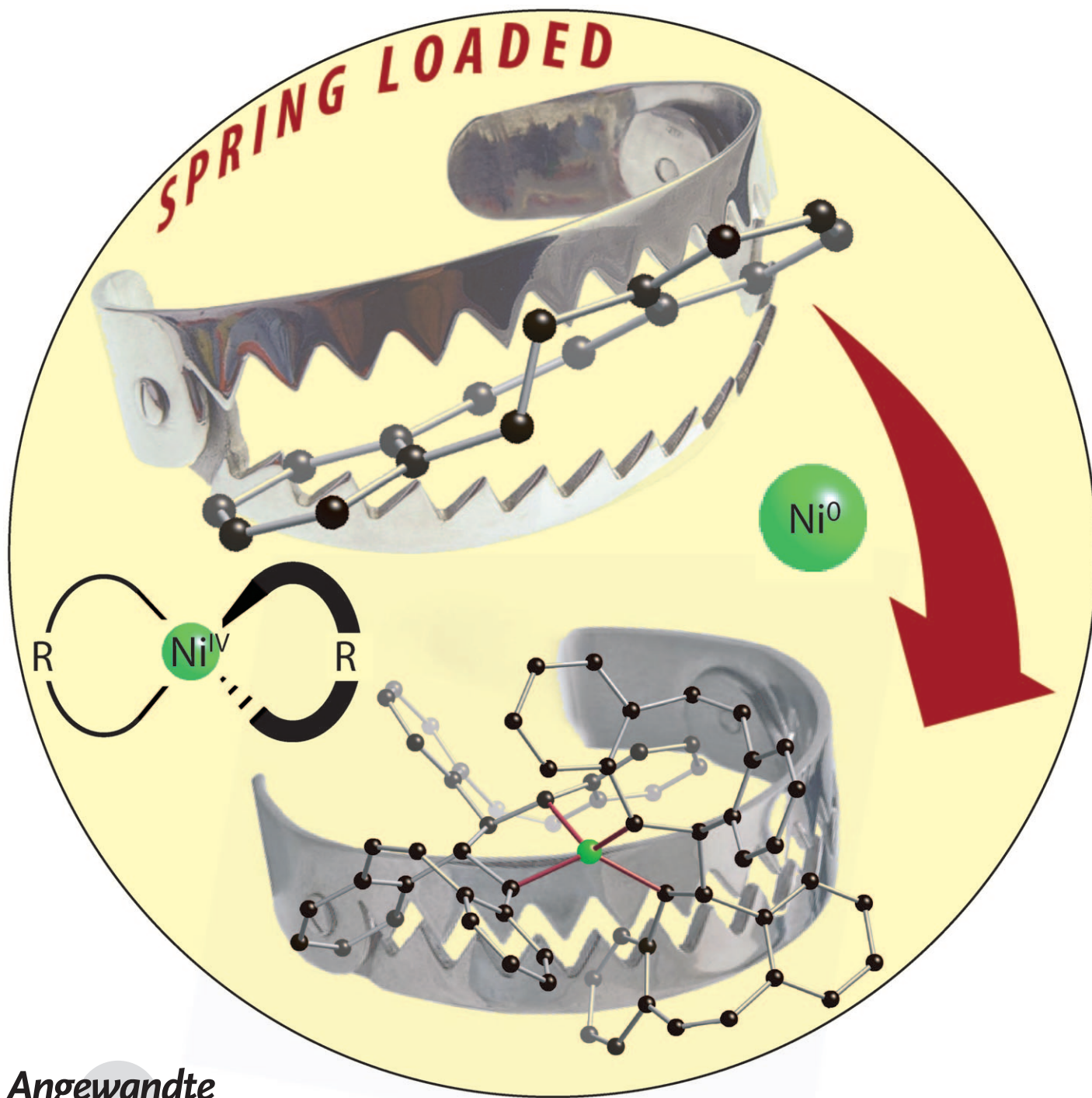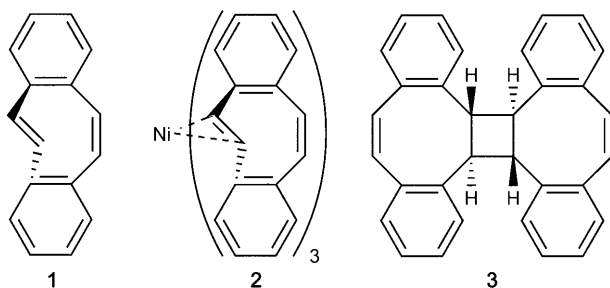# Communications

