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Mono(dinitrogen) and Carbon Monoxide Adducts of Bis(cyclopentadienyl) Titanium Sandwiches

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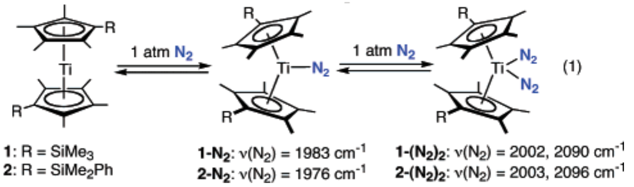
The unique sandwich structure of ferrocene has inspired the preparation of related bis(cyclopentadienyl) complexes with transition metals from across the periodic table.[1] Introduction of sterically demanding cyclopentadienyl rings by Lawless and Mach has provided the first examples of the long sought after titanium sandwiches, (η^5-$C_5Me_4R)_2$Ti (R = alkyl, silyl),[2] allowing exploration of the electronic structure and reactivity of these unique molecules. Investigations from our laboratory have demonstrated that many of these compounds coordinate dinitrogen at low temperature, providing monomeric (η^5-$C_5Me_4R)_2Ti(N_2)_2$ compounds.[3] Here we describe a new entry into the coordination chemistry of group 4 sandwich compounds with the synthesis and characterization of thermally stable *mono*(dinitrogen) and carbonyl adducts of substituted bis(cyclopentadienyl) titanium derivatives along with mixed dinitrogen−carbon monoxide compounds.

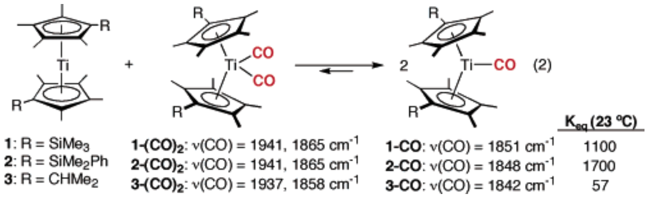
We previously observed that cooling (η^5-$C_5Me_4SiMe_3)_2$Ti to −45 °C produced a single new N≡N stretch centered at 1983 cm^{-1} in the solution infrared spectrum. This band was tentatively assigned to the mono(dinitrogen) compound, (η^5-$C_5Me_4SiMe_3)_2Ti(N_2)$ (eq 1).[3] Warming the sample above this temperature resulted in N_2 loss, complicating both the isolation and further characterization of this unique compound. Alkyl-substituted titanium sandwiches, such as (η^5-$C_5Me_4CHMe_2)_2$Ti (**3**), do not yield observable mono(dinitrogen) complexes upon cooling, forming only the bis(dinitrogen) complex, (η^5-$C_5Me_4CHMe_2)_2Ti(N_2)_2$ (**3-(N$_2$)$_2$**), at −35 °C. As a result, titanocenes bearing more sterically demanding and electron-withdrawing silyl substituents were prepared with the goal of isolating the mono(dinitrogen) compound.



Cooling a pentane solution of (η^5-$C_5Me_4SiMe_2Ph)_2$Ti (**2**) to −35 °C produced a single N≡N infrared stretch centered at 1976 cm^{-1}. Notably, bands for the bis(dinitrogen) complex, **2-(N$_2$)$_2$**, were not observed until the solution was cooled to −60 °C. In preparative experiments, reduction of (η^5-$C_5Me_4SiMe_2Ph)_2$TiCl with excess 0.5% Na(Hg) followed by filtration and recrystallization from pentane at −35 °C under an atmosphere of N_2 furnished red−purple dichroic crystals of **2-N$_2$** in 83% yield. In addition to ^{1}H NMR spectroscopy, diamagnetic **2-N$_2$** was characterized by single-crystal X-ray diffraction (Figure 1). In the solid state, the molecule is C_2 symmetric with the principal axis containing the Ti−N_2 bonds. The Ti(1)−N(1) and N(1)−N(2) distances of 2.016(1) and 1.119(2) Å are consistent with a weakly activated dinitrogen ligand and comparable to the distances found in **3-(N$_2$)$_2$**.[3] Comparison of the IR stretching frequencies of **2-(N$_2$)** (ν_{N2} = 1976 cm^{-1}) to the corresponding bis(dinitrogen) compound, **2-(N$_2$)$_2$** (ν_{N2} = 2003, 2096 cm^{-1}), indicated a more activated N_2 ligand in the former, consistent with increased back-bonding when only one π-acid ligand is present.

