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Synthesis, Structure, and Reactivity of Rare-Earth Metallocene η^3-Propargyl/Allenyl Complexes

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The reaction of the alkyl complexes $Cp^*_2LnCH(SiMe_3)_2$ (Ln = Y **1-Y**, Ce **1-Ce**, La **1-La**; Cp* = η^5-C_5Me_5) and $Me_2Si(\eta^5\text{-}C_5Me_4)_2LnCH(SiMe_3)_2$ (Ln = Ce **5-Ce**) with 1-methylalk-2-ynes $CH_3C{\equiv}CR$ (R = Me **3a**, Et **3b**, ^{n}Pr **3c**, ^{t}Bu **3d**, $SiMe_3$ **3e**, Ph **3f**, C_6H_4Me-2 **3g**, $C_6H_3Me_2$-2,6 **3h**, $C_6H_3{}^iPr_2$-2,6 **3i**, C_6F_5 **3j**) affords the corresponding η^3-propargyl/allenyl complexes $Cp^*_2LnCH_2CCR$ (**4a−j-Ln**) and $Me_2Si(\eta^5\text{-}C_5Me_4)_2CeCH_2CCR$ (**6a−j-Ce**) via propargylic metalation. The hydride complexes $[Cp^*_2Ln(\mu\text{-}H)]_2$ (Ln = Y **2-Y**, Ce **2-Ce**, La **2-La**) react rapidly with **3** to produce mixtures of insertion and propargylic metalation products, and the relative rate of these processes depends on the metal and alkyne substituent. Selected η^3-propargyl/allenyl complexes $Cp^*_2YCH_2CCR$ (R = Me **4a-Y**, Ph **4f-Y**), $Cp^*_2CeCH_2CCR$ (R = Me **4a-Ce**, Ph **4f-Ce**), $Cp^*_2CeCH(Me)CCEt$ (**9b-Ce**), $Cp^*_2LaCH_2CCR$ (R = Ph **4f-La**, $C_6H_3Me_2$-2,6 **4h-La**) are obtained on a preparative scale and characterized by NMR spectroscopy, IR spectroscopy, and cryoscopy. Compounds **4f-Y** and **4f-La** are also characterized by single-crystal X-ray diffraction. The reactions of the η^3-propargyl/allenyl complexes with Brønsted acids, such as alcohols and acetylenes, afford the corresponding substituted allenes ($RCH{=}C{=}CH_2$) and 1-methylalk-2-ynes ($CH_3C{\equiv}CR$) as organic products. The reactions of **4f-Y** and **4f-La** with Lewis bases, such as pyridine and THF, yield the corresponding base adducts. The adduct **4f-La·py** is characterized by single-crystal X-ray diffraction, revealing an η^3-coordinated propargyl/allenyl ligand.

Introduction

In contrast to allenyl and propargyl derivatives of transition metals, alkali metals, and alkaline earth metals,[1] relatively little is known about related rare-earth metal compounds.[2] In general, η^1-allenyl (**I**) and -propargyl (**III**) metal complexes (Chart 1) are known to exhibit interesting structural features and unusual reactivity.[3] An aspect that has received much recent attention is their tautomeric behavior, as metal η^1-propargyls have been shown to undergo both reversible and irreversible tautomerization into metal η^1-allenyls. In addition, various well-characterized delocalized π-bonded η^3-allenyl/propargyl complexes (**II**) are known.[4]

The first reported rare-earth metal allenyl and propargyl derivatives were made from the reaction of Cp^*_2LuMe with allene and 2-butyne, both yielding allenyl products.[5] A facile 1,3-metal shift in the propargyl intermediate to yield the observed allenyl was proposed, but no experimental evidence was given. A decade later, Heeres et al. reported spectroscopi-

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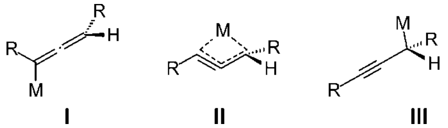
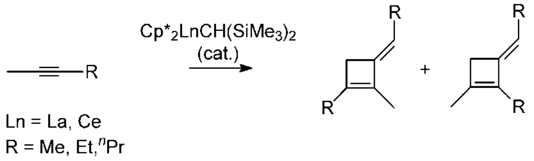
10.1021/om800547n CCC: $40.75

Chart 1. Structural Isomerism in Allenyl/Propargyl Metal Complexes



Scheme 1. Catalytic Cyclodimerization of 1-Methylalk-1-ynes



cally characterized alkyl- and silyl-substituted rare-earth metallocene 2-alkynyls Cp*$_2$LnCH$_2$CCR that were implicated as the active catalyst in the organolanthanide-catalyzed cyclodimerization of alkyl- and silyl-substituted 1-methylalk-2-ynes CH$_3$CCR (Scheme 1).[6] The reactivity of these species remained unexplored and the exact nature of their bonding was unknown, as structural data were lacking.

Since then, only three studies involving well-defined allenyl/propargyl rare-earth metal complexes have appeared in literature, including the spectroscopically characterized yttrium η^1-allenyl species **A**, which is reported to be in a rapid equilibrium with its η^1-propargyl isomer **A′**,[7] some structurally characterized η^3-propargyl samarium half-sandwich complexes (e.g., **B**), incorporating a chelating allenyl/propargyl ligand system,[8] and a divalent ytterbium η^3-propargyl (**C**), which was also structurally characterized (Chart 2).[9] The only other reports regarding propargyl and/or allenyl rare-earth metal complexes involve proposed reactive intermediates in metal-mediated organic synthesis, prepared *in situ* by transmetalation reactions of rare-earth metal salts with organopalladium intermediates[10] or Grignard reagents.[11]

A study on the synthesis, structure, and reactivity of these complexes was initiated to elucidate the nature of the bonding in 2-alkynyl rare-earth metallocenes and investigate their reactive chemistry. The reactions of Cp*$_2$LnCH(SiMe$_3$)$_2$ (**1**) and [Cp*$_2$Ln(μ-H)]$_2$ (**2**) with several 1-methylalk-1-ynes (**3**) were probed as routes toward Lewis-base-free 2-alkynyl rare-earth metal complexes Cp*$_2$LnCH$_2$CCR (**4**). The effects of the metal, ancillary ligand, and alkyne substituent on the rate and selectivity of these reactions are discussed, as well as the structure of the resulting 2-alkynyl rare-earth metal complexes. The reactivity of 2-alkynyl rare-earth metallocenes toward Lewis bases and Brønsted acids was also investigated.

Results and Discussion

Reactions with 1-Methyl-alk-2-ynes on NMR Tube Scale. In this section, the reactions of rare-earth metallocene alkyl and hydride complexes with 1-methylalk-2-ynes on an NMR tube scale are described. Isolation and full characterization of the organometallic products of selected examples are reported in a following section.

(a) Metallocene Alkyls. The alkyl derivatives Cp*$_2$LnCH(SiMe$_3$)$_2$ (**1**) (Ln = Y **1-Y**, Ce **1-Ce**, La **1-La**) reacted with equimolar amounts of 1-methylalk-2-ynes CH$_3$CCR (R = Me **3a**, Et **3b**, ^{n}Pr **3c**, ^{t}Bu **3d**, SiMe$_3$ **3e**, Ph **3f**, C$_6$H$_4$Me-2 **3g**, C$_6$H$_3$Me$_2$-2,6 **3h**, C$_6$H$_3$^{i}Pr$_2$-2,6 **3i**, C$_6$F$_5$ **3j**) to afford the corresponding 2-alkynyl complexes Cp*$_2$LnCH$_2$CCR (**4a**−**j**) and CH$_2$(SiMe$_3$)$_2$, as indicated by *in situ* NMR spectroscopy (Scheme 2). A correlation between the rate of proton transfer and the (kinetic) acidity of the 1-methylalk-2-ynes might be expected.[12] In this study, the rate of propargylic metalation was found to decrease considerably upon increasing the size of the alkyne substituent R and decreasing the ionic size of the metal Ln.[13] For example, the reactions of the cerium (**1-Ce**) and lanthanum (**1-La**) derivatives with 2-butyne (**3a**) were complete within a few hours at room temperature. The smaller yttrium derivative **1-Y**, on the other hand, was unreactive toward **3a**, even after prolonged heating at 80 °C. The rate of propargylic metalation could be increased by employing a large molar excess of substrate, but then propargylic metalation was accompanied by competing catalytic cyclodimerization of the substrate for the reactions of **1-Ce** and **1-La** with less sterically encumbered 1-methylalk-2-ynes. No reaction was observed for **1-Ce** and **1-La** with the more crowded internal alkyne 3-hexyne (**7b**), even after prolonged heating at 50 °C. Nevertheless, for the analogous reactions of **1-Ce** and **1-La** with 2-pentyne (**3b**) and 2-hexyne (**3c**), respectively, complete conversion of **1-Ce** and **1-La** into the corresponding 2-alkynyl derivatives was observed after 15 days at 50 °C. As alkyl groups do not differ significantly in their electronic substituent effects, these reactions appear to be under steric control.[14]

Reactions of the ansa-metallocene alkyl Me$_2$Si(η^5-C$_5$Me$_4$)$_2$CeCH(SiMe$_3$)$_2$ (**5-Ce**) with 1-methylalk-2-ynes **3a**−**j** were conducted in order to investigate the effect of opening

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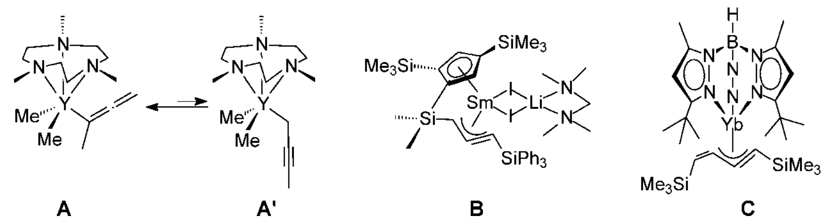
[12] A Hammett plot with a reaction constant ρ of 1.3 was found for the propargylic metalation of substituted 1-phenyl-1-propynes by *n*-BuLi, indicating that this reaction is only mildly accelerated by electron-withdrawing substituents; see: Becker, J. Y. *J. Organomet. Chem.* **1976**, *118*, 247.

[13] Ionic radii for eight-coordinate complexes: La^{3+} (1.160 Å), Ce^{3+} (1.143 Å), and Y^{3+}, see: Shannon, R. D *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

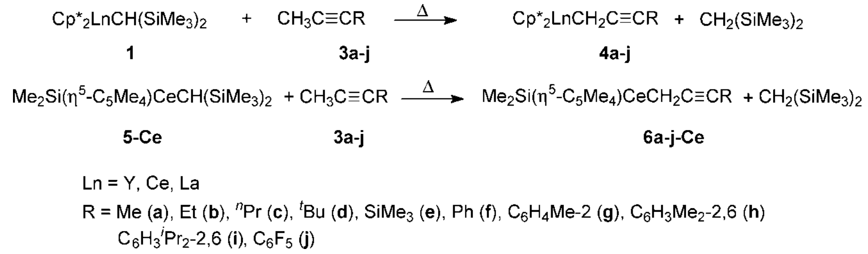
[14] (a) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. (b) Isaacs, N. S. *Physical Organic Chemistry*, 2nd ed.; Longman: Essex, 1996. (c) Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119.

[15] Many examples exist in the literature, demonstrating that the rates of insertion and σ-bond metathesis are greatly influenced upon linking the cyclopentadienyl ligands by a Me$_2$Si group; see:(a) Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147. (b) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103. (c) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111. (d) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108. (e) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241. (f) Shin, J. H.; Parkin, G. *Chem. Commun.* **1999**, 887. (g) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828. (h) Dash, A. K.; Gourevich, I.; Wang, J. Q.; Wang, J.; Kapon, M.; Eisen, M. S. *Organometallics* **2001**, *20*, 5084. (i) Fontaine, F. G.; Tilley, D. T. *Organometallics* **2005**, *24*, 4340.

