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Communication

The Scandium(II) Carbonyl Complex $(C_5H_2{}^tBu_3)_2Sc(CO)$ and Its Isocyanide Analog $(C_5H_2{}^tBu_3)_2Sc(CNC_6H_3Me_2\text{-}2,6)$

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ABSTRACT: Treatment of the scandium(II) metallocene $Cp^{ttt}{}_2Sc$ (Cp^{ttt} = $C_5H_2{}^tBu_3$) with CO or the isocyanide CNXyl (Xyl = $C_6H_3Me_2$-2,6) yields the carbonyl complex $Cp^{ttt}{}_2Sc(CO)$, **1**, or the isocyanide complex $Cp^{ttt}{}_2Sc(CNXyl)$, **2**, which were identified by X-ray crystallography. Isotopic labeling with ^{13}CO shows the CO stretch of **1** at 1875 cm^{-1} shifts to 1838 cm^{-1} in **1-^{13}CO**. The CN stretch in **2** is shifted to 1939 cm^{-1} compared to 2118 cm^{-1} for the free isocyanide. The 80.1 MHz (28.7 G) ^{45}Sc hyperfine coupling in **1** and 74.7 MHz (26.8 G) in **2** are similar to the 82.6 MHz (29.6 G) coupling constant in $Cp^{ttt}{}_2Sc$ and indicate that **1** and **2** are Sc(II) complexes. A comprehensive analysis of the electronic structures of **1** and **2** using DFT calculations is reported.

Carbon monoxide has become a ubiquitous ligand in transition metal chemistry since the discovery of complexes such as $[Pt(CO)Cl_2]_2$ and $Ni(CO)_4$ in the late 1800s.[1] The strong affinity of CO for the d-block elements is largely due to the favorable match of orbital characteristics for effective σ-donor and π-acceptor interactions.[2,3] Although molecular carbonyl complexes have been isolated across the d-block, those of the first element in the transition series, scandium, have been reported only in theoretical studies or in low temperature matrices and gas phase mass spectra.[4−11] Predictions have been made based on the 18-electron "rule"[12] that $[Sc(CO)_7]^{1-}$ and $[Sc(CO)_6]^{3-}$ should be stable[8] and there is mass spectrometry evidence for species such as $Sc(CO)_n{}^+$, $ScO(CO)_n{}^+$, and $ScO(H_2O)(CO)_n{}^+$.[8,9] However, there have been no examples of crystallographically characterized nor even isolable, room temperature stable CO complexes of scandium reported until now. This is, in part, because the most common oxidation state, Sc(III), has no valence electrons available for the π-backbonding interaction that is responsible for the strong binding of CO to transition metals. The CO complexes observed at low temperature involve Sc in the zero or +1 oxidation state and the CO vibrational frequencies in the range 1700−2000 cm^{-1} attributed to these species in the low temperature matrices[5] indicate backbonding to the CO ligands.

While scandium is a transition metal, the reported reaction chemistry of its complexes in the +3 oxidation state resembles that of yttrium and the lanthanides, which is why it is also classified as a rare-earth element.[13,14] Whereas CO complexation by transition metals is common, this is not true for the rare-earth elements which typically react with CO by insertion or reductive homologation reactions.[15−17] No stable carbonyl complexes of the rare-earth metals have been isolated although there is infrared spectroscopic evidence for weak complexation of CO in solution by the Ln(II) metallocenes $Cp^*{}_2Sm$, $Cp^*{}_2Eu$, and $Cp^*{}_2Yb$ (Cp^* = C_5Me_5) with $\tilde{\nu}_{CO}$ of 2114−2153 cm^{-1} compared to 2143 cm^{-1} for free CO.[18−20] However, a series of cyclopentadienyl carbonyl complexes of uranium of formula $Cp^x{}_3U(CO)$ have been reported (Cp^x = $C_5H_4SiMe_3$,[21] C_5Me_4H,[22] and C_5Me_5[23]) with reduced $\tilde{\nu}_{CO}$ of 1900−1976 cm^{-1} attributed to π^* carbonyl orbital interactions with filled cyclopentadienyl ligand orbitals and not the metal orbitals.[24] Recently, the first example of a Sc(II) metallocene was isolated, $Cp^{ttt}{}_2Sc$ (Cp^{ttt} = $C_5H_2{}^tBu_3$),[25] and this provided an opportunity to determine if Sc(II) would react with CO by complexation or reductive homologation as seen with $Cp^*{}_2Sm(THF)_2$[26] and $Cp^{ttt}{}_2Tm$.[27]

