Experimental Section

Materials and Methods

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line, or interfaced to a high vacuum (10^{-5} torr) line, or in a nitrogen filled 'Vacuum Atmospheres' glove box with a medium capacity recirculator (1-2 ppm O_2). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4Å molecular sieve column. Hydrocarbon solvents benzene-d_6, toluene-d_8, thf-d_8 and diethylether-d_{10} were distilled under nitrogen from Na/K alloy. All solvents for vacuum line manipulations were stored in vacuo over Na/K alloy in resealable bulbs. Acetylenic compounds (Aldrich) were dried and stored over activated molecular sieves (4Å), degassed and freshly vacuum-distilled. Commercially available 30% methylaluminoxane in toluene solution was purchased from Witco and the solvent removed through a high vacuum line. The degree of polymerization for MAO was measured by Witco. NMR spectra were recorded on Bruker AM 200 and Bruker AM 400 spectrometers. Chemical shifts for ^{1}H-NMR, ^{13}C-NMR are referenced to internal solvent resonances and are reported relative to tetramethylsilane. GC/MS experiments were conducted in a GCMS (Finnigan Magnum) spectrometer. The NMR experiments were conducted in teflon valve-sealed tubes (J. Young) after vacuum transfer of the liquids in a high vacuum line.

General procedure for the catalytic dimerization of terminal alkynes:

In a typical procedure, the specific amount of the alkyne was vacuum transferred in a high vacuum line into an J. Young NMR tube containing 10 mg of MAO in 0.6 ml of C_6D_6, unless otherwise mentioned. The sealed tube was then kept at room temperature or heated in an oil bath to 78 °C until 100% conversion (yields are given for every specific reaction) of the alkyne was detected by following the disappearance of the acetylenic hydrogen of the alkyne in the ^1H NMR spectra. The organic products were vacuum transferred (10^{-6} mm Hg) to another J. Young NMR tube, sealed and both residue and volatiles were identified by ^1H-, ^{13}C- and 2D-NMR spectroscopy and GC-MS measurements as well as by comparing when possible to the literature known compounds.[1,2]

(1) ***Dimerization of*** ^{i}***PrC≡CH***

(a) According to the general procedure described above, 99.5 % yield was obtained after 24 hours, by the reaction of 0.091 mL (0.89 mmol) of ^{i}PrC≡CH with MAO in C_6D_6 at room temperature, producing the *gem*-$H_2C{=}C(Pr^i)C{\equiv}C(Pr^i)$ (**1**).

1: ^1H NMR (C_6D_6, 200MHz): δ 5.29 (d, J = 1.56 Hz, 1H, *H*CH), 5.06 (d, J = 1.56 Hz, 1H, HC*H*), 2.5 (septet, J = 7.12 Hz, 1H, C*H*Me$_2$), 2.33 (septet, J = 6.73 Hz, 1H, C*H*Me$_2$), 1.10 (d, J = 6.73 Hz, CH(C*H*$_3$)$_2$), 1.06 (d, J = 7.12 Hz, CH(C*H*$_3$)$_2$).

^{13}C NMR (C_6D_6, 50 MHz): δ 139.2 (s, *C*=CH$_2$), 117.0 (t, J = 159 Hz, *C*H$_2$), 96.4 (s, *C*≡CPr^i), 76.6 (s, C≡*C*Pr^i), 35.9 (d, J = 135 Hz, *C*HMe$_2$), 23.3 (q, J = 128 Hz, CH(*C*H$_3$)$_2$), 21.8 (q, J = 128 Hz, CH(*C*H$_3$)$_2$).

GC/MS: m/z 136 (M^+), 135 (M^+ - H), 121 (M^+ - CH_3), 105 (M^+ - $2CH_3$ - H), 93 (M^+ - Pr^i, 100%), 79 (93 - CH_2).

(b) According to the general procedure described above, 99.3% yield was obtained after 1 hour, by the reaction of 0.091 mL (0.89 mmol) of ^{i}PrC≡CH with MAO in C_6D_6 at 78 °C, producing the *gem*-$H_2C{=}C(Pr^i)C{\equiv}C(Pr^i)$ (1).

(c) According to the general procedure described above, 99.3% yield of the *gem*-$H_2C{=}C(Pr^i)C{\equiv}C(Pr^i)$ (1) was obtained by the reaction of 0.091 mL (0.89 mmol) of ^{i}PrC≡CH with MAO in C_6D_6 at 78 °C for 1 hour. The volatiles were vacuum transferred and then another 0.3 ml (2.93 mmol) of ^{i}PrC≡CH and 0.6 mL of C_6D_6 were vacuum transferred into the same NMR tube, sealed and heated to 78 °C for 3 hours, converting the starting alkyne completely into **1**. This procedure were repeated for several times without change in the kinetics (total yield for 10 runs 93.2%).