Chart 2. Examples of Rare-Earth Metal Propargyl and Allenyl Species



Scheme 2. Reactions of the Alkyl Derivatives 1 and 5 with 1-Methylalk-2-ynes CH_3CCR (3a−j) Affording the 2-Alkynyl Derivatives 4a−j and 6a−j, Respectively



the metal coordination sphere at the σ-ligand equatorial girdle.[15] Although the scope of the propargylic metalation of **5-Ce** toward **3a-j** was similar to that of **1-Ce** and **1-La**, the solubility of the formed 2-alkynyl derivatives was very low. For example, the addition of excess 2-butyne (**3a**) to **5-Ce** resulted in the quantitative formation of $CH_2(SiMe_3)_2$ and the deposition of orange crystalline $[Me_2Si(\eta^5\text{-}C_5Me_4)_2CeCH_2CCMe]_n$ (**6a-Ce**), suggesting the formation of an oligomeric product. Unfortunately, the quality of the crystals was insufficient for single-crystal X-ray diffraction. Further heating of the reaction mixture led to catalytic cyclodimerization of **3a** at a reaction rate comparable to the same reaction catalyzed by $Cp^*_2LaCH_2CCMe$ (**4a-La**).[6]

(b) Metallocene Hydrides. In general, the hydride derivatives $[Cp^*_2Ln(\mu\text{-}H)]_2$ (**2**) react rapidly with aliphatic and aromatic 1-methylalk-2-ynes to yield complex, time-dependent reaction mixtures. Reaction mixtures contained significant amounts of *cis*-alkenes in most cases and the relative amount of the *cis*-alkene depended on the metal and the alkyne substituent.[16] The reactions of **2-Y** with **3a−j** were generally less selective for the formation of the corresponding 2-alkynyl derivative than those of **2-Ce** and **2-La**. Also, the composition of the reaction mixtures with **2-Y** did not change in time, contrary to reactions with **2-Ce** and **2-La**.[17] The reactions of **2** with 1-pentafluorophenyl-1-propyne (**3j**) were more complicated, as product analysis indicated that multiple nonselective insertions of the alkyne take place.[18]

NMR tube reactions of the hydride derivatives $[Cp^*_2Ln(\mu\text{-}H)]_2$ (**2**) (Ln = Y **2-Y**, Ce **2-Ce**, La **2-La**) with molar excesses of 1-phenyl-1-propyne (**3f**) produced mixtures that appear to contain three metallocene species, one of them being $Cp^*_2LnCH_2CCPh$ (**4f**), and *cis*-1-phenyl-1-propene. The concentration of **4f** and *cis*-1-phenylprop-1-ene gradually increased over time. Even though the two additional metallocenes in these reaction mixtures could not be identified unambiguously, quenching experiments with methanol-d_4 afforded *cis*-1-phenyl-1-propene-d_1, suggestive of the presence of $Cp^*_2LnC(Ph){=}C(Me)H$ (**8fa**) and $Cp^*_2LnC(Me){=}C(Ph)H$ (**8af**).

These results can be rationalized by three separate pathways by which a monomeric hydride derivative Cp^*_2LnH reacts with **3f** (Scheme 3).[19] Analogous to the above alkyls, Cp^*_2LnH may react with **3f** via propargylic C−H activation, forming $Cp^*_2LnCH_2CCPh$ (**4f-Ln**) and dihydrogen. The formation of **2-La** from the reaction of **4f-La** with excess dihydrogen suggests that propargylic C−H activation by Cp^*_2LaH is reversible.[20] Contrary to the above alkyls, however, insertion of Cp^*_2LnH into the carbon−carbon triple bond of **3f** may also take place: 1,2- and 2,1-insertion give rise to the 1-phenylprop-1-en-2-yl **8fa** and the 1-phenylprop-1-en-1-yl **8af** derivative, respectively. This process is exemplified by the reaction of $[Cp^*_2La(\mu\text{-}H)]_2$ (**2-La**) with diphenylethyne, producing the alkenyl derivative $Cp^*_2LaC(Ph){=}C(Ph)H$ (**8ff-La**) in high isolated yield. The reaction of **8af** and **8fa** with **3f** yields **4f-Ln** and *cis*-1-phenylprop-1-ene. Evidence for this process is provided by the reaction of **8ff-La** with **3f**, producing **4f-La** and *cis*-diphenylethene. Other routes to the formation of *cis*-1-phenylprop-1-ene are plausibly the reactions of **8af** and **8fa** with dihydrogen, formed from propargylic C−H activation of **3f** by Cp^*_2LaH.

Preparative Scale Reactions. The yellow $Cp^*_2YCH_2CCMe$ (**4a-Y**) and orange $Cp^*_2YCH_2CCPh$ (**4f-Y**) yttrium derivatives, the green cerium compounds $Cp^*_2CeCH_2CCMe$ (**4a-Ce**), $Cp^*_2CeCH_2CCPh$ (**4f-Ce**), and $Cp^*_2CeCH(Me)CCEt$ (**9b-Ce**), and the red lanthanum compounds $Cp^*_2LaCH_2CCPh$ (**4f-La**) and $Cp^*_2LaCH_2CCC_6H_3Me_2\text{-}2,6$ (**4h-La**) were obtained as crystalline materials by addition of excess 1-methylalk-2-yne to pentane suspensions of the corresponding hydrides and subsequent crystallization by cooling. The isolated yields of the

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(16) See the Supporting Information.

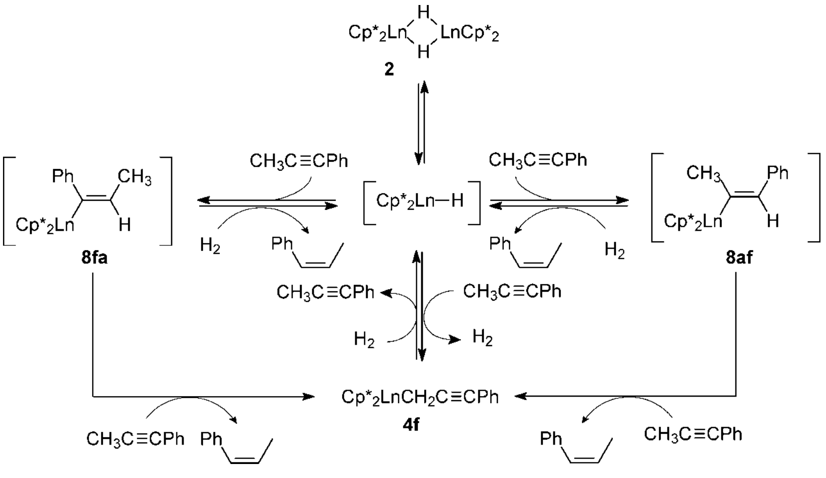
(17) These results are in accordance with the much lower hydrogenation activity of alkenes by **2-Y** relative to **2-La** and **2-Ce**; see: Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111.

(18) GC/GC-MS and NMR analyses indicate the presence of 1-(pentafluorophenyl)prop-1-ene-d_1 and 2,4-bis(pentafluorophenyl)-3-methylhexa-2,4-diene-d_1 after deuterolysis, pointing to mono- and double-insertion products.[16]

(19) Ample evidence exists in the literature that hydride derivatives of rare-earth metallocenes $[Cp^*_2Ln(\mu\text{-}H)]_2$ (**2-Ln**) are present in solution as an equilibrium mixture of dimer and monomer. Dissociation of the dimer $[Cp^*_2Y(\mu\text{-}H)]_2$ to the monomer Cp^*_2YH in reactions of $[Cp^*_2Y(\mu\text{-}H)]_2$ with alkenes has been studied in detail; see: Casey, C. P.; Tunge, J. A.; Lee, T.-Y.; Carpenetti, D. W., III. *Organometallics* **2002**, *21*, 389.

(20) The reversible nature of propargylic metalation was demonstrated by the reaction of $Cp^*_2LaCH_2CCPh$ (**4f-La**) with excess dihydrogen (1 atm). **4f-La** was consumed within several hours, giving rise to *n*-propylbenzene and $[Cp^*_2La(\mu\text{-}H)_2]$ (**2-La**) over the course of 1 day at room temperature.

Scheme 3. Proposed Reaction Sequences for the Reaction of the Hydride Derivatives $[Cp^*_2Ln(\mu\text{-}H)]_2$ (2) with 1-Phenyl-1-propyne (3f)



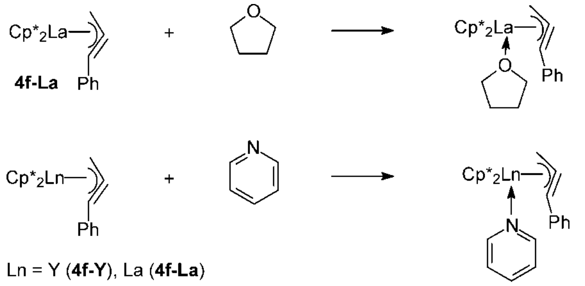
alkyl-substituted derivatives were relatively low, due to the high solubility of the compounds in both aliphatic and aromatic solvents. Molecular weight determinations (cryoscopy in benzene) showed that **4a-Y**, **4f-Y**, **4a-Ce**, **4f-La**, and **9b-Ce** are monomeric in solution.

The phenyl-substituted 2-alkynyl derivatives $Cp^*_2LnCH_2CCPh$ (**4f**) could be prepared in high isolated yields by performing the reaction of the hydride **2** with 1-phenyl-1-propyne (**3f**) while removing the H_2 formed by the reaction by repeated brief evacuations. A more convenient preparative method involves the *in situ* formation of the hydride **2** from the alkyl **1**. This is achieved by replacing the nitrogen atmosphere of a pentane solution of **1** by hydrogen (1 atm), subsequent stirring for 12 h at 0 °C, replacing the hydrogen atmosphere again by nitrogen, and addition of alkyne. A crystalline solid was obtained after complete *in vacuo* removal of the organic compounds in the crude product mixture (e.g., *cis*-1-phenylprop-1-ene, $CH_2(SiMe_3)_2$, unreacted **3f**).

The putative oligomeric 2-butynyl compound $[Me_2Si(\eta^5\text{-}C_5Me_4)_2CeCH_2CCMe]_n$ (**6a-Ce**) was synthesized by addition of excess 2-butyne (**3a**) to a benzene solution of $Me_2Si(\eta^5\text{-}C_5Me_4)_2CeCH(SiMe_3)_2$ (**5-Ce**). Its low solubility impeded the use of NMR spectroscopy and cryoscopy, but elemental analysis, infrared spectroscopy, and its reactivity with 2,6-di-*tert*-butyl-4-methylphenol confirmed its identity (*vide infra*).[21]

Reactivity toward Lewis Bases. (a) Tetrahydrofuran. The reaction of $Cp^*_2LaCH_2CCPh$ (**4f-La**) with an equimolar amount of tetrahydrofuran (THF) in benzene-d_6 revealed a rapid and clean reaction without color change, as indicated by *in situ* ^1H NMR spectroscopy (Scheme 4).[16] The upfield shifts of the THF ^1H and ^{13}C NMR resonances versus free THF (e.g., $\Delta\delta$ −0.55 and −0.04 ppm for the α- and β-carbon, respectively, in the ^{13}C NMR spectrum) are consistent with the coordination to the electrophilic metal center. On the basis of the upfield shift of the propargylic CH_2 carbon resonance vs **4f-La** ($\Delta\delta$ −1.37 ppm) and the similarity of the NMR spectral parameters with the crystallographically characterized pyridine adduct $Cp^*_2La(\eta^3\text{-}CH_2CCPh)\cdot C_5H_5N$ (*vide infra*), an η^3-propargyl/allenyl structure is favored for $Cp^*_2LaCH_2CCPh\cdot C_4H_8O$ (**4f-La**·THF).

Scheme 4. Reactions of 4f-Y and 4f-La with THF and Pyridine



(b) Pyridine. A clean and quantitative reaction was also observed for the reaction of $Cp^*_2LaCH_2CCPh$ (**4f-La**) with an equimolar amount of pyridine (Scheme 4) with *in situ* ^1H NMR spectroscopy. The formation of the corresponding adduct (**4f-La**·py) is indicated by the upfield shifts of the pyridine proton ($\Delta\delta$ −0.12, −0.17, and −0.19 ppm for α-, β-, and γ-C*H*, respectively) and carbon resonances ($\Delta\delta$ −0.55, −0.30, and +1.77 ppm for α-, β-, and γ-*C*H, respectively) upon metal coordination. The changes of the ^1H and ^{13}C NMR resonances of **4f-La** are similar to those observed previously for **4f-La**·THF. A single-crystal X-ray analysis study of **4f-La**·py established unambiguously that the bonding of the propargyl/allenyl ligand in **4f-La**·py is trihapto (*vide infra*).

The reaction of $Cp^*_2YCH_2CCPh$ (**4f-Y**) with pyridine was studied to investigate the effect of metal size on the bonding mode of the η^3-propargyl/allenyl ligand upon Lewis base coordination. NMR spectroscopy indicated that the addition of pyridine (1 equiv) to **4f-Y** led to the rapid and clean formation of the corresponding Lewis base adduct **4f-Y**·py. The Lewis base adduct $Cp^*_2YCH_2CCPh\cdot C_5H_5N$ (**4f-Y**·py) was isolated in reasonable yield (63%) as an off-white thermolabile solid. The increased thermolability of **4f-Y**·py as compared to **4f-La**·py may be explained by an increased nucleophilic character of the propargyl methylene group in the former due to a stonger distortion of the η^3-bonding of the propargyl/allenyl ligand upon coordination of pyridine to the smaller metal. This increased nucleophilicity could induce reactivity with the coordinated

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(21) Attempts to dissolve $[Me_2Si(\eta^5\text{-}C_5Me_4)_2CeCH_2CCMe]_n$ (**6a-Ce**) in THF-d_8 resulted in the formation of free 2-butyne and several broad resonances in the−25 to 15 ppm range of the ^1H NMR spectrum. C−O bond activation of THF-d_8 and the formation of a ring-bridged μ-oxo compound, $[Me_2Si(\eta^5\text{-}C_5Me_4)_2Ce(THF)]_2(\mu\text{-}O)$, is well-possible; see: Booij, M. Ph.D. Thesis 1989, University of Groningen, Chapter 2.

