

# *ansa*-Nickelocenes by the Ring-Closing Metathesis Route: Syntheses, X-ray Crystal Structures, and Physical Properties

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The first *ansa*-nickelocenes,  $[\text{Ni}(\eta^5, \eta^5\text{-C}_5\text{H}_4\text{-CH}_2\text{-CH=CH-CH}_2\text{-C}_5\text{H}_4)]$  (**4**) and  $[\text{Ni}(\eta^5, \eta^5\text{-C}_5\text{H}_4\text{-(CH}_2)_2\text{-CH=CH-(CH}_2)_2\text{-C}_5\text{H}_4)]$  (**5**), and a bridged binickelocene,  $[\text{Ni}_2(\eta^5, \eta^5\text{-C}_5\text{H}_4\text{-(CH}_2)_2\text{-CH=CH-(CH}_2)_2\text{-C}_5\text{H}_4)_2]$  (**6**), were prepared by alkene metathesis of 1,1'-disubstituted nickelocenes. Compound **4** reacts with hydrogen to yield *ansa*-nickelocene **7**, bearing the saturated bridge. The new compounds were characterized by UV-vis, IR, MS, <sup>1</sup>H NMR, magnetic susceptibility, and electrochemical measurements. Crystal and molecular structures of **4**, **6**, and **7** were determined by single-crystal X-ray analysis. These measurements show that the studied *ansa*-nickelocenes exhibit properties similar to those of nickelocene.

## Introduction

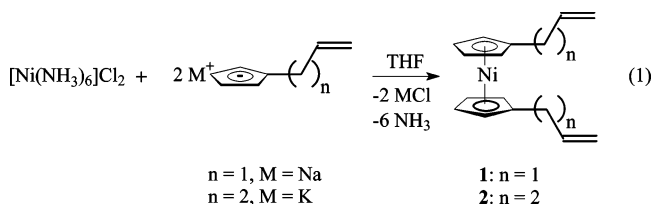
The development of well-defined catalysts that are tolerant to many functional groups has made the alkene metathesis reaction a versatile tool for carbon-carbon bond formation.<sup>1</sup> In recent years metathesis was successfully applied in the transition metal coordination sphere, providing access to novel inorganic and organometallic complexes (Scheme 1).<sup>2</sup> Ring-closing metathesis between two ligands of a coordinately saturated transition metal complex was investigated in most cases (Scheme 1, a). Byproducts arising from intermolecular metathesis reactions, believed to be dimers or oligomers, were often detected in these experiments. In an example of particular interest to our research group, *ansa*-ferrocenes and *ansa*-ruthenocenes were prepared by ring-closing metathesis of 1,1'-bis(alkenyl)metallocenes in good yields (Scheme 1, b).<sup>3</sup> Relatively few reports dealt with ROMP of ferrocene-based monomers<sup>4</sup> or an intermolecular coupling of two monoalkenyl metallocenes (Scheme 1, c).<sup>5</sup>

Bis(cyclopentadienyl)nickel (nickelocene) is the only metallocene with 20 valence electrons.<sup>6</sup> The electronic structure and

bonding of nickelocene has received constant attention since its discovery.<sup>7</sup> To achieve a better understanding of its unique properties, we have decided to synthesize bridged nickelocenes to find out if they possess any slip-fold distortion from the  $\eta^5$ -toward  $\eta^3$ -coordination mode of cyclopentadienyl ligands, as predicted on the basis of the 18-electron rule. We report here alkene metathesis of moderately stable, 20-electron 1,1'-bis(alkenyl)nickelocenes using Grubbs' catalysts.

## Results and Discussion

**Syntheses.** The 1,1'-bis(alkenyl)nickelocenes were obtained in a straightforward procedure from an anhydrous Ni(II) salt and the corresponding alkali metal alkenylcyclopentadienide (eq 1).



The 1,1'-bis(alkenyl)nickelocenes **1** and **2** were isolated by column chromatography on alumina as green oils and characterized by mass spectrometry.

Ring-closing metathesis of **1** using  $[\text{Ru}(\text{=CHPh})\text{Cl}_2(\text{PCy}_3)_2]$  (**3**) as a catalyst in a  $\text{CH}_2\text{Cl}_2$  solution under dilute conditions ( $[\text{Ni}] = 0.026 \text{ mol/L}$ ) afforded the first *ansa*-nickelocene (**4**) in 35% yield (eq 2). The reaction was conveniently followed by EI-MS of the crude reaction mixture aliquots, where the

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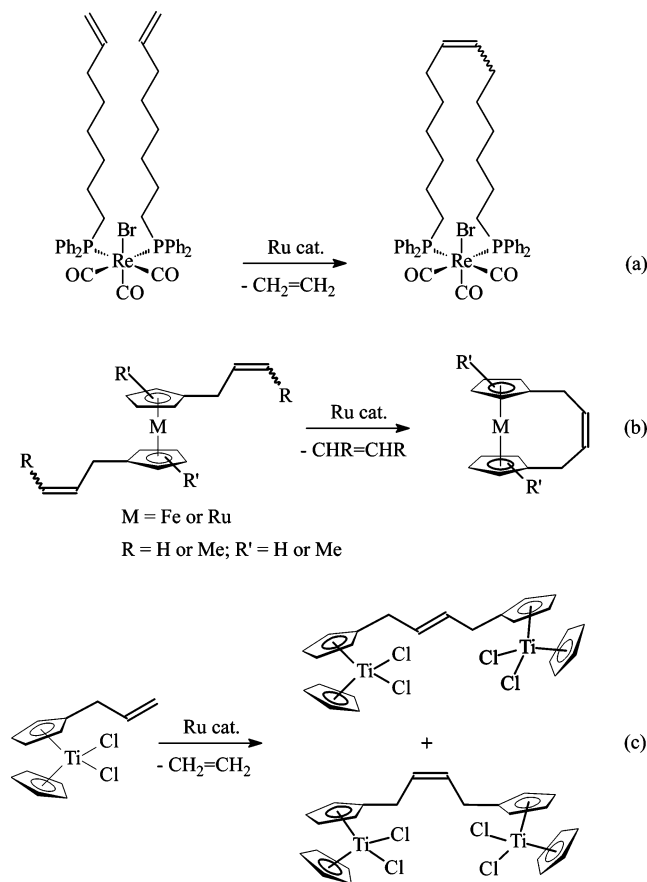
<sup>‡</sup> University of Wrocław.

