced by ligand exchange reactions.

COT is a weak ligand, leading to high-energy nickel cyclooctatetraene complexes, and thus overall high-barrier ethyne coupling steps. Based on our model calculations, NiC_4 ring systems can only be formed with an ethyne spectator ligand. The ethyne COT ligand exchange reactions of nickelacyclopentadienes **7** or **8** to complex **52** are thermodynamically disfavored by more than 25 kJ mol^{-1} (Figure 13). Due to the facile ethyne insertion rearrangement in complex **8**, a ligand exchange equilibrium is not competitive at this point. The sandwich complex **49** features a relative energy almost as high as the ethyne insertion transition state of the proposed mononuclear pathway.

Bis(nickelacyclopentadiene) complex **53** is no alternative in further C_4–C_4 coupling steps either. Despite the very exergonic C–C bond formation to complex **55**, the high Gibbs free energy of the transition state **54** is not competitive.

Nickel metal precipitation: Trinuclear nickel μ-ethyne complexes are potential intermediates in the precipitation of nickel metal from catalytically active Ni^0 species. The low relative free energies and the small Ni–Ni distances in com-

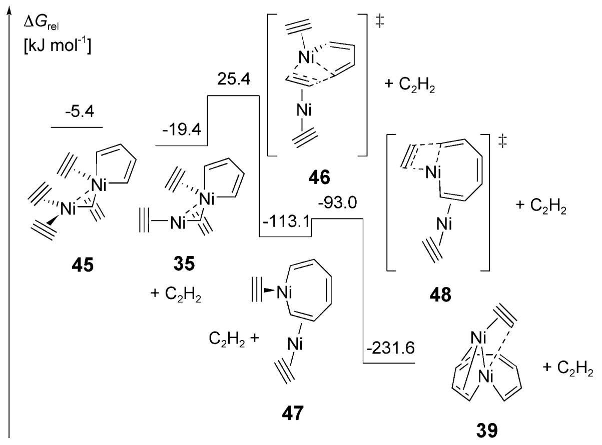


Figure 11. Less favored ethyne insertion cascade for dinuclear complexes.

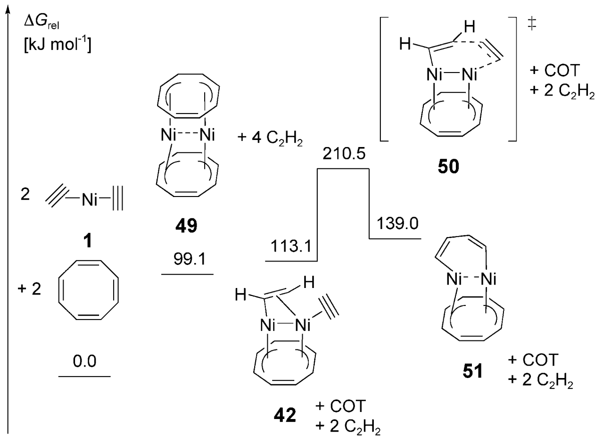


Figure 12. Ethyne coupling across two nickel atoms.

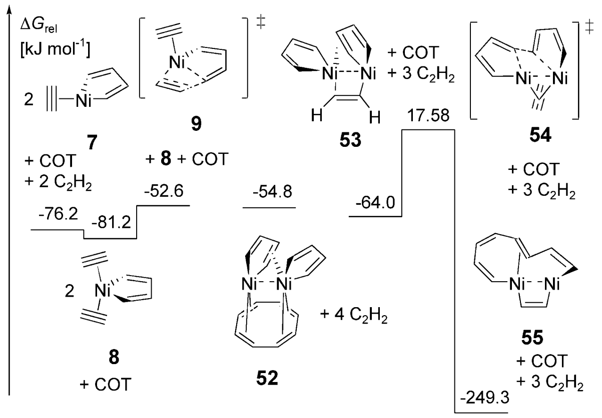


Figure 13. Comparison of mononuclear ethyne insertion and dinuclear C_4–C_4 coupling.

