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Synthesis and Crystallographic Characterization of a Dimeric Alkynide-Bridged Organolanthanide: [(C₅H₅)₂ErC≡CC(CH₃)₃]₂

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[(C₅H₅)₂ErC≡CC(CH₃)₃]₂ has been synthesized by the halide-free reaction of [(C₅H₅)₂ErCH₃]₂ with HC≡CC(CH₃)₃ and characterized by spectroscopic, analytical, and crystallographic methods. The title compound crystallizes from THF in the triclinic space group P1̄ with unit cell dimensions $a = 3.602$ (3) Å, $b = 8.767$ (3) Å, $c = 10.216$ (5) Å, $\alpha = 77.86$ (3)°, $\beta = 84.50$ (3)°, $\gamma = 76.61$ (3)°, and $Z = 1$ (dimer) for $D_c = 1.71$ g cm⁻³. Full-matrix least-squares refinement led to a final R value of 0.065 based on 1321 observed reflections. The two (C₅H₅)₂Er units in the dimer are connected by asymmetrical alkynide bridges with independent Er–C bond lengths of 2.42 (2) and 2.47 (2) Å and Er—C≡C angles of 149 (2) and 115 (2)°. Isopiestic studies indicate that this complex is also dimeric in THF solution. [(CH₃C₅H₄)₂Yb-C≡CC(CH₃)₃]₂ was prepared analogously.

Introduction

Dicyclopentadienyllanthanide complexes of formula (C₅H₅)₂LnR (Ln = lanthanide metal; R = alkyl, aryl, alkynyl) constitute one of the major classes of σ-bonded organolanthanide species. The first alkyl, aryl, and alkynyl derivatives[2] of this general class were initially formulated as 7-coordinate monomeric species.[3] However, a subsequent X-ray crystallographic investigation of the ytterbium and yttrium methyl derivatives [(C₅H₅)₂YbCH₃]₂ and [(C₅H₅)₂YCH₃]₂ indicated that these complexes were dimeric in the solid state when recrystallized from toluene.[4] The yttrium complex was also shown to be dimeric in CH₂Cl₂ solution by observation of the ⁸⁹Y–¹³C coupling in the ¹³C NMR spectrum. In contrast, when dissolved in the coordinating solvent, tetrahydrofuran (THF), the yttrium derivative was found to exist as the monomeric base adduct, (C₅H₅)₂YCH₃(THF). Furthermore, dicyclopentadienyllanthanide methyl complexes, in general, crystallize from THF as the monomeric solvates as evidenced by the absence of the strong infrared absorption at 1190 cm⁻¹ (assignable to a CH deformation mode of a bridging methyl group in the dimer[4]) and by the presence of absorptions characteristic of solvating THF. These data suggested that (C₅H₅)₂LnR complexes are dimeric in nonpolar solvents and monomeric as THF solvates in THF. This general trend is similar to that observed for the chloride analogues, [(C₅H₅)₂LnCl]₂/(C₅H₅)₂LnCl(THF).[5]

We recently reported one counterexample to the above trend, namely, the isolation *from toluene* of a monomeric alkyl complex (C₅H₅)₂Lu(C(CH₃)₃)(THF).[6] We now report the alternative counterexample, namely, the isolation *from THF* of a dimer complex [(C₅H₅)₂ErC≡CC(CH₃)₃]₂ (I).[7] This remarkable result further demonstrates the importance of the ligand vis-à-vis the solvent in the stabilization and dimerization of σ-bonded organolanthanides and indicates how easily structural diversity can be achieved in this simple class of organolanthanide complexes. In this regard, it is interesting to note that the analogous ytterbium octynide complex (C₅H₅)₂YbC≡CC₆H₁₃ is thought to be trimeric based on cryoscopic molecular weight studies, whereas the hexynide,

[(C₅H₅)₂YbC≡CC₄H₉]ₓ, has a measured x value of 2.5.[8] Hence an X-ray structure determination of the title complex has provided an opportunity to determine how such species associate in the solid state.

The bridged-alkynide structure of complex I (Figure 1) is of interest not only with respect to the molecularity of the general class, (C₅H₅)₂LnR, but also in regard to the structures of electron-deficient alkynide-bridged complexes in general. Only a few such complexes have been crystallographically characterized, and these have involved main-group metals exclusively. Methylpropynylberyllium trimethylamine crystallizes as a dimer (II)[9] in which the alkynide group is nearly perpendicular to the metal–metal vector. Diphenyl(phenylethynyl)aluminum forms a dimer in the solid state (III)[10] in which the two metals and the two α-carbons form a rectangular array. An electron diffraction study of dimethylpropynylaluminum suggests an intermediate asymmetric dimeric structure (IV)[11] for this complex in the gas phase. Crystallographic investigation of the congeneric dimethylpropynylindium indicates the oligomeric structure V[12] in which the monomeric units are connected by a metal π interaction with the triple bond. Therefore, an X-ray structure determination of the title complex has also provided an opportunity to extend our knowledge of the structure of electron-deficient alkynide-bridging systems to the f orbital metals.

