Inorg. Chem. **1998,** *37,* 4732−4734

Notes

Cyclopentadienyl−Bis-Aryloxide Titanium Complexes

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Received January 26, 1998

Introduction

In our recent studies of alkylated monocyclopentadienyl−titanium−thiolate complexes, we have observed complex and competing reaction pathways.[1−3] Among the products, we have found evidence of C−H and C−S bond activation as well as reduction of Ti(IV) to Ti(III). Incorporation of the bulky ancillary ligand 2,6-diisopropylaryloxide in analogous systems limited the accessible pathways and thus allowed C−H and C−S bond activation reactions to be studied separately. As part of a more general investigation of Ti−aryloxide derivatives, we have prepared a series of derivatives containing at least two of these aryloxide ligands. Structural data for these compounds provided insight into the electronic and steric features of these ancillary ligands. The implications of these data are considered.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing either Schlenk line techniques or a Vacuum Atmospheres inert atmosphere glovebox. Solvents were reagent grade, distilled from the appropriate drying agents under N_2, and degassed by the freeze−thaw method at least three times prior to use. All organic reagents were purified by conventional methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Avance 300 and 500 MHz instruments. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$. Low- and high-resolution EI mass spectra were obtained employing a Kratos Profile mass spectrometer outfitted with a N_2 glovebag enclosure for the inlet port. $CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2Cl$ was prepared via a known method.[3] Elemental analyses were performed by E+R Microanalytical Laboratory Inc., Corona, NY.

Synthesis of $CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_3$ (1), $CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2(NH(C_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)$ (2), $CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2(SPh)$ (3), and $CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2PHPh$ (4). These compounds were prepared in a similar manner, with the appropriate substitution of $HOC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2$, $H_2NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2$, HSPh, or H_2PPh. Thus only one preparation is described in detail. To $CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2Cl$ (95 mg, 0.19 mmol) dissolved in hexane (2 mL) were added HOR* (33.8 mg, 0.19 mmol) and *t*-BuLi dropwise (110.7 μL of a 1.7 M solution, 0.19 mmol). The reaction mixture was stirred overnight and filtered, and the solvent was removed to reduce the volume to 0.5 mL. Yellow crystals of **1** were obtained in 78% yield. **1**: ^{1}H NMR (C_6D_6, 25 °C) δ 1.22 (d, 36H, $|J_{H-H}| = 6.8$ Hz), 3.68 (sept, 6H, $|J_{H-H}| = 6.8$ Hz), 6.30 (s, 5H), 6.94 (t, 3H, $|J_{H-H}| = 7.6$ Hz), 7.05 (d, 6H, $|J_{H-H}| = 7.6$ Hz). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 23.3, 25.8, 116.4, 121.6, 122.8, 136.7, 162.1. Calcd for $C_{41}H_{56}TiO_3$: (HRMS) 643.3869. Found: 643.3844. Anal. Calcd: C, 76.37; H, 8.75. Found: C, 76.25; H, 8.66. **2**: red crystals, yield = 60%. ^{1}H NMR (C_6D_6, 25 °C): δ 1.17 (d, 12H, $|J_{H-H}| = 7$ Hz), 1.23 (d, 12H, $|J_{H-H}| = 7$ Hz), 1.27 (d, 12H, $|J_{H-H}| = 7$ Hz), 3.48 (sept, 2H, $|J_{H-H}| = 7$ Hz), 3.75 (sept, 4H, $|J_{H-H}| = 7$ Hz), 6.24 (s, 5H), 6.92 (m, 3H), 7.06 (m, 6H), 8.93 (s, 1H). ^{13}C{^{1}H} NMR (C_6D_8, 25 °C): δ 24.3, 24.5, 27.7, 28.7, 116.7, 122.2, 122.7, 123.8, 124.4, 137.7, 139.9, 152.0, 162.6. Calcd for $C_{41}H_{57}TiO_2N$: (HRMS) 644.3709. Found: 644.3690. Anal. Calcd: C, 76.49; H, 8.92; N, 2.18. Found: C, 76.15; H, 8.78; N, 2.01. **3**: red crystals, yield = 86%. ^{1}H NMR (C_6D_6, 25 °C): δ 1.10 (d, 12H, $|J_{H-H}| = 7$ Hz), 1.23 (d, 12H, $|J_{H-H}| = 7$ Hz), 3.72 (sept, 4H $|J_{H-H}| = 7$ Hz), 6.10 (s, 5H), 6.80−6.92 (m, 11H), 7.80 (d, 2H). ^{13}C{^{1}H} NMR (C_6D_8, 25 °C): δ 24.7, 26.5, 117.3, 122.8, 123.8, 125.3, 128.8, 131.2, 138.4, 146.8, 162.7. Calcd for $C_{35}H_{44}TiO_2S$: (HRMS) 576.2542. Found: 576.2533. Anal. Calcd: C, 72.89; H, 7.69. Found: C, 72.59; H, 7.46. **4**: purple crystals, yield = 91%. ^{1}H NMR (C_6D_8, −43 °C): δ 1.29 (d, 12H, $|J_{H-H}| = 6.5$ Hz), 1.25 (d, 12H, $|J_{H-H}| = 6.5$ Hz), 3.60 (sept, 4H, $|J_{H-H}| = 6.5$ Hz), 4.8 (d, 1H, $|J_{P-H}| = 189$ Hz), 5.98 (s, 5H), 7.03 (br, 1H), 7.17 (br, 2H), 7.28 (br, 1H), 7.44 (br, 4H). ^{13}C{^{1}H} NMR (C_6D_8, −43 °C): δ 23.3, 25.8, 116.4, 121.6, 122.8, 132.3(d, $|J_{P-C}| = 31.3$ Hz), 136.7, 162.1. ^{31}P NMR (THF, 25 °C): δ 43.0 (d, $|J_{P-H}| = 189$ Hz). ^{31}P{^{1}H} NMR (THF, 25 °C) δ: 43.0 (s). Calcd for $C_{35}H_{45}TiO_2P$: (HRMS) 576.2637. Found: 576.2622. Anal. Calcd: C, 72.91; H, 7.87. Found: C, 72.73; H, 7.56.