We report here that $Cp^{ttt}{}_2Sc$ readily combines with CO to form $Cp^{ttt}{}_2Sc(CO)$, the first crystallographically characterizable molecular carbonyl complex of scandium and of a rare-earth element. Given the structural and electronic similarities of isocyanide ligands, CNR, to CO, we have also investigated isocyanide reactivity and report the first crystallographically characterized isocyanide complex of scandium, $Cp^{ttt}{}_2Sc(CNXyl)$ (Xyl = $C_6H_3Me_2$-2,6).

Solutions of $Cp^{ttt}{}_2Sc$ in C_6D_6 or *n*-hexane placed under a CO atmosphere rapidly change color from dark red to dark red-orange. ^1H NMR studies in a J. Young tube show that the paramagnetically broadened signals at 0.30 and −0.10 ppm corresponding to the *tert*-butyl groups of $Cp^{ttt}{}_2Sc$ are replaced by new broad signals at 4.58 and 3.65 ppm upon exposure of the solution to CO. This product was identified by X-ray crystallography as the carbonyl complex $Cp^{ttt}{}_2Sc(CO)$, **1**, Figure 1. On a preparative scale, Scheme 1, complex **1** can be isolated as a dark orange powder in 97% yield. Similarly, the reaction between $Cp^{ttt}{}_2Sc$ and CNXyl in *n*-hexane resulted in

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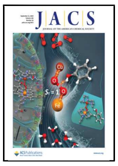

