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Dihydrogen and Silane Addition to Base-Free, Monomeric Bis(cyclopentadienyl)titanium Oxides

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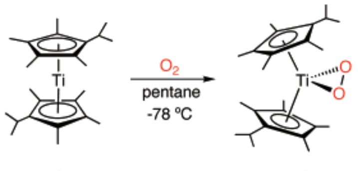
Synthesis of a family of monomeric, base-free bis(cyclopentadienyl)titanium oxide complexes, $(\eta^5\text{-}C_5Me_4R)_2Ti{=}O$ (R = ^iPr, $SiMe_3$, $SiMe_2Ph$), has been accomplished by deoxygenation of styrene oxide by the corresponding sandwich compound. One example, $(\eta^5\text{-}C_5Me_4SiMe_2Ph)_2Ti{=}O$, was characterized by X-ray diffraction. All three complexes undergo clean and facile hydrogenation at 23 °C, yielding the titanocene hydroxy hydride complexes $(\eta^5\text{-}C_5Me_4R)_2Ti(OH)H$. For $(\eta^5\text{-}C_5Me_4SiMe_3)_2Ti{=}O$, the kinetics of hydrogenation were first-order in dihydrogen and exhibited a normal, primary kinetic isotope effect of 2.7(3) at 23 °C consistent with a 1,2-addition pathway. Isotope effects of the same direction but smaller magnitudes were determined for silane addition.

The addition of molecular hydrogen across a metal−oxygen bond is of interest, in part, because of the potential role of this transformation in the hydrogenation of carbon monoxide to methanol.[1] Despite the ubiquity of metal oxides, the direct observation of the addition of dihydrogen across metal−oxygen bonds in homogeneous compounds remains rare. The reduction of permanganate by dihydrogen to MnO_2 has been known for almost a century[2] and is believed to proceed through Mn^V and a [3 + 2] cycloaddition pathway.[3] More recently, Mayer and co-workers discovered the ligand-induced hydrogenation of OsO_4, where kinetic, mechanistic, and density functional theory (DFT) studies also support [3 + 2] cycloaddition.[4] In early transition metal chemistry, hydrogenation of $Cp^*_2Zr({=}O)py$ ($Cp^* = \eta^5\text{-}C_5Me_5$; py = pyridine) proceeds cleanly and yields $[Cp^*_2Zr(H)](\mu_2\text{-}O)[Cp^*_2Zr(OH)]$. This product most likely arises from the initial 1,2-addition of dihydrogen to yield a transient zirconocene hydroxy hydride, which undergoes subsequent chemistry with the base-stabilized oxo to yield the observed product.[5a] The base-stabilized zirconocene oxo also promotes addition chemistry with alkyl halide electrophiles.[5] In this contribution, we describe the synthesis of a family of monomeric, base-free titanocene oxide complexes and report the clean 1,2-addition of dihydrogen and silanes across the Ti=O bond.

The isolation of thermally stable bis(cyclopentadienyl)titanium sandwich compounds, $(\eta^5\text{-}C_5Me_4R)_2Ti$ (R = alkyl, silyl),[6] has provided a rare opportunity to study the fundamental reaction chemistry at a well-defined, divalent titanocene center. The introduction of sterically demanding silyl- and alkylcyclopentadienyl substituents has resulted in the isolation of unusual mono(dinitrogen), mono(carbonyl),[7] and bis(dinitrogen) compounds.[8] On the basis of these observations, the synthesis of monomeric, base-free titanocene oxide complexes was targeted because ligand coordination is typically required to stabilize complexes such as $[(\eta^5\text{-}C_5Me_5)_2Ti{=}O]$.[9]

Ideally, preparation of the desired base-free terminal oxo derivatives could be accomplished directly from dioxygen. Exposure of a pentane solution of $(\eta^5\text{-}C_5Me_4{}^iPr)_2Ti$ (**1**) to a slight excess of dioxygen gas at −78 °C furnished a diamagnetic yellow solid identified as $(\eta^5\text{-}C_5Me_4{}^iPr)_2Ti(\eta^2\text{-}O_2)$ (**1-O₂**) based on NMR spectroscopy, X-ray diffraction, and combustion analysis (eq 1).



