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A Nickel(II)-Cornered Molecular Rectangle with Biscarbene and 4,4'-Bipyridine Bridging Groups

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Summary: Nickelocene reacts with a rigid bisimidazolium salt to give cyclopentadiene and a biscarbene-bridged dinuclear nickel complex, which upon treatment with 4,4'-bipyridine and AgBF_4 yields the CpNi^{II} -cornered molecular rectangle $[\mathbf{1}](\text{BF}_4)_4$.

Metal-directed self-assembly has become an important tool in supramolecular chemistry¹ since J.-M. Lehn first demonstrated the spontaneous formation of a double-helical complex from bipyridine and $\text{Cu}(\text{I})$.² Subsequently, a large number of metal-helicates³ and other three-dimensional supramolecular structures obtained by self-assembly have been described.⁴ Among the first supramolecular assemblies were molecular squares like $[\mathbf{A}]^{8+}$, first synthesized by Fujita et al.⁵ and subsequently studied by Stang et al.⁶ and other research groups (Figure 1).⁷ These molecular squares are built from four end-capped metal components linked by four spacers possessing nitrogen or oxygen donor groups. We became interested in organometallic molecular squares, i.e., in molecules where the 4,4'-bipyridine spacers in $[\mathbf{A}]^{8+}$ are partly or completely substituted for spacers employing carbon atoms to bind to the end-capped metal components. Here we describe the molecular rectangle $[\mathbf{1}](\text{BF}_4)_4$ with rigid biscarbene and 4,4'-bipyridine spacers between the metal centers.

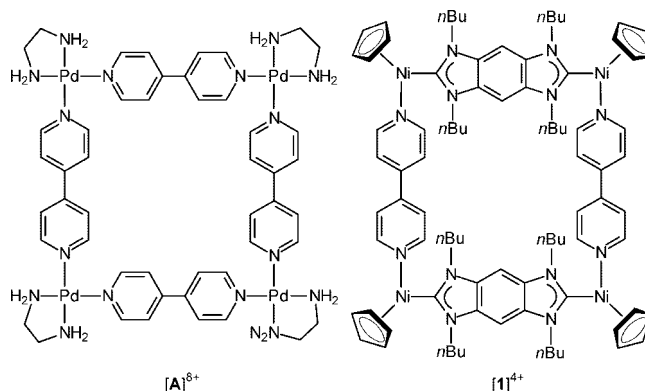


Figure 1. Classical molecular square $[\mathbf{A}]^{8+}$ and the molecular rectangle $[\mathbf{1}]^{4+}$ made up from biscarbene and 4,4'-bipyridine bridging groups.

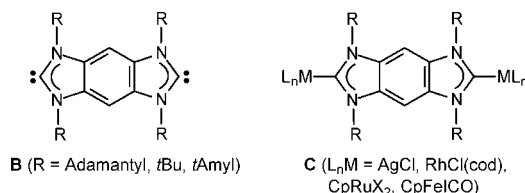


Figure 2. Biscarbenes **B** and their dinuclear metal complexes **C**.

N-Heterocyclic carbenes (NHCs) have developed into an important class of ligands in organometallic chemistry.⁸ Benzannulated N-heterocyclic carbenes,⁹ and their coordination chemistry¹⁰ has also been studied. Bielawski et al. demonstrated that the benzene ring can be substituted with two N-heterocyclic carbene groups, leading to compounds of type **B**,¹¹ which are capable of acting as a bridge between two metal centers, and a number of complexes of type **C** have been prepared (Figure 2).¹²

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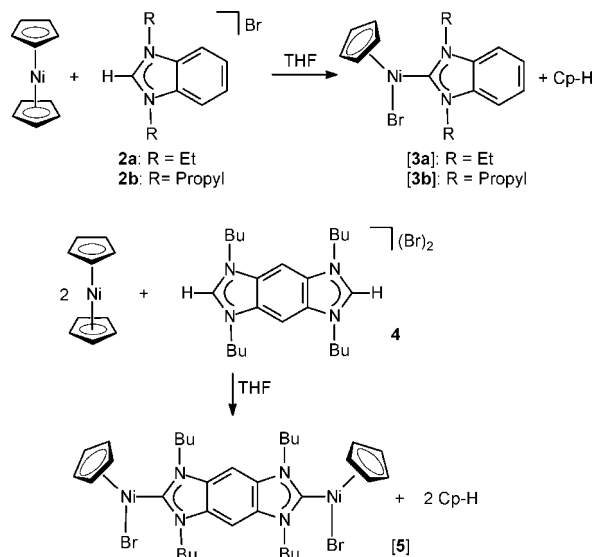
We selected biscarbenes of type **B** as carbon-bound bridging groups to generate novel molecular squares. The apparently simple reaction of bisazolium salts of type **B** with base and end-capped Pd^{II} or Pt^{II} starting materials did not lead to the desired molecular squares. Previously it had been noticed that the Pt^{II} complexes are kinetically rather inert,^{5b} while the reaction of Pd^{II} with benzimidazolium salts and base often yields a mixture of *cis*- and *trans*-dicarbene complexes.¹³

