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Selective Catalytic Cross-Coupling of Ethylene and 2,3-Dimethylbutadiene by Titanium Aryloxide Compounds

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Summary: The 2,3-dimethylbutadiene complex $[(Ar''O)_2Ti(CH_2CMe{=}CMeCH_2)]$ (1) will catalyze the selective cross-coupling of ethylene and 2,3-dimethylbutadiene to produce 4,5-dimethylhexa-1,4-diene.

The use of group 4 metal compounds to carry out selective carbon–carbon bond forming reactions has been and continues to be an extremely active area of research.[1-5] One of the important goals of this area of research is to develop ways of making these coupling reactions catalytic. We wish to report here upon our observation of the titanium aryloxide catalyzed cross-coupling of ethylene and 2,3-dimethylbutadiene to produce exclusively 4,5-dimethylhexa-1,4-diene.[6,7] The ability to carry out this catalytic dimerization appears to be linked to the structure of the titanacycloheptene intermediate.

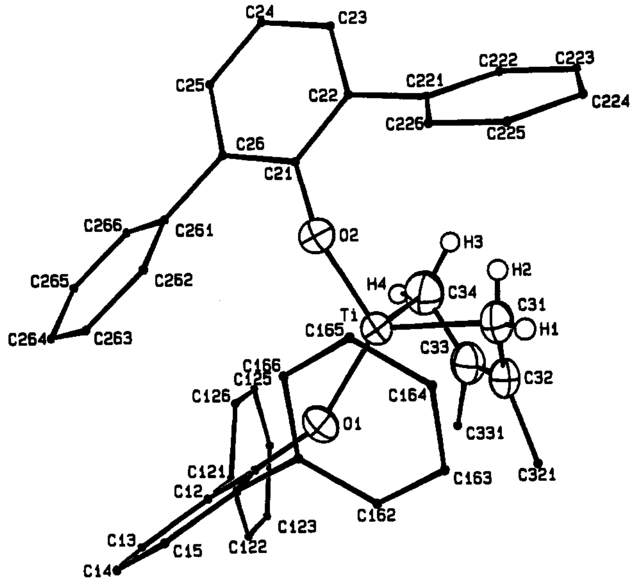

Figure 1. ORTEP view of the titanacycle compound 1. Selected bond distances (Å) and angles (deg): Ti–O(1) = 1.804 (2); Ti–O(2) = 1.843 (2); Ti–C(31) = 2.096 (4); Ti–C(32) = 2.299 (3); Ti–C(33) = 2.290 (4); Ti–C(34) = 2.109 (5); C(31)–C(32) = 1.436 (5); C(32)–C(33) = 1.384 (6); C(33)–C(34) = 1.442 (6); O(1)–Ti–O(2) = 115.2 (1); C(31)–Ti–C(34) = 87.0 (1); Ti–O(1)–C(11) = 151.2 (1); Ti–O(2)–C(21) = 143.6 (2).

Hydrocarbon solutions of the titanacyclopentane complex $[(Ar''O)_2Ti(CH_2)_4]$ ($Ar''O$ = 2,6-diphenylphenoxide)[8] react rapidly with 2,3-dimethylbutadiene to produce 2 equiv of ethylene and the titanacyclopent-3-ene complex $[(Ar''O)_2Ti(CH_2CMe{=}CMeCH_2)]$ (1) (Scheme I).[9] Compound 1 can be obtained as dark purple crystals from a hexane solution. A single-crystal X-ray diffraction analysis of 1 (Figure 1)[10] shows the metallacycle ring to be bent with a fold angle of 75°.[11] The coordination of the butadiene unit to the $[Ti(OAr'')_2]$ fragment is very similar to that reported for related group 4 metal diene complexes, e.g., Cp_2M(diene) and CpMX(diene) (M = Ti, Zr, Hf).[5d,f] The ^1H NMR spectrum of solutions of 1 show well-resolved, nonequivalent α-CH_2 protons indicating that the bent structure is maintained in solution and that flipping of the metallacycle ring is slow on the NMR time scale.[9]

When exposed to an atmosphere of ethylene, compound 1 undergoes a coupling reaction with 1 equiv of C_2H_4 to produce a new metallacyclic compound 2. Both the ^1H and ^{13}C NMR spectra of 2 indicate the presence of two isomers in solution.[12] The major component (80%) of the mixture

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[7] The selective oligomerization of conjugated dienes by titanium has been reported; see ref 5d.

