

# Methanofullerene-Based Palladium Bis(amino)aryl Complexes and Application in Lewis Acid Catalysis

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Synthetic routes have been developed for the attachment of palladium(II) bis(amino)aryl (NCN or C<sub>6</sub>H<sub>2</sub>{CH<sub>2</sub>NMe<sub>2</sub>}<sub>2-2,6</sub>)<sup>-</sup> complexes to C<sub>60</sub>. Using diazo and Bingel addition reactions, various methanofullerene NCN–SiMe<sub>3</sub> compounds (C<sub>60</sub>–L–NCN–SiMe<sub>3</sub>, L = C(Me), C(CO<sub>2</sub>Et)CO<sub>2</sub>CH<sub>2</sub>, and C(Me)C<sub>6</sub>H<sub>4</sub>C≡C) have been prepared and characterized. Electrophilic palladation of these ligands was achieved with Pd(OAc)<sub>2</sub>, leading to the corresponding C<sub>60</sub>–L–NCN·PdCl complexes. These were converted into active Lewis acid catalysts for the aldol condensation and the Michael reaction. Catalytic tests show that the activity of cationic methanofullerene NCN–palladium complexes in the aldol reaction between benzaldehyde and methyl isocyanoacetate is comparable to the parent unsupported NCN palladium complex. However, in the Michael reaction of methyl vinyl ketone and ethyl cyanoacetate, the fullerene catalysts are not only significantly slower but also undergo a deactivation/decomposition process during the reaction. Preliminary retention measurements using a nanofiltration membrane have shown 72% retention of the palladium complex C<sub>60</sub>–C(Me)–(NCN)PdCl.

## Introduction

Various new materials incorporating C<sub>60</sub> have been prepared in the past decade, such as polymeric and dendrimeric structures, donor–acceptor compounds, and new supramolecular architectures.<sup>1</sup> A number of these fullerene compounds have been shown to be active as catalysts in organic synthesis. For example, a C<sub>60</sub> derivative bearing an organofluorine tail catalyzes the photooxygenation of olefins and dienes in a dioxygen atmosphere under mild conditions.<sup>2</sup> The palladium complex C<sub>60</sub>Pd(PPh<sub>3</sub>)<sub>2</sub> has been used in the cyclization reaction of 1-heptene to 1,2-dimethylcyclopentane and in the selective partial hydrogenation of acetylenic alcohols.<sup>3</sup> Palladium polymers of buckminsterfullerene, [C<sub>60</sub>Pd<sub>n</sub>]<sub>m</sub>, catalyze the hydrogenation of olefins and acetylenes under a dihydrogen atmosphere at room temperature.<sup>4</sup> The rhodium complex RhH(CO)(PPh<sub>3</sub>)<sub>2</sub>–(C<sub>60</sub>) was tested as catalyst for the hydroformylation reaction, showing greater thermal stability than RhH(CO)(PPh<sub>3</sub>)<sub>3</sub>.<sup>5</sup>

We have previously explored the synthesis of methanofullerene ligand systems in which C<sub>60</sub> is used as a

molecular scaffold for the attachment of the (potentially) terdentate coordinating, monoanionic bis(amino)aryl ligand NCN ([C<sub>6</sub>H<sub>2</sub>{CH<sub>2</sub>NMe<sub>2</sub>}<sub>2-2,6-R-4</sub>)<sup>-</sup>), as depicted in Figure 1.<sup>6,7</sup> We are interested in these materials, since they can be considered as alternatives for catalysts bonded to carbon supports such as nanotubes and coal fibers. Efforts to prepare organometallic complexes from these methanofullerene NCN ligands were hampered by difficulties of selective cyclometalation at the NCN moiety: i.e., the introduction of the σ M–C bond at the intra-annular position. While these ligands could be metalated with nickel via the oxidative addition reaction of zerovalent nickel salts, this method turned out to be unsuccessful for palladium. Since NCN–palladium complexes, e.g., [(NCN)Pd(H<sub>2</sub>O)] [BF<sub>4</sub>], are active catalysts in various C–C bond formation reactions, such as aldol condensation and the Michael reaction,<sup>8</sup> we wanted to explore other possible pathways to palladated NCN-anchored methanofullerenes. Moreover, attaching NCN–palladium complexes to C<sub>60</sub> will lead to considerable enlargement in size of the catalyst relative to the parent, unsupported species, allowing the application of the methanofullerene complexes for homogeneous catalysis

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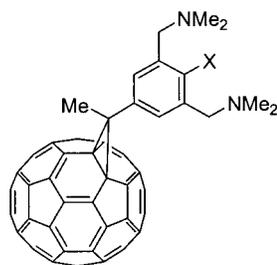
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**Figure 1.** Methanofullerene NCN ligands  $C_{60}-C(Me)-NCN-X$  ( $X = Br, I$ ).

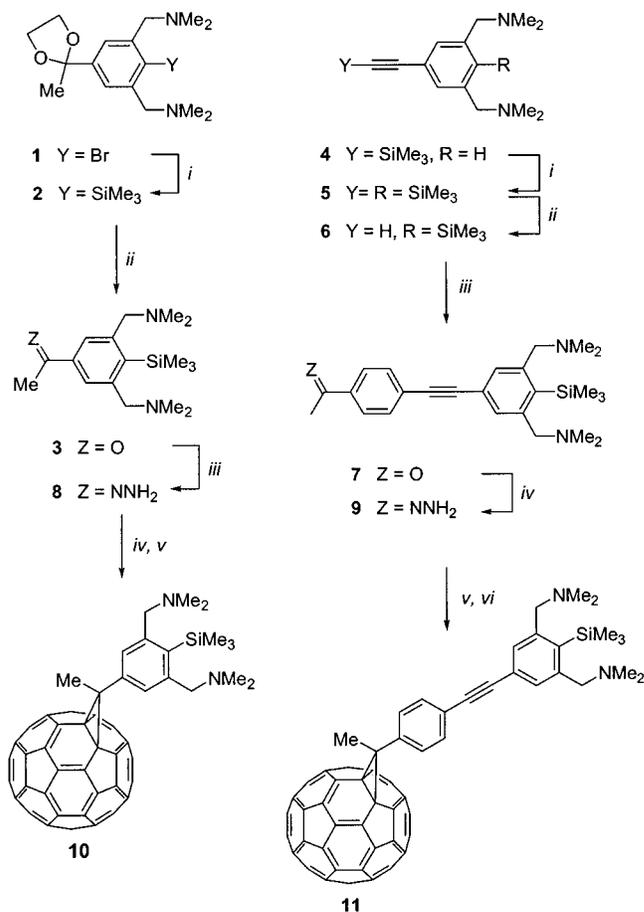
in a nanofiltration membrane reactor. Here, we describe the preparation of novel  $C_{60}$ -anchored NCN-palladium complexes. Moreover, their use as precursor complexes for Lewis acid catalysis and a preliminary retention test using a nanofiltration membrane are also presented.

### Results and Discussion

Previous approaches toward palladated methanofullerene NCN complexes, such as oxidative addition of zerovalent palladium salts or a lithiation-transmetalation step, failed due to interference of the  $C_{60}$  moiety in the methanofullerene NCN ligands  $C_{60}-C(Me)-NCN-X$  ( $X = Br, I$ ).<sup>7</sup> A convenient way to obtain cyclopalladated NCN complexes involves the direct electrophilic palladation reaction of  $NCN-SiMe_3$  with  $Li_2[PdCl_4]$  or  $Pd(OAc)_2$ .<sup>9</sup> The *o*- $CH_2NMe_2$  groups direct the cyclopalladation reaction toward the  $C-SiMe_3$  carbon center exclusively, while no alternative *ortho*-palladation at the 3- or 5-position occurs.<sup>10</sup> This approach circumvents the lithiation/palladation pathway<sup>11</sup> and the use of palladium(0) complexes, such as  $Pd(dba)_2$ ,<sup>12</sup> in the synthesis of NCN-palladium(II) complexes and is, therefore, perfectly suited for palladation of  $C_{60}$ -anchored NCN systems.