For the preparation of biscarbene-bridged molecular squares an end-capped metal component different from (en)Pd^{II} or (en)Pt^{II} had to be developed. It has been reported that Ni(OAc)₂ reacts with benzimidazolium halides with formation of complexes of the type *trans*-[NiX₂(NHC)₂]¹⁴ (NHC = benzimidazolin-2-ylidene, X = Br, I), while the electron-rich nickelocene yields in the reaction with azolium halides complexes of the type [NiX(Cp)(NHC)] (NHC = imidazolin-2-ylidene or imidazolidin-2-ylidene, X = Cl, Br) and cyclopentadiene.¹⁵ We have adapted this method to coordinate a benzimidazolin-2-ylidene ligand obtained from the benzimidazolium salts of type **2** to the {NiX(Cp)} complex fragment, giving complexes of type **[3]** (Scheme 1).

Red complexes of type **[3]** are obtained in yields of about 50% by heating a benzimidazolium salt of type **2** and nickelocene in a THF/DMF solvent mixture (see Supporting Information). The complexes are identified by the characteristic chemical shift for the carbene carbon atom in the ¹³C NMR spectrum (for example δ 179.3 ppm for **[3a]**). The X-ray diffraction structure analysis of **[3a]**¹⁶ reveals a Br–Ni–C_{carbene} angle of 95.63(6)°, which identifies the CpNi complex fragment as a perfectly suited end-capped metal building block for a molecular square (Figure 3). Additional geometric parameters for **[3a]** fall in the range observed for [CpNiX(NHC)] complexes.¹⁵

Complex **[5]** was prepared in analogy to the preparation of complexes of type **[3]** from the bisimidazolium salt **4** and 2 equiv of nickelocene (Scheme 1). As observed for complexes of type **[3]**, the formation of the biscarbene-bridged dinuclear complexes **[5]** can be monitored visually by the color change from green for nickelocene to red for the carbene complexes.

Scheme 1. Preparation of the Half-Sandwich Complexes **3a,b** and of the Dinuclear Complex **5**



Complex **[5]** gives a typical resonance at δ 178.2 ppm for the carbene carbon atom in the ¹³C NMR spectrum (see Supporting Information). The rotation about the Ni–C_{carbene} bond is restricted, which leads to the observation of two resonances for the *N*-CH₂ groups at δ 5.81 and 4.52 ppm in the ¹H NMR spectrum. Similar observations were made with complexes of type **[3]** and related compounds.^{15c}

An X-ray diffraction study with a red crystal of complex **[5]·toluene**¹⁶ showed that the Ni–Br vectors in this compound are oriented in an almost parallel fashion, pointing in the same direction (Figure 4). The structure analysis illustrates that the protons of the *N*-CH₂ groups of the carbene ligand are located in different chemical environments, thus leading to the two

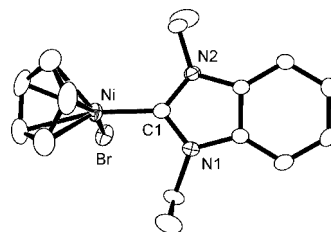


Figure 3. Molecular structure of **[3a]** (50% displacement ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): Ni–Br 2.3368(3), Ni–C1 1.867(2); Br–Ni–C1 95.63(6).

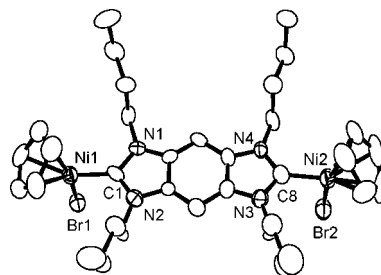


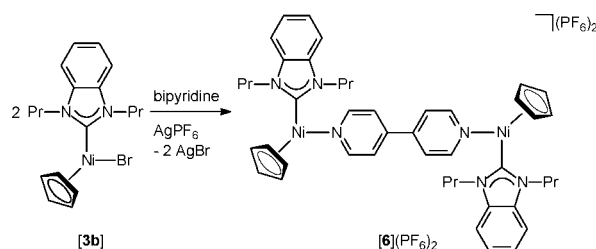
Figure 4. Molecular structure of one of the two independent molecules of **[5]** in the asymmetric unit of **[5]·toluene** (50% displacement ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg) for molecule 1 [molecule 2]: Ni1–Br1 2.321(2) [2.325(2)], Ni2–Br2 2.306(2) [2.322(2)], Ni–C1 1.876(13) [1.862(14)], Ni2–C8 1.871(14) [1.858(13)]; Br1–Ni1–C1 94.1(4) [94.1(4)], Br2–Ni2–C8 93.6(4) [93.8(4)].

