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Propargylic C(sp^3)–H Bond Activation for Preparing η^3-Propargyl/Allenyl Complexes of Yttrium

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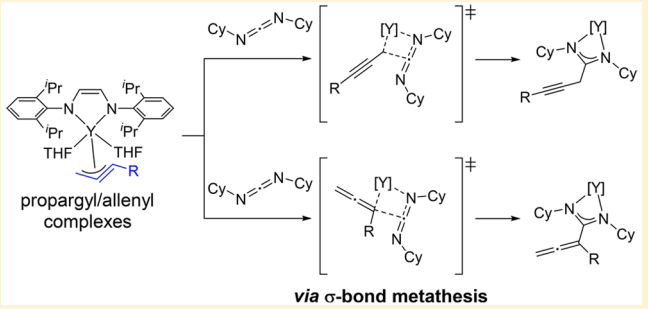
Supporting Information

ABSTRACT: Propargylic C(sp^3)—H bond activation of 1-substituted-1-propynes, such as 1-trimethylsilyl-1-propyne, 2-hexyne, and 1-phenyl-1-propyne, was achieved by treatment with an alkylyttrium complex **8** bearing an ene-diamido ligand to give the corresponding (η^3-propargyl/allenyl)yttrium complexes **7a–c**. A unique delocalized η^3-propargyl/allenyl structure of these three complexes was revealed by NMR spectroscopy and X-ray single crystal analyses. To elucidate the reactivity of the η^3-propargyl/allenyl unit of complexes **7a–c**, we conducted two reactions with *N*-methylaniline and *N*,*N*′-dicyclohexylcarbodiimine. For protonation by *N*-methylaniline, we found that the product distribution of monosubstituted internal alkynes and allenes depended on the substituent on the η^3-propargyl/allenyl moiety: **7a** and **7b** afforded the corresponding internal alkynes as the major products, whereas the major protonation product of **7c** was phenylallene. For the insertion of *N*,*N*′-dicyclohexylcarbodiimine, complex **7a** selectively yielded η^3-{*N*,*N*′-dicyclohexyl-2-(3-trimethylsilylpropargyl)-amidinate}yttrium **12a**, while complex **7c** produced η^3-{*N*,*N*′-dicyclohexyl-2-(1-phenylallenyl)amidinate}yttrium complex **13c**, though complex **7b** gave a mixture of η^3-{*N*,*N*′-dicyclohexyl-2-(3-normalpropylpropargyl)amidinate}yttrium complex **12b** and η^3-{*N*,*N*′-dicyclohexyl-2-(1-normalpropylallenyl)amidinate}yttrium **13b** in an 83:17 ratio. On the basis of the product distributions in these two-types of reactions, (η^3-propargyl/allenyl)yttrium complexes were shifted into preferentially favorable η^1-allenyl species or η^1-propargyl species depending on the substituents prior to the reaction with electrophiles via a four-membered cyclic mechanism.



INTRODUCTION

Propargyl and allenyl functionalities are important structural motifs in pharmaceuticals and other materials, and their versatile reactivity is often used for further chemical transformations.[1,2] These functional groups are catalytically and stoichiometrically introduced via allenyl- and propargyl-metal species, whose reactions with polar and nonpolar unsaturated bonds have been comprehensively well-investigated. In general, a propargyl-metal species gives the corresponding allenyl products, while an allenyl-metal species yields the corresponding propargyl products via cyclic intermediates (Figure 1a and b).[3] Noteworthy is that propargyl-metal complexes and allenyl-metal complexes are in equilibrium, probably through η^3-propargyl/allenyl complexes (Scheme 1),[3b,d−g,j,m,n,4] and recently, some η^3-propargyl/allenyl complexes were prepared by four synthetic routes:[5] (a) oxidative addition of Pt(0) into 1-phenyl-3-bromo-1-propyn followed by replacement of the bromide anion by AgOTf for **1**,[6a] (b) abstraction of a hydroxyl group of prop-2-yl-1-ol in the presence of $HBF_4{\cdot}Et_2O$ for **2**,[7a] (c) transmetalation of $Cp_2ZrMe(Cl)$ with a Grignard reagent, $PhCCCH_2MgBr$, for **3**,[8a] and (d) a propargylic C–H bond activation of internal alkynes by metal alkyl complexes for **4**, **5**, and **6** (Figure 2).[9] Among them, the latter method is regarded as the most straightforward and clean reaction with only the formation of alkanes as byproducts, though only electropositive metal–alkyl complexes have been applicable. Bazan and Bercaw independently prepared η^3-propargyl/allenyl complexes of zirconium **4**[9a] and yttrium **5**[4a] by the corresponding reactions of $Cp^*(TBM)ZrCH_3$ (TBM = tribenzylidenemethane) and

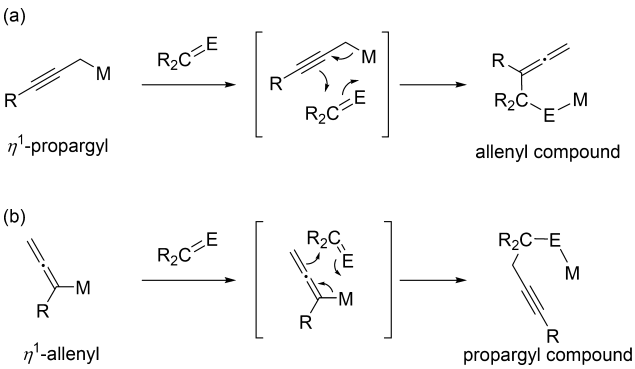


Figure 1. Plausible mechanism for the reaction of propargyl- and allenyl complexes with unsaturated compounds.

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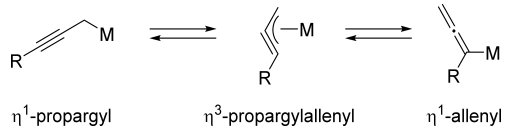
Scheme 1. Equilibrium between Propargyl- and Allenyl-Metal Species via the η^3-Propargyl/Allenyl Moiety



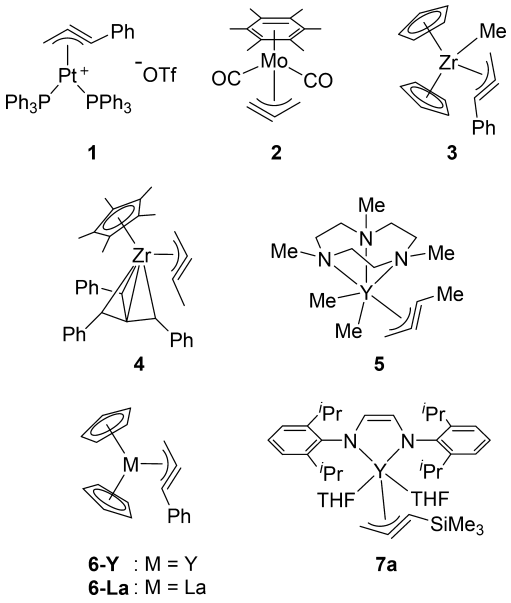
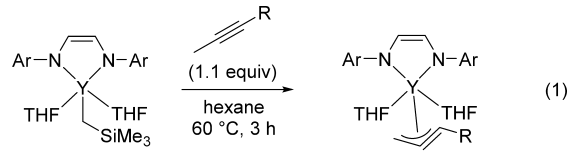


Figure 2. Representative examples of η^3-propargyl/allenyl complexes.

