Synthesis, Structure, and Reactivity of a New Series of Titanium η^2-Olefin and η^2-Ketone Complexes

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Summary: Fragmentation of the titanacyclopentane ring in $[(Ar''O)_2Ti(CH_2)_4]$ ($Ar''O$ = 2,6-diphenylphenoxide) occurs upon addition of PMe_3 to yield the η^2-ethylene complex $[(Ar''O)_2Ti(\eta^2\text{-}C_2H_4)(PMe_3)]$ (1). The reactivity of 1 and its η^2-propene analogue toward $Ph_2C{=}O$ has been investigated.

The synthesis, structure, and ensuing reactivity of unsaturated organic molecules bound to early d-block elements continues to be the focus of much research.[1] In the case of the group 4 metals, a rapidly expanding body of work exists on the bonding and coupling of unsaturated small molecules at $[Cp_2M]$ or $[Cp'_2M]$ metal centers.[2-5]

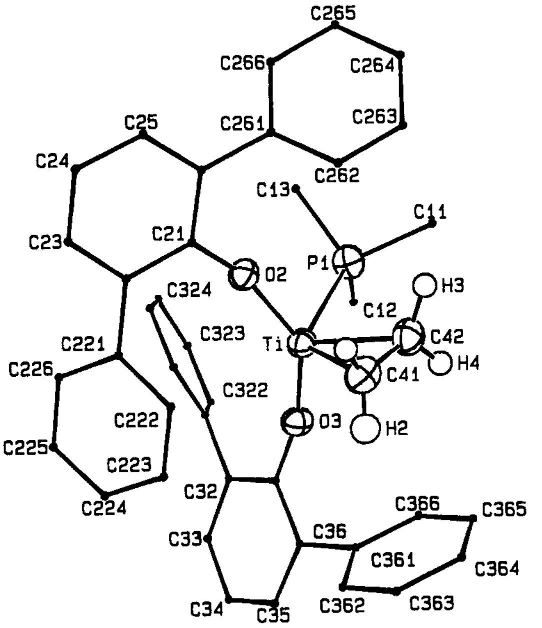
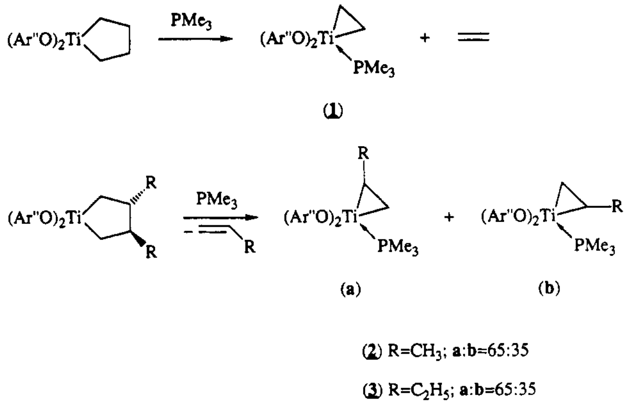


Figure 1. ORTEP view of $[(Ar''O)_2Ti(\eta^2\text{-}C_2H_4)(PMe_2)]$ (**1**). The ethylene hydrogen atoms were located and refined. Selected bond distances (Å) and angles (deg): Ti–O(2), 1.835 (1); Ti–O(3), 1.838 (1); Ti–P(1), 2.5633 (5); Ti–C(41), 2.110 (2); Ti–C(42), 2.148 (2); C(41)–C(42), 1.425 (3); O(2)–Ti–O(3), 140.73 (5); P(1)–Ti–C(41), 122.67 (5); P(1)–Ti–O(42), 83.97 (5); C(41)–Ti–C(42), 39.09 (7); α = 55.6°.

Scheme I



(**2**) R=CH_3; **a**:**b**=65:35

(**3**) R=C_2H_5; **a**:**b**=65:35

We wish to report here on the chemistry of a new series of η^2-olefin complexes of titanium that are supported by

