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Synthesis and X-ray crystal structure of a heterobimetallic bridged alkynide complex $(C_5Me_5)_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li(THF)$

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Abstract

YCl_3 reacts with four equivalents of t-C_4H_9Li to form $Y(CMe_3)_4Li(THF)_4$ (**1**) in high yield. **1** reacts with $HC{\equiv}CCMe_3$ to form $Y(C{\equiv}CCMe_3)_4Li(THF)$ (2) quantitatively. **2** reacts with KC_5Me_5 to form $(C_5Me_5)_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li(THF)$ (3) which can also be prepared from $(C_5Me_5)_2YCl(THF)$ and $LiC{\equiv}CCMe_3$. **3** crystallizes from toluene at $-34°C$ in space group *Cmcm* with $a = 13.363(4)$ Å, $b = 15.918(7)$ Å, $c = 17.453(9)$ Å and $D_{calcd} = 1.07$ g cm^{-3} for $Z = 4$. Least-squares refinement of the model based on 733 reflections converged to a final $R_F = 0.077$. **3** contains a $(C_5Me_5)_2Y$ bent metallocene unit connected to Li via two alkynide bridges. The proximity of the two CMe_3 groups to Li prevents coordination by more than one THF of solvation.

The alkynide ligand, $RC{\equiv}C^-$, has played an important role in the development of the organometallic chemistry of the *f*-orbital elements and related metals [1–12]. Historically, alkynide ligands have often provided the first well-characterized examples of several classes of molecules containing *f*-orbital metal–carbon bonds. This is due in part because (a) alkynides are good σ-bonding ligands [8], (b) there is minimal steric congestion around the carbon donor atom, and (c) desirable steric bulk [13,14] can be provided via the R group of the $RC{\equiv}C^-$ unit. Alkynides also have been found to form strong three center M–C–M bridges with *f*-orbital metals [5,6].

Several years ago we reported the synthesis of the tetraalkynide anions, $Ln(C{\equiv}CR)_4^-$ (Ln = Sm, Er, Lu; R = CMe_3, Ph) [4]. We report here the synthesis of an yttrium analog and its reaction chemistry with the $C_5Me_5^-$ ligand. A bridged heterobimetallic alkynide complex, $(C_5Me_5)_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li(THF)$, is formed with only one THF molecule solvating the lithium ion. An X-ray crystallographic structural determination has shown why this occurs.

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Experimental

The air- and moisture-sensitive complexes described below were handled using Schlenk, vacuum line, and glove box (Vacuum/Atmospheres HE-553 Dri-Lab) techniques. Physical measurement methods and the preparation of YCl_3, KC_5Me_5, and the solvents have been described previously [15]. $(C_5Me_5)_2YCl(THF)$ was prepared by adding THF to $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$ [15]. t-Butyllithium (Aldrich) was freshly sublimed and $HC{\equiv}CCMe_3$ (Aldrich) was dried over molecular sieves and degassed. $LiC{\equiv}CCMe_3$ was prepared from the reaction of $HC{\equiv}CCMe_3$ with ^nBuLi in THF. ^{13}C NMR spectra were run on a General Electric GN-500 spectrometer and assignments were verified using DEPT [16] methods.

$Y(CMe_3)_4Li(THF)_4$ (1) [17–19]. t-Butyllithium (1.02 g, 15.9 mmol) in 20 ml of hexane was slowly added to a suspension of YCl_3 (0.78 g, 3.99 mmol) in 20 ml of THF which had been cooled to −78° C. The mixture was stirred for 1 h at −78° C, the cold bath was removed, and the mixture was stirred for an additional hour. The solution was filtered and the solvent was removed from the filtrate by rotary evaporation to give **1** as an off-white powder (2.36 g, 97%). Anal. Found: Y, 13.7. $C_{32}H_{68}LiO_4Y$ calcd.: Y, 14.5%. ^1H NMR (C_4D_8O) 0.84 (s, CMe_3). IR (KBr): 2970s, 2900s, 2740s, 2670s, 1455m, 1370w, 1250w, 1190w, 1130m, 1045s, 990w, 940w, 920m, 892s, 780s, 675w cm^{-1}.

