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Synthesis and structure of nitrile-solvated rare earth metallocene cations $[Cp_2Ln(NCR)_3][BPh_4]$ ($Cp = C_5Me_5, C_5H_4SiMe_3$; R = Me, ^tBu, Ph)

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A R T I C L E I N F O

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Dedicated to Professor Malcolm Chisholm for being inspirational in so many ways. Your interactive, courageous, and enthusiastic manner of advancing science provides a model for all of us to emulate.

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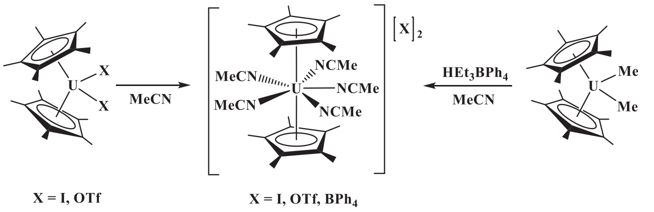
A B S T R A C T

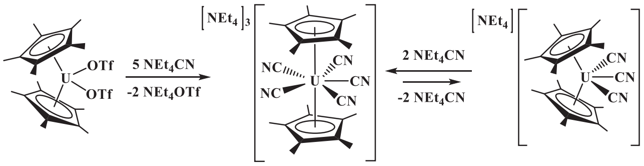
The coordination chemistry of MeCN, ^tBuCN, and PhCN with the cationic rare earth metallocene complexes $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$, **1-Ln** (Ln = Y, La, Gd), has been examined to determine how nitrile coordination will affect the metallocene geometry. Crystallographic determination of geometry was possible for $[(C_5Me_5)_2Ln(NCMe)_3][BPh_4]$ (**2-Y**, **2-Gd**), $[(C_5Me_5)_2Y(NC^tBu)_3][BPh_4]$ (**3-Y**), and $[(C_5Me_5)_2Ln(NCPh)_3][BPh_4]$ (**4-La**, **4-Gd**). In each case, only three nitriles are found to coordinate and the metallocenes are bent with (C_5Me_5 ring centroid)–metal–(C_5Me_5 ring centroid) angles of 137–140°. The THF adduct, $[(C_5Me_5)_2La(NCMe)_2(THF)][BPh_4]$, **5-La**, was also crystallographically characterized. A similar result was observed with the yttrium metallocene of the trimethylsilyl-containing ligand $(C_5H_4SiMe_3)^{1-}$: coordination of only three nitriles is found in $[(C_5H_4SiMe_3)_2Y(NCMe)_3][BPh_4]$, **6-Y**, which has a 136.8° (C_5Me_5 ring centroid)–Y–(C_5Me_5 ring centroid) angle.

1. Introduction

One of the remarkable advances in actinide metallocene chemistry in recent years has been the discovery that the bent metallocene geometry, found in every $(C_5Me_5)_2AnX_nL_m$ complex (An = actinide; X = anionic ligand; L = neutral ligand; $n = 1, 2$; $m = 0–2$) reported since the first example in 1978 [1], could be converted to a structure in which the two cyclopentadienyl planes are parallel, Eq. (1) [2–4]. Although there have been numerous reports of f element cyclooctatetraene (COT)-containing complexes with parallel ring geometries [5–15], as well as nearly parallel geometries obtained with $(COT)Ln(C_5Me_5)$ systems [16–22], bis(pentamethylcyclopentadienyl) complexes of the f elements always had bent metallocene geometries. The conversion of the bent to linear geometry was accomplished by surprisingly simple reactions: addition of acetonitrile (MeCN) to the tetravalent uranium complexes $(C_5Me_5)_2UX_2$ (X = I, OTf) [2] and addition of $HNEt_3BPh_4$ to $(C_5Me_5)_2UMe_2$ in MeCN, Eq. (1) [3]. Metallocenes with parallel C_5Me_5 planes could also be obtained by addition of NEt_4CN to the uranium metallocene $(C_5Me_5)_2U(OTf)_2$, Eq. (2) [4]. In Eq. (2), the linear penta-cyanide complex is found to be in equilibrium with the bent tri-cyanide analog [4].



(1)



(2)

Detailed studies of the bent versus linear metallocene geometries for the uranium metallocenes showed that the structures were highly dependent on reaction conditions, and parallel plane

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structures were favored for U^{4+} and U^{5+}, but not U^{3+} [3,23]. The similarity of the bent metallocene structures $(C_5Me_5)_2UI(NCMe)_2$ [3] and $(C_5Me_5)_2CeI(NCMe)_2$ [24] could indicate that parallel plane metallocenes were also not favored with Ln^{3+} complexes [3].