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[9] Anal. Calcd for $TiC_{42}H_{36}O_2$ (1): C, 81.28; H, 5.85. Found: C, 80.87; H, 5.79. ^1H NMR (C_6D_6, 30 °C): δ 6.87–7.60 (m, aromatics); δ 3.02 (d), 1.35 (d, CH_2); δ 0.77 (s, CH_3). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 129.6 (CMe); δ 87.9 ($^1J(^{13}C-^1H)$ = 138.2, 160.8 Hz, Ti–CH_2); δ 22.4 ($^1J(^{13}C-^1H)$ = 127.6 Hz, CMe).

[10] Crystal data for $TiC_{42}H_{36}O_2$ (1) at −60 °C: a = 35.351 (3) Å, b = 37.927 (3) Å, c = 9.755 (1) Å, V = 13079 (3) Å^3, Z = 16, and ρ_{calcd} = 1.261 g cm^{-3} in space group *Fdd*2. A total of 3167 unique intensities were collected with use of Mo Kα radiation ($4 \le 2\theta \le 50°$), of which 2559 were used in the final refinement. Final residuals are R = 0.032 and R_w = 0.039.

[11] Fold angles of 75.0, 75.7, and 73.2° were reported for the other related structurally characterized titanium butadiene complexes.[4d]

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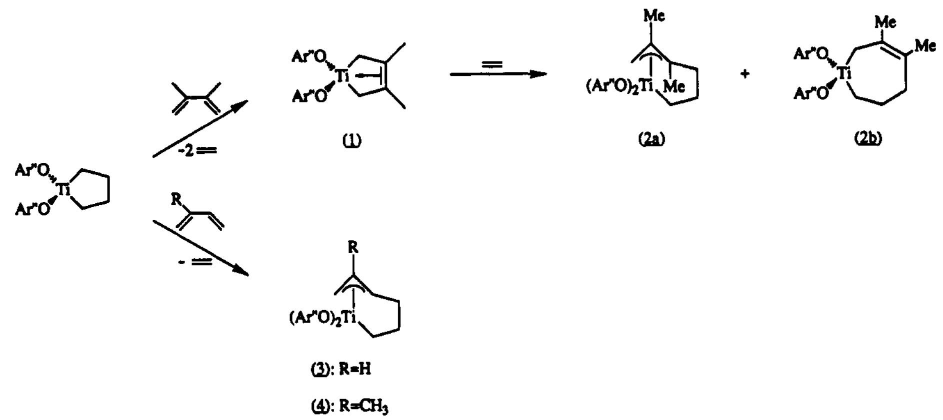
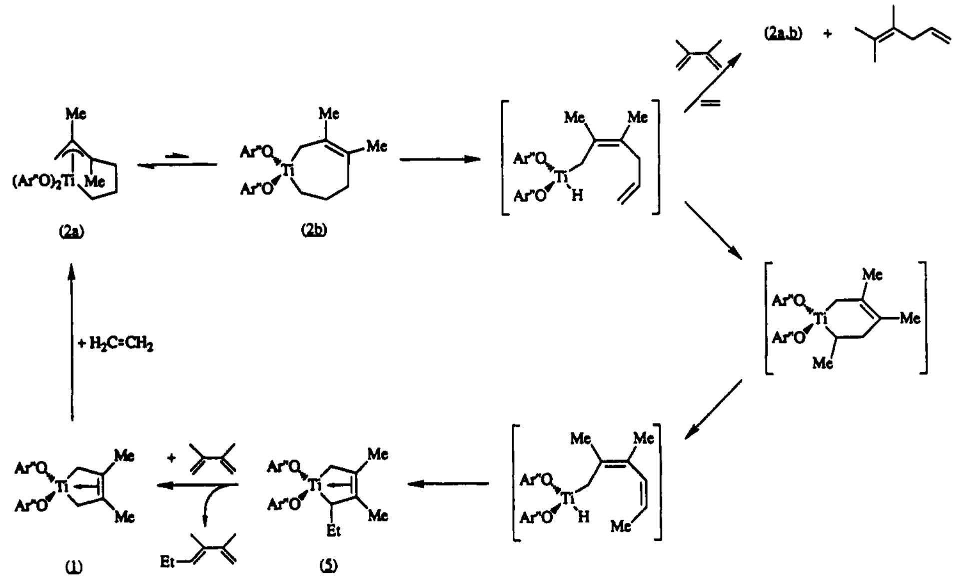
Scheme I



