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# C−H Activation via Carbodiimide Insertion into Yttrium−Carbon Alkynide Bonds: An Organometallic Alder-ene Reaction

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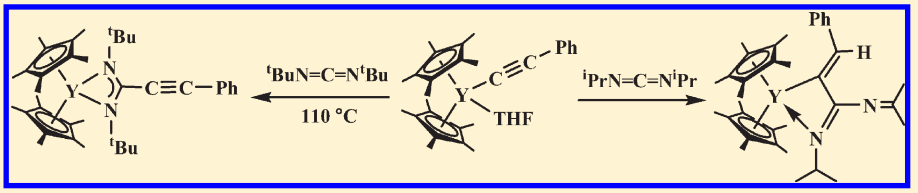
Supporting Information

**ABSTRACT:**




The yttrium alkynide $(C_5Me_5)_2Y(C{\equiv}CPh)(THF)$, **1**, and the related trienediyl $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PhC{=}C{=}C{=}CPh)$, **2**, can be isolated from the reaction of $(C_5Me_5)_2Y(\eta^3\text{-}CH_2CHCH_2)(THF)$ with phenylacetylene in THF and hexane, respectively. Complex **1** reacts with $^t$BuN=C=N$^t$Bu to afford the conventional amidinate insertion product $(C_5Me_5)_2Y[^t$BuNC(C≡CPh)N$^t$Bu-$\kappa^2N,N']$, **3**. However, the analogous reaction with *iso*-propyl and cyclohexyl carbodiimides involves C−H activation and forms the iminovinyl complexes $(C_5Me_5)_2Y[C(=CHPh)C(N=CMe_2)=N^i$Pr-$\kappa^2C,N]$, **4**, and $(C_5Me_5)_2Y\{C(=CHPh)C[N=C(CH_2)_5]=NCH(CH_2)_5\text{-}\kappa^2C,N\}$, **5**, respectively. The reaction is formally a variation of the Alder-ene reaction in which a C−H bond of the carbodiimide (ene) is activated and transferred to the alkynide ligand (enophile) bound to yttrium. The trienediyl **2** reacts with *iso*-propyl carbodiimide via conventional insertion to form a bis(amidinate) product with a trienediyl linker, namely, $(C_5Me_5)_2Y\text{-}[\mu\text{-}\kappa^2\text{-}(^i$PrN)$_2$C−C(Ph)=C=C=C(Ph)−C(N$^i$Pr)$_2$]Y$(C_5Me_5)_2$, **6**. The alkynide ligand in **1** is also modified in the reaction with benzylcyanide that forms an unusual insertion product, the amidonitrile complex $[(C_5Me_5)_2Y\{\mu\text{-}N(H)C(CH_2Ph)=C[C(Ph)=CHPh]C{\equiv}N\}]_2$, **7**.

## INTRODUCTION

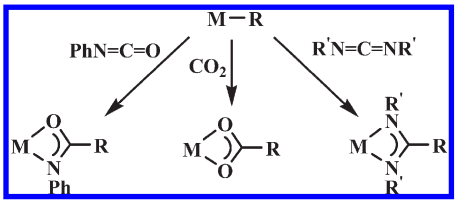
Recent studies in f element chemistry have shown that insertion of carbodiimides, RN=C=NR, into metal carbon bonds is a useful method to change the coordination environment of organometallic complexes.[1−8] Although carbodiimides are isoelectronic versions of common insertion substrates, such as $CO_2$,[9−14] and RNCO,[11,12,15] they offer important alternatives in that the amidinate ligand has substituents on both donor atoms in the products (Scheme 1). In addition to this increased steric control compared to $CO_2$ or PhNCO insertion products, carbodiimides deliver two strongly donating nitrogen atoms.

