

Scheme 3. Transformation of **7** to the vinyl iodide **11** and the following coupling reaction.

easily available in quantity, and the reaction operation is easy.

### Experimental Section

Typical procedure for the site-selective C–C bond formation of **2** with organocuprates (preparation of **3aa**, Table 1, entry 1): To a stirred solution of CuI (1.99 g, 10.4 mmol) in Et<sub>2</sub>O (10 mL) was added a 1.04 M solution of MeLi in ether (20.0 mL, 20.8 mmol) at 0 °C, under argon, to give a homogeneous solution. The solution was cooled to –50 °C, then **2a** (1.90 g, 3.48 mmol) was added to the solution. After stirring at –50 °C for 3 h, the reaction mixture was quenched by the addition of aqueous NH<sub>4</sub>Cl and the organic products were extracted with diethyl ether. The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo to give a crude oil. Chromatography on silica gel (hexane) afforded compound **3aa** (1.35 g, 90%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.16 (s, 9H), 0.85–0.90 (m, 6H), 1.25–1.60 (m, 16H), 1.65 (s, 3H), 2.18 (t, *J* = 8.0 Hz, 2H), 2.51 (t, *J* = 7.1 Hz, 2H), 6.19 ppm (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 0.41, 14.18, 14.21, 19.67, 22.73, 22.76, 27.94, 28.84, 29.45, 29.85, 31.63, 31.91, 36.61, 45.06, 110.59, 131.35, 136.40, 149.32 ppm.

Typical procedure for conversion of **4** into **5** (synthesis of **11**; Scheme 3): To a stirred solution of **7** (0.126 g, 0.345 mmol) in absolute ethanol (6 mL) was added AgNO<sub>3</sub> (0.088 g, 0.518 mmol) at 0 °C. The mixture was stirred for 10 min to ensure complete dissolution. Iodine (0.114 g, 0.449 mmol) was added in one portion and stirred at 0 °C for 20 min. The reaction mixture was diluted with diethyl ether, filtering through a celite pad. The filtrate was washed with sodium thiosulfate solution, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo to give a crude oil. Chromatography on silica gel (hexane) afforded compound **11** (0.118 g, 82%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.86–0.91 (m, 9H), 1.21–1.42 (m, 20H), 1.89 (t, *J* = 7.4 Hz, 2H), 2.05 (t, *J* = 7.1 Hz, 2H), 2.24 (t, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 5.47 ppm (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 14.16, 14.20, 14.23, 22.74, 22.76, 23.13, 27.94, 28.04, 29.20, 29.27, 29.61, 30.75, 31.67, 31.82, 31.86, 35.47, 43.36, 96.24, 121.60, 142.69, 143.15 ppm.

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## Reaction of “[Mn<sup>II</sup>(CH<sub>2</sub>tBu)<sub>2</sub>]” with Bidentate Diimine Ligands: From Simple Base Adducts to C–C Activation of the Ligand\*\*

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Base adducts of dialkyl Mn<sup>II</sup> complexes are typically monomeric tetrahedral high-spin systems;<sup>[1]</sup> our synthetic target is to extend these adducts to bidentate diimine ligands. Gambarotta and co-workers<sup>[2]</sup> recently reported an approach to Mn<sup>II</sup> analogues of Brookhart–Gibson complexes<sup>[3]</sup> and compared their performance in olefin polymerization with those of Fe<sup>II</sup> and Ni<sup>II</sup> catalysts. In this approach, they showed that the reaction of [MnCl<sub>2</sub>L<sub>2</sub>] complexes with organolithium reagents gave the corresponding Mn<sup>I</sup> and Mn<sup>0</sup> alkyl complexes, that is, the lithium reagents alkylate and reduce the Mn<sup>II</sup> dichloro complex. These results have led us to disclose our investigation on the reaction of a bisneopentyl Mn<sup>II</sup> complex with bidentate Schiff base ligands that were designed to generate complexes with structure **1** (Scheme 1). The major difference in our approach is the reaction of diimine ligands

