

tin reagents with unsaturated organic moieties, and heating the CH_2Cl_2 solution under reflux is necessary. In attempted vinylation by $(\text{CH}_2=\text{CH})_4\text{Sn}$ and alkynylation by $\text{HC}\equiv\text{CSiMe}_3$ 1 was recovered quantitatively, apparently due to irreversible formation of the π -complexes. (2) It is noteworthy that silver metal deposited upon mixing HSiEt_3 or R_4Sn with AgSbF_6 , whether 1 was present or not. Furthermore, in model experiments with $\text{Ph}_3\text{CBr}/\text{AgSbF}_6$ or $[\text{Ph}_3\text{C}]\text{PF}_6$ in place of 1/ AgSbF_6 , Ph_3CH was obtained with HSiEt_3 and Et_4Sn , but Ph_3CMe was not formed with Me_4Sn . These results suggest that some Ag-Me species may alkylate 1 to give 4.²⁵ (3) The role of exogenous carbon monoxide in the formation of acyl derivatives, e.g.

9,¹⁸ contrasts with the intramolecular CO migration involved in forming the tricobalt species $[\text{Co}_3(\text{CO})_9(\text{CCO})]^+$, which also is apparently more electrophilic in further reactions to form $\text{Co}_3(\text{CO})_9(\mu_3\text{-CC(O)R})$ compounds.¹ However, similar trapping of external CO by mononuclear $[\text{CpFe}(\text{CO})_2(\text{CH}_2)]^+$ and dinuclear $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\mu\text{-CH})]^+$ has been observed, affording the ketene complex $[\text{CpFe}(\text{CO})_2(\text{CH}_2\text{-C=O})]^+$ ²⁶ and the ketenyl complex $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\mu\text{-CH-C=O})]^+$,²⁷ respectively. Work aimed at the direct observation of intermediates in the triosmium reactions is underway.

Acknowledgment. We are grateful to D. S. Strickland for her preliminary work with $[\text{H}_3\text{Os}_3(\text{CO})_9(\text{CCO})]^+$ and HSiEt_3 . This research was supported by National Science Foundation Grant CHE 89-15349.

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Formation, Fragmentation, and Isomerization of Titanacycle Rings Supported by Aryloxy Ligation

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Received May 18, 1990

Summary: The reactivity of the titanacyclopentadiene ring in $[(\text{Ar}''\text{O})_2\text{Ti}(\text{C}_4\text{Et}_4)]$ can best be explained on the basis of facile fragmentation into a titanium bis(alkyne) complex.

The last few years have seen an intense research interest into the structure and reactivity of metallacycle- and heterometallacycle-containing compounds.¹⁻³ A particu-