$Y(C{\equiv}CCMe_3)_4Li(THF)$ (2). Neat $HC{\equiv}CCMe_3$ (0.73 g, 8.89 mmol) was added at room temperature to a solution of **1** (1.22 g, 1.99 mmol) in 10 ml of THF. The solution was stirred for 1 h and filtered. Rotary evaporation of the filtrate left **2** (0.97 g, 99%). Anal. Found: Y, 17.8. $C_{28}H_{44}LiOY$ calcd.: Y, 18.1%. ^1H NMR (C_4D_8O) 1.16 (s, $C{\equiv}CCMe_3$). $^{13}C\{^1H\}$ NMR (C_4D_8O) 130.5 (d, $J(YC) = 96$ Hz, $\mathit{C}CCMe_3$), 127.2 ($C\mathit{C}CMe_3$), 69.4 (THF), 30.0 ($CC\mathit{C}Me_3$), 34.2 ($CCC\mathit{Me}_3$), 27.6 (THF). IR (KBr): 2980s, 2900s, 2850s, 2040s, 1455m, 1360m, 1245s, 1205s, 1050–1030w, 895w, 705m cm^{-1}.

$(C_5Me_5)_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li(THF)$ (3). A mixture of KC_5Me_5 (140 mg, 0.303 mmol) and **2** (200 mg, 0.406 mmol) in 50 ml of THF was stirred overnight. The THF was removed by rotary evaporation and the resulting white solid was stirred in toluene for 2 h. The solution was centrifuged and the toluene was removed from the supernatant by rotary evaporation to yield a mixture containing **3** (110 mg). Crystals of **3** (50 mg, 21%) were grown from toluene at −34° C. Anal. Found: Y, 14.9. $C_{36}H_{56}LiOY$ calcd.: Y, 14.8%. ^1H NMR (C_4D_8O): 2.00 (s, 30H, C_5Me_5), 1.22 (s, 18H, $CCCMe_3$). ^{13}C NMR (C_4D_8O) 127.0 (d, $J(YC) = 46$ Hz, $\mathit{C}CCMe_3$), 123.3 ($C\mathit{C}CMe_3$), 116.8 (C_5Me_5), 69.4 (THF), 33.9 ($CCC\mathit{Me}_3$, $J(CH)$ 126 Hz), 30.1 ($CC\mathit{C}Me_3$), 27.58 (THF), 13.6 ($C_5\mathit{Me}_5$, $J(CH) = 125$ Hz). IR (KBr): 2940s, 2910s, 2900s, 2860w, 2050m, 2750w, 1635w, 1445m, 1435m, 1355m, 1235s, 1195m, 1000s, 750s, 700m cm^{-1}.

Alternative synthesis of **3** from $(C_5Me_5)_2YCl(THF)$. $LiC{\equiv}CCMe_3$ (94 mg, 1.07 mmol) was added to a solution of $(C_5Me_5)_2YCl(THF)$ (200 mg, 0.428 mmol) in 12 ml THF and the resultant solution was stirred for 26 h. The cloudy solution was centrifuged and the solvent was removed from the supernatant by rotary evaporation. The resultant white solid was extracted with toluene (2 × 10 ml) and centrifuged. The solvent was removed from the supernatant by rotary evaporation to leave **3** as a white microcrystalline powder (232 mg, 90%) identified by NMR spectroscopy.