Formation of amidinate complexes by insertion of a carbodiimide into a metal alkynide bond is less common. However, reactions have been reported for Li,[16] Ca,[17] Y,[18,19] Sm,[20] and U[4] complexes, and in some cases, catalytic formation of the corresponding amidines has been observed.[17−19] For example, Hou and co-workers[18] reported carbodiimide insertion with the bridged yttrium alkynide, $\{[Me_2Si(C_5Me_4)(NPh)]Y(\mu\text{-}C{\equiv}CPh)(THF)\}_2$, to form $[Me_2Si(C_5Me_4)(NPh)]Y[^t$BuNC(C≡CPh)N$^t$Bu-$\kappa^2N,N'](THF)$. Subsequent addition of phenylacetylene liberated the alkynylamidine, $^t$BuN=C(C≡CPh)N(H)$^t$Bu, with concomitant formation of the starting alkynide. Catalysis was possible with a range of substituents on both the carbodiimide and the alkyne components.

We report here on yttrium alkynide carbodiimide insertion chemistry examined as part of a study of the reaction chemistry of $(C_5Me_5)_2Y(C{\equiv}CPh)(THF)$, **1**, the THF analogue of $(C_5Me_5)_2Y(C{\equiv}CPh)(Et_2O)$, previously prepared from $(C_5Me_5)_2Y[CH(SiMe_3)_2]$ and phenylacetylene.[21] Surprisingly, the course of the reaction was highly dependent upon the nature of R in the RN=C=NR substrate. Specifically, C−H bond activation and reduction of the alkynide C≡C bond was observed when the R group was a secondary alkyl. Analysis of the reaction chemistry indicated that this was an organometallic version of the Alder-ene reaction (Scheme 2).[22]

Two examples of the organometallic Alder-ene reaction are described as well as the synthesis and structure of the solvated alkynide precursor, **1**, and the related trienediyl complex, $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PhC{=}C{=}C{=}CPh)$, **2**, obtained by formal coupling of two alkynide ligands in unsolvated

**Scheme 1. Insertion with $CO_2$ and Isoelectronic Analogues**

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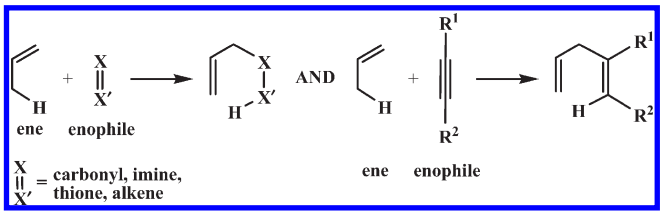
**Scheme 2. General Examples of the Alder-ene Reaction**




"$(C_5Me_5)_2Y(C{\equiv}CPh)$".[21,23] An additional reaction in which insertion leads to an unexpected product and reduction of the triple bond in **1** is also reported: the formation of an amidonitrile complex from **1** and benzylnitrile.

## EXPERIMENTAL SECTION

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line, high-vacuum line, and glovebox techniques under an argon atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories, dried over NaK alloy, degassed by three freeze−pump−thaw cycles, and vacuum-transferred before use. $(C_5Me_5)_2Y(\eta^3\text{-}CH_2CHCH_2)(THF)$ was prepared according to the literature procedure.[24] Cyclohexylcarbodiimide was sublimed ($10^{-5}$ Torr) and *iso*-propyl- and *tert*-butylcarbodiimide, phenylacetylene, and benzylnitrile were stored over molecular sieves overnight and freeze−pump−thaw degassed three times prior to use. All other reagents were purchased from Aldrich and used as received. The $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker GN500 or CRYO500 MHz spectrometer at 298 K, unless otherwise stated, and referenced internally to residual protio-solvent resonances. $^{89}Y$ NMR spectra were recorded on an AVANCE600 MHz spectrometer operating at 29.4 MHz and referenced externally to $Y(NO_3)_3\cdot 6H_2O$ in $D_2O$. HMQC and HMBC experiments were performed to aid in the assignment of spectral resonances. Infrared spectra were recorded as KBr pellets on a Varian FTS 1000 FT-IR spectrometer. Elemental analyses were recorded on a PerkinElmer 2400 Series CHNS elemental analyzer.

