Similar parameters are found for **5** except that the P(1)–Pt–P(2) bond angle is compressed by about 6° in the latter due to the larger steric bulk of the $Co(CO)_4$ ligand. The five-coordinate geometry about Co is best described not as a tbp but as a $Co(CO)_4$ tetrahedron with the Pt atom capping a lower face. Alternatively, the Co geometry could be viewed as a distorted square pyramid (sp) with C(2) at the apical position. The Pt, C(2), and C(3) atoms all lie in the same plane as Co [sum of bond angle is 360 (1)°]. In addition, two of the carbonyls [C(1)–O(1) and C(4)–O(4)] are bent back toward the Pt in an almost semibridging fashion, leading to a slight bending of the Co–C–O angles (about 171°) and Pt–C distances of about 2.6 Å. The other two Co–C–O bond angles are about 178°.[21,22]

Besides the P–N–Pt triangular bonding mode, one of the most unusual features of the Pt complexes **1**, **5**, and **7** is an extremely long Pt–X (X = Cl, I, Co) bond trans to the cyclenP phosphorus [the Pt–Cl distance in **1** is 2.440 (4) Å].[3b] These values are 0.1–0.15 Å longer than typical bonds in related compounds.[23] Spectral measurements also support a weakened Pt–X bond: ν_{PtCl} in **1** is at 249 cm^{-1} [compared to 279 and 303 cm^{-1} in *cis*-$Cl_2Pt(PPh_3)_2$][3b], and as previously noted, the ν_{CO} values in **5** are extremely low. Moreover, once the P–N bond is cleaved, the Pt–X bond length reverts to a normal value [for example, the Pt–Cl bond length in **3** is 2.353 (2) Å]. Long Pt–X bond lengths and low ν_{PtX} values are usually attributed to a strong trans influence of the ligand trans to X; indeed, the Pt–Cl bond length of 2.45 Å and low ν_{PtCl} value of 242 cm^{-1} in *trans*-$ClPt(SiMePh_2)(PMe_2Ph)_2$ were attributed to the large trans influence of Si.[24] However, the trends in these systems cannot be due simply to the pentacoordinated phosphorus since the Pt–Cl bond in **2** (trans to the cyclenP phosphorus) is only slightly lengthened [2.39 (1) Å] and the ν_{PtCl} values are not significantly low (275 and 300 cm^{-1}). Nor is it only the constraint of the three-membered P–N–Pt ring, since the Pt–PPh_3 bond shows no such lengthening. One difference between the pentacoordinate cyclenP ligands in **1** and **2** is its orientation with respect to the platinum coordination plane. In **1**, the N–P–N axial axis of the tbp is in the platinum plane, while in **2** it is perpendicular. This may mean that a tbp phosphorus may be a stronger trans ligand in the former orientation. Support for this comes from the increased cyclenP–Pt bond length in **2** [2.29 (1) Å] compared to 2.22–2.24 Å in the triangular species **3**, **5**, and **7**.

The geometries of cyclenP afford an ideal opportunity to compare the changes in ${}^1J_{PtP}$ with the three observed coordination modes and are illustrated for **1**, **2**, and **3**. Of particular significance is the observation of ${}^1J_{PtP}$ for a tbp phosphorus in **2**, a unique monodentate ligand geometry for phosphorus. The phosphorus geometry in **2** is a distorted tbp, with axial and equatorial N–P–N angles of 167 and 115°, respectively; as noted above, the platinum and two equatorial nitrogens are in the same plane as the phosphorus. Thus, the σ-bonding orbital used by phosphorus to bind to platinum is approximately sp^2 hybridized, to a first approximation. This high degree of s character should lead to a large ${}^1J_{PtP}$ value.[12] Indeed, the observed coupling of 5567 Hz is the largest of any of the derivatives, even though the P–Pt distance is the longest. Cleavage of one P–N bond, as in **3**, results in a more "normal" $R_3P \rightarrow Pt$ binding, with the phosphorus using an approximately sp^3 hybrid orbital. This results in a decrease of about 1000 Hz in the coupling constant. A further 1000-Hz decrease is observed in **1**, which features the P–N–Pt triangular binding mode. This complex is more difficult to treat in a simple hybridization scheme due to the constraints of the three-membered ring. However, the lowering of the coupling constant is consistent with what has been observed before with decreasing chelate ring size: a four-membered ring containing a direct P–Pt bond has a lower coupling constant than a five-membered ring. This has been attributed to angle strain in the smaller ring.[12,16] In **1**, the angle strain is even more pronounced, which should lead to even smaller values. All of the above derivatives have ${}^1J_{PtP}$ values that fall in the expected ranges, except **11**, for which ${}^1J_{PtP}$ is only 3055 Hz. Such a diminution of the coupling constant is due to the trans influence of acetylenide ligands.[25]

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Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances, bond angles, torsion angles, hydrogen atom coordinates, and complete crystallographic data for **5** and **7** (11 pages); tables of observed and calculated structure factors for **5** and **7** (29 pages). Ordering information is given on any current masthead page.

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(21) A similar $Co(CO)_4$ geometry was found in the complex *trans*-$(py)_2Pt[Co(CO)_4]_2$ (py = pyridine): Moras, D.; Dehand, J.; Weiss, R. *C. R. Seances Acad. Sci., Ser. C* **1968**, *267*, 1471.

(22) IR spectra in solution and the solid state are very similar (see Experimental Section). The only significant difference between the solid and solution spectra appears to be a more pronounced splitting of one of the bands in the solid state [the shoulder (in THF) at 1920 cm^{-1} is not evident in more dilute solutions]. This suggests that there is little difference between both structures.

(23) See ref 1b for representative Pt–Cl bonds and ref 21 for Pt–Co bonds.