Scheme II



(**2a**) is formulated as containing a π-allylic metallacycle, while the minor component (**2b**) is its σ-allylic (titanacyclohept-3-ene) isomer. Similar isomers have been observed in the coupling of olefins and butadienes at group 4 metallocene metal centers.[3e]

The addition of either butadiene or 2-methylbutadiene (isoprene) to the titanaycloppentane $[(\mathrm{Ar''O})_2\mathrm{Ti}(\mathrm{CH_2})_4]$ was found to lead directly to coupled products (Scheme I).[13] The product from the reaction of butadiene (**3**) exists in solution as only one detectable isomer, containing the π-allylmetallacycle.[13] Similarly, only one isomer was obtained from the reaction with 2-methylbutadiene, the ethylene being coupled exclusively with the less sterically hindered portion of the diene. The NMR spectroscopic properties of **3** and **4** are very similar to those of the major isomer **2a** formed using 2,3-dimethylbutadiene. Compounds **3** and **4** are stable in benzene solution for days at 25 °C with almost no detectable (^{1}H NMR) decomposition or rearrangements. Furthermore, neither compound will react with excess ethylene or added butadiene (for **3**) or 2-methylbutadiene (for **4**).

Solutions of the isomeric mixture **2a,b** do change over time. Monitoring a ^{1}H NMR solution of **2** in C_6D_6 over hours showed the clean conversion of the isomeric mixture **2a,b** into a single new organometallic product **5**.[14] The spectroscopic properties of deep green solutions of **5** are consistent with its formulation as a new titanacyclopent-3-ene complex $[(\mathrm{Ar''O})_2\mathrm{Ti}(\mathrm{CHEtCMe{=}CMeCH_2})]$ (**5**)

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(12) Anal. Calcd for $\mathrm{TiC_{44}H_{40}O_2}$ (**2**): C, 81.47; H, 6.22. Found: C, 81.28; H, 6.41. Selected ^{1}H NMR (C_6D_6, 30 °C): δ 6.78–7.53 (m, aromatics); δ 2.13 (d), 1.10 (d, Ti$\mathrm{C}H_2$CMe major isomer); δ 0.63 (s), 0.23 (s, C*Me*C*Me* major isomer); δ 1.33 (s), 0.94 (s, C*Me*C*Me* minor isomer). Selected ^{13}C NMR (C_6D_6, 30 °C): major isomer, δ 160.6, 160.5 (Ti-O-*C*), 143.8, 139.4 (*C*Me *C*Me), 140.8, 140.7 (ortho carbons on phenoxides), 133.5, 133.4 (ipso carbons on phenyls of phenoxides), 80.8, 70.6 (Ti–CH_2), 45.2, 36.4 ($\mathrm{TiCH_2}CH_2\mathrm{CH_2}$), 21.2, 21.1 (C*Me* C*Me*); minor isomer, δ 92.1, 75.6 (Ti–CH_2), 36.2, 36.0 ($\mathrm{TiCH_2}CH_2CH_2$), 16.1, 15.5 (C*Me*C*Me*).