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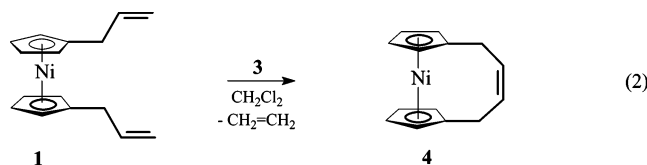
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**Scheme 1. Alkene Metathesis in Metal Coordination Sphere<sup>2c,3,5a</sup>**


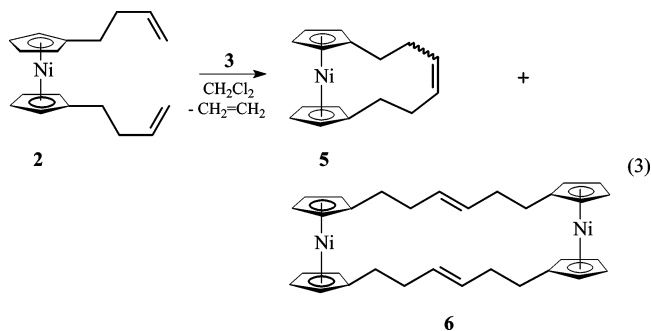
molecular peak of **1** (at  $m/z = 268$ ) and that of **4** (at  $m/z = 240$ ) were clearly observed. Moreover, the molecular peak of a product of cross-metathesis between two molecules of **1** (at  $m/z = 480$ ) was occasionally present in these mass spectra.



This synthesis is quite remarkable taking into account that nickelocene reacts under mild conditions with phosphines in chlorinated solvents<sup>8</sup> and catalyst **3** operates predominantly via a dissociative mechanism, thus liberating the free phosphine in solution.<sup>9</sup> Use of toluene instead of  $\text{CH}_2\text{Cl}_2$  gave similar results, while reactions with the second-generation catalyst  $[\text{Ru}(\text{CHPh})\text{Cl}_2(\text{PCy}_3)(\text{H}_2\text{IMes})]$  ( $\text{H}_2\text{IMes} = 1,3\text{-dimesityl-4,5-dihydroimidazol-2-ylidene}$ ) were less effective than those with **3**.

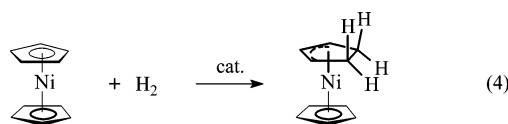
Metathesis of **2** under conditions similar to those for **1** provided the expected *ansa*-nickelocene **5** and a bridged nickelocene **6** (eq 3).

The separation of **6** from **5** was greatly facilitated by complete insolubility of **6** in hexane. Therefore, rather simple workup involving extractions and crystallizations provided compounds **5** and **6** as green, crystalline solids. The structure of **6** was first

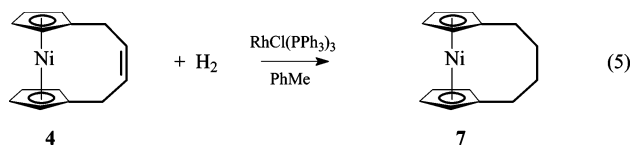


established from its mass spectrum where a weak molecular ion at  $m/z = 536$  ( $^{58}\text{Ni}$ ) was present and confirmed by X-ray diffraction studies.

Having in hand the first *ansa*-nickelocenes, we sought to test their reactivity. Nickelocene reacted with hydrogen under a variety of conditions to afford red, diamagnetic complex ( $\eta^3\text{-cyclopentadienyl})(\eta^5\text{-cyclooctadienyl})\text{nickel}$  in high yield (eq 4).<sup>10</sup>



It seemed interesting to pursue this simplest addition reaction for the *ansa*-analogue **4**. Thus, we found that **4** reacted regioselectively with hydrogen in the presence of Wilkinson's catalyst at ambient temperature to yield green *ansa*-nickelocene **7** with the saturated bridge (eq 5).



**X-ray Crystallography.** The molecular structures of **4**, **6**, and **7** with atom-numbering schemes are depicted in Figures 1, 2, and 3. Selected bond lengths and angles for **4** and **6** are collected in Tables 1 and 2, respectively. Crystal data, data collection, and refinement parameters for **4** and **6** are given in Table 3. Data for **7** are not given owing to a poor refinement of the structure.

There are two independent molecules of **4** in the crystal unit with no major differences between them. The molecular structure of **4** reveals that both cyclopentadienyl rings are flat and not parallel (Figure 1). They are slightly inclined toward the bridge with the angle between the two Cp planes of  $8.1\text{--}(2)^\circ$ . This dihedral angle is somewhat larger than  $4.7^\circ$  reported for *meso*-1,1'-(hex-3-ene-2,5-diyl)ferrocene,<sup>3</sup> which most likely reflects the fact that M–C bonds in nickelocene are longer than those in ferrocene.<sup>11,12</sup> The average Ni–C (2.179 Å) and cyclopentadienyl C–C (1.424 Å) bond distances in **4** agree well with those determined for nickelocene at 101 K (2.185 and 1.423 Å, respectively).<sup>11</sup> Several quantitative measures of a cyclopentadienyl or indenyl ring slippage have been introduced, e.g., the slip vector or the slip value  $\Delta\text{M–C}$ .<sup>13</sup> The  $\Delta\text{M–C}$  value,

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**Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compound 4**

Ni(1)–C(11)	2.160(3)	Ni(1)–C(20)	2.162(3)
Ni(1)–C(12)	2.168(3)	Ni(1)–C(24)	2.168(3)
Ni(1)–C(15)	2.182(3)	Ni(1)–C(21)	2.179(3)
Ni(1)–C(13)	2.190(3)	Ni(1)–C(23)	2.189(3)
Ni(1)–C(14)	2.196(3)	Ni(1)–C(22)	2.192(3)
C(11)–C(12)	1.421(4)	C(20)–C(24)	1.418(4)
C(11)–C(15)	1.432(4)	C(20)–C(21)	1.425(4)
C(12)–C(13)	1.428(4)	C(21)–C(22)	1.419(4)
C(13)–C(14)	1.422(4)	C(22)–C(23)	1.420(4)
C(14)–C(15)	1.422(4)	C(23)–C(24)	1.429(4)
C(11)–C(16)	1.511(4)	C(11)–C(16)–C(17)	112.2(2)
C(16)–C(17)	1.512(4)	C(18)–C(17)–C(16)	125.0(3)
C(17)–C(18)	1.328(4)	C(17)–C(18)–C(19)	125.1(3)
C(18)–C(19)	1.513(4)	C(20)–C(19)–C(18)	113.3(2)
C(19)–C(20)	1.512(4)		
Cp(c)–Ni(1)–Cp(c)		173.46(2)	

