

Preliminary communication

REACTIVITY OF LANTHANIDE CARBON σ BONDS: ALKYL-LANTHANIDE COMPLEXES AS SYNTHETIC PRECURSORS TO LANTHANIDE ALKYNIDES*

WILLIAM J. EVANS* and ANDREA L. WAYDA

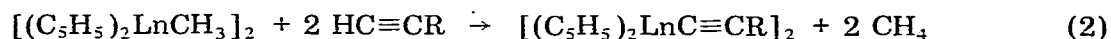
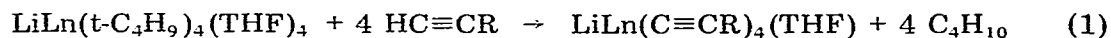
Department of Chemistry, University of Chicago, Chicago, Illinois 60637 (U.S.A.)

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Summary

A general, halide-free synthesis of σ -bonded organolanthanides is demonstrated by the reaction of terminal alkynes with $\text{LiLn}(\text{t-C}_4\text{H}_9)_4(\text{THF})_4$ to form a new series of homoleptic lanthanide alkynide complexes, $\text{LiLn}(\text{C}\equiv\text{CR})_4(\text{THF})_4$, and by the synthesis of $[(\text{C}_5\text{H}_5)_2\text{LnC}\equiv\text{CR}]_2$ from $[(\text{C}_5\text{H}_5)_2\text{LnCH}_3]_2$.

Several types of homoleptic σ -bonded organolanthanide complexes have been synthesized by the reaction of a lanthanide trichloride with an alkyl-lithium reagent [1–3]. Alkyldicyclopentadienyllanthanide compounds have been similarly obtained using $[(\text{C}_5\text{H}_5)_2\text{LnCl}]_2$ precursors [4]. Syntheses of this type are limited to those cases where it is possible to achieve clean separation of the alkyl complex from the by-product LiCl and from the mixed alkyl halide complexes [1] and LiCl adducts [1,5] which are often present. An alternate approach to formation of $\text{Ln}-\text{C}$ σ -bonds, based on organolithium, early transition metal [6] and lanthanide metal chemistry [7–10], is the reaction of the basic alkyl moiety in homoleptic and heteroleptic alkyl-lanthanide complexes with substrates containing acidic hydrogen. Consequently, as part of a general investigation of the reactivity of $\text{Ln}-\text{C}$ σ -bonds, we have examined the reactivity of such complexes toward metallation, as shown in eq. 1 and 2.



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Since the precursors are easily purified, this approach provides a general chloride-free synthesis of homoleptic organolanthanides, exemplified here by the synthesis of a new class of lanthanide alkynides [8,11], $\text{LiLn}[\text{C}\equiv\text{CC}(\text{CH}_3)_3]_4\cdot(\text{THF})$ ($\text{Ln} = \text{Sm}, \text{Er}, \text{Lu}$), and by an alternate synthesis of dicyclopentadienyl-lanthanide alkynides [4,10] based on $[(\text{C}_5\text{H}_5)_2\text{LnCH}_3]_2$ precursors [4].

Reaction of $\text{LiEr}(\text{t-C}_4\text{H}_9)_4(\text{THF})_4$ [3] with an 8-fold molar excess of 3,3-dimethylbut-1-yne (32 equiv.) in tetrahydrofuran (THF) at room temperature for 24 h proceeds according to eq. 1 with complete replacement of the *t*-butyl ligands and formation of 2-methylpropane (identified by gas chromatography). Removal of THF and extraction with pentane, followed by removal of solvent, allows isolation in nearly quantitative yield of pink $\text{LiEr}(\text{C}\equiv\text{CCMe}_3)_4(\text{THF})$, identified by complete elemental analysis (Found: C, 58.46; H, 7.50; Er, 29.70; Li, 1.36; O, 2.98 (by difference). $\text{ErC}_{28}\text{H}_{44}\text{LiO}$ calcd.: C, 58.90; H, 7.77; Er, 29.30; Li, 1.21; O, 2.80%), and the following spectral features. The near infrared visible spectrum (nm (ϵ): 523(12), 520(12), 378(20)) is consistent with Er^{3+} and differs from the starting material [3] in that these reported transitions are not hypersensitive. The room temperature magnetic moment [12], 9.79 BM, is also consistent with Er^{3+} . The infrared spectrum contains a strong sharp $\nu(\text{C}\equiv\text{C})$ absorption at 2050 cm^{-1} (cf. $\text{LiC}\equiv\text{CCMe}_3$, $\nu(\text{C}\equiv\text{C})$ 2025 cm^{-1}) as well as other absorptions indicative of the $\text{C}\equiv\text{CCMe}_3$ moiety (1360, 1240, 1200 cm^{-1}). Absorptions at 1050 and 890 cm^{-1} are consistent with coordinated THF [1]. Hydrolytic decomposition forms 3,3-dimethylbut-1-yne.