$CnYMe_3$ (Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane) with 2-butyne, and Hessen reported two η^3-propargyl/allenyl complexes of group 3 metals, **6-Y** and **6-La**, by treating $Cp^*_2LnCH(SiMe_3)_2$ with 1-phenyl-1-propyne in the presence of hydrogen.[9b] Recently, we synthesized a η^3-propargyl/allenyl yttrium complex **7a** by treating 1-trimethylsilyl-1-propyne with an alkylyttrium complex **8** supported by an ene-diamido ligand,[9c] and expanded our synthetic approach to other (η^3-propargyl/allenyl)yttrium complexes **7b** and **7c** by, respectively, treating **8** with 2-hexyne and 1-phenyl-1-propyne. Moreover, to elucidate the reaction pattern of the η^3-propargyl/allenyl moiety bound to the yttrium atom depending on the substituents, we carried out two reactions of **7a**−**c** with *N*-methylaniline and *N*,*N*′-dicyclohexylcarbodiimine, whose reactions proceeded according to a different pattern than that typically observed for η^1-propargyl- and η^1-allenyl complexes of various transition metals, as depicted in Figure 1.

RESULTS AND DISCUSSION

Synthesis and Characterization of (η^3-Propargyl/allenyl)yttrium Complexes 7b and 7c. The alkylyttrium complex **8** having a dianionic ene-diamido ligand reacted with 2-hexyne and 1-phenyl-1-propyne in hexane at 60 °C for 3 h to give the corresponding (η^3-propargyl/allenyl)yttrium complexes **7b** and **7c** as a consequence of selective C(sp^3)—H bond activation at the propargylic methyl group of the corresponding substituted propynes (eq 1), though we previously reported the synthesis and characterization of complex **7a** obtained in a similar manner.[9c]

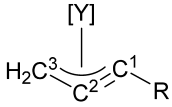


8 (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$)

7a: R = $SiMe_3$ (38% yield)[9c]
7b: R = ^{n}Pr (58% yield)
7c: R = Ph (44% yield)

Complexes **7b** and **7c** were fully characterized as a delocalized π-bonded η^3-propargyl/allenyl structure, as clearly differing from a tautomeric mixture of (η^1-propargyl)yttrium and (η^1-allenyl)yttrium based on the NMR spectral data as well as a crystallographic study of **7c** and **7a** (Tables 1 and 2). Table 1 summarizes the chemical shift values and corresponding $^1J_{C-H}$ and $^1J_{Y-C}$ coupling constants of the η^3-propargyl/allenyl moiety in NMR spectroscopy for **7a**−**7c**, together with some related yttrium complexes such as CnY(η^3-CH_2CCMe) (**5**: Cn = 1,4,7-trimethyl-1,4,7-triazacyclonane)[4a] and $Cp^*_2Y(\eta^3$-CH_2CCPh) (**6-Y**).[9b] Resonances due to methylene protons bound to C^3 and C^3 carbon of the η^3-propargyl/allenyl moiety were observed at δ_H 2.64 and δ_C 40.8 for **7b** and δ_H 3.23 and δ_C 47.7 for **7c**, values that were almost the same as those found for the reported complex **7a** (δ_H 2.60 and δ_C 37.8)[9c] and those of **6-Y** (δ_H 2.60 and δ_C 37.8), while methylene protons bound to C^3 and C^3 carbon of **5** were observed in a lower field (δ_H 3.87 and δ_C 55.5) than those found for **7a**−**7c** and **6-Y**. The C−H coupling constants of methylene bound to C^3 of the η^3-propargyl/allenyl moiety for **7a**−**7c** were ca. 160 Hz assignable to typical sp^2-carbons.[10] Chemical shifts of the quaternary C^2 carbon of **7b** and **7c** were observed at δ_C 151.4 for **7b** and δ_C 163.3 for **7c** values, which were similar to the reported values of

Table 1. ^{1}H and ^{13}C NMR Spectral Data for η^3-Propargyl/Allenylyttrium Moiety of 7a−c, 5, and 6-Y



	7a: R = $SiMe_3$[9c]	**7b**: R = ^{n}Pr	**7c**: R = Ph	**5**[4a]	**6-Y**[9b]
C^1R (δ_C)	107.3	108.5	113.8	109.9	106.8
$^1J_{Y-C}$ (Hz)	12	14	17	- (broad)	11.9
C^2 (δ_C)	162.6	151.4	163.3	169.2	155.1
C^3H_2 (δ_H)	2.60	2.64	3.23	3.87	2.82
C^3 (δ_C)	37.8	40.8	47.7	55.5	49.3
$^1J_{C-H}$ (Hz)	157	158	161	159	159
$^1J_{Y-C}$ (Hz)	3	3	n.d.	Not reported	5

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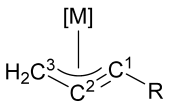
Table 2. Selected Bond Lengths and Angles (Å and Deg) for the η^3-Propargyl/Allenylyttrium Moiety of 7a, 7c, 1, 3, and 6-Y

		7a: R = $SiMe_3$[9c]	7c: R = Ph	1: R = Ph[6a]	3: R = Ph[8a]	6-Y: R = Ph[9b]
	M	Y	Y	Pt	Zr	Y
	M—C1	2.513(4)	2.522(6)	2.186(11)	2.361 (3)	2.560(3)
	M—C2	2.564(4)	2.556(5)	2.150(9)	2.438(3)	2.529(3)
	M—C3	2.916(5)	2.817(6)	2.273(10)	2.658(4)	2.653(3)
	C1—C2	1.256(6)	1.259(8)	1.23(1)	1.259(4)	1.268(4)
	C2—C3	1.343(6)	1.366(8)	1.39(2)	1.344(5)	1.366(4)
	C1—C2—C3	164.4(5)	160.3(6)	148(1)	155.4(3)	155.9(3)

η^3-propargyl/allenyl yttrium complexes **7a** (δ_C 162.6), **5** (δ_C 169.2), and **6-Y** (δ_C 155.1) being completely different from the chemical shifts of quaternary C^2 carbons of typical η^1-propargyl complexes (δ_C 60—100)[3,6a,11] and η^1-allenyl complexes (δ_C 190—210).[3,6a,11b−d] Noteworthy were the $^1J_{Y-C}$ values of C^1 and C^3 carbons, which demonstrated the bonding nature between the carbons of the η^3-propargyl/allenyl moiety and the yttrium center. The $^1J_{Y-C}$ value (3 Hz) was observed for the C^3 carbon of complexes **7a** and **7b**, while the $^1J_{Y-C}$ for the C^3 carbon was not observed for complex **7c**. Much larger $^1J_{Y-C}$ values of **7a** (12 Hz), **7b** (14 Hz), and **7c** (17 Hz) were observed for the C^1 carbon, suggesting that the bond between the C^1 carbon and the yttrium center was stronger than the C^3—Y bond and consistent with the corresponding crystallographic data (vide infra).