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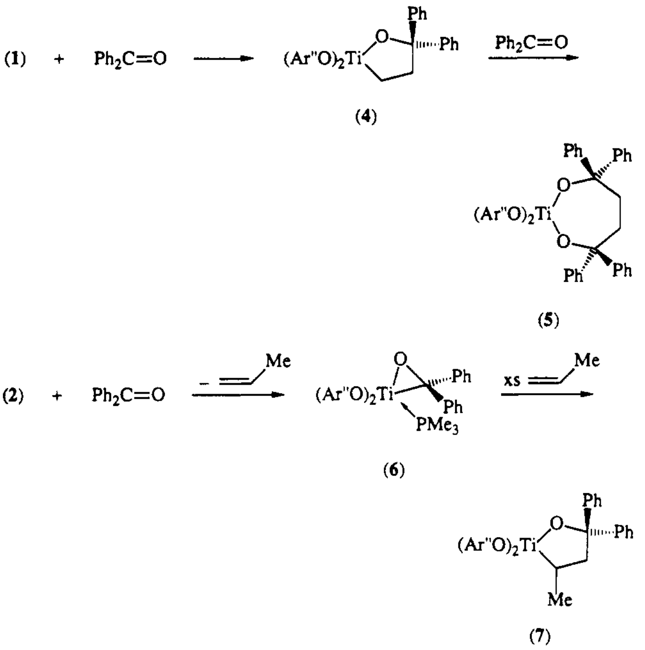
Scheme II



aryloxide ancillary ligands.

The titanacyclopentane complex $[(Ar''O)_2Ti(CH_2)_4]$ ($Ar''O$ = 2,6-diphenylphenoxide)[6] has been shown to be stable in hydrocarbon solution below 60 °C. The addition of PMe_3 to a red solution of this complex rapidly leads to formation of a deep purple solution from which can be isolated the ethylene complex $[(Ar''O)_2Ti(\eta^2\text{-}C_2H_4)(PMe_3)]$ (**1**) as dark red crystals (Scheme I).[7] The solid-state structure of **1**[7] shows a pseudotetrahedral environment about the titanium metal center with the ethylene lying perpendicular to the O–Ti–O plane (Figure 1). The Ti–C distances and elongated C–C distance of 1.425 (3) Å indicate a bonding description involving a titanacyclopropane ring. The only other previously structurally characterized titanium ethylene complex, $[Cp^*_2Ti(C_2H_4)]$, has a C–C distance of 1.438 (5) Å.[8] However, in terms of overall structure, complex **1** bears a striking resemblance to the metallocene olefin compounds of formula $[Cp_2M(olefin)(PMe_3)]$ (M = Zr, Hf).[9,10] The observed solid-state structure of **1** (Figure 1) is maintained in solution, as evidenced by the presence of two nonequivalent CH_2 groups in both the ^1H and ^{13}C NMR spectra.[7] The treatment of hydrocarbon solutions of the 2,3-dialkyltitanacyclopentane substrates $[(Ar''O)_2Ti(CH_2CHRCHRCH_2)]$ (R = CH_3, C_2H_5) with PMe_3 leads to the derivatives $[(Ar''O)_2Ti(\eta^2\text{-}CH_2CHR)(PMe_2)]$ (R = CH_3 (**2**), C_2H_5 (**3**)), which exist as a mixture of two isomers (rotamers) in solution.[9a,11]

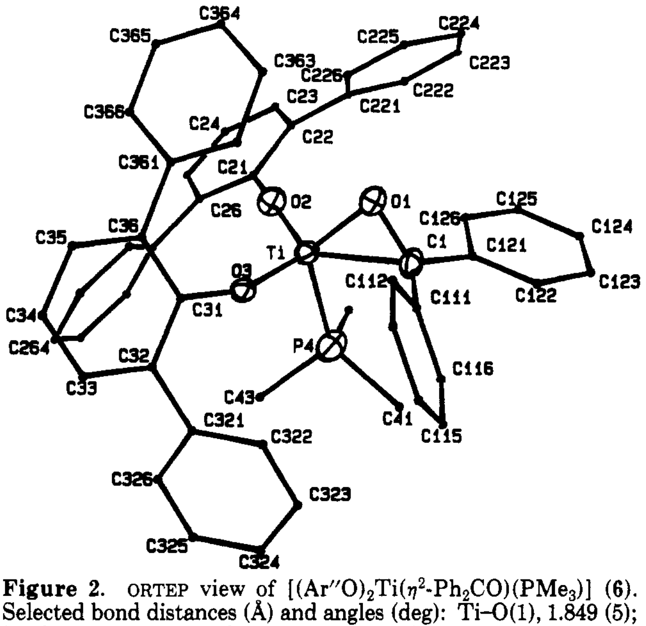


Figure 2. ORTEP view of $[(Ar''O)_2Ti(\eta^2\text{-}Ph_2CO)(PMe_3)]$ (**6**). Selected bond distances (Å) and angles (deg): Ti–O(1), 1.849 (5); Ti–O(2), 1.839 (5); Ti–O(3), 1.817 (4); Ti–C(1), 2.150 (7); Ti–P(4), 2.592 (3); C(1)–O(1), 1.397 (8); O(2)–Ti–O(3), 115.8 (2); P(4)–Ti–O(1), 127.0 (2); P(4)–Ti–C(1), 90.9 (2); C(1)–Ti–O(1), 40.0 (2).