Finally, the study allows us to examine the relative importance of the interaction of carbon–carbon triple bonds with trivalent lanthanide centers. This latter feature is a possible explanation for the high degree of association observed in complexes derived from the reaction of zerovalent lanthanide atoms with a variety of alkynes.[13–16] Hence, the structure of

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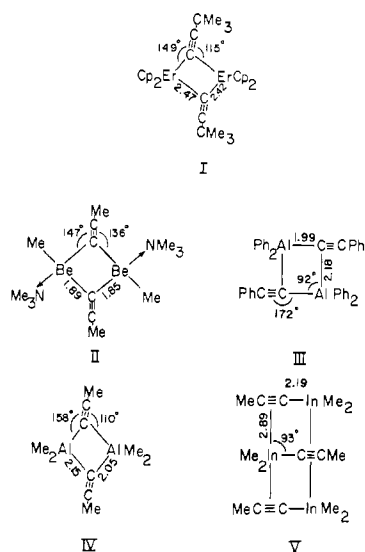
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**Figure 1.** Structures of bridged electron-deficient alkynide complexes.

complex I is of interest as a possible model for these catalytically active complexes.[13,14]

Results and Discussion

Syntheses. Complex I was synthesized as part of our general investigation of the reactivity of lanthanide–carbon σ bonds.[7] This synthesis (eq 1) is based upon our discovery that suitably

$$[(C_5H_5)_2ErCH_3]_2 + 2HC{\equiv}CC(CH_3)_3 \rightarrow$$
$$[(C_5H_5)_2ErC{\equiv}CC(CH_3)_3]_2 + 2CH_4 \quad (1)$$
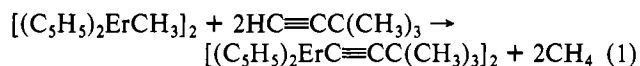
basic alkyl lanthanide precursors will cleanly metalate acidic hydrocarbon substrates at ambient temperature. The reaction was monitored by Toepler pump collection of CH_4 (85% recovered) and by observing the precipitation of the alkynide product, which is less soluble than the methyl precursor in THF. Due to the limited solubility of I, the halide-free synthesis shown in eq 1 is preferable to the alternative synthesis proceeding from a halide precursor (eq 2). Both syntheses

$$[(C_5H_5)_2ErCl]_2 + 2LiC{\equiv}CC(CH_3)_3 \rightarrow$$
$$[(C_5H_5)_2ErC{\equiv}CC(CH_3)_3]_2 + 2LiCl \quad (2)$$
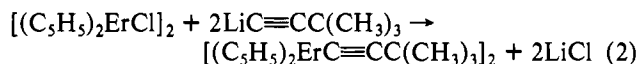
require two steps starting from $HC{\equiv}CC(CH_3)_3$ and $[(C_5H_5)_2ErCl]_2$. However, it is easier to separate LiCl from the more soluble $[(C_5H_5)_2ErCH_3]_2$ intermediate than from the sparingly soluble $[(C_5H_5)_2ErC{\equiv}CC(CH_3)_3]_2$ (as is necessary according to eq 2).

Characterization. Complex I was preliminarily characterized by infrared and near-infrared–visible spectroscopy and by standard analytical methods. The infrared spectrum contained strong absorptions at 1010 and 780 cm^{-1} characteristic of C_5H_5, an absorption at 2050 cm^{-1} characteristic of terminal alkynides (cf. $\nu(C{\equiv}C)$: $LiC{\equiv}CC(CH_3)_3$, 2025 cm^{-1}), and absorptions at 1365, 1360, 1245, and 1205 cm^{-1} characteristic of the $C{\equiv}CC(CH_3)_3$ unit. No evidence for coordinated THF was observed in the infrared spectrum. Complexometric metal analysis supported an empirical formula of $(C_5H_5)_2ErC{\equiv}C$-$C(CH_3)_3$ and isopiestic molecular weight measurements in THF indicated the dimeric nature of the complex (calcd for the dimer, 740; found, 757).

$[(CH_3C_5H_4)_2YbC{\equiv}CC(CH_3)_3]_2$ was synthesized and characterized in an analogous fashion (see Experimental Section).