1 **1-O₂** (1)

In a benzene-d_6 solution at 23 °C, **1-O₂** decomposes over the course of hours. Despite this complication, the solid-

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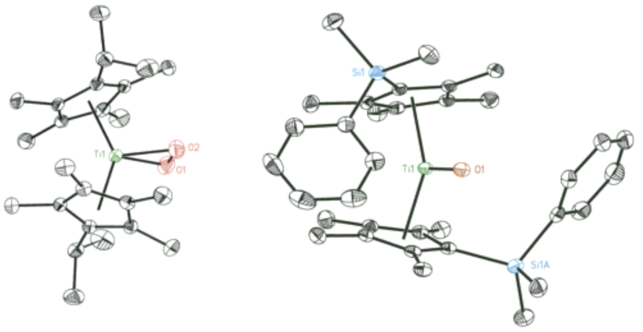
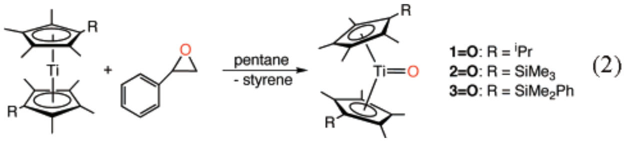


Figure 1. Molecular structure of **1-O$_2$** (left) and **3═O** (right) at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

state structure was determined (Figure 1) and confirms the side-on hapticity of the peroxide ligand. The O−O bond length of 1.441(4) Å, coupled with the Ti−O1 and Ti−O2 distances of 1.906(3) and 1.910(3) Å, is also consistent with a Ti^{IV} center and an $[O_2]^{2-}$ fragment.[10]

Because treatment of the titanium sandwich with dioxygen did not yield the desired terminal oxo compound, O-atom abstraction routes were explored. The addition of 1 equiv of styrene oxide to a pentane solution of **1** immediately released a stoichiometric quantity of styrene and yielded a new C_{2v}-symmetric titanium compound identified as the monomeric oxo species, $(\eta^5\text{-}C_5Me_4{}^iPr)_2Ti{=}O$ (**1═O**). A similar synthetic procedure was used for the preparation of $(\eta^5\text{-}C_5Me_4SiMe_3)_2Ti{=}O$ (**2═O**) and $(\eta^5\text{-}C_5Me_4SiMe_2Ph)_2Ti{=}O$ (**3═O**) (eq 2).

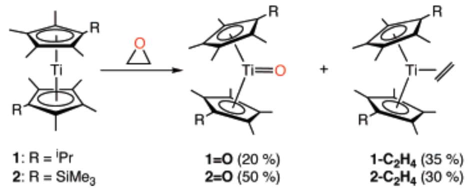


(2)

The relative stability of each oxo derivative is related to the cyclopentadienyl substituent. The least sterically protected member of the series, isopropyl-substituted **1═O**, undergoes decomposition ($t_{1/2} \sim 48$ h) over the course of days at 23 °C in pentane. Two products, $(\eta^5\text{-}C_5Me_4{}^iPr)_2Ti(OH)_2$ (**1-(OH)$_2$**) and $(\eta^5\text{-}C_5Me_4{}^iPr)_4Ti_4O_6$, were cleanly and reproducibly formed in a 4:1 ratio. An unidentified NMR-silent material, accounting for approximately 50% of the mixture, was also obtained and was protonated with HCl to yield a 3:2 mixture of $(\eta^5\text{-}C_5Me_4{}^iPr)_2TiCl_2$ and $(\eta^5\text{-}C_5Me_4{}^iPr)TiCl_3$. The silylated compounds, **2═O** and **3═O**, have proven to be more stable and were isolated in the solid state. At 23 °C, decomposition occurs over the course of weeks and also yields $(\eta^5\text{-}C_5Me_4SiMe_2R)_4Ti_4O_6$ and an NMR-silent material. One of the clusters, $(\eta^5\text{-}C_5Me_4SiMe_3)_4Ti_4O_6$, was characterized by X-ray diffraction[11] and is structurally similar to $(\eta^5\text{-}C_5Me_5)_4Ti_4O_6$.[12]