Two different methods were used for the preparation of  $C_{60}$ -anchored NCN- $SiMe_3$  ligands (or, in general,  $C_{60}-L-NCN-SiMe_3$ ), namely, diazo addition<sup>7,13</sup> and the Bingel cyclopropanation reaction, because the latter is known for its versatility in the synthesis of  $C_{60}$  adducts.<sup>14</sup> Two suitable NCN- $SiMe_3$  precursor compounds were synthesized for diazo addition to  $C_{60}$  (Scheme 1). 4-Bromo-3,5-bis[(dimethylamino)methyl]acetophenone ethylene acetal (**1**) was lithiated at the  $C-Br$  position via lithium bromide exchange with 2 equiv of *t*-BuLi in diethyl ether. Subsequently, reaction of the corresponding lithium compound with trimethylsilyl triflate<sup>15</sup> in THF afforded the  $Me_3Si$ -substituted acetal **2**, which was deprotected with acid into acetophenone **3**. To increase

### Scheme 1. Synthesis of (a, left) **10** and (b, right) **11**<sup>a</sup>



<sup>a</sup> Reagents and conditions for part a: (i) 2 *t*-BuLi,  $Et_2O$ ,  $-78^\circ C$ , 30 min, then  $Me_3SiOTf$ , THF,  $-78^\circ C$  to room temperature; (ii) HCl,  $Et_2O$ , then NaOH,  $Et_2O$ ; (iii)  $N_2H_4 \cdot H_2O$ , EtOH, reflux; (iv)  $MnO_2$ ,  $Et_2O$ , 20 h, then  $C_{60}$ , toluene, 5 h; (v) toluene,  $110^\circ C$ , 5 days. Reagents and conditions for part b: (i) *n*-BuLi, hexanes,  $-78^\circ C$ , then  $Me_3SiOTf$ , THF,  $0^\circ C$ ; (ii) KOH, MeOH; (iii) 4-iodoacetophenone, CuI,  $Pd(PPh_3)_2Cl_2$ , HNET<sub>2</sub>; (iv)  $N_2H_4 \cdot H_2O$ , EtOH, reflux; (v)  $MnO_2$ ,  $Et_2O$ , 20 h, then  $C_{60}$ , toluene, 5 h; (vi) toluene,  $110^\circ C$ , 5 days.

the distance between the NCN and  $C_{60}$  moieties, we introduced a phenylacetylene spacer between the acetyl and the NCN- $SiMe_3$  groups. The *ipso* carbon of 5-[(trimethylsilyl)ethynyl]-1,3-bis[(dimethylamino)methyl]benzene (**4**)<sup>16</sup> was selectively lithiated with *n*-BuLi in hexanes at  $-78^\circ C$ , followed by reaction with trimethylsilyl triflate<sup>15</sup> in THF, giving **5**. The  $Me_3Si$ -protected acetylene functionality in **5** was deprotected with base, affording the free acetylene **6** in 81% yield, which was subsequently coupled to 4-iodoacetophenone using a Pd/Cu catalyst system,<sup>17</sup> affording **7**. The acetyl-functionalized compounds **3** and **7** were quantitatively converted into the corresponding hydrazones **8** and **9** with  $N_2H_4 \cdot H_2O$  and subsequently oxidized with  $MnO_2$  into the diazo compounds, which were reacted in situ with  $C_{60}$ , giving mixtures of the [5,6]-isomers (85–90%) and the [6,6]-isomers (10–15%). Heating these mixtures in toluene for 5 days gave the pure [6,6]-methano-

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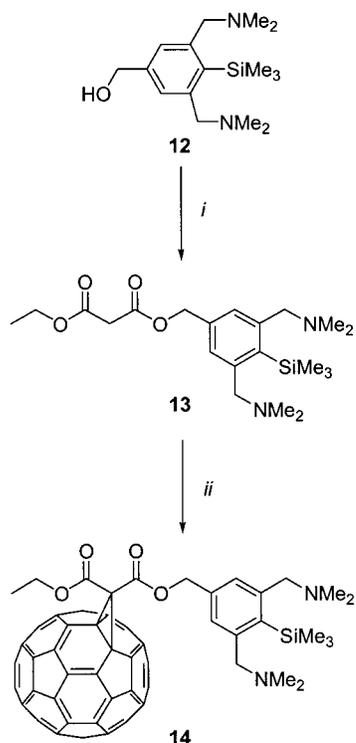
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Scheme 2. Synthesis of **14**<sup>a</sup>

<sup>a</sup> Reagents and conditions: (i) ethyl malonyl chloride, pyridine,  $\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ ; (ii)  $\text{C}_{60}$ ,  $\text{I}_2$ , DBU, toluene, 17 h.

fullerene compounds **10** ( $\text{C}_{60}\text{-C}(\text{Me})\text{-NCN-SiMe}_3$ ) and **11** ( $\text{C}_{60}\text{-C}(\text{Me})\text{-C}_6\text{H}_4\text{C}\equiv\text{C-NCN-SiMe}_3$ ), respectively.

Interestingly, during the isomerization reaction of  $\text{C}_{60}\text{-C}(\text{Me})\text{-NCN-X}$  ( $\text{X} = \text{Br}, \text{I}$ ) compounds, we have observed the significant formation of side products, which was ascribed to (photoinduced) intermolecular reaction of the amine groups with the fullerene moiety.<sup>7,18</sup> However, the [5,6]-isomers of **10** and **11** cleanly isomerize to their [6,6]-isomers without formation of side products. This may be due to an aromatic substitution effect ( $\text{SiMe}_3$  for halide) or a kinetic stabilization of the amine functions through intramolecular interaction of the nitrogen donor atom with the silicon center,<sup>19</sup> which may prevent intermolecular reaction of the amine groups during the isomerization of the fullerene core.

A suitable  $\text{NCN-SiMe}_3$  precursor for Bingel derivatization was prepared by base-assisted reaction of ethyl malonyl chloride with the hydroxyl compound **12**,<sup>20</sup> affording the malonyl- $\text{NCN-SiMe}_3$  derivative **13** (Scheme 2). This was reacted in a one-pot Bingel cyclopropanation reaction with  $\text{I}_2$ , DBU, and  $\text{C}_{60}$  to form the methanofullerene **14** ( $\text{C}_{60}\text{-C}(\text{CO}_2\text{Et})\text{CO}_2\text{CH}_2\text{-NCN-SiMe}_3$ ), which was isolated in 42% yield.

The silane compounds **10**, **11**, and **14** (abbreviated  $\text{C}_{60}\text{-L-NCN-SiMe}_3$ , with  $\text{L} = \text{C}(\text{Me}), \text{C}(\text{Me})\text{C}_6\text{H}_4\text{C}\equiv\text{C}, \text{C}(\text{CO}_2\text{Et})\text{CO}_2\text{CH}_2$ ) reacted quantitatively with  $\text{Pd}(\text{OAc})_2$

in a mixture of 1,2-dichlorobenzene and methanol within 2 h. Subsequent addition of  $\text{LiCl}$  in methanol afforded the corresponding palladium(II) complexes **15–17** (Scheme 3) selectively, without formation of side products. The direct  $\text{C-Si}$  bond activation by  $\text{Pd}(\text{OAc})_2$  is not influenced by the nature of the applied linkers nor, more importantly, by the fullerene moiety, which demonstrates the versatility of this metalation procedure.