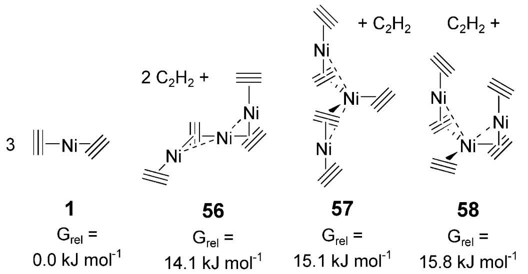
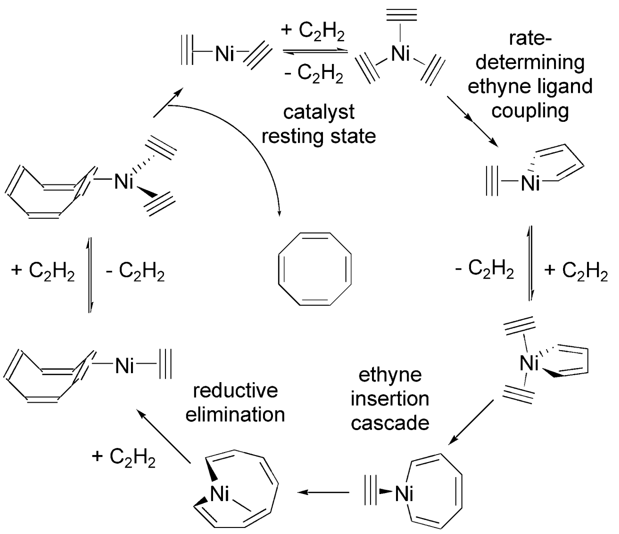


Figure 14. Relative free energies for trinuclear μ-ethyne complexes.

plexes **56**, **57**, and **58** (2.652 Å, 2.669 Å and 2.657 Å/2.704 Å, Figure 14) indicate a facile aggregation route for nickel(0) species towards nickel(0) clusters. Thus, the high relative stability of polynuclear μ-ethyne complexes could well be the origin for irreversible catalyst deactivation by nickel metal precipitation in Ni^0 ethyne reaction mixtures. A derivative of complex **56** with bulky alkyne substituents has been structurally characterized (average Ni–Ni distance 2.56 Å); this underlines the potential role of such aggregates in nickel ethyne reaction mixtures.[36] Hyla—Kryspin and Koch et al. have already characterized binuclear and trinuclear μ-bridged ethyne nickel(0) complexes quantum chemically.[23,33]

The low overall free activation energy of less than 85 $kJ\,mol^{-1}$ computed in this study (Figure 1), and the observed moderate reaction rates can be rationalized by low concentrations of active nickel(0) species in the reaction mixture; this is either due to slow Ni^{II} precatalyst reduction (original Reppe precatalysts) or due to decomposition of active nickel(0) complexes by nickel metal precipitation. Low nickel(0) concentrations would significantly hamper dinuclear pathways, which further supports the mechanistic proposal of a catalytic cycle with mononuclear intermediates (Figure 1 and Scheme 4). Since all nickel coordination sites are mandatory for the catalytic cycle, suitable Ni^0-stabilizing ligands are μ-ethyne metal complex fragments. However, these metal fragments must be redox-inactive under the reaction conditions, catalytically inactive due to only one accessible coordination site, and stable towards acetylide formation. Then, the insertion of μ-ethyne ligands into Ni–C σ-bonds can proceed with sufficiently low barriers, and the cocatalyst can dissociate from the COT product; this is in analogy to ethyne nickel fragments computed in this study.



Scheme 4. Proposed catalytic “octagon“ for ethyne tetramerization.

Solvent effects: In this study, we focused on the energetics under gas-phase conditions. We are aware of the entropic and enthalpic consequences of this gas-phase restriction. Indeed, the solvent choice is an important parameter for the reaction rate and yields.[5,6] THF and even more so 1,4-dioxane[6b] are better solvents than hydrocarbons in the COT synthesis. Hard oxygen donor atoms of ether solvents can form strong hydrogen bonds to ethyne, and support high ethyne concentrations in the reaction mixture. The preference of high ethyne concentrations can be rationalized both by higher equilibrium concentrations of tricoordinated nickel(0) species, and by disfavored μ-ethyne nickel aggregate formation.

Conclusion

From DFT model calculations, we can predict the catalytic COT formation cycle shown in Scheme 4. The catalyst resting state of nickel-catalyzed ethyne tetramerization is a homoleptic ethyne nickel(0) complex, which undergoes a stepwise ethyne ligand C–C coupling reaction. Ethyne coordination to the resulting nickelacyclopentadiene derivative is followed by two rapid ethyne insertions into Ni–C σ-bonds. Then, the nickelacyclononatetraene intermediate coordinates ethyne, and subsequently reductively eliminates COT without a barrier. Finally, associative ligand exchange liberates the COT product and regenerates the catalyst.

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