Synthesis, Structure, and Dynamic Behavior of a New Series of Titanacyclopentane Compounds Containing Ancillary Aryloxide Ligands

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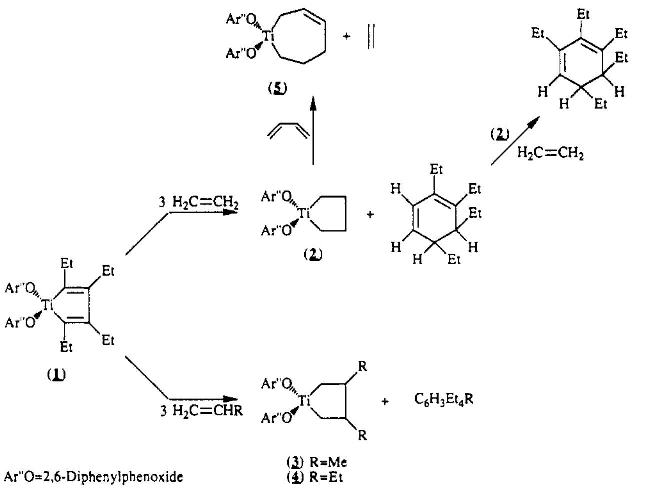
Received September 27, 1990

Summary: A new series of titanacyclopentane compounds have been isolated by reaction of the titanacyclopentadiene complex [Ti(OAr″)$_2$(C$_4$Et$_4$)] (OAr″ = 2,6-diphenylphenoxide) with ethylene, propene, and 1-butene.

The study of metallacyclic compounds of the transition metals remains an extremely active area of research.[1-5] During our studies of the early-transition-metal organometallic chemistry that can be supported by aryloxide ligation,[6] we have isolated a new series of titanacyclopentane complexes. We communicate here the structure, dynamic behavior, and reactivity of these compounds.

Scheme I



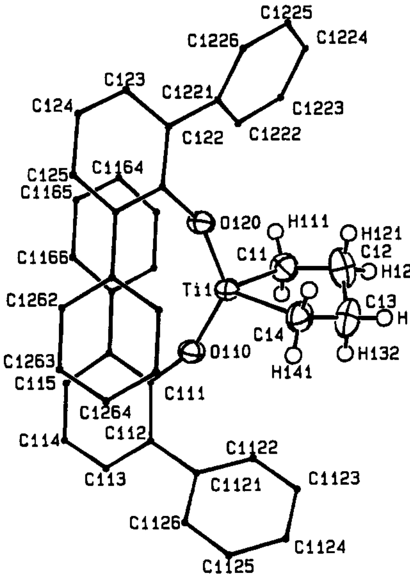


Figure 1. ORTEP view of molecule 1 in the unit cell of 2. Selected bond distances (Å) and angles (deg): Ti(1)-O(110) = 1.799 (1), Ti(1)-O(120) = 1.804 (1), Ti(1)-C(11) = 2.087 (2), Ti(1)-C(14) = 2.084 (2), C(11)-C(12) = 1.510 (3), C(12)-C(13) = 1.511 (4), C(13)-C(14) = 1.517 (3); O(110)-Ti(1)-O(120) = 132.62 (6), C(11)-Ti(1)-C(14) = 85.59 (9). Bond distances and angles for molecule 2 are almost identical.

Exposure of solutions of the titanacyclopentadiene complex [(Ar″O)$_2$Ti(C$_4$Et$_4$)] (1)[7] to an atmosphere of ethylene rapidly results in formation of the titanacyclopentane compound 2 along with 1,2,5,6-tetraethyl-1,3-cyclohexadiene (Scheme I).[8] Although cyclotrimerization of 3-hexyne by 1 is slow,[7] addition of ethylene to a mixture of 3-hexyne and 1 leads to the rapid catalytic formation of 1,2,5,6-tetraethyl-1,3-cyclohexadiene. In the presence

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[8] Anal. Calcd for TiC$_{40}$H$_{34}$O$_2$ (**2**): C, 80.80; H, 5.76. Found: C, 80.69; H, 6.02. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 6.90–7.41 (m, aromatics), 1.98, 1.60 (broad s, C*H*$_2$). Selected ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 160.3 (Ti–O–*C*), 89.7 ($^1J(^{13}$C–^{1}H) = 127.4 Hz, Ti*C*H$_2$), 31.1 ($^1J(^{13}$C–^{1}H) = 127.7 Hz, TiCH$_2$*C*H$_2$).