(24) (a) McWeeny, R.; Mason, R.; Towl, A. D. C. *Discuss. Faraday Soc.* **1969**, *47*, 50. (b) Chatt, J.; Eaborn, C.; Ibekwe, S. *Chem. Commun.* **1966**, 700.

(25) For example, for the complexes *cis*-$L_2Pt[P(C_4H_9)_3]_2$, the ${}^1J_{PtP}$ values are 3500 Hz (L = Cl) and 2219 Hz (L = CCH). See ref 6 and 12b.

Contribution from Rhone-Poulenc, Inc., New Brunswick, New Jersey 08901,
and the Department of Chemistry, University of California, Irvine, California 92717

Reactivity of Ceric Ammonium Nitrate with Sodium Cyclopentadienide. X-ray Crystal Structure of $Ce(NO_3)_3(DME)_2$

Peter S. Gradeff,*[,1a] Kenan Yunlu,[1a] Timothy J. Deming,[1b] Jeffrey M. Olofson,[1b] Joseph W. Ziller,[1b] and William J. Evans*[,1b]

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The reactions of ceric ammonium nitrate (CAN) with 1, 3, 5, and 6 equiv of NaC_5H_5 in THF have been examined. The 6-equiv reaction forms $(C_5H_5)_3Ce(THF)$ in >90% yield in 30–60 min. The 5-equiv reaction forms a cyclopentadienylcerium nitrate complex, $(C_5H_5)_2Ce(NO_3)_2Na(THF)_2$, which decomposes violently upon heating. The 3-equiv reaction forms a cerium(III) nitrate complex of low solubility. A dimethoxyethane (DME) derivative of the latter complex, $Ce(NO_3)_3(DME)_2$, has been characterized by X-ray crystallography. This complex crystallizes from DME at −34 °C in space group $P2_1/n$ with a = 10.4404 (11) Å, b = 15.1301 (21) Å, c = 11.4023 (13) Å, β = 92.431 (9)°, V = 1799.5 (4) Å^3, and D(calcd) = 1.87 g cm^{-3} for Z = 4. The reaction of CAN with 1 equiv of NaC_5H_5 causes reduction of Ce(IV) to Ce(III). $(C_5H_5)_3Ce(THF)$ can also be made from $(NH_4)_2Ce(NO_3)_5$ and 5 equiv of NaCp. A scheme describing the overall CAN/NaC_5H_5 reaction system is presented.

Ceric ammonium nitrate (CAN) is a readily available, stable salt of Ce(IV), which is a potentially valuable precursor to a variety of cerium complexes. Recently, for example, the utility of CAN in the preparation of cerium(IV) alkoxides has been demon-

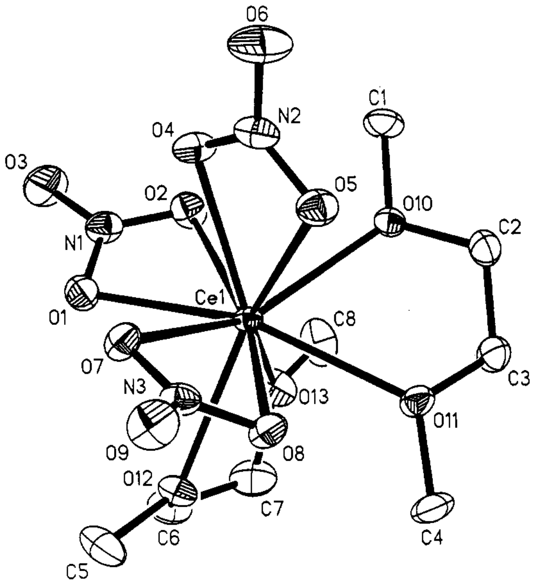

Figure 1. ORTEP diagram of $Ce(NO_3)_3(DME)_2$.

strated.[2-4] To learn more about the reactivity of CAN and to determine if it is a good precursor to Ce(III) as well as Ce(IV) compounds, we have studied its reactivity with the cyclopentadienide ion, $C_5H_5^-$ (Cp). Since 1971, the literature has contained reports of cerium(IV) cyclopentadienide complexes prepared from dipyridinium hexachlorocerate(IV).[5-8] However, in 1983 the synthesis of Cp_4Ce from $(C_5H_6N)_2CeCl_6$ was convincingly refuted by Deacon et al.,[9] who found that the actual reaction product was $Cp_3Ce(THF)$.[10] On this basis, one could expect that CAN would be a precursor to Cp_3Ce, not Cp_4Ce, and preliminary reports indicated this was correct.[11,12] We report here the details of this reaction, including a simplified high-yield synthesis of $Cp_3Ce(THF)$, intermediates in the reaction, and X-ray data on a new cerium(III) nitrate. The overall reaction scheme presented here and the structurally characterized cerium(III) nitrate derivative help explain the general reactivity of CAN and demonstrate that it is a viable precursor to Ce(III) complexes.

Results and Discussion

Synthesis. CAN reacts with NaCp in THF under N_2 in an exothermic reaction that evolves gas. If CAN is treated with 6 equiv of NaCp and if the reaction is worked up after 30–60 min, a >90% yield of $Cp_3Ce(THF)$ (identified by NMR spectroscopy and X-ray crystallography) can be obtained (reaction 1) as well as a high yield of a white salt presumed to be $NaNO_3$. The gas evolved in the reaction is NH_3, and the presence of oily hexane-soluble byproducts is consistent with $C_5H_5^-$ oxidation products.

$$(NH_4)_2Ce(NO_3)_6 + 6NaCp \xrightarrow{THF} Cp_3Ce(THF) + 2NH_3 + 6NaNO_3 + 2CpH + \text{Cp oxidn products} \quad (1)$$

In order to identify intermediate steps in the overall 6-equiv reaction, CAN has also been treated with 1, 3, and 5 equiv of NaCp. These results are consistent with the reactions shown in Scheme I and with the following individual steps. (a) Initially, 1 equiv of NaCp is consumed in a reaction resulting in complete reduction of Ce^{4+} to Ce^{3+} (eq a). An unstable black intermediate is present in this step. (b) Two equivalents of NaCp subsequently reacts with NH_4^+ ions to form NH_3, $NaNO_3$, and CpH, leaving 1 equiv of "$Ce(NO_3)_3(THF)_x$" (eq b). (c) Three equivalents of NaCp replaces the NO_3 groups in "$Ce(NO_3)_3(THF)_x$" to form the observed $Cp_3Ce(THF)$ and more $NaNO_3$ (eq c). The validity of these steps was tested in a variety of ways as described below.