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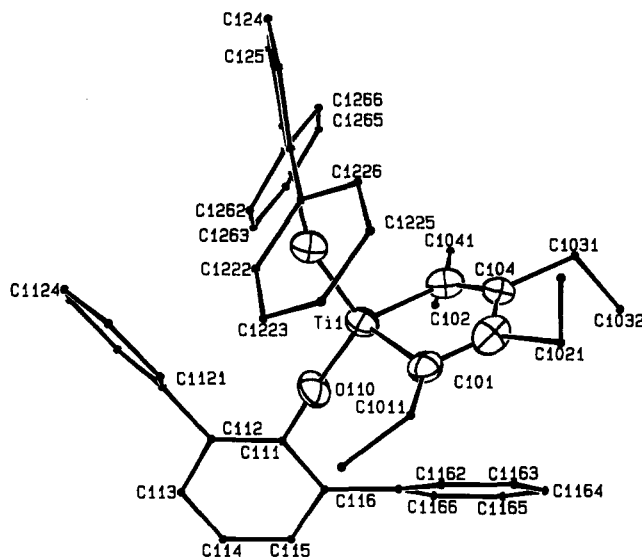
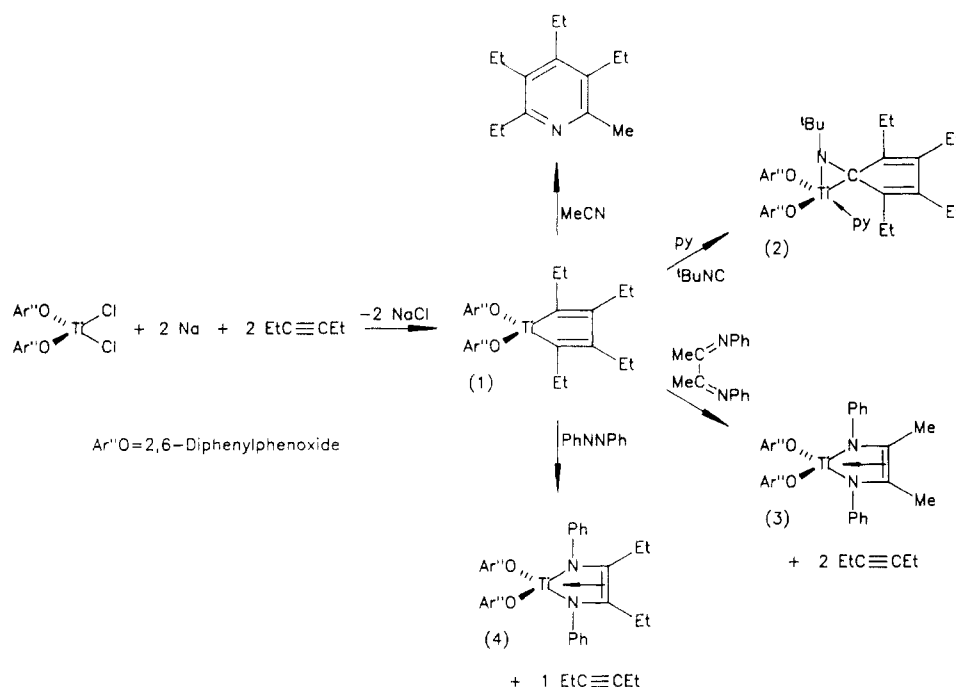


Figure 1. ORTEP view of molecule 1 of $[(\text{Ar}''\text{O})_2\text{Ti}(\text{C}_4\text{Et}_4)]$ (1). Selected bond distances (Å) and angles (deg) for molecules 1 and 2: Ti-O(110) = 1.806 (6), 1.788 (6); Ti-O(120) = 1.804 (6), 1.828 (6); Ti-C(101) = 2.016 (9), 1.983 (9); Ti-C(104) = 1.986 (9), 2.02 (1); C(101)-C(102) = 1.35 (1), 1.33 (1); C(102)-C(103) = 1.52 (1), 1.55 (1); C(103)-C(104) = 1.33 (1), 1.34 (1); O(110)-Ti-O(120) = 116.5 (3), 111.1 (3); C(101)-Ti-C(104) = 94.3 (4), 98.5 (4).

larly well-studied area has been the development of useful synthetic methodologies based upon the reactivity of intermediate metallacyclopentadiene rings formed by intramolecular coupling of two alkyne units at transition-metal centers.⁴⁻⁶ During our studies of the organometallic

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Scheme I



chemistry of titanium that can be supported by aryloxide ligation,⁷ we have isolated and investigated the reactivity of a new titanacyclopentadiene complex. The reactivity of this complex can be explained on the basis of initial fragmentation back into a titanium bis(alkyne) complex and rapid isomerization of subsequent heterometallacycle compounds.

The room-temperature sodium amalgam reduction (2:1 Na:Ti) of toluene solutions of the dichloride $\text{Ti}(\text{OAr}'')_2\text{Cl}_2$ ($\text{OAr}'' = 2,6\text{-diphenylphenoxy}$)⁸ in the presence of 3-hexyne (≥ 2 equiv) leads to formation of the orange titanacyclopentadiene compound $[(\text{Ar}'')_2\text{O}_2\text{Ti}(\text{C}_4\text{Et}_4)]$ (1) in 80–90% yields (Scheme I).⁹ A structural study of 1 (Figure 1)¹⁰ shows the molecule to contain an essentially planar metallacycle ring, in contrast to the case for the