Figure 3 shows the molecular structure of complex **7c**. The selected bond lengths and angles of **7c** are summarized in Table 2 together with those for **7a** and some η^3-propargyl/allenyl complexes **1**, **3**, and **6-Y**. Complex **7c** adopts a distorted trigonal bipyramidal molecular geometry, where the O1 and N2 atoms occupy axial positions, and the yttrium atom has one chelating ene-diamido ligand, two THF, and one η^3-propargyl/allenyl ligand, and the overall structure of **7c** is essentially the same as the reported structure of **7a**. The bond length of C27—C28 (1.366(8) Å) is shorter than that of a typical C−C single bond (1.45 Å) and longer than that of a typical C−C double bond (1.31 Å), while the bond length of C28—C29 (1.259(8) Å) is regarded as an intermediate between a C−C double bond and a C−C triple bond (1.20 Å). Accordingly, the η^3-propargyl/allenyl coordination mode was confirmed based on the observed bond lengths along with a slightly bent C27—C28—C29 angle (160.3(6)°) and larger C28—C29—C30 angle (137.8(6)°) than the ideal angle of sp^2 carbon found for some η^1-allenyl complexes.[12] Furthermore, the bond length of Y−C29 (2.522(6) Å) in **7c** is the shortest among the three yttrium−carbon bonds (Y−C27 = 2.817(5) Å and Y−C28 = 2.556(5) Å), indicating the η^3-propargyl/allenyl coordination mode. Such an observation is in good accord with the large J_{Y-C} value (17 Hz) for a C^1 carbon (vide supra).

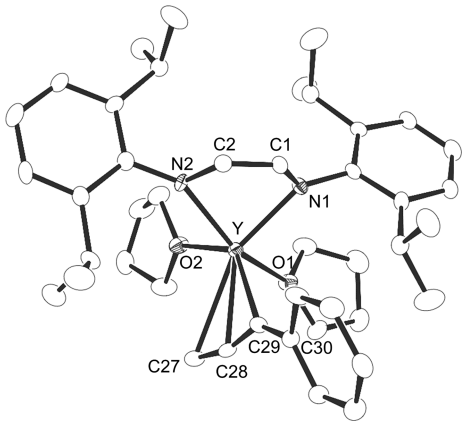
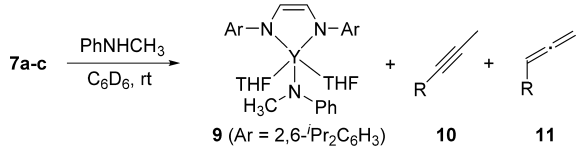


Figure 3. ORTEP drawing of the η^3-propargyl/allenyl-yttrium complex **7c** with 50% thermal ellipsoids. All hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y—N1, 2.200(5); Y—N2, 2.209(5); Y—C27, 2.917(5); Y—C28, 2.556(5); Y—C29, 2.522(6); N1—C1, 1.411(7); N2—C2, 1.413(7); C1—C2, 1.351(9); C27—C28, 1.366(8); C28—C29, 1.259(8); C27—C28—C29, 160.3(6); C28—C29—C30, 137.8(6); O1—Y−N2, 147.97(15); and O2—Y1—N1, 117.81(15).

Protonation and Insertion Reactions of (η^3-Propargyl/allenyl)yttrium Complexes 7a−c. With three (η^3-propargyl/allenyl)yttrium complexes **7a−c** in hand, we conducted protonation by *N*-methylaniline (1 equiv) and an insertion reaction of *N*,*N*′-dicyclohexylcarbodiimide to clarify the substituent-dependent preference of η^1-propargyl or η^1-allenyl species generated *in situ* from η^3-propargyl/allenyl complexes. Protonation of the η^3-propargyl/allenyl moiety bound to the yttrium atom afforded internal alkynes **10** and allenes **11** together with the formation of an amido complex **9** (Scheme 2): reactions of **7a** and **7b**, having electron-donating substituent on the η^3-propargyl/allenyl ligand, with *N*-methylaniline gave the corresponding alkynes, 1-trimethylsilyl-1-propyne (**10a**) and 2-hexyne (**10b**), with contamination of the corresponding minor allenes **11a** and **11b** in the ratios of **10a**/**11a** = 91:9 and **10b**/**11b** = 76:24. On the other hand, treatment of **7c**, which has an electron-deficient group on the η^3-propargyl/allenyl ligand, with *N*-methylaniline mainly producing phenylallene

Scheme 2. Protonation of (η^3-Propargyl/allenyl)yttrium Complexes 7a−c by *N*-Methylaniline



R = $SiMe_3$ **10a:11a** = 91:9
R = ^{n}Pr **10b:11b** = 76:24
R = Ph **10c:11c** = 22:78

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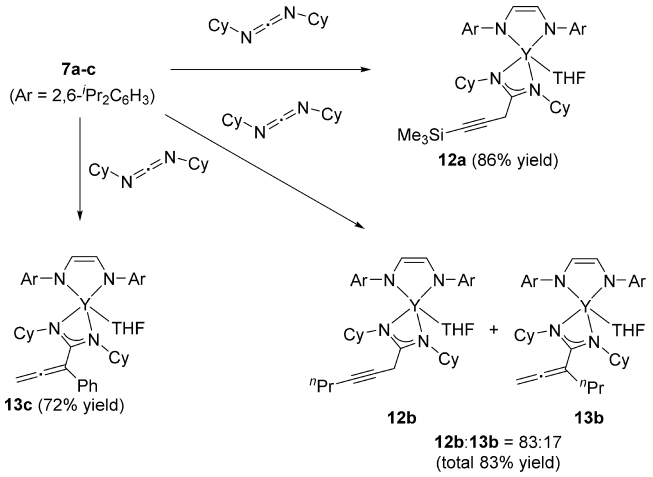
(**11c**) accompanied by a minor product of 1-phenyl-1-propyne (**10c**) in a **10c**/**11c** = 22:78 ratio.

Treatment of **7a** with *N*,*N*′-dicyclohexylcarbodiimide resulted in the selective formation of complex **12a** supported by an η^3-amidinate ligand whose central carbon was attached by a propargyl group with a terminal trimethylsilyl substituent (Scheme 3). The ^{1}H and ^{13}C{^{1}H} NMR spectra of **12a**

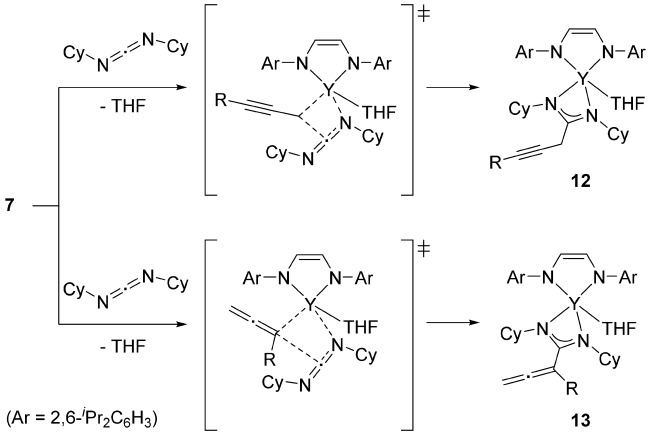
Scheme 3. Reaction of (η^3-Propargyl/allenyl)yttrium Complexes 7a−c and *N*,*N*′-Dicyclohexylcarbodiimide