Scheme I

$$(NH_4)_2Ce(NO_3)_6 + NaCp \xrightarrow{THF} \text{“}CpCe(NO_3)_5(NH_4)_2\text{”} + NaNO_3 \rightarrow (NH_4)_2Ce(NO_3)_5 + \text{Cp oxidn products} \quad (a)$$

$$(NH_4)_2Ce(NO_3)_5 + 2NaCp \xrightarrow{THF} \text{“}Ce(NO_3)_3(THF)_x\text{”} + 2NaNO_3 + 2NH_3 + 2CpH \quad (b)$$

$$\text{“}Ce(NO_3)_3(THF)_x\text{”} + 3NaCp \rightarrow Cp_3Ce(THF) + 3NaNO_3 \quad (c)$$

$$(NH_4)_2Ce(NO_3)_6 + 5NaCp \xrightarrow{THF} Cp_2Ce(NO_3)_2Na(THF)_2 + 4NaNO_3 + 2NH_3 + 2CpH + \text{Cp oxidn products} \quad (d)$$

$$(NH_4)_2Ce(NO_3)_5 + 5NaCp \rightarrow Cp_3Ce(THF) + 5NaNO_3 + 2NH_3 + 2CpH \quad (e)$$

During dropwise addition of the first equivalent of NaCp to CAN, no gas formation is observed and the formation of an unstable species is clearly indicated by color changes. A black color appears upon contact of the NaCp solution with the CAN solution, but this color dissipates almost immediately. It is possible that the black color arises from a charge-transfer absorption in a transient cyclopentadienylcerium(IV) complex such as "$CpCe(NO_3)_5(NH_4)_2$". This possibility is consistent with the observation that Cp_3CeOR complexes are black.[13-16]

The reaction of CAN with the first equivalent of NaCp can be effectively titrated by using this black species as a colorimetric indicator. The black species ceases to form after 1.05–1.15 mol of NaCp is added/mol of CAN. After 1.15 mol of NaCp is added, the solution contains no Ce(IV), as shown by a qualitative test with barium 4-(phenylamino)benzenesulfonate.[17] These results are consistent with eq a in Scheme I, which shows that the first step in this reaction is the reduction of Ce(IV) to Ce(III) by NaCp. This reaction apparently occurs first with little overlap of the subsequent reactions (eq b and c), since the titration shows that an excess of only 0.05–0.15 equiv of NaCp is needed to completely reduce Ce(IV) to Ce(III).

When CAN is treated with 3 equiv of NaCp, the color changes described above occur as NaCp is initially added, but subsequently, vigorous evolution of NH_3 occurs. A precipitate ($NaNO_3$) is formed along with a cerium product of low solubility, which contains no detectable Cp ligands (by NMR spectroscopy and decomposition studies). These results are consistent with a combination of eq a and b, which show "$Ce(NO_3)_3(THF)_x$" as the likely cerium product.[18] Further support for the existence of a species like "$Ce(NO_3)_3(THF)_x$" arises from an X-ray crystallographic study of a dimethoxyethane (DME) analogue, Ce-

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(1) (a) Rhone-Poulenc, Inc. (b) University of California, Irvine.

(2) Gradeff, P. S.; Schreiber, F. G.; Brooks, K. C.; Sievers, R. E. *Inorg. Chem.* **1985**, *24*, 1110–1111.

(3) Gradeff, P. S.; Schreiber, F. G.; Mauermann, H. *J. Less-Common Met.* **1986**, *126*, 335–338.

(4) Deming, T. J.; Olofson, J. M.; Ziller, J. W.; Evans, W. J. *Abstracts of Papers*, 196th National Meeting of the American Chemical Society, Los Angeles, CA; American Chemical Society: Washington, DC, 1988; INOR 221.

(5) Kalsotra, B. L.; Anand, S. P.; Multani, R. K.; Jain, B. D. *J. Organomet. Chem.* **1971**, *28*, 87–89.

(6) Kalsotra, B. L.; Multani, R. K.; Jain, B. D. *Isr. J. Chem.* **1971**, *9*, 569–572; *J. Inorg. Nucl. Chem.* **1973**, *35*, 311–313.

(7) Kapur, S.; Multani, R. K. *J. Organomet. Chem.* **1973**, *63*, 301–303.

(8) Kapur, S.; Kalsotra, B. L.; Multani, R. K.; Jain, B. D. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1689–1691.

(9) Deacon, G. B.; Tuong, T. D.; Vince, D. G. *Polyhedron* **1983**, *2*, 969–970.

(10) Birmingham, J. M.; Wilkinson, G. *J. Am. Chem. Soc.* **1956**, *78*, 42–44.

(11) (a) Gradeff, P. S.; Schreiber, F. G. *NATO ASI Ser., Ser. C* **1984**, *No. 155*. (b) Rhone-Poulenc, Inc., U.S. Patents 4,492,655 and 4,703,109, 1985.