The reaction sequence demonstrated for $\text{Ln} = \text{Er}$ in eq. 1 is also observed for samarium and lutetium. The off-white samarium product and white lutetium product have IR spectra nearly identical to the erbium product, and complexometric metal analysis (Found: Sm, 27.07; Lu, 30.81. $\text{LnC}_{28}\text{H}_{44}\text{LiO}$ calcd.: Sm, 27.14; Lu, 30.24%), magnetic moment [12] (Sm, $\mu_{\text{eff}}^{298} = 1.66$) and ^{13}C NMR measurements ($\text{LiSm}(\text{C}\equiv\text{CCMe}_3)_4(\text{THF})$: (gated decoupled, ppm downfield from TMS, $\text{C}_4\text{D}_8\text{O}$): 32.4 (q, C_δ), 27.7 (s, C_γ), C_α and C_β not observed. Cf. $\text{LiC}\equiv\text{CCMe}_3$: 122.9 (s, C_α or C_β), 115.9 (s, C_β or C_α), 33.1 (q, C_δ), 28.7 (s, C_γ)) are consistent with the formation of analogous products. The solubility of the lutetium derivative diminishes upon prolonged handling.

Reaction 1 is also generally applicable to other alkynes. Using $\text{HC}\equiv\text{CC}_4\text{H}_9$ and $\text{HC}\equiv\text{CC}_6\text{H}_5$, alkynide complexes exhibiting $\nu(\text{C}\equiv\text{C})$ at 2050 and 2040 cm^{-1} , respectively, were obtained. As is common in organolanthanide chemistry, complexes of these less bulky ligands are not as stable as the alkynides derived from 3,3-dimethylbut-1-yne, as evidenced by rapid darkening of these species upon solvent removal.

To further define the general reactivity pattern of lanthanide alkyls shown in eqn. 1, we examined the reaction of alkynes with the monoalkyl lanthanides, $[(\text{C}_5\text{H}_5)_2\text{LnCH}_3]_2$ (eq. 2). As expected, $[(\text{C}_5\text{H}_5)_2\text{ErCH}_3]_2$ [4] reacts with 3,3-dimethylbut-1-yne in THF to form, in 85% yield, CH_4 and $[(\text{C}_5\text{H}_5)_2\text{Er}(\text{C}\equiv\text{CCMe}_3)]_2$, identified by IR ($\nu(\text{C}\equiv\text{C})$ 2050 cm^{-1}), complexometric metal analysis (Found: Er, 44.26. $\text{ErC}_{32}\text{H}_{38}$ calcd.: Er, 44.18%), near infrared and isopiestic molecular weight measurement (in THF). $[(\text{C}_5\text{H}_5)_2\text{Er}(\text{C}\equiv\text{CCMe}_3)]_2$ is only slightly soluble in arene solvents, in contrast to the readily soluble $[(\text{C}_5\text{H}_5)_2\text{ErCH}_3]_2$. As a result, the synthesis of $[(\text{C}_5\text{H}_5)_2\text{Er}(\text{C}\equiv\text{CCMe}_3)]_2$ by this halide-free reaction is preferable to a route in-

volving the reaction of $[(C_5H_5)_2ErCl]_2$ with $LiC\equiv CMe_3$ and subsequent separation of $LiCl$ by arene extraction of the product [4]. Both syntheses require two steps starting from $HC\equiv CMe_3$ and $[(C_5H_5)_2ErCl]_2$, but it is easier to separate by-product $LiCl$ from the methyl intermediate than from the alkynide product. $[(C_5H_4CH_3)_2YbCH_3]_2$ reacts in an analogous manner to form $[(C_5H_4CH_3)_2Yb(C\equiv CMe_3)]_2$ (Found: Yb, 42.34. $YbC_{36}H_{46}$ calcd.: Yb, 41.95%).

Clearly this metallation reactivity is generally applicable to a variety of alkyl-lanthanide/substrate combinations and should be useful not only in generating new classes of lanthanide alkynides but also in the synthesis of a variety of other lanthanide species.

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