**$(C_5Me_5)_2Y(C{\equiv}CPh)(THF)$, 1.** Complex **1** was made by a variation of the synthesis of $(C_5Me_5)_2Y(C{\equiv}CPh)(Et_2O)$ from $(C_5Me_5)_2Y[CH(SiMe_3)_2]$ and phenylacetylene.[21] A solution of HC≡CPh (128 mg, 1.25 mmol) in THF (5 mL) was added to a stirred yellow solution of $(C_5Me_5)_2Y(\eta^3\text{-}CH_2CHCH_2)(THF)$ (500 mg, 1.25 mmol) in THF (10 mL). Within 1 min, gas evolution was observed (presumably propene) and the yellow color faded from the reaction mixture. After the mixture was stirred for 16 h, volatiles were removed under reduced pressure to afford an off-white crystalline solid. This was washed quickly with hexane (3 mL) and the yellow solution saved. The bulk solid was dissolved in hot hexane (3 mL) from which X-ray quality single crystals formed by slow cooling to ambient temperature overnight. Decantation of the mother liquor and drying of the crystals under reduced pressure afforded white **1** (307 mg, 46%). Combination of the mother liquor and original hexane washings, followed by concentration and overnight storage at −30 °C, afforded a second crop of crystalline material (200 mg, 30%). $^1H$ NMR ($C_6D_6$): $\delta$ 7.70 (d, 2H, $^3J_{HH}$ = 7.7 Hz, *o*-Ph), 7.14 (m, 2H, *m*-Ph), 7.03 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *p*-Ph), 3.53 (bs, 4H, THF), 2.10 (s, 30H, $C_5Me_5$), 1.16 (bs, 4H, THF). $^{13}C$ NMR ($C_6D_6$): $\delta$ 147.3 (d, $^1J_{CY}$ = 70.4 Hz, Y−*C*≡CPh), 131.4 (*m*-Ph), 128.6 (*i*-Ph), 128.0 (*o*-Ph), 125.3 (*p*-Ph), 116.9 ($C_5Me_5$), 109.6 (d, $^2J_{CY}$ = 12.6 Hz, Y−C≡*C*Ph), 70.9 and 24.8 (THF), 11.5 ($C_5Me_5$). IR: 2969 s, 2895 s, 2855 s, 2722 w, 1974 m, 1593 m, 1483 s, 1439 m, 1377 m, 1244 w, 1196 m, 1171 w, 1066 w, 1016 s, 929 s, 875 m, 775 m, 757 s, 694 s, 670 w, 617 w, 592 w, 532 m, 519 m $cm^{-1}$. Anal. Calcd for $C_{32}H_{43}OY$: C, 72.15; H, 8.15. Found: C, 71.51; H, 7.97.

**$[(C_5Me_5)_2Y](\mu\text{-}\eta^2{:}\eta^2\text{-}PhC{=}C{=}C{=}CPh)$, 2.** A solution of HC≡CPh (22 mg, 0.21 mmol) in hexane (5 mL) was added to a stirred yellow solution of $(C_5Me_5)_2Y(\eta^3\text{-}CH_2CHCH_2)(THF)$ (100 mg, 0.21 mmol) in hexane (5 mL) with stirring. Within 1 min, gas evolution was observed (presumably propene) and a transient colorless solution formed, which proceeded to turn yellow, then orange, with stirring for 16 h. Volatiles were removed under reduced pressure, affording an orange solid. This was dissolved in hot benzene (3 mL), and X-ray quality single crystals formed by slow cooling to ambient temperature overnight. Decantation of the mother liquor, washing with benzene (2 mL), and drying under reduced pressure afforded orange crystalline **2** (33 mg, 34%). $^1H$ NMR ($C_6D_6$): $\delta$ 7.30 (t, 4H, $^3J_{HH}$ = 7.5 Hz, *m*-Ph), 7.08 (t, 2H, $^3J_{HH}$ = 7.5 Hz, *p*-Ph), 6.75 (d, 4H, $^3J_{HH}$ = 7.5 Hz, *o*-Ph), 2.08 (s, 60H, $C_5Me_5$). $^{13}C$ NMR ($C_6D_6$): $\delta$ 197.9 (d, $^1J_{CY}$ = 37.7 Hz, Y−*C*), 155.2 (d, $^2J_{CY}$ = 3.8 Hz, Y−C≡*C*), 141.4 (*i*-Ph), 131.1, 128.5, 128.2 (Ph−*C*H), 119.2 ($C_5Me_5$), 11.7 ($C_5Me_5$). IR: 3064 w, 3028 w, 2900 m, 2857 m, 2725 w, 1588 w, 1551 m, 1472 m, 1438 m, 1379 m, 1278 w, 1181 w, 1155 w, 1123 w, 1066 w, 1023 w, 990 w, 810 w, 759 m, 681 s, 628 m, 609 m, 593 w, 544 w, 463 w $cm^{-1}$. Anal. Calcd for $C_{56}H_{70}Y_2$: C, 73.02; H, 7.68. Found: C, 74.31; H, 7.76. The $^1H$ NMR spectrum of the mother liquor showed the presence of **1** as a byproduct.