(12) Jacob, K.; Glanz, M.; Tittes, K.; Thiele, K. H. *Z. Anorg. Allg. Chem.* **1988**, *556*, 170–178.

(13) Greco, A.; Cesca, S.; Bertolini, G. *J. Organomet. Chem.* **1976**, *113*, 321–330.

(14) Gulino, A.; Casarin, M.; Conticello, V. P.; Guadiello, J. G.; Mauermann, H.; Fragala, I.; Marks, T. J. *Organometallics* **1988**, *7*, 2360–2364.

(15) Evans, W. J.; Deming, T. J.; Ziller, J. W. *Organometallics*, in press.

(16) Black cerium products were also observed in reactions of $(pyH)_2[CeCl_6]$ with NaCp.[9]

(17) Scott, W. W. *Standard Methods of Chemical Analysis*, 5th ed.; Van Nostrand: Princeton, NJ, 1939; Vol. 1, p 1206.

(18) Complexometric analysis is consistent with x = 1–2.

$(NO_3)_3(DME)_2$ (see below). The "$Ce(NO_3)_3(THF)_x$" product of reaction b reacts with 3 equiv of NaCp to form $Cp_3Ce(THF)$ in 80% yield (eq c). Hence, reactions a–c constitute a stepwise equivalent of reaction 1.

The reaction of 5 equiv of NaCp with CAN (reaction d) proceeds like reactions a–c except that the final product is a new complex formulated as $Cp_2Ce(NO_3)_2Na(THF)_2$ on the basis of analytical and spectroscopic data. *Caution*! This material decomposes explosively upon heating.[19] The proposed formula is consistent with the rather large class of known $(C_5R_5)_2LnX_2M(ether)_2$ complexes, where X is an anion and M is an alkali metal (R = H, Me).[20] The formation of $Cp_2Ce(NO_3)_2Na(THF)_2$ is also consistent with stepwise replacement of NO_3 groups by Cp in eq c.

$Cp_3Ce(THF)$ has also been made from another cerium(III) nitrate complex, $(NH_4)_2Ce(NO_3)_5$, as shown in reaction e. This reaction proceeded like reaction 1 in that it was an exothermic reaction in which gas evolved and precipitate formed ($NaNO_3$). However, no black color was observed initially with this Ce(III) precursor. This result is consistent with the above discussion of eq a, namely that the transient black intermediate is associated with the reduction of Ce(IV) to Ce(III).

Variations in the reaction conditions for the CAN/$C_5H_5^-$ system have been explored beyond those given in the Experimental Section. No advantage was found in the use of larger amounts of THF solvent to solubilize more of the CAN. Reactions in 6 times as much THF gave equivalently high yields of $Cp_3Ce(THF)$ after 30–60 min. On the other hand, longer reaction times, for example 24 h for the CAN/6NaCp reaction, gave lower yields of $Cp_3Ce(THF)$[12] and the formation of dark purple-brown byproducts. Since longer reaction times for the $(NH_4)_2Ce(NO_3)_5$/5NaCp reaction did *not* give these dark byproducts, they may arise from the products of the Ce(IV) oxidation of $C_5H_5^-$ (eq a). If more than 6 equiv of NaCp is reacted with CAN, the complex $Cp_4CeNa(THF)$ is reported to form.[12]

The stepwise nature of the CAN/NaCp reaction is very reasonable and suggests that CAN can easily be used as a precursor to mixed-ligand cerium complexes containing nitrate. Control of product composition can be accomplished by varying the stoichiometry. Note that the limited solubility of CAN in THF does not prevent high-yield reactions from occurring in short reaction times.

Structure. The identity of the $Cp_3Ce(THF)$ product of the CAN/6NaCp reaction was confirmed by X-ray crystallography. The crystals are isostructural with the other crystallographically characterized members of the series $Cp_3Ln(THF)$ in which Ln = La,[21] Nd,[22,23] Pr,[22] Sm,[24] Gd,[25] Y,[21] Yb,[26] and Lu.[27]

In the course of our studies on CAN, the structure of the cerium(III) nitrate, $Ce(NO_3)_3(DME)_2$, obtained as a byproduct in the DME recrystallization of a CAN/$NaOCMe_3$ reaction product, has been determined. This complex, shown in Figure 1, contains a cerium atom surrounded by five bidentate ligands. The structure of this ML_3L_2' complex (L, L′ = chelating ligand) is not easily described. The different sizes and bite angles of the two types of chelates lead to an overall ligand arrangement that does not conform to common coordination geometries.[28]

Table I. Selected Ce–O Bond Lengths (Å) and Angles (deg) in $Ce(NO_3)_3(DME)_2$

Ce(1)–O(1)	2.529 (2)	Ce(1)–O(7)	2.539 (2)
Ce(1)–O(2)	2.606 (2)	Ce(1)–O(8)	2.593 (2)
Ce(1)–O(4)	2.550 (2)	Ce(1)–O(10)	2.563 (2)
Ce(1)–O(5)	2.604 (2)	Ce(1)–O(11)	2.571 (2)
O(1)–Ce(1)–O(2)	49.9 (1)	O(10)–Ce(1)–O(11)	63.1 (1)
O(4)–Ce(1)–O(5)	49.5 (1)	O(12)–Ce(1)–O(13)	62.6 (1)
O(7)–Ce(1)–O(8)	49.9 (1)		

The five chelating ligands roughly describe a trigonal bipyramid in which the nitrate group containing N(2) is at one apical position and the DME ligand containing O(12) and O(13) is at the other apical position. This perspective can also be used to describe a structure for all ten oxygen donor atoms in which six are in a plane with two above and two below. This is not a normal ten-coordinate geometry, however, and the set of six oxygen atoms is not rigorously planar. The best plane formed by the six oxygens O(1), O(2), O(7), O(8), O(10), and O(11) and Ce(1) has a mean deviation of 0.44 Å. The two sets of two oxygen atoms above and below this "plane" are roughly perpendicular: the dihedral angle between the Ce(1), O(4), O(5) plane and the Ce(1), O(12), O(13) plane is 101°.