A Stable Tetraalkyl Complex of Nickel(IV)**

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Herein we describe the reaction of nickel(0) with the strained alkene (5*Z*,11*E*)-dibenzo[*a,e*]cyclooctatetraene (**1**). We have reported on **1**[1] and shown that the strain in the eight-membered ring can be exploited in ring-opening metathesis

ture of this nickel alkene complex tris((5*Z*,11*E*)-dibenzo-[*a,e*]cyclooctatetraene)nickel(0) (**2**) is shown in Figure 1 a.

The structure of **2** is noteworthy in at least three aspects: the coordination of the C≡C bonds, the steric protection of
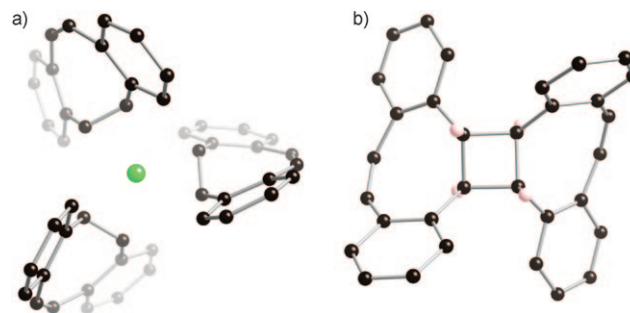

Figure 1. Molecular structures determined from the crystal structures of a) **2** (Ni–C bonds not shown) and b) **3** (C black, H pink, Ni green). Some hydrogen atoms have been removed to clarify the view.

polymerization (ROMP). To characterize the strain-based reactivity more thoroughly, we have examined the behavior of **1** in the presence of homogeneous nickel(0). The study of reactions of alkenes with complexes of zerovalent nickel has a long and colorful history;[2] we show herein that the strained alkene **1** allows us to create and crystallographically study the first tetraalkyl complex of nickel(IV).

We prepared **1** by the method described previously. It is a mixture of two enantiomers defined by the helicity arising from the *trans* double bond in the eight-membered ring.[3] To solubilize the Ni⁰ precursor, [Ni(cod)₂] (cod = 1,5-cyclooctadiene) is treated with one equivalent of tri(*tert*-butyl)phosphine (P*t*Bu₃) in cyclohexane to give a pale yellow solution, presumably of [Ni(cod)(P*t*Bu₃)].[4] When a cyclohexane solution of **1** is added to this Ni⁰ complex, the resulting solution darkens to maroon, and over time pale yellow crystals deposit. The crystallographically determined struc-

the Ni center, and the chirality of the complex. Although either the *cis* or the *trans* double bond in **1** could coordinate to the Ni center, it is exclusively the *trans* bond that does so. This result is not surprising inasmuch as the orbitals of the *trans* π bond point radially from the center of the eight-membered ring while those of the *cis* π bond are perpendicular to the average plane of the ring. Hence the *trans* bond is much less sterically hindered. When it coordinates to the Ni atom, the C≡C bond lengthens considerably (1.32 Å in **1** vs. 1.40 Å in **2**). Lengthening of datively bonded π bonds is expected,[5] but the extent of the lengthening in the present case highlights the relief of the strain in **1** upon complexation. Also indicative of this relief is the partial change in hybridization of the carbon atoms bound to the nickel center, as is demonstrated by the shifts seen in the ¹³C NMR spectra. The resonance of the carbon atoms in the *trans* double bond in the ¹³C NMR spectra moves substantially from 137.8 ppm in the unbound form to 74.9 ppm upon binding to nickel in **2** (see the Supporting Information). This dramatic shift indicates that the structure may be better described as a metallocyclopropane instead of a simple alkene datively bonded to a metal center.[6]

The three very bulky alkene ligands protect the Ni atom quite well. This is apparent from the crystal structure, and it is verified by the comparative air-stability of **2**. Although Ni⁰ complexes are usually quite sensitive to air oxidation,[7] **2** is stable as a solid for (at least) several weeks in the laboratory ambient. In the future, this nickel species may be useful as a robust precursor to Ni⁰ catalysts.