Structure. A single crystal of I was obtained by slow diffusion of pentane into a THF solution maintained at 0 °C and was examined by X-ray diffraction methods. The dimeric structure of this molecule in the solid state was confirmed as
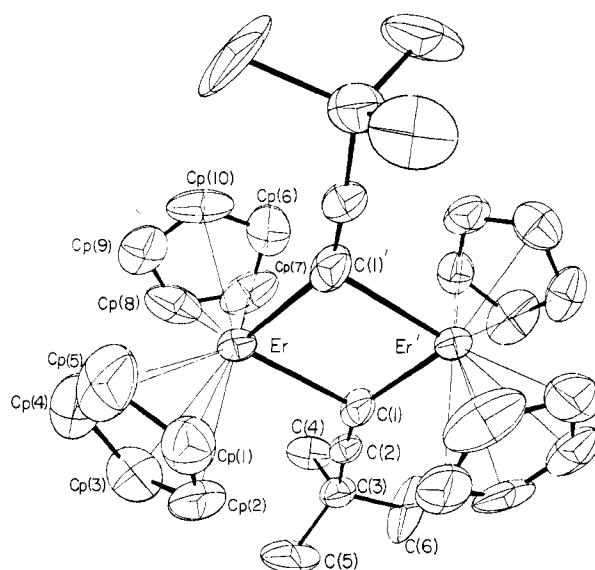

Figure 2. ORTEP plot of the molecular structure of $[(C_5H_5)_2ErC{\equiv}CC(CH_3)_3]_2$.

Table I. Bond Lengths (A) and Angles (Deg) for $[(C_5H_5)_2ErC{\equiv}CC(CH_3)_3]_2$

atoms	dist	atoms	dist
Er–Er'[a]	3.657 (2)	Er–Cp(1)	2.61 (3)
Er–Cp(2)	2.66 (2)	Er–Cp(3)	2.60 (3)
Er–Cp(4)	2.61 (3)	Er–Cp(5)	2.60 (3)
Er–Cp(6)	2.65 (2)	Er–Cp(7)	2.62 (3)
Er–Cp(8)	2.63 (2)	Er–Cp(9)	2.65 (2)
Er–Cp(10)	2.62 (2)	Er–C(1)'	2.47 (2)
Er–C(1)	2.42 (2)	Cp(1)–Cp(2)	1.37 (4)
Cp(1)–Cp(5)	1.42 (4)	Cp(2)–Cp(3)	1.43 (4)
Cp(3)–Cp(4)	1.46 (4)	Cp(4)–Cp(5)	1.39 (4)
Cp(6)–Cp(7)	1.47 (5)	Cp(6)–Cp(10)	1.40 (4)
Cp(7)–Cp(8)	1.44 (4)	Cp(8)–Cp(9)	1.40 (4)
Cp(9)–Cp(10)	1.32 (4)	C(1)–C(2)	1.26 (3)
C(2)–C(3)	1.42 (3)	C(3)–C(4)	1.57 (3)
C(3)–C(5)	1.56 (3)	C(3)–C(6)	1.58 (3)
Er–Cent(1)[b]	2.325	Er–Cent(2)	2.345

atoms	angle	atoms	angle
C(1)–Er–C(1)'	83.4 (7)	Cp(2)–Cp(1)–Cp(5)	109 (3)
Cp(1)–Cp(2)–Cp(3)	108 (2)	Cp(2)–Cp(3)–Cp(4)	107 (2)
Cp(3)–Cp(4)–Cp(5)	107 (2)	Cp(1)–Cp(5)–Cp(4)	109 (3)
Cp(7)–Cp(6)–Cp(10)	105 (3)	Cp(6)–Cp(7)–Cp(8)	107 (3)
Cp(7)–Cp(8)–Cp(9)	106 (3)	Cp(8)–Cp(9)–Cp(10)	111 (3)
Cp(6)–Cp(10)–Cp(9)	111 (3)	Er–C(1)–Er'	96.6 (7)
Er'–C(1)–C(2)	149 (2)	Er–C(1)–C(2)	115 (2)
C(1)–C(2)–C(3)	176 (2)	C(2)–C(3)–C(4)	108 (2)
C(2)–C(3)–C(5)	111 (2)	C(4)–C(3)–C(5)	110 (2)
C(2)–C(3)–C(6)	106 (2)	C(4)–C(3)–C(6)	107 (2)
C(5)–C(3)–C(6)	114 (2)	Cent(1)–Er–Cent(2)	130.2
Cent(1)–Er–C(1)	110	Cent(2)–Er–C(1)	111
Cent(1)–Er–C(1)'	107	Cent(2)–Er–C(1)'	105

[a] Primed atoms are related to those given in the table by the center of symmetry. [b] Cent(1) is the centroid of the cyclopentadienyl ring defined by Cp(1)–Cp(5). Both rings are planar to within 0.02 A.

shown in the ORTEP plot in Figure 2. Important structural parameters are listed in Table I.

