ORGANOMETALLICS

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

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between the metallocenes which, in the case of the iron derivatives, is more pronounced for **5d** ($\Delta E_{1/2}$ = 345 mV) than for the silyl-bridged compound **3** with M = Fe ($\Delta E_{1/2}$ = 210 mV[14]).

While **5d,e** are diamagnetic, the paramagnetic compounds **5a,b,c** showed striking differences when studied by ^{1}H NMR spectroscopy. The paramagnetic ^{1}H NMR shifts at 298 K[15] of **5b** (δ^{para}_{298} = −39.3/−60.4 (H2–5), 36.7 (CH_3)) and of **5c** (δ^{para}_{298} = 319 (H2–5), 111.1 (CH_3)) are very similar to those found for substituted mononuclear cobaltocenes and vanadocenes.[16] In particular, the signals for H2–5 of **5c** are not resolved, as is found for many other vanadocenes.[16] It follows that **5b,c** have two and six unpaired electrons, respectively, and that the electron spin coupling is very small. This has been confirmed by a temperature-dependence study, according to which the δ^{para} values closely follow the Curie law.

In contrast, the ^{1}H NMR spectrum of **5a** (Figure 1) is much different from what is known for substituted nickelocenes.[16] The signal shifts of H2–5 (δ^{para}_{298} = −122.1/−100.6) and of CH_3 (δ^{para}_{298} = 117.9) are only about half as big as usual, and the signals are much narrower. The temperature dependence of the proton signal shifts is also shown in Figure 1. There is no linear correlation of δ^{para} with $1/T$ and, hence, a strong deviation from Curie behavior. Instead, all absolute shift values increase with the temperature after passing through a minimum. This is characteristic of a strong antiferromagnetic coupling. The coupling can be adjusted by substitution. Thus, for the parent binickelocene $(CpNi)_2C_{10}H_8$[5a] the signal shifts of H2–5 (δ^{para}_{298} = −160.7/−132.8) and of Cp (δ^{para}_{298} = −140.8) are also far from those of simple nickelocenes. However, the proton signals of the fulvalene ligand are more shifted than in the case of **5a**, which means that the antiferromagnetic coupling is somewhat smaller.

Unlike the predominantly Coulombic interaction between the metallocene moieties, which are rather similar (cyclic voltammetry), the magnetic exchange varies. In the decamethylbimetallocenes the latter effect is so pronounced that the influence of the metal on the magnetism may be studied conveniently. We are currently extending this work to other paramagnetic bimetallocenes.

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[14] Atzkern, H.; Hiermeier, J.; Köhler, F. H.; Steck, A. *J. Organomet. Chem.* **1991**, *408*, 281.

[15] The signal shifts were measured relative to the solvent signal and calculated relative to the corresponding signal shifts of **5d**. Shifts to low frequency have a negative sign.

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Formation, Fragmentation, and Isomerization of Azatitanacycle Rings Supported by Aryloxide Ligation

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Summary: The ethylene complex $[(Ar''O)_2Ti(\eta^2\text{-}C_2H_4)(PMe_3)]$ (Ar″O = 2,6-diphenylphenoxide) reacts with $PhCH_2N{=}CHPh$ to produce the 2-azatitanacyclopentane complex $[(Ar''O)_2Ti(CH_2CH_2CHPhNCH_2Ph)]$, which undergoes coupling reactions with alkynes and benzonitrile to produce new azametallacycles with loss of ethylene.

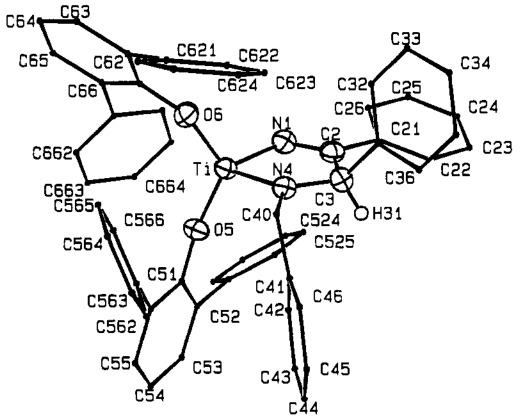

Figure 1. ORTEP view of **4** emphasizing the central coordination sphere. Selected bond distances (Å) and angles (deg): Ti–O(5), 1.816 (2); Ti–O(6), 1.829 (2); Ti–N(1), 1.910 (2); Ti–N(4), 1.886 (2); N(1)–C(2), 1.277 (3); C(2)–C(3), 1.529 (4); C(3)–N(4), 1.466 (3); O(5)–Ti–O(6), 124.10 (8); N(1)–Ti–N(4), 81.9 (1).