The chirality of **2** is also interesting. As mentioned earlier, ligand **1** is chiral. The unit cell in the crystal of **2** contains four individual complexes. As shown in Figure 1 a, each of these nickel tris(alkene) complexes is homochiral in the sense that each of the alkene ligands around a particular Ni center has the same absolute stereochemistry. This results in a nickel-centered three-bladed propeller. Two of each enantiomer of the propeller complex are present in the unit cell. Thus, the crystalline material exists as the racemate.

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We next turn our attention to the reactivity of **2**. When heated to 60°C in benzene, **2** disappears, and the product subsequently identified as the cyclobutane **3** appears.[8] The yield of this reaction is 42%. The crystallographically determined structure shows the product to be the *trans,-trans,trans*-cyclobutane (Figure 1b). This stereochemistry is significant because, as we reported previously, the thermal cyclodimerization of **1** in the absence of any metal catalysis gives the *cis,cis,trans*-cyclobutane.[9] Thus, the metal center clearly directs a different dimerization. In this new dimerization, the metal facilitates the formation of what would be a thermally forbidden (2s + 2s) cyclization product.[10] It is also significant that in the nickel-based dimerization we observe no cyclobutane derivatives that would arise from the direct combination of one right-handed (Δ) enantiomer and one left-handed (Λ) enantiomer. This, too, suggests that the cyclodimerization is intramolecular with respect to **2**.

Given the literature precedents,[2,10] we believe that the production of **3** occurs in two steps: first, two of the coordinated alkene ligands combine to form a nickelacyclopentane, and subsequently this nickel dialkyl complex reductively eliminates the cyclobutane. To test this hypothesis, we attempted to trap the nickelacycle with 2,2′-bipyridine (bipy), as shown in Scheme 1.[11,12] The reaction of [(bipy)Ni(cod)]
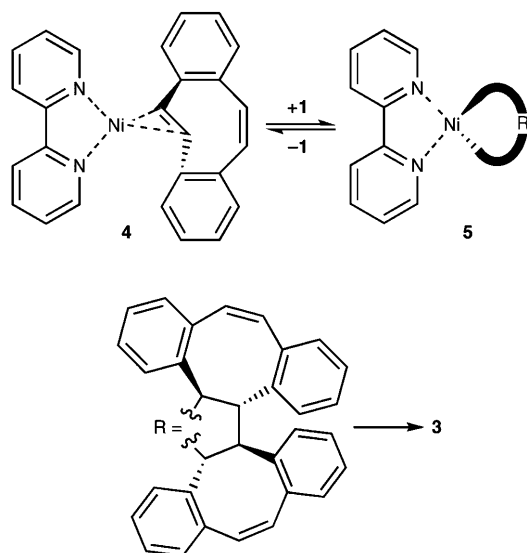
Scheme 1. Reaction of **4** to form nickelacycle **5** (not isolated), which reductively eliminates cyclobutane **3**.

with one equivalent of **1** gives a dark-colored complex that was identified crystallographically as the mono(alkene) adduct **4** (Figure 2). The ^{1}H NMR spectrum of **4** showed broad resonances in the aromatic region. Thermolysis of **4** gives **3**, presumably through a metallacyclic intermediate such as **5**. Again, exclusively **3**, the *trans,trans,trans*-cyclobutane isomer, is formed. Therefore, this process occurs through exchange of ligands such that a single nickel center contains two alkene ligands and another one contains two bipy ligands. Once the second alkene is bound, the ligands may easily slip to form the metallacyclopentane and then eliminate from the
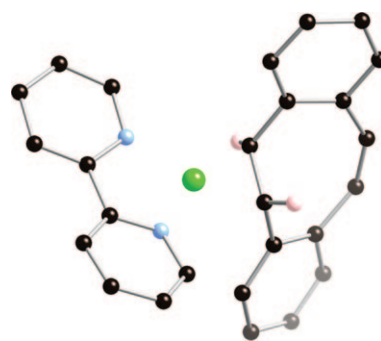
Figure 2. View of **4** taken from the crystal structure (N blue, C black, H pink, Ni green). Some hydrogen atoms have been removed to clarify the view.

crowded metal center as a cyclobutane derivative. Furthermore, when we heated a mixture of **2** and bipy, the solution turned a characteristic green color[13] and gave resonances in the NMR spectrum consistent with a nickelacyclopentane **5**.[14]

We were curious about the intense red color that initially forms in the combination of **1** with [Ni(cod)(P*t*Bu$_3$)], so we mixed the two in various proportions. When we use a two-fold excess of **1**, dark red crystals of a new complex **6** (Figure 3) form along with colorless crystals of cyclobutane dimer **3**.

