

Syntheses, Structural Characterization, and Kinetic Investigations of Metalla[3]triangulanes: Isoelectronic Nickel(0) and Copper(I) Complexes with Bicyclopropylidene (bcp) and Dicyclopropylacetylene (dcpa) as Ligands

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The kinetics of the reactions between [Ni(bipy)(COD)] and bicyclopropylidene (bcp), dicyclopropylacetylene (dcpa) and 1,4-dimethoxy-2-butyne (dmbu) were investigated using stopped-flow techniques. Similar to previous studies the results support an associative mechanism (activation parameters for bcp: $\Delta H^\ddagger = 46 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta S^\ddagger = -69 \pm 8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) and therefore allowed to postulate a more general reaction mechanism for the reaction pathway. The products, the

nickel(0) complexes [Ni(bipy)(bcp)] and [Ni(bipy)(dcpa)], could be structurally characterized and the molecular structures are presented. In addition, the corresponding copper(I) complexes [Cu(bipy)(bcp)]PF₆ and [Cu(bipy)(dcpa)]PF₆ were also structurally characterized and their reactivity towards dioxygen was investigated. A detailed discussion of the structural properties and comparisons to similar literature-known olefinic complexes with transition metals are presented.

Introduction

As has been stated before,^[1] transition metal-catalyzed cocyclizations, which are formal cycloaddition reactions, of alkenes and alkynes as well as other unsaturated building blocks, are outstanding examples for synthetic efficiency. These reactions are highly atom economical and use simple starting materials under mild conditions to form complex cyclic and oligocyclic compounds. Since the synthesis of bicyclopropylidene (bcp, **1**, Scheme 1) has been reported and optimized,^[2,3] this alkene as well as its derivatives became versatile C₆ building blocks for organic synthesis.^[4,5,6] For example, methylenecyclopropane, especially **1** and its derivatives, are predestined for the

formation of new cyclopropyl group-containing compounds.^[7] Alkene **1** can undergo cocyclizations under palladium, nickel and cobalt catalysis.^[8] However, despite the fundamental interest in the mechanism of these reactions, so far only metalla-[3]triangulanes **1-Ti**, **1-Co** and **1-Pt**, i.e. transition metal complexes of titanium(II),^[9] cobalt(I)^[9,10] and platinum(0),^[11,12] respectively (Scheme 1) with **1** as a ligand have been isolated and structurally characterized, yet little is known about the mechanism of the formation of these complexes.

On the other hand, the twofold cyclopropyl-substituted alkyne, dicyclopropylacetylene (dcpa, **2**, Scheme 1), attracted our attention as an interesting building block and versatile precursor as well. Synthesis of the hydrocarbon **2** was first

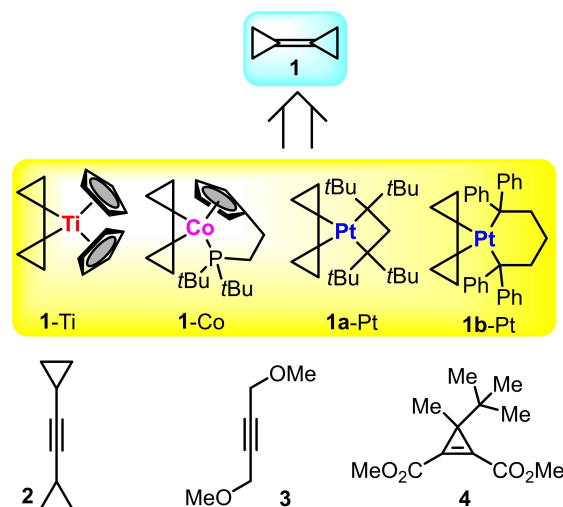
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Scheme 1. Bicyclopropylidene (**1**) and two alkynes **2** and **3**, employed as ligands in the current work in comparison to dimethyl 3-methyl-3-tert-butylcycloprop-1-ene-1,2-dicarboxylate (**4**).^[13]

reported in 1970^[14] and has been improved more recently.^[15–17] For example, this compound was applied in the preparation of perspirocyclopropanated cyclic oligoacetylenes^[17] and other compounds with several cyclopropane moieties on adjacent carbon atoms under appropriate conditions.^[18] Interestingly, cobalt(I)-catalyzed Z-regioselective hydrosilylation of **2** proceeds with retention of both cyclopropanes and affords (dicyclopropylvinyl)silanes which are valuable starting materials in organic syntheses.^[19] To the best of our knowledge and in line with the Cambridge Structural Database (CSD), no crystal structures of metal complexes with **2** as a ligand have been reported so far.