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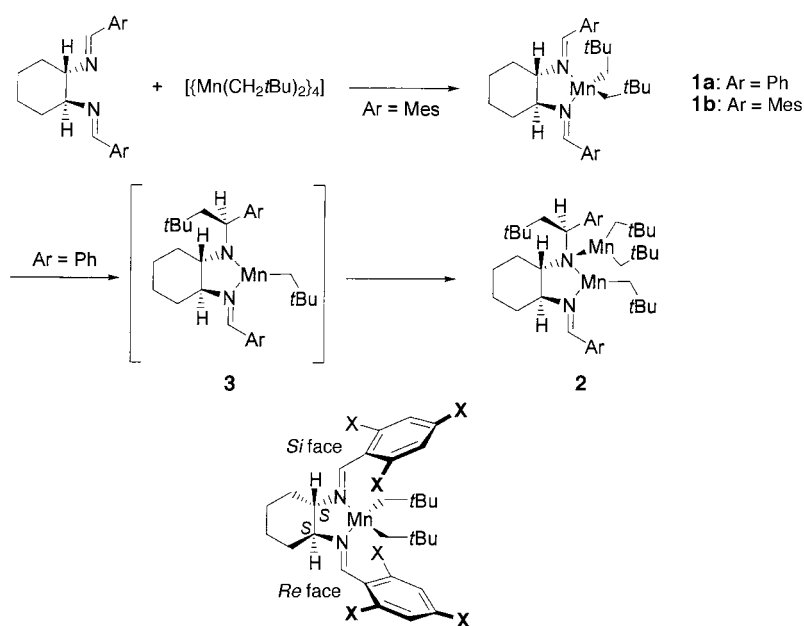
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with manganese(II) dialkyl complexes, which proceeds without reduction. Depending on the structure of the ligand it is possible to isolate either the desired base adduct or compounds in which the imine functional group is alkylated.

A brown solution of  $[\text{Mn}(\text{CH}_2\text{tBu})_2]$  (1 equiv) in toluene was added to a colorless solution of *trans*-*N,N*-bis(benzylidene)-1,2-cyclohexanediamine in toluene, and the solution turned dark-purple. After 12 h, removal of toluene and addition of pentane led to precipitation of unconsumed ligand (excess ligand: vide infra). After complete removal of the ligand and concentration to dryness, a concentrated solution of the solid in toluene was cooled to  $-30^\circ\text{C}$  to give single crystals as brown rectangular parallelepipeds (20%). However, X-ray analysis revealed the presence of **2** (Figure 1) with a structure that was dramatically different from that of the expected **1a**.<sup>[4]</sup> Complex **2** is dinuclear, and the Mn–Mn distance of 2.822 Å implies that there is no metal–metal bond. Mn(1) is bound to one neopentyl ligand as well as to an imino and an amido ligand, whereas Mn(2) is bonded to the electron lone pair of the nitrogen atom of this amido group, but retains the two neopentyl ligands. Complex **2** is probably obtained via the expected **1a** (Scheme 1), which then undergoes migration of the neopentyl ligand onto the imine group<sup>[5]</sup> to generate a mononeopentyl  $\text{Mn}^{\text{II}}$  complex with one imine and one amido ligand, which further reacts with the putative “ $[\text{Mn}(\text{CH}_2\text{tBu})_2]$ ” to give **2**. Thus, two equivalents of “ $[\text{Mn}(\text{CH}_2\text{tBu})_2]$ ” are required for each equivalent of ligand. This suggested reaction pathway is, however, difficult to substantiate, since starting material and product(s) contain high-spin  $\text{Mn}^{\text{II}}$ . Moreover, **2** was isolated as a single stereoisomer. The stereochemistry at the carbon center corresponds to the attack of the neopentyl fragment



Scheme 1. Generation of **2** via **1**, through migration of a neopentyl group and further reaction with the putative “ $[\text{Mn}(\text{CH}_2\text{tBu})_2]$ ”.

from the *Si* face of the imine moiety, that is, the face with the methine hydrogen atom rather than the C–C framework of the cyclohexane ring.