displayed a singlet resonance at δ_H 3.12 and a triplet resonance at δ_C 17.1 ($^1J_{C-H}$ = 125 Hz) assignable to a methylene moiety between the amidinate moiety and the C≡C moiety, clearly indicating that *N*,*N*′-dicyclohexylcarbodiimide was inserted into the η^1-propargylyttrium species of **7a**. Complex **7b** was found to give a propargyl-attached complex **12b** as a major product (83% selectivity) with the same tendency as **7a**. In sharp contrast, the reaction of **7c** with *N*,*N*′-dicyclohexylcarbodiimide yielded η^3-*N*,*N*′-dicyclohexyl-2-(1-phenylallenyl)amidinate yttrium complex **13c** as a single product in 72% isolated yield, in which the C═N bond of *N*,*N*′-dicyclohexylcarbodiimide inserted into a preferential (η^1-allenyl)yttrium species of **7c** (Scheme 3). Complex **13c** was characterized by its ^{1}H and ^{13}C{^{1}H} NMR spectra: a singlet signal due to the typical terminal vinylidene protons was observed at δ_H 4.97, and the internal carbon and terminal vinylidene carbon of the allenyl unit were observed as a singlet signal at δ_C 205.3 and a triplet resonance at δ_C 79.3 with a large $^1J_{C-H}$ coupling constant ($^1J_{C-H}$ = 168 Hz).[11] The molecular structure of **13c** was determined by a preliminary X-ray diffraction study of the single crystal (Figure S23),[13] though the structural feature of **13c** was not precisely discussed due to its low accuracy, indicating that the yttrium atom adopts a five-coordinated distorted trigonal bipyramidal structure surrounded by one enediamido, one allenylamidinate, and one THF, and the allenyl carbon with a phenyl group attaches to the central carbon atom of the η^3-amidinate ligand.

These two reactions and bonding characteristics, evidenced from the NMR spectroscopy, led us to propose a four-membered cyclic mechanism for the reactions of η^3-propargyl/allenylyttrium complexes with electrophiles, such as *N*-methylaniline and *N*,*N*′-dicyclohexylcarbodiimine, reflecting the substituent-dependent preference of the reactive species, i.e., η^1-propargylyttrium or η^1-allenylyttrium derived from η^3-propargyl/allenylyttrium. Complexes **7a** and **7b** favored the η^1-propargyl form as the active species because of the formation of the corresponding alkynes as major products and a smaller $^1J_{Y-C}$ value (12 Hz for **7a** and 15 Hz for **7b**) for the C^1 carbon and an observable $^1J_{Y-C}$ value (3 Hz for **7a** and **7b**) for the C^3 carbon in NMR spectroscopy. In contrast, the major product of the reaction of **7c** with *N*-methylaniline was phenylallene (**11c**), and the $^1J_{Y-C}$ value (17 Hz) for the carbon (C^1), as well as the lack of a coupling constant for the C^3 carbon in NMR spectroscopy for **7c**, suggested the favorable contribution of the allenyl canonical form for **7c**; therefore, we assumed that the preference of the active species of **7c** was an η^1-allenyl species prior to being protonated via a typical four-membered δ-bond metathesis pathway.[14] On the basis of these preferences of the reactive species for protonation, it was assumed that the η^1-propargyl species for **7a** and **7b** reacted with *N*,*N*′-dicyclohexylcarbodiimide to give the corresponding (η^3-propargylamidinate)yttrium complexes **12a** and **12b** via a four-membered cyclic transition state, while the preference of η^1-allenyl species for **7c** selectively yields the (η^3-allenylamidinate)yttrium complex **13c** as the major product through the same cyclic transition state (Scheme 4).

Scheme 4. Proposed Reaction Mechanism to Give Amidinate Complexes 12 and 13



CONCLUSION

We demonstrated that a unique propargylic C(sp^3)-H bond activation was applicable for preparing (η^3-propargyl/allenyl)-yttrium complexes **7a−c** by treating the alkylyttrium complex **8** with the corresponding internal alkynes, such as 1-trimethylsilyl-1-propyne, 1-hexyne, and 1-phenyl-1-propyne. On the basis of the two types of reactions of **7a−c** with *N*-methylaniline and *N*,*N*′-dicyclohexylcarbodiimine, we proposed a four-membered cyclic mechanism for the protonation and insertion with selectivity in which the propargyl canonical form produced internal alkynes upon protonation and η^3-{*N*,*N*′-dicyclohexyl-2-(3-substitutedpropargyl)amidinate}yttrium complexes **12** for the insertion reactions, whereas the allenyl canonical form afforded allenes upon protonation and η^3-{*N*,*N*′-dicyclohexyl-2-(1-substitutedallenyl)amidinate}yttrium complexes **13** for the insertion reaction, presumably consistent with the general tendency that early transition metal complexes favor σ-bond metathesis and a four-membered cyclic transition state in polymerization and amine-insertion reactions.[15] This is the first example of a regioselective insertion reaction of the C═N bond into the η^3-propargyl/allenyl complex. It is

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noteworthy that such selectivity is clearly distinguished from the general tendency that η^1-propargyl complexes of late-transition metals afford the corresponding allenyl products, while η^1-allenyl complexes of late-transition metals favorably yield the corresponding propargyl products via cyclic intermediates, as demonstrated in Figure 1a and b.

EXPERIMENTAL SECTION

General. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under argon using the standard Schlenk technique or argon-filled glovebox. Yttrium complexes **7a** and **8** were prepared according to the literature.[9c] Dicyclohexylcarbodiimide and *N*-methylaniline were purchased and purified by distillation over CaH_2. Hexane, pentane, toluene, and benzene-d_6 were distilled over CaH_2 and thoroughly degassed by trap-to-trap distillation before use. NMR spectra were recorded on a Bruker AV 400 MHz spectrometer in a 5 mm NMR tube. Chemical shifts were reported in parts per million and referenced to a residual proton signal of the solvent (^{1}H benzene-d_6, δ = 7.16; chloroform, δ = 7.26) or the solvent itself ($^{13}C\{^1H\}$ benzene-d_6, δ = 128.06; chloroform, δ = 77.16). Melting points were recorded by a BUCHI Melting Point M-565. The elemental analyses were recorded by using PerkinElmer 2400 at the Faculty of Engineering Science, Osaka University.

Preparation of (2,6-^{i}Pr$_2$C$_6$H$_3$-DAD)Y(buten-2-ynyl)(THF)$_2$ (7b). To a solution of **8** (200 mg, 0.287 mmol) in hexane was added a solution of 2-hexyne (25.9 mg, 0.316 mmol) via syringe at room temperature. The color of the reaction mixture turned to brown. The reaction mixture was stirred at 60 °C for 3 h, and then all volatiles were evaporated. After drying the remaining solid *in vacuo*, **7b** was isolated as a brown powder in 58% yield (115 mg, 0.166 mmol), mp 78−80 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 1.04 (t, 3H, $^3J_{HH}$ = 7.2 Hz, $CH_3CH_2CH_2$), 1.10 (br s, 8H, β-CH_2 of THF), 1.38 (d, 24H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.67 (sext, $^3J_{HH}$ = 7.2 Hz, 2H, $CH_3CH_2CH_2$), 2.30 (tt, $^3J_{HH}$ = 7.1 Hz, $^5J_{HH}$ = 2.7 Hz, 2H, $CH_3CH_2CH_2$), 2.65 (t, $^5J_{HH}$ = 2.8 Hz, 2H, YCH_2), 3.53 (br s, 8H, α-CH_2 of THF), 3.82 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 5.70 (s, 2H, CH═CH), 7.14 (t, 2H, $^3J_{HH}$ = 8.0 Hz, *p*-Ar), 7.24 (t, 4H, $^3J_{HH}$ = 8.0 Hz, *m*-Ar). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 30 °C): δ 14.2 (q, $^1J_{CH}$ = 121 Hz, $CH_3CH_2CH_2$), 25.2 (t, $^1J_{CH}$ = 133 Hz, β-CH_2 of THF), 25.4 (q, $^1J_{CH}$ = 123 Hz, $CH(CH_3)_2$), 25.8 ($CH_3CH_2CH_2$), 28.4 (d, $^1J_{CH}$ = 124 Hz, $CH(CH_3)_2$), 28.8 (t, $^1J_{CH}$ = 129 Hz, $CH_3CH_2CH_2$), 40.9 (dt, $^1J_{CH}$ = 157 Hz, $^1J_{YC}$ = 3 Hz, YCH_2C), 71.0 (t, $^1J_{CH}$ = 148 Hz, α-CH_2 of THF), 108.6 (d, $^1J_{YC}$ = 14 Hz, $YCH_2C{\equiv}C$), 113.5 (dd, $^1J_{CH}$ = 165 Hz, $^2J_{YC}$ = 2 Hz, CH = CH), 122.1 (d, $^1J_{CH}$ = 157 Hz, *p*-Ar), 123.4 (d, $^1J_{CH}$ = 152 Hz, Hz *m*-Ar), 143.8 (*o*-Ar), 151.4 ($YCH_2C{\equiv}C$), 152.6 (d, $^2J_{YC}$ = 4 Hz, *ipso*-Ar). Anal. Calcd for $C_{40}H_{61}N_2O_2Y$: C, 69.54; H, 8.90; N, 4.06. Found: C, 69.15; H, 8.85; N, 4.45. Small deviation of the E.A. values is due to high sensitivity of **7b** to air.