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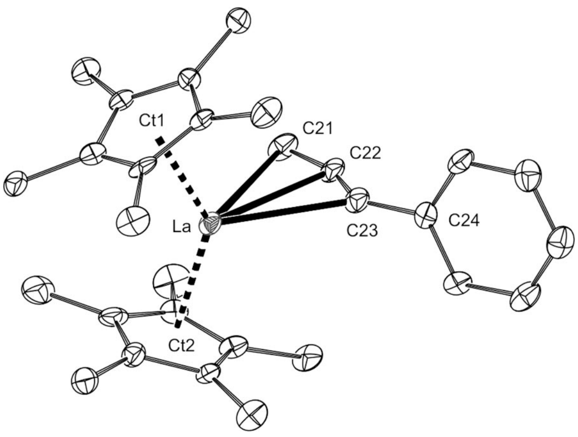

Figure 1. Thermal ellipsoid plot of Cp*$_2$LaCH$_2$CCPh (**4f-La**) (drawn at a 50% probability level). Hydrogen atoms are omitted for clarity.

pyridine ligand, as is observed frequently for rare-earth metal alkyl and hydride species.[22] Attempts to obtain single crystals of **4f-Y**·py suitable for X-ray analysis failed. Freshly prepared **4f-Y**·py turned dark red within hours upon standing at room temperature, and the decomposition products defied unambiguous characterization.

X-ray Crystal Structures of Cp*$_2$YCH$_2$CCPh (4f-Y), Cp*$_2$LaCCPh (4f-La), and Cp*$_2$LaCH$_2$CCPh·py (4f-La·py). The geometries of the bent metallocene fragments in **4f-Y**, **4f-La**, and **4f-La**·py are similar to that in other lanthanum[23] and lanthanide metallocenes.[24] However, the Cp* ligands are in the less common eclipsed conformation in **4f-La**·py. The molecular structure of **4f-La** is shown in Figure 1, and selected bond distances and angles for **4f-Y** and **4f-La** are given in Table 1. The phenyl-substituted propargyl/allenyl ligands are clearly bound in an η^3-mode.[3] The backbone of the η^3-propargyl/allenyl ligands is virtually coplanar with the metal center (e.g., atom displacements from the least-squares plane: La 0.000, C21 0.001, C22 0.003, C23 0.002 Å for **4f-La**). This structural feature is believed to be typical of η^3-propargyl/allenyl complexes.[3d−f]

The crystallographic C21−C22 and C22−C23 bond distances of 1.36(1) and 1.23(1) Å, respectively, are intermediate between those generally accepted for C−C single (1.45 Å) and double (1.31 Å) and double and triple (1.20 Å) bonds, respectively, and the C$_3$ ligand backbone is thus consistent with resonance between propargyl and allenyl structures. The bond angles C21−C22−C23 of 156° and 159° for **4f-Y** and **4f-La**, respectively, indicate a considerable deviation from linearity at the central carbon atom, which is typical for η^3-propargyl/allenyl complexes.[3d−f]

The solid-state molecular structure of **4f-La**·py is depicted in Figure 2, and selected bond distances and angles are given in Table 1. It is interesting to note that pyridine coordinates at the more substituted side of the η^3-propargyl/allenyl ligand, suggesting that the coordination of Lewis bases is controlled by electronic factors rather than steric factors. The solid-state structures of **4f** and **4f-La**·py reveal several changes upon pyridine coordination. First, a slight distortion of the coplanar arrangement of the metal center with the η^3-propargyl/allenyl carbon backbone is seen (atom displacements from the least-squares plane relative to **4f-La**·py: La Δ +0.002, C26 Δ +0.010, C27 Δ +0.018, C28 Δ +0.010 Å). An apparent shift toward a more propargyl-like structure is also observed, as evidenced by the increased distances between lanthanum and the terminal carbon (Δ 0.08(1) Å).

Spectroscopic Characterization. (a) NMR Spectroscopy. Selected ^{1}H and ^{13}C NMR resonances of several Cp*$_2$LnCH$_2$CCR complexes are shown in Table 2. The diamagnetic yttrium and lanthanum Cp*$_2$LnCH$_2$CCR complexes exhibit equivalent Cp* and CH$_2$ resonances in the ^{1}H and ^{13}C NMR spectrum. No ^{1}H and ^{13}C NMR resonances attributable to distinct η^1-propargyl and η^1-allenyl forms of Cp*$_2$YCH$_2$CCPh (**4f-Y**), Cp*$_2$LaCH$_2$CCPh (**4f-La**), and Cp*$_2$LaCCC$_6$H$_3$Me$_2$-2,6 (**4h-La**) were observed at temperatures down to −80 °C. These observations, together with the solid-state structures of **4f-La** and **4f-Y**, suggest that the Cp*$_2$LnCH$_2$CCR compounds have a static η^3-propargyl structure and do not exist as a rapid equilibrium mixture of distinct η^1-propargyl and η^1-allenyl species in solution, but additional experiments would be needed to settle this issue more rigorously. The NMR data of the present rare-earth metal complexes compare well with those of reported (phenyl-substituted) allenyl and propargyl transition metal complexes[3,4] and are consistent with an η^3-allenyl/propargyl structure.[14,25]

Although the chemical shifts of the *C*H$_2$ propargyl carbon resonances (C-1, δ 42−56 ppm) of the Cp*$_2$LnCH$_2$CCR complexes are in the range of metal-bound *s*p^3 carbons in rare-earth metallocenes, such as Cp*$_2$Y(CH$_2$C$_6$H$_3$Me$_2$-3,5)[26] (δ 47.35 ppm, $^1J_{CH} = 133.4$ Hz) and Cp*$_2$LaCH(SiMe$_3$)$_2$[27] (δ 44.64 ppm, $^1J_{CH} = 93.0$ Hz), the corresponding first-order carbon−hydrogen coupling constants $^1J_{CH}$ (156.7−162.5 Hz) are significantly larger. These unusually large $^1J_{CH}$ values suggest that the C−H bonds of the propargylic carbon have considerably more s character and are close to that of an sp^2 carbon (typically 156 Hz).[28]

Yttrium-89 has a nucleus with $I = 1/2$ in a natural abundance of 100%, and coupling interactions in Cp*$_2$YCH$_2$CCR (R = Me **4a-Y**, Ph **4f-Y**) are observed with the propargyl (C-1) and terminal carbon atom (C-3) of the CH$_2$CCR ligand (Table 2). The absence of an observable J_{YC} on the central carbon (C-2) of CH$_2$CCR is in agreement with the nature of metal η^3-

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[23] (a) Heeres, H. J.; Meetsma, A.; Teuben, J. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 420. (b) Scholz, A.; Smola, A.; Scholz, J.; Loebel, J.; Schumann, H.; Thiele, K.-H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 435. (c) Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275. (d) Thiele, K.-H.; Bambirra, S.; Sieler, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 2886. (e) Evans, W. J.; Davis, B. L.; Nyce, G. W.; Perotti, J. M.; Ziller, J. W. *J. Organomet. Chem.* **2003**, *677*, 89.

[24] Evans, W. J.; Foster, S. E. *J. Organomet. Chem.* **1992**, *433*, 79.

[25] Extensive studies in organolithium chemistry have shown that the central carbon (C-2, δ 165−180 ppm for allenyl) and the propargyl carbon (C-1, δ 90−100 ppm) are very sensitive indicators of allenylic and propargylic structures. For examples, see:(a) Reich, H. J.; Holladay, J. E. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2365. (b) Reich, H. J.; Thompson, J. L. *Org. Lett.* **2000**, *2*, 783. (c) Reich, H. J.; Holladay, J. E.; Walker, T. G.; Thompson, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 9769. (d) Reich, H. J.; Holladay, J. E.; Mason, J. D.; Sikorsko, W. H. *J. Am. Chem. Soc.* **1995**, *117*, 12137. (e) Reich, H. J.; Holladay, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 8470. (f) Lambert, C.; von Ragué Schleyer, P.; Würthwein, E.-U. *J. Org. Chem.* **1993**, *58*, 6377.

[26] den Haan, K. H. Ph.D. Thesis, University of Groningen, 1986, Chapter 6.

[27] Booij, M. Ph.D. Thesis, University of Groningen, 1989, Chapter 7.

[28] Such an unambiguous interpretation is complicated by the fact that inductive/field effects originating from polar substituents influence $^1J_{CH}$ values to such an extent that the $^1J_{CH}$ values mostly do not reflect the true hybridization state of the carbon; see: (a) Kalinowski, H.-O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; Wiley: Chichester, 1991; Chapter 4. (b) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; Wiley-VCH: Weinheim, 1998; Chapter 3.3; p 97.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in $Cp^*_2LnCH_2CCPh$ (Ln = Y 4f-Y, La 4f-La) and $Cp^*_2LaCH_2CCPh(C_5H_5N)$ (4f-La·py)[a]

4f-Y		4f-La		4f-La·py	
		Bond Lengths			
C21−C22	1.366(4)	C21−C22	1.362(10)	C26−C27	1.356(4)
C22−C23	1.268(4)	C22−C23	1.234(10)	C27−C28	1.248(4)
C23−C24	1.462(4)	C23−C24	1.465(9)	C28−C29	1.454(4)
Y−C21	2.653(3)	La−C21	2.811(6)	La−C26	2.822(3)
Y−C22	2.529(3)	La−C22	2.695(7)	La−C27	2.726(3)
Y−C23	2.560(3)	La−C23	2.740(7)	La−C28	2.823(3)
av Y−C(Cp*)	2.654(4)	av La−C(Cp*)	2.806(16)	av La−C(Cp*)	2.841(7)
	2.652(4)	av La−C(Cp*)	2.780(16)	av La−C(Cp*)	2.852(7)
Y−Ct1	2.362(3)	La−Ct1	2.535(3)	La−Ct1	2.571
Y−Ct2	2.362(3)	La−Ct2	2.509(4)	La−Ct2	2.584
				La−N	2.743(2)
		Bond Angles			
Ct1−Y−Ct2	139.3(1)	Ct1−La−Ct2	137.1(1)	Ct1−La−Ct2	134.2
C21−C22−C23	155.9(3)	C21−C22−C23	159.3(7)	C26−C27−C28	161.0(3)
C22−C23−C24	141.5(3)	C22−C23−C24	141.2(7)	C27−C28−C29	142.8(3)
Y−C21−C22	70.2(2)	La−C21−C22	71.0(4)	La−C26−C27	71.9(2)
Y−C23−C22	74.7(2)	La−C23−C22	74.9(4)	La−C28−C27	72.7(2)

[a] Cp*1 = C1−C5, Cp*2 = C11−C15, Ct = centroid.

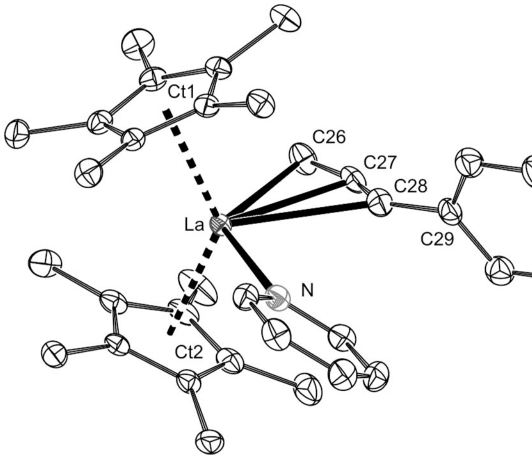

Figure 2. Molecular structure of **4f-La·py** with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

CH_2CCR bonding.[29] The yttrium−carbon couplings of the propargyl carbon CH_2 (8.1 Hz for **4a-Y** and 5.2 Hz for **4f-Y**) are notably smaller than those of yttrocene-bound sp^3 carbons, such as $Cp^*_2Y(CH_2C_6H_3Me_2\text{-}3,5)$[30] ($^1J_{YC}$ = 23.2 Hz) and $Cp^*_2YCH(SiMe_3)_2$[31] ($^1J_{YC}$ = 36.6 Hz), but are comparable to those of the terminal carbons of the allyl group in $Cp^*_2Y(\eta^3\text{-}C_3H_5)$[32] ($^1J_{YC}$ = 3.8 Hz).

The NMR spectra of the paramagnetic cerium compounds show strongly shifted and broadened resonances. Proton−proton coupling cannot be observed in most cases, and shift−structure relations are not evident.[33] Nonetheless, practically all protons are observable in the ^{1}H NMR spectra, exhibiting correct integrated intensities.[14] Noteworthy are the strongly high-field shifted α-carbon protons of $Cp^*_2CeCH_2CCMe$ (**4a-Ce**) and $Cp^*_2CeCH_2CCPh$ (**4f-Ce**), at δ −30.5 (lw = 38 Hz, lw = line width of the resonances at half-maximum) and δ −35.4 ppm (lw = 78 Hz), respectively. The α-proton of $Cp^*_2CeCH(Me)CCEt$ (**9b-Ce**) is found at δ −11.2 ppm (lw = 43 Hz). The NMR data for **9b-Ce** clearly demonstrate that the α-carbon is asymmetric, resulting in diastereotopic CH_2 protons and inequivalent Cp* rings.