(2) ***Dimerization of ^{n}BuC≡CH***

(a) According to the general procedure described above, 99.7% yield was obtained after 24 hours, by the reaction of 0.096 mL (0.84 mmol) of ^{n}BuC≡CH with MAO in C_6D_6 at room temperature, producing the *gem*-$H_2C{=}C(Bu^n)C{\equiv}C(Bu^n)$ (**2**).

2: ^{1}H NMR (C_6D_6, 200 MHz): δ 5.35 (d, J = 2.03 Hz, 1H, *H*CH), 5.06 (d, J = 2.03 Hz, 1H, HC*H*), 2.13 (t, J = 6.9 Hz, 4H, CH_2), 1.56 (quintet, J = 7.4 Hz, 4H, CH_2), 1.32 (m, 4H, CH_2), 0.85 (t, J = 7.3 Hz, 3H, CH_3), 0.77 (t, J = 7.3 Hz, 3H, CH_3).

^{13}C NMR (C_6D_6, 50 MHz): δ 133.0 (s, *C*=CH_2), 119.4 (t, J = 158 Hz, CH_2), 89.8 (s, *C*≡CBu^n), 81.4 (s, C≡*C*Bu^n), 37.7 (t, J = 123.5 Hz, CH_2), 31.2 (t, J = 123.5 Hz, CH_2), 30.7 (t, J = 128 Hz, CH_2), 22.3 (t, J = 128 Hz, CH_2), 22.2 (t, J = 128 Hz, CH_2), 19.2 (t, J = 128 Hz, CH_2), 14.0 (q, J = 125 Hz, CH_3), 13.6 (q, J = 125 Hz, CH_3).

GC/MS: m/z 164 (M^+), 149 (M^+ - CH_3), 135 (M^+ - C_2H_5), 121 (M^+ - C_3H_7), 107 (M^+ - Bu^n, 100%), 93 (M^+ - Bu^n - CH_2), 78 (M^+ - Bu^n - C_2H_5).

(b) According to the general procedure described above, 99.2 % yield was obtained after 1 hour, by the reaction of 0.096 mL (0.84 mmol) of $^nBuC{\equiv}CH$ with MAO in C_6D_6 at 78 °C, producing the *gem*-$H_2C{=}C(Bu^n)C{\equiv}C(Bu^n)$ (**2**).

(3) ***Dimerization of $^tBuC{\equiv}CH$***

(a) According to the general procedure described above, 99.4% yield was obtained after 10-days, by the reaction of 0.092 mL (0.797 mmol) of $^tBuC{\equiv}CH$ with MAO in C_6D_6 at room temperature, producing the *gem*-$H_2C{=}C(Bu^t)C{\equiv}C(Bu^t)$ (**3**).

3: ^1H NMR (C_6D_6, 200 MHz): δ 5.31 (d, J = 1.3 Hz, 1H, *H*CH), 5.1 (d, J = 1.3 Hz, 1H, HC*H*), 1.19 (s, 9H, $C(CH_3)_3$), 1.15 (s, 9H, $C(CH_3)_3$).

^{13}C NMR (C_6D_6, 50 MHz): δ 142.4 (s, $C{=}CH_2$), 116.0 (t, J = 159 Hz, CH_2), 99.2 (s, $C{\equiv}CBu^t$), 79.7 (s, $C{\equiv}CBu^t$), 32.9 (s, CMe_3), 31.9 (s, CMe_3), 30.9 (q, J = 124 Hz, CH_3), 29.2 (q, J = 124 Hz, CH_3).

GC/MS: m/z 164 (M^+), 149 (M^+ - CH_3, 100%), 134 (M^+ - $2CH_3$), 133 (M^+ - $2CH_3$ - H), 121 (M^+ - C_3H_7), 107 (M^+ - Bu^t), 91 (M^+ - Bu^t - CH_4).

(b) According to the general procedure described above, the reaction of 0.092 mL (0.797 mmol) of $^tBuC{\equiv}CH$ with MAO in C_6D_6 at 78 °C for 1 hour produced the *gem*-$H_2C{=}C(Bu^t)C{\equiv}C(Bu^t)$ (**3**) dimer in 41.7% yield. The reaction mixture was reflux for 12 hours to complete 99.7 % yield into **3**.

(4) ***Dimerization of PhC≡CH***

(a) According to the general procedure described above, 98.9% yield was obtained after 36 hours, by the reaction of 0.14 mL (1.3 mmol) of PhC≡CH with MAO in C_6D_6 at room temperature, producing the *gem*-$H_2C=C(Ph)C≡C(Ph)$ (**4**).