With regard to the interesting structural properties of transition metal complexes of **1** and **2** and their potential catalytic activities, the formation of nickel(0) and copper(I) complexes with these ligands were studied.

Results and Discussion

Synthesis and Structural Characterization of Nickel(0) Complexes [Ni(bipy)(bcp)] (1-Ni) and [Ni(bipy)(dcpa)] (2-Ni)

The complexes 1-Ni and 2-Ni were obtained by mixing [Ni(bipy)(COD)] (**5**) with an excess of the respective ligand **1** or **2** in either diethyl ether or tetrahydrofuran.^[20,21] While easily prepared, the two complexes are extremely sensitive towards dioxygen, which therefore precluded their full characterization. However, it was possible to crystallize both 1-Ni and 2-Ni, and

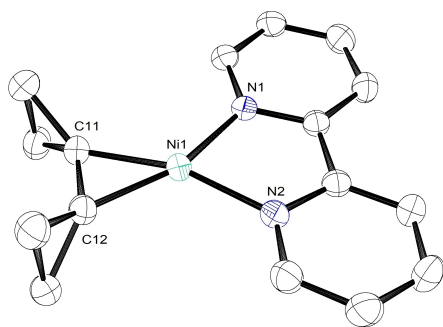


Figure 1. ORTEP plot of the complex 1-Ni. Ellipsoids at 50% probability, hydrogen atoms omitted for clarity.

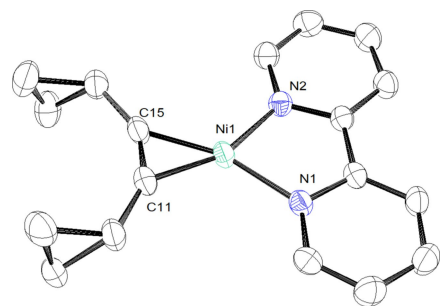


Figure 2. ORTEP plot of complex 2-Ni. Ellipsoids at 50% probability, hydrogen atoms omitted for clarity.

their molecular structures are presented in Figure 1 and Figure 2 (crystallographic data are reported in the Supporting Information).

The green colored complex 1-Ni shows the typical η^2 -binding motif of the alkene, and the trigonal coordination geometry characteristic for a metalla[3]triangulane. In addition, a severe bending of the cyclopropane moieties is revealed in the molecular structure. This is a consequence of the strong back-bonding effect^[9,10] which also leads to a remarkably longer double bond [1.422(4) Å, 9.0%] of the coordinated ligand (Table 1) in comparison to the free molecule of **1** [1.304(2) Å].^[4,22] Interestingly, the elongation of the C=C distances in 1,5-cyclooctadiene [1.340(3) Å],^[23] ethylene [1.337(2) Å], butadiene [1.342(1) Å],^[24] and styrene [1.325(2) Å]^[25] upon formation of similar nickel complexes is equal to $\Delta = 0.053$,^[26] 0.055,^[27] 0.073,^[28] and 0.118 Å.^[27] Notably, the latter value is the same as $\Delta = 0.118$ Å caused by effect of spirocyclopropanes in 1-Ni. Comparable lengths of the double bonds of 1.441(8) Å^[11] and 1.427(3) Å^[12] were observed for the previously reported platinum(0) complexes **1a**-Pt and **1b**-Pt, respectively. In addition, the proximal bonds of the ring spiro-annellated to the nickelacyclopropane moiety (average 1.496 Å) are slightly shortened as compared to the distal C–C bonds (average 1.520 Å); the latter, however, are shortened in comparison to the normal C–C bond (1.544 Å). This can be attributed to the hybridization change of the spiro carbon atoms from sp^2 to $sp^{3[15,17]}$ and is a common phenomenon in triangulane structural features.^[6] The nickel-carbon distances in the complex 1-Ni are 1.883(2) Å and 1.895(2) Å. The average Ni–C distance of 1.889 Å in spirocyclopropanated complex 1-Ni is shorter than the distances in analogous three-coordinate Ni complexes with ordinary alkenes (1.921–2.064 Å),^[26–29] probably due to the enhanced contribution of π back-donation. Also, the angle C–Ni–C in the nickelacyclopropane moiety of 1-Ni (44.2°) turned out to be the largest one in comparison with the sequence of complexes with cyclooctadiene (39.6°),^[26] ethylene (42.4°)^[27] and styrene (43.4°).^[27]