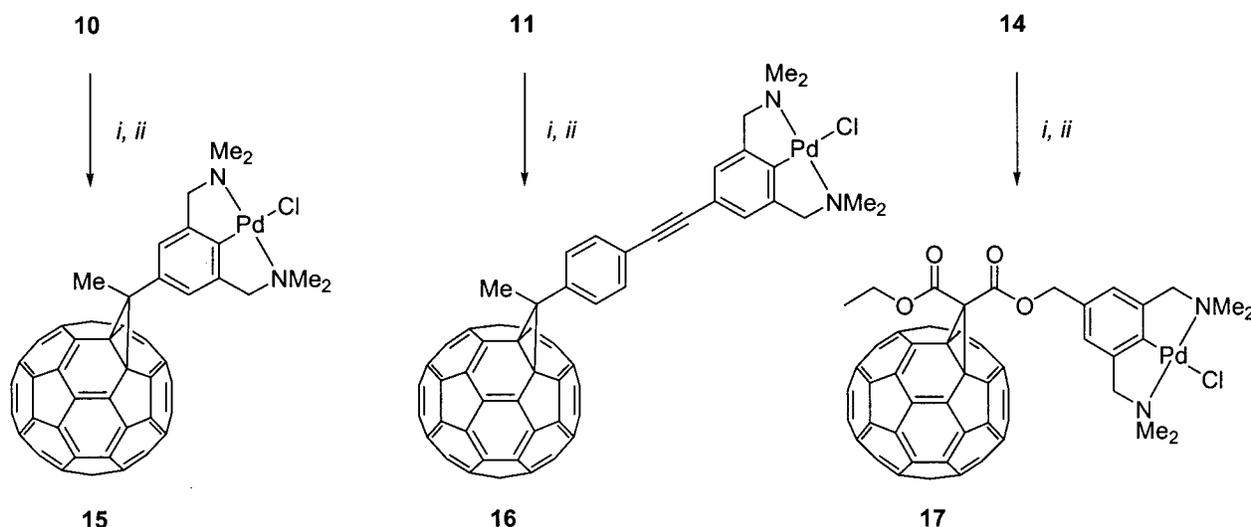
Methanofullerenes  $\text{C}_{60}\text{-L-NCN-SiMe}_3$  and their corresponding palladium complexes were characterized by NMR spectroscopy, mass spectroscopy, and elemental analysis, and the results are consistent with the structures depicted. MALDI-TOF mass spectral analysis in a 9-nitroanthracene matrix gave the correct molecular ions for all  $\text{C}_{60}\text{-L-NCN-SiMe}_3$  compounds; for the palladium complexes, the characteristic molecular ion minus chloride fragment was observed. For all fullerene derivatives,  $^1\text{H}$  NMR spectroscopy at  $25^\circ\text{C}$  showed singlet resonances for the  $\text{CH}_2$  and  $\text{NMe}_2$  groups. When a toluene- $d_8$  solution of **15** was cooled, these resonances decoalesced into an AB pattern ( $T_c = 225\text{ K}$ ,  $\Delta G^\ddagger = 46\text{ kJ/mol}$ ) and two singlets ( $T_c = 213\text{ K}$ ,  $\Delta G^\ddagger = 45\text{ kJ/mol}$ ), respectively. This observation can be explained by the hindered rotation of the  $(\text{NCN})\text{PdCl}$  unit about the  $(\text{Me})\text{C-C}(\text{NCN})$  bond, as was observed for the analogous  $\text{C}_{60}\text{-C}(\text{Me})\text{-}(\text{NCN})\text{NiBr}$  complex.<sup>7</sup> For silane **10**, similar fluxional behavior was observed (Figure 2). At  $-90^\circ\text{C}$ , besides broadening of the resonances due to viscosity changes, the singlet resonance of the  $\text{CH}_2$  protons had decoalesced into an AB pattern ( $T_c = 208\text{ K}$ ,  $\Delta G^\ddagger = 45\text{ kJ/mol}$ ), whereas the dimethylamino resonance showed no decoalescence upon lowering the temperature. Analogously to palladium complex **15**, rotation about the  $(\text{Me})\text{C-C}(\text{NCN})$  bond has become blocked at this temperature, leading to inequivalent aryl- $\text{CH}_2$  protons (AB pattern). The observation of just one resonance for the  $\text{NMe}_2$  groups, even at  $183\text{ K}$ , can be explained by dynamic coordination of the dimethylamino fragments to the silicon center.<sup>19</sup> The  $\text{NMe}_2$  groups displace each other for coordination to silicon, while rapid pyramidal inversion at the N centers takes place, giving rise to only one resonance in the  $^1\text{H}$  NMR spectrum. For **11** and **14** and the corresponding palladium complexes **16** and **17**, no decoalescence of the  $\text{CH}_2$  and  $\text{NMe}_2$  signals upon lowering the temperature to  $-90^\circ\text{C}$  was observed. Only line broadening of the observed resonances took place, which rather was due to increased viscosity of the sample solutions. The use of the phenylacetylene and malonyl spacers results in the disappearance of the hindered rotation of the  $\text{NCN}$  unit observed for **10** and **15**. The  $^{29}\text{Si}$  NMR spectra of **10**, **11**, and **15** showed one resonance for the  $\text{SiMe}_3$  group which was observed at  $-6.8$ ,  $-7.0$ , and  $-7.3\text{ ppm}$ , respectively ( $\text{CDCl}_3$ ). These resonances are high field shifted with respect to, for example,  $\text{Me}_3\text{SiPh}$  ( $\delta -4.1$ ,  $\text{CDCl}_3$ ), which indicates an increased electron density at the silicon center due to the interaction of one or both  $\text{CH}_2\text{NMe}_2$  N-donor substituents with the silicon center.

**Application of Metalated Complexes in Lewis Acid Catalysis.** The  $\text{C}_{60}\text{-L-(NCN)PdCl}$  complexes **15–17** were used as catalyst precursors in two Lewis acid catalyzed transformations, namely the Michael addition of methyl vinyl ketone with ethyl cyanoacetate

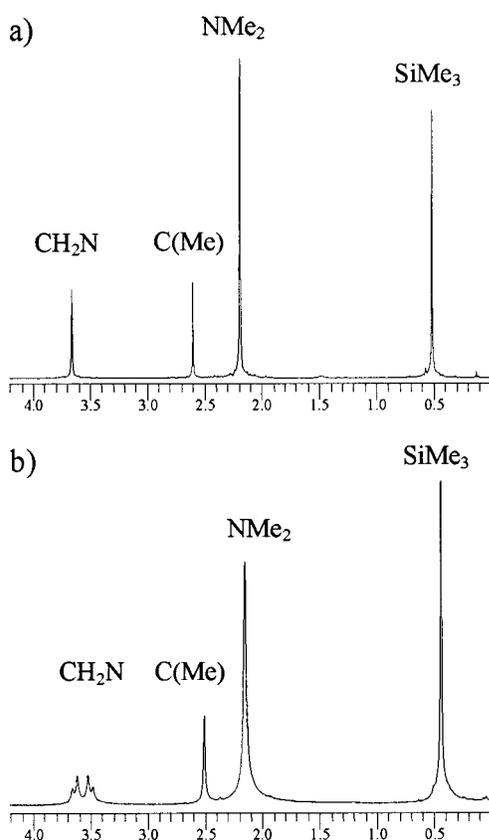
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Scheme 3. Synthesis of Palladium Complexes 15–17<sup>a</sup>

<sup>a</sup> Reagents and conditions: (i) Pd(OAc)<sub>2</sub>, 1,2-dichlorobenzene, 2 h; (ii) LiCl, MeOH, 20 h.



**Figure 2.** Variable-temperature <sup>1</sup>H NMR of **10** at (a) 25 °C and (b) –90 °C in CD<sub>2</sub>Cl<sub>2</sub>/CS<sub>2</sub> (1/1).

and the aldol condensation of benzaldehyde and methyl isocyanoacetate (Scheme 4). These were chosen as representative test reactions for the comparison of C<sub>60</sub>-functionalized catalysts with the unsupported parent analogues.

To this end, the neutral palladium complexes **15**–**17** were converted into the corresponding cationic aqua complexes with AgBF<sub>4</sub> (Scheme 5). The resultant cationic species **18**–**20** were characterized with <sup>1</sup>H NMR spectroscopy only and were freshly prepared prior to use in the catalytic reactions. The cationic palladium complexes are in general less soluble in common organic

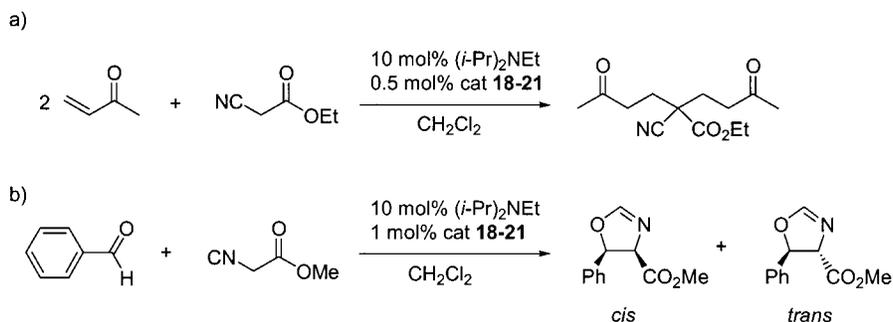
solvents than the neutral palladium complexes but were dissolved completely under catalytic conditions.

All catalytic reactions were performed in CH<sub>2</sub>Cl<sub>2</sub> with 10 mol % of Hünig's base ((*i*-Pr)<sub>2</sub>NEt) at 20 °C. The reactions were monitored with <sup>1</sup>H NMR spectroscopy; the reported reaction rates are calculated from conversion values of the first 2 h of the reaction. The results for the Michael addition are shown in Table 1 and are compared with those for the parent complex [(NCN)-Pd(H<sub>2</sub>O)][BF<sub>4</sub>] (**21**) (Figure 3).<sup>11</sup> The Michael reactions catalyzed by methanofullerenes **18**–**20** are significantly slower than the reaction catalyzed by **21**. Moreover, during the catalytic experiments the formation of a brown precipitate in the initially clear reaction mixtures was observed when **18**–**20** were used as catalysts. Simultaneously, gradual deactivation of the catalyst was observed. However, the reaction did not stop completely, and the conversion still remained considerably faster than the uncatalyzed reaction. The formation of a precipitate was not observed in the blank reaction or with **21**. Whether this decomposition reaction can be circumvented by using catalytic systems with larger linkers between the NCN palladium moiety and the C<sub>60</sub> group or whether this decrease is intrinsic to the presence of a fullerene unit is unclear.