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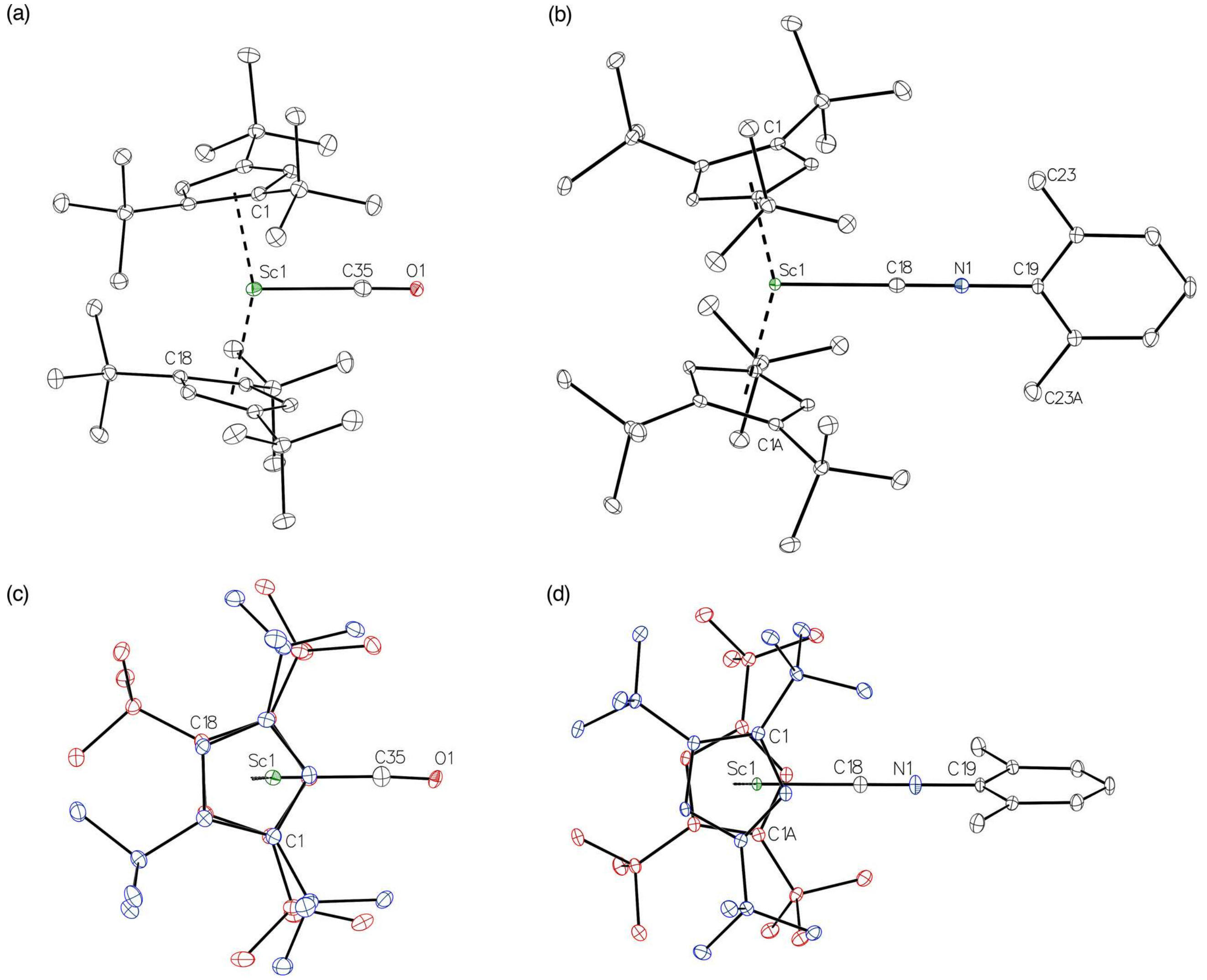
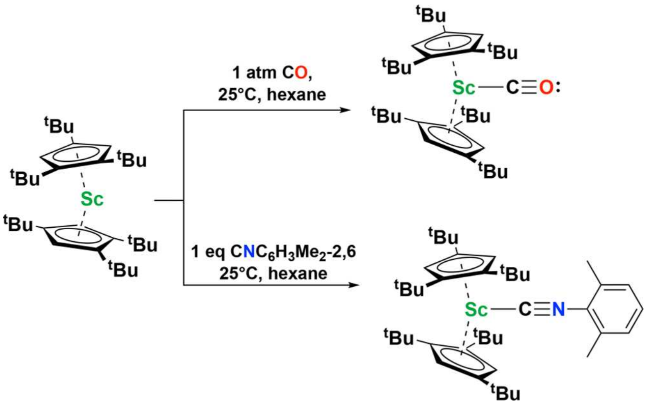


Figure 1. Side (a, b) and top (c, d) views of $C_{pttt}{}^2Sc(CO)$, **1**, and $C_{pttt}{}^2Sc(CNXyl)$, **2**, respectively. In the top views, the carbon atoms are colored blue for the upper ring and red for the lower ring. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are not shown for clarity.

Scheme 1. Synthetic Routes to the Scandocene Carbonyl Complex 1 and Isocyanide Complex 2



an immediate color change to dark blue and afforded dark blue crystals of the complex $Cp^{ttt}{}_2Sc(CNXyl)$, **2**, Figure 1, in 81% yield.