Reaction of a more highly substituted bisbenzylidene ligand ( $\text{Ar} = \text{mesityl (Mes)}$ ) with “ $[\text{Mn}(\text{CH}_2\text{tBu})_2]$ ” gave the desired base adduct **1b** in 36% yield of isolated product. X-ray analysis shows that the geometry of the complex is a distorted tetrahedron with a wide C–Mn–C bond angle of  $146.4^\circ$  (Figure 2).<sup>[4]</sup> The methyl substituents of the aromatic ring probably shield the imino group (see Scheme 1 and Figure 2) and thus prevent the migration of the neopentyl ligand to the imino group.

To understand the scope of this chemistry further, we also investigated the reaction of the Brookhart imino ligand with

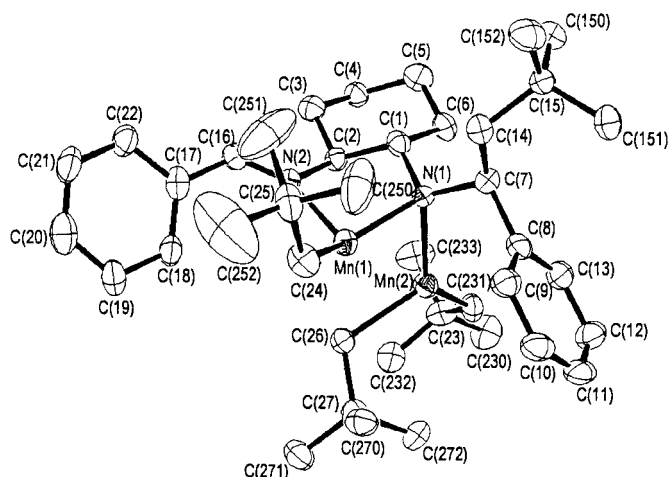


Figure 1. Thermal-ellipsoid plot of **2**. Selected bond lengths [Å] and angles  $^\circ$ : Mn(1)–C(24) 2.121(5), Mn(1)–C(26) 2.419(5), Mn(1)–N(1) 2.132(4), Mn(1)–N(2) 2.242(4), Mn(2)–C(26) 2.223(5), Mn(2)–C(231) 2.122(5), Mn(2)–N(1) 2.129(4); N(1)–Mn(1)–N(2) 79.35(2), N(1)–Mn(1)–C(24) 142.63(2), N(2)–Mn(1)–C(24) 118.48(2), N(1)–Mn(2)–C(26) 104.05(2), N(1)–Mn(2)–C(231) 129.99(2), C(26)–Mn(2)–C(231) 123.8(2).

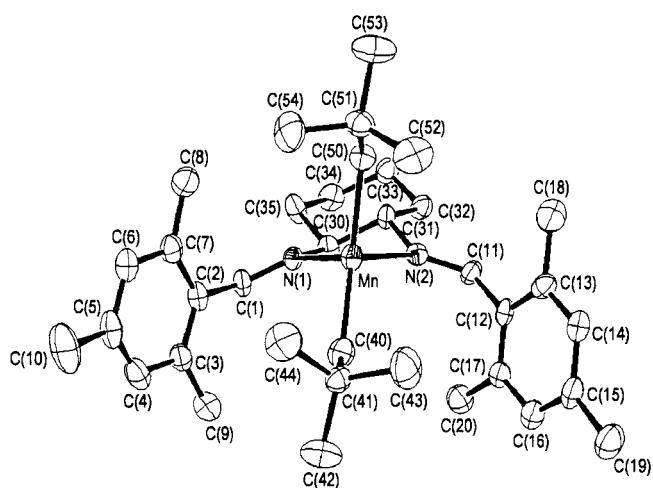


Figure 2. Thermal-ellipsoid plot of **1b**. Selected bond lengths [Å] and angles  $^\circ$ : Mn–C(40) 2.141(6), Mn–C(50) 2.165(6), Mn–N(1) 2.344(4), Mn–N(2) 2.279(4); C(40)–Mn–C(50) 146.4(2), C(40)–Mn–N(1) 102.1(2), C(40)–Mn–N(2) 110.3(2), C(50)–Mn–N(1) 105.62(2), C(50)–Mn–N(2) 95.71(2), N(1)–Mn–N(2) 73.12(2).