Some differences in the bond lengths of spirocyclopropane-annellated 1-Ni in comparison to the rather similarly strained cyclopropanefused 4-Ni are noted.^[13] The cyclopropene ligand **4** is substituted with two methoxycarbonyl groups, a methyl and a *tert*-butyl substituent (Scheme 1). The nickelabicyclobutane moiety in 4-Ni has slightly elongated nickel-C_{olefin} bond lengths with 1.897(5) Å. However, the former olefinic C–C bond length is 1.437(9) Å and even remarkably longer than the one in 1-Ni,

Table 1. Selected bond lengths (Å) in metalla[3]triangulanes 1-Met.^[a]

Compound ^a	C=C	C–C _{dist.}	C–C _{vic.}	C–Met	Ref.
1-Co	1.401(5)	1.499(12)	1.482(5)	1.960(4)	[9]
1a-Pt	1.441(8)	1.504(7)	1.482(5)	2.052(3)	[11]
1b-Pt	1.427(3)	1.518(3)	1.488(4)	2.077(3)	[12]
				2.050(3)	
1-Ni	1.422(4)	1.524(4)	1.496(4)	1.883(2)	This work
		1.515(4)		1.895(2)	
1-Cu	1.364(3)	1.531(2)	1.476(2)	1.961(2)	This work

[a] Not reported for 1-Ti.

being in the range of typical sp^3 - sp^3 carbon-carbon bond lengths. A strong bending of the residual groups is again observable in their structure.

The binding motif in **2-Ni** is similar to that in complex **1-Ni** with regard to the trigonal-planar coordination geometry and the strong outward bending of the two cyclopropyl rings.^[20] The internal C–C bond distance with 1.283(3) Å is again significantly longer than the C≡C triple bond of the free alkyne molecule [1.197(3) Å, calculated data,^[30] $\Delta = 0.086$ Å], and the metal-carbon bond distances are 1.851(3) Å and 1.854(3) Å. Similar values have been reported previously by J. J. Eisch et al. for the elongated C≡C triple bond in the corresponding complex of diphenylacetylene [1.294(4) Å^[31] vs. 1.206(2) Å in the parent tolan;^[32] $\Delta = 0.088$ Å]. The metal-carbon bond lengths in **2-Ni** differ from 1.846(6) Å to 1.859(9) Å for the two independent molecules of the complex in the asymmetric cell. The angles C–Ni–C in the nickelacyclopentadiene moiety of **2-Ni** (40.5°) and of diphenylacetylene-derived complex (40.8°)^[31] are of virtually the same value.

Molecular structures of the Cu(I) complexes with the unsaturated ligands 1 and 2. Since only a few examples of structurally characterized metal complexes with the ligands **1** and **2** have been reported so far, it looked promising to also prepare the corresponding Cu(I) complexes and analyze the structural and kinetic similarities and differences. Both complexes [Cu(bipy)(bcp)]PF₆ (**1-Cu**) and [Cu(bipy)(dcpa)]PF₆ (**2-Cu**) were obtained by mixing the copper(I) salt [Cu(MeCN)₄](PF₆) with 2,2'-bipyridine and an excess of either the alkene **1** or the alkyne **2**. Similar to the nickel compounds described above, it was not possible to fully characterize these complexes. However, after subsequent crystallization efforts, the molecular structures could be solved;^[20] the cations of both complexes **1-Cu** and **2-Cu** are presented in Figure 3. It is obvious that the structures of both complexes are very similar to their nickel analogues. The basic structural motifs are the same, e.g. the nearly trigonal planar coordination geometry and the outward bending of the spirocyclopropane moieties. Due to the high symmetry of the structure of the copper alkene complex **1-Cu**, the pairs of two adjacent Cu–N [1.976(2) Å] and Cu–C [1.961(2) Å] bonds are of the same length.

The C=C double bond in **1-Cu** with a length of 1.364(3) Å is elongated (4.5%) in comparison to that in the free ligand [1.304(2) Å]. This is due to the same effect as discussed above,

the change of hybridization from sp^2 to sp^3 . For comparison, in the previously discussed complexes **1-Co**,^[9] **1-Pt**^[11,12] and **1-Ni** (this work) the C=C bonds varied from 1.401(5) to 1.441(8) Å (Table 1). This nicely shows the differences in the mode of coordination of three different metal centers resulting in different elongations of the double bonds. In a similar copper (I)-ethylene complex supported by a neutral amino ligand, the C=C bond length is 1.359(7) Å.^[33] This is only slightly longer than in a free ethylene molecule [1.337(2) Å], but being close to those in the complex **1-Cu** reported here. Therefore, compound **1-Cu** can be less well regarded as a member of the family of metalla[3]triangulanes. On the other hand, the difference between the elongated distal [1.531(2) Å] and the shortened vicinal [1.476(2) Å] bonds is the biggest in this series and not in line with the geometries of cyclopropanes with electron acceptors.^[34] The metal-ethylene bonding is in a similar dimension and shows a Cu–C bond length of 1.961(2) Å.