0276-7333/91/2310-0015$02.50/0

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of excess ethylene, **2** will catalytically convert 1,2,5,6-tetraethyl-1,3-cyclohexadiene *into* 1,2,3,5,6-pentaethyl-1,3-cyclohexadiene. Reaction of **1** with propene or 1-butene yields the substituted titanacyclopentane compounds **3** and **4**, respectively.[9] In the room-temperature 200-MHz ^{1}H NMR spectrum of **2**, the methylene protons of the metallacycle ring appear as two broad, equal-intensity signals at δ 1.60 and 1.98 ppm. Selective irradiation of either of these peaks results in almost complete loss of intensity for the other signal. Furthermore, spin magnetization transfer is found to occur at room temperature not only between the α- and β-methylene protons but also between the metallacycle ring protons and free ethylene in solution. A variable-temperature ^{1}H NMR study of toluene-d_8 solutions of **2** in the presence of ethylene shows that coalescence of the two methylene signals occurs at 55 °C. At temperatures above 40 °C, broadening of the signal due to the free ethylene protons is also observed. These observations can be rationalized in terms of rapid fragmentation of the titanacyclopentane ring to generate a bis(ethylene) complex. Rotation of the ethylene units followed by coupling back to **2** accounts for exchange of methylene units in the titanacyclopentane ring, while a somewhat slower dissociation of the bound ethylene ligands accounts for exchange with free C_2H_4.[10] The rate of exchange of methylene groups at 55 °C is calculated to be 187 s^{-1}, yielding an estimate of $\Delta G^{\ddagger}$ for the exchange process of 15.9 (5) kcal mol^{-1}. This exchange rate is considerably faster than a value of 6.5 (2) × 10^{-3} min^{-1} at 50 °C reported by Negishi et al. for the isomerization of a hafnacyclopentane ring.[5c] In the ^{13}C NMR spectrum of **2**, the two triplets at δ 89.7 ppm ($^1J(^{13}C-^1H) = 127.7$ Hz) and δ 31.1 ppm ($^1J(^{13}C-^1H) = 127.7$ Hz) confirm a titanacyclopentane structure in solution. In the solid state, **2** crystallizes with two independent molecules in the unit cell (Figure 1).[11] The [(Ar″O)$_2$Ti] unit in pseudotetrahedral **2** is unexceptional, while the titanacyclopentane ring is puckered in a manner observed for other metallacyclopentane compounds.

The solution NMR spectra of the substituted titanacyclopentane compounds **3** and **4** indicate the presence of more than one isomer. In both cases the major isomer (80%) is the trans-2,3-disubstituted species.[9]

Hydrocarbon solutions of **2** in the absence of added C_2H_4 undergo decomposition over hours at 25 °C to produce the new organometallic product **5** along with detectable amounts of ethane (Scheme I). In the presence of added ethylene (1–5 equiv), **2** is more stable in solution. However, over days decomposition to **5** takes place along with the formation of ethane and 1-butene. The identification of **5** as the titanacyclohept-3-ene species [(Ar″O)$_2$Ti(CH$_2$CH=CHCH$_2$CH$_2$CH$_2$)] is based upon its NMR spectra.[12] The formation of **5** via a titanacyclopent-3-ene (1,3-butadiene) complex is strongly indicated by the fact that addition of 1,3-butadiene to **2** rapidly produces **5** in quantitative yield.[13]

Acknowledgment. We thank the National Science Foundation (Grant CHE-8915573) for support of this research. We also thank Joe Mickiewicz for his assistance with the variable-temperature NMR study.

Supplementary Material Available: Variable-temperature ^{1}H NMR spectra of **2**, a 2D NMR spectrum of **5**, and tables of fractional coordinates, anisotropic thermal parameters, and full bond distances and angles for **2** (28 pages); a table of observed and calculated structure factors for **2** (46 pages). Ordering information is given on any current masthead page.