(13) A preliminary X-ray diffraction study on compound **4** confirms the stereochemistry of this ring. Anal. Calcd for $\mathrm{TiC_{42}H_{36}O_2}$ (**3**): C, 81.28; H, 5.85. Found: C, 81.37; H, 5.92. ^{1}H NMR (C_6D_6, 30 °C): δ 6.79–7.41 (m, aromatics); δ 4.36 (td, ^1J(trans) = 16 Hz, ^1J(cis) = 8.5 Hz, $\mathrm{TiCH_2C}H$); δ 3.21 (ddd, $\mathrm{TiCH_2CHC}H$); δ 2.25 (m), 2.20 (m, $\mathrm{TiCH_2C}H_2$; δ 1.90 (dd), 0.84 (dd, $\mathrm{TiC}H_2\mathrm{CH}$); δ 1.77 (dtd), 1.57 (ddt, $\mathrm{TiCH_2CH_2C}H_2$); δ 1.69 (broad d), –0.24 (dt, $\mathrm{TiC}H_2\mathrm{CH_2}$). Selected ^{13}C NMR ($C_6D_6$, 30 °C): δ 160.4, 160.3 (Ti–O–*C*); δ 140.7, 140.4 (ortho carbons on phenoxides); δ 133.5, 133.4 (ipso carbons on phenyls of phenoxides); δ 136.3, 135.6 ($\mathrm{TiCH_2}C\mathrm{H}C\mathrm{H}$); δ 77.7, 77.2 (Ti–CH_2); δ 45.3, 35.8 ($\mathrm{TiCH_2}CH_2CH_2$). Anal. Calcd for $\mathrm{TiC_{43}H_{38}O_2}$ (**4**): C, 81.38; H, 6.03. Found: C, 81.27; H, 6.00. ^{1}H NMR (C_6D_6, 30 °C): δ 6.76–7.55 (m, aromatics); δ 2.89 (dd, $\mathrm{CMeC}H$); δ 2.18 (d), 0.87 (d, $\mathrm{TiC}H_2\mathrm{CMe}$); δ 2.12 (m), 1.9 (m, $\mathrm{TiCH_2CH_2C}H_2$); δ 1.9 (m), 1.26 (m, $\mathrm{TiCH_2C}H_2\mathrm{CH_2}$); δ 1.62 (m), –0.06 (m, $\mathrm{TiC}H_2\mathrm{CH_2CH_2}$); δ 0.70 (s, C*Me*). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 160.1 (Ti–O–*C*); δ 140.7 (ortho carbons on phenyls of phenoxides); δ 143.6 (*C*MeCH); δ 131.8 (CMe*C*H); δ 82.3, 72.0 (Ti-CH_2); δ 43.9, 31.3 ($\mathrm{TiCH_2}CH_2CH_2$); δ 18.6 (C*Me*).

(14) ^{1}H NMR of **5** (C_6D_6, 30 °C): δ 6.81–7.67 (m, aromatics); δ 2.80 (d), 1.18 (d, Ti–$\mathrm{C}H_2$); δ 1.82 (t, Ti–C*H*Et); δ 1.70 (dp), 1.42 (p, $\mathrm{CHC}H_2\mathrm{CH_3}$); δ 0.68 (t, $\mathrm{CH_2C}H_3$); δ 0.81 (s), 0.62 (s, C*Me*C*Me*). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 160.7 (Ti–O–*C*); δ 141.1, 140.3 (ortho carbons on phenoxides); δ 134.2, 131.8 (ipso carbons on phenyls of phenoxides); δ 127.8, 127.2 (*C*Me*C*Me); δ 108.4 (Ti*C*HEt); δ 88.3 ($\mathrm{Ti}CH_2$); δ 24.5 ($CH_2\mathrm{CH_3}$); δ 23.1 ($\mathrm{CH_2}CH_3$); δ 16.1, 15.5 (C*Me*C*Me*). ^{1}H NMR (C_6D_6, 30 °C) for 1-ethyl-2,3-dimethylbutadiene: δ 5.59 (t, C*H*Et); δ 5.06 (s), 4.90 (s, $\mathrm{C}H_2\mathrm{CMe}$); δ 2.01 (p, $\mathrm{C}H_2\mathrm{CH_3}$); δ 1.88 (s), 1.75 (s, C*Me*C*Me*); δ 0.90 (t, $\mathrm{CH_2C}H_3$).

(Scheme II). Addition of 2,3-dimethylbutadiene to **5** leads to the regeneration of **1** and 1-ethyl-2,3-dimethylbutadiene.