Preparation of (2,6-^{i}Pr$_2$C$_6$H$_3$-DAD)Y(3-(phenyl)prop-2-ynyl)-(THF)$_2$ (7c). To a solution of **8** (300 mg, 0.432 mmol) in hexane was added 1-phenyl-1-propyne (50.2 mg, 0.432 mmol) via syringe at room temperature. The color of the reaction mixture turned to orange. The reaction mixture was stirred at 60 °C for 3 h, and then all volatiles were evaporated. After drying the remaining solid in vacuo, **7c** was isolated as an orange powder in 44% yield (139 mg, 0.192 mmol), mp 85−87 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 1.08 (br s, 8H, β-CH_2 of THF), 1.30 (d, 24H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 3.24 (s, 2H, YCH_2), 3.58 (br s, 8H, α-CH_2 of THF), 3.77 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 5.80 (s, 2H, CH = CH), 6.98 (t, 1H, $^3J_{HH}$ = 7.2 Hz, *p*-Ph), 7.11−7.16 (m, 4H, *p*-Ar and *m*-Ph), 7.22 (d, 4H, $^3J_{HH}$ = 7.6 Hz, *m*-Ar), 7.45 (d, 2H, $^3J_{HH}$ = 7.2 Hz, *o*-Ph). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 25.2 (t, $^1J_{CH}$ = 134 Hz, β-CH_2 of THF), 25.3 (q, $^1J_{CH}$ = 120 Hz, $CH(CH_3)_2$), 28.5 (d, $^1J_{CH}$ = 127 Hz, $CH(CH_3)_2$), 47.7 (t, $^1J_{CH}$ = 156 Hz, $YCH_2C{\equiv}C$), 71.2 (t, $^1J_{CH}$ = 151 Hz, α-CH_2 of THF), 113.7 (dd, $^1J_{CH}$ = 165 Hz, $^2J_{YC}$ = 2 Hz, CH = CH), 113.8 (d, $^1J_{YC}$ = 17 Hz, $YCH_2C{\equiv}C$), 122.3 (d, $^1J_{CH}$ = 157 Hz, *p*-Ar), 123.4 (d, $^1J_{CH}$ = 152 Hz, *m*-Ar), 125.4 (d, $^1J_{CH}$ = 160 Hz, *p*-Ph), 128.5 (d, $^1J_{CH}$ = 157 Hz, *m*-Ph), 130.3 (d, $^1J_{CH}$ = 158 Hz, *o*-Ph), 135.6 (*i*-Ph), 143.8 (*o*-Ar), 152.5 (d, $^2J_{YC}$ = 3.9 Hz, *i*-Ar), 163.4 ($YCH_2C{\equiv}C$). Anal. Calcd for $C_{43}H_{59}N_2O_2Y$: C, 71.25; H, 8.20; N, 3.86. Found: C, 71.39; H, 8.0; N, 3.86. The small deviation of the E.A. values is due to the high sensitivity of **7c** to air.

Preparation of (2,6-^{i}Pr$_2$C$_6$H$_3$-DAD)Y[(NCy)$_2$C−CH$_2$C≡CSiMe$_3$)](THF)$_2$ (12a). **7a** (68.2 mg, 9.45 μmol) and *N*,*N*′-dicyclohexylcarbodiimide (18.9 mg, 9.17 μmol) were reacted in benzene at room temperature for 3 h. Then, all volatiles were evaporated. The remaining solid was dried to give **12a** as a brown powder in 89% yield (72.1 mg, 8.43 μmol), mp 97−99 °C (dec). ^{1}H NMR (400 MHz, C_6D_6 and 14 equiv of THF-d_8, 30 °C): δ 0.16 (s, 9H, $Si(CH_3)_3$), 0.96−1.11 (br m, 2H, Cy), 1.11−1.31 (br m, 8H, Cy), 1.35 (d, 24H, $^3J_{HH}$ = 6.4 Hz $CH(CH_3)_2$), 1.45 (br s, 8H, β-CH_2 of THF and THF-d_8), 1.52−1.61 (br m, 2H, Cy), 1.64−1.75 (br m, 4H, Cy), 1.82−1.88 (br m, 4H, Cy), 3.21 (br m, 2H, Cy), 3.25 (s, 2H, $CH_2C{\equiv}CSi$), 3.56 (br m, 8H, α-CH_2 of THF + THF-d_8), 3.75 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 5.61 (s, 2H, CH═CH), 7.06 (t, 2H, $^3J_{HH}$ = 7.6 Hz, *p*-Ar), 7.20 (d, 4H, $^3J_{HH}$ = 7.6 Hz, *m*-Ar). ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 0.24 (s, 9H, $Si(CH_3)_3$), 0.92−1.04 (m, 2H, Cy), 1.09 (br s, 4H, β-CH_2 of THF), 1.15−1.33 (br m, 8H, Cy), 1.34−1.62 (br m, 26H, $CH(CH_3)_2$ and Cy), 1.61−1.75 (br s, 4H, Cy), 1.77−1.98 (br s, 4H, Cy), 3.03−3.40 (br, 2H, Cy), 3.20 (s, 2H, $CH_2C{\equiv}CSi$), 3.57 (br s, 4H, α-CH_2 of THF), 3.67 (br s, 4H, $CH(CH_3)_2$), 5.69 (s, 2H, CH═CH), 7.10 (t, 2H, $^3J_{HH}$ = 7.2 Hz, *p*-Ar), 7.27 (d, 4H, $^3J_{HH}$ = 7.2 Hz, *m*-Ar). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 0.2 (q, $^1J_{CH}$ = 131 Hz, $Si(CH_3)_3$), 17.3 (td, $^1J_{CH}$ = 134 Hz, $^3J_{YC}$ = 2 Hz, $CCH_2C{\equiv}CSi$), 25.2 (β-CH_2 of THF), 25.4 ($CH(CH_3)_2$), 26.3 (2 carbon of Cy), 28.4 (br, $CH(CH_3)_2$), 37.1 (t, $^1J_{CH}$ = 126 Hz, Cy), 56.9 (d, $^1J_{CH}$ = 126 Hz, Cy), 70.8 (α-CH_2 of THF), 86.0 ($CCH_2C{\equiv}CSi$), 102.2 (t, $^2J_{CH}$ = 12 Hz, $CCH_2C{\equiv}CSi$), 114.0 (d, $^1J_{CH}$ = 166 Hz, CH═CH), 121.2 (d, $^1J_{CH}$ = 161 Hz, *p*-Ar), 123.5 (br d, $^1J_{CH}$ = 149 Hz, *m*-Ar), 141.2 (br s, *o*-Ar), 150.9 (d, $^2J_{YC}$ = 3 Hz, *i*-Ar), 171.2 (s, $CCH_2C{\equiv}CSi$). Anal. Calcd for $C_{49}H_{77}N_4OSiY$: C, 68.82; H, 9.08; N, 6.55. Found: C, 68.98; H, 10.12; N, 6.54. A small deviation of the E.A. values is due to high sensitivity of **12a** to air.