X-ray Data Collection and Reduction. X-ray quality crystals of **1**−**4** were obtained directly from the preparation as described above. The crystals were manipulated and mounted in capillaries in a glovebox, a dry, O_2-free environment thus being maintained for each crystal. Diffraction experiments were performed on a Rigaku AFC6 diffractometer equipped with graphite-monochromatized Mo Kα radiation or on a Siemens SMART system CCD diffractometer. When the Rigaku diffractometer was used, the initial orientation matrices were obtained from 20 machine-centered reflections selected by an automated peak search routine. These data were used to determine the crystal systems. Automated Laue system check routines around each axis were consistent with the crystal system. Ultimately, 25 reflections ($20° < 2\theta < 25°$) were used to obtain the final lattice parameters and the orientation matrices. Crystal data are summarized in Table 1. The observed extinctions were consistent with the space groups in each case. The data sets were collected in three shells ($4.5° < 2\theta < 45−50.0°$), and three standard reflections were recorded every 197 reflections. Fixed scan rates were employed. Up to 4 repetitive scans of each reflection at the respective scan rates were averaged to ensure meaningful statistics. The number of scans of each reflection was determined by the intensity. The intensities of the standards showed no statistically significant change over the duration of the data collections. The data were processed using the TEXSAN crystal solution package operating on a SGI Challenger mainframe with remote X-terminals. The reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinements.