The titanacyclopropane ring in **1** undergoes ring expansion with Ph_2CO to initially produce the 2-oxatitanacyclopentane **4**[12] (Scheme II), in which the PMe_3 ligand has been displaced. The ^1H NMR spectrum of **4** shows two well-resolved triplets at δ 3.34 and 1.47 ppm for the two methylene groups.[12] The two CH_2 carbon atoms are observed at δ 53.0 and 82.2 ppm in the ^{13}C NMR spectrum with $^1J(^{13}C–^1H)$ couplings of 132.2 and 131.0 Hz, respectively, consistent with their sp[2] nature within the metallacycle ring. Further treatment of **4** with Ph_2CO leads to further ring expansion to the 2,7-dioxatitanacycloheptane compound **5** (Scheme II).[13]

In contrast to this behavior, reaction of the propene complex **2** with Ph_2CO results in formation of the η^2-benzophenone complex **6** as the major product (Scheme II).[14] The exposure of solutions of **6** to an atmosphere of

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(7) Anal. Calcd for $TiC_{41}H_{39}O_2P$ (**1**): C, 76.63; H, 6.12; P, 4.82. Found: C, 76.99; H, 6.14; P, 4.58. ^1H NMR (C_6D_6, 30 °C): δ 6.87–7.36 (aromatics) 1.72 (td, $^1J_{^1H-^{31}P}$ = 6.8 Hz, CH_2 adjacent to P), 0.51 (t, CH_2 away from P), 0.22 (d, $^1J_{^1H-^{31}P}$ = 6.8 Hz, PMe_3). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 160.0 (ipso OAr''), 78.0 ($^1J_{^{13}C-^{31}P}$ = 5.9 Hz, $^1J_{^{13}C-^1H}$ = 148 Hz, CH_2 adjacent to P), 67.0 ($^1J_{^{13}C-^1H}$ = 150 Hz, CH_2 away from P), 12.5 ($^1J_{^{13}C-^{31}P}$ = 15.7 Hz, $^1J_{^{13}C-^1H}$ = 128 Hz, PMe_3). ^{31}P NMR (C_6D_6, 30 °C): δ 2.43 (PMe_3). X-ray crystal data for **1** at –50 °C: a = 10.796 (1) Å, b = 10.8433 (7) Å, c = 16.352 (3) Å, α = 80.81 (1)°, β = 88.72 (1)°, γ = 63.972 (8)°, Z = 2, d_{calcd} = 1.259 g cm^{-3} in space group $P\bar{1}$ (No. 2). Of the 4441 unique data collected with Mo Kα radiation ($4° \leq 2\theta \leq 45°$), the 3942 with $I > 3\sigma(I)$ were used in the final refinements to yield R = 0.037 and R_w = 0.055. Hydrogen atoms on the ethylene were refined; all other hydrogens were placed in ideal positions and were not refined.

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(11) Anal. Calcd for $TiC_{42}H_{41}O_2P$ (**2**): C, 76.82; H, 6.29; P, 4.72. Found: C, 76.83; H, 6.46; P, 4.98. ^1H NMR (C_6D_6, 30 °C): major isomer, δ 6.8–7.6 (aromatics), 1.61 (m), 1.48 (m, CH_2), 1.43 (d, $CHMe$), 0.53 (m, $CHMe$), 0.14 (d, PMe_3); minor isomer, δ 6.8–7.6 (aromatics), 2.32 (m, $CHMe$), 1.04 (d, $CHMe$), 0.90 (dd), 0.44 (dd, CH_2), 0.02 (PMe_3). Selected ^{13}C NMR (C_6D_6, 30 °C): major isomer, δ 80.7 ($^1J_{^{13}C-^{31}P}$ = 5.5 Hz, $^1J_{^{13}C-^1H}$ = 148 Hz, CH_2), 76.2 ($^1J_{^{13}C-^1H}$ = 148 Hz, $CHMe$), 22.6 ($CHMe$), 12.5 ($^1J_{^{13}C-^{31}P}$ = 15.5 Hz, $^1J_{^{13}C-^1H}$ = 129 Hz, PMe_3); minor isomer, δ 89.2 ($^1J_{^{13}C-^{31}P}$ = 6.4 Hz, $^1J_{^{13}C-^1H}$ = 148 Hz, $CHMe$), 74.0 ($^1J_{^{13}C-^1H}$ = 147 Hz, CH_2), 20.9 ($CHMe$), 12.8 ($^1J_{^{13}C-^{31}P}$ = 17.4 Hz, $^1J_{^{13}C-^1H}$ = 129 Hz, PMe_3). ^{31}P NMR (C_6D_6, 30 °C): major isomer, δ 2.19 (PMe_3); minor isomer, δ 1.40 (PMe_3).