The isolation and crystallographic characterization of **2-(N$_2$)** prompted exploration into the synthesis of related titanocene monocarbonyl derivatives. Unlike the dicarbonyl compounds, which have been known for decades,[4] titanocene monocarbonyls have eluded isolation despite being implicated as intermediates in both ligand substitution[5] and catalytic reactions.[6] The parent compound, (η^5-$C_5H_5)_2$Ti(CO) (ν_{CO} = 1890 cm^{-1}), has only been observed by IR spectroscopy in an argon matrix at 12 K[7] and examples of mono CO adducts of titanium fulvalene compounds are known.[8] Isolobal (η^5-$C_5Me_5)_2Si(N_2)$ (ν_{N2} = 2046 cm^{-1}) and (η^5-$C_5Me_5)_2$Si(CO) (ν_{CO} = 2065 cm^{-1}) have also been observed in situ in liquid Xe.[9]

Addition of a stoichiometric quantity of CO gas to **2** furnished the desired monocarbonyl complex, **2-CO**, although the product was contaminated with significant amounts of **2-(CO)$_2$** and unreacted **2**. An improved synthetic method has been devised whereby an equimolar mixture of **2** and **2-(CO)$_2$** was mixed for 18 h and formed **2-CO** as the predominant product (eq 2).



In contrast to the dinitrogen compound, **2-CO** is isolable at 23 °C. The solid-state structure (Figure 1) is similar to that of **2-N$_2$** with idealized C_2 symmetry. The Ti(1)−C(10) and C(10)−O(1) bond lengths of 1.9786(19) and 1.151(2) Å, respectively, are comparable to the values of 2.0065(18) and 1.150(2) Å found in **1-(CO)$_2$**. The synthetic procedure used to isolate **2-CO** appears general as **1-CO**, and the alkyl-substituted compound, **3-CO**, were prepared by mixing the sandwich and the corresponding dicarbonyl (eq 2). For these examples, isolation of the titanocene monocarbonyls in pure form has proven difficult as the product is in equilibrium with the starting materials. Equilibrium constants for each reaction were determined at 23 °C by ^{1}H NMR spectroscopy and are reported in eq 2. In general, introduction of larger, more electron-withdrawing silyl substituents into the cyclopentadienyl ligands favors the monocarbonyl more than in the purely alkylated case.

To probe the pathway of formation for the titanocene monocarbonyl compounds, a series of isotopic labeling studies were conducted. Treatment of **3-(^{13}CO)$_2$** with 1 atm of CO produced isotopic exchange over the course of hours, furnishing a near statistical mixture of the isotopologs of **3-(CO)$_2$** and free ^{13}CO as judged by ^{13}C NMR spectroscopy. Mixing equimolar quantities of **2-(^{13}CO)$_2$** and **3-(CO)$_2$** also resulted in isotopic exchange, forming

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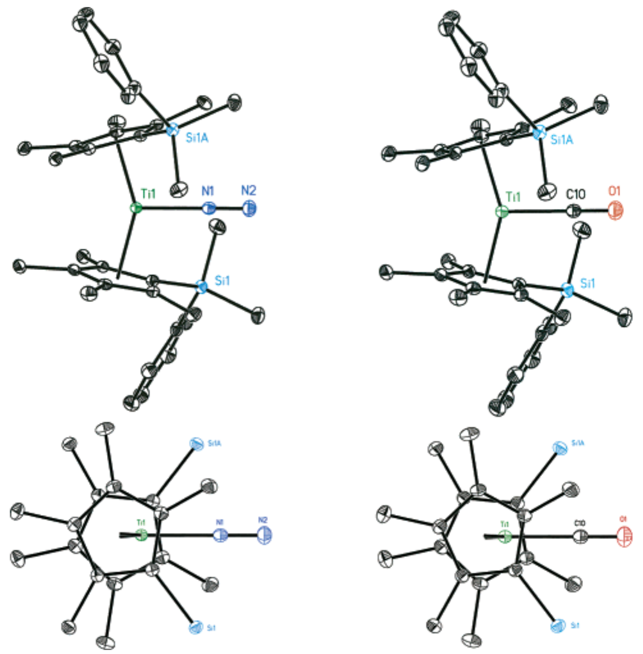

Figure 1. Molecular structures of **2-N_2** (left) and **2-CO** (right) at 30% probability ellipsoids with top views shown below. Hydrogen atoms and silyl substituents in the top views are omitted for clarity.

a near statistical mixture of labeled and natural abundance titanocene dicarbonyl compounds. The converse experiment, mixing **3-(^{13}CO)$_2$** and **2-(CO)$_2$**, produced the same outcome. These results, in combination with previously reported kinetic data for substitution of (η^5-C_5H_5)$_2$Ti(CO)$_2$ with ^{13}CO,[5] are consistent with a pathway whereby the monocarbonyl derivatives are formed by initial CO dissociation from the dicarbonyl compounds followed by trapping of the free ligand by the titanium sandwich.