The EPR spectrum of **1**, Figure 2a, shows an isotropic eight-line pattern centered at $g_{iso} = 1.996$ with a ^{45}Sc (100%, $I = 7/2$) hyperfine coupling constant of $A_{iso} = 80.1$ MHz (28.7 G). This is similar to the EPR spectrum of $Cp^{ttt}{}_2Sc^{II}$ ($g_{iso} = 1.99$, $A_{iso} = 82.6$ MHz (29.6 G))[21] and is consistent with the presence of a $3d^1$ Sc(II) ion in **1**. Complex **2** has a similar EPR spectrum, Figure 2c, with $g_{iso} = 1.994$ with a coupling constant of $A_{iso} = 74.7$ MHz (26.8 G). In the ^{13}CO analog, **1-^{13}CO**, prepared analogously, coupling to the ^{13}C nucleus is seen, Figure 2b, and the observed spectrum was reproduced when modeled anisotropically with the following parameters: $g_1 = 1.997$, $g_2 = 1.996$, $A_1(^{45}Sc) = 78.2$ MHz (28.0 G), $A_2(^{45}Sc) = 83.3$ MHz (29.8 G), $A_1(^{13}C) = 19.6$ MHz (0.7 G), $A_2(^{13}C) = 22.3$ MHz (0.8 G). The *ca.* 20 MHz ^{13}C hyperfine coupling in **1-^{13}CO** is comparable to the 16 MHz coupling observed in "$Nb(^{13}CO)$" in argon at 4 K.[4] The Evans method[28−30] magnetic moments of 1.5 μB in **1** and 1.9 μB for **2** are consistent with the 1.73 μB spin-only magnetic moment of one unpaired electron and match the $3d^1$ electron configuration indicated by the EPR spectra.

Complex **1** has a bent metallocene structure with a terminal CO ligand bound to Sc through the carbon atom, Figure 1a. The Sc atom is in a trigonal planar environment between the two ring centroids and the CO ligand which is bound symmetrically as expected based on the Lauher-Hoffmann

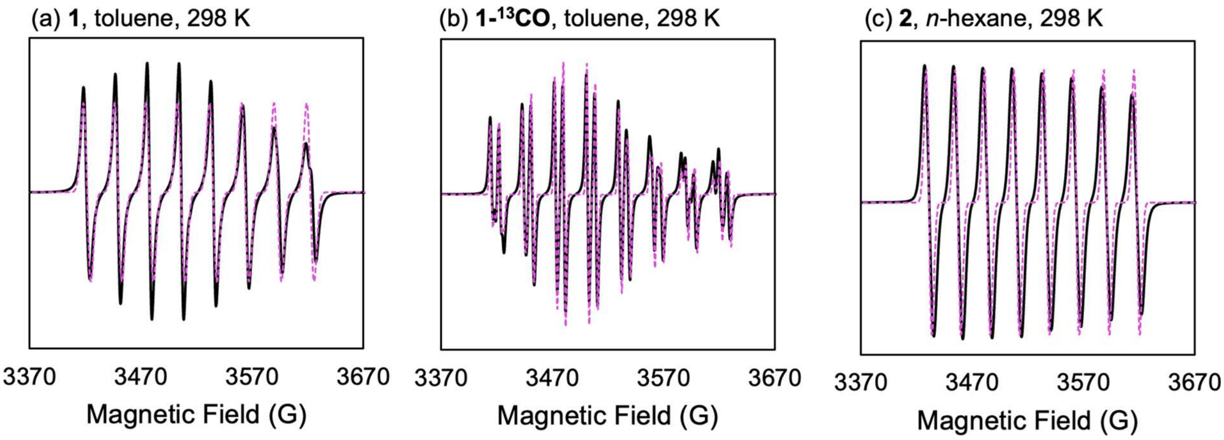


Figure 2. Experimental (black) and simulated (magenta) X-band (9.84 GHz) CW EPR spectra of (a) 1, *ca.* 3 mM in toluene at 298 K; (b) **1-^{13}CO**, *ca.* 3 mM in toluene at 298 K; (c) 2, *ca.* 3 mM in *n*-hexane at 298 K.

Table 1. Structural and Spectroscopic Parameters for 1, 2, and Selected Related Compounds