Reaction of 7b with *N*,*N*′-Dicyclohexylcarbodiimide. **7b** (87.4 mg, 0.127 mmol) and *N*,*N*′-dicyclohexylcarbodiimide (25.6 mg, 0.124 mmol) were reacted in benzene at room temperature for 3 h. Then, all volatiles were evaporated. The remaining solid was dried to give a brown solid in total 86% yield. Analysis of the product by ^{1}H NMR in C_6D_6 showed the presence of two compounds in a **12b**/**13b** = 83:17 ratio, as evidenced by two sets of signals attributable to the ligand backbone proton (CH═CH). The major product appears to be **12b**. ^{1}H NMR (400 MHz, C_6D_6, 30 °C) major product: δ 0.94 (t, 3H, $^3J_{HH}$ = 7.2 Hz, $CH_3CH_2CH_2$), 1.12 (br s, 4H, β-CH_2 of THF), 1.18−1.35 (m, 8H, Cy), 1.36−1.63 (br m, 30H, $CH(CH_3)_2$, Cy, and $CH_3CH_2CH_2$), 1.64−1.78 (br s, 4H, Cy), 1.82−2.00 (m, 4H, Cy), 2.07 (t, 2H, $^3J_{HH}$ = 6.8 Hz, $CH_3CH_2CH_2$), 3.18 (s, 2H, $YCH_2C{\equiv}C$), 3.31 (br s, 2H, Cy), 3.61 (br s, 4H, α-CH_2 of THF), 3.68 (br s, 4H, $CH(CH_3)_2$), 5.70 (s, 2H, CH═CH), 7.10 (t, 2H, $^3J_{HH}$ = 7.6 Hz, *p*-Ar), 7.27 (d, 4H, $^3J_{HH}$ = 7.6 Hz, *m*-Ar). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 13.7 ($CH_3CH_2CH_2$), 16.2 (d, $^3J_{YC}$ = 3 Hz, $CCH_2C{\equiv}C^nPr$), 21.2 ($CH_3CH_2CH_2$), 22.6 ($CH_3CH_2CH_2$), 25.2 (β-CH_2 of THF), 25.4 ($CH(CH_3)_2$), 26.3 (2 carbon of Cy), 29.1 ($CH(CH_3)_2$), 37.2 (Cy), 56.8 (Cy), 70.9 (α-CH_2 of THF), 75.9 ($CCH_2C{\equiv}C^nPr$), 81.4 ($CCH_2C{\equiv}C^nPr$), 114.1 (CH═CH), 121.2 (*p*-Ar), 123.5 (br, *m*-Ar), 141.5 (br, *o*-Ar), 150.9 (d, $^2J_{YC}$ = 4 Hz, *ipso*-Ar), 172.7 (d, $^2J_{YC}$ = 2 Hz, $CCH_2C{\equiv}C^nPr$). Selected ^{1}H NMR data for the minor product **13b**: ^{1}H NMR (400 MHz, C_6D_6, 30 °C) δ 0.98 (t, 3H, $^3J_{HH}$ = 7.2 Hz, $CH_3CH_2CH_2$), 2.11−2.19 (m, 2H, $CH_3CH_2CH_2$), 4.69 (t, 2H, $^5J_{HH}$ = 4.0 Hz, $H_2C{=}C{=}C$), 5.76 (s, 2H, CH═CH). Selected ^{13}C NMR data for minor product **13b**: ^{13}C NMR (100 MHz, C_6D_6, 30 °C) δ 76.5 ($H_2C{=}C{=}C$), 98.0 (d, $^3J_{YC}$ = 3 Hz, $H_2C{=}C{=}C$), 174.1 ($H_2C{=}C{=}C(^nPr)C$), 203.6 ($H_2C{=}C{=}C$).

Preparation of (2,6-^{i}Pr$_2$C$_6$H$_3$-DAD)Y[(NCy)$_2$C−C(Ph)═C═CH$_2$)](THF) (13c). **7c** (148 mg, 0.204 mmol) and *N*,*N*′-dicyclohexylcarbodiimide (42.1 mg, 0.204 mmol) were reacted in benzene at room temperature for 3 h. All volatiles were evaporated, and the remaining solid was dried to give **13c** as a brown powder in 74% yield (130 mg, 0.151 mmol), mp 120−122 °C (dec). ^{1}H NMR (400 MHz, C_6D_6 + 9 eq. of THF, 30 °C): δ 0.99−1.89 (m, Cy, $CH(CH_3)_2$, and β-

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CH_2 of THF, integration is not given due to broadness in this region), 3.18−3.28 (br m, 2H, Cy), 3.57 (br s, 10H, α-CH_2 of THF and THF-d_8), 3.75 (sept, 4H, $^3J_{HH}$ = 6.4 Hz, $CH(CH_3)_2$), 5.00 (s, 2H, H_2C═C═C), 5.74 (s, 2H, CH═CH), 7.04−7.12 (m, 3H, *p*-Ph and *p*-Ar), 7.22−7.30 (m, 6H, *m*-Ar and *m*-Ph), 7.59 (d, 2H, $^3J_{HH}$ = 6.8 Hz, *o*-Ph). ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 0.98−1.89 (m, Cy, $CH(CH_3)_2$, and β-CH_2 of THF, integration is not given due to broadness in this region), 3.26−4.13 (br m, 10H, Cy, α-CH_2 of THF, and $CH(CH_3)_2$), 4.98 (s, 2H, H_2C═C═C), 5.80 (s, 2H, CH═CH), 7.06 (t, 1H, $^3J_{HH}$ = 7.6 Hz, *p*-Ph), 7.14 (*p*-Ar, overlapped with C_6D_6), 7.25−7.32 (m, 6H, *m*-Ar and *m*-Ph), 7.64 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *o*-Ph). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 25.3 (br, β-CH_2 of THF), 26.1 (br, $CH(CH_3)_2$, 2 carbon of Cy), 28.4 (br, $CH(CH_3)_2$), 37.1 (br, Cy), 58.2 (d, $^1J_{CH}$ = 129 Hz, Cy), 71.1 (br, α-CH_2 of THF), 79.0 (t, $^1J_{CH}$ = 170 Hz, H_2C═C═C), 102.0 (d, $^3J_{YC}$ = 3 Hz, H_2C═C═C), 114.3 (br d, $^1J_{CH}$ = 151 Hz, CH═CH), 121.5 (d, $^1J_{CH}$ = 164 Hz, *p*-Ar), 123.5 (br, *m*-Ar), 126.4 (d, $^1J_{CH}$ = 158 Hz, *o*-Ph), 129.2 (*m*-Ph), 133.9 (*i*-Ph), 141.8 (br, *o*-Ar), 150.8 (d, $^2J_{YC}$ = 3 Hz, *i*-Ar), 171.7 (d, $^2J_{YC}$ = 1 Hz, H_2C═C═C(Ph)C), 205.4 (t, $^2J_{CH}$ = 3 Hz H_2C═C═C), *p*-Ph signal is overlapped with the C_6D_6 signal.