**$(C_5Me_5)_2Y[^tBuNC(C{\equiv}CPh)N^tBu\text{-}\kappa^2N,N']$, 3.** Toluene solutions of **1** (100 mg, 0.19 mmol in 5 mL) and $^tBuN{=}C{=}N^tBu$ (30 mg, 0.19 mmol in 5 mL) were combined in a Schlenk tube equipped with a greaseless stopcock. The colorless reaction mixture turned yellow after heating at 110 °C for 2 h. The solvent was removed under reduced pressure to afford a yellow solid. X-ray quality single crystals were obtained overnight from a concentrated hexane solution at −30 °C. Separation of the mother liquor, followed by washing with cold hexane (3 mL) and drying under reduced pressure, afforded **3** as a yellow crystalline solid (79 mg, 68%). $^1H$ NMR ($C_6D_6$): $\delta$ 7.45 (m, 2H, Ph−*CH*), 6.98 (m, 3H, Ph−*CH*), 2.10 (s, 30H, $C_5Me_5$), 1.60 [bs $\nu_{1/2}$ = 28.5 Hz, 18H, $C(CH_3)_3$]. $^{13}C$ NMR ($C_6D_6$): $\delta$ 152.5 (NCN), 130.8, 129.1, and 128.5 (Ph−*CH*), 122.5 (*i*-Ph), 117.9 ($C_5Me_5$), 97.8 (C≡CPh), 84.5 (d, $^3J_{CY}$ = 6.3 Hz, *C*≡CPh), 52.8 [$C(CH_3)_3$], 31.8 [broad, $C(CH_3)_3$], 12.3 ($C_5Me_5$). IR: 3068 w, 2977 m, 2903 m, 2859 m, 2723 w, 2210 m, 1617 w, 1597 w, 1574 w, 1492 m, 1421 s, 1384 s, 1356 s, 1226 m, 1197 s, 1072 m, 1025 w, 915 w, 892 w, 870 w, 797 w, 755 m, 705 m, 688 m, 593 w, 549 w, 530 w, 464 w $cm^{-1}$. Anal. Calcd for $C_{37}H_{53}N_2Y$: C, 72.28; H, 8.71; N, 4.56. Found: C, 71.75; H, 8.99; N, 4.47.