(12) Anal. Calcd for $TiC_{51}H_{40}O_3$ (**4**): C, 81.81; H, 5.38. Found: C, 81.62; H, 5.20. ^1H NMR (C_6D_6, 30 °C): δ 6.85–7.38 (aromatics), 3.34 (t), 1.47 (t, CH_2). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 160.0 (ipso OAr''), 148.6 (ipso $OCPh_2$), 92.4 ($OCPh_2$), 82.2 ($^1J_{^{13}C-^1H}$ = 132 Hz, $TiCH_2$), 53.0 ($^1J_{^{13}C-^1H}$ = 131 Hz, $TiCH_2CH_2$).

(13) Anal. Calcd for $TiC_{64}H_{50}O_4$ (**5**): C, 82.57; H, 5.41. Found: C, 82.82; H, 5.51. ^1H NMR (C_6D_6, 30 °C): δ 6.78–7.41 (aromatics), 2.51 (s, CH_2). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 160.0 (ipso OAr''), 147.5 (ipso $OCPh_2$), 95.1 ($OCPh_2$), 38.0 (CH_2).

(14) Anal. Calcd for $TiC_{52}H_{45}O_3P$ (**6**): C, 78.38; H, 5.69; P, 3.89. Found: C, 79.27; H, 5.90; P, 3.73. ^1H NMR (C_6D_6, 30 °C): δ 6.79–7.49 (aromatics), –0.23 (d, PMe_3). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 160.5 (ipso OAr''), 145.5 (ipso $OCPh_2$), 12.0 (d, PMe_3).

propene results in formation of the 2-oxametallacyclopentane species **7** as a mixture of two isomers.[15] Compound **7** was observed as a minor component in the formation of **6**. The major isomer of metallacycle **7** contains the methyl group attached to the carbon atom bound to the titanium metal center (i.e. the 5-methyl regioisomer). A single-crystal X-ray diffraction analysis of **6**[16] shows some similarities to the structure of **1**. The η^2-bound benzophenone lies perpendicular to the O–Ti–O planes, making both aryloxide ligands equivalent. Although many η^2-aldehyde derivatives of the group 4 metals are known,[17] compound **6** represents the first structurally characterized monomeric η^2-ketone complex of a group 4 metal. The C–O distance of 1.397 (8) Å in **6** is slightly longer than the value of 1.338 (2) Å in the zirconocene η^2-ketene complex $[Cp^*_2Zr(OCCH_2)(py)]$.[18]

Acknowledgment. We thank the National Science Foundation (Grant CHE-8915573) for support of this research.

Supplementary Material Available: Tables of crystal data and data collection parameters, positional parameters, general temperature factors, and bond distances and angles for **1** and **6** (41 pages). Ordering information is given on any current masthead page.

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[15] ^{1}H NMR (C_6D_6, 30 °C) for **7**: 5-methyl isomer, δ 6.7–7.5 (aromatics), 3.25 (dd), 2.94 (dd, C*H*$_2$), 1.88 (m, C*H*Me), 0.60 (d, CH*Me*); 4-methyl isomer, δ 6.7–7.5 (aromatics), 3.69 (M, C*H*Me), 1.12 (dd), 0.99 (dd, C*H*$_2$), 0.93 (d, CH*Me*). Selected ^{13}C NMR (C_6D_6, 30 °C; only 5-methyl isomer assignable): δ 159.7 (ipso O*Ar''*), 149.4, 148.6 (ipso OC*Ph*$_2$), 95.4 (Ti*C*HMe), 89.8 (O*C*Ph$_2$), 59.0 (*C*H$_2$), 21.8 (TiCH*Me*).

[16] X-ray crystal data for $TiC_{52}H_{45}O_3P$ (**6**) at −75 °C: $a = 9.910$ (1) Å, $b = 10.757$ (3) Å, $c = 19.942$ (3) Å, $\alpha = 89.23$ (2)°, $\beta = 76.73$ (1)°, $\gamma = 82.50$ (2)°, $Z = 2$, $d_{calcd} = 1.290$ g cm^{-3} in space group $P\bar{1}$ (No. 2). Of the 5364 unique data collected with Mo Kα radiation ($4° \le 2\theta \le 45°$), the 2585 with $I > 3\sigma(I)$ were used in the final refinement to yield $R = 0.059$ and $R_w = 0.065$. Hydrogen atoms were placed in ideal positions and were not refined.