In complex **2-Cu** comparable structural properties can be found, and the ligand again shows a strong outward bending of the cyclopropane rings (Figure 3). The coordinated C–C triple bond is slightly longer (3.1%) than in the free alkyne [1.234(5) vs. 1.197(3) Å].^[30] This is in the same dimension as in a copper-acetylene complex with a C–C triple bond of 1.188(11) vs. 1.204(3) Å^[33] showing a slightly shorter bond length in contrast to the previously observed trend.^[34] In regard to the Cu–C bond lengths of 1.951(4) and 1.962(4) Å, the values are nearly identical with those in the copper complex of **1** and the known copper-acetylene complex.^[33] In general, the trend of the structures reported here and those of similar complexes can be summarized with the fact, that copper(I), in sharp contrast to nickel and other metal ions, does not exhibit strong π -backbonding interactions leading to shorter metal-carbon and remarkably longer carbon-carbon double and triple bonds in the metal-coordinated molecules.

Kinetic Investigation of the Formation of the Ni(0) Complexes

The reactions of [Ni(bipy)(COD)] (**5**) with **1** and **2** can be monitored spectroscopically to obtain a better mechanistic understanding with the stopped-flow technique, as has been described previously in detail for the reactions of **5** with benzaldehyde, propionaldehyde and isoprene.^[35] Due to the

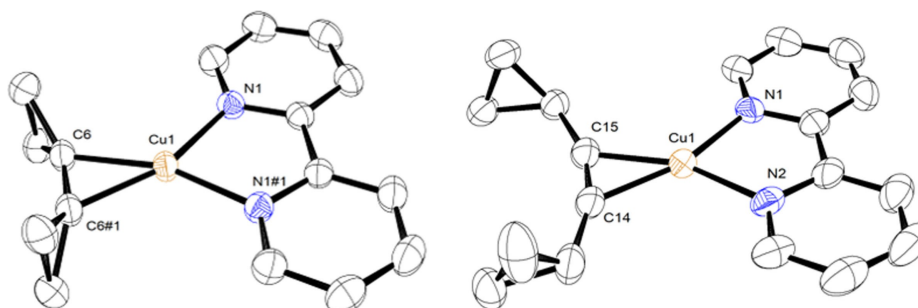


Figure 3. ORTEP plots of complexes **1-Cu** (left) and **2-Cu** (right). Ellipsoids at 50% probability, hydrogen atoms and counter anions omitted for clarity.

extreme sensitivity of the Ni(0) complexes towards dioxygen, these reactions cannot easily be monitored.^[36] However, by using air-tight glass syringes filled in a glove box, prior to the measurements and special reaction conditions to suppress side reactions this problem could be overcome.^[21] Time-resolved spectra for the reaction of **5** with **1** are presented in Figure 4.

In case of complex 1-Ni, the decrease of the absorbance maxima at 354 and 561 nm are characteristic for the disappearance of the precursor complex [Ni(bipy)(COD)] (**5**), whereas the increase of the absorbance at 430 nm indicates the formation

of 1-Ni. Isosbestic points at 390 nm and 478 nm disclose that no spectroscopically observable intermediates are formed. The kinetic measurements were carried out under pseudo first-order conditions, which were ensured by an excess of ligand **1**. The plot of absorbance vs. time at 561 nm was fitted to a single one-exponential function which allowed the determination of the pseudo first-order rate constants k_{obs} (see inset in Figure 4) leading to the simple rate equation of $v = k_{\text{obs}} \times [\mathbf{5}]$. All reactions were measured at four different temperatures with five different ligand concentrations. From a plot of k_{obs} vs $[\mathbf{1}]$ (Figure 5) a linear dependence with no intercept was observed confirming an irreversible reaction with the following rate law (eq. 1):

$$-\frac{d[\text{Ni(bipy)(COD)}]}{dt} = v = k_2 \cdot [\mathbf{5}] \cdot [\mathbf{1}] \quad (1)$$

From the slopes in Figure 5, second order rate constants k_2 ($k_{\text{obs}} = k_2 \cdot [\mathbf{1}]$) were calculated and used for the Eyring plot presented in Figure 6. Activation parameters were determined leading to an activation enthalpy of $\Delta H^\ddagger = 46.4 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ and an activation entropy of $\Delta S^\ddagger = -69 \pm 8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. The negative activation entropy supports an associative or associative interchange mechanism with a highly ordered transition state.