Diffraction experiments performed on a Siemens SMART System CCD diffractometer involved collecting a hemisphere of data in 1329 frames with 10 s exposure times. A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing package. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package operating on a SGI computer.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[4] The Ti atom positions were determined using direct methods employing either the

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S0020-1669(98)00084-6 CCC: $15.00

Table 1. Crystallographic Data[a]

	1	**2**	**3**	**4**
formula	$C_{41}H_{56}O_3Ti$	$C_{41}H_{57}O_2NTi$	$C_{35}H_{44}O_2STi$	$C_{35}H_{45}O_2PTi$
fw	644.796	643.811	576.700	577.624
a, Å	10.519(6)	15.2195(2)	11.74(1)	10.8826(2)
b, Å	19.28(1)	14.2922(2)	14.15(1)	
c, Å	19.093(5)	18.5400(4)	10.264(8)	49.7421(11)
α, deg			92.66(7)	
β, deg	97.46(4)	107.610(7)	102.44(7)	
γ, deg			78.73(7)	
V (Å^3)	3839(3)	3869.1(2)	1632(2)	5101.8(2)
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P6_1$
Z	4	4	2	6
μ, cm^{-1}	2.57	2.68	1.73	3.25
data collected	7471	21120	6052	14195
data $F_o^2 > 3\sigma(F_o^2)$ 799	2147	825	4236	
D_{calcd} (g cm^{-1})	1.12	1.32	1.17	1.13
R (%)	9.70	7.70	9.10	9.25
R_w(%)	8.30	6.70	6.90	22.94[a]
goodness of fit	2.510	2.080	2.030	1.601

[a] All data were collected at 24 °C. The marked *R* value is based on all data. $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum(|F_o| - |F_c|)^2|/\sum|F_o|^2]^{0.5}$, GOF = $\sum(|F_o| - |F_c|)/\sigma)/(n - \mathrm{m})$.

SHELXTL or Mithril direct methods routines. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $\omega(|F_o| - |F_c|)^2$ where the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, the number of non-hydrogen atoms assigned anisotropic temperature factors was determined so as to maintain a reasonable data:variable ratio. The remaining atoms were assigned isotropic temperature factors. Empirical absorption corrections were applied to the data sets based either on ψ-scan data or on a DIFABS calculation and employing the software resident in the TEXSAN or SHELXTL packages. Hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen atom contributions were calculated, but not refined. The final values of *R*, R_w, and the goodness of fit in the final cycles of the refinements are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Tables of crystallographic data have been deposited as Supporting Information.

Results and Discussion

Nucleophilic substitution reactions employing $CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2Cl$, base, and the appropriate reagent offer facile access to the series of compounds $CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_3$ (**1**), $CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2(NH(C_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)$ (**2**), $CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2(SPh)$ (**3**), and $CpTi(OC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2PHPh$ (**4**) (Figures 1−4). ^1H and ^{13}C NMR data were consistent with the above formulations. In the case of **4**, ^{31}P NMR revealed a resonance at 43.0 ppm with a single P−H coupling of 189 Hz, consistent with the formation of the Ti(IV) phosphide derivative.

It is noteworthy that, while reactions analogous to those described above are commonplace in early metal chemistry, typically reactions of phosphides with Ti(IV) reagents lead to reduction. In fact, the only known examples of Ti(IV)−P σ-bonded compounds are the di- and triphosphinato derivatives of the forms $Cp_2Ti[(PR_2)_2]$[5] and $Cp_2Ti[(PR_2)_3$.[6] Thus, compound **4** is the first structurally characterized Ti(IV)−phosphide derivative. We have previously noted that the incorporation of aryloxides as ancillary ligands helps to fend off reduction. Clearly, the isolation of **4** supports this view.