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Paramagnetic Decamethylbimetallocenes

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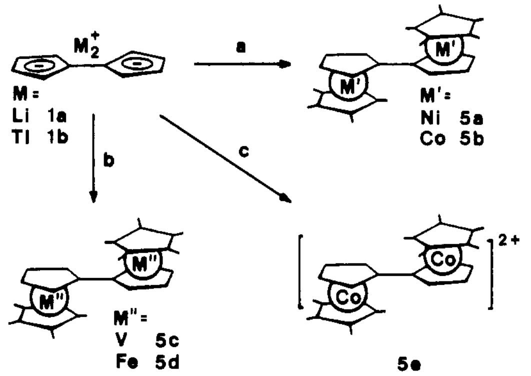
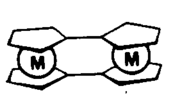
Summary: The paramagnetic decamethylbimetallocenes $(Cp^*M)_2C_{10}H_8$ have been synthesized for M = Ni, Co, and V together with the diamagnetic reference compounds having M = Fe and Co$^+$. The potentials of four electron transfers for Ni and Co$^+$ and of two for Fe (cyclic voltammetry) imply similar intramolecular interaction for all bimetallocenes. ^{1}H NMR spectroscopy shows paramagnetism for Co and V and antiferromagnetism for Ni.

Scheme I[a]



[a] Legend: (a) M = Li, Cp*Ni(acac), or Cp*Co(acac), THF, −78 °C; (b) M = Li, Cp*Li and $VCl_2(THF)_n$ or Cp*Na and $Fe_2Cl_4(THF)_3$, THF, 25 °C; (c) M = Tl, $[Cp^*CoCl]_2$, THF, −35 °C, NH_4PF_6.

The chemistry of organometallic π-complexes derived from the fulvalene dianion (**1**) has experienced a remarkable renaissance because it allows the assembly of at least two metal fragments in close proximity.[1] What makes such an arrangement attractive is the study of conceivable successive stoichiometric or catalytic reactions at two metal centers, a reactivity that may be different from that of mononuclear π-complexes, and the interaction between the two metals that has been studied by various methods.[1] Our interest in fulvalene complexes is focused on the latter area and dates back to the investigation of bis(fulvalene)dimetal compounds **2**, which in the case of Cr, V, and Ni show sizable antiferromagnetic coupling[2] rather than diamag-



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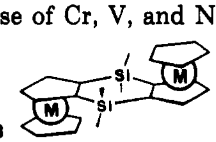

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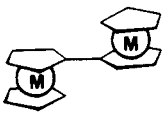
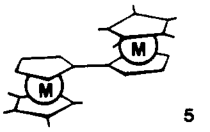


4



5

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[1] Recent examples are: (a) Herberhold, M.; Brendel, H.-D.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 1652. (b) Schottenberger, H.; Ingram, G.; Obendorf, D.; Tessadri, R. *Synlett* **1991,** 905. (c) Jutzi, P.; Schnittger, J.; Neumann, B.; Stammler, H.-G. *J. Organomet. Chem.* **1991,** *410,* C13. (d) Webb, R. J.; Geib, S. J.; Staley, D. L.; Rheingold, A. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1990,** *112,* 5031. (e) Watanabe, M.; Kawata, S.; Sano, H.; Motoyama, I. *J. Organomet. Chem.* **1990,** *399,* 301. (f) McGovern, P. A.; Vollhardt, K. P. C. *Synlett* **1990,** 493. (g) Rausch, M. D.; Spink, W. C.; Conway, B. G.; Rogers, R. D.; Atwood, J. L. *J. Organomet. Chem.* **1990,** *383,* 227. (h) Wielstra, Y.; Gambarotta, S.; Spek, A. L.; Smeets, W. J. J. *Organometallics* **1990,** *9,* 2142. (i) Dong, T.-Y.; Hwang, M.-Y.; Hsu, T.-L.; Schei, C.-C.; Yeh, S.-K. *Inorg. Chem.* **1990,** *29,* 80. (j) Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1989,** *111,* 4784. (k) Astruc, D.; Guillin, J.; Varret, F.; Trautwein, A. X.; Villeneuve, G. *J. Am. Chem. Soc.* **1989,** *111,* 5800. (l) McManis, G. E.; Nielson, R. M.; Weaver, M. J. *Inorg. Chem.* **1988,** *27,* 1827. (m) Herrmann, W. A.; Andrejewski, D.; Herdtweck, E. *J. Organomet. Chem.* **1987,** *319,* 183. (n) Schwarzhans, K. E.; Scholz, W. *Monatsh. Chem.* **1987,** *118,* 875.

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