Table 1

Crystal structure and data collection parameters for $(C_5Me_5)_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li(THF)$ (3)

formula	$C_{36}H_{56}LiOY$
molecular weight	600.69
space group	*Cmcm*
cell constants: *a*, Å	13.363(4)
b, Å	15.918(7)
c, Å	17.453(9)
cell volume, $Å^3$	3712
Z	4
D_{calcd}, g cm^{-3}	1.07
temp, ° C	24
μ, cm^{-1}	16.0
min-max trans coeff	0.744–0.834
radiation	Mo-K_α, 0.71073 Å
type of scan	θ–2θ
scan width, deg	-1.2 in 2θ from K_{α_1} to $+1.2$ from K_{α_2}
scan speed, deg/min	2–16
data collection range	$4° < 2\theta < 45°$
total unique data	1398
observed data	733
no. of parameters varied	106
R(F)	0.077
R_w(F)	0.092
GOF	2.29
max shift in final cycle	0.11

X-ray Crystallography of $(C_5Me_5)_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li(THF)$ *(3).* Procedures for data collection and reduction have been previously described [20]. A crystal measuring 0.31 × 0.31 × 0.33 mm was sealed under nitrogen in a glass capillary and

Table 2

Final fractional coordinates for $(C_5Me_5)_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li(THF)$

Y(1)	0.0000	0.0975(1)	0.7500
Li(1)	0.0000	0.2923(28)	0.7500
O(1)	0.0000	0.4151(10)	0.7500
C(1)	0.0000	0.2078(11)	0.8419(11)
C(2)	0.0000	0.2571(11)	0.8969(12)
C(3)	0.0000	0.3101(13)	0.9697(12)
C(4)	0.0961(16)	0.3690(13)	0.9674(12)
C(5)	0.0000	0.2565(19)	1.0341(14)
C(6)	0.1438(9)	−0.0111(9)	0.7129(8)
C(7)	0.1739(12)	0.0645(13)	0.6848(11)
C(8)	0.1964(16)	0.1150(13)	0.7500
C(9)	0.1270(15)	−0.0901(13)	0.6608(16)
C(10)	0.1912(18)	0.0859(22)	0.6024(13)
C(11)	0.2382(18)	0.2044(15)	0.7500
C(12)	0.0885(14)	0.4650(13)	0.7500
C(13)	0.0499(17)	0.5542(17)	0.7500

mounted on a Syntex $P2_1$ diffractometer. Lattice parameters were determined at 25 °C from the angular settings of 15 computer-centered reflections. Data were collected by the θ–2θ scan technique in bisecting geometry. Relevant crystal and data collection parameters are given in Table 1. During data collection, the intensities of three standard reflections showed no significant fluctuations. An absorption correction was applied. Systematic absences indicated either space group $Cmc2_1$ or *Cmcm*. Satisfactory solution and refinement established the space group as *Cmcm*. MULTAN [21] and difference Fourier techniques were used to locate all nonhydrogen atoms which were refined with anisotropic thermal parameters by use of full-matrix least-squares methods. No hydrogen atoms were located. Atomic scattering factors were taken from ref. 22. A final difference map contained no recognizable features. Fractional coordinates are given in Table 2.

Discussion

Synthesis. Yttrium trichloride reacts with four equivalents of $LiCMe_3$ in THF at −78 °C (eq. 1) to form the homoleptic tetrakis-t-butyl complex $Y(CMe_3)_4Li(THF)_4$ (**1**) analogous to the known series of $Ln(CMe_3)_4Li(THF)_4$ complexes (Ln = Sm [17], Yb [17], Er [17], Lu [18,19]). The ^1H NMR spectrum of **1** contains a singlet at 0.84

$$YCl_3 + 4\ LiCMe_3 \xrightarrow{THF} Y(CMe_3)_4Li(THF)_4 + 3\ LiCl \qquad (1)$$

for the t-butyl protons which compares well with the 0.95 resonance of the crystallographically characterized $[Lu(CMe_3)_4][Li(Me_2NCH_2CH_2NMe_2)_2]$ [19].