One of the monomeric terminal oxo compounds, **3═O**, was characterized by X-ray diffraction (Figure 1) and exhibits idealized C_2 molecular symmetry, with the Ti═O bond serving as the principal axis. The Ti═O bond length of 1.670(2) Å is statistically equivalent to the Ti═O distance of 1.665(3) Å for pyridine-stabilized $(\eta^5\text{-}C_5Me_5)_2Ti({=}O)L$[9b] and is similar to those reported in non-cyclopentadienyl-ligated titanium oxides.[13]

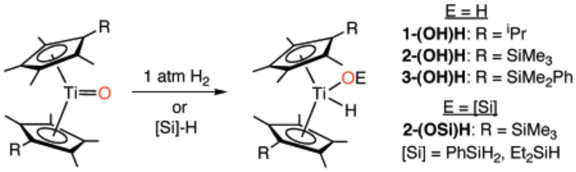
Attempts to prepare **1═O** and **2═O** by O-atom abstraction from ethylene oxide (EO) produced a different outcome. Treatment of **1** with 1 equiv of EO yielded 20% **1═O** and 35% $(\eta^5\text{-}C_5Me_4{}^iPr)_2Ti(\eta^2\text{-}CH_2{=}CH_2)$ (**1-C$_2$H$_4$**). The remaining 45% was an unidentified NMR-silent product that converted to $(\eta^5\text{-}C_5Me_4{}^iPr)_2TiCl_2$ and $(\eta^5\text{-}C_5Me_4{}^iPr)TiCl_3$ upon treatment with HCl. Performing a similar experiment with **2** yielded 50% **2═O**, 30% **2-C$_2$H$_4$**, and 20% NMR-silent material (eq 3). Similar results were obtained when the order of addition was reversed.



(3)

Both **1-C$_2$H$_4$** and **2-C$_2$H$_4$** were independently prepared by treating **1** and **2** with ethylene, respectively. Observation of the olefin complexes following the addition of EO to **1** and **2** suggests that, for smaller O-atom donors, epoxide coordination is slow compared to ring-opening and olefin loss, allowing ethylene capture by the unreacted sandwich. Because the amount of the ethylene complex remains essentially constant, the relative amount of NMR-silent material formed from **1** and **2** likely reflects the stability of **1═O** versus **2═O**.

With monomeric, base-free titanocene oxo complexes in hand, fundamental 1,2-addition chemistry of the Ti═O bond was explored. The addition of dihydrogen to **1═O**, **2═O**, or **3═O** furnished the corresponding titanocene hydroxy hydride compounds, $(\eta^5\text{-}C_5Me_4R)_2Ti(OH)H$ (eq 4). The observation of clean hydrogenation chemistry highlights the importance of base-free titanium oxo compounds because the ligand-stabilized variant, $(\eta^5\text{-}C_5Me_5)_2Ti({=}O)L$, yields a mixture of products including $(\eta^5\text{-}C_5Me_5)_2Ti(OH)_2$ and $(\eta^5\text{-}C_5Me_5)_2Ti(OH)H$ upon dihydrogen addition.[14]



(4)

Both primary and secondary silanes also produced clean 1,2-addition chemistry. The addition of either $PhSiH_3$ or Et_2SiH_2 to **2═O** yielded the corresponding titanocene siloxy

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hydride complex, **2-(OSi)H**, as judged by NMR and IR spectroscopies (eq 4). No reaction was observed upon addition of the tertiary silane Et_3SiH.

The mechanism of both dihydrogen and silane addition to **2═O** was investigated in more detail. In a pentane solution, **2═O** exhibits a weak band ($\epsilon = 170\ cm^{-1}\ M^{-1}$) centered at 746 nm assigned as a ligand-to-metal charge transfer. The low intensity of the peak is likely the result of a symmetry-forbidden excitation from the $^1A_1$ state to the $^1A_2$ state. A depiction of the DFT-computed frontier molecular orbitals for this compound is reported in the Supporting Information. Monitoring the disappearance of this band as a function of time in the presence of 370 equiv of dihydrogen at 23 °C yielded a pseudo-first-order rate constant of $8.5(5) \times 10^{-3}\ s^{-1}$ for Ti═O hydrogenation. The corresponding experiment with dideuterium gas produced a value of $3.2(2) \times 10^{-3}\ s^{-1}$ and a normal, primary kinetic isotope effect of 2.7(3) at 23 °C. Attempts to measure the pressure dependence of dihydrogen on the observed rate constants have met with mixed success. At high pressures ($P_{H_2} > 0.537$ atm; 225 equiv), a linear correlation is observed and is reproducible.[11] At lower pressures, significant deviations are observed. The origin of this behavior is not completely understood but is likely due to inefficient gas mixing with the pentane solution.

