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Facile Access to Tetravalent Cerium Compounds: One-Electron Oxidation Using Iodine(III) Reagents

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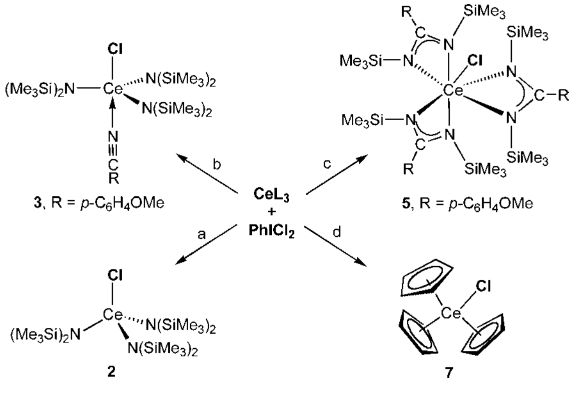
Abstract: Readily accessible and easy-to-use phenyliodine(III) dichloride, $PhICl_2$, has been established as an innovative and superior reagent for the one-electron oxidation of cerium(III) complexes, comprising amide, amidinate, and cyclopentadienyl derivatives. Its use allowed the successful synthesis and structural characterization of the first members of three new classes of chloro-functionalized (organo)cerium(IV) compounds, including the long sought-after Cp_3CeCl.

Due to their high oxidation potential, cerium(IV) compounds are widely used in various areas of chemistry and technology. Important fields of application include organic synthesis,[1] bioinorganic chemistry,[2] materials science,[3] and industrial catalysis (automotive three-way catalysts, oxygen storage, etc.).[4] More recently, soluble cerium(IV) compounds are increasingly employed for the production of ceria nanoparticles.[5] Thus, there is a constant demand for new, well-defined cerium(IV) species. The long-known cerium(IV) alkoxides form a well-investigated class of compounds which are useful precursors for the metal−organic chemical vapor deposition (MOCVD) production of thin CeO_2 layers.[6] In sharp contrast, the road to other classes of cerium(IV) species, especially amides[7−10] and organometallics,[11] is rocky and unpredictable. In particular, the most logical synthesis route, i.e., the one-electron oxidation of Ce(III) precursors, is often severely hampered by either the unavailability of suitable oxidants or erratic reaction pathways. Certainly, the most prominent examples were published by Lappert et al., emphasizing the considerable difficulties involved in the synthesis of the cerium(IV) silylamide $[(Me_3Si)_2N]_3CeCl$ (**2**).[7,10] The synthesis of purple **2** was achieved using the uncommon oxidant $TeCl_4$, with optimized yields around 25%.

We now report that phenyliodine(III) dichloride, $PhICl_2$, can be successfully employed as an innovative and superior reagent for the one-electron oxidation of cerium(III) precursors, comprising amide, amidinate, and cyclopentadienyl derivatives.

The hypervalent organoiodine(III) compound $PhICl_2$ has several advantages: (a) it is readily accessible from cheap, commercially available starting materials;[12] (b) solid $PhICl_2$ can easily be employed in exact stoichiometric amounts; (c) liquid, highly soluble, and volatile iodobenzene would be the only iodine-containing byproduct; and (d) several transition metal complexes have been successfully oxidized using $PhICl_2$.[13] All these assumptions could be verified by a test reaction with the silylamide $[(Me_3Si)_2N]_3Ce$ (**1**). Treatment of a toluene solution of **1** with the calculated amount of $PhICl_2$ in toluene (Scheme 1, path a) resulted in an immediate color change from orange to purple. Pure **2** could be isolated in 10% yield in a very simple manner by crystallization from the concentrated reaction mixture at −20 °C.[14] The organoiodine(III) route can be also utilized to access novel five-coordinate cerium(IV) amido species (Scheme 1, path b). Dark red-brown **3** was isolated in 45% yield by adding *p*-anisonitrile to a toluene solution of **1** prior to treatment with $PhICl_2$.[14] An X-ray diffraction study revealed the presence of the first functional cerium(IV) amide displaying trigonal-bipyramidal coordination geometry (Figure 1). At 2.6443(7) Å, the Ce−Cl distance in **3** is slightly longer than that in **2** (2.597(2) Å).[6]

Scheme 1. Synthesis of Ce(IV) Compounds by Reaction of $[(Me_3Si)_2N]_3Ce$ (**1**, a: toluene), $[(Me_3Si)_2N]_3Ce/(N{\equiv}CR)$ (**1**, b: toluene, R $=p\text{-}C_6H_4OMe$), $[p\text{-}MeOC_6H_4C(NSiMe_3)_2]_3Ce(N{\equiv}CR)$ (**4**, c: pentane, R $=p\text{-}C_6H_4OMe$), and Cp_3Ce (**6**, d: toluene) with $PhICl_2$



In order to prove a more general applicability of this route, we examined the oxidizability of two other cerium(III) benchmark complexes. In recent years, lanthanide amidinates have gained

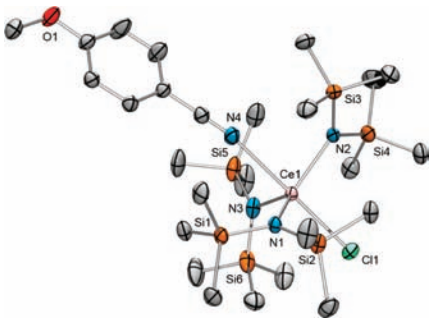


Figure 1. Molecular structure of $[(Me_3Si)_2N]_3CeCl(N{\equiv}CC_6H_4OMe\text{-}p)$ (**3**).