Protonation of 7a−c. To a solution of **7a−c** (1.5×10^{-2} mmol) in C_6D_6 (0.5 mL) was added *N*-methylaniline (1.5×10^{-2} mmol). The solution was transferred into an NMR tube and analyzed by NMR spectroscopy. In all cases, amidoyttrium complex **9** was observed together with the protonated organic products: for the amidoyttrium complex **9**, ^{1}H NMR (400 MHz, C_6D_6, 30 °C) δ 1.06 (br s, 8H, β-CH_2 of THF), 1.34 (d, 24H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 2.96 (s, 3H, NCH_3), 3.55 (br s, 8H, α-CH_2 of THF), 3.68 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 5.67 (s, 2H, CH═CH), 6.60 (d, 2H, $^3J_{HH}$ = 8.0 Hz, *o*-Ph), 6.67 (t, 1H, $^3J_{HH}$ = 8.0 Hz, *p*-Ph), 7.09−7.16 (m, 2H, *p*-Ar), 7.24 (d, 4H, $^3J_{HH}$ = 7.2 Hz, *m*-Ar), 7.30 (t, 2H, $^3J_{HH}$ = 8.0 Hz, *m*-Ph).

The spectroscopic data for alkyne **10a**: ^{1}H NMR (400 MHz, C_6D_6, 30 °C) δ 0.20 (s, 9H, $Si(CH_3)_3$), 1.51 (s, 3H, CH_3C≡CSi); for allene **11a**, ^{1}H NMR (400 MHz, C_6D_6, 30 °C) δ 0.10 (s, 9H, $Si(CH_3)_3$), 4.28 (d, 2H, $^4J_{HH}$ = 7.2 Hz, H_2C═C═CH), 4.89 (t, 1H, $^4J_{HH}$ = 7.6 Hz, H_2C═C═CH).

The spectroscopic data for alkyne **10b**: ^{1}H NMR (400 MHz, C_6D_6, 30 °C) δ 0.89 (t, 3H, $^3J_{HH}$ = 7.2 Hz, $CH_3CH_2CH_2$), 1.39−1.44 (m, 2H, $CH_3CH_2CH_2$), 1.57 (t, $^5J_{HH}$ = 2.8 Hz, 3H, CH_3C≡CCH_2), 1.99−2.06 (m, 2H, $CH_3CH_2CH_2$); for allene **11b**, ^{1}H NMR (400 MHz, C_6D_6, 30 °C) δ 0.83 (t, 3H, $^3J_{HH}$ = 7.6 Hz, $CH_3CH_2CH_2$), 1.39−1.44 (m, 2H, $CH_3CH_2CH_2$), 1.81−1.93 (m, 2H, $CH_3CH_2CH_2$), 4.59−4.63 (m, 2H, H_2C═C═CH), 5.00−5.06 (m, 1H, H_2C═C═CH).

The spectroscopic data for alkyne **10c**: ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 1.65 (s, 3H, CH_3C≡C), 6.96−7.02 (m, 3H, *m*- and *p*-Ph), 7.47 (d, $^3J_{HH}$ = 8.0 Hz, *o*-Ph); for allene **11c**, ^{1}H NMR (400 MHz, C_6D_6, 30 °C) δ 4.85 (d, 2H, $^4J_{HH}$ = 6.8 Hz, H_2C═C═CH), 6.04 (t, 1H, $^4J_{HH}$ = 6.8 Hz, H_2C═C═CH), 7.09−7.15 (m, 2H, Ph), 7.21−7.26 (m, 3H, Ph).

X-ray Crystallographic Analysis. All crystals were handled similarly. The crystals were mounted on the CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 113(2) K. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo−Kα (0.71075 Å) radiation. Crystal data and structure refinement parameters are listed in Supporting Information. The structures were solved by SHELXL-97[16] and SIR2008,[17] refined on F^2 by a full-matrix least-squares method, using SHELXL-97.[16] Non-hydrogen atoms were anisotropically refined. H atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(Fo^2 - Fc^2)^2]$ ($w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(Fo^2,0) + 2Fc^2)/3$ with $\sigma^2(Fo^2)$ from counting statistics. The functions *R*1 and *wR*2 were $(\Sigma||Fo| - |Fc||)/\Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2/\Sigma(wFo^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecule.[18]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00395.

NMR spectra for the metal complexes and protonation of **7a−c** by $PhNHCH_3$ (PDF)

Accession Codes

CCDC 1551191−1551192 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) See some selected reviews: (a) Hoffmann-Röder, A.; Krause, N. *Angew. Chem., Int. Ed.* **2004**, *43*, 1196−1216. (b) Alcaide, B.; Almendros, P.; Aragoncillo, C. *Chem. Soc. Rev.* **2010**, *39*, 783−816. (c) Pinho e Melo, T. M. V. D. *Monatsh. Chem.* **2011**, *142*, 681−697. (d) Adams, C. S.; Weatherly, C. D.; Burke, E. G.; Schomaker, J. M. *Chem. Soc. Rev.* **2014**, *43*, 3136−3163. (e) Tejedor, D.; Méndez-Abt, G.; Cotos, L.; García-Tellado, F. *Chem. Soc. Rev.* **2013**, *42*, 458−471. (f) Tsuji, J.; Mandai, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *34*, 2589−2612. (g) Vizer, S. A.; Sycheva, E. S.; Al-Quntar, A.; Kurmankulov, N. B.; Yerzhanov, K. B.; Dembitsky, V. M. *Chem. Rev.* **2015**, *115*, 1475−1502. (h) Yoshida, M. *Chem. Pharm. Bull.* **2012**, *60*, 285−299. (i) Müller, T. J. *Eur. J. Org. Chem.* **2001**, *2001*, 2021−2033. (j) Arshadi, S.; Vessally, E.; Edjlali, L.; Ghorbani-Kalhor, E.; Hosseinzadeh-Khanmiri, R. *RSC Adv.* **2017**, *7*, 13198−13211.

(2) (a) Castelhano, A. L.; Pliura, D. H.; Taylor, G. J.; Hsieh, K. C.; Krantz, A. *J. Am. Chem. Soc.* **1984**, *106*, 2734−2735. (b) Buynak, J. D.; Borate, H. B.; Husting, C.; Hurd, T.; Vallabh, J.; Matthew, J.; Lambert, J.; Siriwardane, U. *Tetrahedron Lett.* **1988**, *29*, 5053−5056. (c) Marshall, J. A.; Wang, X.-J. *J. Org. Chem.* **1990**, *55*, 6246−6248. (d) Aurrecoechea, J. M.; Fananas-San Antón, R. *J. Org. Chem.* **1994**, *59*, 702−704. (e) Ruan, R.; Zhang, J.; Zhou, X.; Cai, R. *Chem. Commun.* **2002**, 538−539. (f) Adams, C. S.; Boralsky, L. A.; Guzei, I. A.; Schomaker, J. M. *J. Am. Chem. Soc.* **2012**, *134*, 10807−10810.