The ^{1}H and ^{13}C NMR resonances of **4f-La** shift in a similar fashion upon coordination of pyridine or THF. The upfield shift of the propargylic CH_2 carbon resonance and the increase in its corresponding first-order carbon, hydrogen coupling constant ($^1J_{CH}$) suggest an increase in propargylic character of the η^3-CH_2CCPh ligand in **4f-La·py** and **4f-La·THF** relative to **4f-La** (Table 2). The upfield shifts of the CH_2CC carbon resonances upon coordination of pyridine are larger for **4f-Y·py** than for **4f-La·py**, suggesting that the shift toward more propargylic character of the CH_2CCPh ligand in $Cp^*_2LnCH_2CCPh\cdot py$ is influenced by steric factors. IR spectroscopy also points to a substantial increase of propargylic character in **4f-Y** upon coordination of pyridine (*vide infra*), but the overall η^3-coordination of the CH_2CCPh ligand in **4f-Y·py** is clearly indicated by the coupling between yttrium and the propargyl and terminal carbon atoms.

(b) Infrared Spectroscopy. Infrared spectroscopy has been widely used as a diagnostic tool in determining the relative contribution of allenylic and propargylic structures.[1] In the 1890−2000 cm^{-1} region of the infrared spectrum, strong and medium absorptions were observed for the present

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(29) According to several molecular orbital studies, the η^3-CH_2CCR ligand binds mainly through its terminal carbons, while the π-bond of the carbon−carbon triple bond does not interact significantly with the metal fragment. For examples, see:(a) Jemmis, E. D.; Chandrasekhar, J.; von Ragué Schleyer, P. *J. Am. Chem. Soc.* **1979**, *101*, 2848. (b) Carfagna, C.; Deeth, R. J.; Green, M.; Mahon, M. F.; McInnes, J. M.; Pellegrini, S.; Woolhouse, C. B. *J. Chem. Soc., Dalton Trans.* **1995**, 3975. (c) Graham, J. P.; Wojcicki, A.; Bursten, B. E. *Organometallics* **1999**, *18*, 837.

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(31) den Haan, K. H.; de Boer, J. L.; Teuben, J. H. *Organometallics* **1986**, *5*, 1726.

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(33) (a) Evans, W. J.; Meadows, J. M.; Kosta, A. G.; Gloss, G. L. *Organometallics* **1985**, *4*, 324. (b) Fischer, R. D. *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; T. J. Marks, I. L. Fragala, Eds.; D. Reidel: Dordrecht, 1985; p 277. (c) Evans, W. J.; Hozbor, M. A. *J. Organomet. Chem.* **1987**, *326*, 299.

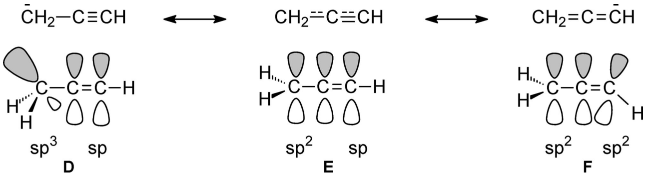
(34) Infrared absorptions at 1850−1900 cm^{-1} are assigned to allenyl structures and those >2000 cm^{-1} to propargyl structures in organolithium chemistry; see:(a) Jaffe, F. *J. Organomet. Chem.* **1970**, *23*, 53–62. (b) Priester, W.; West, R.; Chwang, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 8413. (c) West, R.; Jones, P. C. *J. Am. Chem. Soc.* **1969**, *91*, 6156. (d) Klein, J.; Becker, J. Y. *J. Chem. Soc., Chem. Commun.* **1973**, 576. For examples of organozinc and -magnesium compounds, see: (e) ref 1b. For examples of organotitanium compounds, see: (f) Ishiguro, M.; Ikeda, N.; Yamamoto, H. *J. Org. Chem.* **1982**, *47*, 2225. (g) Furuta, K.; Ishiguro, M.; Haruta, R.; Ikeda, N.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2768.

Table 2. NMR Data for Selected $Cp^*_2LnCH_2CCR$ Complexes[a]

entry	$Cp^*_2LnCH_2CCR$	CH_2	C-1 ($^1J_{CH}$, $^1J_{YC}$)	C-2	C-3 ($^1J_{YC}$)
1	$Cp^*_2YCH_2CCMe$ (**4a-Y**)	2.16	42.0 (154, 8.1)	137.3	94.9 (8.0)
2	$Cp^*_2YCH_2CCPh$ (**4f-Y**)	2.82	49.3 (159.1, 5.2)	155.1	106.8 (11.9)
3	$Cp^*_2YCH_2CCPh \cdot C_5H_5N$ (**4f-Y**·py)	2.71	47.2 (157.2, 7.7)	151.6	104.9
4	$Cp^*_2LaCH_2CCMe$ (**4a-La**)	2.30	50.9 (155)	139.7	102.5
5	$Cp^*_2LaCH_2CCPh$ (**4f-La**)	2.82	54.0 (158.3)	152.2	112.8
6	$Cp^*_2LaCH_2CCPh \cdot C_4H_8O$ (**4f-La**·THF)	2.95	52.6 (n.d.)	n.o.	n.o.
7	$Cp^*_2LaCH_2CCPh \cdot C_5H_5N$ (**4f-La**·py)	3.16	51.1 (159.5)	152.2	n.o.
8	$Cp^*_2LaCH_2CCC_6H_3Me_2$-2,6 (**4h-La**)	2.71	49.0 (156.9)	149.3	105.8
9	$Cp^*_2LaCH_2CCC_6H_3{}^iPr_2$-2,6 (**4i-La**)	2.68	47.7 (156.7)	145.6	100.3
10	$Cp^*_2LaCH_2CCC_6F_5$ (**4j-La**)	3.08	55.8 (162.5)	165.2	108.8

[a] NMR measurements in C_6D_6 at 25 °C under a nitrogen atmosphere. The chemical shifts are reported in ppm and the coupling constants in Hz. n.d. = not determined, n.o. = not observed.

Scheme 5. Hybridization of the Terminal Carbon Atoms in the Limiting Structures of the Prop-2-ynyl/Allenyl Anion



Cp'_2LnCH_2CCR complexes.[14] Comparison with reported data indicates that these values are intermediate of those typically observed for η^1-propargyl (2100−2215 cm^{-1}) and η^1-allenyl metal complexes (1800−1920 cm^{-1}).[34]

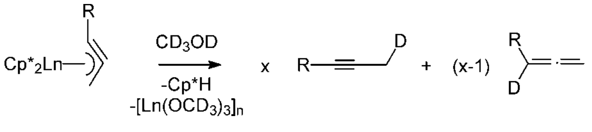
A shift of the C≡C stretch from 1944 cm^{-1} to 1973 cm^{-1} is observed upon coordination of pyridine to the metal center in **4f-La**, indicating an increase in the propargylic bonding character of the η^3-CH_2CCPh ligand. A larger shift from 1923 cm^{-1} to 2148 cm^{-1} points to an even higher degree of propargylic character of the η^3-CH_2CCPh ligand in **4f-Y** upon coordination of pyridine.

(c) Substituent Effects. The ^1H NMR data of the propargyl derivatives $Cp^*_2LnCH_2CCR$ reveal that the propargylic CH_2 resonances move upfield with increasing *ortho*-substitution in the $Cp^*_2LaCH_2CCC_6H_3R_2$-2,6 (R = H **4f-La**, Me **4h-La**, ^{i}Pr **4i-La**) series, while substitution of the phenyl group by a pentafluorophenyl group has the opposite effect (Table 2). The ^{13}C NMR data of the η^3-CH_2CCR ligand of the $Cp^*_2LaCH_2CCR$ complexes show a similar trend. The CH_2 and CH_2CC resonances shift upfield, while the CH_2CC resonances shift downfield upon increasing the steric bulk at the *ortho*-positions of the phenyl group. A reverse change is observed (i.e., the CH_2 and CH_2CC resonances shift downfield and the CH_2CC resonance shifts upfield), when the phenyl group in $Cp^*_2LaCH_2CCPh$ is replaced by a pentafluorophenyl group.

The first-order carbon−hydrogen couplings ($^1J_{CH}$ in Hz) of the propargylic carbon in the $Cp^*_2LaCH_2CCR$ series decrease in the following order: C_6F_5 (163) > C_6H_5 (158) > $C_6H_3Me_2$-2,6 (157) > $C_6H_3{}^iPr_2$-2,6 (157).[14] Under the assumption that the polar effects of the metal center are constant in the series $Cp^*_2LaCH_2CCR$, this decrease in $^1J_{CH}$ arguably reflects a change in hybridization, pointing to a change from a sp^2-type carbon in **E** and **F** to a more sp^3-type carbon in **D** (Scheme 5).[35]

On the basis of the $^1J_{CH}$ value of the methyl group, the relative σ-electron-withdrawing ability of the substituent R on the alkynes CH_3CCR was found to increase in the following order: **3h** ($C_6H_3Me_2$-2,6, 131.0) ≈ **3i** ($C_6H_3{}^iPr_2$-2,6, 131.0) < **3f** (Ph, 131.4) < **3j** (C_6F_5, 133.0).[14,36] In this light, structurally diagnostic spectroscopic parameters of the $Cp^*_2LaCH_2CCR$ complexes, such as (1) the proton chemical shift of the CH_2 group, (2) the carbon chemical shifts of the η^3-CH_2CCR ligand, and (3) the first-order carbon−hydrogen coupling constant of the CH_2 group, correlate well with the σ-electron-withdrawing ability of the ligand, revealing that the bonding character of the η^3-CH_2CCR ligand in $Cp^*_2LaCH_2CCR$ complexes is mainly influenced by the electronic effects of the alkyne substituent R.[37] The (steric) effect of the di-*ortho*-isopropyl groups in **3i** as compared to the di-*ortho*-methyl groups in **3h** is relatively small on the above structurally diagnostic spectroscopic parameters.

Scheme 6. Reaction of $Cp^*_2Ln(\eta^3$-$CH_2CCR)$ with Methanol-d_4 to Produce Acetylenic and Allenylic Protonolysis Products



Reactions with Brønsted Acids. (a) Methanol. When the $Cp^*_2LnCH_2CCR$ complexes were allowed to react with methanol-d_4, rapid reactions occurred, as indicated by instantaneous color changes to light yellow. The organic reaction products were identified as the acetylenic ($RCCCH_2D$) and allenylic ($RCD=C=CH_2$) deuterolysis products of the η^3-CH_2CCR ligand (Scheme 6). Analogous reactions with methanol were conducted, and the ratios of acetylenic and allenylic products were determined by *in situ* ^1H NMR spectroscopy (using appropriate long pulse delays to avoid signal saturation under the present anaerobic conditions). The results reveal that the influence of metal size (entries 1and 2, Table 3) and the electronic substituent effect of the alkyne substituent (entries 2 and 6) is small on the relative amount of acetylenic quenching product. More pronounced effects are observed for the steric effect of the alkyne substituent (entries 2 and 5).

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(36) The validity of the linear relationship between the rate of proton transfer from a carbon acid and the first-order carbon−hydrogen coupling constant of the corresponding carbon ($^1J_{CH}$) has been demonstrated by many studies. For reviews on carbon acids, see: (a) Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic Press: New York, 1965. (b) Jones, J. R. *The Ionisation of Carbon Acids*; Academic Press: London, 1973. (c) Reutov, O. A.; Beletskaya, I. P.; Butin, K. P. *CH-Acids*; Pergamon Press: Oxford, 1978. (d) Stewart, R. *The Proton: Applications to Organic Chemistry*; Academic Press: New York, 1985. (e) For examples, see: Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1963**, *85*, 2022. (f) Closs, G. L.; Larrabee, R. B. *Tetrahedron Lett.* **1965**, 287. (g) Streitweiser, A., Jr.; Caldwell, R. A.; Young, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 529. (h) Maksić, Z. B.; Eckert-Maksić, M. *Tetrahedron* **1969**, *25*, 5113. (i) Maksić, Z. B.; Randić, M. *J. Am. Chem. Soc.* **1973**, *95*, 6522. (j) Luh, T.-Y.; Stock, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 3712.