4: ^1H NMR (C_6D_6, 200 MHz): δ 7.69 - 7.74 (m, 4H, *o-H*-Ph), 7.4 - 7.6 (m, 4H, *m-H*-Ph), 6.69 - 6.98 (m, 2H, *p-H*-Ph), 5.74 (s, 1H, *H*CH), 5.68 (s, 1H, HC*H*).

^{13}C NMR (C_6D_6, 50 MHz): δ 137.8 (s, *C*=CH2), 132.0, 128.7, 128.6, 128.5, 128.3, 126.5 (*C*H-Ph), 130.6 (s, *C*C_5H_5), 120.8 (t, J = 160 Hz, *C*H_2), 91.5 (s, C≡*C*Ph), 89.4 (s, *C*≡CPh).

GC/MS: m/z 204 (M^+), 203 (M^+ - H, 100%), 190 (M^+ - CH_2), 126 (M^+ - C_6H_6), 101 ($PhC≡C^+$).

(b) According to the general procedure described above, 99.4% was obtained after 2 hours, by the reaction of 0.14 mL (1.3 mmol) of PhC≡CH with MAO in C_6D_6 at 78 °C, producing exclusively the *gem*-$H_2C=C(Ph)C≡C(Ph)$ (**4**).

(5) ***Dimerization of MeC≡CH***

According to the general procedure described above, 97.4% yield was obtained after 2-days, by the reaction of MeC≡CH (0.68 mmol) with MAO (0.172 mmol) in C_6D_6 at room temperature, producing the *gem*-$H_2C=C(Me)C≡C(Me)$ (**5**).

5: ^1H NMR (C_6D_6, 200 MHz): δ 5.29 (s, 1H, *H*CH), 5.01 (s, 1H. HC*H*), 1.77 (s, 3H, CH_3), 1.57 (s, 3H, CH_3).

^{13}C NMR (C_6D_6, 50 MHz): δ 134.2 (s, *C*=CH_2), 120.2 (t, J = 159 Hz, *C*H_2), 90.5 (s, *C*≡CMe), 85.1 (s, C≡*C*Me), 3.7 (q, J = 131 Hz, *C*H_3), 2.7 (q, J = 131 Hz, *C*H_3).

(6) *Dimerization of p-^{t}Bu-PhC≡CH*

According to the general procedure described above, 99.1% yield was obtained after 1 hour, by the reaction of 0.078 mL (0.571 mmol) of *p*-^{t}Bu-PhC≡CH with MAO in C_6D_6 at 78 °C, producing the *gem*-H_2C=C(Ph-Bu^t-*p*)C≡C(Ph-Bu^t-*p*) (**6**).

6: ^{1}H NMR (C_6D_6, 200 MHz): δ 7.76 (d, J = 8.34 Hz, 2H, *o-H*-Ph), 7.53 (d, J = 8.21 Hz, 2H, *o-H*-Ph), 7.26 (d, J = 8.34 Hz, 2H, *m-H*-Ph), 7.13 (d, J = 8.21 Hz, 2H, *m-H*-Ph), 5.81 (s, 1H, *H*CH), 5.74 (s, 1H, HC*H*), 1.21 (s, 9H, C(CH_3)$_3$), 1.12 (s, 9H, C(CH_3)$_3$).

^{13}C NMR (C_6D_6, 50 MHz): δ 135.3 (s, *C*=CH_2), 131.9, 126.4, 125.6 (C*H*-Ph), 131.4 (s, *C*C_5H_4Bu^t-*p*), 119.7 (t, J = 156.1 Hz, CH_2), 91.6 (s, *C*≡C), 89.1 (s, C≡*C*), 34.6 (s, *C*Me_3), 31.4 (q, J = 125 Hz, C(CH_3)$_3$), 31.2 (q, J = 125 Hz, C(*C*H_3)$_3$).

GC/MS: m/z 316 (M^+), 301 (M^+ - CH_3, 100%), 273 (M^+ - C_3H_7), 202 (M^+ - 2Bu^t), 182 (^{t}BuPhC≡C^+), 170 (^{t}BuPhC$^+$), 134 (^{t}BuPh$^+$), 77 ($C_6H_5^+$).

(7) *Dimerization of TMSC≡CH*

According to the general procedure described above, 100% conversion was obtained after 72 hours, by the reaction of 0.117 mL (0.83 mmol) of TMSC≡CH with MAO (0.172 mmol) in C_6D_6 at 78 °C, producing a mixture of the following dimers (yield in %); *gem*-H_2C=C(TMS)C≡C(TMS) (7, 43.6%), *trans*-(TMS)CH=CHC≡C(TMS) (**8**, 32.9%) and *cis*-(TMS)CH=CHC≡C(TMS) (**9**, 23.5%).[2] No reaction was observed at room temperature.