An alternative view of $Ce(NO_3)_3(DME)_2$ involves considering the small-bite NO_3 ligands as occupying just one coordination site. In the past, nitrate groups often have been considered to occupy one coordination position,[29–33] and a particularly pertinent example is $(Ph_3EtP)_2Ce(NO_3)_5$, which was described as a trigonal bipyramid.[33] Since $(Ph_3EtP)_2Ce(NO_3)_5$ is a homoleptic system, it is much more symmetric than the mixed-ligand complex $Ce(NO_3)_3(DME)_2$.

If one considers the NO_3 ligands to occupy one site and the DME ligands to occupy two sites, $Ce(NO_3)_3(DME)_2$ can be viewed as a seven-coordinate complex. A distorted pentagonal-bipyramidal geometry can be envisioned in which the nitrate ligands containing N(2) and N(3) and the O(12), O(13), and O(10) atoms comprise the pentagonal plane (mean deviation from the plane containing Ce(1) of 0.35 Å) and O(11) and the nitrate containing N(1) are the apical ligands. The 150° N(1)(nitrate)–Ce(1)–O(11) angle shows that this view is also not close to the idealized geometry. Nevertheless, this may be the best description of this structure.

In contrast to the irregularity of the overall geometry, the bond distances and angles are quite regular (Table I and supplementary material). The three O–Ce–O angles of the nitrate ligands are very similar, 49.9 (1), 49.9 (1) and 49.5 (1)°, and the O–Ce–O angles of the DME ligands, 62.6 (1) and 63.1 (1)°, are very close in size. The N–O distances for oxygen atoms attached to cerium fall in a narrow range of 1.264 (4)–1.277 (4) Å, and the other N–O distances are 1.218 (3)–1.225 (4) Å. The O–N–O angles for the oxygen atoms coordinated to the cerium are 116.4 (2)–116.6 (2)°, whereas the other O–N–O angles are 121.4 (3)–122.1 (3)°. These variations in the nitrate parameters are typical for bidentate NO_3 ligands.[32]

The average Ce–O(nitrate) distance of 2.57 (3) Å in $Ce(NO_3)_3(DME)_2$ can be compared to the Ce–O(nitrate) average distances of 2.569 (15) Å in $(Ph_3EtP)_2Ce(NO_3)_5$,[33] 2.64 (2) Å

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(19) Gradeff, P. S. *Chem. Eng. News* **1988**, *66* (Aug 1), 2.

(20) For example: Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1980**, *19*, 2190–2191. Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271–3278. Tilley, T. D.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3267–3270. Schumann, H.; Lauke, H.; Hahn, E.; Heeg, M. J.; van der Helm, D. *Organometallics* **1985**, *4*, 321–324. Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103–8110. Hazin, P. N.; Huffman, J. C.; Bruno, J. W. *Organometallics* **1987**, *6*, 23–27. Lappert, M. F.; Singh, A.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1981**, 1191–1193.

(21) Rogers, R. D.; Atwood, J. L.; Emad, A.; Sikora, D. J.; Rausch, M. D. *J. Organomet. Chem.* **1981**, *216*, 383–392.

(22) Fan, Y.; Lu, P.; Jin, Z.; Chen, W. *Sci. Sin., Ser. B (Engl. Ed.)* **1984**, *27*, 993–1001.

(23) Benetello, F.; Bombieri, G.; Castellani, C. B.; Jahn, W.; Fischer, R. D. *Inorg. Chim. Acta* **1984**, *95*, L7–L10.

(24) Deacon, G. B.; Koplick, A. J.; Tuong, T. D. *Aust. J. Chem.* **1984**, *37*, 517–525.

(25) Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Organomet. Chem.* **1980**, *192*, 65–73.

(26) Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. J.; Bott, S. G.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 4983–4994.

(27) Ni, C.; Deng, D.; Quian, C. *Inorg. Chim. Acta* **1985**, *110*, L7–L10.

(28) cf: Favas, M. C.; Kepert, D. L. *Prog. Inorg. Chem.* **1981**, *28*, 309–367.

(29) Cotton, F. A.; Goodgame, D. M. L.; Soderberg, R. H. *Inorg. Chem.* **1963**, *2*, 1162–1166.

(30) Bergman, J. G., Jr.; Cotton, F. A. *Inorg. Chem.* **1966**, *5*, 1208–1213.

(31) Taylor, J. C.; Mueller, M. H.; Hitterman, R. L. *Acta Crystallogr.* **1966**, *20*, 842–851.

(32) Addison, C. C.; Garner, C. D.; Logan, N.; Wallwork, S. C. *Q. Rev., Chem. Soc.* **1971**, *25*, 289–322 and references therein.

(33) Al-Karaghouli, A. R.; Wood, J. S. *J. Chem. Soc., Dalton Trans.* **1973**, 2318–2321.

in $[Ce(NO_3)_6]_2Mg_3(H_2O)_{24}$,[34] and 2.666 Å in $[Ce(NO_3)_4(H_2O)_2(4,4'\text{-bipyridine})]^-$.[35] Assuming again that the NO_3 ligand occupies one site, these cerium(III) nitrates are five-, six-, and seven-coordinate, respectively. Interestingly, the Ce–O(nitrate) distance in $Ce(NO_3)_3(DME)_2$ is closer to that of the five-coordinate complex than to that of the seven-coordinate complex.