The last few years have seen an expansion of interest in the chemistry of transition-metal metallacyclic compounds.[1] In the case of the group 4 metals extremely useful synthetic methodologies have been built up around the formation and reactivity of metallacycle rings containing the metallocene (Cp_2M) subunit.[2-6] Recently our group has been exploring the reactivity of unsaturated

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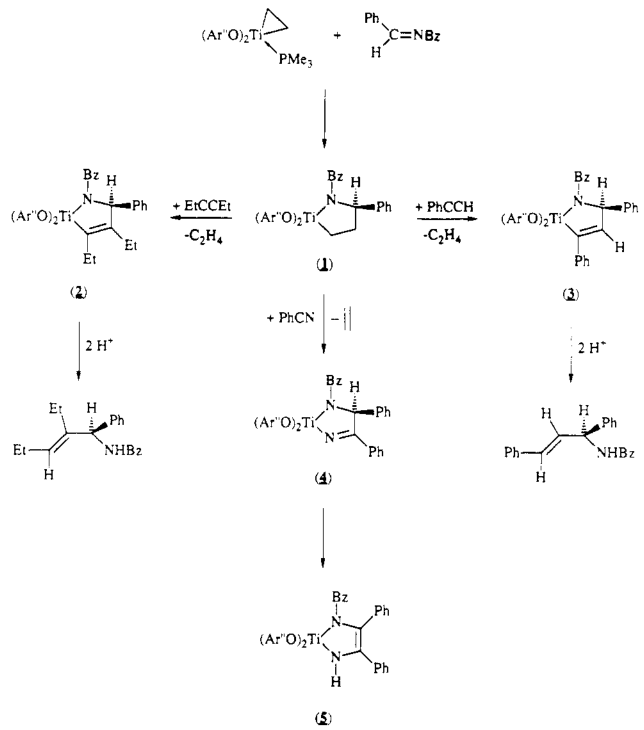
organic molecules bound to titanium aryloxide fragments such as [Ti(OAr″)$_2$] (OAr″ = 2,6-diphenylphenoxide).[7] We wish to report here on the formation and reactivity of a series of azatitancycle compounds formed by the coupling of unsaturated organic substrates by this metal fragment.

Scheme I



A benzene solution of the deep purple η^2-ethylene complex [(Ar″O)$_2$Ti(η^2-C$_2$H$_4$)(PMe$_3$)][8] reacts slowly with 1 equiv of PhCH$_2$N=CHPh to produce a light orange solution of the 2-azatitanacyclopentane complex [(Ar″O)$_2$Ti(CH$_2$CH$_2$CHPhNCH$_2$Ph)] (**1**; Scheme I).[9] Both the ^{1}H and ^{13}C NMR spectra of **1** are consistent with its formulation as a metallacyclic compound and not a mixed-olefin, Schiff base complex.[9] However, the CH$_2$CH$_2$ fragment within **1** can readily be displaced by other unsaturated molecules. Heating a mixture of **1** and 3-hexyne or phenylacetylene in benzene at 80 °C for 15 min results in elimination of 1 equiv of ethylene and formation of the corresponding 2-azatitanacyclopent-4-ene complexes **2**[10] and **3**[11] (Scheme I). The coupling reaction with PhC≡CH was found to be highly regioselective, producing only the 3,5-regioisomer (Scheme I)[12] with no evidence for the formation of the other regioisomer after **3** was heated at 80 °C for hours. The regiochemistry was confirmed by hydrolysis of the metallacyclic compounds **2** and **3** to produce the corresponding allylic amines (Scheme I).[13]

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(9) Anal. Calcd for TiC$_{58}$H$_{49}$NO$_2$ (**1**·C$_6$H$_6$): C, 82.94; H, 5.88; N, 1.67. Found: C, 82.63; H, 5.95; N, 2.05. ^{1}H NMR (C$_6$D$_6$, 30 °C; δ): 6.63–7.43 (aromatics); 3.89 (d), 3.24 (d, C*H*$_2$Ph); 3.75 (t, C*H*Ph); 2.21 (m, TiCH$_2$C*H*$_2$); 1.39 (m), 1.15 (m, TiC*H*$_2$). Selected ^{13}C NMR (C$_6$D$_6$, 30 °C; δ): 160.4, 160.1 (Ti–O–*C*); 85.9 (Ti*C*H$_2$); 64.2 (*C*HPh); 57.1 (*C*H$_2$Ph); 33.7 (TiCH$_2$*C*H$_2$).