(8) ***Dimerization of olefin functionalized substituted terminal alkynes***

(a) According to the general procedure described above, 99.5% yield was obtained after 20 hours, by the reaction of 0.078 mL (0.826 mmol) of $H_2C{=}C(Me)C{\equiv}CH$ with MAO in C_6D_6 at room temperature, producing quantitative the *gem*-$H_2C{=}C(C(Me){=}CH_2)C{\equiv}C\text{-}C(Me){=}CH_2$(**10**).

10: ^{1}H NMR (C_6D_6, 200 MHz): δ 5.5 (s, 1H, *H*CH), 5.27 (s, 1H, HC*H*), 5.84 (s, 1H, *H*CH), 5.07 (s, 1H, HC*H*), 5.34 (s, 1H, *H*CH), 5.02 (s, 1H, HC*H*), 1.75 (s, 3H, CH_3), 1.69 (s, 3H, CH_3).

^{13}C NMR (C_6D_6, 50 MHz): δ 140.9 (s, 2 *C*(Me)=CH_2), 132.5 (s, *C*=CH_2), 121.8 (s, CH_2), 120.8 (s, CH_2), 117.32 (s, CH_2), 92.2 (s, *C*≡C), 87.6 (s, C≡*C*), 23.37 (s, CH_3), 19.26 (s, CH_3).

GC/MS: m/z 132 (M^+), 117 (M^+ - CH_3, 100%), 103 (M^+ - C_2H_5), 91 (M^+ - C_3H_5), 77 (M^+ - C_4H_7), 63 (M^+ - C_5H_7).

(b) According to the general procedure described above, 99.2% yield was obtained after 2 hours, by the reaction of 0.078 mL (0.826 mmol) of $H_2C{=}C(Me)C{\equiv}CH$ with MAO in C_6D_6 at 78 °C, producing the *gem*-$H_2C{=}C(C(Me){=}CH_2)C{\equiv}C\text{-}C(Me){=}CH_2$(**10**).

General procedure for the preparative scale for the catalytic dimerization of terminal alkynes:

In a typical procedure, 200 mg (3.45 mmol) of dry MAO was charged into a 50 mL heavy duty glass schlenk flask in the glovebox. The flask was connected to a Schlenk line and 2 mL of benzene were syringed into the flask followed by 21.5 mmols of the corresponding terminal alkyne RC≡CH (R = ^{i}Pr, ^{t}Bu, ^{n}Bu, Ph, ^{t}BuPh, CH_2=C(Me)). The reaction mixture was heated at 70°C for 12h, cooled to room temperature and open to air. 20 mL of 1N HCl/MeOH (50:50) was added slowly to the reaction mixture and the organic and aqueous layers were separated. The organic layer was dried with $MgSO_4$ and filtered. The low boiling volatiles were removed by flash distillations and the geminal dimer was vacuum transfer at 100°C (oil temperature) at 10^{-4} mmHg to obtain quantitatively yield (99%). For the alkyne R = CH_2=C(Me) the reaction is carried out at room temperature to obtain the geminal dimer.

(9) Stoichiometric reaction of MAO and ^{i}PrC≡CD

Into a glovebox, 22 mg (0.38 mmol) of dry MAO was charged into a J-Young NMR tube. The tube was then connected to a high vacuum line and 0.08 mL (0.76 mmol) of ^{i}PrC≡CD and 0.6 mL of C_6D_6 were vacuum transfer to the NMR tube. The tube was sealed, heated and maintained at room temperature for 36 hours. After the first half an hour of the reaction CH_3D was already observed along with small amounts of the corresponding dideuterium geminal dimer $D_2C{=}C(^iPr)C{\equiv}CPr^i$, as confirmed by ^2H NMR spectroscopy. The amount of the dimer increase gradually with time. The deuterium NMR of the geminal dimer is:

^2H NMR (C_6D_6, 61.2 MHz): δ 5.26 (s, 1D), 5.05 (s, 1D).

^{13}C NMR (C_6D_6, 50 MHz): δ 139.0 (s, *C*=CD_2), 106.8 (quintet, J = 23.9 Hz, CD_2), 96.5 (s, *C*≡CPr^i), 79.6 (s, C≡CPr^i), 35.8 (d, J = 135 Hz, *C*HMe$_2$), 23.2 (q, J = 128 Hz, $CH(CH_3)_2$), 21.8 (q, J = 128 Hz, $CH(CH_3)_2$).