Overall behavior, rate constants and activation parameters fit quite well with the data reported previously for the formation of other related nickel(0) complexes (Table 2). Therefore, the same mechanism can be postulated for the formation reaction (Scheme 2). For the transition state, a partial decoordination (**5 A**) of the leaving ligand COD followed by coordination of the attacking alkene in **5B** is assumed, which emphasizes the associative element of the reaction mechanism. After the

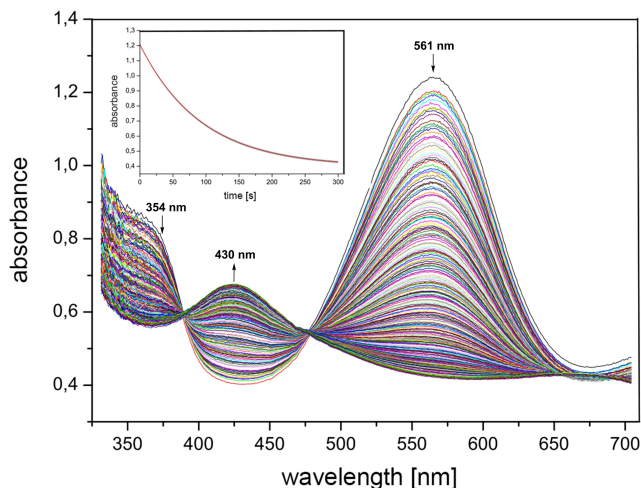


Figure 4. Time-resolved UV-vis spectra of the reaction of **5** with ligand **1** in THF; concentrations: $[\mathbf{5}] = 0.25 \text{ mM}$, $[\mathbf{1}] = 30 \text{ mM}$, $T = -20.2^\circ \text{C}$, $t = 299.5 \text{ s}$, $\Delta t = 1 \text{ s}$. Inset: Absorbance vs. time trace at 561 nm with single one-exponential fit (red).

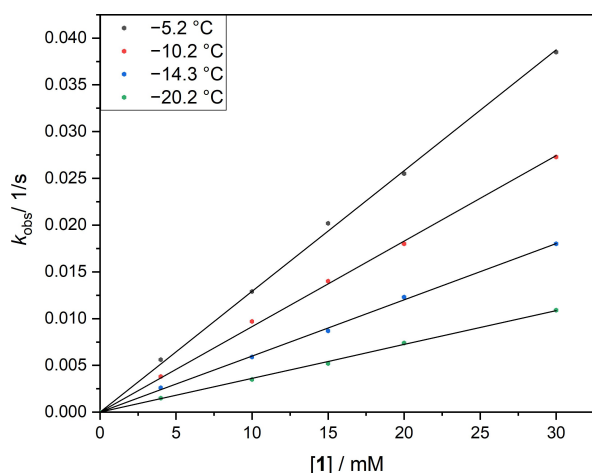


Figure 5. Plot of k_{obs} vs. concentration of 1-Ni at four temperatures for second-order rate constant determination with linear fits (black lines).

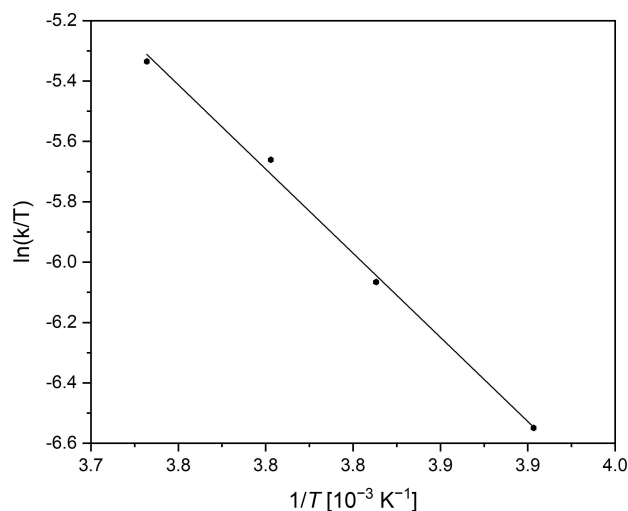
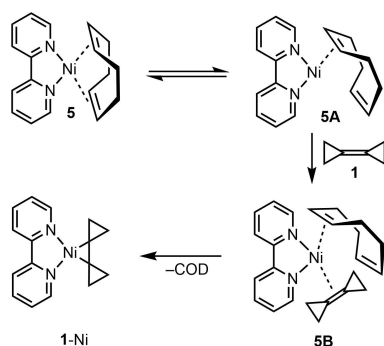


Figure 6. Eyring plot of the reaction to 1-Ni and linear fit (black line).