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eminent importance both as highly effective catalysts for polymerization reactions and as volatile precursors for MOCVD and atomic layer deposition processes.[15] While lanthanide amidinates in the oxidation states +2 and +3 are well established, cerium(IV) amidinate complexes remained unknown. The superior performance of the organoiodine(III) route was further proven by the synthesis and structural characterization of the first cerium(IV) amidinate complex. $[p\text{-MeOC}_6H_4C(NSiMe_3)_2]_3Ce(N{\equiv}CR)$ (**4**, R = $p\text{-C}_6H_4OMe$) was oxidized with $PhICl_2$ in pentane, resulting in clean formation of the corresponding Ce(IV) amidinate $[p\text{-MeOC}_6H_4C(NSiMe_3)_2]_3CeCl$ (**5**), which was isolated as dark red-brown block-like crystals in 61% yield (Scheme 1, path c).[14] The presence of the first chloro-functional cerium(IV) amidinate was clearly confirmed by a single-crystal X-ray diffraction study (Figure 2; Ce−Cl = 2.659(1) Å).

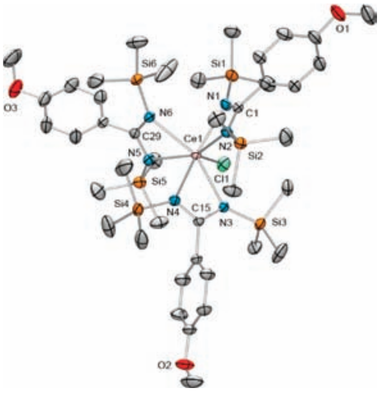

Figure 2. Molecular structure of $[p\text{-MeOC}_6H_4C(NSiMe_3)_2]_3CeCl$ (**5**).

A further example of the versatility of $PhICl_2$ as an oxidant was demonstrated by the synthesis and structural characterization of organometallic tris(cyclopentadienyl)cerium(IV) chloride, the long sought-after cerium(IV) analogue of $(C_5H_5)_3UCl$.[16] Addition of 0.5 equiv of $PhICl_2$ to a toluene solution of $(C_5H_5)_3Ce$ (**6**) produced an immediate color change from yellow to black (Scheme 1, path d). Black crystals were isolated, after removal of the volatiles, from a concentrated toluene solution at −35 °C in 15% yield.[14] Diamagnetic $(C_5H_5)_3CeCl$ (**7**) displays a singlet at δ 4.74 in the ^{1}H NMR spectrum in C_6D_6 (cf. paramagnetic **6**: δ 2.22 ppm[18]). X-ray diffraction analysis revealed these crystals to be $(C_5H_5)_3CeCl$ (Figure 3). The Ce−Cl bond distance of 2.6666(7) Å appears slightly elongated compared to those of complexes **3** and **5** but shorter than in $[\{N[CH_2CH_2N{=}CH(2\text{-O-}3,5\text{-}t\text{Bu}_2C_6H_2)]_3\}CeCl$ (2.7930(9) Å).[17]

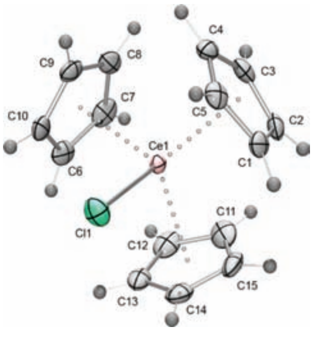

Figure 3. Molecular structure of $(C_5H_5)_3CeCl$ (**7**).

Notably, **7** was first described in 1971,[19a] but that report was later refuted by Deacon et al.[19b] Only two well-defined Ce(IV) cyclopentadienyl complexes, $(C_5H_5)_3Ce(O\textit{i}Pr)$[11a] and $(C_5H_5)_3Ce(O\textit{t}Bu)$,[11b] are known so far. Thus, compound **7** is not only the first new tris(cyclopentadienyl)cerium(IV) complex reported in more than 20 years but also the first chloro-functional species of this type for which a promising derivative chemistry can be envisioned.

In summary, we have discovered an innovative and generally applicable synthesis route that enables facile access to known and novel tetravalent cerium complexes. This organoiodine(III)-based oxidation protocol appears to be quite general and thus opens the door for future investigations in the field of Ce(IV) amides, amidinates, and organometallics. Work focused on extending this chemistry to other classes of Ce(IV) species and iodine(III) reagents, such as PhIO and $PhIO_2$, is currently underway. It takes little imagination to foresee that the new synthetic route could also have a bright future in high-valent organoactinide chemistry.

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Supporting Information Available: X-ray structural data, in CIF format, for **3**, **5**, and **7**; experimental details on the preparation and characterization of **3**−**5** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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