(10) Intermolecular Diels-Alder reactions

According to the general procedure described above, 0.078 mL (0.826 mmol) of $H_2C{=}C(Me)C{\equiv}CH$ were vacuum transferred into a J. Young NMR tube containing 10 mg of MAO (0.172 mmol) in 0.6 ml of C_6D_6. The sealed NMR tube was kept at 78 °C and the reaction was followed at regular interval by monitoring the intensity of the new signals appeared. Quantitative formation (yield > 99.5%) of head-to-tail dimer *gem*-$H_2C=C(C(Me)=CH_2)C\equiv C-C(Me)=CH_2$ (**10**) was observed after 2-hours of heating. Further heating of the reaction mixture for another 3 hours leads to the complete disappearance of **10** with the formation of intermolecular Diels-Alder adduct **11** (yield 99.1). The adduct **11** was also prepared independently by heating compound **10** in C_6D_6 at 78 °C for 2 hours (yield 98.5%).

11: ^1H NMR (C_6D_6, 200 MHz): δ 5.35 (s, 1H, *H*CH), 5.25 (s, 1H, *H*CH), 5.04 (s, 1H, *H*CH), 4.96 (s, 1H, *H*CH), 4.94 (s, 1H, *H*CH), 4.82 (s, 1H, *H*CH), 2.68 (m, 2H, CH_2), 2.27 (bs, 1H, *H*CH), 2.19 (bs, 1H, *H*CH), 1.9 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 1.71(s, 3H, CH_3), 1.56 (m, 2H, CH_2).

^{13}C NMR (C_6D_6, 50MHz): δ 147.6 (s, 2 *C*(Me)=CH_2), 138.6 (s, sp^2C), 121.8 (s, sp^2C), 120.8 (s, =CH_2), 120.4 (s, =CH_2), 114.5 (s, sp^2C), 110.6 (s, =CH_2), 93.7 ($C\equiv C$), 93.0 ($C\equiv C$), 89.7 (s, $C\equiv C$), 83.9 (s, $C\equiv C$), 42.5 (s, CH_2), 32.9 (s, sp^3C) 31.9 (s, CH_2), 28.4 (s, CH_2), 23.8 (s, 2 CH_3), 22.1 (s, CH_3), 19.6 (s, CH_3).

GC/MS: m/z 264 (M^+), 263 (M^+ - H), 249 (M^+ - CH_3), 236 (M^+ - $2CH_3$), 221 (M^+ - $3CH_3$), 207 (M^+ - 3Me - CH_2), 193 (M^+ - 3Me - $2CH_2$), 179 (M^+ - 3Me - $3CH_2$), 91 ($H_2C=C(Me)-C(=CH_2)C\equiv C^+$), 77 (91 - CH_2), 65 ($H_2C=C(Me)C\equiv C^+$), 53 ($H_2C=C(Me)C^+$).

(11) Intermolecular cross Diels-Alder reactions.

According to the general procedure described above, quantitative yield (>99%) was obtained after 24 hours, by the reaction of 0.118 mL (12.4 mmol) of $H_2C=C(Me)C\equiv CH$ with MAO (1.72 mmol) in C_6H_6 at room temperature, producing *gem*-$H_2C=C(C(Me)=CH_2)C\equiv C$-

C(Me)=CH_2 (**10**). Then of 1.17 mL (11.6 mmol) of HC≡CCO_2Et was vacuum transferred into the NMR tube, sealed and heated at 78 °C for 5 hours leading to the formation of the intermolecular Diels-Alder adduct **11** (78%) and the cross Diels-Alder adduct **16** (22%). The ratio between **11** and **16** were measured from NMR and GC-MS spectroscopy. Compound **16** was clean by a base separation flash chromatography with silica eluted with hexane and followed by ether. The ether was removed in a roto-evaporator to obtain 10% yield of the isolated compound.

16: ^1H NMR (C_6D_6, 200 MHz): δ 6.79 (m, 1H, HC=), 5.24 (s, 1H, *H*CH), 4.82 (s, 1H, *H*CH), 4.02 (q, J = 7.05 Hz, OCH_2CH_3), 2.83 (bs, 4H, CH_2), 1.81 (bs, 6H, CH_3), 0.99 (t, J = 7.05 Hz, OCH_2CH_3).

^{13}C NMR (C_6D_6, 50 MHz): δ 166.0 (s, *C*O), 138.5 (s, sp^2C), 135.1 (s, =*C*H), 134.7 (s, sp^2C), 120.8 (s, =CH_2), 114.5 (s, sp^2C), 111.1 (s, sp^2C), 93.9 (s, *C*≡C), 88.6 (s, C≡*C*), 60.2 (s, OCH_2), 32.2 (s, CH_2), 31.66 (s, CH_2), 23.7 (s, CH_3), 21.3 (s, CH_3), 14.3 (s, OCH_2CH_3).