Table 2. Activation parameters for the formation of complexes 1-Ni, 3-Ni in comparison to selected literature examples.

	bcp (1)	dmbu (3)	dimethyl 3-methyl-3- <i>tert</i> -butylcycloprop-1-ene-1,2-dicarboxylate (4) ^[38]	benzaldehyde ^[39]	isoprene ^[35]
$\Delta H^\ddagger [\text{kJ} \cdot \text{mol}^{-1}]$	46.4 ± 2.0	47.2 ± 3.0	28.0 ± 1.6	47.8 ± 0.4	35.0 ± 5.0
$\Delta S^\ddagger [\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}]$	-69 ± 8	-68 ± 10	-128 ± 5	-47 ± 1	-79 ± 16



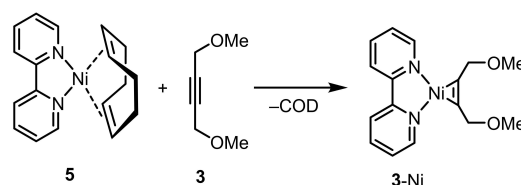
Scheme 2. Proposed mechanism for the formation of complex 1-Ni, as supported by the results of the kinetic measurements.

complete removal of the COD ligand, the final complex 1-Ni is formed in the last step.

Quite unexpectedly, in contrast to the kinetic study of **5** reacting with **1**, the investigation of the analogous reaction of the precursor complex **5** with **2** turned out to be more problematic. Although the reaction could be followed using the stopped-flow technique,^[20] decomposition reactions hampered clean fitting of the data (time resolved UV-vis spectra are presented in Figure S1, Supporting Information). Again, a decrease of the band at 561 nm was observed for this reaction. This indicated the consumption of the precursor complex, whereas appearance of the bands at 410 and 805 nm showed the formation of the new complex **2-Ni**. Isosbestic points were observed at 390 and 485 nm. The reactions had to be carried out at higher temperatures (10 to 25 °C vs. –5 to –20 °C), and observed reaction rates of **5** with **2** were somewhat slower in comparison with **1**. Despite applying pseudo first order conditions by using an excess of the ligand, no adequate fits of the absorbance vs. time plots were possible. Ignoring this and using k_{obs} values from poor fits to a single exponential function led to a plot of k_{obs} vs $[2]$ with a linear behavior with an intercept (see Figure S2, Supporting Information). This indicates either a reversible formation of **2-Ni** or a reaction type that would be independent from the concentration of **2**. As described in detail previously for related systems (e.g. isoprene in Table 2)^[35] most likely it indicates a reversible reaction step. That no satisfying fits could be obtained is a consequence of decomposition reactions that seem to be more problematic here due to the higher temperatures that were necessary for the measurements. In contrast to our previous studies adding a tenfold excess of COD in this case did not prevent decomposition of **5** and thus did not solve the problem.

To find out whether this might be a general problem with coordinating alkynes in Ni(0) chemistry or a specific one for ligand **2**, another simple alkyne, 1,4-dimethoxy-2-butyne (**3**) was employed for the reaction with the precursor **5** (Scheme 3).

The time-resolved spectra of this reaction (see Figure S3, Supporting Information) with bands at 420 and 675 nm show the formation of the new complex $[\text{Ni}(\text{bipy})(\text{dmbu})]$ (**3-Ni**) comparable to the other two complexes described above.^[21]



Scheme 3. Reaction of **5** with 1,4-dimethoxy-2-butyne (**3**) to form **3-Ni**.

Unfortunately, no crystals of this complex could be obtained that were suitable for structural determination. The higher reaction temperatures applied are responsible for the blurred isosbestic points at 385 and 475 nm due to the slow decomposition of **5**. However, despite the observed decomposition and in contrast to the reaction with **2**, the decrease of the time trace at 561 nm could again be fitted to a single one-exponential function and the pseudo first-order rate constants k_{obs} could be determined from the plots with varying temperatures and ligand concentrations (see Figure S4, Supporting Information). The reaction is irreversible, as confirmed by the missing intercept of the linear fits, but in general very similar to the reaction with ligand **1**. This is again supported by the activation parameters that were calculated for the reaction with **3** as $\Delta H^\ddagger = 47.2 \pm 3.0 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta S^\ddagger = -68 \pm 10 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, nearly identical to the data obtained for the reaction with **1**, despite the structural difference of the ligand scaffold.