Bond Lengths. The Er–C distances for the cyclopentadienyl ring carbons are unexceptional. The average distance, 2.62 A, falls within the expected range based on an average ionic cyclopentadienyl carbon radius of 1.64 ± 0.04 Å[17] and an 8-coordinate Er^{3+} radius of 1.004 Å.[18]

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The Er–C bond lengths for the alkynide carbons (C(1), C(1)′), 2.42 (2) and 2.47 (2) Å, respectively, are much larger than those of the two other structurally characterized f element alkynides, $(C_5H_5)_3UC\equiv CC_6H_5$ (VI), 2.33 Å,[19] and $(C_5H_5)_3UC\equiv CH$ (VII), 2.36 Å,[20] even though the Er^{3+} radius is smaller than that of U^{4+} (1.05 Å). This is not unexpected, however, since metal–carbon bond distances for electron-deficient bridging ligands are typically longer than those for terminal ligands. For example, the bridge and terminal methyl carbon distances in trimethylaluminum are 2.124 and 1.952 Å,[21] respectively. Similarly, the Yb–C distance in the unbridged $[Li(THF)_4][Yb(CH(Si(CH_3)_3)_2)_3Cl]$ (VIII) is 2.38 Å,[22] whereas $(C_5H_5)_2Yb(CH_3)_2Al(CH_3)_2$ (IX) has Yb–C bond lengths of 2.56 and 2.61 Å,[23] and $[(C_5H_5)_2YbCH_3]_2$ (X) has Yb–C distances of 2.49 and 2.54 Å.[4] Hence the structure of I conforms to this trend.

Comparison of alkynide–metal vs. alkyl–metal bond lengths in previously studied nonbridged f element complexes has shown that the alkynides form shorter bonds. For example, the uranium–carbon bond lengths in alkynides VI and VII, 2.33 and 2.36 Å, are shorter than the uranium–carbon distances in analogous alkyl and aryl complexes: 2.48 Å in $(C_5H_5)_3UCH_2C(CH_3)\!=\!CH_2$,[24] 2.46 Å in $(C_5H_5)_3U(n\text{-Bu})$, and 2.55 Å in $(C_5H_5)_3U(p\text{-xylyl})$.[25] A similar comparison of alkynide vs. alkyl distances can now be made for bridged f element systems, and the trend persists. The Ln–C distances of 2.42 (2) and 2.47 (2) Å for I are significantly shorter than those for the methyl-bridged complexes IX (2.56, 2.61 Å) and X (2.49, 2.54 Å). As a consequence of the opposing trends that (1) alkynide Ln–C bond lengths are shorter than alkyl and aryl bond lengths and that (2) bridging distances are longer than terminal distances, the Ln–C bond lengths in I are in the same range as some lanthanide carbon bonds in complexes with terminal ligands only: $[Li(THF)_4][Lu(C_6H_3(CH_3)_2)_4]$, 2.45 Å,[26] and $(C_5H_5)_2Lu(C(CH_3)_3)(THF)$, 2.47 Å.[6]

Alkynide Bridge. The mode of alkynide bridging in complex I does not conform exactly to any of the structures previously characterized by X-ray diffraction (II, III, V).[9,10,12] The most similar previously reported structure is that proposed for IV from electron diffraction data.[11] With Er–C(1)′ and Er–C(1) bond lengths of 2.42 (2) and 2.47 (2) Å and Er′–C(1)–C(2) and Er–C(1)–C(2) angles of 149 and 115°, respectively, the bridge is clearly asymmetric. The importance of these asymmetries can be evaluated by comparing the bond lengths and angles of the other bridging complexes.

The difference in the Er–C bond distances of 0.05 Å is virtually the same as that found in the methyl-bridged lanthanide complexes IX (0.05 Å)[23] and X (0.05 Å).[4] In other bridged organolanthanides, variations as large as 0.08 Å (in the cerium chloride bridges of $[C_8H_8CeCl(THF)_2]_2$)[27] and as small as 0.01 Å (in $[(C_5H_5)_2YCH_3]_2$)[4] have been found, whereas the cyclopentadienyl chloride dimers $[(C_5H_5)_2ScCl]_2$[28]

and $[(CH_3C_5H_4)_2YbCl]_2$[29] are symmetrical. In the main-group complexes, the symmetrically bridged $[CH_3C\equiv C\text{-}Be(CH_3)(N(CH_3)_3)]_2$ (II) exhibits a 0.04-Å difference in Be–C bond lengths,[9] whereas the asymmetrically bridged $[(CH_3)_2AlC\equiv C(CH_3)]_2$ (IV) has a 0.10-Å difference.[11] Hence, I has differences in Er–C bond distances in the alkynide bridge which are in the middle of the range of observed variations in bridging bond lengths. These distances clearly indicate a strong interaction of the α-carbon atom, C(1), with both erbium centers.