GC/MS: m/z 230 (M^+), 215 (M^+ - CH_3), 201 (M^+ - CH_3CH_2), 185 (M^+ - OEt), 157 (M^+ - OEt - CO), 142 (M^+ - CO_2Et - CH_3, 100%), 115 (M^+ - HCO_2Et - MeC=CH_2), 103 (115 - C), 91 (115 - C≡C).

(12) Effect of solvents on the dimerization of ^iPrC≡CH

(a) According to the general procedure described above, 99.3% yield was obtained after 1 hour, by the reaction of 0.091 mL (0.89 mmol) of ^iPrC≡CH with MAO in C_6D_6 at 78 °C, producing the *gem*-H_2C=C(Pr^i)C≡C(Pr^i) (**1**).

(b) According to the general procedure described above, 98.9% yield was obtained after 1 hour, by the reaction of 0.079 mL (0.774 mmol) of ^{i}PrC$\equiv$CH with MAO in toluene-d_8 at 78 °C, producing the *gem*-$H_2C{=}C(Pr^{i})C{\equiv}C(Pr^{i})$ (**1**).

(c) According to the general procedure described above, 99% was obtained after 3 hours, by the reaction of 0.08 mL (0.8 mmol) of ^{i}PrC$\equiv$CH with MAO (0.172 mmol) in cyclohexane-d_{12} at 78 °C, producing the *gem*-$H_2C{=}C(Pr^{i})C{\equiv}C(Pr^{i})$ (**1**).

(d) Accordingly to the general procedure described above, 0.078 mL (0.768 mmol) of ^{i}PrC$\equiv$CH were vacuum transferred into an J. Young NMR tube containing 10 mg of MAO (0.172 mmol) in 0.6 mL of THF-d_6 or diethylether-d_{10}. No change in the alkyne concentration was observed by keeping the NMR tube either at room temperature for 2-days or at the corresponding reflux temperatures for 24 hours.

(13) Cross dimerization of ^{i}PrC$\equiv$CH with ^{t}BuC$\equiv$CH

(a) According to the general procedure described above, 0.098 mL (0.96 mmol) of ^{i}PrC$\equiv$CH and 0.11 mL (0.96 mmol) of ^{t}BuC$\equiv$CH were vacuum transferred into an J. Young NMR tube containing 10 mg of MAO (0.172 mmol) in 0.6 mL of C_6D_6. The NMR tube was kept at reflux for 12 hours leading to complete a conversion (based on the dissapearence of the terminal alkyne protons by ^{1}H-NMR), producing the *gem*-$H_2C{=}C(Pr^{i})C{\equiv}C(Pr^{i})$ (**1**; 34.2%), *gem*-$H_2C{=}C(Bu^{t})C{\equiv}C(Bu^{t})$ (**3**; 28.9%), *trans*-$H(Bu^{t})C{=}CHC{\equiv}C(Bu^{t})$ (**12**; 1.5%), the cross dimer *gem*-$H_2C{=}C(Pr^{i})C{\equiv}C(Bu^{t})$ (**13**; 28%) and *gem*-$H_2C{=}C(Bu^{t})C{\equiv}C(Pr^{i})$ (**14**; 6.5%).

12: Compound **12** was prepared independently following the procedure (**c**) in reference 1b and compared by retention time and in the pattern of the mass spectrum by GC/MS.

GC/MS: m/z 164 (M^+), 149 (M^+ - CH3,), 134 (M^+ - $2CH_3$), 133 (M^+ - $2CH_3$ - H), 121 (M^+ - C_3H_7), 107 (M^+ - Bu^t, 100%), 91 (M^+ - Bu^t - CH_4).

13: ^1H NMR (C_6D_6, 200 MHz): δ 5.23 (d, J = 2.51 Hz, 1H, *H*CH), 5.04 (d, J = 2.51 Hz, 1H, *H*CH), 2.32 (septet, J = 6.48 Hz, 1H, C*H*Me_2), 1.17 (s, 9H, $C(CH_3)_3$), 1.08 (d, J = 6.48 Hz, 6H, $CH(CH_3)_2$).

^{13}C NMR (C_6D_6, 50 MHz): δ 139.1 (s, *C*=CH_2), 116.9 (t, J = 160 Hz, CH_2), 96.4 (s, *C*≡C), 78.9 (s, C≡*C*), 35.9 (d, J = 135 Hz, *C*HMe_2), 31.9 (s, *C*Me_3), 31.2 (q, J = 124 Hz, $C(CH_3)_3$), 21.8 (q, J = 128 Hz, $CH(CH_3)_2$).