(10) Anal. Calcd for TiC$_{56}$H$_{49}$NO$_2$ (**2**): C, 82.44; H, 6.05; N, 1.72. Found: C, 82.84; H, 6.27; N, 1.87. ^{1}H NMR (C$_6$D$_6$, 30 °C; δ): 6.76–7.61 (aromatics); 4.35 (s, C*H*Ph); 3.14 (d), 2.90 (d, C*H*$_2$Ph); 1.40 (q), 1.26 (m, C*H*$_2$CH$_3$); 0.55 (t), 0.40 (t, CH$_2$C*H*$_3$). Selected ^{13}C NMR (C$_6$D$_6$, 30 °C; δ): 218.2 (Ti*C*Et); 160.7, 160.4 (Ti–O–*C*); 139.8 (TiCEt*C*Et); 61.7 (*C*H$_2$Ph); 55.5 (*C*HPh); 27.2, 23.8 (*C*H$_2$CH$_3$); 14.8, 13.1 (CH$_2$*C*H$_3$).

(11) Anal. Calcd for TiC$_{58}$H$_{45}$NO$_2$ (**3**): C, 83.34; H, 5.43; N, 1.68. Found: C, 83.00; H, 5.54; N, 1.17. ^{1}H NMR (C$_6$D$_6$, 30 °C; δ): 6.43–7.61 (aromatics); 6.74 (d, TiCPhC*H*); 4.50 (d, C*H*Ph); 3.23 (d), 3.05 (d, C*H*$_2$Ph). Selected ^{13}C NMR (C$_6$D$_6$, 30 °C; δ): 207.5 (Ti*C*Ph); 160.9, 160.6 (Ti–O–*C*); 138.4 (TiCPh*C*H); 58.9 (*C*HPh); 56.6 (*C*H$_2$Ph).

(12) Similar regioselectivity has been observed previously; see: (a) Buchwald, S. L.; Wannamaker, M. W.; Watson, B. T. *J. Am. Chem. Soc.* **1989**, *111*, 776. (b) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486.

Reaction of 1 with benzonitrile also occurs with elimination of ethylene to produce the 2,5-diazatitanacyclopent-2-ene complex 4 (Scheme I).[14] Compound 4 is sufficiently stable to be isolated. However, over days in solution it was found to isomerize to the 2,5-diazatitanacyclopent-3-ene derivative 5 (Scheme I),[15] which was more readily purified as its pyridine adduct **6**.[16] The kinetic product 4 was subjected to a single-crystal X-ray diffraction analysis.[17] Previous work has shown that 2,5-diazatitanacyclopent-3-ene (ene–diamido) derivatives such as 5 are bent with fold angles close to 50°.[18] In contrast, the metallacyclic ring in 4 is rigorously planar (Figure 1). The coordination environment about titanium is pseudotetrahedral. While the two Ti–N distances of 1.886 (2) and 1.910 (2) Å are comparable to those found in ene–diamido compounds of titanium,[18] the C–N distances of 1.277 (3) and 1.466 (3) Å are consistent with the structure shown for 4 (Scheme I).

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

Supplementary Material Available: Text describing the X-ray diffraction study and tables of crystal data and data collection parameters, positional parameters, general temperature factors, and bond distances and angles for 4 (23 pages). Ordering information is given on any current masthead page.

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[13] High-resolution MS for $CHEtCEtCHPhNHCH_2Ph$: calcd, 280.2062; found, 280.2062. ^1H NMR (C_6D_6, 30 °C; δ): 7.04–7.42 (aromatics); 5.62 (t, C*H*Et); 4.41 (s, C*H*Ph); 3.63 (dd, $C\mathit{H}_2Ph$); 1.97 (m, $C\mathit{H}_2CH_3$); 1.32 (broad, N*H*); 0.94 (t), 0.80 (t, CH_2CH_3). Selected ^{13}C NMR (C_6D_6, 30 °C; δ): 68.7 (*C*HPh); 52.2 ($\mathit{C}H_2Ph$); 21.6, 21.4 ($\mathit{C}H_2CH_3$); 14.9, 14.5 ($CH_2\mathit{C}H_3$). High-resolution MS for $CHPhCHCHPhNHCH_2Ph$: calcd, 299.1674; found, 299.1668. ^1H NMR (C_6D_6, 30 °C; δ): 7.0–7.45 (aromatics); 6.51 (d, =C*H*Ph); 6.25 (dd, =C*H*); 4.26 (d, NC*H*Ph); 3.65 (s, $NC\mathit{H}_2Ph$); 1.89 (broad, N*H*). Selected ^{13}C NMR (C_6D_6, 30 °C; δ): 65.1 (N*C*HPh); 51.8 ($N\mathit{C}H_2Ph$).