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 6**

Ni(1)–C(14)	2.149(4)	Ni(1)–C(24)	2.174(4)
Ni(1)–C(13)	2.165(3)	Ni(1)–C(23)	2.175(4)
Ni(1)–C(15)	2.171(4)	Ni(1)–C(25)	2.178(4)
Ni(1)–C(12)	2.205(4)	Ni(1)–C(26)	2.187(3)
Ni(1)–C(11)	2.227(4)	Ni(1)–C(22)	2.199(3)
C(11)–C(12)	1.425(5)	C(22)–C(23)	1.425(5)
C(11)–C(15)	1.425(5)	C(22)–C(26)	1.428(5)
C(12)–C(13)	1.421(5)	C(23)–C(24)	1.424(5)
C(13)–C(14)	1.424(5)	C(24)–C(25)	1.411(4)
C(14)–C(15)	1.427(5)	C(25)–C(26)	1.420(5)
C(11)–C(16)	1.515(5)	C(11)–C(16)–C(17)	114.5(3)
C(16)–C(17)	1.523(5)	C(18)–C(17)–C(16)	111.9(3)
C(17)–C(18)	1.506(5)	C(19)–C(18)–C(17)	124.6(4)
C(18)–C(19)	1.323(5)	C(18)–C(19)–C(20)	126.4(4)
C(19)–C(20)	1.503(5)	C(19)–C(20)–C(21)	111.6(3)
C(20)–C(21)	1.531(5)	C(22)–C(21)–C(20)	114.7(3)
C(21)–C(22)	1.499(5)		
Cp(c)–Ni(1)–Cp(c)		176.77(3)	

i.e., the difference between the average Ni–C distances to C(13) and C(14) and those to C(11), C(12), and C(15) (and the corresponding carbon atoms for the second ligand), is ca. 0.02 Å for both rings and indicates that **4** is a true  $\eta^5$ – $\eta^5$  complex. The bond angles in the Cp ligands average at the expected 108.0°, with the smallest angle of 107.2(2)° and 107.3(2)° at the bridging carbon atoms. Carbon–carbon bond distances in the Cp ring are somewhat irregular and show minor allyl-ene distortion.<sup>14</sup> Cyclopentadienyl rings in nickelocene are staggered; however, complex **4** is in an eclipsed conformation, which we assume is caused by the rigid bridge. The stereochemistry of the double bond in crystalline **4** is *cis*, analogously to the other *ansa*-metallocenes obtained by the metathesis route.<sup>3</sup> It is of interest to note that in the case of 1,1'-(2-buten-1,4-diyl)-ferrocene that was prepared from the dianion of 1,4-bis-(cyclopentadienyl)but-2-ene, one isomer, presumed to be *cis*, was obtained regardless of the configuration of the starting hydrocarbon.<sup>15</sup>

The centrosymmetric molecule of **6** consists of two nickelocenes coupled by two 3-hexenylene bridges with *trans* stereochemistry at the double bonds (Figure 2). The Cp ligands and the bridges are in an eclipsed conformation. The rings are flat and slightly inclined with a dihedral angle of 5.4(2)°. The rings are tilted in the direction opposite those in **4**; that is, the longest Ni–C distances are those to C(11) and C(22). A similar distortion was observed in a trimetallic Ni–Fe–Ni bridged

metallocene with a rigid *cis/trans* configuration.<sup>16</sup> Thus, we attribute this bending to the steric repulsion of the bridging hydrocarbon chains. Average Ni–C (2.183 Å) and C–C cyclopentadienyl (1.423 Å) bond lengths are the same as in nickelocene. Cyclopentadienyl rings are regular with the exception of one short C(24)–C(25) bond of 1.411(4) Å. Interestingly, there are notable differences in the Ni–C bond lengths for one of the ligands from 2.149(4) to 2.227(4) Å ( $\Delta M-C = 0.04$  Å), suggesting partial electron localization.

The structure of the compound **7** could not be fully determined owing to the poor crystal quality and the weak diffracting power caused by a disorder of bridging carbon atoms. However, the atom connectivity is undoubtedly correct (Figure 3). The structural parameters of the nickelocene part of **7** are well refined and reveal that cyclopentadienyl rings are parallel within experimental error. In contrast with complex **4**, Cp rings in **7** are twisted toward a staggered conformation by 17°. We assume that these structural features are caused by the increased flexibility of the saturated bridge of **7** in comparison to the unsaturated one of **4**.

**Physical and Spectroscopic Properties.** Compound **4** is a dark green, paramagnetic solid (mp = 95–97 °C), stable under an inert atmosphere, and soluble in common organic solvents. Magnetic susceptibility measurements in a toluene solution by the Evans' method<sup>17</sup> for **4** ( $\mu = 2.65 \mu_B$  at 295 K) and **5** ( $\mu = 2.95 \mu_B$  at 291 K) are consistent with the presence of two unpaired electrons per molecule. Similarly to the reported mass spectra of nickelocene,<sup>18</sup> the mass spectra of **4**, **5**, and **7** exhibit intense molecular peaks at  $m/z = 240$  (100% rel int),  $m/z = 268$  (90% rel int), and  $m/z = 242$  (100% rel int), respectively. Besides the weak molecular ion, the mass spectrum of compound **6** is virtually identical to that of **5**, proving that it breaks into two molecules of **5** under the EI conditions. As anticipated, the IR spectra of **4** (Figure S1; see Supporting Information) and **5** are considerably more complex than the IR spectra of nickelocene<sup>19</sup> owing to the presence of a noncoordinated C=C bond and departure from the cylindrical symmetry. Our tentative assignments are based on those for the parent compound. The UV–vis spectra of all new compounds (Figures S2–S5; see Supporting Information) exhibit three strong absorptions in the range 200–800 nm similar to the spectra of nickelocene.<sup>20</sup> The <sup>1</sup>H NMR spectra of **4**, **5**, and **7** were recorded in C<sub>6</sub>D<sub>6</sub> solutions (see Table 4). The nonequivalent cyclopentadienyl protons are resolved and appear as two signals at low frequency (below –250 ppm), which is in good agreement with data reported for nickelocene and its substituted analogues.<sup>16,21</sup> The olefinic protons in **4** and **5** are detected as singlets at 12 ppm, while signals at –5.0 ppm in **5** and –1.15 ppm in **7** were assigned to the bridging methylene groups. The  $\alpha$ -methylene protons, which are expected to give signals at high frequency (above 200 ppm), are observed at 139 ppm only for complex **7**. We did not detect any <sup>13</sup>C signals for the studied compounds.