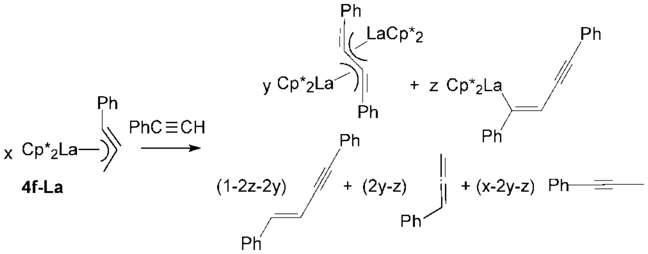
(37) Electronic substituent effects in propargyl−allenyl equilibria are not without precedent; see: Miao, W.; Chung, L. W.; Wu, Y.-D.; Chan, T. H. *J. Am. Chem. Soc.* **2004**, *126*, 13326.

Table 3. Alkyne/Allene Ratios for the Reaction of $Cp^*_2LnCH_2CCR$ (4) with Methanol (MeOH), 2,6-Di-*tert*-butyl-4-methylphenol (ArOH), and Phenylacetylene (PhCCH)[a]

entry	compound	alkyne:allene (MeOH)	alkyne:allene (ArOH)	alkyne:allene (PhCCH)
1	$Cp^*_2YCH_2CCPh$ (**4f-Y**)	1.0:1.0	0.8:1.0	n.d.
2	$Cp^*_2LaCH_2CCPh$ (**4f-La**)	1.1:1.0	1.0:1.0	0.2:1.0
3	$Cp^*_2CeCH_2CCPh$ (**4f-Ce**)	n.d.	1.0:1.0	n.d.
4	$Cp^*_2LaCH_2CCC_6H_3Me_2$-2,6 (**4h-La**)	1.1:1.0	n.d.	n.d.
5	$Cp^*_2LaCH_2CCC_6H_3{}^iPr_2$-2,6 (**4i-La**)	0.6:1.0	n.d.	n.d.
6	$Cp^*_2LaCH_2CCC_6F_5$ (**4j-La**)	1.2:1.0	n.d.	n.d.

[a] Reactions conducted in benzene-d_6 at room temperature. The ratios were determined by *in situ* ^1H NMR spectroscopy. n.d. = not determined.

Scheme 7. Reaction of $Cp^*_2La(\eta^3-CH_2CCPh)$ (4f-La) with Phenylacetylene to Produce Acetylenic and Allenylic Protonolysis Products alongside Products from Catalytic Dimerization of Phenylacetylene



(b) 2,6-Di-*tert*-butyl-4-methylphenol. To study the effect of a sterically more hindered alcohol than methanol, analogous reactions with 2,6-di-*tert*-butyl-4-methylphenol (HOAr) were performed. These reactions were also rapid, forming the corresponding Cp^*_2LnOAr (**10**) compounds quantitatively. The results reveal that the effect of a sterically more hindered alcohol is small on the regioselectivity of the protonolysis reaction (entries 1 and 2, Table 3).

(c) Phenylacetylene. When a stoichiometric amount of phenylacetylene was added to a benzene-d_6 solution of **4f-La** at room temperature, the orange solution turned immediately dark red. Only 57% of **4f-La** was consumed upon complete conversion of phenylacetylene, as determined by *in situ* ^1H NMR spectroscopy. NMR and GC-MS analysis revealed products previously observed in the lanthanocene-catalyzed oligomerization reaction of phenylacetylene (Scheme 7),[38] while the protonated η^3-propargyl/allenyl ligand was converted into phenylallene and 1-phenyl-1-propyne in a 1.00:0.20 ratio, respectively. When **4f-La** was allowed to react with a 2- and 10-fold molar excess of phenylacetylene, the complete consumption of phenylacetylene was accompanied by a mere 80% and 88% conversion of **4f-La**, respectively. It seems therefore that protonolysis of **4f-La** by phenylacetylene is slow relative to oligomerization of phenylacetylene catalyzed by monomeric $Cp^*_2LaCCPh$.

(d) Mechanism. The formation of allenylic and acetylenic quenching products in the reaction of Cp'_2LnCH_2CCR complexes with Brønsted acids may be rationalized by initial Lewis base coordination (Scheme 8). Nucleophilic attack at the metal center may take place at the substituted side or at the unsubstituted side of the η^3-propargyl/allenyl ligand.[39] The formation of the Lewis base adducts is plausibly followed by the electrophilic attack of the hydroxyl proton on the most polarized carbon of the η^3-propargyl/allenyl ligand. As a result, the η^1-allenyl-like Lewis base adduct **G**, formed from nucleophilic base attack at the unsubstituted side of the η^3-propargyl/allenyl ligand, will give rise to the allenylic quenching product upon protonolysis, and the η^1-propargyl-like Lewis base adduct **H**, formed from nucleophilic base attack at the substituted side of the η^3-propargyl/allenyl ligand, will give rise to the acetylenic quenching product.

The solid-state structure of $Cp^*_2LaCH_2CCPh \cdot C_5H_4N$ (**4f-La·py**) showed that pyridine is coordinated to the metal center at the more substituted side of the η^3-propargyl/allenyl ligand (*vide supra*). Although this finding suggests that the coordination of Lewis bases is controlled by electronic factors rather than steric factors, more experiments are needed to determine whether the regioselectivity of the protonolysis reaction of the Cp'_2LnCH_2CCR complexes is under electronic or steric control. It should be noted that the catalytic cyclodimerization of 1-methylalk-2-ynes is presently believed to involve alkyne insertion into the propargylic $Ln-CH_2$ bond and the allenylic La−CH(R) bond of Cp'_2LnCH_2CCR complexes.[40] As alkyne insertion reasonably proceeds via initial Lewis base coordination,[41] the side of Lewis base coordination at the metal center may also control the regioselectivity of the reaction of **4f-La** with 1-methylalk-2-ynes.

Conclusions

Novel rare-earth metallocene η^3-propargyl/allenyl derivatives have been prepared via the reactions of the alkyl derivatives $Cp^*_2LnCH(SiMe_3)_2$ or hydride derivatives$[Cp^*_2Ln(\mu\text{-}H)]_2$ with the corresponding 1-methylalk-2-ynes CH_3CCR. Spectral and structural analysis provided evidence for a static η^3-bonding description of the propargylic/allenylic ligand in $Cp^*_2LnCH_2CCR$. NMR spectroscopy revealed that changes toward a more propargylic or a more allenylic character of the η^3-CH_2CCR ligand in $Cp^*_2LaCH_2CCR$ complexes are brought about mainly by the electronic effects of the alkyne substituent R. Despite the η^3-bonding of the propargyl/allenyl ligands, the compounds can still accommodate an additional Lewis base ligand. Reactions of the $Cp^*_2LnCH_2CCR$ complexes with Brønsted acids produce both acetylenic ($CH_3C{\equiv}CR$) and

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[39] Coordination of Lewis bases along the line perpendicular to the Cp(centroid)−Ln−Cp(centroid) plane allows for a good overlap between the lowest unoccupied molecular orbital (LUMO), approximately of a z^2 type, and the lone pair of the Lewis base, as demonstrated by MO analyses of d^0 metallocenes and $Cp_2Y(\eta^3-CH_2CCPh)$.[14] For examples, see:(a) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (b) Steigerwald, M. L.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 308. (c) Ortiz, J. V.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 2095. (d) Rabaâ, H.; Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 4327. (e) Rappé, A. K. *J. Am. Chem. Soc.* **1987**, *109*, 5605.

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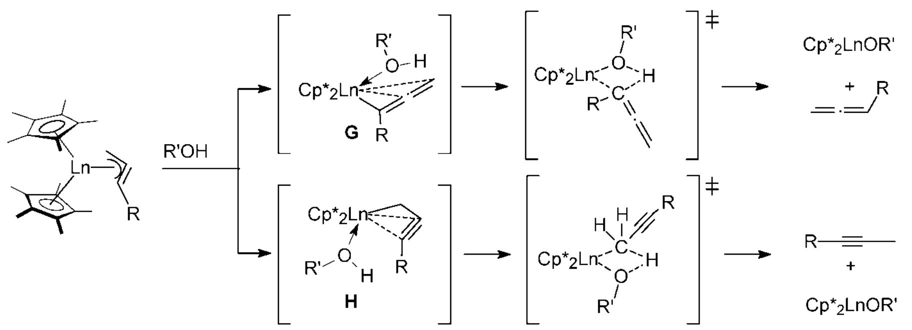
Scheme 8. Proposed Mechanism for the Reactions of the Cp*$_2$Ln(η^3-CH$_2$CCR) Complexes with Alcohol R′OH



allenylic (CH$_2$=C=CHR) protonolysis products. Rare-earth metallocene η^3-propargyl/allenyl species are likely to be involved in the catalytic cyclodimerization of 1-methylalk-1-ynes. The catalytic cyclodimerization of methylarylalkynes by these compounds will be reported separately.

Experimental Section

General Considerations. All reactions and manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk, vacuum line, and glovebox techniques. Deuterated solvents were dried over Na/K alloy prior to use. Other solvents were dried by percolation over columns of aluminum oxide, BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (4 Å) (pentane) or by distillation from Na/K alloy (THF, cyclohexane). The compounds Cp*$_2$LnCH(SiMe$_3$)$_2$ (Ln = Y,[42] Ce,[43] La[44]), [Cp*$_2$Ln(μ-H)]$_2$ (Ln = Ce,[40] La[41]), Me$_2$Si(Cp″H)$_2$,[45] LiCH(SiMe$_3$)$_2$,[46] 2-(prop-1-ynyl)toluene,[47] 2,6-dimethyliodobenzene,[48] 1-(2,6-dimethylphenyl)-1-propyne,[44] *n*-butyl nitrite,[49] copper bronze,[50] and propynyl copper(I)[51] were prepared according to literature procedures. Reagents were purchased from Aldrich and Acros Organics and were used as received unless stated otherwise. Hydrogen (Hoek-Loos, 99.995%) was dried by passing the gas over a column filled with LiAlH$_4$. Diphenylethyne (Aldrich) was purified by sublimation before use. Dimethyl sulfoxide was dried at least three times on freshly activated 4 Å molecular sieves.[52]

Physical and Analytical Measurements. NMR spectra were recorded on a Varian VXR-300 (FT, 300 MHz, ^{1}H; 75 MHz, ^{13}C), a Varian XL-400 (FT, 400 MHz, ^{1}H; 100 MHz, ^{13}C), or a Varian Inova 500 (FT, 500 MHz, ^{1}H; 125.7 MHz, ^{13}C) spectrometer. NMR experiments on air-sensitive samples were conducted in flame-sealable tubes or tubes equipped with a Teflon valve (Young). The ^{1}H NMR spectra were referenced to resonances of residual protons in deuterated solvents and reported in ppm relative to tetramethylsilane (δ 0.00 ppm). The coupling constants *J* and the line width (lw) of the resonances at half-maximum are given in Hz. The ^{13}C NMR spectra were referenced to carbon resonances of deuterated solvents. ^{19}F NMR spectra were referenced internally to hexafluorobenzene in CDCl$_3$ (δ −163.0 ppm). IR spectra of pure compounds and KBr pellets or Nujol solutions of the samples were recorded on a Mattson 4020 Galaxy FT-IR or a Pye-Unicam SP3-300 spectrophotometer. The elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim an der Ruhr, or the Microanalytical Department of the University of Groningen. All found percentages are the average of at least two independent determinations. GC analyses were performed on a HP 6890 instrument with a HP-1 dimethylpolysiloxane column (19095 Z-123). GC-MS spectra were recorded at 70 eV using a HP 5973 mass-selective detector attached to a HP 6890 GC as described above. Vacuum sublimations were carried out by using a homemade sublimation apparatus. Molecular weights were determined by cryoscopy in benzene.

Preparation of [Me$_2$Si(η^5-C$_5$Me$_4$)$_2$Ce(μ-Cl)]$_2$. A suspension of 2.76 g (11.2 mmol) of CeCl$_3$ and 3.83 g (12 mmol) of Me$_2$Si(η^5-C$_5$Me$_4$)$_2$Li$_2$ in THF (200 mL) was heated under reflux for 5 days. The resulting orange suspension was evaporated to dryness and sublimed under vacuum (0.01 mmHg) at 225 °C. This afforded 0.84 g (0.9 mmol, 16%) of [Me$_2$Si(η^5-C$_5$Me$_4$)$_2$Ce(μ-Cl)]$_2$ as pink crystals.

IR (Nujol, [cm^{-1}]): 2700 (w), 2120 (w), 1310 (m), 1250 (m), 1140 (m), 1120 (m), 1010 (m), 840 (s), 800 (s), 770 (m), 750 (m), 680 (s), 450 (s). Anal. Calcd for C$_{20}$H$_{30}$CeClSi: C, 50.65; H, 6.38. Found: C, 50.20; H, 6.52. [Me$_2$Si(η^5-C$_5$Me$_4$)$_2$Ce(μ-Cl)]$_2$ is insufficiently soluble for NMR and cryoscopy.

