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Diene Complexes of Pentamethylcyclopentadienyltitanium Chloride. Synthesis and First X-Ray Structure of Titanium-Diene Complexes

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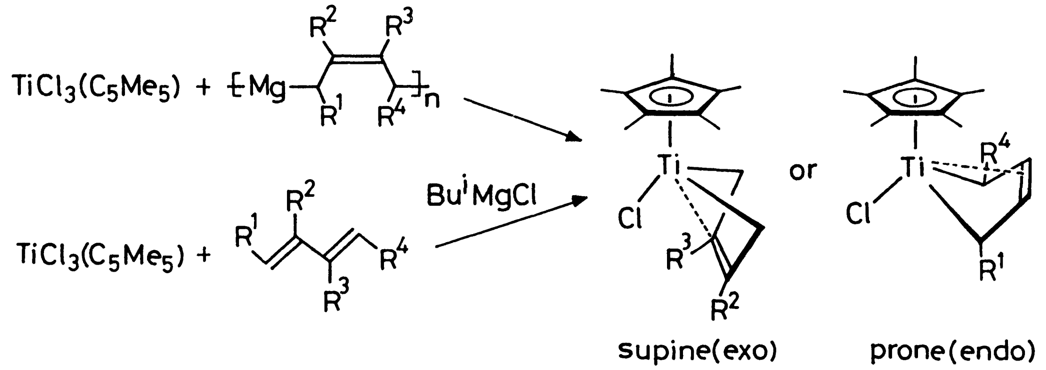
A series of titanium-diene complexes has been prepared by the reaction with $TiCl_3(C_5Me_5)$ and (2-butene-1,4-diyl)magnesium derivatives and the first X-ray structure analysis of titanium-diene complex, $TiCl(C_5Me_5)$(*s-cis*-butadiene), revealed novel prone(endo) geometry for diene coordination.

The recent accelerated progress in group 4A-5A early transition metal organometallic chemistry has proved many important structural aspects together with their versatile reactivities toward electrophiles, which have not been observed for middle and late transition metal complexes.$^{1)}$ Metal-diene complexes are one of the most extensively investigated series of this class of metal complexes and characteristic supine(exo) oriented η^4-metallacyclo-3-pentene structure has been reported for $TaCl_2L$(diene)($L=C_5H_5$ or C_5Me_5)$^{2)}$ and more recently for $HfCl(C_5Me_5)$-(2,3-dimethylbutadiene)$^{3)}$ based on the X-ray structure analysis.

Since the highly active oligo- and polymerizations of conjugated dienes have been known to be effectively catalyzed by Ti or V species presumably *via* an intermediate involving a diene-coordinated organometallics, the preparation and full-characterization of first row transition metal-diene complexes are of fundamental significance. We have found that titanium-diene complexes of the type $TiCl(C_5Me_5)$-(diene) are available as air and moisture sensitive blue crystals in ca. 50% yield, when the reaction of $TiCl_3(C_5Me_5)$ with (2-butene-1,4-diyl)magnesium or reaction of $TiCl_3(C_5Me_5)$ with i-BuMgCl (2 equivalent) in the presence of a conjugated diene was performed under the highly controlled conditions with appropriate purification methods.$^{4)}$ The resulting $TiCl(C_5Me_5)$(isoprene)(1) and $TiCl(C_5Me_5)$(2,3-dimethylbutadiene)(2) exhibit conventional supine geometry as confirmed in terms of ^1H NMR spectroscopy$^{5)}$ by reference to the NMR parameters of well characterized $HfCl(C_5Me_5)$-(2,3-dimethylbutadiene) and $TaCl_2(C_5Me_5)$(diene), while $TiCl(C_5Me_5)$(butadiene)(3) and $TiCl(C_5Me_5)$(1,4-diphenylbutadiene)(4) show quite different chemical shift values,$^{6)}$ possibly due to the novel prone(endo) structure. In order to establish the exact molecular structures of 3 and 4, the X-ray crystal structure analysis of $TiCl(C_5Me_5)$(butadiene)(3) has been carried out.