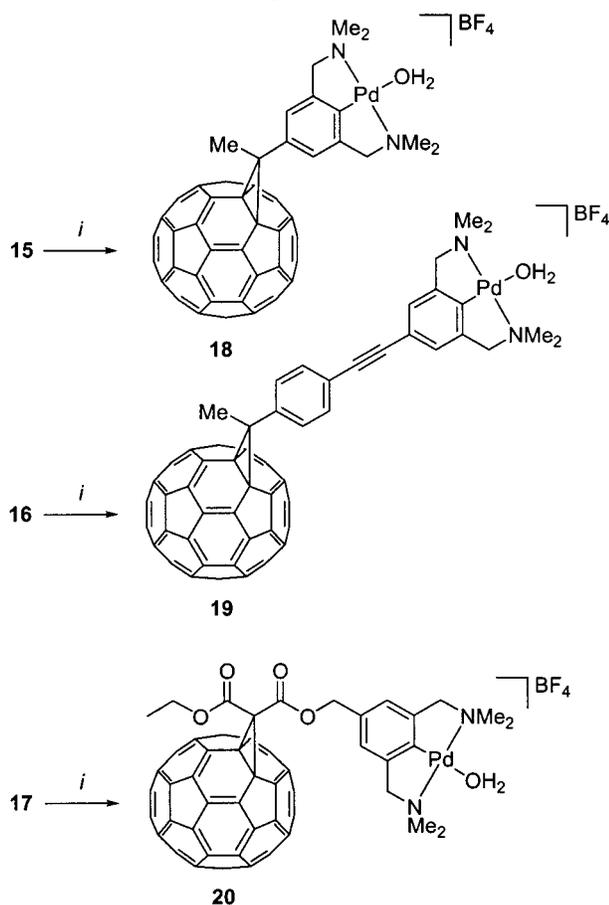
No such deactivation process was observed using the palladium catalysts in the aldol condensation of benzaldehyde and methyl isocyanoacetate. Here, the reported reaction rates (Table 2) do not differ substantially from each other, and more importantly, they are in the same order of magnitude as for the parent complex **21**. Also, the *cis/trans* ratios of the oxazoline products are nearly identical. These results show that, in the aldol condensation, the presence of the fullerene moiety, the nature of the linker, and the distance between the catalytic site and the fullerene do not influence the catalytic behavior. Thus, C<sub>60</sub> acts as a potentially useful catalyst support.

To gain insight into whether these methanofullerene palladium catalysts are applicable in a nanomembrane reactor, the retention of palladium(II) complex **15** was determined. The concentration of **15** in CH<sub>2</sub>Cl<sub>2</sub> solution was determined before and after passing through a

**Scheme 4. Lewis Acid Catalyst Reactions: (a) Double Michael Reaction of Methyl Vinyl Ketone with Ethyl Cyanoacetate; (b) Aldol Condensation Reaction of Benzaldehyde and Methyl Isocyanoacetate**



**Scheme 5. Synthesis of Cationic Palladium Catalysts 18–20<sup>a</sup>**



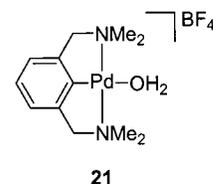
<sup>a</sup> Reagents and conditions: (i) AgBF<sub>4</sub>, wet acetone.

**Table 1. Michael Reaction Catalyzed by 18–21**

catalyst	10 <sup>4</sup> <i>k</i> (s <sup>-1</sup> ) <sup>a</sup>	<i>t</i> <sub>1/2</sub> (min) <sup>b</sup>
<b>18</b>	1.1	105
<b>19</b>	0.9	128
<b>20</b>	0.9	128
<b>21</b>	2.8 <sup>c</sup>	41
blank reaction	2.3 <sup>d</sup>	5023

<sup>a</sup> *k* is the reaction rate, based on a first-order reaction in ethyl cyanoacetate. <sup>b</sup> *t*<sub>1/2</sub> = (ln 2)/(60*k*). <sup>c</sup> From ref 8c. <sup>d</sup> Based on a conversion of 20% after 17 h.

nanofiltration membrane<sup>21</sup> using UV–vis spectroscopy ( $\lambda = 327$ ,  $\epsilon = 3.8 \times 10^4$  mol L<sup>-1</sup>). The retention of **15** by this membrane was found to be 72%. This moderate



**Figure 3.**

**Table 2. Aldol Condensation Catalyzed by 18–21**

catalyst	10 <sup>3</sup> <i>k</i> (s <sup>-1</sup> ) <sup>a</sup>	<i>t</i> <sub>1/2</sub> (min) <sup>b</sup>	cis/trans <sup>c</sup>
<b>18</b>	4.0	173	0.33
<b>19</b>	4.5	154	0.30
<b>20</b>	4.2	165	0.29
<b>21</b>	4.3	161	0.35
blank reaction	0 <sup>d</sup>		

<sup>a</sup> *k* is the reaction rate, based on a first-order reaction in methyl isocyanoacetate. <sup>b</sup> *t*<sub>1/2</sub> = (ln 2)/(60*k*). <sup>c</sup> Determined by <sup>1</sup>H NMR spectroscopy after 100% conversion. <sup>d</sup> No conversion was observed after 24 h.

retention demonstrates that the size of these types of molecules (for **15** calculated<sup>22</sup> as 1.5 × 1.0 × 1.0 nm) needs to be significantly larger for useful retention in a continuous-flow process. For example, the presented synthetic routes toward the C<sub>60</sub>-L-(NCN)PdCl complexes could be applied to introduce more catalytic centers per C<sub>60</sub> unit. In this respect, the use of 4,4'-disubstituted benzophenones<sup>23</sup> or 1,3-disubstituted malonate compounds as anchoring precursors could be used, since the electrophilic palladation reaction of the presented C<sub>60</sub>-L-NCN-SiMe<sub>3</sub> compounds has been shown to be a versatile tool for the introduction of catalytically active metal centers in the N,C,N-terdentate chelating capacity of the NCN unit. Additionally, the C<sub>60</sub> moiety in these methanofullerene metal complexes may be used as a scaffold for new functionalities, such as dendrimers and polymers.<sup>24</sup> This not only enlarges the size of the catalyst molecule but also shields the C<sub>60</sub> surface from the reaction mixture, creating an inert catalyst scaffold.

## Experimental Section

**General Comments.** All experiments were conducted under a dry dinitrogen atmosphere using standard Schlenk techniques. Solvents were dried over appropriate materials

(22) Spartan 5.1.1 (SGI).

(23) See for example: Avent, A. G.; Birkett, P. R.; Paolucci, F.; Roffia, S.; Taylor, R.; Wachter, N. K. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1409.

(24) (a) Herzog, A.; Hirsch, A.; Vostrowsky, O. *Eur. J. Org. Chem.* **2000**, 171. (b) Nierengarten, J.-F. *Chem. Eur. J.* **2000**, *6*, 3667.

and distilled prior to use.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra were recorded at 298 K (unless stated otherwise) on a Varian Inova 300 MHz or on a Varian Mercury 200 MHz NMR spectrometer. All NMR chemical shifts are in ppm referenced to residual solvent signal ( $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$ ) or to TMS ( $^{29}\text{Si}\{^1\text{H}\}$ ). The starting materials 4-bromo-3,5-bis[(dimethylamino)methyl]acetophenone ethylene acetal (**1**),<sup>7</sup> 5-[(trimethylsilyl)ethynyl]-1,3-bis[(dimethylamino)methyl]benzene (**4**),<sup>16</sup> 3,5-bis[(dimethylamino)methyl]-4-(trimethylsilyl)benzyl alcohol (**12**),<sup>20</sup> and  $(\text{NCN})\text{PdH}_2\text{O}[\text{BF}_4]$  (**21**)<sup>11</sup> were synthesized according to literature procedures. MALDI-TOF mass spectra were acquired using a Voyager-DE BioSpectrometry Workstation mass spectrometer (PerSeptive Biosystems Inc., Framingham, MA). Sample solutions were prepared in  $\text{CH}_2\text{Cl}_2$  with an approximate concentration of  $1\text{ g L}^{-1}$ . As the matrix, 9-nitroanthracene (9-NA) was used with an approximate concentration of  $40\text{--}50\text{ g L}^{-1}$ . An  $0.5\ \mu\text{L}$  aliquot of the sample solution and  $0.5\ \mu\text{L}$  of the matrix solution were combined on a gold MALDI target and analyzed after evaporation of the solvent. Elemental analyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium (Mülheim, Germany).