Preparation of Me$_2$Si(η^5-C$_5$Me$_4$)$_2$CeCH(SiMe$_3$)$_2$ (5-Ce). A 381 mg (0.40 mmol) amount of [Me$_2$Si(η^5-C$_5$Me$_4$)$_2$Ce(μ-Cl)]$_2$ and 128 mg (0.77 mmol) of LiCH(SiMe$_3$)$_2$ were suspended in toluene (20 mL). After stirring for 24 h at room temperature, a red-purple solution containing a white precipitate had formed. The solvent was removed *in vacuo*, and the residue was extracted with pentane (30 mL). Concentration and cooling to −80 °C gave 261 mg (0.44 mmol) of **5-Ce** as purple crystals. A second workup gave another 31 mg. Total yield: 292 mg (0.49 mmol, 61%).

^{1}H NMR (300 MHz, C$_6$D$_6$, 21 °C): δ 10.76 (s, C*H*$_3$, 6 H, lw = 12 Hz), 3.96 (s, C*H*$_3$, 6 H, lw = 20 Hz), −3.09 (m, C*H*$_3$, 6 H, lw = 31 Hz), −4.92 (s, C*H*$_3$, 6 H, lw = 14 Hz), −8.57 (s, SiC*H*$_3$, 18 H, lw = 37 Hz), −13.97 (s, C*H*$_3$, 6 H, lw = 22 Hz). The resonance due to CeC*H* was not observed. IR (Nujol, [cm^{-1}]): 2710 (w), 2130 (w), 1310 (m), 1250 (m), 1240 (m), 1120 (m), 1060 (m), 1020 (sh), 840 (s), 820 (s), 810 (sh), 770 (m), 750 (m), 680 (m), 570 (m), 460 (m). Anal. Calcd for C$_{27}$H$_{49}$CeSi$_3$: C, 54.22; H, 8.26; Ce, 23.43. Found: C, 54.49; H, 8.35; Ce, 23.82.

Preparation of 2,6-Diisopropyliodobenzene. A 500 mL, three-neck, round-bottomed flask, equipped with a gas-inlet adaptor, drop funnel, and a Teflon-coated stir bar, was charged with 2 g of freshly

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prepared copper bronze and placed in a nitrogen atmosphere. A 16.52 g (99.5 mmol) sample of KI, 8.30 g (32.7 mmol) of iodine, and 50 mL of dry DMSO were added, and the resulting mixture was stirred and heated to 60 °C. After addition of 20 g of freshly prepared *n*-butylnitrite a solution of 12.1 g (68.2 mmol) of 2,6-diisopropylaniline in 30 mL of DMSO was added dropwise. The reaction mixture was stirred for 2 h at 60 °C. The reaction was stopped by adding aqueous solutions of sodium chloride and sodium bisulfite. Filtration, separation, drying over $MgSO_4$, and rotatory evaporation gave a yellow oil, which was purified with column chromatography (silica, hexanes). Yield: 15.2 g (78%) of a light yellow, viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.20 (m, C*H*, 1 H), 7.04 (m, C*H*, 2 H), 3.37 (septet, $^3J_{HH} = 6.8$ Hz, 2 H), 1.20 (d, $^3J_{HH} = 6.8$ Hz, 6 H). ^{13}C NMR (125.7 MHz, $CDCl_3$, 25 °C): δ 23.37 (q, $^1J_{CH} = 126.8$ Hz, *C*H_3), 39.41 (d, $^1J_{CH} = 128.2$ Hz, *C*H), 109.14 (m, *C*I), 123.79 (d, $^1J_{CH} = 156.4$ Hz, *C*H), 128.30 (d, $^1J_{CH} = 160.2$ Hz, *C*H), 151.12 (m, *C*). IR (neat, [cm^{-1}]): 2950 (m), 2915 (m), 2850 (m), 2230 (w), 1907 (w), 1665 (w), 1490 (m), 1463 (m), 1365 (m), 1105 (w), 1020 (m), 910 (m), 872 (m), 835 (s), 790 (m), 728 (s). GC-MS, *m*/*z* (relative intensity): 290 (1), 289 (9), 288 (M$^+$, 70), 274 (13), 273 (M$^+$ − CH_3, 100), 146 (10), 145 (8), 133 (9), 131 (33), 128 (14), 117 (21), 115 (23), 105 (10), 91 (28). Anal. Calcd for $C_{12}H_{17}I$ (288.17): C, 50.02; H, 5.95. Found: C, 50.15; H, 6.07.

Preparation of 1-(2,6-Diisopropylphenyl)-1-propyne (3i). A 8.6 g (84 mmol) amount of freshly prepared propynyl copper(I) was brought in a 400 mL Schlenk flask, equipped with a Teflon-coated stir bar, and evacuated. After addition of 240 mL of dry pyridine and 3.0 g (10 mmol) of 2,6-diisopropyliodobenzene the reaction mixture was heated at reflux at 120 °C for 10 days. The mixture was quenched with water. Addition of petroleum ether (40−60), filtration, extraction of the organic layer with petroleum ether (40−60), drying over $MgSO_4$, and rotatory evaporation afforded a yellow oil, which was purified by means of column chromatography (neutral alumina) with petroleum ether. Yield: 1.58 g (76%) of a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 1.24 (d, $^3J_{HH} = 6.9$ Hz, CH(C*H*$_3$)$_2$, 6 H), 2.13 (s, ArCC*H*$_3$, 3 H), 3.52 (septet, $^3J_{HH} = 6.9$ Hz, C*H*Me$_2$, 2 H), 7.18 (d, $^3J_{HH} = 7.8$ Hz, *m*-C*H*, 2 H), 7.30 (t, $^3J_{HH} = 7.8$ Hz, *p*-C*H*, 1 H). ^{13}C NMR (125.7 MHz, $CDCl_3$, 25 °C): δ 4.55 (q, $^1J_{CH} = 131.4$ Hz, CC*C*H$_3$), 23.61 (qdq, $^1J_{CH} = 125.8$ Hz, $^2J_{CH} = 5.1$ Hz, $^3J_{CH} = 5.1$ Hz, *C*H$_3$), 31.92 (dsept, $^1J_{CH} = 128.7$ Hz, $^2J_{CH} = 4.0$ Hz, *C*HMe$_2$), 76.73 (q, $^2J_{CH} = 4.6$ Hz, CH$_3$*C*), 93.76 (q, $^3J_{CH} = 10.7$ Hz, Ar*C*), 121.64 (m, *i*-C), 122.32 (ddd,, $^1J_{CH} = 158.5$ Hz, $^2J_{CH} = 4.8$ Hz, $^3J_{CH} = 7.9$ Hz, *m*-*C*H), 127.55 (d, $^1J_{CH} = 159.9$ Hz, *p*-CH), 150.52 (m, *o*-*C*). IR (neat, [cm^{-1}]): 2962 (s), 2870 (m), 2243 (w), 1575 (w), 1463 (m), 1362 (m), 1253 (w), 1179 (w), 1107 (w), 1060 (w), 935 (w), 801 (m), 754 (m), 483 (s). GC-MS, *m*/*z* (relative intensity): 201 (8), 200 (M$^+$, 51), 185 (M$^+$ − CH_3, 33), 158 (12), 157 (67), 156 (11), 155 (15), 154 (9), 153 (19), 152 (16), 151 (4), 144 (14), 143 (100), 141 (37), 129 (38), 128 (70), 115 (36), 91 (9). HR-MS: $C_{15}H_{20}$, calc. 200.15650, found 200.15734.

Reactions of Cp*$_2$LnCH(SiMe$_3$)$_2$ (Ln = Y, Ce, La) and Me$_2$Si(η^5-C$_5$Me$_4$)$_2$CeCH(SiMe$_3$)$_2$ with Excess MeCCR (R = Me, Et, Pr, Ph, SiMe$_3$, and ^{t}Bu). NMR tubes were loaded with solutions of ~0.05 mmol of Cp*$_2$LnCH(SiMe$_3$)$_2$ and Me$_2$Si(η^5-C$_5$Me$_4$)$_2$-CeCH(SiMe$_3$)$_2$ in 0.5 mL of benzene-*d*$_6$. Excess MeCCR (~0.9 mmol) was added, and the tubes were flame-sealed and kept in an oven at 80 °C. The reactions were monitored by ^{1}H NMR spectroscopy.

Reactions of [Cp*$_2$Ln(μ-H)]$_2$ (Ln = Y, Ce, La) with Excess MeCCR (R = Me, Et, Pr, Ph, SiMe$_3$, and ^{t}Bu). NMR tubes were loaded with solutions of ~0.03 mmol of [Cp*$_2$Ln(μ-H)]$_2$ in 0.5 mL of benzene-*d*$_6$. Excess MeCCR (~0.15 mmol) was added, and the tubes were flame-sealed and kept at room temperature. The reactions were monitored by ^{1}H NMR spectroscopy.

Preparation of Cp*$_2$YCH$_2$CCMe (4a-Y). A solution of 694 mg (1.34 mmol) of Cp*$_2$YCH(SiMe$_3$)$_2$ in pentane (35 mL) was stirred under H$_2$ (1 atm) for 3 h at room temperature, during which a white precipitate of [Cp*$_2$Y(μ-H)]$_2$ was formed. The hydrogen atmosphere was replaced by nitrogen, and 2-butyne (0.85 mL, 11 mmol) was added at 0 °C. The reaction mixture was stirred for 15 min, during which hydrogen evolved and a clear yellow solution was formed. Concentration and cooling to −80 °C gave 107 mg (0.26 mg) of **4a-Y** as pale yellow crystals. A second crop gave another 45 mg (0.11 mmol). Total yield: 152 mg (0.37 mmol, 28%). Complex **4a-Y** is extremely soluble, and this hampers purification and isolation considerably.

IR (cm^{-1}): 2720 (w), 1975 (m), 1930 (w), 1230 (w), 1020 (m), 710 (m), 600 (w). ^{1}H NMR (300 MHz, C$_6$D$_6$, 21 °C): δ 1.54 (t, $^5J_{HH} = 2.6$ Hz, 3 H, C*H*$_3$), 1.92 (s, 30 H, Cp*), 2.16 (t, $^5J_{HH} = 2.6$ Hz, $^2J_{YH} = 0.6$ Hz, 2 H, C*H*$_2$). ^{13}C NMR (75 MHz, C$_6$D$_6$, 21 °C): δ 8.4 (q, $^1J_{CH} = 130$ Hz, *C*H$_3$), 11.0 (q, $^1J_{CH} = 125$ Hz, C$_5$(*C*H$_3$)$_5$), 42.33 (dt, $^1J_{CH} = 154$ Hz, $^1J_{YC} = 8.1$ Hz, *C*H$_2$C≡C), 94.9 (d, $^1J_{YC} = 8.0$ Hz, CH$_2$C≡*C*), 116.9 (s, *C*$_5$Me$_5$), 137.3 (s, *C*≡CCH$_3$). Anal. Calcd for $C_{24}H_{35}Y$ (412.45): C, 69.89; H, 8.55. Found: C, 69.54; H, 8.41; MW, 433 ± 34.

Preparation of Cp*$_2$CeCH$_2$CCMe (4a-Ce). 2-Butyne (1.7 mL, 23 mmol) was added to a solution of 1.02 g (1.79 mmol) of Cp*$_2$CeCH(SiMe$_3$)$_2$ in benzene (25 mL). After stirring for 16 h at room temperature, a green solution had formed. Concentration and crystallization at 10 °C gave 51 mg (0.11 mmol, 6%) of **4a-Ce** as sticky green crystals. Complex **4a-Ce** is extremely soluble, and this hampers purification and isolation considerably. IR (cm^{-1}): 2140 (m), 1965 (m), 1260 (m), 1080 (m), 1010 (s), 800 (m), 670 (w), 620 (w), 570 (s). ^{1}H NMR (300 MHz, C$_6$D$_6$, 21 °C): δ 2.5 (s, Cp*, 30 H, lw = 14 Hz), −9.6 (s, C*H*$_3$, 3 H, lw = 3 Hz), −30.5 (s, 2 H, C*H*$_2$, lw = 80 Hz). Anal. Calcd for $C_{24}H_{35}Ce$ (463.66): C, 62.17; H, 7.61. Found: C, 61.68; H, 7.28.