As originally predicted by Lauher and Hoffmann,[10] the HOMO of the monocarbonyl (and likewise the mono(dinitrogen)) derivative is an essentially linear combination of a titanocene b_2 molecular orbital with the in-plane π^* orbital of the CO ligand (Figure S7). Despite an energetically accessible LUMO ($\Delta E_{\mathrm{HOMO/LUMO}} = 20-22$ kcal) of principally titanocene $1a_1$ character, addition of σ-ligands, such as PMe$_3$, tetrahydrothiophene, and *N*,*N*-dimethylaminopyridine, to either **2-CO** or **3-CO** produced no change in the ^{1}H NMR spectrum even upon cooling to −80 °C.

Treatment of **3-(CO)** with the strongly σ-donating, weakly π-acidic ^{t}BuNC furnished a new C_1 symmetric compound identified as **3-(CN^{t}Bu)(CO)** based on NMR and IR spectroscopies. Although observable for minutes at 23 °C in benzene-d_6 solution, this compound decomposed to **3-(CO)$_2$** and unidentified titanocene species over time. Coordination of a weak π-acid suggested that mixed carbonyl dinitrogen compounds could be synthesized. Indeed, mixing a titanocene bis(dinitrogen) compound such as **3-(N_2)$_2$** with **3-(CO)$_2$** and monitoring the reaction mixture by in situ IR spectroscopy at −78 °C in pentane solution produced four new bands over the course of 1 h assigned as **3-(N_2)(CO)**. The silyl-substituted titanocenes, **1-(N_2)(CO)** and **2-(N_2)(CO)**, were observed in a similar manner. In each case, warming the sample above −20 °C resulted in disappearance of the N_2−CO complex;[3] however, subsequent cooling regenerated the compound. In general, the mixed N_2−CO derivatives have lower frequency N_2 and CO bands than the corresponding bis(dinitrogen) and dicarbonyl compounds (Table S1). In conclusion, our studies once again highlight the ability to control the nature of N_2 coordination by careful manipulation of cyclopentadienyl substituents.[11] In the present case, introduction of extreme steric bulk has opened a new chapter in group 4 metallocene dinitrogen and carbonyl chemistry with the isolation of unique examples of mono(dinitrogen) and carbonyl compounds that were computationally predicted nearly 3 decades ago.

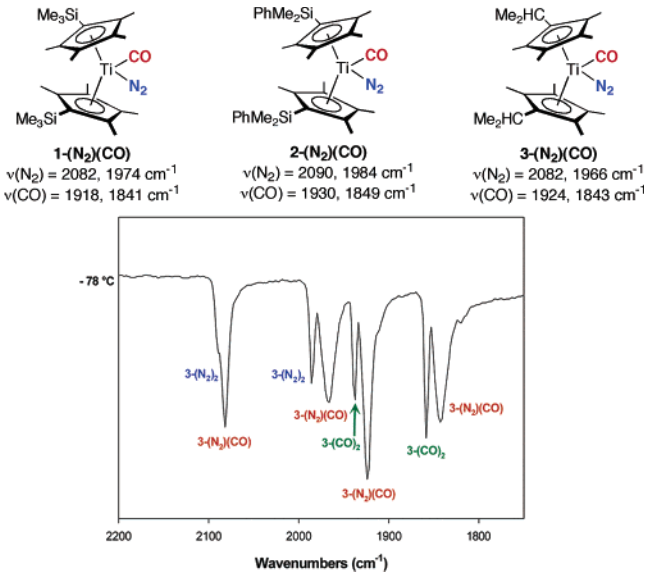

Figure 2. Mixed titanocene N_2−CO compounds and detection of **3-(N_2)(CO)** by IR spectroscopy.

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Supporting Information Available: Experimental procedures, DFT results, and crystallographic data for **2-N_2**, **2-CO**, and **1-(CO)$_2$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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