A search of the Cambridge Structural Database revealed no Ce(III)–DME complexes with which to compare the 2.57 (3) Å average Ce–O(DME) distances. This average is identical with the Ce–O(nitrate) average and is reasonable compared to the 2.68–2.69 Å Ln–O(DME) distances in $\{[(Me_3Si)_2N]SmI(DME)(THF)\}_2$[36] and $[(Me_3Si)_2N]_2Eu(DME)_2$,[37] when the differences in oxidation state and coordination number are considered.[38]

Conclusion

CAN reacts with NaCp in a multistep reaction to give $Cp_3Ce(THF)$ in high yield. The overall reaction can be experimentally broken into distinct steps as shown in Scheme I. CAN, therefore, appears to be a viable starting material for the syntheses of a variety of cerium complexes containing both mixtures of nitrate and other anionic ligands and nitrate-free systems.

Experimental Section

The syntheses and subsequent manipulations of the complexes described below were conducted with the rigorous exclusion of air and water by using Schlenk-line and glovebox (Vacuum/Atmospheres HE-553 Dri-Lab) techniques.

Materials. Toluene, hexane, and THF were distilled from sodium benzophenone ketyl. C_6D_6 was vacuum-transferred from sodium benzophenone ketyl. Anhydrous ceric ammonium nitrate (Rhone-Poulenc) was stored under nitrogen until used. Sodium cyclopentadienide was prepared from the reaction of sodium hydride with freshly cracked cyclopentadiene in THF and was dried on a high-vacuum line before use.

Physical Measurements. Infrared spectra[39] and complexometric titration[40] data were obtained as previously described. ^1H NMR spectra were recorded by using a Bruker WM 250-MHz spectrometer and were referenced to residual protons in C_6D_6 (δ 7.15) or β-methylene protons in THF-d_8 (δ 1.79). ^{13}C NMR spectra were obtained on QE 300-MHz and GN 500-MHz NMR spectrometers. Complete elemental analyses were obtained from Dornis and Kolbe.

Synthesis of $(C_5H_5)_3Ce(THF)$ from CAN. Under nitrogen, NaC_5H_5 (723 mg, 8.21 mmol) suspended in 7 mL of THF in an addition funnel was added over a 1-min period to a stirred suspension of CAN (750 mg, 1.37 mmol) in 4 mL of THF in a 250-mL Schlenk flask containing a stir bar. An exothermic reaction occurred, the solution initially became black, and gas was evolved. Shortly after all of the NaC_5H_5 was added, the solution became orange-yellow. After 30–60 min of additional stirring, the mixture was filtered to give a tan precipitate and an orange-yellow filtrate. The precipitate was washed with 20 mL of THF and then was dried and weighed (615.4 mg, compared to 697.5 mg expected for $NaNO_3$, an 88% yield). The solvent was removed from the filtrate by rotary evaporation (while the flask was heated with a 50 °C H_2O bath) to give a tan powder. The powder was washed with hexane and extracted into toluene. Removal of toluene by rotary evaporation gave pure $(C_5H_5)_3Ce(THF)$ (517 mg, 1.27 mmol, 92%) as a tan powder. As previously reported,[9,24] the complex is not soluble in alkanes and violently decomposes in air. ^1H NMR (C_6D_6): δ 7.67 ($\Delta\nu_{1/2}$ = 20 Hz, C_5H_5), −4.3 ($\Delta\nu_{1/2}$ = 17 Hz, THF), −10.2 ($\Delta\nu_{1/2}$ = 49 Hz, THF). ^{13}C NMR (C_6D_6): δ 147.4 (C_5H_5); THF not observed. Recrystallization of the powder from warm THF gave orange-yellow X-ray-quality platelets. The space group was $P2_1/n$ with unit cell constants a = 8.339 (4) Å, b = 24.637 (16) Å, c = 8.432 (8) Å, β = 101.64 (6)°, and V = 1697 (2) Å^3. The compound was isostructural with the other crystallographically characterized $(C_5H_5)_3Ln(THF)$ species (Ln = La,[21] Nd,[22,23] Pr,[22] Sm,[24] Gd,[25] Y,[21] Yb,[26] Lu[27]).

Table II. Crystallographic Data for $Ce(NO_3)_3(DME)_2$

formula	$CeC_8H_{20}N_3O_{13}$	cell vol, Å^3	1799.5 (4)
mol wt	506.4	mol/unit cell	4
space group	$P2_1/n$	D(calcd), Mg m^{-3}	1.87
		temp, K	213
cell consts		μ(calcd), mm^{-1}	2.45
a, Å	10.4404 (11)	radiation (λ, Å)	Mo Kα (0.710730)
b, Å	15.1301 (21)		
c, Å	11.4023 (13)		
β, deg	92.431 (9)		

Synthesis of $(C_5H_5)_3Ce(THF)$ from $(NH_4)_2Ce(NO_3)_5$. Under N_2, NaCp (362.4 mg, 4.11 mmol) suspended in 30 mL of THF in an addition funnel was added dropwise to a stirred suspension of $(NH_4)_2Ce(NO_3)_5$[41] (400 mg, 0.823 mmol) in 20 mL of THF in a 250-mL Schlenk flask. An exothermic reaction occurred, gas was evolved, and the suspension initially was colorless. Shortly after all of the NaCp was added, the solution became orange-yellow. After 17 h of additional stirring, the mixture was filtered to give a white precipitate and an orange filtrate. The precipitate was dried and weighed (276 mg, compared to 350 mg expected for $NaNO_3$, a 79% yield). The solvent was removed from the filtrate by rotary evaporation (while the flask was heated with a 50 °C H_2O bath) to give a tan powder. The powder was washed with hexane and then extracted into toluene. Removal of toluene by rotary evaporation gave $Cp_3Ce(THF)$ as a tan powder (260 mg, 77% yield), which was identified by ^1H NMR spectroscopy.