These results indicate that the problems with the kinetic measurements for **2** as a ligand are not basic and caused by an alkyne moiety, but more likely are created specifically by the ligand **2** itself; probably due to steric encumbrance caused by the cyclopropyl groups, although the steric substituent constant of a cyclopropyl group, as defined by Beckhaus, is only slightly larger (1.33 versus 0.89) than that of an ethyl substituent.^[37]

In summary, the kinetic studies for the reaction of **5** with several quite different ligands **L** showed that a general mechanism for the formation of the complexes $[\text{Ni}(\text{bipy})(\text{L})]$ can be postulated (Scheme 2 with $\text{L} = 1$).

Oxygenation Reactions of 1-Cu and 2-Cu. The ability of copper(I) complexes to stabilize a variety of “dioxygen adduct” intermediates has been investigated in great detail by us and others.^[40] In this context, the lability of the bonding of **1** and **2** in these complexes prompted us to examine an oxygenation reaction of the latter. However, no intermediate complex was detectable in a benchtop experiment in which complexes **1-Cu** and **2-Cu** had been treated with dioxygen in acetone at –80 °C. Only a color change of the solution to a pale blue color could be observed caused by simple oxidation to the corresponding copper(II) complex. Furthermore, no oxidation of **1** and **2** was observed either. Workup of the solution of **2-Cu** after oxidation led to the isolation of crystals of a copper(II) bipyridine complex, in which two $\text{Cu}(\text{II})(\text{bipy})$ units are bridged by two hydroxide anions. The molecular structure of this complex could be determined, however no full refinement was performed on this compound because there are numerous examples of this complex type, e.g. $[(\text{bipy})\text{Cu}(\text{OH})_2\text{Cu}(\text{bipy})](\text{ClO}_4)_2$ ^[41] reported in the crystallographic database.

Conclusion

Herein, we demonstrated that bicyclopropylidene (bcp) as well as dicyclopropylacetylene (dcpa), both valuable building blocks in organic syntheses, can be utilized as η^2 -coordinating ligands for transition metal complexes. Copper(I) complexes of both ligands, [Cu(bipy)(bcp)]PF₆ and [Cu(bipy)(dcpa)]PF₆, could be structurally characterized, however they turned out to be less interesting with regard to oxygenation chemistry (probably the consequence of 2,2'-bipyridine as a co-ligand). The molecular structures of the nickel(0) complexes, [Ni(bipy)(bcp)] and [Ni(bipy)(dcpa)], were determined as well and as expected turned out to be similar to the analogous copper complexes. The results of a detailed kinetic analysis on the formation of these two complexes are in line with previous studies of related complexes and underline a general mechanism for these reactions. In contrast to the copper complexes, [Ni(bipy)(bcp)] and [Ni(bipy)(dcpa)] might become useful in future catalytic applications. While extremely reactive, complexes of this type have been tested in the past for e.g. activation of otherwise quite unreactive carbon dioxide.^[35,39] The problems with regard of handling these compounds can be overcome by starting with stable nickel(II) compounds and reducing these electrochemically thus performing electrocatalysis.^[42]

Experimental Section

General Methods. Commercially available reagents were used as obtained without further purification, unless otherwise stated. Anhydrous solvents were purchased from Acros Organics and further distilled three times over drying agents under Schlenk conditions. All experiments with air-sensitive compounds were carried out employing standard Schlenk techniques or in a glove box (MBraun, Garching, Germany; O₂ & H₂O < 0.1 ppm) under an argon atmosphere. The ligands **1**^[3] and **2**^[17] were prepared as described previously. Complex **5** was chosen as a versatile precursor by us and others before,^[26] therefore **5**^[43] and [Cu(MeCN)₄]PF₆^[44] were synthesized according to the corresponding published procedures.

Low Temperature Stopped-Flow Measurements. Variable temperature stopped-flow measurements allowed the collection of time-resolved UV-vis spectra of the precursor complex reactions with the corresponding alkenes or alkynes as described previously.^[35,39] The solutions were prepared in a glove box and transferred to the low-temperature stopped-flow instrument using glass syringes. The reactions were studied under pseudo-first-order conditions with an excess of ligand solution. Temperatures were varied from –20 to 35 °C. Time-resolved UV-vis spectra of these reactions were recorded with a home-built stopped-flow unit or with a modified Hi-Tech SF-3 L low-temperature stopped-flow unit (Salisbury, UK) equipped with a J&M TIDAS 16–500 photodiode array spectrophotometer (J&M, Aalen, Germany).^[45] Data fitting was performed using the integrated Kinetic Studio 4.0 software package (TgK Scientific, Bradford-on-Avon, UK) and Origin 2018 (OriginLab Corporation, Northampton, USA).