**$(C_5Me_5)_2Y[C(=CHPh)C(N{=}CMe_2){=}N^iPr\text{-}\kappa^2C,N]$, 4.** Portionwise addition of a THF solution of $^iPrN{=}C{=}N^iPr$ (24 mg, 0.19 mmol in 5 mL) to a stirred THF solution of **1** (100 mg, 0.19 mmol in 5 mL) elicited an immediate color change to bright yellow. After stirring at room temperature for 16 h, volatiles were removed under reduced pressure to afford a yellow solid (108 mg), which was dissolved in hot hexane (2 mL) and stored overnight at −30 °C. An amorphous yellow solid was isolated after decantation of the mother liquor. Washing in cold hexane (2 mL) and drying under reduced pressure afforded yellow **4** (76 mg, 69%). $^1H$ NMR ($C_6D_6$): $\delta$ 7.44 (d, 1H, $^3J_{HY}$ = 5.6 Hz, YC=*CH*), 7.41 (d, 2H, $^3J_{HH}$ = 7.5 Hz, *o*-Ph), 7.27 (m, 2H, *m*-Ph), 7.16 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *p*-Ph) partially obscured by solvent, 3.49 [sept, 1H, $^3J_{HH}$ = 6.5 Hz, NC*H*$(CH_3)_2$], 2.05 (s, 30H, $C_5Me_5$), 1.71 [s, 6H, N=C($CH_3$)$_2$], 1.16 [d, 6H, $^3J_{HH}$ = 6.5 Hz, NCH($CH_3$)$_2$]. $^{13}C$ NMR ($C_6D_6$): $\delta$ 180.3 (d, $^1J_{CY}$ = 42.8 Hz, Y−*C*), 174.9 (NCN), 163.5 [N=*C*$(CH_3)_2$], 143.7 (YC=*CH*), 141.7 (d, $^3J_{CY}$ = 1.2 Hz, *i*-Ph), 128.4 (*o*-Ph), 127.8 (*m*-Ph), 127.3 (*p*-Ph), 117.3 ($C_5Me_5$), 48.2 [NCH$(CH_3)_2$], 25.4 [N=C-$(CH_3)_2$], 23.1 [NCH$(CH_3)_2$], 11.7 ($C_5Me_5$). $^{89}Y$ ($C_6D_6$): $\delta$ −24.2. $^1H\{^{89}Y\}$ ($C_6D_6$): $\delta$ 7.44 (s, 1H, YC=*CH*), 7.41 (d, 2H, $^3J_{HH}$ = 7.5 Hz, *o*-Ph), 7.27 (m, 2H, *m*-Ph), 7.16 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *p*-Ph) partially obscured by solvent, 3.49 [sept, 1H, $^3J_{HH}$ = 6.5 Hz, NC*H*$(CH_3)_2$], 2.05 (s, 30H, $C_5Me_5$), 1.71 [s, 6H, N=C($CH_3$)$_2$], 1.16 [d, 6H, $^3J_{HH}$ = 6.5 Hz,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NCH($CH_3$)$_2$]. A $^{89}$Y−$^1$H HMQC experiment confirmed the coupling between yttrium and (C═C*H*) and revealed the presence of weak coupling to [NC*H*(CH$_3$)$_2$] and (C$_5$*Me*$_5$). IR: 2971 m, 2906 s, 2859 s, 2724 w, 1677 s, 1596 w, 1509 s, 1440 m, 1371 m, 1329 w, 1279 w, 1228 m, 1212 m, 1170 w, 1121 w, 1068 w, 1023 w, 969 w, 924 w, 894 w, 853 w, 793 w, 755 m, 692 s, 618 w, 589 w, 516 w, 502 m, 487 m, 474 m cm$^{-1}$. Anal. Calcd for $C_{35}H_{49}N_2Y$: C, 71.64; H, 8.43; N, 4.78. Found: C, 71.43; H, 9.18; N, 4.72.