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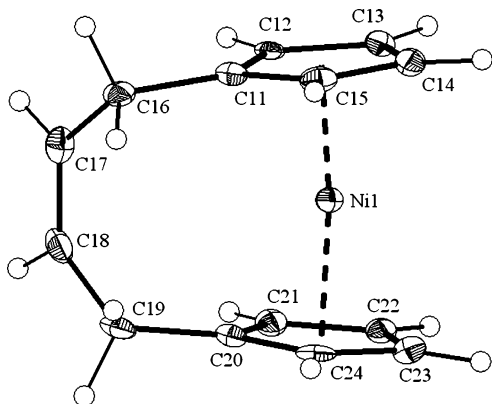
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Table 3. Crystal Data and Structure Refinement for **4** and **6**

	<b>4</b>	<b>6</b>
empirical formula	C <sub>14</sub> H <sub>14</sub> Ni	C <sub>32</sub> H <sub>36</sub> Ni <sub>2</sub>
cryst size (mm)	0.4 × 0.15 × 0.15	0.324 × 0.207 × 0.098
cryst syst	monoclinic	monoclinic
space group	P2 <sub>1</sub> /c (no. 14)	P2 <sub>1</sub> /c (no. 14)
unit cell dimens		
<i>a</i> (Å)	11.041(4)	16.487(5)
<i>b</i> (Å)	14.857(5)	7.617(4)
<i>c</i> (Å)	13.732(5)	10.600(4)
β (deg)	110.50(5)	108.05(3)
volume (Å <sup>3</sup> )	2109.9(13)	1265.7(9)
<i>Z</i>	4	2
fw	240.96	538.03
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.517	1.412
temperature (K)	100(2)	100(2)
absorp coeff (mm <sup>-1</sup> )	1.797	1.506
<i>F</i> (000)	1008	568
radiation	Mo Kα (λ = 0.71073 Å, graphite monochromator)	
θ range (deg)	3.09–28.09	3.35–26.98
scan type	ω	ω
absorp corr <i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.5784, 0.8721	0.658, 0.832
index ranges	–14 ≤ <i>h</i> ≤ 14 –16 ≤ <i>k</i> ≤ 19 –18 ≤ <i>l</i> ≤ 17	–21 ≤ <i>h</i> ≤ 21 –9 ≤ <i>k</i> ≤ 9 –10 ≤ <i>l</i> ≤ 13
no. of reflns collected	15 685	7704
no. of unique data	4925, <i>R</i> <sub>int</sub> = 0.0306	2761, <i>R</i> <sub>int</sub> = 0.0394
refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>	
no. of data/restraints/params	4925/0/271	2761/0/154
goodness-of-fit on <i>F</i> <sup>2</sup> <sup>a</sup>	0.956	1.222
final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] <sup>b</sup>	<i>R</i> <sub>1</sub> = 0.0352 <i>wR</i> <sub>2</sub> = 0.0833	<i>R</i> <sub>1</sub> = 0.0400 <i>wR</i> <sub>2</sub> = 0.1005
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0844 <i>wR</i> <sub>2</sub> = 0.0958	<i>R</i> <sub>1</sub> = 0.0507 <i>wR</i> <sub>2</sub> = 0.1026
largest resid (e Å <sup>-3</sup> )	0.798/–0.279	0.613/–0.463
weights <i>a</i> ; <i>b</i> <sup>c</sup>	0.0459; 0.0	0.0085; 4.0339

<sup>a</sup> GooF =  $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ . <sup>b</sup>  $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ ,  $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ . <sup>c</sup>  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = [2F_c^2 + \max(F_o^2, 0)]/3$ .



**Figure 1.** ORTEP drawing of the molecular structure of **4**. The thermal displacement ellipsoids are drawn at the 50% probability level.

**Electrochemical Measurements.** The present series of new nickelocenes offers the opportunity to bridge the gap between the very extensive electrochemical information on the most common first-row transition metal metallocenes (i.e., ferrocenes and cobaltocenes) and more limited information on nickelocenes.<sup>22,23</sup> As an introduction to the forthcoming description of the redox properties of all nickelocenes described herein, we investigated the electrochemical behavior of *ansa*-nickelocene **4**.

In most organic solvents nickelocene displays the reversible sequence Ni(II)/Ni(III)/Ni(IV),<sup>22a–d</sup> and in a few cases the

partially chemically reversible Ni(II)/Ni(I) reduction has also been observed.<sup>22c,h</sup> Figure 4 compares the cyclic voltammetric behavior of nickelocene and **4** in THF solutions. In view of the high sensitivity of nonaqueous solutions of **4** to traces of water or dioxygen, preliminary measurements were carried out at low temperature (253 K) in order to slow the eventual decomposition of the complex.

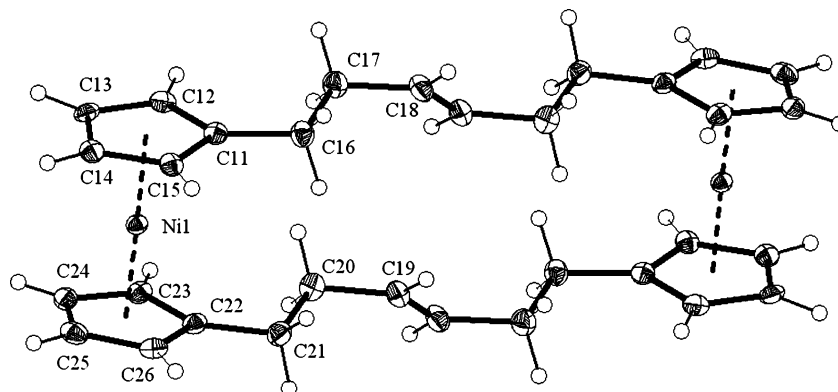
From a qualitative viewpoint, the two voltammetric profiles are substantially similar, and analysis<sup>24</sup> of the cyclic voltammetric responses pertinent to the Ni(II)/Ni(III) oxidation of **4** with scan rates varying from 0.02 to 0.2 V s<sup>-1</sup> confirms the occurrence of a simple diffusion-controlled process (the current ratio  $i_{pc}/i_{pa}$  is constantly equal to 1 and the current function  $i_{pa}xv^{-1/2}$  remains constant). The very large peak-to-peak separations suggest a quasi-reversible process (which would imply significant structural reorganizations accompanying the one-electron removal);<sup>24</sup> however, under the same experimental