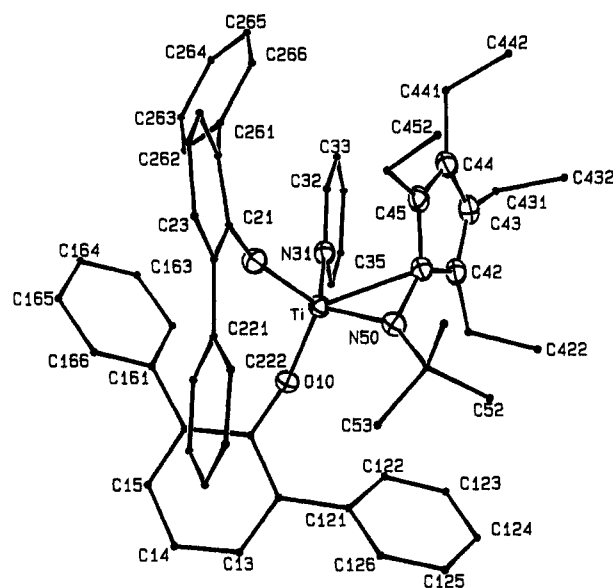


Figure 2. ORTEP view of $[(Ar''O)_2Ti(\eta^2-BuNCC_4Et_4)(py)]$ (**2**). Selected bond distances (Å) and angles (deg): Ti–O(10) = 1.861 (2); Ti–O(20) = 1.841 (2); Ti–N(31) = 2.142 (2); Ti–N(50) = 1.860 (2); Ti–C(41) = 2.262 (3); C(41)–N(50) = 1.417 (3); O(10)–Ti–O(20) = 111.36 (8); C(41)–Ti–N(50) = 36.68 (9).

folded tungstacyclopentatriene compound $[(Ar''O)_2W-(C_4Et_4)]$,^{5b,11} Compound 1 shows many of the reactions typical of other metallacyclopentadiene complexes.⁴⁻⁶ Hence, treatment with excess 3-hexyne at 110 °C leads to the catalytic formation of hexaethylbenzene, while treatment with MeCN leads to the liberation of the corresponding substituted pyridine (Scheme I). Reaction of 1 with Bu^tNC in the presence of an additional 1 equiv of C₅H₅N (py) rapidly leads to the formation of the new iminocyclopentadiene complex $[(Ar''O)_2Ti(\eta^2-Bu^tNCC_4Et_4)(py)]$ (2; Scheme I)¹² which has been struc-

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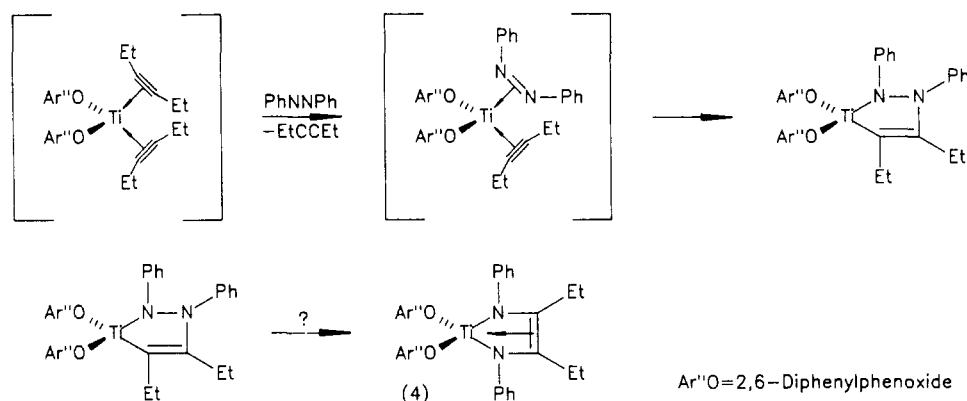
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(9) Anal. Calcd for $\text{TiC}_{48}\text{H}_{46}\text{O}_2$ (1): C, 82.03; H, 6.60. Found: C, 81.43; H, 6.83. ^1H NMR data (C_6D_6 , 30 $^\circ\text{C}$): δ 6.86–7.48 (m, phenyl protons), δ 2.02 (q), 1.59 (q, CH_2CH_3); 0.87 (t), 0.42 (t, CH_2CH_3). Selected ^{13}C NMR data (C_6D_6 , 30 $^\circ\text{C}$): δ 231.3 (Ti–C); 136.3 (Ti–C=C); 160.0 (Ti–O–C); 28.4, 20.9 (CH_2CH_3); δ 14.9, 13.9 (CH_2CH_3).