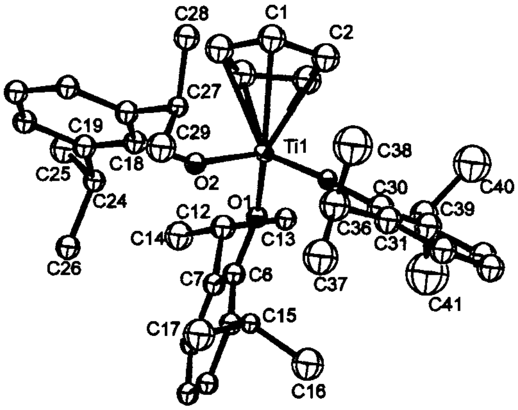

Figure 1. ORTEP drawing of **1**; 30% thermal ellipsoids are shown, and hydrogen atoms are omitted for clarity. Distances (Å): Ti(1)−O(1) 1.80(2), Ti(1)−O(2) 1.79(2), Ti(1)−O(3) 1.80(2). Angles (deg): O(1)−Ti(1)−O(2) 102.7(8), O(1)−Ti(1)−O(3) 101.7(8), O(2)−Ti(1)−O(3) 103.8(8), Ti(1)−O(1)−C(6) 152(1), Ti(1)−O(2)−C(18) 145(1), Ti(1)−O(3)−C(30) 163(1).

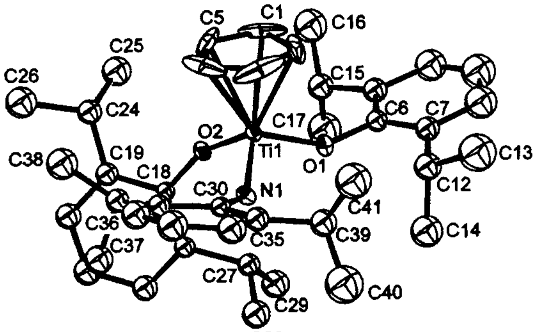

Figure 2. ORTEP drawing of **2**; 20% thermal ellipsoids are shown, and hydrogen atoms are omitted for clarity. Distances (Å): Ti(1)−O(1) 1.844(6), Ti(1)−O(2) 1.850(6), Ti(1)−N(1) 1.900(7). Angles (deg): O(1)−Ti(1)−O(2) 101.6(3), O(1)−Ti(1)−N(1) 103.4(3), O(2)−Ti(1)−N(1) 104.6(3), Ti(1)−O(1)−C(6) 147.0(6), Ti(1)−O(2)−C(18) 147.1(5), Ti(1)−N(1)−C(30) 138.6(6).

Crystallographic studies of **1**−**4** were performed, and in each case the results confirmed the formulations above. The molecular structure of each of these compounds is best described

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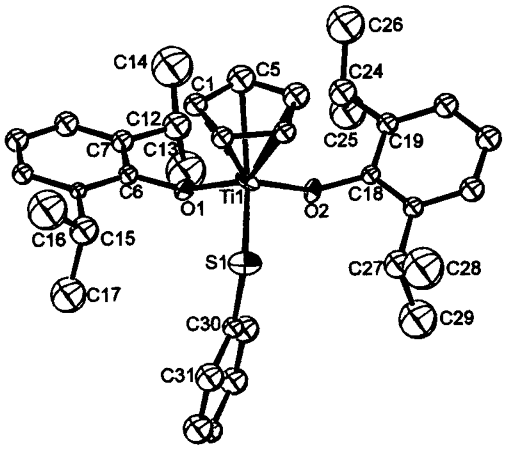

Figure 3. ORTEP drawing of **3**; 20% thermal ellipsoids are shown, and hydrogen atoms are omitted for clarity. Distances (Å): Ti(1)−S(1) 2.349(7), Ti(1)−O(1) 1.80(2), Ti(1)−O(2) 1.81(1). Angles (deg): S(1)−Ti(1)−O(1) 105.9(5), S(1)−Ti(1)−O(2) 105.8(5), O(1)−Ti(1)−O(2) 105.0(8), Ti(1)−S(1)−C(30) 107.2(7), Ti(1)−O(1)−C(6) 150(1), Ti(1)−O(2)−C(18) 144(1).