As expected [4,5,8,23], complex **1** reacts with $HC{\equiv}CCMe_3$ in THF at room temperature (eq. 2) to form the alkynide complex $Y(C{\equiv}CCMe_3)_4Li(THF)$ (**2**) analogous to the lanthanide complexes $Ln(C{\equiv}CCMe_3)_4Li(THF)$ (Ln = Sm, Er, Lu) [4]. The IR spectrum of **2** shows an absorption at 2040 cm^{-1} which is identical to the $\nu(C{\equiv}C)$ absorption found for $[(C_5H_5)_2Lu(C{\equiv}CCMe_3)]_2$ [24] and $[(C_5Me_5)_2Yb]_2(\mu\text{-}C{\equiv}CPh)_4Yb$ [25]. This absorption is also close to the 2050 cm^{-1} band found for each of the $Ln(C{\equiv}CCMe_3)_4Li(THF)$ complexes [4], $[(C_5H_5)_2ErC{\equiv}CCMe_3]_2$ [6], and $[(MeC_5H_4)_2YbC{\equiv}CCMe_3]_2$ [6] and the 2025 cm^{-1} band found for $[(C_5Me_5)Eu(\mu\text{-}C{\equiv}CPh)(THF)_2]_2$ [25] and $LiC{\equiv}CCMe_3$. The absorption is at lower frequency than the 2065–2080 cm^{-1} absorptions in $(C_5Me_5)_2YC{\equiv}CR(L)$ (R = Me, Ph, $SiMe_3$; L = Et_2O, THF) [8]. In comparison, $HC{\equiv}CCMe_3$ has $\nu(C{\equiv}C)$ at 2110

$$Y(CMe_3)_4Li(THF)_4 + 4\ HC{\equiv}CCMe_3 \xrightarrow{THF} Y(C{\equiv}CCMe_3)_4Li(THF) + 4\ HCMe_3 \qquad (2)$$

cm^{-1}. The ^1H NMR spectrum of **2** contains a singlet at 1.16 indicating that in solution the t-butyl groups are equivalent. The resonance is comparable to the δ 1.21 signal found for the t-butyl group in $[(C_5H_5)_2LuC{\equiv}CCMe_3]_2$ [24]. The ^{13}C NMR spectrum of **2** contains a doublet at 130.5 ppm assignable to the α carbon of the alkynide ligand. The splitting is due to ^{89}Y–^{13}C coupling (100% naturally abundant ^{89}Y has $I = 1/2$) and indicates that each alkynide ligand is interacting with just one yttrium center. The 96 Hz J(YC) coupling constant is the largest observed to date. $(C_5Me_5)_2Y(C{\equiv}CR)(OR'_2)$ complexes exhibit J(FC) values of 70 to 75 Hz for the alkynide ligands [8].

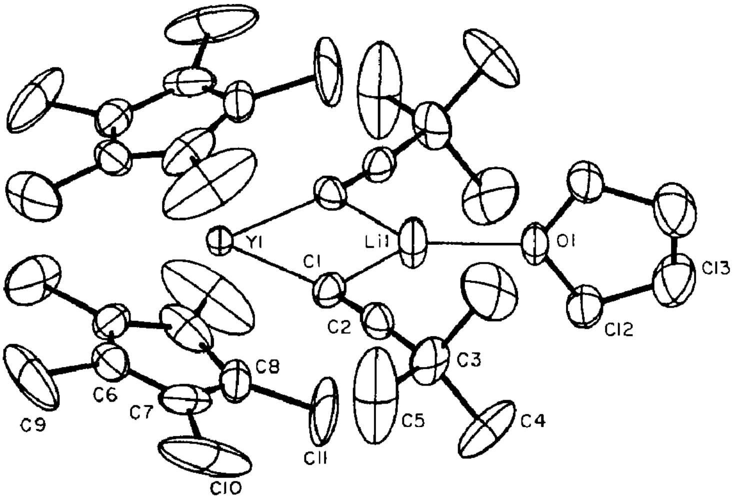


Fig. 1. ORTEP diagram of $(C_5Me_5)_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li(THF)$.

Complexometric analysis of **2** showed only one THF of solvation. This result is identical to that found for the $Ln(C{\equiv}CCMe_3)_4Li(THF)$ complexes [4], but differs from the $Ln(CMe_3)_4Li(THF)_4$ [17] and $[Ln(CMe_3)_4][Li(Me_2NCH_2CH_2NMe_2)_2]$ [18,19] complexes. The apparent deficiency in coordinating ligands for lithium can be explained in terms of lithium alkyne interactions of the type observed in the structure described below.