Kinetic isotope effects were also determined for silane addition. Measuring the product ratio following the addition of 10 equiv of an equimolar mixture of $PhSiH_3/PhSiD_3$ to **2═O** yielded a kinetic isotope effect of 1.5(1) at 23 °C. Control experiments were conducted and did not produce crossover between the isotopologues of the products. A similar value of 1.2(1) (23 °C) was measured using the same procedure as for the addition of Et_2SiH_2/Et_2SiD_2. Kinetic isotope effects of this direction and magnitude are comparable to those measured for silane addition to the putative $(\eta^5\text{-}C_5Me_5)_2Ti{=}S$ complex[14] and are significantly smaller than that for dihydrogen/dideuterium addition, possibly as a result of a less symmetric transition structure arising from the addition of a relatively polar Si−H bond.

The relative rate of dihydrogen 1,2-elimination from **1-(OH)H** was probed by exchange NMR spectroscopy. No cross-peaks between the Ti−H and O−H bonds were observed up to 90 °C (mixing time 700 ms), demonstrating that intramolecular exchange does not occur on the NMR time scale. Similar behavior was observed with **2-(OSi)H**. These barriers are higher than those reported for the analogous sulfido complex $(\eta^5\text{-}C_5Me_5)_2Ti(SH)H$, where the intramolecular process occurred on the NMR time scale, implicating an $\eta^2\text{-}H_2$ intermediate.[14] The higher barrier for 1,2-elimination in **1-(OH)H** is consistent with a dominant ground-state effect resulting from a stronger O−H bond as compared to an S−H bond. Intermolecular exchange, as judged by isotopic exchange between **1-(OD)D**[16] and free dihydrogen, occurs over the course of hours at 23 °C. The converse experiment, dideuterium addition to **1-(OH)H**, also produced isotopic exchange with no evidence for competing cyclometalation. Similar experiments with isotopologues of **2-(OSi)H** (Si = $PhSiH_2$) and free silane also established that intermolecular exchange occurs with a higher barrier because crossover was observed only upon heating to 70 °C for several hours.

Attempts were also made to activate C−H bonds of saturated and unsaturated hydrocarbons with **2═O**. No changes were observed upon the addition of excesses (typically 10 equiv) of CH_4, ethylene, or benzene (neat), despite the established propensity for these molecules to participate in 1,2-addition chemistry.[17] Warming these mixtures simply hastened decomposition of the titanocene oxide. This lack of reactivity contrasts the facile C−H chemistry observed with transiently generated titanocene alkylidene complexes[18] and unsaturated imide compounds[19] and is likely a result of stronger Ti═E π bonding for the oxo derivative. For dihydrogen and silanes, rupture of relatively weak H−H and Si−H bonds, coupled with the formation of strong O−H and Si−O linkages, renders these reactions spontaneous.

In summary, the introduction of large alkyl- and silylcyclopentadienyl substituents has resulted in stabilization of monomeric, base-free titanocene oxide complexes. These molecules undergo facile 1,2-addition of dihydrogen and Si−H bonds of primary and secondary silanes but are unreactive toward C−H bonds of saturated and unsaturated hydrocarbons because of their inability to overcome strong Ti═O π bonding.

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Supporting Information Available: Experimental procedures, kinetic data, and crystallographic data for **1-O$_2$** and **3═O** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 636540 contains the supplementary data for **2-cluster** and can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (12 Union Road, Cambridge CB2 1EZ, U.K.; tel +44 1223 336408; fax +44 1223 336033).

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