(10) Crystal data for $\text{TiC}_{14}\text{H}_{46}\text{O}_2$ (1) at 20 °C: $a = 12.627$ (3) Å, $b = 17.378$ (4) Å, $c = 17.739$ (3) Å, $\alpha = 90.41$ (2)°, $\beta = 94.68$ (2)°, $\gamma = 92.89$ (2)°, $V = 3874$ (3) Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.205$ g cm⁻³ in space group $P1$. A total of 10 099 unique intensities were collected by using Mo $K\alpha$ radiation ($4^\circ \leq 2\theta \leq 45^\circ$), of which 3481 with $I > 3\sigma(I)$ were used in the final refinement. Final residuals are $R = 0.075$ and $R_w = 0.080$. The unit cell contains two independent molecules.

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Scheme II



turally characterized (Figure 2).¹³ Besides the normal coordination of the pyridine and aryloxy ligands, the titanium metal center in **2** can be seen to be bound to the imine function of the iminocyclopentadiene molecule in an $\eta^2(\text{C},\text{N})$ fashion. The structural features and reactivity of directly related η^2 -imine (azametallacyclopropane) complexes have been discussed.^{7a}

A number of reactions of metallacycle **1**, however, can be seen to proceed via fragmentation back into its component alkyne units.¹⁴ Hence, treatment of C_6D_6 solutions of **1** with the 1,4-diaza-1,3-butadiene compound $\text{PhN}=\text{CMeCMe}=\text{NPh}$ can be shown to lead to the enediamido compound $[(\text{Ar}'\text{O})_2\text{Ti}(\text{PhNCMe}=\text{CMeNPh})]$ (**3**)¹⁵ and 2 equiv of 3-hexyne at room temperature. The analogous enediamido compound $[(\text{Ar}'\text{O})_2\text{Ti}(\text{PhNC}=\text{C}(\text{Et})\text{NPh})]$ (**4**) is also formed when titanacyclopentadiene **1** is heated with azobenzene ($\text{PhN}=\text{NPh}$) at 110 °C for 60 min.¹⁶⁻¹⁸

Monitoring the reaction by ^1H NMR spectroscopy shows the formation of 3-hexyne as well as smaller amounts of hexethylbenzene. A viable pathway for the formation of **4** from **1** + $\text{PhN}=\text{NPh}$ involves initial fragmentation of **1** to a bis(alkyne) intermediate. Displacement of one of the alkyne groups by $\text{PhN}=\text{NPh}$ followed by intramolecular coupling leads to a diazametallacyclopentene ring (Scheme II). This step, which has been recently demonstrated by Bergman et al.,¹⁹ leads to a 2,3-diazametallacyclopentene complex. Formation of the observed, final enediamido (2,5-diazametallacyclopentene) compound would then require a previously uncharacterized isomerization process (Scheme II). Further synthetic and mechanistic studies of this reactivity are in progress.

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

Registry No. **1**, 127998-83-8; **2**, 127998-80-5; **3**, 127998-81-6; **4**, 127998-82-7; $\text{Ti}(\text{OAr}')_2\text{Cl}_2$, 110300-61-3; Bu^tNC , 7188-38-7; $\text{PhN}=\text{CMeCMe}=\text{NPh}$, 5393-49-7; $\text{PhN}=\text{NPh}$, 103-33-3; $\text{CH}_3\text{CH}_2\text{COCH}(\text{NPh})\text{CH}_2\text{CH}_3$, 127998-79-2; 3-hexyne, 928-49-4.

Supplementary Material Available: Tables of crystal data and data collection parameters, positional parameters, general temperature factors, and bond distances and angles for **1** and **2** (37 pages); tables of observed and calculated structure factors (58 pages). Ordering information is given on any current masthead page.

(12) Anal. Calcd for $\text{TiC}_{58}\text{H}_{80}\text{N}_2\text{O}_2$ (**2**): C, 80.53; H, 6.99; N, 3.24. Found: C, 80.29; H, 7.01; N, 3.62. ^1H NMR (C_6D_6 , 30 °C): δ 8.51 (d, ortho protons on pyridine); 6.3–7.7 (m, aromatics); 1.69 (m, CH_2CH_3); 1.03 (broad t, CH_2CH_3); δ 0.64 (s, Bu^tN). Selected ^{13}C NMR data (C_6D_6 , 30 °C): δ 160.6 (Ti–O–C); 139.6, 132.7 (CCH_2CH_3); δ 115.2 (Bu^tNC); δ 65.1 (Me_3C); 31.7 (Me_3C); 19.4, 18.1 (CH_2CH_3); 16.5 (CH_2CH_3).