supine(exo) prone(endo)

1, $R^1=R^{3\sim4}=H$, $R^2=CH_3$ 3, $R^{1\sim4}=H$

2, $R^1=R^4=H$, $R^{2\sim3}=CH_3$ 4, $R^{2\sim3}=H$, $R^1=R^4=C_6H_5$

Crystal Data of 3: $C_{14}H_{21}ClTi$, M=272.6, monoclinic, space group $P2_1/c$, a=6.999(1), b=14.625(3), c=13.842(2) Å, β=95.61(2)°, U=1410.0(4) Å^3, Z=4, D_c=1.284 g cm^{-3}, μ(Mo$K\alpha$)=7.9 cm^{-1}. The X-ray diffraction data were measured on a Rigaku automated, four-circle diffractometer with Zr-filtered Mo$K\alpha$ radiation by the use of crystal sealed in a thin-walled glass capillary tube under argon. A total of 4106 independent reflections was collected up to 2θ=60° by the θ-2θ scan method, of which 2367 were observed reflections [$|F_o|>3\sigma(F_o)$]. The crystal structure was solved by the conventional heavy atom method and was refined by the full-matrix least-squares (XRAY-76).[7] The final R (R_w) index is 0.083 (0.087). The weighting scheme applied was $w=[\sigma^2(F_o)+0.003(F_o)^2]^{-1}$.

Figure 1 shows an ORTEP drawing[8] of complex 3 with the numbering scheme of atoms. It is evident that the complex 3 consists of the expected prone structure where the butadiene ligand assumes the *s-cis* geometry. The dihedral angle between the planes of cyclopentadienyl and diene ligands is 20.2°. Although closely related $Zr(C_5Me_5)_2$(butadiene) and $Zr(C_5H_5)_2$(1,4-diphenylbutadiene) favor the *s-trans*-diene coordination, the present titanium-diene complexes always prefer the *s-cis*-diene coordination. The titanium atom is in the pseudo-tetrahedral geometry if the C_5Me_5 ligand is considered to occupy one coordination site and the butadiene ligand two coordination sites at its C(1) and C(4) atoms. The terminal C-C bonds, C(1)-C(2) [1.416(14) Å] and C(3)-C(4) [1.418(14) Å], are slightly longer than the inner C(2)-C(3) bond [1.400(14) Å], indicating the presence of substantial contribution of metallacyclo-3-pentene structure, which is generally recognized for zirconium-, hafnium-,and tantalum-diene complexes. The mean distance of terminal C-C bond [1.417 Å] is the shortest among the values in the early transition metal-diene complexes, *i.e.* the distances vary in a range of 1.420-1.473 Å for zirconium-diene complexes,[9] 1.429-1.478 Å for hafnium derivatives,[9] and 1,456-1.500 Å in the case of tantalum complexes.[9] The mean distance of Ti-C(1) and Ti-C(4) bonds [2.184 Å] is a little shorter than the corresponding distance of Ti-C(2) and Ti-C(3) bonds [2.285 Å]. The former value is comparable with usual Ti-C bond distances observed in $Ti(C_5Me_5)_2$(ethylene) [2.160 Å][10] and titanacyclobutane $Ti(C_5H_5)_2(CH_2C(Me)_2CH_2)$ [2.138, 2.152 Å],[11] but is shorter than those in $Ti(C_5H_5)_2$-(1,2-dimethylallyl) [2.34, 2.35 Å].[12]