Since an extensive series of unsolvated metallocene cations of the formula $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ are available [25–28] and contain labile $(BPh_4)^{1-}$ anions, it was of interest to determine how nitrile coordination would affect their structure. Formation of bent metallocene base adducts of these cations, i.e., $[(C_5Me_5)_2LnL_2][BPh_4]$, are known for L = $OPPh_3$ [29], tetrahydrothiophene [30], THF [31], pyridine [32], acetone [32], and NH_3 [33], but the effect of coordination of cylindrical nitriles was unknown. If metallocenes with parallel rings could be obtained for highly paramagnetic lanthanides, it would provide a new class of rare earth metallocenes with axial symmetry [5,34].

Although no metallocenes with parallel rings have been observed for +3 metal complexes of the f elements, the use of the $(BPh_4)^{1-}$ precursors had not been examined. We report here the structures of products from adding nitriles to $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ as well as to the Me_3Si-substituted cyclopentadienyl system $[(C_5H_4SiMe_3)_2Y(THF)_2][BPh_4]$. Since the key point of comparison is the bent versus linear geometry, and since both structures would have similar NMR spectral patterns when observable in the systems with lower magnetic moments, X-ray crystallographic data were essential to evaluate the differences in rare earth versus actinide chemistry.

2. Experimental details

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under a dinitrogen atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were dried over NaK alloy, degassed by three freeze–pump–thaw cycles, and vacuum transferred before use. Acetonitrile, *t*-butyl nitrile, and benzonitrile were dried over molecular sieves and degassed by three freeze–pump–thaw cycles. $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$, **1**, (Ln = Y, **1-Y**; La, **1-La**; Gd, **1-Gd**) [25,26] and $(C_5H_4SiMe_3)_3Y$ [35] were synthesized according to literature procedures. The $Nd_2Fe_{14}B$ magnets used in the crystallizations were obtained from United Nuclear Scientific Equipment and Supplies [36]. ^1H NMR spectra were recorded on Bruker GN500 or CRYO500 MHz spectrometers (^{13}C NMR at 126 MHz) at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. IR samples were prepared as KBr pellets on a Varian 1000 FT-IR system. Elemental analyses were conducted on a Perkin–Elmer 2400 Series II CHNS elemental analyzer, but were complicated by variable amounts of nitriles in the samples.

2.1. $[(C_5H_4SiMe_3)_2Y(THF)_2][BPh_4]$ [37]

HEt_3NBPh_4 (167 mg, 0.4 mmol) was added to a yellow THF solution (5 mL) of $(C_5H_4SiMe_3)_3Y$ [35] (200 mg, 0.4 mmol). The solution became colorless and was left to stir overnight. Removal of THF via reduced pressure afforded white solids which were washed with hexane and dried to yield $[(C_5H_4SiMe_3)_2Y(THF)_2][BPh_4]$ (270 mg, 76%) as a white solid. ^1H NMR (THF-d_8): δ 7.32 (br s, 8H, *o*-B*Ph*$_4$), 6.90 (t, $^3J_{HH}$ = 7.0 Hz, 8H, *m*-B*Ph*$_4$), 6.75 (t, $^3J_{HH}$ = 7.0 Hz, 4H, *p*-B*Ph*$_4$), 6.74 (br s, 4H, $C_5H_4SiMe_3$), 6.32 (br s, 4H, $C_5H_4SiMe_3$), 0.31 (s, 18H, $C_5H_4SiMe_3$). ^{13}C NMR (THF-d_8): δ 165.3 (B*Ph*$_4$), 129.1 (B*Ph*$_4$), 125.9 (B*Ph*$_4$), 124.0 ($C_5H_4SiMe_3$), 123.3 ($C_5H_4SiMe_3$), 122.1 (B*Ph*$_4$), 117.6 ($C_5H_4SiMe_3$), 0.5 ($C_5H_4SiMe_3$). IR: 3642w, 3456w, 3104m, 3054s, 3033s, 2982s, 2957s, 2899s, 2496w, 2423w, 2235w, 2090w, 1944w, 1882w, 1819w, 1764w, 1699w, 1580m, 1480s, 1445m, 1427s, 1405m, 1364m, 1345m, 1311m, 1247s, 1177s, 1153m, 1066s, 1043s, 995s, 953m, 906s, 837s, 802s, 742s, 705s, 627m, 606s cm^{-1}. *Anal.* Calc. for $C_{48}H_{62}BO_2Si_2Y$: C, 69.72; H, 7.56. Found: C, 69.89; H, 7.49%.