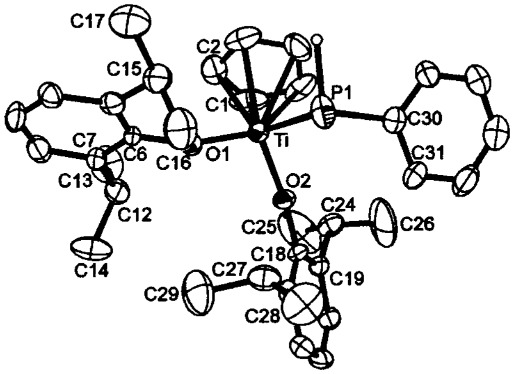

Figure 4. ORTEP drawing of **4**; 20% thermal ellipsoids are shown, and hydrogen atoms are omitted for clarity. Distances (Å): Ti(1)−O(2) 1.805(5), Ti(1)−O(1) 1.819(5), Ti(1)−P(1) 2.543(3). Angles (deg): O(2)−Ti(1)−O(1) 105.4(2),O(2)−Ti(1)−P(1) 97.3(2),O(1)−Ti(1)−P(1) 98.6(2), C(30)−P(1)−Ti(1) 100.7(3),C(6)−O(1)−Ti(1) 155.6(5),C(18)−O(2)−Ti(1) 171.6(5).

as that of a distorted “three-legged piano stool”. The Ti−O bonds in **1**, **3**, and **4** are comparable, averaging 1.80(2) Å. These values compare to those found in a variety of related compounds including CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)Cl(SPh), [CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(SCHCH$_3$)]$_2$, CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(SCH$_2$Ph)$_2$, CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(SCH$_2$CH$_3$)$_2$, and [CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)(μ-S)]$_2$. In contrast, the Ti−O distances in compound **2** are slightly longer, being 1.844(6) and 1.850(6) Å, suggesting a weaker Ti−O interaction. These observations are also consistent with the diminished Ti−O−C angles, which are 147.0(6)° and 147.1(5)° in **2**. In contrast, the Ti−O−C angles in **1**, **3**, and **4** range from 150(1)° to 171.6(5)°. While all of these Ti−O−C angles are certainly greater than those expected from a pyramidal oxygen atom, these angles do not correlate with the corresponding Ti−O distances. Thus, the proposition of Ti−O π-bonding is not supported by these structural data.

In the case of compounds **2**−**4** the Ti−N, Ti−S, and Ti−P distances are 1.900(7), 2.349(7), and 2.543(3) Å and are comparable to those found in CpTiCl$_2$NHNMe$_2$,[7] CpTi(OC$_6$H$_3$-2,6-*i*-Pr$_2$)Cl(SPh),[1] and Cp$_2$Ti[(PPh)]$_2$,[5] respectively. The Ti−N−C angle in **2** is 138.6(6)°, and the angles about N sum to 359.2°. In addition, the NCH plane is correctly oriented so as to permit a π interaction with the 1e$_2$ molecular orbitals of the CpTiL$_3$ unit. Certainly, in other systems early metal−nitrogen π bonding has been substantiated previously.[8] Nonetheless, workers have demonstrated that planarity at N is sterically favorable for early metal amides and thus not necessarily an indication of π bonding.[9,10] In the case of **4**, the angles about P sum to 297°. These metric parameters and the orientation of the phosphorus substituents discount any Ti−P π interaction. Similarly, for **3**, the geometry about sulfur does not abide with π donation.

In general, the structural data show no correlation of the angles about oxygen and the Ti−O distances. Furthermore, the structures of compounds **3** and **4** provide no evidence of Ti−S or Ti−P π bonding. It is clear that these observations support the argument, originally put forward by others, that steric factors play a large role in determining the geometry of early metal complexes.[9−11] In this regard, it is interesting that the steric congestion associated with three bulky ancillary ligands in **1**−**4** gives similar ligand orientations. In each case for **1**−**4**, two of the aryl rings of the ligands are very approximately parallel to the cyclopentadienyl ring while the third ring is oriented almost perpendicular to these planes. This packing arrangement presumably dictates the Ti−E−C angles (E = O, N, S, P) and alleviates the steric congestion, accommodating the proximate isopropyl groups which crowd around the metal center.

Acknowledgment. This work was supported by the NSERC of Canada.

Supporting Information Available: X-ray crystallographic files, in CIF format, for compounds **1**−**4** are available on the Internet only. Access information is given on any current masthead page.

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