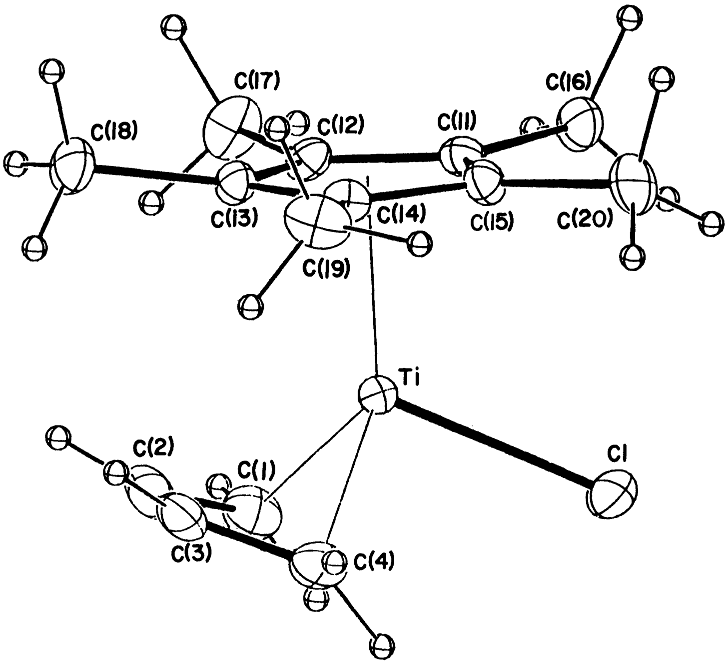


Fig. 1. Molecular structure of $TiCl(C_5Me_5)$(butadiene) (3) drawn by the thermal ellipsoids for nonhydrogen atoms at 20% probability level and by the spheres with radius of 1 $Å^2$ for hydrogen atoms.

Especially noteworthy is the large bite angle (β) defined by C(1)-Ti-C(4). The value for the complex 3 [88.3(4)°] is the largest among the angles observed for *s-cis*-coordinated metal-diene complexes, *i.e.* 5.5-13.2° larger than the values reported for zirconium- and hafnium-diene complexes$^{9)}$ and 10.4-16.9° larger than the angles reported for tantalum-diene complexes.$^{9)}$ The remarkably large bite angle may arise from relatively short M-C(1) and M-C(4) distances as a result of small ionic radius of titanium atom and a long nonbonded distance between C(1) and C(4). Actually the M-C(terminal) bond distance of the present complex is much shorter than the M-C(terminal) bonds observed for other early transition metal-diene complexes, which distributed from 2.251 Å in $Ta(C_5Me_5)(C_6H_{10})(C_4H_6)^{2)}$ to 2.371 Å in $Hf(Me_2PCH_2CH_2PMe_2)$(butadiene)$_2$.$^{13)}$ The nonbonded C(1)··C(4) distance in the present complex [3.041(15) Å] is longer than the corresponding distance in $TaCl_2(C_5H_5)$(butadiene) [2.694(16) Å, β=73.3°] or that in $Fe(CO)_3$(butadiene) [2.83 Å, β=82.6°]$^{14)}$ accompanied with the expansion of bond angles around the C(2) and C(3) atoms in the diene ligand [124.7(9)° and 126.1(9)°].

The dihedral angle between the planes defined by the Ti, C(1), and C(4) atoms and the C(1), C(2), C(3), and C(4) atoms, is 105.0°, the magnitude of which is similar to those found in other early transition metal-diene complexes but larger than those in the corresponding complexes of late transition metals.$^{9)}$

The X-ray structure analysis of complex 3 revealed the unique coordination geometry for diene ligand, which has the substantial σ^2,π-η^4-metallacyclo-3-pentene structure even though there observed a remarkable tendency to behave as π^2-η^4-metal-diene species. The present X-ray together with NMR studies reveal that the steric repulsions between the pentamethylcyclopentadienyl ligand and substituents on the diene ligand may act as the crucial factor in determining the supine or prone geometry of the coordinated diene, *i.e.* the alkyl substitution on the C(2) and/or C(3) atoms bring about the supine geometry while the substitution on the C(1) and/or C(4) atoms or nonsubstitution on the C(2) and C(3) atoms always lead to the prone geometry.

References

1) For example; R. R. Schrock, *Acc. Chem. Res.*, 12, 98 (1979); M. E. Thompson and J. E. Bercaw, *Pure Appl. Chem.*, 56, 1 (1984); H. Yasuda, K. Tatsumi, and A. Nakamura, *Acc. Chem. Res.*, 18, 120 (1985).