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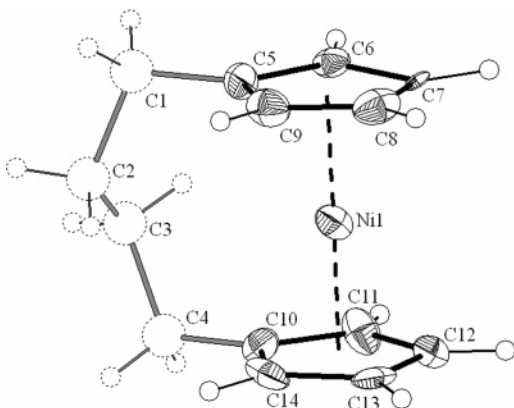
(23) For dinickelocenes see: (a) Smart, J. C.; Pinsky, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 1009. (b) Hudeczek, P.; Köhler, F. H. *Organometallics* **1992**, *11*, 1773. (c) Schottenberger, H.; Ingram, G.; Obendorf, D. *J. Organomet. Chem.* **1992**, *426*, 109.

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**Figure 2.** ORTEP drawing of the molecular structure of **6**. The thermal displacement ellipsoids are drawn at the 50% probability level.



**Figure 3.** ORTEP drawing of the molecular structure of **7**. The thermal displacement ellipsoids are drawn at the 50% probability level. Bridging atoms are shown without ellipsoid representation owing to poor refinement of the structure.

**Table 4.**  $^1\text{H}$  NMR Data for Compounds **4**, **5**, and **7** in  $\text{C}_6\text{D}_6$  at 296 K<sup>a</sup>

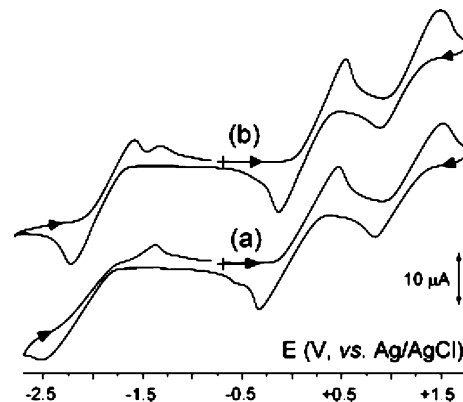
position of nuclei	<b>4</b>	<b>5</b>	<b>7</b>
$\text{C}_5\text{H}_4\text{-CH}_2\text{-}$	-252 (636)	-278 (775)	-253 (736)
	-266 (756) <sup>b</sup>	-296 (876) <sup>b</sup>	-258 (739) <sup>b</sup>
$\text{C}_5\text{H}_4\text{-CH}_2\text{-}$	<i>c</i>	<i>c</i>	139 (259)
$\text{-CH=}$	12.0 (23)	11.9 (47)	
$\text{C}_5\text{H}_4\text{-CH}_2\text{-CH}_2\text{-}$		-5.0 (38)	-1.15 (62)

<sup>a</sup> Experimental chemical shifts in ppm relative to the residual signal of  $\text{C}_6\text{D}_6$  (at 7.15 ppm). Signal half-width in Hz in parentheses. <sup>b</sup> Integration ratio 1:1. <sup>c</sup> Not observed.

conditions, ferrocene displays a quite similar trend (see Table 5). This suggests that the shape of the waves is due to the high resistivity of the THF solution, which is further increased by the low-temperature experiment (as a matter of fact, this prevented the possibility of accurate measurements at higher scan rates).

Such findings, together with the fact that the Ni(II)/Ni(III) oxidation of **4** is easier by about 0.15 V with respect to nickelocene (Table 5), are strongly reminiscent of the redox behavior of the *ansa*-ferrocenes  $[\text{Fe}(\eta^5, \eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_3\text{C}_5\text{H}_4)]$  and  $[\text{Fe}(\eta^5, \eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_4\text{C}_5\text{H}_4)]$ , which oxidize at less positive potentials than ferrocene by 0.07 and 0.08 V, respectively,<sup>25,26</sup> while maintaining the  $\eta^5\text{-}\eta^5$ -coordination.<sup>25,27</sup>

A further observation is concerned with the markedly lower chemical reversibility of the Ni(II)/Ni(I) couple of **4** (which also



**Figure 4.** Cyclic voltammograms recorded at a gold electrode in THF solutions of (a) **4** ( $1.1 \times 10^{-3}$  mol/L) and (b)  $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$  ( $0.9 \times 10^{-3}$  mol/L).  $[\text{NBu}_4][\text{PF}_6]$  (0.2 mol/L) supporting electrolyte.  $T = 253$  K. Scan rate  $0.2$  V  $\text{s}^{-1}$ .

gives rise to some electrode poisoning effects) with respect to that of nickelocene. From a speculative viewpoint, it seems reasonable to argue that while the structural constraints of the 2-buten-1,4-diyl bridge can withstand the decrease of the ionic radius upon Ni(II)/Ni(III) oxidation, they cannot withstand the increase of the ionic radius upon Ni(II)/Ni(I) reduction.

As discussed above, the cyclic voltammetric measurements were cautiously performed at low temperature. Nevertheless, a fast examination of **4** was also carried out at room temperature. Deaerated THF solutions of the compound **4** as well as the mono- and dications are sufficiently stable at room temperature on the cyclic voltammetric time scale, even if the need for electrode cleaning prevented further measurements (Figure S6, which also shows calibration with respect to the ferrocene/ferrocenium couple; see Supporting Information).