KC_5Me_5 reacts with complex **2** via net displacement of two alkynide ligands to form $(C_5Me_5)_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li(THF)$ (**3**) (eq. 3). Complex **3** can also be prepared from $(C_5Me_5)_2YCl(THF)$ and $LiC{\equiv}CCMe_3$ according to eq. 4. In the latter

$$Y(C{\equiv}CCMe_3)_4Li(THF) + KC_5Me_5 \xrightarrow{THF,\ C_7H_8} (C_5Me_5)_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li(THF) \quad (3)$$

$$(C_5Me_5)_2YCl(THF) + 2\ LiC{\equiv}CCMe_3 \longrightarrow (C_5Me_5)_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li(THF) \quad (4)$$

reaction, a slight excess of the lithium reagent favors **3** over alternatives such as $[(C_5Me_5)_2Y(\mu\text{-}C{\equiv}CCMe_3)]_n$ and provides **3** in high yield.

The ^1H NMR spectrum of **3** was consistent with the formula given, the IR spectrum had an absorption at 2050 cm^{-1} consistent with a $\nu(C{\equiv}C)$ vibration, and complexometric analysis was consistent with a single THF of solvation. Complex **3** was fully identified by X-ray crystallography as described below.

Structure. The structure of **3** is shown in Fig. 1. The molecule has crystallographic *mm* symmetry: one mirror plane contains Y(1), Li(1), C(1), C(2), C(3), C(5) and O(1) and the other contains Y(1), Li(1), O(1), C(8) and C(11). The THF molecule is disordered across the latter mirror plane and Fig. 1 shows only the average of THF positions. Bond distances and angles are given in Tables 3 and 4.

The geometry around yttrium is typical of eight coordinate $(C_5Me_5)_2Ln(L)(L')$ complexes in that the two ring centroids, C(1) and C(1′) define a distorted tetrahedron. As shown in Table 5 [26–29] the 2.65(1) average Y–C(ring) distance

Table 3

Bond distances (Å) for $(C_5Me_5)_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li(THF)$

Y(1)–C(1)	2.38(2)
Y(1)–C(6)	2.66(1)
Y(1)–C(7)	2.64(1)
Y(1)–C(8)	2.64(2)
Y(1)–Li(1)	3.10(5)
Li(1)–O(1)	1.96(5)
Li(1)–C(1)	2.09(3)
Li(1)–C(2)	2.62(2)
O(1)–C(12)	1.43(2)
C(1)–C(2)	1.24(2)
C(2)–C(3)	1.52(3)
C(3)–C(5)	1.41(3)
C(3)–C(4)	1.59(2)
C(6)–C(6′)	1.30(3)
C(6)–C(7)	1.36(2)
C(6)–C(9)	1.57(2)
C(7)–C(8)	1.43(2)
C(7)–C(10)	1.50(2)
C(8)–C(11)	1.53(3)
C(12)–C(13)	1.51(3)
C(13)–C(13′)	1.33(5)
Y(1)–ring centroid	2.38

Table 4

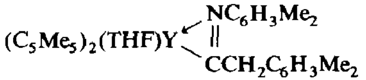
Bond angles (deg) for $(C_5Me_5)_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li(THF)$