2) H. Yasuda, K. Tatsumi, T. Okamoto, K. Mashima, K. Lee, A. Nakamura, Y. Kai, N. Kanehisa, and N. Kasai, *J. Am. Chem. Soc.*, 107, 2410 (1985).

3) J. Blenkers, B. Hessen, F. van Bolhuis, A. J. Wagner, and J. H. Teuben, *Organometallics*, 6, 459 (1987).

4) Coinciding with our work, the complex 2 has been prepared by Teuben *et al.*$^{3)}$ in the similar manner. See for our preliminary reports; H. Yamamoto, T. Okamoto, H. Yasuda, and A. Nakamura, 53rd Annual Meet. Chem. Soc. Japan, (1986) Abstr. 2M02; H. Yamamoto, H. Yasuda, and A. Nakamura, 4th IUPAC Symposium on Organomet. Chem. Directed Toward Org. Synthesis, Vancouver (1987), Abstr. PS1-47.

5) 1: ^{1}H NMR (C_6D_6,90 MHz) δ 1.09 (m, -(Me)C=C$\underline{H}_2$ anti, 1H), 1.17 (m, -CH=C$\underline{H}_2$ anti, 1H), 2.81 (m, -(Me)C=C$\underline{H}_2$ syn, 1H), 2.95 (m, -CH=C$\underline{H}_2$ syn, 1H), 5.66 (t, J= 10 Hz, -C$\underline{H}$=CH_2, 1H), 1.98 (s, -($\underline{Me}$)C=CH_2, 3H), 1.93 (s, $C_5\underline{Me}_5$, 15H).
   2: mp 133.5-134.0 °C; ^{1}H NMR (C_6D_6, 100 MHz) δ 1.42 (dd, J=-9.0 Hz, J=1.8 Hz, =C$\underline{H}_2$ anti, 2H), 2.75 (dd, J=-9.0 Hz, J=1.8 Hz, =C$\underline{H}_2$ syn, 2H), 1.86 (s, -($\underline{Me}$)C=CH_2, 6H), 1.88 (s, $C_5\underline{Me}_5$, 15H).

6) 3: mp(dec.) 125.1-126.3 °C; ^{1}H NMR (C_6D_6, 500 MHz) δ 3.16 (m, =C$\underline{H}_2$ syn, 2H), 3.71 (m, -C$\underline{H}$=, 2H), 3.82 (m, =C$\underline{H}_2$ anti, 2H), 1.61 (s, $C_5\underline{Me}_5$, 15H).
   4: mp(dec.) 219.3-220.0 °C; ^{1}H NMR (C_6D_6, 100 MHz) δ 4.22 (m, -C$\underline{H}$=CHPh, 2H), 6.73 (m, -CH=C$\underline{H}$Ph, 2H), 7.15 (m, -CH=CH$\underline{Ph}$, 10H), 1.45 (s, $C_5\underline{Me}_5$, 15H).

7) J. M. Stewart, "XRAY-76," Report TR-446, University of Maryland, MD (1976).

8) C. K. Johnson, "ORTEP-II," Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN (1974).

9) H. Yasuda, A. Nakamura, Y. Kai, and N. Kasai, "Topics in Physical Organometallic Chemistry," ed by M. F. Gielen, Freund Publishing House LTD., London (1987), Vol. 2, p. 179.

10) S. A. Cohen, P. R. Auburn, and J. E. Bercaw, *J. Am. Chem. Soc.*, 105, 1136 (1983).

11) J. B. Lee, G. J. Gajda, W. P. Schaefer, T. R. Howard, T. Ikariya, D. A. Straus, and R. H. Grubbs, *J. Am. Chem. Soc.*, 103, 7358 (1981).

12) R. B. Helmholdt, F. Jellinek, H. A. Martin, and A. Vos, *Recl. Trav. Chim. Pays-Bas*, 86, 1263 (1976).

13) S. S. Wreford and J. F. Whitney, *Inorg. Chem.*, 20, 3918 (1981).

14) O. S. Mills and G. Robinson, *Acta Crystallogr.*, 16, 758 (1963).

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