GC/MS: m/z 150 (M^+), 149 (M^+ - H), 135 (M^+ - CH_3, 100%), 119 (M^+ - $2CH_3$ - H), 107 (M^+ - Pr^i), 93 (M^+ - Bu^t), 91 (M^+ - Pr^i - CH_2), 79 (M^+ - Bu^t - CH_2), 57 ($^tBu^+$).

14: Compound **14** was prepared independently following the procedure (**12**) in reference 1c to obtain the bis(acetylide)uranium complex (**A**). Then, a 50 mL Schlenk flask was charged into a glovebox with 50 mg (0.085 mmol) of complex **A**. A 10 mL portion of C_6H_6 was added to the Schlenk flask by vacuum transfer at –78°C followed by 0.02 mL (0.192 mmol) of $^tBuC{\equiv}CH$. The reaction mixture was heated to reflux for 4 hours, cooled to room temperature and quenched by adding 3.5 mL of water. The solvent was removed by flash evaporation and the residue was vacuum transfer (50°C at 10^{-1} mmHg) to obtain 22 mg (78%) yield of **14**.

Compound **14** was compared by retention time and in the pattern of the mass spectrum by GC/MS.

GC/MS: m/z 150 (M^+), 149 (M^+ - H), 135 (M^+ - CH_3), 119 (M^+ - $2CH_3$ - H), 107 (M^+ - Pr^i), 93 (M^+ - Bu^t), 91 (M^+ - Pr^i - CH_2), 79 (M^+ - Bu^t - CH_2, 100%), 57 ($^tBu^+$).

(b) According to the general procedure described above, 0.078 mL (0.768 mmol) of $^iPrC{\equiv}CH$ and 0.088 mL (0.768 mmol) of $^tBuC{\equiv}CH$ were vacuum transferred into an J. Young NMR tube containing 10 mg of MAO (0.172 mmol) in 0.6 mL of C_6D_6. The NMR tube was kept at 78 °C and the reaction was stopped after 2 hours. The complete disappearance of only $^iPrC{\equiv}CH$ signals was verified by ^1H NMR, producing *gem*-$H_2C{=}C(Pr^i)C{\equiv}C(Pr^i)$ (**1**; 60.63%), *gem*-$H_2C{=}C(Bu^t)C{\equiv}C(Bu^t)$ (**3**; 2.8%), the cross dimer *gem*-$H_2C{=}C(Pr^i)C{\equiv}C(Bu^t)$ (**13**; 30.6%) and *gem*-$H_2C{=}C(Bu^t)C{\equiv}C(Pr^i)$ (**14**; 6.0%).

(c) According to the general procedure described above, 100% conversion was obtained after 12 hours, by the reaction of 0.117 mL (1.14 mmol) of $^iPrC{\equiv}CH$ and 0.065 mL (0.57 mmol) of $^tBuC{\equiv}CH$ with MAO (0.172 mmol) in C_6D_6 at 78 °C, producing *gem*-$H_2C{=}C(Pr^i)C{\equiv}C(Pr^i)$ (**1**; 64%), *gem*-$H_2C{=}C(Bu^t)C{\equiv}C(Bu^t)$ (**3**; 8.7%). the cross dimer *gem*-$H_2C{=}C(Pr^i)C{\equiv}C(Bu^t)$ (**13**; 22.6%) and *gem*-$H_2C{=}C(Bu^t)C{\equiv}C(Pr^i)$ (**14**; 4.7%).

(d) According to the general procedure described above, 0.039 mL (0.384 mmol) of $^iPrC{\equiv}CH$ and 0.088 ml (0.768 mmol)of $^tBuC{\equiv}CH$ were vacuum transferred into an J. Young NMR tube containing 10 mg of MAO (0.172 mmol) in 0.6 mL of C_6D_6. The NMR tube was kept at 78 °C and the reaction was stopped after 30 min. The complete disappearance of the acetylenic signals of $^iPrC{\equiv}CH$ was verified by ^1H NMR, producing *gem*-$H_2C{=}C(Pr^i)C{\equiv}C(Pr^i)$ (**1**; 40.9%), *gem*-$H_2C=C(Bu^t)C\equiv C(Bu^t)$ (**3**; 6.5%), the cross dimer *gem*-$H_2C=C(Pr^i)C\equiv C(Bu^t)$ (**13**; 43.5%) and *gem*-$H_2C=C(Bu^t)C\equiv C(Pr^i)$ (**14**; 9.2%).

(14) Cross dimerization of $^iPrC\equiv CH$ with $PhC\equiv CH$.