(3) (a) Walker, M. E. *Chem. Rev.* **1992**, *92*, 97−112. (b) Nakagawa, T.; Kasatkin, A.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 3207−3210. (c) Usanov, D. L.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 8169−8172. (d) Fandrick, D. R.; Fandrick, K. R.; Reeves, J. T.; Tan,

DOI: 10.1021/acs.organomet.7b00395
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Z.; Johnson, C. S.; Lee, H.; Song, J. J.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* **2010**, *12*, 88−91. (e) Sai, M.; Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 3294−3298. (f) Wisniewska, H. M.; Jarvo, E. R. *Chem. Sci.* **2011**, *2*, 807−810. (g) Fandrick, D. R.; Saha, J.; Fandrick, K. R.; Sanyal, S.; Ogikubo, J.; Lee, H.; Roschangar, F.; Song, J. J.; Senanayake, C. H. *Org. Lett.* **2011**, *13*, 5616−5619. (h) Ardolino, M. J.; Morken, J. P. *J. Am. Chem. Soc.* **2012**, *134*, 8770−8773. (i) Vieira, E. M.; Haeffner, F.; Snapper, M. L.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2012**, *51*, 6618−6621. (j) Bejjani, J.; Botuha, C.; Chemla, F.; Ferreira, F.; Magnus, S.; Pérez-Luna, A. *Organometallics* **2012**, *31*, 4876−4885. (k) Muñoz-Bascõn, J.; Sancho-Sanz, I.; Álvarez-Manzaneda, E.; Rosales, A.; Oltra, J. E. *Chem. - Eur. J.* **2012**, *18*, 14479−14486. (l) Fandrick, K. R.; Ogikubo, J.; Fandrick, D. R.; Patel, N. D.; Saha, J.; Lee, H.; Ma, S.; Grinberg, N.; Busacca, C. A.; Senanayake, C. H. *Org. Lett.* **2013**, *15*, 1214−1217. (m) Mszar, N. W.; Haeffner, F.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2014**, *136*, 3362−3365. (n) Ruiz-Muelle, A. B.; Oña-Burgos, P.; Ortuño, M. A.; Oltra, J. E.; Rodríguez-García, I.; Fernández, I. *Chem. - Eur. J.* **2016**, *22*, 2427−2439.

(4) (a) Hajela, S.; Schaefer, W. P.; Bercaw, J. E. *J. Organomet. Chem.* **1997**, *532*, 45−53. (b) Reich, H.; Thompson, J. *Org. Lett.* **2000**, *2*, 783−786. (c) Jammi, S.; Mouysset, D.; Siri, D.; Bertrand, M. P.; Feray, L. *J. Org. Chem.* **2013**, *78*, 1589−1603.

(5) (a) Kurosawa, H.; Ogoshi, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 973−984. (b) Chen, J.-T. *Coord. Chem. Rev.* **1999**, *192*, 1143−1168. (c) Wojcicki, A. *Inorg. Chem. Commun.* **2002**, *5*, 82−97.

(6) (a) Blosser, P. W.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1993**, *12*, 1993−1995. (b) Stang, P. J.; Crittell, C. M.; Arif, A. M. *Organometallics* **1993**, *12*, 4799−4804. (c) Baize, M. W.; Blosser, P. W.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1996**, *15*, 164−173. (d) Tsutsumi, K.; Ogoshi, S.; Nishiguchi, S.; Kurosawa, H. *J. Am. Chem. Soc.* **1998**, *120*, 1938−1939. (e) Yabe-yoshida, M.; Kabuto, C.; Kabuto, K.; Kwon, E.; Sakaba, H. *J. Am. Chem. Soc.* **2009**, *131*, 9138−9139.

(7) (a) Krivykh, V. V.; Taits, E. S.; Petrovskii, P. V.; Struchkov, Y. T.; Yanovskii, A. I. *Mendeleev Commun.* **1991**, *1*, 103−104. (b) Casey, C. P.; Selmeczy, A. D.; Nash, J. R.; Yi, C. S.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1996**, *118*, 6698−6706. (c) Taits, E. S.; Petrovskii, P. V.; Krivykh, V. K. *Russ. Chem. Bull.* **1999**, *48*, 1774−1781.

(8) (a) Blosser, P. W.; Gallucci, J. C.; Wojcicki, A. *J. Am. Chem. Soc.* **1993**, *115*, 2994−2995. (b) Blosser, P. W.; Gallucci, J. C.; Wojcicki, A. *J. Organomet. Chem.* **2000**, *597*, 125−132. (c) Denomme, D. R.; Dumbris, S. M.; Hyatt, I. F. D.; Abboud, K. A.; Ghiviriga, I.; McElwee-White, L. *Organometallics* **2010**, *29*, 5252−5256.

(9) (a) Rodriguez, G.; Bazan, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 343−352. (b) Norambuena, V. F. Q.; Heeres, H. J.; Meetsma, A.; Teuben, J. H.; Hessen, B. *Organometallics* **2008**, *27*, 5672−5683. (c) Kaneko, H.; Nagae, H.; Tsurugi, H.; Mashima, K. *J. Am. Chem. Soc.* **2011**, *133*, 19626−19629.

(10) Karplus, M.; Grant, I. *Proc. Natl. Acad. Sci. U. S. A.* **1959**, *45*, 1269−1273.

(11) (a) Ungváry, F.; Wojcicki, A. *J. Organomet. Chem.* **1990**, *396*, 95−104. (b) Elsevier, C. J.; Kleijn, H.; Boersma, J.; Vermeer, P. *Organometallics* **1986**, *5*, 716−720. (c) Keng, R.-S.; Lin, Y.-C. *Organometallics* **1990**, *9*, 289−291. (d) Shuchart, C. E.; Willis, R. R.; Wojcicki, A. *J. Organomet. Chem.* **1992**, *424*, 185−198.

(12) (a) Ihara, E.; Tanaka, M.; Yasuda, H.; Kanehisa, N.; et al. *J. Organomet. Chem.* **2000**, *613*, 26−32. (b) Blosser, P. W.; Calligaris, M.; Schimpff, D. G.; Wojcicki, A. *Inorg. Chim. Acta* **2001**, *320*, 110−116. (c) Hughes, R. P.; Larichev, R. B.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2006**, *25*, 3943−3947. (d) Fan, G.; Xie, X.; Liu, Y.; Li, Y. *Organometallics* **2013**, *32*, 1636−1642. (e) Johnson, A.; Laguna, A.; Concepcion Gimeno, M. *J. Am. Chem. Soc.* **2014**, *136*, 12812−12815.

(13) See Supporting Information.

(14) Waterman, R. *Organometallics* **2013**, *32*, 7249−7263.

(15) (a) Nugent, W. A.; et al. *Organometallics* **1983**, *2*, 161−162. (b) Amin, S. B.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 10102−10103. (c) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203−219. (d) Fu, P.-F.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 10747−10748. (e) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880−1889. (f) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22−29.

(16) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112−122.

(17) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Siliqi, D.; Spagna, R. *J. Appl. Crystallogr.* **2007**, *40*, 609−613.

(18) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.

DOI: 10.1021/acs.organomet.7b00395
Organometallics XXXX, XXX, XXX−XXX