C(1)–Y(1)–C(1′)	84.8(10)
O(1)–Li(1)–C(1)	130.0(11)
C(1)–Li(1)–C(1′)	100.0(22)
C(2)–Li(1)–C(2′)	155.3(23)
C(12)–O(1)–C(12′)	112.2(19)
C(12)–O(1)–Li(1)	123.9(10)
C(2)–C(1)–Li(1)	100.7(16)
C(1)–C(2)–C(3)	174.3(18)
C(5)–C(3)–C(2)	109.2(18)
C(5)–C(3)–C(4)	112.1(14)
C(2)–C(3)–C(4)	107.8(12)
C(4)–C(3)–C(4′)	107.7(22)
C(6′)–C(6)–C(7)	111.1(11)
C(6′)–C(6)–C(9)	125.4(13)
C(7)–C(6)–C(9)	122.9(18)
C(6)–C(7)–C(8)	105.9(17)
C(6)–C(7)–C(10)	126.4(24)
C(8)–C(7)–C(10)	127.3(22)
C(7)–C(8)–C(7′)	106.0(21)
C(7)–C(8)–C(11)	127.0(11)
O(1)–C(12)–C(13)	103.9(16)
C(13′)–C(13)–C(12)	110.0(11)
Cn[a]–Y(1)–Cn	138.3
Cn–Y(1)–C(1)	105.2

[a] Cn = C_5Me_5 ring centroid.

Table 5

Structural parameters for trivalent $(C_5Me_5)_2Y$ complexes

Complex	Coordination number	Average Y–C(ring) distances (Å)	Range of Y–C(ring) distances (Å)	(Ring Centroid)–Y–(Ring Centroid) Angle (Deg)	Y–C(σ) bond distance (Å)	Reference
$\underline{(C_5Me_5)_2Y}(\mu\text{-Cl})YCl(C_5Me_5)_2$	7	2.60(2)	2.56(2)–2.63(2)	139.3		15
$(C_5Me_5)_2Y[N(SiMe_3)_2]$	7 [a]	2.682(4) 2.678(4)	2.632(7)–2.737(7)	132.3		26
$(C_5Me_5)_2Y[CH(SiMe_3)_2]$	7 [a]	2.668(7)	2.637(6)–2.692(6)	134.4	2.468(7)	26
$(C_5Me_5)_2Y(\mu\text{-Cl})\underline{YCl(C_5Me_5)_2}$	8	2.67(1)	2.66(2)–2.69(2)	135.8		15
$(C_5Me_5)_2YCl(THF)$	8	2.66(2)		136.4		27
$(C_5Me_5)_2YMe(THF)$	8	2.66(5)	2.51(3)–2.74(2)	1370.0	2.44(2)	28
$(C_5Me_5)_2Y(\mu\text{-C}{\equiv}CCMe_3)_2Li(THF)$	8	2.65(1)	2.64(2)–2.66(1)	138.3	2.38(2)	This work
 $(C_5Me_5)_2(THF)Y\begin{matrix}\swarrow NC_6H_3Me_2\\ \Vert\\ \searrow CCH_2C_6H_3Me_2\end{matrix}$	9	2.728(4)	2.685(3)–2.782(3)	132.0	2.392(3)	29

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[a] Does not include agostic hydrogen interactions.

and the 138.3° (ring centroid)-Y-(ring centroid) angle are normal for trivalent eight coordinate $(C_5Me_5)_2Y$ complexes. Complex **3** is unusual in that the C_5Me_5 rings are eclipsed with respect to each other [30–34]. Eclipsed rings in $(C_5Me_5)_2Ln(L)(L')$ complexes often result from steric congestion caused by the other ligands in the molecule. For example, a structural study on a series of $(C_5Me_5)_2Ln(\mu$-halide$)_2Li(ether)_2$ complexes found that the rings became eclipsed when the halide was a large iodide [30]. The ORTEP diagram supports the view that **3** is sterically crowded. No unusually short (ring methyl)–(alkynide methyl) distances were observed, but the C(11)–C(1) nonbonding distance is only 3.56 Å.