## Conclusions

This work demonstrates that moderately stable, 20-electron *ansa*-nickelocenes **4** and **5** could be synthesized in synthetically useful yields by ring-closing metathesis in the metal coordination sphere. The bridged binickelocene **6** was also obtained as a result of an intermolecular metathesis reaction. Hydrogenation of the double bond in **4** provides a synthetic route to *ansa*-nickelocene with a saturated bridge. The new compounds show only minor distortions from the sandwich structure in the solid state and are  $\eta^5\text{-}\eta^5$  complexes. Spectroscopic and electrochemical mea-

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**Table 5. Formal Electrode Potentials (V, vs Ag/AgCl) and Peak-to-Peak Separations (mV) for the Redox Changes Exhibited by 4 and Related Species in THF Solution at Various Temperatures (K)**

complex	$E^{\circ'}_{M(IV)/M(III)}$	$\Delta E_p^a$	$E^{\circ'}_{M(III)/M(II)}$	$\Delta E_p^a$	$E^{\circ'}_{M(II)/M(I)}$	$\Delta E_p^a$	T	ref
4	+1.18	500	+0.07	540	-2.50 <sup>b,c</sup>	-	253	this work
	+0.90	200 <sup>d</sup>	0.00	230 <sup>d</sup>	-	-	298	this work
[Ni(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ]	+1.21	435	+0.22	430	-1.91 <sup>e</sup>	411	253	this work
	+0.92	148	+0.12	160	-1.77 <sup>e</sup>	190	298	this work
			-0.1		-1.7 <sup>e</sup>		298	22c
	+0.85		0.01		-1.80 <sup>e</sup>		298	22h
[Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ]			+0.56	538			253	this work
			+0.59	210			298	this work

<sup>a</sup> Measured at 0.1 V s<sup>-1</sup>. <sup>b</sup> Peak-potential value for irreversible processes. <sup>c</sup> Measured at 0.1 V s<sup>-1</sup>. <sup>d</sup> Measured at 0.02 V s<sup>-1</sup>. <sup>e</sup> Partially chemically reversible (see text)

measurements reported herein indicate that properties of all studied ansa-nickelocenes are analogous to those of nickelocene.

## Experimental Section

**General Considerations.** All manipulations were carried out under an atmosphere of purified argon using standard Schlenk techniques. Solvents were dried and distilled under argon employing standard drying agents.<sup>28</sup> Allylcyclopentadiene,<sup>29</sup> (but-3-enyl)cyclopentadiene,<sup>30</sup> [Ni(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub>,<sup>31</sup> [NiBr<sub>2</sub>·2DME],<sup>32</sup> [Ru(=CHPh)-Cl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>] (**3**),<sup>33</sup> and [Ru(=CHPh)Cl<sub>2</sub>(PCy<sub>3</sub>)(H<sub>2</sub>IMes)]<sup>34</sup> were prepared according to the published procedures. H<sub>2</sub>O for hydrolysis and deactivation of Al<sub>2</sub>O<sub>3</sub> was distilled under Ar. Al<sub>2</sub>O<sub>3</sub> (Aldrich, neutral) was heated at 250–300 °C for 5 h, cooled to ambient temperature under a stream of Ar, repeatedly evacuated and back-filled with Ar, and deactivated with 5 wt % of H<sub>2</sub>O. All other reagents were commercial and used as received. Electrochemical measurements were performed in freshly distilled (from sodium benzophenone) THF containing [NBu<sub>4</sub>][PF<sub>6</sub>] (Fluka, electrochemical grade) as a supporting electrolyte. Mass spectra (EI, 70 eV) were measured on an AMD-604 mass spectrometer. <sup>1</sup>H NMR spectra and magnetic susceptibility measurements were taken on a Mercury-400BB spectrometer. Melting points were determined in sealed capillaries. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. UV–vis spectra were measured on a Varian Cary 5000 spectrometer. Elemental analyses were performed on a Vario EL instrument from Elementar. Satisfactory elemental analyses could not be obtained for compounds **1** and **2** because they are oils.

**1,1'-Bis(allyl)nickelocene (1).** Allylcyclopentadiene (4.448 g, 41.96 mmol) was added dropwise to a suspension of NaH (1.007 g, 41.96 mmol) in 35 mL of THF at 0 °C. When the addition was complete, the cooling bath was removed and the reaction mixture was stirred at room temperature until gas evolution stopped. This red solution of sodium allylcyclopentadienide was added to a solution of [NiBr<sub>2</sub>·2DME] (8.337 g, 20.91 mmol) in THF (30 mL). The reaction mixture was stirred at 40 °C for 8 h and then at room temperature for 3 days. A green solution and a white precipitate were formed. Hexane (15 mL) and water (15 mL) were added. The organic layer was separated, reduced in volume to ca. 10 mL, and purified by column chromatography on Al<sub>2</sub>O<sub>3</sub> using hexane as the mobile phase. A green band was collected, which yielded an oil

after the solvent removal. Crystallization from hexane at -78 °C afforded 4.056 g (15.09 mmol, 72% yield) of **1** as a green oil. Mp: ca. 0–5 °C (bath int). MS (EI, 70 eV) *m/z* (rel int, %) (<sup>58</sup>Ni): 268 (M<sup>+</sup>, 100), 227 ([M - C<sub>3</sub>H<sub>5</sub>]<sup>+</sup>, 17), 164 ([NiC<sub>8</sub>H<sub>10</sub>]<sup>+</sup>, 55), 162 ([NiC<sub>8</sub>H<sub>8</sub>]<sup>+</sup>, 29), 136 ([NiC<sub>6</sub>H<sub>6</sub>]<sup>+</sup>, 38), 124 ([NiC<sub>5</sub>H<sub>6</sub>]<sup>+</sup>, 31), 58 (Ni<sup>+</sup>, 26). HRMS for C<sub>16</sub>H<sub>18</sub><sup>58</sup>Ni: calc 268.07620; found 268.07656. A similar procedure employing [Ni(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub> as a substrate provided **1** in 55% yield.

**1,1'-Bis(but-3-enyl)nickelocene (2).** Freshly cut potassium (ca. 2.0 g, excess) was added to a solution of (but-3-enyl)cyclopentadiene (1.861 g, 15.51 mmol) in THF (40 mL) at -30 °C.<sup>35</sup> The resulting mixture was gradually warmed to 0 °C over a period of 6 h, during which time a bright yellow solution was obtained. This solution was added to a suspension of [Ni(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub> (1.805 g, 7.78 mmol) in THF (40 mL). The reaction mixture was heated to reflux for 2 h and stirred overnight at room temperature. Volatiles were removed under vacuum, and the resulting oily residue was extracted with hexane (20 mL), filtered, and reduced in volume to ca. 10 mL. Column chromatography on Al<sub>2</sub>O<sub>3</sub>, eluting with hexane, afforded 0.852 g (2.88 mmol, 37% yield) of **2** as a green oil. MS (EI, 70 eV) *m/z* (rel int, %) (<sup>58</sup>Ni): 296 (M<sup>+</sup>, 72), 255 ([M - C<sub>3</sub>H<sub>5</sub>]<sup>+</sup>, 20), 240 ([M - C<sub>4</sub>H<sub>8</sub>]<sup>+</sup>, 4.8), 177 ([NiC<sub>5</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>CH=CH<sub>2</sub>]<sup>+</sup>, 100), 137 ([NiC<sub>6</sub>H<sub>7</sub>]<sup>+</sup>, 46), 124 ([NiC<sub>5</sub>H<sub>6</sub>]<sup>+</sup>, 8.8), 58 (Ni<sup>+</sup>, 24). HRMS for C<sub>18</sub>H<sub>22</sub><sup>58</sup>Ni: calc 296.10750; found 296.10649.

