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Formation, fragmentation, and isomerization of titanacycle rings supported by aryloxide ligation

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tin reagents with unsaturated organic moieties, and heating the CH_2Cl_2 solution under reflux is necessary. In attempted vinylation by $(CH_2{=}CH)_4Sn$ and alkynylation by $HC{\equiv}CSiMe_3$ **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 $Ph_3CBr/AgSbF_6$ or $[Ph_3C]PF_6$ 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 $[Co_3(CO)_9(CCO)]^+$, which also is apparently more electrophilic in further reactions to form $Co_3(CO)_9(\mu_3\text{-}CC(O)R)$ compounds.[1] However, similar trapping of external CO by mononuclear $[CpFe(CO)_2(CH_2)]^+$ and dinuclear $[Cp_2Fe_2(CO)_3(\mu\text{-}CH)]^+$ has been observed, affording the ketene complex $[CpFe(CO)_2(CH_2{=}C{=}O)]^+$[26] and the ketenyl complex $[Cp_2Fe_2(CO)_3(\mu\text{-}CH{=}C{=}O)]^+$,[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 $[H_3Os_3(CO)_9(CCO)]^+$ 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 Aryloxide Ligation

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Summary: The reactivity of the titanacyclopentadiene ring in $[(Ar''O)_2Ti(C_4Et_4)]$ 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 particularly 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

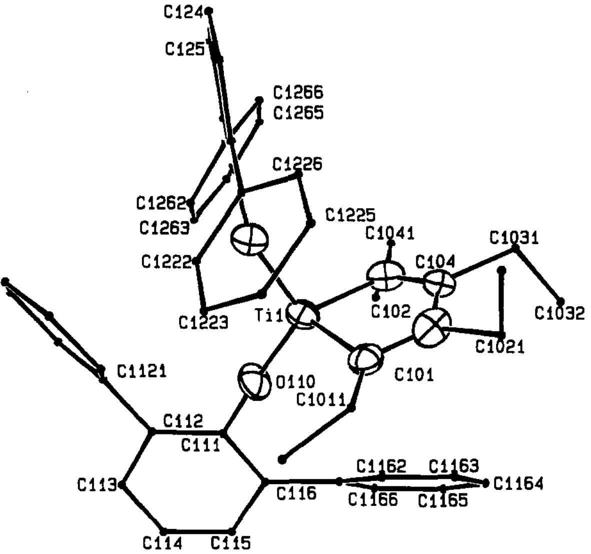

Figure 1. ORTEP view of molecule 1 of $[(Ar''O)_2Ti(C_4Et_4)]$ (1). Selected bond distances (Å) and angles (deg) for molecules 1 and 2: Ti–O(110) = 1.806 (6), 1.788 (6); Ti–O(120) = 1.804 (6), 1.828 (6); Ti–C(101) = 2.016 (9), 1.983 (9); Ti–C(104) = 1.986 (9), 2.02 (1); C(101)–C(102) = 1.35 (1), 1.33 (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).

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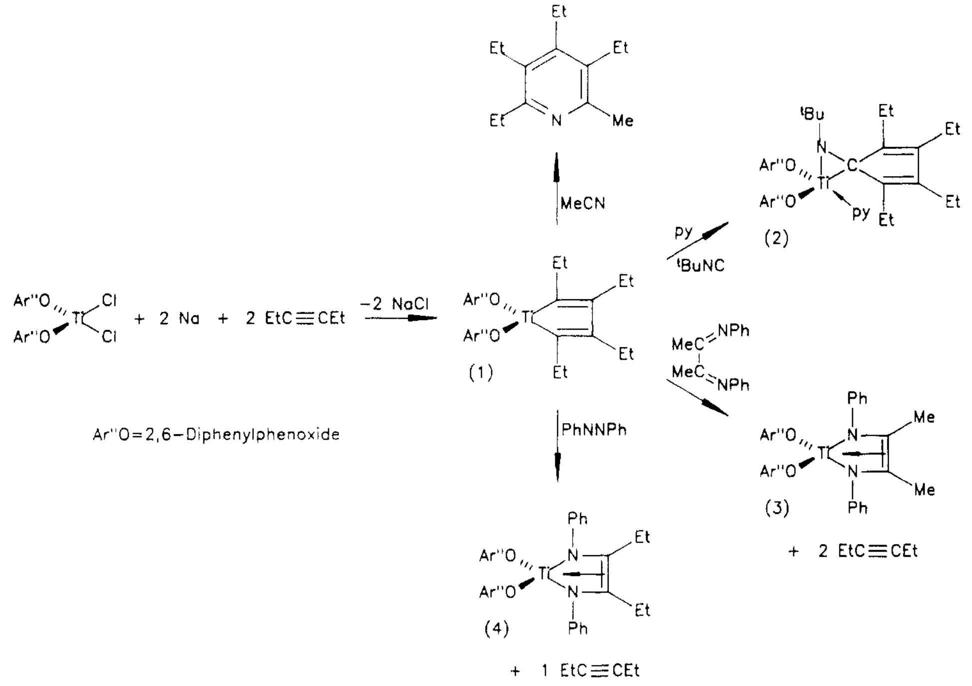
Scheme I