The difference in Er—C≡C angles found for I is large compared to that expected for bridging alkynides which have no π component in bonding. If the bridges in I were symmetric and if the triple bond was perpendicular to the Er–Er vector, an Er–C(1)–C(2) angle of 132° might be expected. II. which has been considered as the closest example of such a structure,[9] has angles of 147 and 136°, a difference of 11°. In contrast, the title complex has a difference of 34°.

In the other extreme, if I contained one pure single bond and the bridge was effected by π interaction with the second erbium atom, an Er–C(1)–C(2) angle of 180° might be expected. Hence, the angle observed in I is 31° from the π-bonded extreme. The closest example of such a π-bonded structure is $[(C_6H_5)_2AlC\equiv CC_6H_5]_2$ (III), which has an Al—C≡C angle of 172°. In this structure, however, the primary interaction is with the α-carbon atom only.

The bridging arrangement found for I is clearly a compromise between a symmetric bridge and a π-bonded structure. With an Er–C(2)′ distance of ~3.2 Å, there is little η^2 interaction of the triple-bond π orbitals with the trivalent erbium center. The observed angles in I are most similar to those proposed for IV, 158 and 110°, respectively.[11] In that case, the bonding was described in covalent terms as one normal Al–C single bond and one bridging C→Al dative bond involving the electron pair in the C≡C multiple bond. Such covalent descriptions are not usually applied to organolanthanide complexes, however.[17] To determine whether or not this is a reasonable description for lanthanide alkynides will require evaluation of additional factors such as the importance of the steric bulk of the *tert*-butyl group in determining the structure of I.

Conclusion

Crystallographic determination of the structure of dimeric $[(C_5H_5)_2ErC\equiv CC(CH_3)_3]_2$, crystallized from THF, taken with the structural determination of the monomeric $(C_5H_5)_2Lu(C(CH_3)_3)(THF)$,[6] crystallized from toluene, clearly demonstrates the variability in structure which can be easily obtained in $(C_5H_5)_2LnR$ complexes by changing the R group. The alkynide ligand is obviously useful in forming bridged bimetallic structures in the presence of coordinating solvents. Such a feature could possibly be exploited for both synthetic and catalytic purposes. The detailed structure of complex I, which is intermediate between a symmetric bridged structure and an asymmetric π-bonded structure, suggests that, as is found for organoaluminum complexes, a variety of geometries may be accessible for bridged electron-deficient lanthanide complexes. Accordingly, determination of the relative importance of σ and π bonding in these complexes must await further structural studies. A simple π interaction between the trivalent lanthanide center and the alkyne triple bond is not indicated by this structure and hence is unlikely to be the explanation for the high degree of association in lanthanide metal alkyne cocondensation products.[13–16]

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Experimental Section

General. All compounds described below are extremely air and moisture sensitive. Therefore, the syntheses of these compounds and manipulations involving these materials are conducted with use of standard Schlenk and high-vacuum-line techniques or are performed in the recirculating nitrogen atmosphere of a Vacuum Atmospheres HE-43 Dri-Lab.

Tetrahydrofuran (THF) and toluene are distilled from solutions of potassium benzophenone ketyl. Pentane is washed with sulfuric acid, dried over $MgSO_4$, refluxed over finely divided $LiAlH_4$, and vacuum transferred. $ErCl_3 \cdot xH_2O$ and $YbCl_3 \cdot xH_2O$ (Research Chemicals, Phoenix, AZ) are dehydrated by the method of Taylor and Carter[30] and stored under nitrogen. 3,3-Dimethylbut-1-yne (Chemical Samples) is dried over activated Linde 4-Å molecular sieves and degassed by vacuum transfer. $[(C_5H_5)_2ErCH_3]_2$ and $[(C_5H_4C-H_3)_2YbCH_3]_2$ are prepared by slight modification of the method of Ely and Tsutsui[3] (the compounds are obtained in pure form by several cycles of toluene extraction and solvent removal rather than by Soxhlet extractions).