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[9] Anal. Calcd for $TiC_{42}H_{38}O_2$ (**3**): C, 81.02; H, 6.15. Found: C, 81.21; H, 6.56. ^{1}H NMR (C_6D_6, 30 °C): trans isomer δ 6.88–7.48 (m, aromatics), 2.04 (m, C*H*Me), 1.88 (t), 1.24 (dd, TiC*H*$_2$), 0.93 (d, CH*Me*). Selected ^{13}C NMR (C_6D_6, 30 °C): trans isomer δ 160.1 (Ti–O–*C*) 98.0 ($^1J(^{13}C-^1H) =$ 129.2 Hz, Ti*C*H$_2$), 44.8 ($^1J(^{13}C-^1H) =$ 126.2 Hz, *C*HMe), 23.3 (CH*Me*). Anal. Calcd for $TiC_{44}H_{42}O_2$ (**4**): C, 81.22; H, 6.51. Found: C, 81.54; H, 6.91. ^{1}H NMR (C_6D_6, 30 °C): trans isomer δ 6.88–7.48 (m, aromatics), 2.03 (m, C*H*Et), 1.85 (t), 1.22 (m, TiC*H*$_2$), 1.22 (m, C*H*$_2$CH$_3$), 0.60 (t, CH$_2$C*H*$_3$). Selected ^{13}C NMR (C_6D_6, 30 °C): trans isomer δ 160.2 (Ti–O–*C*) 95.0 ($^1J(^{13}C-^1H) =$ 126.5 Hz, Ti*C*H$_2$), 48.7 ($^1J(^{13}C-^1H) =$ 126.8 Hz, *C*HEt) 28.9 (*C*H$_2$CH$_3$), 18.1 (CH$_2$*C*H$_3$).

[10] The fragmentation and isomerization of metallacyclopentane rings has been well documented.[5]

[11] Crystal data for $TiC_{40}H_{34}O_2$ (**2**) at −61 °C: $a = 10.047$ (1) Å, $b =$ 14.625 (2) Å, $c = 22.415$ (2) Å, $V = 3088$ (1) Å^3, $Z = 4$, $\rho_{calcd} = 1.211$ g cm^{-3} in space group $P\bar{1}$. A total of 8046 unique intensities were collected with use of Mo Kα radiation ($4 \le 2\theta \le 45°$), of which 6555 with $I > 3\sigma(I)$ were used in the final refinement. Final residuals are $R = 0.033$ and $R_W =$ 0.049.

[12] Anal. Calcd for $TiC_{42}H_{36}O_2$ (**5**): C, 81.28; H, 5.85. Found: C, 81.27; H, 5.92. ^{1}H NMR (C_6D_6, 30 °C): δ 6.8–7.5 (m, aromatics), 4.41 (td, TiCH$_2$C*H*), 3.21 (broad td, TiCH$_2$CHC*H*), 2.27 (m, TiCH$_2$C*H*$_2$), 1.94 (dd), 0.86 (dd, TiCH$_2$CH), 1.7 (m, TiCH$_2$CH$_2$C*H*$_2$), 1.7 (m), −0.18 (m, TiC*H*$_2$CH$_2$). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 160.4, 160.3 (Ti–O–*C*), 136.3, 135.6 (TiCH$_2$*C*H*C*H), 77.7, 77.2 (Ti–*C*H$_2$), 45.3, 35.8 (TiCH$_2$*C*H$_2$-*C*H$_2$).

[13] The formation of 1,3-butadiene from a titanacyclopentane compound has precedence.[5b]

Platinum-Complex-Catalyzed Dehydrogenative Double Silylation of Acetylenes, Dienes, and Olefins with Bis(hydrosilane) Compounds

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Received July 25, 1990

Summary: Acetylenes, dienes, and olefins underwent dehydrogenative double silylation with bis(hydrosilane) species in the presence of platinum complex catalysts to give disilacyclic compounds in good yields.

The synthesis of silicon compounds is a rapidly growing field relevant to silicon-based functional polymers, selective organic synthesis, and biological activity.[1] Of particular importance among complex-catalyzed syntheses of silicon compounds is the double silylation of unsaturated hy-

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