Complex **6** is a nickelaspirocyclononane, a tetraalkyl complex of nickel(IV). We were able to grow crystals of **6** suitable for X-ray diffraction analysis from saturated cyclohexane solutions. The structure is shown in Figure 3. The bond length of what was once the *trans* double bond of the ligand has grown to 1.52 Å. The new carbon–carbon bond formed between adjacent ligands also has a bond length of
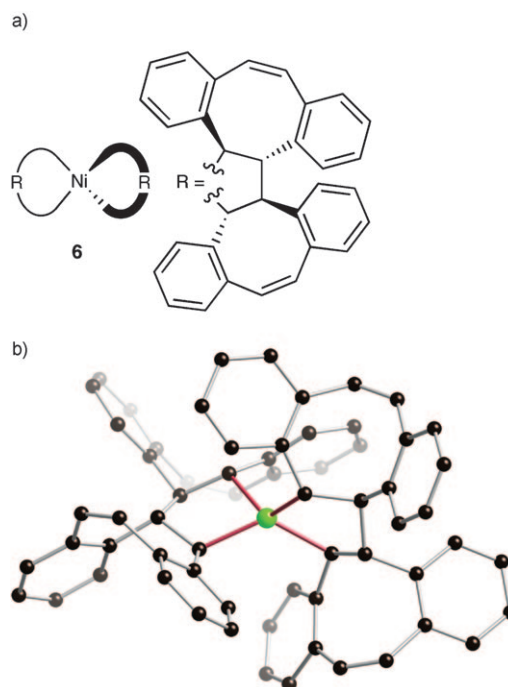
Figure 3. a) Chemical structure of homoleptic spirocycle **6**. b) Molecular structure determined from the crystal structure of **6** (C black, Ni green). Hydrogen atoms have been removed to clarify the view.

1.52 Å. This relaxation of the rigid ring structure may be driving this reaction along with the formation of new carbon–carbon bonds between ligands. As with initial binding, the release of strain from the ligand greatly disfavors the reverse transformation. It is remarkable that the C−C bond-forming step occurs twice to give a metallaspirocycle.

Complex **6** contains two metallacyclopentane units and, especially in view of the very high nominal oxidation state of the nickel center, seemed to be a candidate for reductive elimination. This reaction, we hypothesized, might form product **3** and possibly regenerate **1**, but when **6** is heated to 60 °C in benzene in an NMR tube, no reaction was observed after one hour. This result is quite surprising, as Ni[II] nickel-acyclopentanes thermolyze easily.[2] Complex **6** is air-stable at room temperature as a solid and in benzene or hexane solution. The complex may be heated to above 290 °C before decomposition is observed. The thermal and oxygen stability of this molecule may partially be a result of the near complete shielding of the metal center by its rigid, bulky ligands.

To our knowledge, **6** is the first example of an all-alkyl complex of Ni[IV].[15] The space-filling representation shows that the Ni coordination environment is crowded; this crowding unquestionably contributes to the stability and lack of reactivity of this compound. The Ni(C₄)₂ core of the spirocycle of **6** is shown in Figure 4 a and selected angles are given in Table 1. At first glance these data suggest that the coordination around the Ni center may be idealized as tetrahedral; however, on closer inspection it is clear that the distortion from the ideal is severe. Rather than six C-Ni-C angles at 109.5°, there are four wide (122–129°) and two narrow (80–81°) angles. This finding is perhaps not surprising, owing to the requirements of the five-membered rings.