The C(1)–Y–C(1′) angle of 84.8(10)° is smaller than normal for $(C_5Me_5)_2Y(L)(L')$ complexes. For example, $(C_5Me_5)_2YCl(THF)$ [27] has Cl–Y–O angles of 89.6(2) and 90.5(2)°, $(C_5Me_5)_2YMe(THF)$ [28] has a C(Me)–Y–O angle of 90.3(4)°, and $(C_5Me_5)_2ClY(\mu\text{-}Cl)Y(C_5Me_5)_2$ [15] has a Cl–Y–Cl(μ) angle of 93.4(2)°. However, small (σ-ligand)–Ln–(σ-ligand) angles have been observed in other lanthanide systems, e.g., 81.5(2) and 84.0(2)° in $[(C_5Me_5)_2Sm(\mu\text{-}Cl)]_3$ [35], 73.36(3)° in $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2AlCl_2$ [30], 76.0(5)° in $(C_5Me_5)_2Lu(\mu\text{-}CH_2)_2PMe_2$ [36], and 73.6(1)° in $(C_5Me_5)_2Lu(\mu\text{-}SCMe_3)_2Li(THF)_2$ [37]. As might be expected, these small angles are more common for systems in which the two σ-bound ligands are bridging.

The 2.38(2) Å yttrium alkynide bond is short compared to the other Y–C(σ) bonds in Table 5. Alkynide ligands typically form shorter metal–carbon bonds than alkyls [5], but bridging ligands generally form longer bonds than terminal groups [5,38]. The fact that the Y–C(σ) bridging bond in **3** is shorter than the Y–C(σ) terminal bonds in the other complexes in Table 5 is further evidence that the alkynide ligand is a powerful σ-bonding ligand.

Perhaps the most unusual feature in the structure of **3** is the formally three-coordinate lithium ion. The closest Li–ligand interactions are the 2.09(3) Å Li–C(1) and Li–C(1′) distances and the 1.96(5) Å Li–O distance. The latter distance is identical to the Li–O distance in $\{[(C_5H_5)_2Y(\mu\text{-}OMe)]_3(\mu_3\text{-}H)\}_2\{Li(THF)_3\}_2$ [39] and shorter than the 2.036(3)–2.044(30 Å lengths in $[Li(THF)_2(mesityl)]_2$ [40]. The Li–C(1) distance is short compared to Li–C distances in ether-solvated organolithium complexes, e.g., $[Li(Et_2O)benzyl]_x$ (2.189(8)-2.229(8) Å) [40], $[Li(THF)_2(mesityl)]_2$ (2.271(3)–2.279(3) Å) [40], $[PhLi(Et_2O)]_4$ (2.33 Å) [41], and $[PhLi(Et_2O)]_3(LiBr)$ (2.15–2.33 Å) [41].

Coordination of lithium to C(2) and C(2′) may also be occurring, but the 2.62(2) Å Li–C(2) and Li–C(2′) distances are long in comparison to the Li–C(1) distance and the Li–C lengths given above. The Li–C(2) distance is also long compared to Li–C(η) distances in lithium cyclopentadienyl complexes which range from 2.257(10)–2.54(6) Å [39,42–44].

Regardless of the importance of the Li–C(2) interaction, the proximity of the CMe_3 groups to lithium prevents approach by more than one THF molecule. As a result, a mono solvate is isolated. The same situation may occur in the $Ln(C{\equiv}CCMe_3)_4Li(THF)$ complexes [4]. One reason that crystallographic characterization of the latter complexes has proven difficult may be that with a tetrahedral arrangement of ligands around the metal, the Li(THF) unit can disorder over six identical positions. In contrast, the formally dianionic $Yb(C{\equiv}CPh)_4^{2-}$ part of $[(C_5Me_5)_2Yb]_2(\mu\text{-}C{\equiv}CPh)_4Yb$ [25] is coordinated to two formally cationic $(C_5Me_5)_2Yb^+$ units. The presence of two sterically bulky cations limits the number of positions available to the cations and, hence, a crystallographically characterizable complex resulted [25].

Conclusion

The synthesis of complex **3** shows that C_5Me_5 groups can displace the strongly binding alkynide ligands in organolanthanide complexes and that the $Ln(C{\equiv}CR)_4Li(THF)$ complexes are reactive toward bulky reagents. The structure of **3** demonstrates one way in which mono-THF solvated lithium derivatives of organolanthanides can form and shows how steric factors can be used to control the coordination number of a second metal in a bimetallic system.

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