	M−C (Å)	C−O (Å)	M−C−O (deg)	$\tilde{\nu}_{CO}$ (cm^{-1})	^{45}Sc A_{iso} (MHz)	ref
CO	—	1.128	—	2143	—	33, 34
Cp$^{ttt}{}_2$Sc(CO), **1**	2.168(3)	1.078(3)	176.5(2)	1875	80.1	This work
1, DFT	2.158	1.164	179.9	1849	80.0	
$(C_5Me_4SiPhMe_2)_2$Ti(CO)	1.979(2)	1.151(2)	180	1848	—	37
$[Me_4C_2(C_5H_4)_2]$Cr(CO)	1.85(1)	1.16(1)	178.4(9)	1905	—	39
	M−C (Å)	C−N (Å)	M−C−N (deg)	$\tilde{\nu}_{CN}$ (cm^{-1})	—	
CNXyl	—	1.160(4)	—	2118	—	36
Cp$^{ttt}{}_2$Sc(CNXyl), **2**	2.213(3)	1.176(4)	180	1939	74.7	This work
2, DFT	2.183	1.199	180	1936	71.2	
Cp*$_2$Ti(CNXyl)$_2$	2.025(2)	1.183(2)	174.1(1)	2115	—	38
	2.071(2)	1.196(2)	178.3(1)			
$[Me_4C_2(C_5H_4)_2]$Cr(CNXyl)	1.892(7)	1.195(7)	180	2006,[a] 1980[b]	—	48
Cp$^{ttt}{}_2$Sm(CNXyl)	2.749(4)	1.142(5)	180	2140	—	43
Cp$^{ttt}{}_2$Yb(CNXyl)	2.588(5)	1.150(6)	180	2140	—	43

[a] nujol mull. [b] THF solution.

model for a bent metallocene bound to a single σ-donor, π-acceptor ligand.[31] Table 1 summarizes the metrical data and makes comparisons with the few available related compounds. The Sc1−C35−O1 angle in 1 is nearly linear at 176.5(5)° and the 170.6° Cp^{ttt}(centroid)−Sc−Cp^{ttt}(centroid) angle of Cp$^{ttt}{}_2$Sc has narrowed to 157.5° in **1**. The 2.21 Å Sc−Cp^{ttt}(centroid) distances in **1** are elongated compared to the 2.16 Å distance in Cp$^{ttt}{}_2$Sc and are closer to the 2.23 Å distances in the Sc(III) iodide precursor Cp$^{ttt}{}_2$ScI.[25] The 2.168(2) Å Sc1−C35 distance is the first experimental Sc(II)−C(CO) distance. In comparison, the *calculated* Sc−C separations for neutral Sc(CO)$_x$ fall in a wide range from 2.075 for x = 1 to 2.292 for x = 7, while the x = 3 or 4 values are *ca.* 2.15 Å. For comparison, the Sc(III)-C(Me) single bond in Cp*$_2$ScMe is 2.24(1) Å.[32]

The infrared spectrum of **1** contains a strong absorbance at 1875 cm^{-1} that shifts to 1838 cm^{-1} in **1-^{13}CO**, which is close to the calculated shift of 1834 cm^{-1}. This band is assigned to the C−O stretching vibration and is significantly red-shifted in comparison to the 2143 cm^{-1} stretch of free CO and 2096 cm^{-1} in ^{13}CO.[33]

Density functional theory (DFT) calculations on **1** and **2** reproduced the key structural parameters in the two compounds, Tables 1, S3, and S4, except for the C−O bond distance in **1** discussed below. The DFT-calculated IR stretch (1849 cm^{-1}) and hyperfine coupling constant (80.0 MHz) also matched the experimental, as did the analogs for **2**, Table 1. The HOMOs of both **1** and **2**, Figure 3, clearly show significant π back-bonding from a scandium 3d orbital to the π* orbital of the CO ligand, which is consistent with the reduced IR stretching frequency compared to free CO. The 1.164 Å predicted C−O distance from the DFT geometry optimization is also consistent with this backbonding. This suggests that the 1.078 Å value from the diffraction data, which is shorter than the 1.128 Å distance in free CO,[34] could be a consequence of unresolved disorder of the CO moiety rather than representative of the true bond distance. We note that there are over 1000 examples of such short CO distances reported in the Cambridge Structural Database.[35]