(13) Crystal data for $\text{TiC}_{58}\text{H}_{80}\text{N}_2\text{O}_2$ (**2**) at –105 °C: $a = 12.554$ (4) Å, $b = 17.934$ (5) Å, $c = 21.567$ (6) Å, $\beta = 102.39$ (2)°, $V = 4742$ (5) Å³, $Z = 4$, $d_{\text{calc}} = 1.211$ g cm^{–3} in space group $P2_1/n$. A total of 6424 unique intensities were collected by using Mo K α radiation ($4 \leq 2\theta \leq 45^\circ$), of which 4739 with $I > 3\sigma(I)$ were used in the final refinement. Final residuals are $R = 0.040$ and $R_w = 0.055$.

(14) Fragmentation of metallacyclopentane rings into component olefin groups is well-known; for example see: (a) Takahashi, T.; Fujimori, T.; Seki, T.; Saburi, M.; Uchida, Y.; Rousset, C. J.; Negishi, E. *J. Chem. Soc., Chem. Commun.* 1990, 182 and references therein. Isomerization of metallacyclopentadiene rings has been demonstrated; see: (b) Strickler, J. R.; Bruck, M. A.; Wigley, D. E. *J. Am. Chem. Soc.*, in press.

(15) Anal. Calcd for $\text{TiC}_{52}\text{H}_{42}\text{N}_2\text{O}_2$ (**3**): C, 80.61; H, 5.46; N, 3.62. Found: C, 80.59; H, 5.61; N, 3.91. ^1H NMR (C_6D_6 , 30 °C): δ 6.15–7.33 (m, aromatics); δ 1.38 (s, CCH_3). Selected ^{13}C NMR data (C_6D_6 , 30 °C): δ 160.4, 158.6 (Ti–O–C); δ 112.3 (CCH_3); δ 14.4 (CCH_3).

(16) The NMR spectra of both **3** and **4** indicate they adopt a nonplanar ground state-structure.^{3a}

(17) Anal. Calcd for $\text{TiC}_{54}\text{H}_{46}\text{N}_2\text{O}_2$ (**4**): C, 80.78; H, 5.78; N, 3.49. Found: C, 80.97; H, 5.79; N, 3.37. ^1H NMR (C_6D_6 , 30 °C): δ 6.25–7.44 (m, aromatics); δ 2.05, 1.59 (ABX₃ pattern of CH_2CH_3); δ 0.51 (t, CH_2CH_3). Selected ^{13}C NMR data (C_6D_6 , 30 °C): δ 160.4, 159.5 (Ti–O–C); δ 118.7 (CET); δ 20.6 (CH_2CH_3); δ 14.0 (CH_2CH_3).

(18) The stereochemistry of **4** was further confirmed by its hydrolysis to produce 4-(phenylamino)-3-hexanone ($\text{CH}_3\text{CH}_2\text{COCH}(\text{NPh})\text{CH}_2\text{CH}_3$). High-resolution MS: calcd, m/e 191.1310; found, m/e 191.1310. Selected ^1H NMR data (C_6D_6 , 30 °C): δ 4.15 (broad d, NH); δ 3.62 (q, CH); δ 1.94 (ABX₃, OCH_2CH_3); δ 1.53 (m), 1.19 (m, diastereotopic CHCH_2CH_3); δ 0.86 (t, CH_2CH_3); δ 0.63 (t, CHCH_2CH_3). ^{13}C NMR (C_6D_6 , 30 °C): δ 147.9 (ipso carbon on phenyl); δ 130.1 (ortho carbon on phenyl); δ 118.5 (para carbon on phenyl); δ 113.8 (meta carbon on phenyl); δ 68.6 (O=C–); δ 63.7 (NCH); δ 32.0, 24.9 (CH_2CH_3); δ 9.5, 7.8 (CH_2CH_3).

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