Synthesis of $Cp_2Ce(NO_3)_2Na(THF)_2$. Under N_2, NaCp (602.5 mg, 6.84 mmol) suspended in 30 mL of THF in an addition funnel was added over a 1-min period to a stirred suspension of CAN (750 mg, 1.37 mmol) in 20 mL of THF in a 250-mL Schlenk flask. An exothermic reaction occurred, the solution initially became black, and gas was evolved. Shortly after all of the NaCp was added, the solution became orange-yellow. After 30–60 min of additional stirring, the mixture was filtered to give a tan precipitate and an orange-yellow filtrate. The precipitate was dried and weighed (551 mg, compared to 465 mg expected for $NaNO_3$, a 118% yield, i.e., not just $NaNO_3$). The solvent was removed from the filtrate by rotary evaporation (while the flask was heated with a 50 °C H_2O bath) to give a tan powder. The powder was washed with hexane and toluene and then extracted into THF. Removal of solvent by rotary evaporation gave a tan powder (516 mg, a 67% yield). The product decomposed violently when placed under vacuum into a 100–110 °C oil bath.[19] ^1H NMR (THF-d_8): δ 9.0 ($\Delta\nu_{1/2}$ = 32 Hz, C_5H_5). ^{13}C NMR (THF-d_8): δ 155.5 (C_5H_5), 69.4 (THF), 27.7 (THF). IR (KBr): 2980 m, 1480 br, s, 1340 s, 1270 s, 1020 s, 860 m, 780 s cm^{-1}. Anal. Calcd for $CeC_{18}H_{26}NaN_2O_8$: Ce, 24.97; C, 38.49; H, 4.63; Na, 4.10; N, 5.00. Found: Ce, 25.55; C, 38.88; H, 4.30; Na, 4.11; N, 6.41.

Collection of X-ray Diffraction Data and Structure Solution for $Ce(NO_3)_3(DME)_2$. A clear prism of approximate dimensions 0.27 × 0.43 × 0.44 mm immersed in Paratone-N (Exxon lube oil additive) and mounted on a glass fiber was transferred to a Syntex P2$_1$ diffractometer that was equipped with a modified LT-1 apparatus. Subsequent setup operations (determination of accurate unit cell dimensions and orientation matrix) and collection of low-temperature (213 K) intensity data were carried out by using standard techniques similar to those of Churchill.[42] Final cell parameters are based on a least-squares analysis of 25 reflections in well-separated regions of reciprocal space, all having 30° < 2θ < 34°. Details are given in Table II and in the supplementary material.

All 5735 data were corrected for the effects of absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale by means of a Wilson plot. A careful survey of a preliminary data set revealed the systematic extinctions $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$; the diffraction symmetry was $2/m$. The centrosymmetric monoclinic space group $P2_1/n$, a nonstandard setting of $P2_1/c$ (C_{2h}^5; No. 14), was thus uniquely defined.

All crystallographic calculations were carried out by using either our locally modified version of the UCLA Crystallographic Computing Package[43] or the SHELXTL PLUS program set.[44] Analytical scattering factors for neutral atoms were used throughout the analysis;[45a] both the

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(34) Zalkin, A.; Forrester, J. D.; Templeton, D. H. *J. Chem. Phys.* **1963**, *39*, 2881–2891.

(35) Bukowska-Strzyzewska, M.; Tosik, A. A. *Inorg. Chim. Acta* **1978**, *30*, 189–196.

(36) Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 575–579.

(37) Tilley, T. D.; Zalkin, A.; Andersen, R. A.; Templeton, D. H. *Inorg. Chem.* **1981**, *20*, 551–554.

(38) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751–767.

(39) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008–2014.

(40) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115–4119.

(41) Gradeff, P. S.; Yunlu, K. Manuscript in preparation.

(42) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265–271.

(43) "UCLA Crystallographic Computing Package"; University of California: Los Angeles, CA, 1981. Strouse, C. Personal communication.

(44) Nicolet Instrument Corp., Madison, WI, 1988.

(45) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974: (a) pp 99–101; (b) pp 149–150.

real ($\Delta f'$) and the imaginary ($i\Delta f''$) components of anomalous dispersion[45b] were included. The quantity minimized during least-squares analysis was $\sum w(F_o - F_c)^2$ where $w^{-1} = \sigma^2(F) + 0.0003F^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares methods. Hydrogen atom contributions were included by using a riding model with $d(\text{C-H}) = 0.96$ Å and $U(\text{iso}) = 0.08$ Å^2. Refinement of positional and anisotropic thermal parameters led to convergence with $R_F = 3.0\%$, $R_{wF} = 3.9\%$, and GOF = 1.62 for 227 variables refined against those 5038 data with $|F_o| > 1.0\sigma(|F_o|)$ ($R_F = 2.4\%$ and $R_{wF} = 3.7\%$ for those 4490 data with $|F_o| > 6.0\sigma(|F_o|)$). A final difference Fourier synthesis showed no significant features, $\rho(\max) = 0.87$ e Å^{-3}.