Infrared spectra are recorded as Nujol mulls (NaCl plates, Barnes Engineering, Presslok holder) on a Perkin-Elmer 283 infrared spectrophotometer. Near-IR–visible spectra are recorded on a Cary 14 recording spectrophotometer using THF solutions of the compounds contained in 2-mm Teflon-capped quartz cells. Gas chromatographic analyses are performed on a Hewlett Packard 5830A equipped with a thermal conductivity detector using a 6 ft × $^1/_4$ in. 5-Å molecular sieve column and a 20% tricresylphosphate on 60/80 Chromosorb W/dimethyldichlorosilane treated column. Complexometric metal analyses are conducted as follows: ca. 50-mg samples of the compounds are weighed in porcelain crucibles in the drybox. The samples are removed to a tube or muffle furnace and ashed at 500–700 °C until the sample has been completely converted to the oxide. The samples are then cooled, dissolved in deionized water and HCl, and titrated directly for rare-earth content with a 0.01 M Na_2EDTA solution with xylenol orange as indicator and hexamethylenetetramine as buffer. Isopiestic molecular weight measurements are performed in a commercially obtained Signer molecular weight apparatus (SGA) which has been modified for use with air-sensitive samples. In use, the apparatus is thermostated at 20 °C in a recirculating water bath. Ferrocene (Aldrich, purified by sublimation) is used as the internal standard.

$[(C_5H_5)_2ErC\equiv CC(CH_3)_3]_2$. $[(C_5H_5)_2ErCH_3]_2$ (0.3200 g, 1.024 mM) is dissolved in THF and placed in one arm of a glass H-tube fitted with a coarse frit between the two tube arms and equipped with Ace Teflon stopcocks. A 2-mL (1.339 g, 16.30 mM) sample of 3,3-dimethylbut-1-yne is added to the other tube arm. The apparatus is closed and removed to the vacuum line where the two sides of the H-tube are frozen (–196 °C) and the apparatus evacuated. Subsequently, the arm containing the alkyne reagent is warmed, permitting the quantitative transfer of the alkyne to the reaction arm. Upon warming, bubbling is observed in the clear pink solution. After the solution is stirred overnight at ambient temperature, a pink precipitate is present in the tube. After 2 days of total reaction time, the volatile product of the reaction, CH_4, is quantitatively measured by cooling the solution to –196 °C and removing the volatile gas by Toepler pump. CH_4 (identified by gas chromatography on a 5-Å molecular sieve column thermostated at 35 °C) is isolated in 85% yield. The apparatus is then removed to the drybox where the resulting pink slurry is filtered. The remaining pink powder is completely soluble in additional THF. The solutions are combined and solvent removed to yield a pale pink free-flowing powder which is insoluble in pentane, slightly soluble in toluene and moderately soluble in THF. The compound is further purified by slow diffusion of pentane into a THF solution of the material thermostated at 0 °C. Pink rodlike crystals separate after several days time. Anal. Calcd for $Er_2C_{32}H_{48}$: Er, 44.18. Found: Er, 44.25. IR (Nujol mull, cm^{-1}) 3095 w, 2050 s, 1760 w, 1650 w, 1540 w, 1365 s, 1360 s, 1245 s, 1205 m, 1010 s, 780 s. Near-IR–VIS (THF, nm): 525, 382. Molecular weight for $[(C_5H_5)_2ErC\equiv CC-(CH_3)_3]_2$: calcd, 757; found, 740.

$[(C_5H_4CH_3)_2YbC\equiv CC(CH_3)_3]_2$. $[(C_5H_4CH_3)_2YbCH_3]_2$ (0.3303 g, 0.95 mM) is dissolved in 20 mL THF and placed in a 100-mL Schlenk flask equipped with a Teflon stir bar. 3,3-Dimethylbut-1-yne (4 mL, 2.68 g, 32.6 mM) is added to a 100-mL Schlenk addition funnel

Table II. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compd	$[(C_5H_5)_2ErC\equiv CC(CH_3)_3]_2$
mol wt	757
space group	$P\bar{1}$
cell constants	
a, Å	8.602 (3)
b, Å	8.767 (3)
c, Å	10.216 (5)
α, deg	77.86 (3)
β, deg	84.50 (3)
γ, deg	76.61 (3)
cell V, Å^3	731.9
molecules/unit cell	1
ρ(calcd), g cm^{-3}	1.71
μ(calcd), cm^{-1}	59.2
radiation	Mo Kα
max/crystal dimens, mm	0.75 × 0.40 × 1.50
scan width, deg	0.80 + 0.20 tan θ
std reflctns	200, 020, 002
decay of stds	±2%
reflctns measd	2050
2θ range, deg	46
obsd reflctns	1321
no. of parameters varied	154
GOF	3.41
R	0.065
R_w	0.069