**3,5-Bis[(dimethylamino)methyl]-4-(trimethylsilyl)acetophenone Ethylene Acetal (2).** To a solution of **1** (2.70 g, 7.56 mmol) in hexanes (50 mL) at  $-78\text{ }^\circ\text{C}$  was added 9.0 mL of a 1.7 M solution of *t*-BuLi in pentane (15.3 mmol). The solution was warmed to  $0\text{ }^\circ\text{C}$  over 3 h, and trimethylsilyl trifluoromethanesulfonate ( $\text{Me}_3\text{SiOTf}$ ) (2.9 mL, 15.1 mmol) in THF (20 mL) was added. The solution was stirred at ambient temperature for 20 h, and then all volatiles were removed in vacuo. Subsequently,  $\text{Et}_2\text{O}$  (50 mL) and 1 M aqueous NaOH (50 mL) were added. The organic layer was isolated, and the water layer extracted with  $\text{Et}_2\text{O}$  ( $2 \times 50\text{ mL}$ ). The organic layers were combined, dried over  $\text{MgSO}_4$ , and filtered, and all volatiles were evaporated in vacuo, yielding a yellow oil. This was chromatographed over silica gel using  $\text{Et}_2\text{O}$ /hexanes/ $\text{NET}_3$  (49/49/2 vol %) as eluent, yielding **2** as an analytically pure yellow oil (2.02 g, 76%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.37 (s, 2H, Ar H), 4.00 (m, 2H, acetal), 3.77 (m, 2H, acetal), 3.50 (s, 4H,  $\text{CH}_2\text{N}$ ), 2.09 (s, 12H,  $\text{NCH}_3$ ), 1.64 (s, 3H,  $\text{CH}_3$ ), 0.36 (s, 9H,  $\text{SiCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  146.5, 142.8, 138.0, 125.2 (Ar C), 108.7 ( $\text{CCH}_3$ ), 65.4 ( $\text{CH}_2\text{N}$ ), 64.4 (acetal), 44.9 ( $\text{NCH}_3$ ), 27.2 ( $\text{CCH}_3$ ), 3.1 ( $\text{SiCH}_3$ ). Anal. Calcd for  $\text{C}_{19}\text{H}_{34}\text{BN}_2\text{O}_2\text{Si}$ : C, 65.09; H, 9.78; N, 7.99. Found: C, 64.98; H, 9.72; N, 7.86.

**3,5-Bis[(dimethylamino)methyl]-4-(trimethylsilyl)acetophenone (3).** To a solution of **2** (2.78 g, 7.93 mmol) in  $\text{Et}_2\text{O}$  (40 mL) at  $0\text{ }^\circ\text{C}$  was added 1 M aqueous HCl (40 mL). The reaction mixture was stirred for 1 h, and the acidic layer was separated. The ethereal layer was extracted with 1 M aqueous HCl (20 mL), and 2 M aqueous NaOH was added to the aqueous fraction at  $0\text{ }^\circ\text{C}$  until pH  $>11$  was reached (70 mL). The solution was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 75\text{ mL}$ ). The organic layers were combined, dried over  $\text{MgSO}_4$ , and filtered, and all volatiles were evaporated in vacuo, affording **3** as a yellow oil (2.13 g, 88%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.84 (s, 2H, Ar H), 3.56 (s, 4H,  $\text{CH}_2\text{N}$ ), 2.59 (s, 3H,  $\text{COCH}_3$ ), 2.12 (s, 12H,  $\text{NCH}_3$ ), 0.38 (s, 9H,  $\text{SiCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  198.9 (CO), 147.2, 145.8, 136.7, 127.5 (Ar C), 65.2 ( $\text{CH}_2\text{N}$ ), 45.1 ( $\text{NCH}_3$ ), 26.8 ( $\text{COCH}_3$ ), 2.9 ( $\text{SiCH}_3$ ). Anal. Calcd for  $\text{C}_{17}\text{H}_{30}\text{N}_2\text{OSi}$ : C, 66.61; H, 9.87; N, 9.14. Found: C, 66.71; H, 9.96; N, 8.91.

**2-(Trimethylsilyl)-5-[(trimethylsilyl)ethynyl]-1,3-bis[(dimethylamino)methyl]benzene (5).** To a solution of **4** (5.98 g, 20.7 mmol) in hexanes (50 mL) at  $-78\text{ }^\circ\text{C}$  was added 13.6 mL of a 1.6 M solution of *n*-BuLi in pentane (21.8 mmol). The solution was warmed to  $0\text{ }^\circ\text{C}$  over 4 h, and a solution of  $\text{Me}_3\text{SiOTf}$  (4.80 mL, 24.9 mmol) in THF (40 mL) was added. The solution was stirred for 3 h, and all volatile components were evaporated in vacuo. Pentane (70 mL) and 1 M aqueous NaOH (70 mL) were added, and the organic layer was separated. The aqueous layer was extracted with pentane ( $2 \times 50\text{ mL}$ ). The organic fractions were combined, dried over  $\text{MgSO}_4$ , and filtered. Removal of all volatiles in vacuo yielded

**5** as a yellow oil (5.25 g, 70%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.70 (s, 2H, Ar H), 3.35 (s, 4H,  $\text{CH}_2\text{N}$ ), 1.91 (s, 12H,  $\text{NCH}_3$ ), 0.40 (s, 9H,  $\text{SiCH}_3$ ), 0.23 (s, 9H,  $\text{C}\equiv\text{CSiCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  147.3, 140.2, 132.3, 123.7 (Ar C), 106.5, 94.6 ( $\text{C}\equiv\text{C}$ ), 65.4 ( $\text{CH}_2\text{N}$ ), 44.9 ( $\text{NCH}_3$ ), 3.7 ( $\text{SiCH}_3$ ), 0.1 ( $\text{C}\equiv\text{CSiCH}_3$ ). Anal. Calcd for  $\text{C}_{20}\text{H}_{36}\text{N}_2\text{Si}_2$ : C, 66.60; H, 10.06; N, 7.77. Found: C, 66.46; H, 10.16; N, 7.63.

**1,3-Bis[(dimethylamino)methyl]-4-ethynyl-2-(trimethylsilyl)benzene (6).** To a solution of **5** (5.25 g, 14.6 mmol) in MeOH (100 mL) was added a solution of KOH (1.22 g, 21.8 mmol) in MeOH (40 mL). The reaction mixture was stirred overnight, and water was added (50 mL). The volume of the reaction mixture was reduced to 50 mL in vacuo and extracted with  $\text{Et}_2\text{O}$  ( $3 \times 50\text{ mL}$ ). The organic fractions were combined, dried over  $\text{MgSO}_4$ , and filtered. Removal of all volatiles in vacuo yielded **6** as a yellow oil (3.40 g, 81%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.43 (s, 2H, Ar H), 3.48 (s, 4H,  $\text{CH}_2\text{N}$ ), 3.04 (s, 1H,  $\text{HC}\equiv\text{C}$ ), 2.11 (s, 12H,  $\text{NCH}_3$ ), 0.35 (s, 9H,  $\text{SiCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  147.3, 140.3, 132.3, 122.6 (Ar C), 84.2, 78.0 ( $\text{C}\equiv\text{C}$ ), 65.4 ( $\text{CH}_2\text{N}$ ), 44.6 ( $\text{NCH}_3$ ), 3.1 ( $\text{SiCH}_3$ ). Anal. Calcd for  $\text{C}_{17}\text{H}_{28}\text{N}_2\text{Si}$ : C, 70.77; H, 9.78; N, 9.71. Found: C, 70.64; H, 9.89; N, 9.79.