In the presence of excess 2,3-dimethylbutadiene, solutions of **2a,b** will absorb ethylene leading to the formation of 4,5-dimethylhexa-1,4-diene.[15] At 25 °C this reaction is slow, but at 70 °C a mixture of **2a,b** (25 mg; 0.039 mmol) and 2,3-dimethylbutadiene (150 μL; 1.33 mmol) in C_6D_6 (0.7 mL total volume) was found to produce 13.7 equiv of 4,5-dimethylhexa-1,4-diene in 100 min when exposed to 1 atm of ethylene,[16] with greater than 95% of **2a,b** still present in solution.

We believe that both the rearrangement of **2** to **5** and the catalytic cross-coupling of 2,3-dimethylbutadiene and ethylene proceed via the σ-allylic metallacyclic intermediate **2b** (Scheme II). In the absence of 2,3-dimethylbutadiene/C_2H_4, the dimethyltitanacyclohept-3-ene can rearrange via a series of β-hydrogen abstraction/reinsertion steps to generate **5**. However, the initial intermediate alkyl-hydride compound can eliminate 4,5-dimethylhexa-1,4-diene directly in the presence of 2,3-dimethylbutadiene/C_2H_4 to regenerate **2a,b**. The fact that the entire mixture of **2a,b** will cleanly convert to **5** suggests that **2a** and **2b** are in equilibrium with one another. We are currently investigating the scope and stereochemistry of this catalytic cross-coupling reaction.[17]

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Supplementary Material Available: Text describing the data collection, structure solution, and refinement and listings of crystal data, fractional coordinates, anisotropic thermal parameters, and full bond distances and angles for the X-ray diffraction study of 1 (20 pages); a table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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[15] NMR data for 4,5-dimethylhexa-1,4-diene are as follows. ^{1}H NMR (C_6D_6 30 °C): δ 5.74 (m, $=CH$); δ 5.00 (m, $=CH_2$); δ 2.72 (broad d, CH_2); δ 1.58 (broad s, $Me_2C{=}CMe$). ^{13}C NMR (C_6D_6, 30 °C): δ 137.1 ($=CH$); δ 125.9, 125.7 ($Me_2C{=}CMe$); δ 115.0 ($=CH_2$); δ 39.4 (CH_2); δ 20.7, 20.3, 18.6 ($Me_2C{=}CMe$).

[16] The catalytic cross-coupling of ethylene and 2,3-dimethylbutadiene can also be achieved using the titanacyclopentadiene complex $[Ar''O)_2Ti(C_4Et_4)]$ as catalyst precursor. This complex has been shown to react with ethylene to produce $[Ar''O)_2Ti(CH_2)_4]$.[8]

[17] The reaction of 2,3-dimethylbutadiene with propene has been shown to produce exclusively 2,4,5-trimethylhexa-1,4-diene in the presence of 1.

Stereoselectivity in the Catalytic Oligomerization of Phenylsilane

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Summary: A variety of chiral and achiral zirconocene complexes were investigated for the stereoselective dehydrogenative coupling of phenylsilane. Polymerization of $PhSiH_3$ with *rac*-(EBI)$ZrCl_2$/2BuLi or $Cp_2Zr(H)Cl$ yields a stereoregular polymer by ^{29}Si NMR spectroscopy. These results suggest that the stereogenic centers of the growing polymer chain may play a role in the stereochemistry of phenylsilane polymerization. A syndiotactic microstructure for the polyphenylsilanes is tentatively assigned on the basis of comparisons of their ^{29}Si NMR chemical shifts with those of known stereoregular cyclic oligomers.

Polysilanes constitute a novel class of σ-conjugated polymers with unusual electronic properties;[1] these materials absorb strongly in the ultraviolet region, and their electronic properties are sensitive to both the chain length and conformation of the polymer.[2] Because the stereochemistry of macromolecules strongly influences their conformational properties, stereoregular polysilanes should exhibit unique electronic and photochemical properties. Unfortunately, current synthetic methods, such as the Wurtz coupling of dichlorosilanes, show little stereoselectivity.[3]

Harrod's discovery[4] of homogeneously catalyzed silane oligomerization reactions with group 4 metallocenes has stimulated considerable interest in the development of catalytic routes to silicon polymers.[5,6] In view of the remarkable advances in stereospecific olefin polymerization with early-transition-metal metallocenes,[7] we were prompted to investigate the influence of metallocene structure on the stereochemistry of phenylsilane polymerization.

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