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Supplementary Material Available: Tables of complete crystallographic data, positional parameters, bond distances, bond angles, thermal parameters, and H atom coordinates (4 pages); a list of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

Contribution from Ames Laboratory,[1] U.S. DOE, and Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Tetrakis(pyridine)tetrachloro(μ-chloro)(μ-hydrido)ditungsten(*W*–*W*) and Its 4-Ethylpyridine Homologue. Compounds Derived from a Quadruply Bonded Dimer by Ligand Exchange and Oxidative Addition of Hydrogen Chloride

Richard T. Carlin and Robert E. McCarley*

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Reaction of $W_2(mhp)_4$ (mhp = anion of 6-methyl-2-hydroxypyridine) with $(CH_3)_3SiCl$ and pyridine in the presence of methanol provides the light brown compound $W_2HCl_5(NC_5H_5)_4$. The 4-ethylpyridine adduct $W_2HCl_5(NC_5H_4C_2H_5)_4$ is obtained by ligand exchange at 100 °C. Brown crystals of the latter are monoclinic, space group *C*2/*c*, with *a* = 11.883 (3) Å, *b* = 13.213 (3) Å, *c* = 21.727 (4) Å, β = 96.39 (3)°, and *Z* = 4. Structure refinement revealed an edge-shared bioctahedral arrangement with one H atom and one Cl atom in bridging positions between the metal atoms. The Cl atoms all occupy positions in the equatorial plane, and the 4-ethylpyridine ligands occupy the axial positions of the dimer. The short W–W distance, 2.516 (2) Å, is consistent with a W–W multiple bond. Comparison of the infrared spectra of the hydride and deuteride derivatives confirms the presence of a bridging H atom and indicates an isostructural arrangement for the pyridine and 4-ethylpyridine derivatives, as do electronic reflectance spectra.

Introduction

The chemistry of quadruply bonded tungsten dimers is a relatively new area of study. Of particular interest is the readily obtained $W_2(mph)_4$, where mhp is the anion of 2-hydroxy-6-methylpyridine.[2] This compound has been found to undergo a number of reactions, including ligand exchange with bidentate ligands in which the quadruple bond remains intact[3,4] and metal–metal bond cleavage by π-acceptor ligands to form monomeric tungsten(II) derivatives.[5] Intermediate between these two extremes are the reactions in which the W_2^{4+} core is oxidized to form a compound with a metal–metal bond of order less than four. This has been observed when $W_2(mhp)_4$ or $W_2(dmhp)_4$ is treated with hydrogen halide in alcohol solutions to form the tungsten(III) compounds $W_2HCl_5(dppm)_2$[6] and $Cs_3W_2X_9$,[7] and the tungsten(IV) complex $W_2X_4(OR)_4(ROH)_2$,[8] and in this laboratory when $W_2(mhp)_4$ is reacted with $AlCl_3$ in diglyme to produce the one-electron-oxidized species $W_2Cl_2(mhp)_3$ with a bond order of 3.5.[9]

In this paper, we wish to report the synthesis and structure of another W(III) dimer. The preparation involves the oxidation of the quadruple bond to a bond of lower order.

Experimental Section

Materials. $W_2(mhp)_4$ was prepared by the established procedure.[2] Pyridine and 4-ethylpyridine were dried by refluxing over CaH_2 followed by distillation. Absolute ethanol and anhydrous diethyl ether were used from the bottles without further purification.

Analyses. Tungsten analyses were performed by decomposing samples with nitric acid and igniting them in tared porcelain crucibles to tungsten trioxide. Chlorine analyses were carried out by first decomposing samples in absolute ethanol by using KOH/H_2O_2. The resulting solutions were evaporated to near dryness, water was added, and the remainder of the ethanol was boiled off. Following acidification with dilute nitric acid, potentiometric titrations with a standard silver nitrate solution were performed.

Physical Measurements. Standard infrared spectra were obtained on a Beckman IR 4250 spectrometer using both Nujol and fluorocarbon mulls on CsI or KBr plates. Fourier transform infrared spectra were obtained on an IBM IR/90 spectrometer using Nujol mulls on either CsI plates or polyethylene disks. X-ray photoelectron spectra were measured with an AEI-200B instrument using Al Kα radiation (1486.6 eV). Beckman DU and Cary 14 spectrophotometers were used to measure the reflectance and solution UV–visible spectra, respectively.

Synthesis of $W_2(\mu\text{-H})(\mu\text{-Cl})Cl_4(py)_4$. In a typical reaction, 3 g (3.75 mmol) of $W_2(mph)_4$ and a magnetic stirring bar were introduced under nitrogen atmosphere into a 100-mL reaction flask equipped with a water jacket. Approximately 30 mL of dry pyridine was added either by syringe from a storage flask or by fresh distillation from CaH_2. The reaction flask was then evacuated on a vacuum line, and 6 mL (47.2 mmol) of trimethylchlorosilane were vacuum distilled into the flask. The mixture was refluxed under nitrogen for ca. 6 h. It was then cooled to below reflux and 1 mL of methanol was added by syringe while a nitrogen flush was maintained. The mixture was refluxed for an additional 10 h, cooled to room temperature, and filtered. The resulting solid was washed with absolute ethanol and anhydrous diethyl ether and then vacuum-dried, giving the desired product, $W_2HCl_5(py)_4$, as a light brown powder in ca. 65% yield. Anal. Calcd for $W_2Cl_5C_{20}H_{21}N_4$: W, 42.64; Cl, 20.55; C, 27.86; H, 2.45; N, 6.50. Found: W, 42.1; Cl, 20.6; C, 27.80; H, 2.42; N, 6.46.

An oxidation state determination was also performed by decomposing samples in a standard acidic Ce(IV) solution to oxidize tungsten to

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(2) Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.

(3) Cotton, F. A.; Niswander, R. H.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3541.

(4) Sattelberger, A. P.; McLaughlin, K. W. *J. Am. Chem. Soc.* **1981**, *103*, 2880.

(5) Mailki, W. S.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 1380.

(6) Fanwick, P. E.; Harwood, W. S.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 242.

(7) DeMarco, D.; Nimry, T.; Walton, R. A. *Inorg. Chem.* **1980**, *19*, 575.

(8) Anderson, L. B.; Cotton, F. A.; DeMarco, D.; Fang, A.; Ilsley, W. H.; Kolthammer, B. W. S.; Walton, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 5078.

(9) Ryan, T.; McCarley, R. E. To be submitted for publication.

0020-1669/89/1328-2604$01.50/0