**5-[4'-(Acetophenone)ethynyl]-1,3-bis[(dimethylamino)methyl]-2-(trimethylsilyl)benzene (7).** To a solution of 4-iodoacetophenone (2.80 g, 11.4 mmol) and **6** (3.30 g, 11.4 mmol) in  $\text{Et}_2\text{NH}$  (90 mL) was added solid  $\text{PdCl}_2(\text{PPh}_3)_2$  (80 mg, 0.11 mmol) and CuI (11 mg, 0.057 mmol). The reaction mixture was stirred overnight and filtered over a small bed of silica gel. All volatile components were removed in vacuo. The remaining crude product was dissolved in  $\text{CH}_2\text{Cl}_2$  (50 mL), and 2 M aqueous HCl (50 mL) was added. The aqueous fraction was isolated and the organic layer extracted with 4 M aqueous HCl ( $2 \times 30\text{ mL}$ ). Aqueous NaOH (4 M) solution was added to the combined aqueous layers until pH  $>12$  was reached, whereafter the aqueous solution was extracted with  $\text{Et}_2\text{O}$  ( $3 \times 50\text{ mL}$ ). The organic fractions were combined, dried over  $\text{MgSO}_4$ , and filtered. Removal of all volatiles in vacuo afforded **7** as a yellow oil (2.89 g, 63%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.90 (d, 2H,  $^3J = 8.7\text{ Hz}$ , Ar H), 7.56 (d, 2H,  $^3J = 8.1\text{ Hz}$ , Ar H), 7.48 (s, 2H, Ar H), 3.50 (s, 4H,  $\text{CH}_2\text{N}$ ), 2.57 (s, 3H,  $\text{COCH}_3$ ), 2.12 (s, 12H,  $\text{NCH}_3$ ), 0.36 (s, 9H,  $\text{SiCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  196.6 (CO), 146.5, 140.2, 135.8, 131.4, 130.8, 128.0, 127.9, 122.2 (Ar C), 92.9, 88.7 ( $\text{C}\equiv\text{C}$ ), 64.8 ( $\text{CH}_2\text{N}$ ), 44.8 ( $\text{NCH}_3$ ), 26.2 ( $\text{COCH}_3$ ), 2.9 ( $\text{SiCH}_3$ ). Anal. Calcd for  $\text{C}_{25}\text{H}_{34}\text{N}_2\text{OSi}$ : C, 73.84; H, 8.43; N, 6.89. Found: C, 73.76; H, 8.51; N, 6.88.

**3,5-Bis[(dimethylamino)methyl]-4-(trimethylsilyl)acetophenone hydrazone (8).** To a solution of **3** (0.62 g, 2.0 mmol) in ethanol (25 mL) was added  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  (0.21 g, 4.1 mmol). The reaction mixture was heated at  $79\text{ }^\circ\text{C}$  for 2 h, whereafter all volatile components were removed in vacuo. The product was dissolved in  $\text{CH}_2\text{Cl}_2$  (25 mL), dried over  $\text{MgSO}_4$ , filtered, and evaporated in vacuo, yielding **8** as a light yellow oil (0.65 g, quantitative yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.55 (s, 2H, Ar H), 5.33 (s, 2H,  $\text{N}_2\text{H}_2$ ), 3.52 (s, 4H,  $\text{CH}_2\text{N}$ ), 2.12 (s, 3H,  $\text{CCH}_3$ ), 2.10 (s, 12H,  $\text{NCH}_3$ ), 0.35 (s, 9H,  $\text{SiCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  147.5, 146.7, 138.9, 138.8 (Ar C), 125.2 ( $\text{CN}_2\text{H}_2$ ), 65.5 ( $\text{CH}_2\text{N}$ ), 40.1 ( $\text{NCH}_3$ ), 11.7 ( $\text{CCH}_3$ ), 3.1 ( $\text{SiCH}_3$ ). Anal. Calcd for  $\text{C}_{17}\text{H}_{32}\text{N}_4\text{Si}$ : C, 63.70; H, 10.06; N, 17.48. Found: C, 63.65; H, 9.97; N, 17.28.

**5-[4'-(Acetophenone hydrazone)ethynyl]-1,3-bis[(dimethylamino)methyl]-2-(trimethylsilyl)benzene (9).** To a solution of **7** (0.95 g, 2.36 mmol) in anhydrous ethanol (20 mL) was added  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  (124  $\mu\text{L}$ , 2.47 mmol). The reaction mixture was heated at reflux for 22 h, and all volatile components were removed in vacuo. The crude product was dissolved in  $\text{CH}_2\text{Cl}_2$  (40 mL), dried on  $\text{MgSO}_4$ , and filtered. Removal of the solvent in vacuo gave **9** as a waxy solid (0.89 g, 90%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.63 (d, 2H,  $^3J = 8.4\text{ Hz}$ , Ar H), 7.49 (d, 2H,  $^3J = 8.1\text{ Hz}$ , Ar H), 7.48 (s, 2H, Ar H), 5.41 (s, 2H,  $\text{NNH}_2$ ), 3.51 (s, 4H,  $\text{CH}_2\text{N}$ ), 2.13 (s, 12H,  $\text{NCH}_3$ ), 2.12 (s, 3H,  $\text{CCH}_3$ ), 0.37 (s, 9H,  $\text{SiCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  146.6, 146.3,

139.6, 138.9, 131.5, 130.9, 125.3, 123.0, 122.9 (CCH<sub>3</sub> and Ar C), 90.6, 89.7 (C≡C) 65.0 (CH<sub>2</sub>N), 44.1 (NCH<sub>3</sub>), 11.3 (CCH<sub>3</sub>), 3.1 (SiCH<sub>3</sub>). Anal. Calcd for C<sub>25</sub>H<sub>36</sub>N<sub>4</sub>Si: C, 71.38; H, 8.63; N, 13.32. Found: C, 71.46; H, 8.56; N, 13.25.

**1,2-Dihydro-61-methyl-61-(3,5-bis[(dimethylamino)methyl]-4-(trimethylsilyl)phenyl)-1,2-methano[60]-fullerene (10).** A suspension of **8** (335 mg, 1.05 mmol), MnO<sub>2</sub> (0.45 g, 5.3 mmol), Na<sub>2</sub>SO<sub>4</sub> (0.74 gr, 5.3 mmol), and a freshly prepared saturated solution of KOH in ethanol (0.5 mL) in Et<sub>2</sub>O (60 mL) was stirred in the dark for 20 h. The reaction mixture was filtered over a G4 glass frit and slowly added to a solution of C<sub>60</sub> (1.50 g, 2.10 mmol) in *o*-dichlorobenzene (500 mL). The reaction mixture was stirred for 5 h, and all volatiles were removed under reduced pressure. The remaining product was chromatographed over silica gel. Elution with toluene afforded 0.84 g of C<sub>60</sub>; subsequent elution with toluene/MeOH (95/5 vol %) yielded a mixture of [5,6]- and [6,6]-isomers of **10** as a brown solid. This was dissolved in toluene (1 L) and heated to 110 °C until the isomerization of the [5,6]-isomer into the [6,6]-isomer was complete (5 days, monitored with <sup>1</sup>H NMR). The reaction mixture was filtered over a G4 glass frit, and the solvent was removed in vacuo. The crude product was dissolved in CS<sub>2</sub> (40 mL) and filtered, and pentane was added (80 mL), resulting in the precipitation of **10** as a brown solid which was dried in vacuo (0.70 g, 66%, 76% based on reacted C<sub>60</sub>). <sup>1</sup>H NMR (CS<sub>2</sub>/C<sub>6</sub>D<sub>6</sub> (3/1)): δ 7.88 (s, 2H, Ar H), 3.52 (s, 4H, CH<sub>2</sub>N), 2.41 (s, 3H, CH<sub>3</sub>), 2.04 (s, 12H, NCH<sub>3</sub>), 0.40 (s, 9H, SiCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CS<sub>2</sub>/C<sub>6</sub>D<sub>6</sub> (3/1)): δ 149.27, 148.33, 147.09, 146.21, 145.42, 145.38, 145.36, 145.28, 145.07, 145.04, 144.99, 144.88, 144.65, 144.63, 144.23, 143.99, 143.35, 143.32, 143.26, 143.21, 143.18, 142.57, 142.41, 142.40, 142.28, 141.29, 140.95, 139.42, 138.46, 138.26, 137.56, 131.41, 129.26, 125.67 (C<sub>60</sub> C and Ar C), 81.10 (C<sub>60</sub> sp<sup>3</sup>), 65.54 (CH<sub>2</sub>N), 47.88 (bridgehead C), 45.23 (NCH<sub>3</sub>), 22.43 (CH<sub>3</sub>), 3.69 (SiCH<sub>3</sub>). <sup>29</sup>Si NMR (CDCl<sub>3</sub>): δ -6.8. MALDI-TOF-MS (9-NA): *m/z* 1011.2 (M<sup>+</sup>). Anal. Calcd for C<sub>77</sub>H<sub>30</sub>N<sub>2</sub>Si: C, 91.46; H, 2.99; N, 2.77. Found: C, 91.18; H, 3.15; N, 2.79.