Complex **2** has a bent metallocene structure similar to that of **1**, Figure 1b. The 153.5° Cp^{ttt}(centroid)−Sc−Cp^{ttt}(centroid) angle is smaller than in Cp$^{ttt}{}_2$Sc and **1**, which is consistent with the larger CNXyl ligand. The 2.22 Å Sc−Cp^{ttt}(centroid) distance is equivalent to that in **1** and the 2.213(3) Å Sc1−C18 bond length is the first reported Sc(II)−C(CNR) distance. The Sc1−C18−N1 and C18−N1−C19 angles lie along a 2-fold rotation axis which makes them exactly 180°. The 1.176(4) Å C18−N1 and 1.385(3) Å N1−C19 distances are similar to those in the free isocyanide, 1.160(4) and 1.399(3) Å.[36] However, the CN stretching frequency of 2118 cm^{-1} for free CNXyl is significantly lowered to 1939

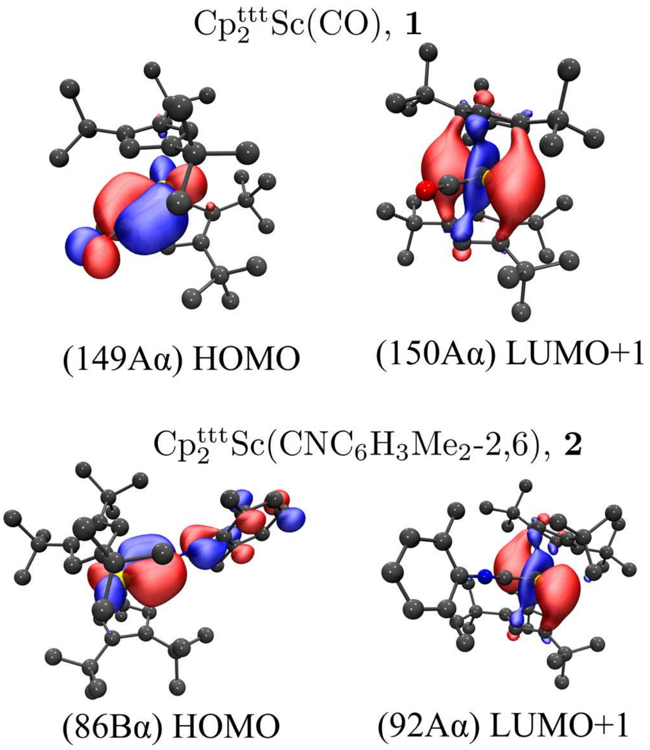


Figure 3. Kohn−Sham frontier molecular orbitals of 1 and 2 from DFT calculations using a TPSSh def2-TZVP basis set for Sc and def2-SV(P) basis sets for C, H, N, O. A contour value of 0.04 was used and H atoms were omitted for clarity.

cm^{-1} in **2** (DFT-calculated: 1936 cm^{-1}). In both **1** and **2** the two Cp^{ttt} ligands are nearly eclipsed, Figures 1c and 1d.

The Sc−C(CO or CNXyl) bonds in **1** and **2** are longer than those in structurally related Ti and Cr complexes, Table 1, as expected due to the decreasing metal size across the row. The *ca.* 0.05 Å shorter distance in **1** versus **2** is similar to the 1.979(2) Å Ti−C(CO) distance in $(C_5Me_4SiPhMe_2)_2$Ti(CO)[37] versus the 2.025(2) and 2.071(2) Å Ti−C(CNXyl) lengths in $Cp^*{}_2Ti(CNXyl)_2$.[38] The shift of the CO stretch in **1** is comparable to those in $(C_5Me_4SiPhMe_2)_2$Ti(CO)[37] and $[Me_4C_2(C_5H_4)_2]$Cr(CO),[39] which appear at 1848 and 1905 cm^{-1}. These are very different from the CO stretches observed in solution for lanthanide metallocenes under CO, "$Cp^*{}_2$Yb(CO)" (2114 cm^{-1}), "$Cp^*{}_2Yb(CO)_2$" (2172 cm^{-1}), "$Cp^*{}_2$Sm(CO)" (2153 cm^{-1}), and "$Cp^*{}_2$Eu(CO)" (2150 cm^{-1}).[18,19] In these lanthanide complexes, π-backbonding from the 4f orbitals is negligible and contraction of the C−O bond due to polarization by the positively charged metal atom is likely the dominant effect.[20,40−42]