[14] Anal. Calcd for $TiC_{63}H_{50}N_2O_2$ ($4\cdot C_6H_6$): C, 82.70; H, 5.51; N, 3.06. Found: C, 83.32; H, 5.78; N, 2.99. ^1H NMR (C_6D_6, 30 °C; δ): 6.73–7.62 (aromatics); 5.81 (s, C*H*Ph); 3.72 (d), 2.96 (d, $C\mathit{H}_2Ph$); 161.4, 160.7 (Ti–O–*C*); 90.6 (*C*HPh); 53.5 ($\mathit{C}H_2Ph$).

[15] (a) Isomerization of a 2-azatitanacyclopent-2-ene ring has been reported; see: Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006. (b) For the isomerization of 2-azametallacyclopentene rings see: Strickler, J. R.; Wigley, D. E. *Organometallics* **1990**, *9*, 1605 and references therein.

[16] ^1H NMR for **5** (C_6D_6, 30 °C; δ): 6.36–7.36 (aromatics); 4.21 (s, $C\mathit{H}_2Ph$). Selected ^{13}C NMR for **5** (C_6D_6, 30 °C; δ): 159.2 (Ti–O–*C*); 117.0, 115.0 (TiNH*C*Ph*C*Ph); 58.4 ($\mathit{C}H_2Ph$). Anal. Calcd for $TiC_{62}H_{49}N_3O_2$ (**6**): C, 81.30; H, 5.39; N, 4.59. Found: C, 81.67; H, 5.57; N, 4.49. ^1H NMR for **6** (C_6D_6, 30 °C; δ): 9.91 (broad N*H*); 6.13–7.60 (aromatics); 4.62 (s, $C\mathit{H}_2Ph$). Selected ^{13}C NMR for **6** (C_6D_6, 30 °C; δ): 160.6 (Ti–O–*C*); 56.4 ($\mathit{C}H_2Ph$).

[17] X-ray crystal data for $TiC_{63}H_{50}N_2O_2$, ($4\cdot C_6H_6$) at −50 °C: a = 10.149 (2) Å, b = 13.738 (2) Å, c = 17.774 (2) Å, α = 94.55 (1)°, β = 101.53 (1)°, γ = 93.66 (1)°, Z = 2, d_{calcd} = 1.260 g cm^{-3} in space group $P\bar{1}$ (No. 2). Of the 6271 unique data collected with Mo Kα radiation ($4° \le 2\theta \le 45°$), the 4728 with $I > 3\sigma(I)$ were used in the final refinements to yield R = 0.035 and R_w = 0.038. Hydrogen atoms were placed in ideal positions and were not refined.

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Articles

Rhenium–Platinum Mixed-Metal Clusters. Synthesis and Solid-State Structural Characterization of $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$ and of $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$

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The reaction of $[Re_2(\mu\text{-}H)_2(CO)_8]$ with 1 equiv of $Pt(COD)_2$ (COD = 1,5-cyclooctadiene) affords quantitatively the triangular cluster $[Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)]$, characterized spectroscopically and by X-ray analysis. The crystals are monoclinic, space group $P2_1$, with a = 7.217 (3) Å, b = 17.081 (5) Å, c = 8.577 (3) Å, β = 109.96 (3)°, and Z = 2. The refinements, based on 2037 significant reflections, gave final agreement indices R and R_w of 0.021 and 0.025, respectively. The ligand COD can be easily substituted by two PPh_3 molecules. On the contrary, the reaction with 2 equiv of CO, at 190 K, leads to the substitution of COD by one CO and one $HRe(CO)_5$ molecule, giving the complex $[Re_3Pt(\mu\text{-}H)_3(CO)_{14}]$, whose structure has been elucidated by X-ray analysis. It gives triclinic crystals, space group $P\bar{1}$, with a = 11.764 (1) Å, b = 13.737 (4) Å, c = 15.787 (3) Å, α = 64.83 (2)°, β = 83.36 (1)°, γ = 89.19 (2)°, and Z = 4. The refinements, based on 4461 significant reflections, gave final agreement indices R and R_w of 0.031 and 0.032, respectively. The structure contains a tetrametal cluster consisting of a Re_2Pt triangle plus a Re atom, which belongs to an unusual $HRe(CO)_5$ two-electron donor ligand, bound to the platinum atom. The ^1H NMR spectrum of this complex shows, at 180 K, the presence of two isomers.

We are currently investigating rational approaches to the synthesis of Re–Pt mixed-metal clusters, as potential models or precursors to catalytic species. Following the method developed by the Stone group,[1] trimetallacyclo-

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