**1,2-Dihydro-61-methyl-61-(4-{3,5'-bis[(dimethylamino)methyl]-4'-(trimethylsilyl)phenylethynyl}phenyl)-1,2-methano[60]fullerene (11).** Compound **11** was synthesized similarly to **10**, starting from **9** (390 mg, 0.94 mmol), MnO<sub>2</sub> (1.22 g, 14.02 mmol), Na<sub>2</sub>SO<sub>4</sub> (2.00 gr, 14.02 mmol), a freshly prepared saturated solution of KOH in EtOH (0.5 mL), and C<sub>60</sub> (1.22 g, 1.69 mmol). The reaction mixture was chromatographed over silica gel. Elution with toluene afforded C<sub>60</sub> (0.86 g); subsequent elution with toluene/MeOH (95/5 vol %) gave a mixture of the [5,6]- and [6,6]-isomers of **11** as a brown solid. This was dissolved in 400 mL of toluene and heated to 110 °C until the isomerization of the [5,6]-isomer into the [6,6]-isomer was complete (5 days, monitored with <sup>1</sup>H NMR). The solvent was removed and the residue chromatographed over silica gel using toluene/MeOH (95/5 vol %) as eluent, yielding **11** as a brown solid (372 mg, 36%, 67% based on reacted C<sub>60</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.86 (s, 2H, Ar H), 7.59 (d, 2H, <sup>3</sup>J = 8.7 Hz, Ar H), 7.50 (d, 2H, <sup>3</sup>J = 8.7 Hz, Ar H), 3.45 (s, 4H, CH<sub>2</sub>N), 2.13 (s, 3H, CH<sub>3</sub>), 2.00 (s, 12H, NCH<sub>3</sub>), 0.47 (s, 9H, SiCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 148.62, 147.91, 146.64, 145.85, 145.18, 145.12, 145.08, 145.04, 144.79, 144.73, 144.67, 144.47, 144.37, 144.01, 143.74, 143.09, 142.99, 142.29, 142.20, 142.16, 140.98, 140.81, 139.89, 139.37, 138.06, 137.54, 132.05, 131.93, 130.99, 130.54, 127.11, 123.25, 122.90 (C<sub>60</sub> C and Ar C), 90.7, 89.3 (C≡C), 80.7 (C<sub>60</sub> sp<sup>3</sup>), 65.1 (CH<sub>2</sub>N), 47.3 (bridgehead C), 45.1 (NCH<sub>3</sub>), 22.4 (CH<sub>3</sub>), 3.2 (SiCH<sub>3</sub>). <sup>29</sup>Si NMR (CDCl<sub>3</sub>): δ -7.0. MALDI-TOF-MS (9-NA): *m/z* 1112.5 (M<sup>+</sup>). Anal. Calcd for C<sub>85</sub>H<sub>34</sub>N<sub>2</sub>Si: C, 91.87; H, 2.98; N, 2.52. Found: C, 91.65; H, 2.92; N, 2.43.

**1-{3,5-Bis[(dimethylamino)methyl]-4-(trimethylsilyl)benzyloxy}-3-ethoxymalonate (13).** To a solution of **12** (1.84 g, 6.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) at 0 °C was added pyridine (0.53 mL, 6.56 mmol) and a solution of ethyl malonyl chloride (1.50 g, 9.99 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The mixture was stirred

for 16 h and evaporated in vacuo. The residue was dissolved in Et<sub>2</sub>O and the solution washed with 4 M aqueous NaOH until the organic layer became clear (4 × 50 mL). The organic fraction was dried over MgSO<sub>4</sub>, filtered, and evaporated in vacuo. The crude product was purified using column chromatography with silica gel and CH<sub>2</sub>Cl<sub>2</sub>/MeOH (95/5 vol %) as eluent, yielding **13** as a yellow oil (0.90 g, 35%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.27 (s, 2H, Ar H), 5.12 (s, 2H, OCH<sub>2</sub>), 4.18 (q, 2H, <sup>3</sup>J = 7.2 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 3.50 (s, 4H, CH<sub>2</sub>N), 3.40 (s, 3H, COCH<sub>2</sub>CO), 2.12 (s, 12H, NCH<sub>3</sub>), 1.24 (t, 3H, <sup>3</sup>J = 6.9 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 0.33 (s, 9H, SiCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 166.4, 166.3 (CO), 146.9, 138.9, 135.1, 127.8 (Ar C), 67.0 (OCH<sub>2</sub>-CH<sub>3</sub>) 65.2 (CH<sub>2</sub>N), 61.4 (OCH<sub>2</sub>) 45.2 (NCH<sub>3</sub>), 41.2 (COCH<sub>2</sub>CO), 14.0 (OCH<sub>2</sub>CH<sub>3</sub>), 3.1 (SiCH<sub>3</sub>). Anal. Calcd for C<sub>21</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub>Si: C, 61.73; H, 8.88; N, 6.86. Found: C, 61.67; H, 8.94; N, 6.81.

**1,2-Dihydro-61-(ethoxycarbonyl)-61-(3,5-bis[(dimethylamino)methyl]-4-(trimethylsilyl)benzyloxy-carbonyl)-1,2-methano[60]fullerene (14).** To a solution of C<sub>60</sub> (0.51 g, 0.70 mmol), I<sub>2</sub> (0.37 g, 1.41 mmol), and **13** (0.29 g, 0.70 mmol) in toluene (600 mL) was added a solution of DBU (0.65 mL, 4.3 mmol) in toluene (30 mL). The reaction mixture was stirred for 17 h and poured on top of a silica gel column. Unreacted C<sub>60</sub> (0.10 g) was eluted using toluene as mobile phase; **14** was eluted using toluene/MeOH (95/5 vol %). The solvents were evaporated in vacuo, and the crude product was washed with hexanes (40 mL) and dried in vacuo, yielding **14** as a light brown solid (0.33 g, 42%, 50% based on reacted C<sub>60</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.42 (s, 2H, Ar H), 5.48 (s, 2H, OCH<sub>2</sub>), 4.52 (q, 2H, <sup>3</sup>J = 7.2 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 3.51 (s, 4H, CH<sub>2</sub>N), 2.12 (s, 12H, NCH<sub>3</sub>), 1.41 (t, 3H, <sup>3</sup>J = 7.2 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 0.35 (s, 9H, SiCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 163.5 (CO), 147.03, 145.33, 145.24, 145.16, 144.87, 144.67, 144.60, 144.58, 144.50, 143.88, 143.06, 142.98, 142.95, 142.21, 141.87, 140.93, 140.84, 139.63, 139.31, 138.79, 134.50, 128.63 (C<sub>60</sub> C and Ar C), 71.6 (C<sub>60</sub> sp<sup>3</sup>), 68.9 (OCH<sub>2</sub>), 65.2 (CH<sub>2</sub>N), 63.4 (OCH<sub>2</sub>CH<sub>3</sub>), 52.2 (bridgehead C), 45.2 (NCH<sub>3</sub>), 14.2 (OCH<sub>2</sub>CH<sub>3</sub>), 3.2 (SiCH<sub>3</sub>). <sup>29</sup>Si NMR (CDCl<sub>3</sub>): δ -7.3. MALDI-TOF-MS (9-NA): *m/z* 1127.1 (M<sup>+</sup>). Anal. Calcd for C<sub>81</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>Si: C, 86.31; H, 3.04; N, 2.49. Found: C, 86.14; H, 2.97; N, 2.51.