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(16) Crystal data for **[1](BF₄)₄·2acetone**: C₉₄H₁₂₄N₁₂B₄F₁₆Ni₄O₂, monoclinic, *P*2₁/*n*, *a* = 16.368(2) Å, *b* = 16.892(2) Å, *c* = 18.687(3) Å, β = 100.086(2)°, *V* = 5087.2(12) Å³, *Z* = 2, *T* = 153(2) K, *D*_{calcd} = 1.329 g cm^{−3}, *R*(*F*) = 0.0959 for 5168 observed intensities (*I* ≥ 2σ(*I*)) collected in the range 3.1° ≤ 2θ ≤ 51.7°. The asymmetric unit contains two acetone molecules, one of which is disordered. The nondisordered acetone molecule is located inside the molecular rectangle. Crystal data for **[3a]**: C₁₆H₁₉N₃BrNi, orthorhombic, *P*2₁2₁2₁, *a* = 10.2497(4) Å, *b* = 10.7909(5) Å, *c* = 14.1980(6) Å, *V* = 1570.35(12) Å³, *Z* = 4, *T* = 153(2) K, *D*_{calcd} = 1.599 g cm^{−3}, *R*(*F*) = 0.0257 for 4293 observed intensities (*I* ≥ 2σ(*I*)) collected in the range 4.7° ≤ 2θ ≤ 62.0°. Crystal data for **[5]·toluene**: C₄₁H₅₆N₄Br₂Ni₂, monoclinic, *P*2₁/*c*, *a* = 17.3023(14) Å, *b* = 23.345(2) Å, *c* = 23.266(2) Å, β = 96.0980(19)°, *V* = 9344.4(13) Å³, *Z* = 8, *T* = 153(2) K, *D*_{calcd} = 1.254 g cm^{−3}, *R*(*F*) = 0.0859 for 6801 observed intensities (*I* ≥ 2σ(*I*)) collected in the range 2.4° ≤ 2θ ≤ 48.4°. The asymmetric unit contains two almost identical molecules of **[5]** and two molecules of toluene. Crystal data for **[6](PF₆)₂·H₂O**: C₄₆H₅₆N₆F₁₂Ni₂OP₂, monoclinic, *P*2₁/*n*, *a* = 18.765(5) Å, *b* = 10.511(3) Å, *c* = 25.588(7) Å, β = 104.416(4)°, *V* = 4888(2) Å³, *Z* = 4, *T* = 153(2) K, *D*_{calcd} = 1.517 g cm^{−3}, *R*(*F*) = 0.0714 for 3285 observed intensities (*I* ≥ 2σ(*I*)) collected in the range 2.4° ≤ 2θ ≤ 47.0°. The asymmetric unit contains one molecule of **[6](PF₆)₂** and one disordered water molecule.

Scheme 2. Preparation of the Dinuclear Complex [6](PF₆)₂

different resonances observed in the ¹H NMR spectrum. At ambient temperature rotation about the Ni–C_{carbene} bond is restricted and the two Ni–Br bonds are locked in the parallel orientation depicted in Figure 4. This parallel preorientation is helpful for the construction of a molecular square, as it effectively prevents the formation of oligomeric reaction products. It will be important to avoid the rotation about the Ni–C_{carbene} bond, which is best achieved by employing ambient reaction temperatures for reactions involving complex [5].

Next we studied the substitution reaction of a bromo ligand from complexes of type [NiBr(Cp)(NHC)] for a pyridine donor (Scheme 2). Reaction of complex [3b] with 4,4'-bipyridine and a stoichiometric amount of AgPF₆ leads to the dinuclear complex [(Cp)(NHC)Ni(*μ*-4,4'-bipyridine)Ni(NHC)(Cp)](PF₆)₂ [6](PF₆)₂ (see Supporting Information). Related bipyridine-bridged dinuclear complexes have been described.¹⁷

The structure analysis of [6](PF₆)₂·H₂O¹⁶ (Figure 5) shows C_{carbene}–Ni–N_{bipyridine} angles of 98.4(3)° and 96.9(3)°. The carbene ligands are arranged in an *anti*-orientation relative to the Ni–Ni vector. Use of the bipyridine bridging unit for the formation of a molecular square would require rotation about the Ni–N bond, which due to the low steric demand of the bipyridine ligand is much easier than rotation about the Ni–C_{carbene} bond. This assumption is corroborated by the ¹H NMR spectrum of [6](PF₆)₂ (see Supporting Information), where due to a restricted rotation about the Ni–C_{carbene} bond two resonances were detected for the *N*-CH₂ groups, while only one resonance was detected for all four bipy_{ortho} protons.