"[Mn(CH<sub>2</sub>tBu)<sub>2</sub>]"]. In this case the reaction yield is higher (51 % of single crystals), but structural analysis again showed major reorganization of the putative base adduct by carbon–carbon migration within the ligand (Figure 3).<sup>[4]</sup> The reaction probably involves adduct formation followed by the events outlined in Scheme 2. Migration of one neopentyl ligand in **4**

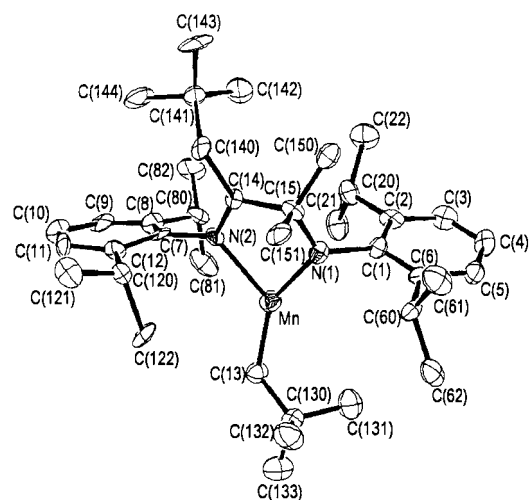
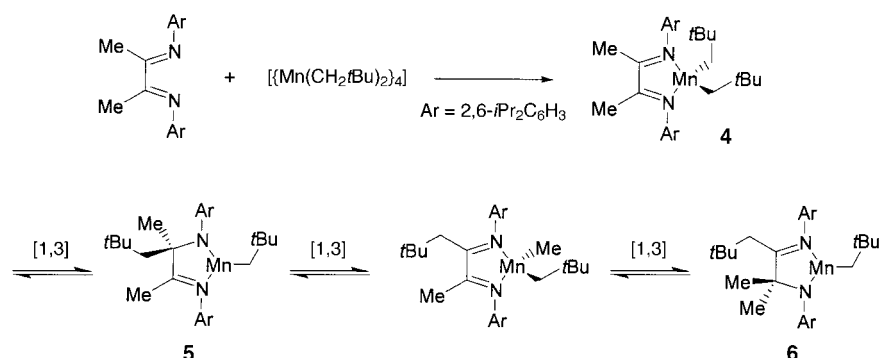


Figure 3. Thermal ellipsoid plot of **6**. Selected bond lengths [Å] and angles [°]: Mn–C(13) 2.105(3), Mn–N(1) 1.960(2), Mn–N(2) 2.185(3); C(13)–Mn–N(1) 150.86(12), C(13)–Mn–N(2) 129.68(11), N(1)–Mn–N(2) 79.11(10).



Scheme 2. Proposed mechanism for the migration reaction.

onto the imino group to give **5** is apparently followed by a 1,2-migration to the vicinal imino group. This rearrangement could also be a two-step process involving successive reversible 1,3-migration of the Me group from the C atom to the Mn atom and then to the other C atom to give an apparent overall 1,2-migration. Complex **6** has an Mn<sup>II</sup> center in a trigonal environment with an imino, an amido, and a neopentyl ligand, like in **2**, but does not undergo further reaction with "[Mn(CH<sub>2</sub>tBu)<sub>2</sub>]", probably because the 2,6-diisopropylphenyl substituent prevents access to the lone pair of the amido ligand.

In conclusion, we have shown that diimine Mn<sup>II</sup> dialkyl complexes are accessible without reduction of the Mn center, which demonstrates the importance to access perhydrocarbyl metal complexes with the appropriate oxidation state. We have also demonstrated the necessity to protect the imino group with bulky substituents to avoid their reaction with

metal–carbon bonds. Most interestingly, we have uncovered pathways in which the C=N bonds undergo alkylation to amido groups. These reactions might be important deactivation pathways in some olefin polymerization reactions.<sup>[6]</sup>

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