**1,2-Dihydro-61-methyl-61-[4-{chloropalladio}-3,5-bis[(dimethylamino)methyl]phenyl]-1,2-methano[60]-fullerene (15).** To a solution of **10** (264 mg, 0.26 mmol) in *o*-dichlorobenzene (40 mL) was added a solution of Pd(OAc)<sub>2</sub> (61 mg, 0.27 mmol) in MeOH (25 mL). The reaction mixture was stirred for 2 h, and LiCl (56 mg, 1.3 mmol) was added. The reaction mixture was stirred for an additional 20 h, whereafter all volatiles were removed in vacuo. The remaining black solid was washed with MeOH (2 × 25 mL) and Et<sub>2</sub>O (25 mL). The crude product was dissolved in CS<sub>2</sub> (10 mL), and the solution was filtered over a G4 glass frit, precipitated with pentane (80 mL), and dried in vacuo, yielding **15** as a brown solid (203 mg, 71%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.39 (s, 2H, Ar H), 4.13 (s, 4H, CH<sub>2</sub>N), 2.97 (s, 12H, NCH<sub>3</sub>), 2.49 (s, 3H, CCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 156.56, 148.89, 148.13, 145.80, 145.20, 145.16, 145.10, 145.03, 144.76, 144.68, 144.45, 144.31, 143.96, 143.11, 143.02, 142.97, 142.29, 142.20, 142.12, 140.94, 140.74, 137.96, 137.63, 135.94, 122.32 (C<sub>60</sub> C and Ar C), 81.1 (C<sub>60</sub> sp<sup>3</sup>), 74.8 (CH<sub>2</sub>N), 53.3 (NCH<sub>3</sub>), 47.9 (bridgehead C), 23.1 (CH<sub>3</sub>). MALDI-TOF-MS (9-NA): *m/z* 1045.3 ([M - Cl]<sup>+</sup>). Anal. Calcd for C<sub>74</sub>H<sub>21</sub>N<sub>2</sub>CIPd: C, 82.31; H, 1.96; N, 2.59. Found: C, 82.19; H, 2.04; N, 2.46.

**1,2-Dihydro-61-methyl-61-(4-{4'-[chloropalladio]-3',5'-bis[(dimethylamino)methyl]phenylethynyl}phenyl)-1,2-methano[60]fullerene (16).** Compound **16** was synthesized similar to **15**, starting from **11** (106 mg, 0.094 mmol), Pd(OAc)<sub>2</sub> (23 mg, 0.10 mmol), and LiCl (23 mg, 0.53 mmol), yielding **16** as a light brown solid (63 mg, 57%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.99 (d, 2H, <sup>3</sup>J = 8.7 Hz, Ar H), 7.66 (d, 2H, <sup>3</sup>J = 8.4 Hz, Ar H), 7.01 (s, 2H, Ar H), 4.02 (s, 4H, CH<sub>2</sub>N), 2.91 (s, 12H, NCH<sub>3</sub>), 2.55 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 158.63, 147.84, 145.80, 145.20, 145.13, 145.06, 145.04, 144.78, 144.70, 144.49,

144.38, 144.02, 143.75, 143.12, 143.07, 143.03, 143.00, 142.98, 142.29, 142.15, 141.02, 140.81, 139.38, 138.07, 137.49, 132.14, 131.76, 131.03, 123.21, 122.91, 118.99 ( $C_{60}$  C and Ar C), 90.9, 88.1 ( $C\equiv C$ ), 80.6 ( $C_{60}$   $sp^3$ ), 74.5 ( $CH_2N$ ), 53.1 ( $NCH_3$ ), 47.3 (bridgehead C), 22.4 ( $CH_3$ ). MALDI-TOF-MS (9-NA):  $m/z$  1144.2 ( $[M - Cl]^+$ ). Anal. Calcd for  $C_{82}H_{25}ClN_2Pd$ : C, 83.47; H, 2.14; N, 2.37. Found: C, 83.40; H, 2.08; N, 2.29.

**1,2-Dihydro-61-(ethoxycarbonyl)-61-[4-[chloropalladio]-3,5-bis(dimethylamino)methyl]benzyloxycarbonyl]-1,2-methano[60]fullerene (17).** Complex **17** was synthesized using the same procedure as used for **15**, starting from **14** (172 mg, 0.153 mmol),  $Pd(OAc)_2$  (36 mg, 0.16 mmol), and LiCl (33 mg, 0.77 mmol), yielding **17** as a brown solid (153 mg, 84%).  $^1H$  NMR ( $CD_2Cl_2$ ):  $\delta$  6.94 (s, 2H, Ar H), 5.39 (s, 2H,  $OCH_2$ ), 4.50 (q, 2H,  $^3J = 7.2$  Hz,  $OCH_2CH_3$ ), 4.00 (s, 4H,  $CH_2N$ ), 2.89 (s, 12H,  $NCH_3$ ), 1.39 (t, 3H,  $^3J = 7.2$  Hz,  $OCH_2CH_3$ ).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ ):  $\delta$  163.55, 163.45 (CO), 157.99, 145.36, 145.30, 145.24, 145.20, 145.14, 145.10, 145.00, 144.92, 144.72, 144.69, 144.63, 144.51, 144.37, 143.90, 143.83, 143.17, 143.14, 143.10, 143.06, 142.92, 142.23, 142.16, 141.90, 141.71, 141.02, 140.85, 139.37, 138.61, 131.10, 121.07 ( $C_{60}$  C and Ar C), 74.7 ( $CH_2N$ ), 71.5 ( $C_{60}$   $sp^3$ ), 69.4 ( $OCH_2$ ), 63.4 ( $OCH_2CH_3$ ), 53.2 ( $NCH_3$ ), 52.2 (bridgehead C), 14.2 ( $OCH_2CH_3$ ). MALDI-TOF-MS (9-NA):  $m/z$  1160.8 ( $[M - Cl]^+$ ). Anal. Calcd for  $C_{78}H_{25}ClN_2O_4Pd$ : C, 78.34; H, 2.11; N, 2.34. Found: C, 78.30; H, 2.04; N, 2.38.

**Synthesis of Lewis Acid Catalysts 18–20. General Procedure.** To a solution of **15** (149 mg, 0.138 mmol) in  $CH_2Cl_2$  was added 1.25 mL of a  $AgBF_4$  solution in wet acetone (33.8 mg/mL). The reaction mixture was stirred for 30 min and evaporated to dryness in vacuo, and the residue was extracted with  $CH_2Cl_2$  (50 mL). The red solution was filtered through Celite and evaporated in vacuo, yielding **18** as a dark brown solid (70%).  $^1H$  NMR ( $CD_2Cl_2$ ):  $\delta$  7.43 (s, 2H, Ar H), 4.13 (s, 4H,  $CH_2N$ ), 2.93 (s, 12H,  $NCH_3$ ), 2.50 (s, 3H,  $CH_3$ ). Data for **19** (starting from **16**, 62%) are as follows.  $^1H$  NMR ( $CD_2Cl_2$ ):  $\delta$  7.99 (d, 2H,  $^3J = 8.4$  Hz, Ar H), 7.67 (d, 2H,  $^3J =$

8.1 Hz, Ar H), 7.03 (s, 2H, Ar H), 4.02 (s, 4H,  $CH_2N$ ), 2.89 (s, 12H,  $NCH_3$ ), 2.55 (s, 3H,  $CH_3$ ). Data for **20** (starting from **17**, 65%) are as follows.  $^1H$  NMR ( $CD_2Cl_2$ ):  $\delta$  6.97 (s, 2H, Ar H), 5.41 (s, 2H,  $OCH_2$ ), 4.51 (q, 2H,  $^3J = 7.2$  Hz,  $OCH_2CH_3$ ), 4.00 (s, 4H,  $CH_2N$ ), 2.86 (s, 12H,  $NCH_3$ ), 1.40 (t, 3H,  $^3J = 76.9$  Hz,  $OCH_2CH_3$ ).

**Catalytic Tests.** The reagents used in the catalytic tests were distilled prior to use (methyl vinyl ketone, ethyl cyanoacetate, benzaldehyde, and diisopropylethylamine), except for methyl isocynoacetate, which was used as received.

**(i) General Procedure for the Michael Addition Reaction.** To a clear  $CH_2Cl_2$  solution of catalyst (8  $\mu$ mol), methyl vinyl ketone (0.40 mL, 4.8 mmol), and ethyl cyanoacetate (170  $\mu$ L, 1.60 mmol) in  $CH_2Cl_2$  (5 mL) was added (*i*-Pr) $_2$ NEt (28  $\mu$ L, 0.16 mmol). Reaction mixture samples (100  $\mu$ L) were taken from the stirred reaction mixture at regular intervals (20–30 min). After careful removal of the volatile components under a stream of nitrogen, the sample was analyzed by  $^1H$  NMR ( $CDCl_3$ ).

**(ii) General Procedure for the Aldol Condensation Reaction.** To a clear  $CH_2Cl_2$  solution of catalyst (16  $\mu$ mol), methyl isocynoacetate (145  $\mu$ L, 1.60 mmol), and benzaldehyde (165  $\mu$ L, 1.60 mmol) in  $CH_2Cl_2$  (5 mL) was added (*i*-Pr) $_2$ NEt (28  $\mu$ L, 0.16 mmol). Reaction mixture samples (100  $\mu$ L) were taken from the stirred reaction mixture at regular intervals (20–30 min). After careful removal of the volatile components under a stream of nitrogen, the sample was analyzed by  $^1H$  NMR ( $CDCl_3$ ).

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