The molecular structures of [5] and [6]²⁺ and particularly the C_{carbene}–Ni–N_{pyridine} angles of about 90° in [6]²⁺ confirm the suitability of the {CpNi} complex fragment for the generation of molecular rectangles using two biscarbene ligands of type **B** and two 4,4'-bipyridine ligands. In fact, abstraction of the bromo ligands from [5] with AgBF₄ and subsequent reaction with 4,4'-bipyridine gives the air- and water-stable complex [1](BF₄)₄ in 43% yield (Figure 6). The X-ray diffraction structure analysis¹⁶ shows the cation [1]⁴⁺ residing on a crystallographic inversion center. The biscarbene ligands are arranged in an almost coplanar fashion. The Ni1–Ni2 and Ni1–Ni2* separations (10.910(2) and 10.380(2) Å, respectively) are almost equidistant in spite of the different bridging groups. This geometric property justifies the description of [1]⁴⁺ as a molecular square. However, since the bridging groups are different, we suggest naming [1]⁴⁺ a molecular rectangle. The N–Ni–C_{carbene} angles (94.6(3)° and 95.4(3)°) in [1]⁴⁺ are only marginally smaller than the N_{bipyridine}–Ni–C_{carbene} angles in [6]²⁺, indicating the presence of a strain-free cation, [1]⁴⁺. Additional bond parameters in [1]⁴⁺ fall in the range previously observed for related complexes.

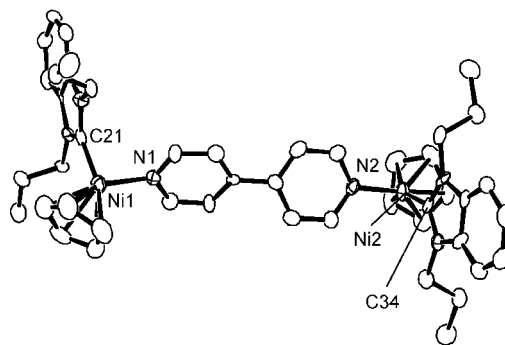


Figure 5. Molecular structure of [6]²⁺ in [6](PF₆)₂·H₂O (50% displacement ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): Ni1–N1 1.937(7), Ni1–C21 1.904(9), Ni2–N2 1.915(7), Ni2–C34 1.874(10); N1–Ni1–C21 98.4(3), N2–Ni2–C34 96.9(3).

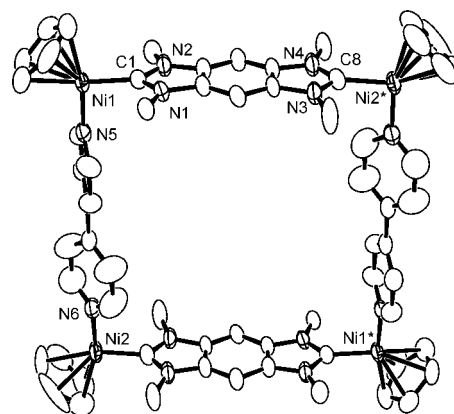


Figure 6. Molecular structure of [1]⁴⁺ in [1](BF₄)₄·2acetone (50% displacement ellipsoids, hydrogen atoms omitted). Only one atom of each of the *N*-butyl substituents is depicted for clarity. Selected bond lengths (Å) and angles (deg): Ni1–C1 1.876(7), range Ni1–C_{Cp} 2.024(10)–2.149(7), Ni1–N5 1.913(6), Ni2–C8 1.892(7), range Ni2–C_{Cp} 2.057(13)–2.136(11), Ni2–N6 1.906(7); C1–Ni1–N5* 94.6(3), C8–Ni2–N6 95.4(3).

In conclusion, we have demonstrated the use of a rigid biscarbene ligand and end-capped CpNi^{II} metal components for the construction of a molecular rectangle. In contrast to molecules of type [A]⁸⁺ the biscarbene/bipyridine-bridged molecular rectangle [1]⁴⁺ carries only a +4 charge due to the negatively charged metal-capping group. Further research is directed toward substitution of the 4,4'-bipyridine ligands for another biscarbene ligand.

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Supporting Information Available: A detailed description of the experimental procedures including spectroscopic and analytical details for all new compounds and X-ray crystallographic files for compounds [1](BF₄)₄·2acetone, [3a], [5]·toluene, and [6](PF₆)₂·H₂O in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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