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 $Ti(OAr'')_2Cl_2$ (OAr'' = 2,6-diphenylphenoxide)[8] in the presence of 3-hexyne (≥2 equiv) leads to formation of the orange titanacyclopentadiene compound $[(Ar''O)_2Ti(C_4Et_4)]$ (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 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 C_5H_5N (py) rapidly leads to the formation of the new iminocyclopentadiene complex $[(Ar''O)_2Ti(\eta^2\text{-}Bu^tNCC_4Et_4)(py)]$ (2; Scheme I),[12] which has been struc-

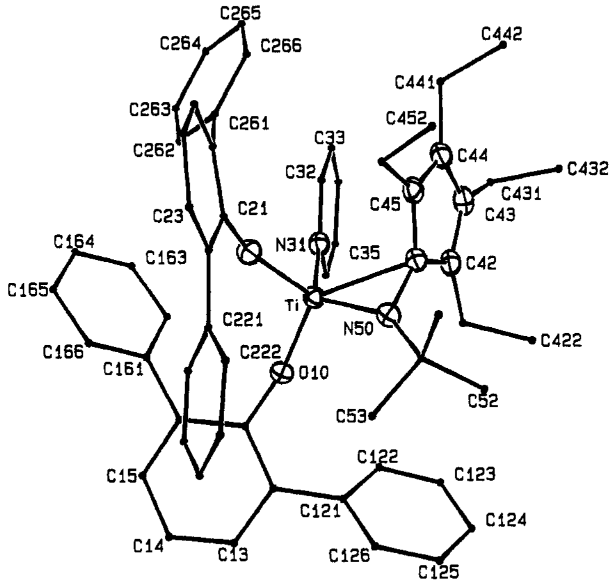


Figure 2. ORTEP view of $[(Ar''O)_2Ti(\eta^2\text{-}Bu^tNCC_4Et_4)(py)]$ (2). Selected bond distances (Å) and angles (deg): Ti–O(10) = 1.861 (2); Ti–O(20) = 1.841 (2); Ti–N(31) = 2.142 (2); Ti–N(50) = 1.860 (2); Ti–C(41) = 2.262 (3); C(41)–N(50) = 1.417 (3); O(10)–Ti–O(20) = 111.36 (8); C(41)–Ti–N(50) = 36.68 (9).

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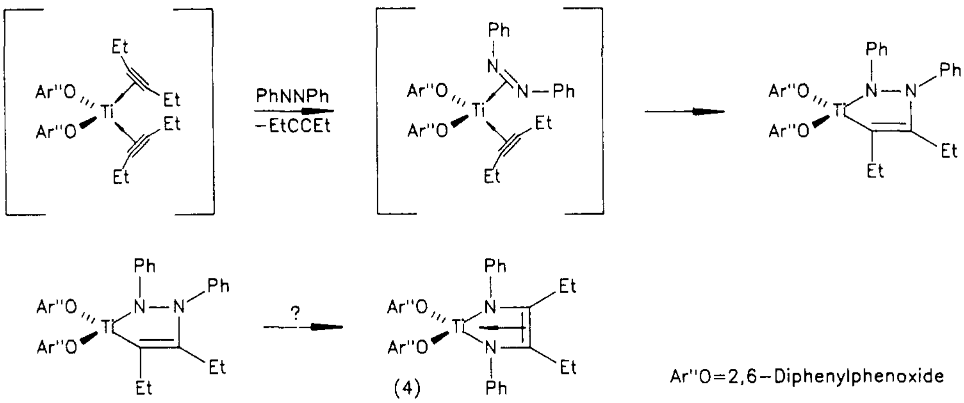
(9) Anal. Calcd for $TiC_{48}H_{46}O_2$ (1): C, 82.03; H, 6.60. Found: C, 81.43; H, 6.83. ^1H NMR data (C_6D_6, 30 °C): δ 6.86–7.48 (m, phenyl protons), δ 2.02 (q), 1.59 (q, CH_2CH_3); 0.87 (t), 0.42 (t, CH_2CH_3). Selected ^{13}C NMR data (C_6D_6, 30 °C): δ 231.3 (Ti—C); 136.3 (Ti—C=C); 160.0 (Ti-O-C); 28.4, 20.9 (CH_2CH_3); δ 14.9, 13.9 (CH_2CH_3).

(10) Crystal data for $TiC_{48}H_{46}O_2$ (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) Å^3, $Z = 4$, $d_{calcd} = 1.205$ g cm^{-3} in space group $P\bar{1}$. A total of 10099 unique intensities were collected by using Mo Kα radiation (4° ≤ 2θ ≤ 45°), 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.