According to the general procedure described above, 100% conversion was obtained after 12 hours, by the reaction of 0.078 mL (0.768 mmol) of $^iPrC\equiv CH$ and 0.042 mL (0.358 mmol) of $PhC\equiv CH$ with MAO (0.172 mmol) in C_6D_6 at 78 °C, producing *gem*-$H_2C=C(Pr^i)C\equiv C(Pr^i)$ (**1**; 47.2%) and the cross dimer *gem*-$H_2C=C(Pr^i)C\equiv C(Ph)$ (**15**; 46.8%).

15: ^{1}H NMR (C_6D_6, 200 MHz): δ 7.36 - 7.44 (m, 2H, *m-H*-Ph), 6.93 - 6.97 (m, 3H, *o-p*-H-Ph), 5.42 (d, J = 1.62 Hz, 1H, *H*CH), 5.15 (d, J = 1.62 Hz, 1H, *H*CH), 2.36 (septet, J = 6.69 Hz, C*H*Me$_2$), 1.14 (d, J = 6.69 Hz, CH(C*H*$_3$)$_2$).

^{13}C NMR (C_6D_6, 50 MHz): δ 138.7 (s, *C*=CH$_2$), 131.89, 128.3, 128.2 (*C*H-Ph), 132.3 (s, *C*C$_5$H$_5$), 118.8 (t, J = 160 Hz, *C*H$_2$), 90.8 (s, *C*≡C), 89.4 (s, C≡*C*), 35.8 (d, J = 135 Hz, C*H*Me$_2$), 21.8 (q, J = 128 Hz, CH(*C*H$_3$)$_2$).

GC/MS: m/z 170 (M^+, 100%), 155 ($M^+ - CH_3$), 141 ($M^+ - C_2H_5$), 127 ($M^+ - Pr^i$), 115 ($M^+ - C_4H_7$), 102 ($M^+ - Pr^i - C_2H$), 91 ($C_7H_7^+$), 77 ($C_6H_5^+$).

(15) Controlling reaction of Me_3Al with $^iPrC\equiv CH$

(a) A 50 mL Schlenk tube was charged with 1 mL of 2M solution of Me_3Al in toluene (2 mmol) and then 0.078 mL (0.768 mmol) of $^iPrC\equiv CH$ was vacuum transferred into the flash. The reaction mixture was stirred at room temperature for 24 h or heated at 90 °C for 24 h. Neither change in the concentration of the alkyne nor any new signals were detected in the ^{1}H NMR spectra. To the reaction mixture was added 20 μL of H_2O (1.15 mmol) at 10 °C and the reaction mixture was allowed to stirred at room temperature for 4 h. A 40% yield of the *gem*-$H_2C{=}C(Pr^i)C{\equiv}C(Pr^i)$ dimer (1) was determined by ^1H NMR spectroscopy.

(b) A 50 mL Schlenk tube was charged with 1 mL of 2M solution of Me_3Al in toluene (2 mmol) and then 20 μL of H_2O (1.15 mmol) was added at 10 °C and the reaction mixture was stirred at room temperature for 12 h. The solvent was removed in vacuo and a 4 mL portion of C_6D_6 was added to the Schlenk tube by vacuum transfer at -78 °C. Then 0.118 mL (1.15 mmol) of $^iPrC{\equiv}CH$ were vacuum transferred into the tube and the reaction mixture were stirred at room temperature for 12 h leading to the quantitative formation of *gem*-$H_2C{=}C(Pr^i)C{\equiv}C(Pr^i)$ (**1**).

Kinetic Study of the dimerization of isopropylacetylene by MAO

In a typical experiment, an NMR sample was prepared as described in the typical NMR scale catalytic reactions section and maintained at -78°C until kinetic measurements were initiated. The sealed tube was kept inside the probe of the NMR instrument and at a regular time intervals NMR data were acquired using eight scans with a long pulse delay to avoid saturation of the signal. The kinetics were usually monitored by the intensity changes in the substrate resonances and in the product resonances over 3 or more half-lives. The substrate concentration (C) was measured from the area (A_s) of the ^1H-normalized signal of the solvent (A_b). All the data collected could convincingly least-squares-fit (R>0.98) to eq 1, where C_0 ($C_0 = A_{s0}/A_{b0}$) is the initial concentration of substrate and C(A_s/A_b) is the substrate concentration at time t.

$$mt = \log(C/C_0) \qquad (1)$$

The ratio of catalyst to substrate was accurately measured by calibration with internal $FeCp_2$. Turnover frequencies (N_t, h^{-1}) were calculated from the least-squares determined slopes (m) of the resulting plots. The termodynamic parameters are calculated by running the same reaction at different temperatures.

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