2.2. $[(C_5Me_5)_2Gd(NCMe)_3][BPh_4]$, **2-Gd**

An excess of MeCN (~0.3 mL, 6 mmol) was added dropwise to a cloudy pale yellow mixture of **1-Gd** (77 mg, 0.10 mmol) in toluene (2 mL) until the solution became colorless and transparent. The solution was stored at −35 °C for 24 h and yielded X-ray quality crystals of **2-Gd** (85 mg, 95%). IR: 3053m, 2979m, 2918s, 2857m, 2300w, 2270m, 1578w, 1480m, 1427m, 1265w, 1181w, 1148w, 1030w, 849w, 732s, 707s, 607m cm^{-1}. Partial desolvation occurred upon drying the crystals as evident from the elemental analysis data. *Anal.* Calc. for $C_{50}H_{59}N_3BGd$, **2-Gd**: C, 69.02; H, 6.84; N, 4.83. Found: C, 68.92; H, 6.91; N, 3.91%. *Anal.* Calc. for **2-Gd**–(0.5 MeCN): C, 69.27; H, 6.82; N, 4.12.

2.3. $[(C_5Me_5)_2La(NCMe)_3][BPh_4]$, **2-La**

Following the procedure for **2-Gd** above, MeCN (~1 mL, 20 mmol) was added to **1-La** (100 mg, 0.14 mmol) in toluene. The colorless transparent solution was stored at −35 °C for several days and yielded colorless microcrystalline solids of **2-La** (30 mg, 25%). ^1H NMR (acetonitrile-d_3): δ 7.28 (s, 8H, *o*-B*Ph*$_4$), 7.00 (t, $^3J_{HH}$ = 7.5 Hz, 8H, *m*-B*Ph*$_4$), 6.85 (t, $^3J_{HH}$ = 7.2 Hz, 4H, *p*-B*Ph*$_4$), 1.91 (s, 30H, C_5Me_5). ^{13}C NMR (acetonitrile-d_3): δ 136.7 (B*Ph*$_4$), 130.0 (B*Ph*$_4$), 126.6 (B*Ph*$_4$), 122.8 (C_5Me_5), 120.7 (B*Ph*$_4$), 11.2 (C_5Me_5). IR: 3056m, 2982m, 2920s, 2856m, 2297m, 2265s, 1578m, 1479m, 1428m, 1266m, 1182w, 1147w, 1066w, 1031m, 929w, 846w, 732s, 704s, 606m cm^{-1}. *Anal.* Calc. for $C_{50}H_{59}N_3BLa$, **2-La**: C, 70.51; H, 6.98; N, 4.93. Found: C, 69.92; H, 6.44; N, 5.42%. *Anal.* Calc. for **2-La**·(0.5 MeCN): C, 70.22; H, 6.99; N, 5.62. Since it proved difficult to obtain X-ray quality crystals of this complex from MeCN alone, THF (5 mL) was added to a concentrated mixture of **2-La** in toluene and MeCN and a crystalline sample was obtainable. Crystals of the THF substitution product, $[(C_5Me_5)_2La(NCMe)_2(THF)][BPh_4]$, **5-La**, were isolated. Although the crystallographic data confirm the structure, these data were not of high enough quality to discuss metrical parameters.

2.4. $[(C_5Me_5)_2Y(NCMe)_3][BPh_4]$, **2-Y**

Following the procedure for **2-Gd** above, MeCN (~1 mL, 20 mmol) was added to **1-Y** (100 mg, 0.15 mmol) in toluene. After stirring the colorless transparent mixture for 5 min, a pale precipitate was observed. THF (~2 mL) was added dropwise to this mixture while stirring until the solution became colorless and transparent again. The solution was stored at −35 °C for several days and yielded colorless crystals of **2-Y** (95 mg, 74%). Although the crystallographic data confirm the structure of **2-Y**, these data were not of high enough quality to report metrical values. ^1H NMR (acetonitrile-d_3): δ 7.28 (s, 8H, *o*-B*Ph*$_4$), 7.00 (t, $^3J_{HH}$ = 7.5 Hz, 8H, *m*-B*Ph*$_4$), 6.85 (t, $^3J_{HH}$ = 7.2 Hz, 4H, *p*-B*Ph*$_4$), 1.85 (s, 30H, C_5Me_5). ^{13}C NMR (acetonitrile-d_3): δ 136.8 (B*Ph*$_4$), 129.3 (B*Ph*$_4$), 126.6 (B*Ph*$_4$), 122.8 (B*Ph*$_4$), 117.8 (C_5Me_5), 11.7 (C_5Me_5). IR: 3052s, 2979s, 2909s, 2855s, 2723w, 2281m, 2272s, 1578m, 1478s, 1426s, 1379m, 1266w, 1181w, 1147m, 1065m, 1030m, 846m, 733s, 704s, 606s cm^{-1}. *Anal.* Calc. for $C_{50}H_{59}N_3BY\cdot MeCN$, **2-Y**·MeCN: C, 74.11; H, 7.42; N, 6.65. Found: C, 74.03; H, 7.63; N, 6.51%.