Preparation of Cp*$_2$CeCH(Me)C(Et) (9b-Ce). 3-Hexyne (1 mL, 8.8 mmol) was added to a suspension of 369 mg (0.45 mmol) of [Cp*$_2$Ce(μ-H)]$_2$ in pentane (5 mL). The mixture was stirred for 60 h at room temperature, during which a green solution and a small amount of a green solid were formed. Filtration, concentration (to ~3 mL), and cooling to −80 °C gave 203 mg (0.41 mmol, 46%) of **9b-Ce** as green crystals. IR (cm^{-1}): 2720 (w), 2130 (w), 1890 (s), 1570 (w), 1380 (m), 1310 (w), 1060 (w), 1020 (m), 910 (w), 800 (w), 720 (m), 590 (w), 520 (w), 460 (w). ^{1}H NMR (300 MHz, C$_6$D$_6$, 21 °C): δ 3.16 (s, Cp*, 15 H, lw = 11 Hz), 2.54 (s, Cp*, 15 H, lw = 11 Hz), −2.73 (s, 3 H, C*H*$_3$, lw = 13 Hz), −4.29 (s, 1 H, C*H*$_2$, lw = 31 Hz), −6.32 (s, 1 H, C*H*$_2$, lw = 32 Hz), −11.2 (s, 1 H, C*H*, lw = 43 Hz), −13.2 (s, 3 H, C*H*$_3$, lw = 9 Hz). ^{13}C NMR (75 MHz, C$_6$D$_6$, 21 °C): δ −13.3 (t, $^1J_{CH} = 134$ Hz, *C*H$_2$), 7.8 (q, $^1J_{CH} = 125$ Hz, C$_5$(*C*H$_3$)$_5$), 11.0 (q, $^1J_{CH} = 125$ Hz, C$_5$(*C*H$_3$)$_5$), 27.9 (q, $^1J_{CH} = 126$ Hz, *C*H$_3$), 132.8 (d, $^1J_{CH} = 153$ Hz, *C*H), 146.5 (s, C′), 201.3 (s, *C*$_5$(CH$_3$)$_5$), 216.6 (s, *C*$_5$(CH$_3$)$_5$), 390.0 (s, C′), 480.1 (q, $^1J_{CH} = 123$ Hz, *C*H$_3$). Anal. Calcd for $C_{26}H_{39}Ce$ (491.71): C, 63.51; H, 8.00; Ce, 28.50; MW, 491.69. Found: C, 63.38; H, 7.94; Ce, 28.36; MW, 491 ± 32 (cryoscopy in benzene).

Preparation of [Me$_2$Si(η^5-C$_5$Me$_4$)$_2$CeCH$_2$CCMe]$_n$ (6a-Ce). 2-Butyne (0.5 mL, 6.4 mmol) was added to a solution of Me$_2$Si(η^5-C$_5$Me$_4$)$_2$CeCH(SiMe$_3$)$_2$ (118 mg, 0.20 mmol) in benzene (10 mL). The solution was stirred at room temperature for 24 h, during which orange crystals deposited. Isolation gave 65 mg (0.13 mmol, 65%) of **6a-Ce** as orange crystals. IR and elemental analysis indicated the presence of lattice benzene (1/3 C$_6$H$_6$/Ce). IR (cm^{-1}): 2720 (w), 2000 (s), 1400 (w), 1310 (m), 1245 (m), 1230 (m), 1120 (w), 1000 (m), 830 (s), 815 (s), 770 (m), 750 (m), 670 (s), 590 (m), 520 (s), 460 (s). The compound is insufficiently soluble for NMR and cryoscopy. Anal. Calcd for $C_{26}H_{37}CeSi$ (517.78): C, 60.30; H, 7.20; Ce, 27.06. Found: C, 60.42; H, 7.08; Ce, 26.29.

Preparation of $Cp^*_2YCH_2CCPh$ (4f-Y). Hydrogen at a pressure of 1 bar was supplied to a solution of $Cp^*_2YCH(SiMe_3)_2$ (0.58 g, 1.12 mmol) in hexanes (5 mL). Stirring for 3 h at room temperature produced a light yellow suspension. The hydrogen atmosphere was replaced by nitrogen, and 1-phenyl-1-propyne (0.2 mL, 1.60 mmol) was added. Immediately, a red suspension formed. The suspension was stirred for 30 min at room temperature, during which it was degassed several times. The solid was separated by decantation and filtration. Subsequent *in vacuo* removal of the solvent yielded a red crystalline material (0.49 g, 92% yield). Crystals suitable for X-ray analysis were obtained by recrystallization in toluene at low temperature.

^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 1.93 (s, Cp*, 30 H), 2.82 (s, CH_2, 2 H), 6.98 (t, $^3J_{HH} = 7.5$ Hz, *p*-Ph, 1 H), 7.09 (t, $^3J_{HH} =$ 7.5 Hz, *m*-Ph, 2 H), 7.19 (d, $^3J_{HH} = 7.8$ Hz, *o*-Ph, 2 H). ^{13}C NMR (125.7 MHz, C_6D_6, 25 °C): δ 11.15 (q, $^1J_{CH} = 125.6$ Hz, $C_5(CH_3)_5$), 49.33 (dt, $^1J_{CH} = 159.1$ Hz, $^1J_{YC} = 5.2$ Hz, $CH_2C\equiv C$), 106.79 (d, $^1J_{YC} = 11.9$ Hz, $CH_2C\equiv C$), 117.78 (m, C_5Me_5), 126.69 (dt, $^1J_{CH}$ = 160.8, $^3J_{CH} = 7.7$ Hz, *p*-CH), 128.60 (dd, $^1J_{CH} = 159.4$ Hz,$^3J_{CH}$ = 7.6 Hz, *m*-CH), 132.40 (dtd, $^1J_{CH} = 159.1$ Hz, $^3J_{CH} = 7.1$ Hz, $^4J_{CH} = 1.4$ Hz, *o*-CH), 132.77 (tdd, $^2J_{CH} = 3.7$ Hz, $^3J_{CH} = 8.1$ Hz, $^4J_{CH} = 2.0$ Hz, *i*-C), 155.09 (t, $^2J_{CH} = 2.5$ Hz, $CH_2C\equiv C$). IR (Nujol, [cm^{-1}]): 2924 (m), 2856 (m), 2727 (m), 1923 (m), 1592 (m), 1544 (m), 1455 (m), 1378 (m), 1269 (m), 1154 (m), 1065 (m), 1021 (m), 916 (w), 846 (w), 768 (m), 698 (m), 627 (m), 482 (s). Anal. Calcd for $C_{29}H_{37}Y$ (474.52): C, 73.41; H, 7.86. Found: C, 73.24; H, 7.89.

Preparation of $Cp^*_2CeCH_2CCPh$ (4f-Ce). 1-Phenyl-1-propyne (0.5 mL 4.00 mmol) was added to a suspension of 374 mg (0.46 mmol) of $[Cp^*_2Ce(\mu\text{-}H)]_2$ in pentane (20 mL). After stirring for 3 h at room temperature, a grass-green solution was formed. Filtration, concentration, and cooling to −80 °C gave 268 mg (0.51 mmol, 56%) of **4f-Ce** as green crystals. IR (cm^{-1}): 3050 (w), 2710 (w), 2120 (w), 1930 (s), 1580 (m), 1550 (w), 1480 (m), 1150 (w), 1060 (w), 1020 (w), 900 (w), 760 (s), 740 (m), 710 (w), 690 (s), 600 (w), 510 (w), 450 (w). ^{1}H NMR (300 MHz, C_6D_6, 21 °C): δ 3.53 (t, $^3J_{HH} = 7.0$ Hz, 1 H, *p*-CH, lw = 3 Hz), 2.91 (s, Cp*, 30 H, lw = 28 Hz), 2.8 (s, 2 H, *m*-CH, lw = 10 Hz), −7.65 (s, 2 H, *o*-CH, lw = 20 Hz), −35.4 (s, 2 H, CH_2, lw = 78 Hz). Anal. Calcd for $C_{29}H_{37}Ce$ (525.73): C, 66.25; H, 7.09; Ce, 26.65; MW, 525.71. Found: C, 67.23; H, 7.07; Ce, 25.86; MW, 530 ± 31 (cryoscopy in benzene).

Preparation of $Cp^*_2LaCH_2CCPh$ (4f-La). Hydrogen at a pressure of 1 bar was supplied to a solution of $Cp^*_2LaCH(SiMe_3)_2$ (0.82 g, 1.42 mmol) in pentane (5 mL). Stirring for 2 h at room temperature produced a yellow suspension. The hydrogen atmosphere was replaced by nitrogen, and 1-phenyl-1-propyne (0.4 mL, 3.20 mmol) was added. Immediately, a deep red suspension formed. The suspension was stirred for 1 h at room temperature, during which it was degassed several times. The solid was separated by decantation and filtration. Subsequent *in vacuo* removal of the solvent yielded a red crystalline material (0.68 g, 91% yield). Crystals suitable for X-ray analysis were obtained by recrystallization in toluene at low temperature.

^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.92 (s, Cp*, 30H), 2.82 (s, CH_2, 2H), 6.99 (t, $^3J_{HH} = 7.3$ Hz, *p*-H, 1 H), 7.12 (dd, $^3J_{HH} =$ 7.2 Hz, $^3J_{HH} = 7.3$ Hz, *m*-H, 2 H), 7.24 (d, $^3J_{HH} = 7.2$ Hz, *o*-H, 2 H). ^{13}C NMR (125.7 MHz, C_6D_6, 25 °C): δ 10.61 (q, $^1J_{CH} = 124.5$ Hz, $C_5(CH_3)_5$), 54.02 (t, $^1J_{CH} = 158.3$ Hz, $CH_2C\equiv C$), 112.76 (m, $CH_2C\equiv C$), 119.46 (m, C_5Me_5), 126.19 (dt, $^1J_{CH} = 161.8$ Hz, $^3J_{CH}$ = 7.4 Hz, *p*-CH), 128.71 (dd,$^1J_{CH} = 153.0$ Hz, $^3J_{CH} = 8.0$, *m*-CH), 130.84 (dtd,$^1J_{CH} = 159.9$ Hz, $^3J_{CH} = 7.0$ Hz, $^2J_{CH} = 1.4$ Hz, *o*-CH), 132.39 (t,$^3J_{CH} = 7.1$ Hz, *i*-C), 152.19 (s, $CH_2C\equiv C$). IR (Nujol, [cm^{-1}]): 2920 (m), 2850 (m), 1944 (s), 1587 (m), 1550 (w), 1455 (s), 1380 (m), 1260 (w), 1090 (w), 1065 (w), 1020 (m), 900 (w), 760 (s), 690 (m), 600 (s), 450 (m). Anal. Calcd for $C_{29}H_{37}La$ (524.52): C, 66.41; H, 7.11. Found: C, 66.24; H, 7.00.

Preparation of $Cp^*_2LaCH_2CCC_6H_3Me_2$-2,6 (4h-La). Hydrogen (1 bar) was applied to a solution of $Cp^*_2LaCH(SiMe_3)_2$ (0.56 g, 0.98 mmol) in hexanes (5 mL). The yellow suspension was stirred for 2 h at room temperature. The hydrogen atmosphere was replaced by nitrogen, and 1-(2,6-dimethylphenyl)-1-propyne (0.21 g, 1.46 mmol) was added. The suspension was stirred overnight at room temperature and degassed several times. After overnight stirring, the suspension turned deep red. The reaction mixture was extracted with hexanes and evaporated to dryness, forming a deep red oil. Crystallization from hexanes at low temperature yielded a red crystalline material (0.12 g, 22% yield). Crystals suitable for X-ray analysis were obtained by recrystallization in toluene and cooling the solution.

^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.92 (s, Cp*, 30 H), 2.18 (s, CH_3, 6 H), 2.71 (s, CH_2, 2 H), 6.94 (s, CH, 3 H). ^{13}C NMR (125.7 MHz, C_6D_6, 25 °C): δ 11.10 (q, $^3J_{CH} = 124.8$ Hz, $C_5(CH_3)_5$), 22.36 (q, $^3J_{CH} = 125.5$ Hz, CH_3), 49.12 (t, $^1J_{CH} = 156.9$ Hz, $CH_2C\equiv C$), 105.81 (t, $^3J_{CH} = 7.0$ Hz, $CH_2C\equiv C$), 119.04 (m, C_5Me_5), 127.14 (d, $^1J_{CH} = 159.0$, *p*-CH), 128.31 (d, $^1J_{CH} = 156.9$, *m*-CH), 130.96 (m, *i*-CH), 140.74 (m, *o*-CH), 149.28 (t, $^2J_{CH} =$ 2.6 Hz, $CH_2C\equiv C$). IR (Nujol, [cm^{-1}]): 2925 (s), 2853 (s), 2725 (w), 1975 (m), 1786 (w), 1566 (w), 1465 (s), 1377 (m), 1260 (w), 1168 (w), 1093 (w), 1020 (m), 779 (m), 720 (m), 500 (s). Anal. Calcd for $C_{31}H_{41}La$ (552.57): C, 67.38; H, 7.48. Found: C, 67.29; H, 7.54.

Preparation of $Cp^*_2LaC(Ph){=}C(Ph)H$ (8ff-La). To a suspension of $[Cp^*_2La(\mu\text{-}H)]_2$ (35.0 mg, 42.6 μmol) in cyclohexane (5 mL) was added diphenylacetylene (15.2 mg, 85.3 μmol). The light yellow suspension turned into an orange solution immediately. Removal of the solvent *in vacuo* gave a yellow solid in quantitative yield. Isolated yield: 49.2 mg (98%).

