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

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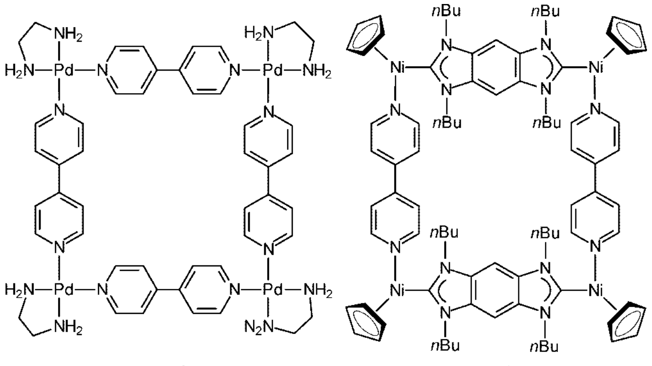
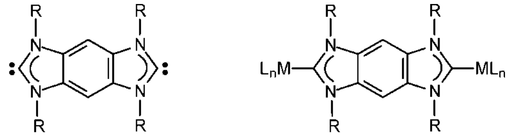
*Summary: Nickelocene reacts with a rigid bisimidazolium salt to give cyclopentadiene and a biscarbene-bridged dinuclear nickel complex, which upon treatment with 4,4′-bipyridine and $AgBF_4$ yields the $CpNi^{II}$-cornered molecular rectangle [**1**]$(BF_4)_4$.*

Metal-directed self-assembly has become an important tool in supramolecular chemistry[1] since J.-M. Lehn first demonstrated the spontaneous formation of a double-helical complex from bipyridine and Cu(I).[2] Subsequently, a large number of metal-helicates[3] and other three-dimensional supramolecular structures obtained by self-assembly have been described.[4] Among the first supramolecular assemblies were molecular squares like [**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 [**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 [**1**]$(BF_4)_4$ with rigid biscarbene and 4,4′-bipyridine spacers between the metal centers.



[**A**]$^{8+}$ [**1**]$^{4+}$

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



B (R = Adamantyl, *t*Bu, *t*Amyl) **C** (L_nM = AgCl, RhCl(cod), $CpRuX_2$, CpFeICO)

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 chemistry[10] 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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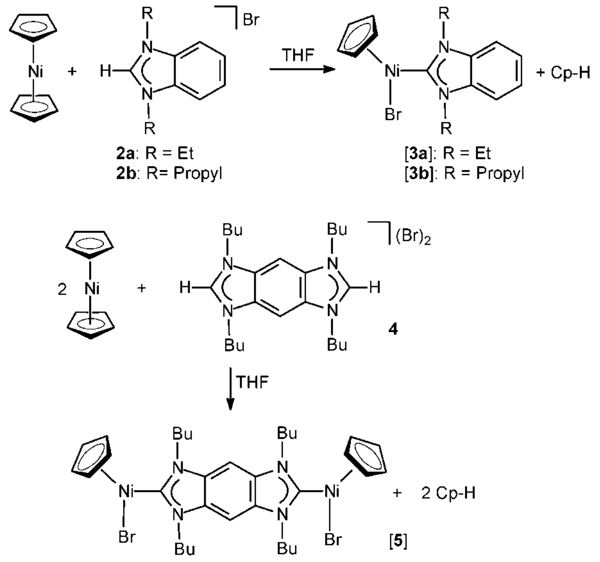
We selected biscarbenes of type **B** as carbon-bound bridging groups to generate novel molecular squares. The apparently simple reaction of bisazolium salts of type **B** with base and end-capped Pd^{II} or Pt^{II} starting materials did not lead to the desired molecular squares. Previously it had been 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*-[NiX$_2$(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 ^{13}C NMR spectrum (for example δ 179.3 ppm for [**3a**]). The X-ray diffraction structure analysis of [**3a**][16] reveals a Br−Ni−C$_{\text{carbene}}$ 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 ^{13}C NMR spectrum (see Supporting Information). The rotation about the Ni−C$_{\text{carbene}}$ bond is restricted, which leads to the observation of two resonances for the *N*-CH$_2$ groups at δ 5.81 and 4.52 ppm in the ^{1}H 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*-CH$_2$ groups of the carbene ligand are located in different chemical environments, thus leading to the two

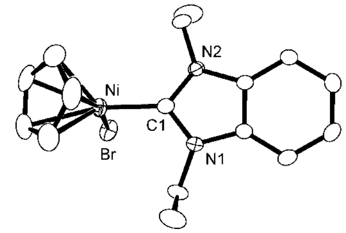


Figure 3. Molecular structure of [**3a**] (50% displacement ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): Ni−Br 2.3368(3), Ni−C1 1.867(2); Br−Ni−C1 95.63(6).