Single-Crystal X-ray Structure Determinations. The diffraction experiments were carried out under inert conditions at 193 K on a Siemens SMART CCD 1000 diffractometer and a STOE IPDS diffractometer using graphite monochromated Mo- K α radiation (λ = 0.71073 Å). The structures were solved by direct methods using

SHELXS and refined against F² on all data by full-matrix least squares with SHELXL.^[46] Details of the crystal and refinement data are described in the Supporting Information.

8,11-Diaza-8:9,10:11-dibenzo-7-nickelatrispiro[2.0.2⁴.0.4⁷.0³] undeca-8,10-diene [Ni(bipy)(bcp)] (1-Ni): To a stirred suspension of [Ni(bipy)(COD)] (200 mg, 619 μ mol) in Et₂O (10 mL) was added **1** (210 mg, 246 μ L, 2.62 mmol) and the reaction mixture was stirred until the solution turned dark green. The green solid was filtered off, washed with Et₂O two times and dried in vacuo. Yield: 94 mg (51 %). Suitable crystals for X-ray characterization where obtained by vapor diffusion of *n*-pentane into a solution in THF. ¹H NMR (400 MHz, acetone-d₆): δ = 8.91 (d, 2 H), 8.15 (m, 4 H), 7.55 (t, 2 H), 0.67 (s, 4 H), 0.22 (s, 4 H) ppm.

8,11-Diaza-8:9,10:11-dibenzo-7-nickelatrispiro[2.0.2⁴.0.4⁷.0³] undeca-8,10-diene Hexafluorophosphate [Cu(bipy)(bcp)]PF₆ (1-Cu): [Cu(MeCN)₄]PF₆ (37.2 mg, 0.10 mmol) and 2,2'-bipyridine (15.6 mg, 0.10 mmol) were dissolved in acetone (3 mL). After addition of **1** (16.0 mg, 18.7 μ L, 0.2 mmol), the reaction mixture was stirred for an additional 10 min until the color of the solution turned to pale yellow. Vapor diffusion of diethyl ether into the solution yielded single crystals of the complex suitable for X-ray characterization. ¹H NMR (400 MHz, acetone-d₆): δ = 8.96 (d, 2 H), 8.70 (d, 2 H), 8.36 (t, 2 H), 7.87 (t, 2 H), 1.59 (br s, 8 H) ppm. ¹³C NMR (100 MHz, acetone-d₆): δ = 153.9, 151.1, 143.1, 129.3, 124.3, 9.1 ppm.

[Ni(bipy)(dcpa)] (2-Ni): To a stirred solution of [Ni(bipy)(COD)] (3.2 mg, 9.9 μ mol) in THF (2 mL), a solution of alkyne **2** (106 mg, 1.0 mmol) in THF (2 mL) was added dropwise at –20 °C. The resulting solution was stirred for two hours and filtered through a pad of zeolite. Diffusion of *n*-pentane into the solution at –5 °C afforded the single crystals suitable for X-ray structure determination.

[Cu(bipy)(dcpa)]PF₆ (2-Cu): [Cu(MeCN)₄]PF₆ (37.2 mg, 0.1 mmol) and 2,2'-bipyridine (15.6 mg, 0.10 mmol) were dissolved in acetone (3 mL). Alkyne **2** (38.8 mg, 365 μ mol) was added and after 10 minutes stirring the solution turned pale yellow. Crystals of the yellow-orange solid suitable for X-ray characterization were obtained by slow diffusion of diethyl ether into the solution at –5 °C during several days.

Attempted Isolation of Crystalline [Ni(bipy)(dmbu)] (3-Ni): To a stirred solution of [Ni(bipy)(COD)] (25.8 mg, 79.8 μ mol) in THF was added ligand **3** (2 mL) (116 mg, 1.02 mmol). The resulting dark red solution was stirred for one hour. Diffusion of *n*-pentane into the solution at –20 °C did not result in crystals suitable for X-ray structure determination so far.

Deposition Numbers 2052272 (1-Ni), 2052271 (2-Ni), 2052273 (1-Cu), and 2052274 (2-Cu) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

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