^{1}H NMR (500 MHz, C_7D_{14}, 25 °C): δ 7.40 (s, **D**), 7.22 (t, **G**), 7.20 (t, **A**), 7.07 (m, **F**), 6.95 (m, **B**), 6.91 (d, **E**), 6.73 (m, **C**), 1.77 (s, Cp*, 30 H). ^{13}C NMR (125.7 MHz, C_7D_{14}, 25 °C): δ 10.51 (q, $^1J_{CH} = 125.4$ Hz, C_5Me_5), 120.60 (s, C_5Me_5), 122.97 (dt, $^1J_{CH} =$ 148.6 Hz, $^3J_{CH} = 7.1$ Hz, 3), 124.25 (d, overlap hampered determination of coupling constants, 2), 125.53 (ddd, $^1J_{CH} = 153.5$ Hz, $^3J_{CH} = 6.2$ Hz, $^3J_{CH} = 6.2$ Hz, 8), 126.18 (dt, $^1J_{CH} =$ 162.2 Hz, $^3J_{CH} = 7.3$ Hz, 9), 129.58 (dd, $^1J_{CH} = 156.1$ Hz, $^3J_{CH} =$ 7.9 Hz, 1), 130.83 (dd, $^1J_{CH} = 158.6$ Hz, $^3J_{CH} = 7.9$ Hz, 10), 133.72 (dt, $^1J_{CH} = 147.5$ Hz, $^3J_{CH} = 4.1$ Hz, 6), 146.25 (q, $^3J_{CH} = 6.6$, 7), 150.83 (q, $^3J_{CH} = 7.5$ Hz, 4), 217.47 (s, 5). ^{1}H−^{13}C gHSQC (500.0 MHz, 125.7 MHz, C_7D_{14}, 25 °C): $\mathbf{A}_1$, $\mathbf{B}_2$, $\mathbf{C}_{3,}$ $\mathbf{D}_6$, $\mathbf{E}_8$, $\mathbf{F}_8$, $\mathbf{G}_{10}$. ^{1}H−^{13}C gHMBC (500.1 MHz, 125.7 MHz, C_7D_{14}, 25 °C): $\mathbf{A}_{2-4}$, $\mathbf{B}_{1,3}$, $\mathbf{C}_{1-5,}$ $\mathbf{D}_{3-8}$, $\mathbf{E}_{6-9}$, $\mathbf{F}_{8,10}$, $\mathbf{G}_{7-9}$. Anal. Calcd for $C_{34}H_{41}La$ (588.61): C, 69.38; H, 7.02. Found: C, 69.51; H, 6.90.

Reactions of Cp'_2LnCH_2CCR with MeOH, CD_3OD, and ArOH. NMR Scale. Samples (0.04−0.08 mmol) of methanol, methanol-d_4, or 2,6-di-*tert*-butyl-4-methylphenol (ArOH) were added to equimolar amounts of Cp'_2LnCH_2CCR at room temperature in benzene-d_6 (0.5 mL). Reaction took place immediately, and Cp^*_2LnOAr compounds were formed quantitatively together with a mixture of allenylic and acetylenic quenching products (Table 3). These reaction products were identified by comparison with literature or authentic samples.

Preparation of Cp^*_2YOAr (10-Y). To a stirred pentane solution of $Cp^*_2YCH(SiMe_3)_2$ (302 mg, 0.58 mmol) was added 128 mg (0.58 mmol) of ArOH. The solution was stirred for 48 h at room temperature. A slightly orange solution had formed, which was concentrated to ~1 mL and subsequently cooled to −80 °C. Isolation gave 205 mg (0.35 mmol, 60%) of the title compound as white crystals. ^{1}H NMR (C_6D_6): δ 7.13 (s, 2H, m-C_6H_2), 2.37 (s, 3H, p-Me), 1.88 (s, 30H, C_5Me_5); 1.46 (s, 18H, t-Bu). ^{13}C NMR (C_6D_6): δ 160.5 (s, i-C_6H_2), 135.2 (s, o-C_6H_2), 125.8 (d, $J = 151$ Hz, m-C_6H_2), 123.5 (s, p-C_6H_2), 119.4 (s, C_5Me_5), 35.6 (s, t-Bu), 31.6 (q, J = 124 Hz, t-Bu), 21.6 (q, J = 124 Hz, p-Me), 11.6 (q, J = 125 Hz, C_5Me_5). Anal. Calcd for $C_{35}H_{53}YO$ (578.71): C, 72.64; H, 9.23; Y, 15.36. Found: C, 72.40; H, 9.16; Y, 15.57.

Preparation of Cp*$_2$CeOAr (10-Ce). Aryloxide **10-Ce** was prepared by a similar procedure to **10-Y** by using 1.809 g (3.2 mmoL) of Cp*$_2$CeCH(SiMe$_3$)$_2$ and 698 mg (3.2 mmol) of ArOH. Workup gave **10-Ce** as red crystals in 68% yield (1.36 g, 2.2 mmol). IR (cm^{-1}): 2730 (w), 2130 (w), 2120 (w), 1740 (w), 1600 (w), 1410 (s), 1370 (m), 1260 (s), 1240 (s), 1210 (m), 1110 (m), 1010 (m), 860(m), 820 (m), 800 (m), 520 (m). ^{1}H NMR (benzene-d_6): δ 8.39 (s, 2 H, lw = 2 Hz, m-C_6H_2), 3.31 (s, 3 H, lw = 2 Hz, p-Me), 2.71 (s, 30 H, lw = 5 Hz, C_5Me_5), −7.12 (s, 18 H, lw = 35 Hz, t-Bu). Anal. Calcd for $C_{35}H_{53}CeO$ (629.92): C, 66.73; H, 8.48; Ce, 22.25. Found: C, 66.81; H, 8.45; Ce, 22.29.

Preparation of Cp*$_2$LaOAr (10-La). To a stirred solution of Cp*$_2$LaCH(SiMe$_3$)$_2$ (219 mg, 0.38 mmol) in pentane (20 mL) was added 82 mg (0.37 mmol) of ArOH. The reaction mixture was stirred for 2 h at room temperature. Concentration to ca. 3 mL and cooling to −80 °C gave 101 mg (0.16 mmol, 43%) of **25** as white crystals. IR (cm^{-1}): 2720 (w), 1750 (w), 1590 (w), 1425 (s), 1360 (m), 1260 (s), 1230 (s), 1210 (m), 1120 (m), 1020 (w), 860 (m), 820 (m), 800 (m), 530 (m), 510 (w). ^{1}H NMR (benzene-d_6, 21 °C): δ 7.14 (s, 2 H, m-C_6H_2), 2.35 (s, 3 H, p-Me), 1.89 (s, 30 H, C_5Me_5), 1.44 (s, 18 H, t-Bu). ^{13}C NMR (benzene-d_6, 21 °C): δ 158.4 (s, i-C_6H_2), 135.5 (s, o-C_6H_2, 125.8 (d, J = 151 Hz, m-C_6H_2), 123.6 (s, p-C_6H_2), 120.9 (s, C_5Me_5), 35.1 (s, CMe_3), 32.0 (q, J = 125 Hz, CMe_3), 21.5 (q, J = 125 Hz, p-Me), 11.1 (q, J = 125 Hz, C_5Me_5). Anal. Calcd for $C_{35}H_{53}LaO$ (628.71): C, 66.86; H, 8.50; La, 22.09. Found: C, 66.60; H, 8.32; La, 21.96.

Preparation of Cp*$_2$La(η^3-CH$_2$CCPh)(py) (4f-La·py). Pyridine (8.0 μL, 98 μmol) was added with a microsyringe to a solution of Cp*$_2$LaCH$_2$CCPh (50 mg, 95 mmol) in hexanes (2 mL) in the glovebox. Stirring for 2 h at room temperature produced a clear, light yellow solution. Cooling and concentrating the solution *in vacuo* afforded yellow crystals suitable for X-ray analysis. Isolated yield: 52 mg (90%).

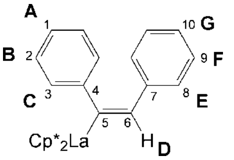
^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.94 (s, Cp*, 30H), 3.16 (s, CH_2, 2H), 6.51 (ddd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 4.5 Hz, $^4J_{HH}$ = 1.5 Hz, β-H, 2 H), 6.81 (tt, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.9 Hz, γ-H, 1 H), 6.96 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.2 Hz, *p*-H, 1 H), 7.13 (d, $^3J_{HH}$ = 7.4 Hz, *m*-H, 2 H), 7.24 (d, $^3J_{HH}$ = 7.9 Hz, *o*-H, 2 H), 8.40 (dd, $^3J_{HH}$ = 4.5 Hz, $^3J_{HH}$ = 1.9 Hz, α-H, 2 H). ^{13}C NMR (125.7 MHz, C_6D_6, 25 °C): δ 11.55 (q, $^1J_{CH}$ = 125.1 Hz, $C_5(CH_3)_5$), 51.07 (t, $^1J_{CH}$ = 159.5 Hz, CH_2CC), 117.96 (m, C_5Me_5), 123.72 (d, $^1J_{CH}$ = 153.6 Hz, *p*-CH), 123.79 (d, $^1J_{CH}$ = 165.6 Hz, β-CH), 128.58 (*m*- and *o*-CH), 136.43 (m, *i*-C), 137.04 (d, $^1J_{CH}$ = 163.3 Hz, α-CH), 152.16 (s, $CH_2C{\equiv}C$). The signal corresponding to CH_2CC was not observed. IR (Nujol, [cm^{-1}]): 2923 (s), 2853 (s), 2713 (m), 1973 (m), 1741 (w), 1653 (w), 1591 (m), 1459 (s), 1377 (m), 1215 (m), 1150 (m), 1067 (m), 1021 (m), 898 (m), 838 (m), 748 (m), 694 (m), 686 (m), 477 (s). Anal. Calcd for $C_{34}H_{42}LaN$ (603.62): C, 67.65; H, 7.01. Found: C, 67.51; H, 6.90.

X-ray Crystallography. In the glovebox, the crystals were transferred from the reaction vessels to a Petri dish filled with a small amount of light mineral oil. A suitable crystal was chosen by examination under a microscope. This crystal was attached to glass fiber, which was mounted in a cold nitrogen stream on a Bruker[53] SMART APEX CCD diffractometer for data collection. Data collection and structure solution were conducted at the University of Groningen. The structures were solved by Patterson methods, and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.[54] Relevant crystal and data collection parameters are given in Table 4.

Table 4. Summary of Crystallographic Data of Cp*$_2$Ln(η^3-CH$_2$CCPh) (Ln = Y 4f-Y, La 4f-La) and [Cp*$_2$La(η^3-CH$_2$CCPh)(NC$_5$H$_5$)] (4f-La·py)

	4f-Y	**4f-La**	**4f-La**·py
molecular formula	$C_{29}H_{37}Y$	$C_{29}H_{37}La$	$C_{34}H_{42}LaN$
fw	474.52	524.52	603.62
T, K	100(1)	100(1)	100(1)
cryst syst	orthorhombic	orthorhombic	triclinic
space group	$Pca2a_1$	$Pna2_1$	$P\bar{1}$
a, Å	16.4646(9)	20.064(1)	8.7176(4)
b, Å	10.5009(6)	10.051(2)	9.6510(4)
c, Å	14.7315(8)	12.233(3)	18.4634(9)
α, deg			78.405(1)
β, deg			87.337(1)
γ, deg			72.103(1)
V, Å^3	2547.0(2)	2466.9(8)	1447.86(11)
Z	4	4	2
ρ_{calc}, g cm^{-1}	1.237	1.412	1.385
F(000)	1000	1072	620
μ(Mo Kα), cm^{-1}	23.02	17.44	14.97
θ range, deg	2.30, 28.28	2.27, 27.48	2.26, 28.28
$wR(F^2)$	0.0685	0.0990	0.0666
refined reflns	6224	5124	6986
refined params	419	276	493
$R(F)$ for $F_o > 4.0\ \sigma(F_o)$	0.0297	0.0463	0.0307
GooF	1.030	1.025	1.028
weighting (a, b)	0.0393, 0.0	0.0, 0.0	0.0316, 0.0

Scheme 9. Numbering Scheme of Cp*$_2$LaC(Ph)=CH(Ph) (8ff-La)



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Supporting Information Available: More detailed experimental procedures are given, as well as spectroscopic data of representative transition metal complexes (for reference) and aromatic 1-methylalk-2-ynes. Graphic representations of the dependence of the proton chemical shift of the CH$_2$ group, the carbon chemical shifts of the C$_3$ ligand, and the first-order carbon−hydrogen coupling constant of the CH$_2$ group in Cp*$_2$LaCH$_2$CCR complexes versus the first-order carbon−hydrogen coupling constant of the CH$_3$ group of the corresponding neutral ligand CH$_3$CCR. The solid-state structure of Cp*$_2$Y(η^3-CH$_2$CCPh) (**4f-Y**) is shown as well. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800547N

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[53] *SMART, SAINT, SADABS, XPREP, and SHELXK/NT. Smart Apex Software Reference Manuals*; Bruker AXS Inc.: Madison, WI, 2000.

[54] Beurskens, P. T.; Beurskens, G.; De Gelder, R.; García-Granda, S.; Gould, R. O.; Israël, R.; Smits, J. M. M. *The DIRDIF-99 Program System*; University of Nijmegen, The Netherlands, 1999.