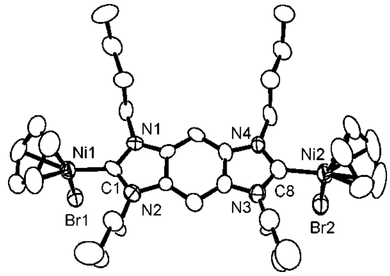


Figure 4. Molecular structure of one of the two independent molecules of [**5**] in the asymmetric unit of [**5**]·toluene (50% displacement ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg) for molecule 1 [molecule 2]: Ni1−Br1 2.321(2) [2.325(2)], Ni2−Br2 2.306(2) [2.322(2)], 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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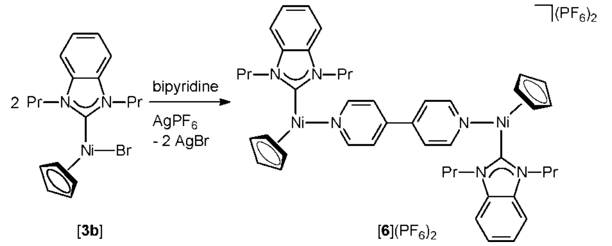
[16] Crystal data for [**1**](BF$_4$)$_4$·2acetone: C$_{94}$H$_{124}$N$_{12}$B$_4$F$_{16}$Ni$_4$O$_2$, monoclinic, $P2_1/n$, a = 16.368(2) Å, b = 16.892(2) Å, c = 18.687(3) Å, β = 100.086(2)°, V = 5087.2(12) Å^3, Z = 2, T = 153(2) K, D_{calcd} = 1.329 g cm^{-3}, $R(F)$ = 0.0959 for 5168 observed intensities ($I \geq 2\sigma(I)$) 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**]: C$_{16}$H$_{19}$N$_2$BrNi, orthorhombic, $P2_12_12_1$, a = 10.2497(4) Å, b = 10.7909(5) Å, c = 14.1980(6) Å, V = 1570.35(12) Å^3, Z = 4, T = 153(2) K, D_{calcd} = 1.599 g cm^{-3}, $R(F)$ = 0.0257 for 4293 observed intensities ($I \geq 2\sigma(I)$) collected in the range 4.7° ≤ 2θ ≤ 62.0°. Crystal data for [**5**]·toluene: C$_{41}$H$_{56}$N$_4$Br$_2$Ni$_2$, monoclinic, $P2_1/c$, a = 17.3023(14) Å, b = 23.345(2) Å, c = 23.266(2) Å, β = 96.0980(19)°, V = 9344.4(13) Å^3, Z = 8, T = 153(2) K, D_{calcd} = 1.254 g cm^{-3}, $R(F)$ = 0.0859 for 6801 observed intensities ($I \geq 2\sigma(I)$) 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**](PF$_6$)$_2$·H$_2$O: C$_{46}$H$_{56}$N$_6$F$_{12}$Ni$_2$OP$_2$, monoclinic, $P2_1/n$, a = 18.765(5) Å, b = 10.511(3) Å, c = 25.588(7) Å, β = 104.416(4)°, V = 4888(2) Å^3, Z = 4, T = 153(2) K, D_{calcd} = 1.517 g cm^{-3}, $R(F)$ = 0.0714 for 3285 observed intensities ($I \geq 2\sigma(I)$) collected in the range 2.4° ≤ 2θ ≤ 47.0°. The asymmetric unit contains one molecule of [**6**](PF$_6$)$_2$ and one disordered water molecule.

Scheme 2. Preparation of the Dinuclear Complex [6](PF_6)$_2$



different resonances observed in the ^{1}H 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 $AgPF_6$ leads to the dinuclear complex [(Cp)(NHC)Ni(μ-4,4′-bipyridine)Ni(NHC)(Cp)](PF_6)$_2$ [**6**](PF_6)$_2$ (see Supporting Information). Related bipyridine-bridged dinuclear complexes have been described.[17]

The structure analysis of [**6**](PF_6)$_2$·H_2O[16] (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 ^{1}H NMR spectrum of [**6**](PF_6)$_2$ (see Supporting Information), where due to a restricted rotation about the Ni−$C_{carbene}$ bond two resonances were detected for the *N*-CH_2 groups, while only one resonance was detected for all four bipy-H_{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 $AgBF_4$ and subsequent reaction with 4,4′-bipyridine gives the air- and water-stable complex [**1**](BF_4)$_4$ in 43% yield (Figure 6). The X-ray diffraction structure analysis[16] 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.

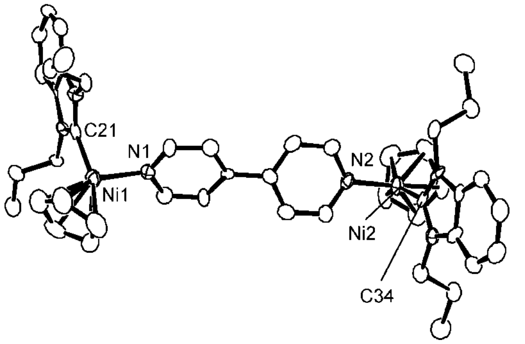


Figure 5. Molecular structure of [**6**]$^{2+}$ in [**6**](PF_6)$_2$·H_2O (50% displacement ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): Ni1−N1 1.937(7), Ni1−C21 1.904(9), Ni2−N2 1.915(7), Ni2−C34 1.874(10); N1−Ni1−C21 98.4(3), N2−Ni2−C34 96.9(3).

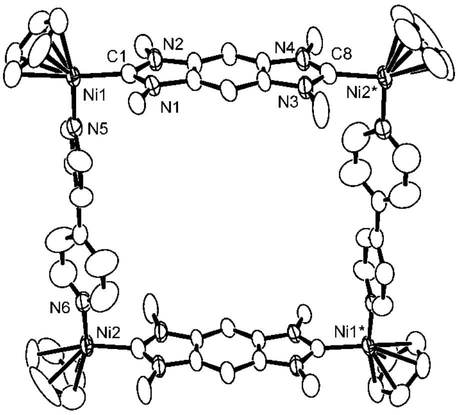


Figure 6. Molecular structure of [**1**]$^{4+}$ in [**1**](BF_4)$_4$·2acetone (50% displacement ellipsoids, hydrogen atoms omitted). Only one atom of each of the *N*-butyl substituents is depicted for clarity. Selected bond lengths (Å) and angles (deg): Ni1−C1 1.876(7), range Ni1−C_{Cp} 2.024(10)−2.149(7), 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**](BF_4)$_4$·2acetone, [**3a**], [**5**]·toluene, and [**6**](PF_6)$_2$·H_2O in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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