Table III. Final Fractional Coordinates for $[(C_5H_5)_2ErC\equiv CC(CH_3)_3]_2$

atom	x/a	y/b	z/c
Er	0.4026 (1)	0.5558 (1)	0.1554 (1)
Cp(1)	0.165 (3)	0.427 (3)	0.130 (3)
Cp(2)	0.257 (4)	0.311 (3)	0.221 (3)
Cp(3)	0.259 (3)	0.375 (3)	0.338 (3)
Cp(4)	0.151 (3)	0.532 (4)	0.317 (3)
Cp(5)	0.098 (3)	0.562 (4)	0.139 (4)
Cp(6)	0.577 (4)	0.776 (4)	0.119 (4)
Cp(7)	0.629 (4)	0.659 (4)	0.240 (4)
Cp(8)	0.499 (5)	0.677 (4)	0.340 (3)
Cp(9)	0.378 (3)	0.799 (3)	0.278 (4)
Cp(10)	0.419 (4)	0.851 (3)	0.151 (3)
C(1)	0.626 (3)	0.352 (3)	0.084 (2)
C(2)	0.699 (2)	0.254 (2)	0.178 (2)
C(3)	0.784 (3)	0.134 (2)	0.279 (2)
C(4)	0.866 (3)	0.218 (3)	0.366 (3)
C(5)	0.670 (4)	0.038 (3)	0.370 (3)
C(6)	0.923 (4)	0.030 (4)	0.202 (3)

containing 20 mL of THF. The funnel is fitted to the reaction flask and the assembly removed to the Schlenk line. The alkyne solution is slowly dripped into the red-orange $[(C_5H_4CH_3)_2YbCH_3]_2$ solution (maintained at 0 °C). The resulting bright orange-yellow solution is allowed to warm slowly to ambient temperature and is stirred for an additional day. The reaction solution is then removed to the drybox where solvent removal yields pure bright orange $[(C_5H_4CH_3)_2Yb-C\equiv CC(CH_3)_3]_2$. Anal. Calcd for $Yb_2C_{36}H_{46}$: Yb, 41.95. Found: Yb, 42.34. IR (Nujol mull, cm^{-1}) 3095 w, 2050 s, 1360 s, 1265 m, 1240 s, 1205 m, 1100 m, br, 1070 m, 1045 m, 1030 s, 935 m, 830 s, 770 s. Near-IR–VIS (THF, nm) 922, 950, 985, 988. Molecular weight for $[(C_5H_4CH_3)_2YbC\equiv CC(CH_3)_3]_2$: Calcd, 825; Found, 845.

X-ray Data Collection, Structure Determination, and Refinement for $[(C_5H_5)_2ErC\equiv CC(CH_3)_3]_2$. Single crystals of the air-sensitive compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 15 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table II.

Data was collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. This method has been previously described.[31] A summary of data collection parameters is given in Table II. The intensities were corrected for Lorentz, polarization, and absorption

(30) Taylor, M. D.; Carter, C. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 387.

(31) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 46.

effects. For the latter, an empirical method similar to that of Churchill was employed.[32]

Calculations were carried out with the SHELX system of computer programs.[33] Neutral-atom scattering factors for Er and C were taken from Cromer and Waber,[34] and the scattering for erbium was corrected for the real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[35] Scattering factors for H were from ref 36.

The position of the erbium atom was revealed by the inspection of a Patterson map. A difference Fourier map phased on the erbium atom readily revealed the positions of the nonhydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum ||F_o| - |F_c||/\sum|F_o| = 0.095$. The hydrogen atoms of the cyclopentadienyl rings were placed at calculated positions 1.00 Å from the bonded carbon atoms and were not refined. The methyl hydrogen

atoms could not be located. Refinement of the nonhydrogen atoms with anisotropic temperature factors led to final values of $R = 0.065$ and $R_w = 0.069$. A final difference Fourier showed no feature greater than 0.6 e/Å³. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or (sin θ)/λ was noted. The final values of the positional parameters are given in Table III.[37]

Registry No. I, 76747-86-9; [(C₅H₄CH₃)₂YbC≡CC(CH₃)₃]₂, 76565-31-6; [(C₅H₅)₂ErCH₃]₂, 61127-35-3; [(C₅H₄CH₃)₂YbCH₃]₂, 76158-22-0.

Supplementary Material Available: Listings of structure factor amplitudes and anisotropic thermal parameters (9 pages). Ordering information is given on any current masthead page.

(32) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957.
(33) SHELX, a system of computer programs for X-ray structure determination by G. M. Sheldrick, 1976.
(34) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.
(35) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
(36) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 72.