**1,1'-(2-Buten-1,4-diyl)nickelocene (4).** A solution of 1,1'-bis(allyl)nickelocene **1** (1.539 g, 5.74 mmol) in 120 mL of CH<sub>2</sub>Cl<sub>2</sub> was added to a solution of [Ru(=CHPh)Cl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>] **3** (0.2802 g, 0.340 mmol, 5.9 mol %) in 100 mL of CH<sub>2</sub>Cl<sub>2</sub>. The resulting mixture was stirred at room temperature for 4 days and at reflux for 3 h. Because the reaction was incomplete as judged by EI-MS of the crude reaction mixture samples, solid [Ru(=CHPh)Cl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>] (0.0302 g, 0.0377 mmol) was added and the reaction mixture stirred for another 5 days at room temperature with degassing under a stream of Ar. Volatiles were removed under vacuum to yield a red-brown, solid residue, which was treated with hexane (2 × 30 mL). The green supernatant was filtered through a short column of alumina and reduced in volume. Crystallization at -78 °C gave 0.481 g (2.00 mmol, 35% yield) of **4** as green needles. Mp: 95–97 °C (dec). MS (EI, 70 eV) *m/z* (rel int, %) (<sup>58</sup>Ni): 240 (M<sup>+</sup>, 100), 174 ([Ni(C<sub>5</sub>H<sub>4</sub>-C<sub>4</sub>H<sub>4</sub>)]<sup>+</sup>, 91), 162 ([NiC<sub>8</sub>H<sub>8</sub>]<sup>+</sup>, 12), 136 ([NiC<sub>6</sub>H<sub>6</sub>]<sup>+</sup>, 16), 58 (Ni<sup>+</sup>, 25). HRMS for C<sub>14</sub>H<sub>14</sub><sup>58</sup>Ni: calc 240.04490; found 240.04508. FT-IR (CCl<sub>4</sub>)  $\nu$  (cm<sup>-1</sup>): 3096 (w, C–H stretch), 3024 (s, C–H stretch), 2910 (vs, C–H stretch), 2845 (s, C–H stretch), 1629 (w, C=C stretch) 1448 (vs, asym. C–C stretch), 1039 (s, C–H bend), 1027 (vs, C–H bend), 944 (s, C–H bend), 617 (w,  $\gamma$ -C–H), 590 (s). UV–vis (2,2,4-trimethylpentane)  $\lambda_{max}$  (nm): 199, 304, 675. Anal. Calcd for C<sub>14</sub>H<sub>14</sub>Ni: C, 69.79; H, 5.86. Found: C, 69.50; H, 6.02. Crystals suitable for X-ray diffraction were grown from a solution in hexane at -30 °C.

**1,1'-(3-Hexen-1,6-diyl)nickelocene (5) and Binickelocene (6).** A solution of 1,1'-bis(but-3-enyl)nickelocene (**2**) (0.852 g, 2.88

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mmol) in  $\text{CH}_2\text{Cl}_2$  (40 mL) was added to a solution of  $[\text{Ru}(\text{=CHPh})\text{-Cl}_2(\text{PCy}_3)_2]$  (**3**) (0.1320 g, 0.160 mmol, 5.6 mol %) in  $\text{CH}_2\text{Cl}_2$  (40 mL). The reaction was stirred at room temperature for 6 days while ethene was removed by degassing and saturating with Ar.  $[\text{Ru}(\text{=CHPh})\text{Cl}_2(\text{PCy}_3)_2]$  (0.0417 g, 0.051 mmol, 1.6 mol %) dissolved in 10 mL of  $\text{CH}_2\text{Cl}_2$  was added and the mixture stirred for another 2 days. The volatiles were removed under vacuum. Hexane ( $3 \times 40$  mL) was added to the resulting brown, solid residue, and the supernatant was filtered through a short bed of  $\text{Al}_2\text{O}_3$ , concentrated, and placed at  $-78$  °C. Green crystals of **5** were collected, washed with hexane, and dried under vacuum. Yield: 0.234 g (0.873 mmol), 30%. Decomposition was observed at  $80$ – $90$  °C. MS (EI, 70 eV)  $m/z$  (rel int, %) ( $^{58}\text{Ni}$ ): 268 ( $\text{M}^+$ , 90), 214 ( $[\text{M} - \text{C}_4\text{H}_6]^+$ , 19), 190 ( $[\text{M} - \text{C}_6\text{H}_6]^+$ , 51), 188 ( $[\text{NiC}_{10}\text{H}_{10}]^+$ , 32), 186 ( $[\text{NiC}_{10}\text{H}_8]^+$ , 18), 174 ( $[\text{NiC}_9\text{H}_8]^+$ , 12), 136 ( $[\text{NiC}_6\text{H}_6]^+$ , 100), 124 ( $[\text{NiC}_5\text{H}_6]^+$ , 10), 58 ( $\text{Ni}^+$ , 50). HRMS for  $\text{C}_{16}\text{H}_{18}^{58}\text{Ni}$ : calc 268.07620; found 268.07709. FT-IR ( $\text{CCl}_4$ )  $\nu$  ( $\text{cm}^{-1}$ ): 3099 (w, C–H stretch), 2987 (w, C–H stretch), 2944 (s, C–H stretch), 2916 (vs, C–H stretch), 2855 (s, C–H stretch), 1447 (s, asym. C–C stretch), 1436 (vs, asym. C–C stretch), 1045 (m, C–H bend), 1027 (s, C–H bend), 970 (vs, C–H bend), 933 (w,  $\gamma$  = C–H), 882 (w,  $\gamma$  = C–H), 516 (w). UV–vis (2,2,4-trimethylpentane)  $\lambda_{\text{max}}$  (nm): 198, 319, 720. Anal. Calcd for  $\text{C}_{16}\text{H}_{18}\text{Ni}$ : C, 71.44; H, 6.74. Found: C, 70.91; H, 6.89.