Although there are no isolated CO complexes of lanthanides for comparison with **1**, the isocyanides $Cp^{ttt}{}_2$Sm(CNXyl) and $Cp^{ttt}{}_2$Yb(CNXyl)[43] have been structurally characterized and can be compared with $Cp^{ttt}{}_2$Sc(CNXyl), **2**, Table 1. Although isocyanides are electronically similar to CO, their chemistry is influenced by the nature of the substituent group on nitrogen and does not always parallel that of CO.[44,45] The C−N distances in **2** and the $Cp^{ttt}{}_2$Ln(CNXyl) complexes (Ln = Sm, Yb)[43] are not significantly altered compared to the free isocyanide. However, the CN stretch in **2** is significantly red-shifted whereas the absorbance for the lanthanide compounds is blue-shifted to 2140 cm^{-1}. It should be noted that since isocyanides are strong σ-donors and weaker π-acceptors than CO,[44] the degree of π-backbonding does not correlate as well with the C−N distance or the CN stretching frequency.[46,47] For example, the C−N distances in $Cp^*{}_2Ti(CNXyl)_2$ and $[Me_4C_2(C_5H_4)_2]$Cr(CNXyl)[48] are longer than in **2**, but the C−N stretching frequencies at 2115 cm^{-1} and 2006/1980 cm^{-1} for these compounds are not as drastically shifted as in **2**. The DFT calculations on the C−N distance and stretching frequency match the experimental data, Table 1.

The formation of the stable carbonyl complex **1**, demonstrates for the first time the ability of scandium to form classical transition metal carbonyl complexes. While a member of the d-block, scandium typically shows chemistry similar to the lanthanides, although this has been historically dominated by the +3 ions of these elements. For the Sc(II) ion, the $3d^1$ electron configuration matches transition metal chemistry better than the $4f^n$ electron configurations of the Ln(II) ions of Eu, Yb, Sm, and Tm. Interestingly, the $\{[(Me_3Si)_2N]_3Ln^{II}\}^{1-}$ anions (Ln = Y, Gd, Dy, Ho, Tm, Lu) which have d^1 ground states, $4d^1$ for Y and $5d^14f^n$ for the lanthanides, also differ from the chemistry of $3d^1$ $Cp^{ttt}{}_2$Sc in that they reduce CO to $(CO)^{1-}$ and $(OC{\equiv}CO)^{2-}$, rather than form Ln(II) carbonyl complexes like **1**.[49,50] It remains to be seen if carbonyl complexation occurs with other complexes of scandium(II) or other rare-earth metal $Cp^{ttt}{}_2$Ln complexes and what factors such as reduction potential or ground state electron configuration favor their formation.

In conclusion, the reaction of the scandium(II) metallocene $Cp^{ttt}{}_2$Sc with CO generates the first stable scandium carbonyl complex, $Cp^{ttt}{}_2$Sc(CO) with significant π-backbonding to the CO ligand as evidenced by infrared spectroscopy. The first isolable scandium isocyanide complex $Cp^{ttt}{}_2$Sc(CNXyl) also readily forms from $Cp^{ttt}{}_2$Sc. The EPR spectra of these compounds are consistent with Sc(II) in each complex. Hence, although the chemistry of Sc(III) mimics lanthanide chemistry and leads to the classification of scandium as a rare-earth element, with Sc(II) and its d^1 electron configuration, the chemistry resembles that of its neighboring elements in the d-block. The capacity of $Cp^{ttt}{}_2$Sc to form scandium(II) metallocene complexes may provide a platform to study ligand effects on hyperfine coupling constants with d^1 metals and learn how to make better qubits from these systems.[51−54]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c09021.

> Synthetic and X-ray crystallographic details and the EPR, infrared, UV−visible, NMR spectroscopy data, and computational results and details (PDF)

Accession Codes

CCDC 2367164−2367165 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare the following competing financial interest(s): Principal Investigator Filipp Furche has an equity interest in TURBOMOLE GmbH. The terms of this arrangement have been reviewed and approved by the University of California, Irvine, in accordance with its conflict of interest policies.

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