(37) See paragraph at the end of paper regarding supplementary material.

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Aluminated Metal Alkylidyne Complexes. 2.[1] Crystal and Molecular Structure of W(CAl₂Me₄Cl)(CH₃)(PMe₃)₂(η²-C₂H₄)

MELVYN ROWEN CHURCHILL* and HARVEY J. WASSERMAN

The dialumina–methylidyne complex W(CAl₂Me₄Cl)(CH₃)(PMe₃)₂(η²-C₂H₄) has been investigated by a single-crystal X-ray diffraction study. This complex crystallizes in the centrosymmetric triclinic space group P1̄ (No. 2) with $a = 10.385$ (2) Å, $b = 14.554$ (5) Å, $c = 8.717$ (2) Å, $\alpha = 78.40$ (2)°, $\beta = 68.55$ (2)°, $\gamma = 78.53$ (2)°, and $Z = 2$. Diffraction data were collected with a Syntex P2₁ automated diffractometer using Mo Kα radiation, and the structure was refined to R_F = 2.7% and R_{wF} = 2.9% for all 3111 data with 3.5° < 2θ < 45° (R_F = 2.4% and R_{wF} = 2.8% for those 2923 reflections with $|F_o| > 3.0\sigma(|F_o|)$). The trimethylphosphine ligands occupy axial sites about a (distorted) trigonal-bipyramidal W(IV) atom, with W–P(1) = 2.496 (2) Å and W–P(2) = 2.502 (2) Å. The equatorial sites are occupied by a methyl group (W–C(4) = 2.211 (6) Å), an η²-ethylene ligand, which lies perpendicular to the equatorial coordination plane (W–C(1) = 2.181 (7) Å, W–C(2) = 2.187 (7) Å), and a CAl₂Me₄Cl ligand (W–C(3) = 1.813 (5) Å). The W–(CAl₂Me₄Cl) fragment is discussed, and it is concluded that the best simple description of the bonding involves a W≡C:⁻ system linked by a three-center, two-electron bond to the two aluminum atoms of a [Me₂Al(μ-Cl)AlMe₂⁺] moiety. The molecule is thus closely related to a mononuclear "bare" carbide (i.e., M≡C:⁻).

Introduction

We have previously reported the results of X-ray structural analyses of the simple tungsten methylidyne complex W(≡CH)(Cl)(PMe₃)₄ (1) and of a mixture of the aluminated derivatives W(≡CH·AlMe₂Cl)(Cl)(PMe₃)₃ (2a) and W(≡CH·AlMeCl₂)(Cl)(PMe₃)₃ (2b).[1-3] These species were prepared by Schrock and co-workers[2] who have extended this work to prepare a dialuminated complex of stoichiometry W(CAl₂Me₄Cl)(CH₃)(PMe₃)₂(η²-C₂H₄) (3), as indicated in Scheme I. We now report the results of a single-crystal X-ray diffraction study of the unusual dialuminated tungsten alkylidyne complex 3.
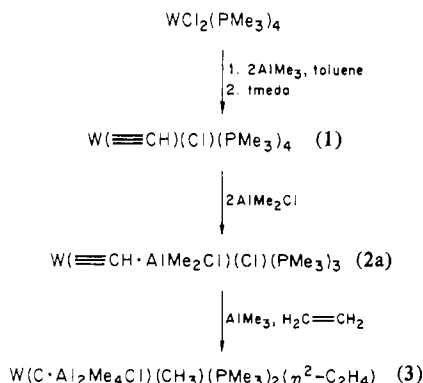
(1) The following paper should be considered as Part 1 of this series: Churchill, M. R.; Rheingold, A. L.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 3392.
(2) Sharp, P. R.; Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 965.
(3) The crystal studied contained ~82% of W(≡CH·AlMe₂Cl)(Cl)(PMe₃)₃ and ~18% of W(≡CH·AlMeCl₂)(Cl)(PMe₃)₃ (see ref 1 and 2).

Scheme I

WCl₂(PMe₃)₄

↓ 1. 2AlMe₃, toluene
2. tmeda

W(≡CH)(Cl)(PMe₃)₄   (1)

↓ 2AlMe₂Cl

W(≡CH·AlMe₂Cl)(Cl)(PMe₃)₃   (2a)

↓ AlMe₃, H₂C=CH₂

W(C·Al₂Me₄Cl)(CH₃)(PMe₃)₂(η²-C₂H₄)   (3)

Experimental Section

A. Data Collection. The compound was supplied by Professor R. R. Schrock of MIT. The sample consisted of large aggregates of pale yellow crystals, individually ranging in size from about 0.2 to 0.5 mm.