(11) Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* 1988, *110*, 8235.

Scheme II



turally characterized (Figure 2).[13] Besides the normal coordination of the pyridine and aryloxide ligands, the titanium metal center in **2** can be seen to be bound to the imine function of the iminocyclopentadiene molecule in an η^2(C,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 PhN=CMeCMe=NPh can be shown to lead to the enediamido compound [(Ar″O)$_2$Ti(PhNCMe=CMeNPh)] (**3**)[15] and 2 equiv of 3-hexyne at room temperature. The analogous enediamido compound [(Ar″O)$_2$Ti(PhNCEt=CEtNPh)] (**4**) is also formed when titanacyclopentadiene **1** is heated with azobenzene (PhN=NPh) at 110 °C for 60 min.[16–18] Monitoring the reaction by ^{1}H 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** + PhN=NPh involves initial fragmentation of **1** to a bis(alkyne) intermediate. Displacement of one of the alkyne groups by PhN=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.

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

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(12) Anal. Calcd for TiC$_{58}$H$_{60}$N$_2$O$_2$ (**2**): C, 80.53; H, 6.99; N, 3.24. Found: C, 80.29; H, 7.01; N, 3.62. ^{1}H NMR (C_6D_6, 30 °C): δ 8.51 (d, ortho protons on pyridine); 6.3–7.7 (m, aromatics); 1.69 (m, C*H*$_2$CH$_3$); 1.03 (broad t, CH$_2$C*H*$_3$); δ 0.64 (s, Bu^{t}N). Selected ^{13}C NMR data (C_6D_6, 30 °C): δ 160.6 (Ti–O–*C*); 139.6, 132.7 (*C*CH$_2$CH$_3$); δ 115.2 (Bu^{t}N*C*); δ 65.1 (Me$_3$*C*); 31.7 (*Me*$_3$C); 19.4, 18.1 (*C*H$_2$CH$_3$); 16.5 (CH$_2$*C*H$_3$).

(13) Crystal data for TiC$_{58}$H$_{60}$N$_2$O$_2$ (**2**) at −105 °C: a = 12.554 (4) Å, b = 17.934 (5) Å, c = 21.567 (6) Å, β = 102.39 (2)°, V = 4742 (5) Å^3, Z = 4, d_{calcd} = 1.211 g cm^{-3} in space group $P2_1/n$. A total of 6424 unique intensities were collected by using Mo Kα radiation ($4 \le 2\theta \le 45°$), 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 TiC$_{52}$H$_{42}$N$_2$O$_2$ (**3**): C, 80.61; H, 5.46; N, 3.62. Found: C, 80.59; H, 5.61; N, 3.91. ^{1}H NMR (C_6D_6, 30 °C): δ 6.15–7.33 (m, aromatics); δ 1.38 (s, CC*H*$_3$). Selected ^{13}C NMR data (C_6D_6, 30 °C): δ 160.4, 158.6 (Ti–O–*C*); δ 112.3 (*C*CH$_3$); δ 14.4 (C*C*H$_3$).

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

(17) Anal. Calcd for TiC$_{54}$H$_{46}$N$_2$O$_2$ (**4**): C, 80.78; H, 5.78; N, 3.49. Found: C, 80.97; H, 5.79; N, 3.37. ^{1}H NMR (C_6D_6, 30 °C): δ 6.25–7.44 (m, aromatics); δ 2.05, 1.59 (ABX$_3$ pattern of C*H*$_2$CH$_3$); δ 0.51 (t, CH$_2$C*H*$_3$). Selected ^{13}C NMR data (C_6D_6, 30 °C): δ 160.4, 159.5 (Ti–O–*C*); δ 118.7 (*C*Et); δ 20.6 (*C*H$_2$CH$_3$); δ 14.0 (CH$_2$*C*H$_3$).

(18) The stereochemistry of **4** was further confirmed by its hydrolysis to produce 4-(phenylamino)-3-hexanone (CH$_3$CH$_2$COCH(NHPh)-CH$_2$CH$_3$). High-resolution MS: calcd, m/e 191.1310; found, m/e 191.1310. Selected ^{1}H NMR data (C_6D_6, 30 °C): δ 4.15 (broad d, N*H*); δ 3.62 (q, C*H*); δ 1.94 (ABX$_3$, OCC*H*$_2$CH$_3$); δ 1.53 (m), 1.19 (m, diastereotopic CHC*H*$_2$CH$_3$); δ 0.86 (t, CH$_2$C*H*$_3$); δ 0.63 (t, CHCH$_2$C*H*$_3$). ^{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 (N*C*H); δ 32.0, 24.9 (*C*H$_2$CH$_3$); δ 9.5, 7.8 (CH$_2$*C*H$_3$).

(19) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 894.