To gain more insight into the bonding in this complex, we performed density functional theory (DFT) calculations on **6**
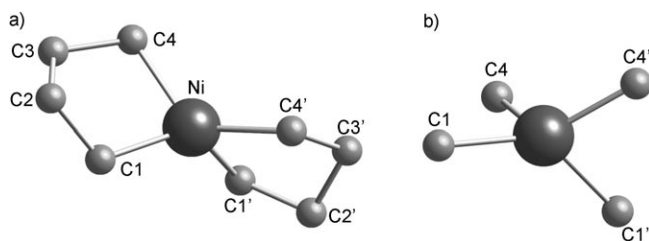
and some related compounds. Starting with the observed molecular geometry, we reoptimized the full geometry at the B3LYP/6-31G**/LACVP level (see the Supporting Information). As expected, the DFT-optimized geometry of **6** is essentially identical to the experimentally observed one, particularly with respect to the Ni coordination geometry. This result convinced us of the reliability of this level of DFT for this particular study.

We then optimized the geometry of the model molecule Ni(C₄H₈)₂ (**7**) that is, the simple "parent" nickelaspirocyclo-nonane. Its full geometry is shown in the Supporting Information; bond angles in the core of **6** are compared to **7** in Table 1. The coordination around the Ni center is quite similar in **6** and **7**; the distortion from the tetrahedral ideal is as significant in the sterically unencumbered model **7** as it is in the sterically congested prototype **6**. This finding naturally implies that the distortion is not strictly due to steric interactions among the dibenzocyclooctatetraene substituents.

To test if this structural motif is intrinsic to Ni[IV] complexes with four alkyl substituents, we examined the simplest version, Ni(CH₃)₄ (Figure 4 b). The distribution of bond angles around the Ni center in tetramethyl nickel is quite similar to that in **6**. Table S1 in the Supporting Information tabulates selected bond angles. We conclude that the distinctly non-tetrahedral coordination in **6** is simply characteristic of the electronic structure of Ni[IV]. According to both EPR spectroscopy and bulk magnetic susceptibility measurements, **6** is diamagnetic. This finding is consistent with the sharp peaks in the NMR spectra. Given these data, the simplest interpretation is that the four Ni−C bonds in **6** are simple, two-electron covalent bonds, each between a carbon atom and an otherwise low-spin d⁶ Ni atom. This situation is quite remarkable, especially in view of the stability of **6** with respect to oxidation, hydrolysis, and thermolysis.

In conclusion, we have described the synthesis and structural features of nickel complexes using the strained, chiral alkene (5Z,11E)-dibenzo[a,e]cyclooctatetraene. We have synthesized an air-stable homochiral Ni⁰ alkene complex that eliminates coupled alkenes to form cyclobutane derivatives in a thermally disallowed cyclization. With an excess of the alkene ligand, we have prepared and characterized the first all-alkyl Ni[IV] species. This new Ni[IV] complex was shown to be remarkably stable. These organometallic complexes represent relatively stable chiral structures that may find application as catalysts in the case of the Ni⁰ alkene complex or as building blocks for elaborate organometallic frameworks in the case of the robust Ni[IV] species.

Figure 4. a) The Ni(C₄)₂ core of the spirocycle in **6**, as determined by X-ray crystallography. b) Structure of Ni(CH₃)₄ determined with DFT.

Table 1: Comparison of the bond angles [°] from the core of the spirocycle in **6** and the model compound **7**.

	6[b]	**7**
C1-Ni-C4	80.6 (79.8)	77.8
C1-Ni-C1′	124.0 (124.0)	109.6
C1-Ni-C4′	129.1 (127.7)	126.3
C4-Ni-C1′	122.8 (123.3)	1120.9
C4-Ni-C4′	126.7 (128.4)	144.4
C1′-Ni-C4′	80.2 (80.3)	78.7

[a] The atom numbers correspond to the model in Figure 4 a. [b] The first values are from the crystal structure; the values in parentheses are taken from the DFT calculations.
Hydrogen atoms have been removed to clarify the view.

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[8] The appearance of the cyclobutane dimer was monitored by ¹H NMR spectroscopy. The conversion was complete after 30 min at 60°C in benzene. The solution turned dark red in color; however, no nickelaspirocyclononane **6** was observed, and we concluded that the color is a result of colloidal nickel.

[9] Subsequent to our synthesis of **1**[1] and the disclosure that it thermally forms cyclobutanes, others have verified this finding (J. Bornhoeft, J. Siegwarth, C. Nather, R. Herges, *Eur. J. Org. Chem.* **2008**, 1619). Compound **3** is produced in minute amounts in these thermal reactions.

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