During the hexane extraction of this reaction mixture a green solid, remaining in the Schlenk tube, was noticed. This solid was recovered by extraction with THF (40 mL). The resulting solution was filtered through a short bed of  $\text{Al}_2\text{O}_3$ , concentrated to a small volume, layered with hexane (40 mL), and placed at  $0$  °C for 1 week. A solid that precipitated was separated (0.060 g, 0.111 mmol), then redissolved in toluene and further purified by column chromatography on  $\text{Al}_2\text{O}_3$  using toluene as the mobile phase. Repeated crystallizations from toluene/THF provided small, light green crystals of **6**. Decomposition was observed at  $160$ – $170$  °C. MS (EI, 70 eV)  $m/z$  (rel int, %) ( $^{58}\text{Ni}$ ): 536 ( $\text{M}^+$ , 1.7), 268 ( $[\text{Ni}(\text{C}_5\text{H}_4(\text{CH}_2)_2\text{CH})_2]^+$ , 100), 190 ( $[\text{NiC}_{10}\text{H}_{12}]^+$ , 47), 188 ( $[\text{NiC}_{10}\text{H}_{10}]^+$ , 31), 186 ( $[\text{NiC}_{10}\text{H}_8]^+$ , 18), 174 ( $[\text{NiC}_9\text{H}_8]^+$ , 10), 136 ( $[\text{NiC}_6\text{H}_6]^+$ , 82), 124 ( $[\text{NiC}_5\text{H}_6]^+$ , 8.9), 58 ( $\text{Ni}^+$ , 25). HRMS for  $\text{C}_{32}\text{H}_{36}^{58}\text{Ni}_2$ : calc 536.15240; found 536.15426. UV–vis (THF)  $\lambda_{\text{max}}$  (nm): 207, 312, 681. Anal. Calcd for  $\text{C}_{32}\text{H}_{36}\text{Ni}_2$ : C, 71.44; H, 6.74. Found: C, 71.12; H, 6.65. Crystals suitable for X-ray diffraction were grown from a toluene/THF solution at  $-30$  °C.

**1,1'-(Butan-1,4-diyl)nickelocene (7)**, *ansa*-Nickelocene (**4**) (0.224 g, 0.929 mmol) and  $[\text{RhCl}(\text{PPh}_3)_3]$  (0.102 g, 0.110 mmol) were dissolved in toluene (50 mL). The resulting solution was stirred under an atmosphere of  $\text{H}_2$  overnight at room temperature. The volatiles were removed under reduced pressure, and the solid residue was extracted with hexane ( $2 \times 40$  mL). The combined extracts were filtered through a short bed (3 cm) of  $\text{Al}_2\text{O}_3$  and reduced in volume. Crystallization at  $-20$  °C afforded green crystals of **7** (0.127 g, 56% yield). Mp:  $85$ – $90$  °C (dec). MS (EI, 70 eV)  $m/z$  (rel int, %) ( $^{58}\text{Ni}$ ): 242 ( $\text{M}^+$ , 100), 214 ( $[\text{M} - \text{C}_2\text{H}_4]^+$ , 7.0), 174

( $[\text{Ni}(\text{C}_5\text{H}_4 - \text{C}_4\text{H}_4)]^+$ , 9.9), 162 ( $[\text{NiC}_8\text{H}_8]^+$ , 38), 136 ( $[\text{NiC}_6\text{H}_6]^+$ , 43), 124 ( $[\text{NiC}_5\text{H}_6]^+$ , 17), 58 ( $\text{Ni}^+$ , 26). HRMS for  $\text{C}_{14}\text{H}_{16}^{58}\text{Ni}$ : calc 242.06055; found 242.05959. UV–vis (2,2,4-trimethylpentane)  $\lambda_{\text{max}}$  (nm): 199, 310, 673. Anal. Calcd for  $\text{C}_{14}\text{H}_{16}\text{Ni}$ : C, 69.21; H, 6.64. Found: C, 68.87; H, 6.84.

**Electrochemical Measurements.** Cyclic voltammetric measurements were carried out in a three-electrode, *nonisothermic* cell, which, when necessary, was refrigerated at 253 K (cooled ethanol was forced to flow through a thermostatic jacket surrounding the working electrode and the counterelectrode).<sup>24</sup> The saturated calomel electrode (SCE) was used as a reference electrode. Platinum or gold electrodes were used as working electrodes. A platinum spiral encircling the working electrode was used as a counterelectrode. The THF/ $[\text{NBu}_4][\text{PF}_6]$  (0.2 mol/L) solution was deaerated and maintained under argon.

**Crystal Structure Determination of 4 and 6.** Crystals of **4** and **6** were mounted onto a glass fiber and then flash-frozen to 100 K (Oxford Cryosystem cryostream cooler). Preliminary examination and intensity data collections were carried out on a Kuma KM4CCD  $\kappa$ -axis diffractometer with graphite-monochromated Mo  $\text{K}\alpha$  radiation. Crystals were positioned 65 mm from the KM4CCD camera. The data were corrected for Lorentz, polarization, and absorption effects. Data reduction and analysis were carried out with the Kuma Diffraction (Wrocław) programs.<sup>36</sup> The structures were solved by direct methods and refined by the full-matrix least-squares method on all  $F^2$  data using the SHELXTL programs.<sup>37</sup> In all compounds non-hydrogen atoms were refined with anisotropic displacement parameters for molecules. The carbon-bonded hydrogen atoms were included in calculated positions and refined using a riding model.

**Crystal Structure Determination of 7.** The crystal was mounted onto a glass fiber and then flash-frozen to 100 K (Oxford Cryosystem cryostream cooler). Preliminary examination and intensity data collections were carried out on a Kuma KM4CCD  $\kappa$ -axis diffractometer with graphite-monochromated Mo  $\text{K}\alpha$  radiation. The structure was solved by direct methods and refined by the full-matrix least-squares method on all  $F^2$  data using the SHELXTL programs.<sup>37</sup> The poor crystal quality and the weak diffracting power of compound **7** allowed only for partial structure determination. Compound **7** crystallized in the orthorhombic crystal system, space group  $Pbca$ ,  $a = 7.8230(7)$  Å,  $b = 11.1250(12)$  Å,  $c = 25.423(2)$  Å. The high-temperature factors of C1, C2, C3, and C4 carbon atoms suggest their disorder, which, unfortunately, could not be resolved. However, the connectivity and other broad structural features of the main complex are well refined and undoubtedly correct.

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**Supporting Information Available:** CIF file for the structural analysis for **4** and **6**, IR spectrum of **4**, UV–vis spectra of **4**–**7**, cyclic voltammogram of **4** at room temperature, MS spectra, and HRMS reports for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(36) Oxford Diffraction. *CrysAlis CCD* and *CrysAlis RED*, Versions 1.171; Oxford Diffraction Ltd: Abingdon, Oxfordshire, England, 2004.

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