**(C$_5$Me$_5$)$_2$Y{C(═CHPh)C[N═C(CH$_2$)$_5$]═N(Cy)-κ$^2$*C,N*}, 5.** Portionwise addition of a THF solution of CyN═C═NCy (39 mg, 0.19 mmol in 5 mL) to a stirred THF solution of **1** (100 mg, 0.19 mmol in 5 mL) elicited an immediate color change to bright yellow. After stirring at room temperature for 16 h, volatiles were removed under reduced pressure to afford a yellow solid (125 mg). This was dissolved in hot hexane (2 mL) and stored overnight at ambient temperature. The X-ray quality yellow single crystals of **5** were isolated from solution by decantation of the mothor liquor, washed in cold hexane (2 mL), and dried under reduced pressure (85 mg, 68%). $^1$H NMR (C$_6$D$_6$): δ 7.55 (d, 1H, $^3J_{HY}$ = 5.6 Hz, YC═C*H*), 7.45 (d, 2H, $^3J_{HH}$ = 7.5 Hz, *o*-Ph), 7.29 (m, 2H, *m*-Ph), 7.17 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *p*-Ph) partially obscured by solvent, 3.32 [m, 1H, NC*H*(CH$_2$)$_5$], 2.08 (s, 30H, C$_5$*Me*$_5$), 2.30−1.10 (m, 20H, C*H*$_2$). $^{13}$C (C$_6$D$_6$): δ 180.6 (d, $^1J_{CY}$ = 42.8 Hz, Y-*C*), 174.7 (NCN), 169.5 [N═*C*(CH$_2$)$_5$], 143.9 (YC═*C*H), 141.7 (d, $^3J_{CY}$ = 1.2 Hz, *i*-Ph), 128.5 (*o*-Ph), 127.9 (*m*-Ph), 127.4 (*p*-Ph), 117.3 (*C*$_5$Me$_5$), 57.7 [NCH(CH$_2$)$_5$], 36.7, 33.0, 27.8, 26.0, 25.7, and 25.1 (CH$_2$), 11.8 (C$_5$*Me*$_5$). $^{89}$Y (C$_6$D$_6$): δ −23.8. $^1$H{$^{89}$Y} (C$_6$D$_6$): δ 7.55 (s, 1H, YC═C*H*), 7.45 (d, 2H, $^3J_{HH}$ = 7.5 Hz, *o*-Ph), 7.29 (m, 2H, *m*-Ph), 7.17 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *p*-Ph) partially obscured by solvent, 3.32 [m, 1H, NC*H*(CH$_2$)$_5$], 2.08 (s, 30H, C$_5$*Me*$_5$), 2.30−1.10 (m, 20H, C*H*$_2$). A $^{89}$Y−$^1$H HMQC experiment also confirmed the coupling between yttrium and (C═C*H*) and revealed the presence of weak coupling to [NC*H*(CH$_2$)$_5$] and (C$_5$*Me*$_5$). IR: 3057 w, 3020 w, 2934 s, 2854 s, 2723 w, 1670 s, 1597 w, 1514 s, 1443 m, 1364 w, 1347 w, 1280 w, 1254 w, 1229 w, 1200 m, 1178 m, 1127 w, 1107 w, 1074 w, 1024 w, 994 w, 972 w, 922 w, 887 w, 845 w, 780 m, 750 m, 693 s, 591 w, 578 w, 508 m, 470 m cm$^{-1}$. Anal. Calcd for $C_{41}H_{57}N_2Y$: C, 73.83; H, 8.63; N, 4.20. Found: C, 73.62; H, 8.79; N, 4.20.

**NMR Scale Synthesis of (C$_5$Me$_5$)$_2$Y[μ-κ$^2$-($^i$PrN)$_2$C−C(Ph)═C═C═C(Ph)−C(N$^i$Pr)$_2$]Y(C$_5$Me$_5$)$_2$, 6.** Neat $^i$PrN═C═N$^i$Pr (3.3 μL, 0.02 mmol) was added to an NMR tube fitted with a Young's tap containing an orange C$_6$D$_6$ (1 mL) solution of **2** (10 mg, 0.01 mmol). The tube was sealed and heated at 100 °C for 7 days, over which time the color of the solution faded and a few X-ray quality orange crystals formed.

**[(C$_5$Me$_5$)$_2$Y{μ-N(H)C(CH$_2$Ph)═C[C(Ph)═CHPh]C≡N}]$_2$, 7.** Portionwise addition of a toluene solution of PhCH$_2$C≡N (66 mg, 0.56 mmol in 5 mL) to a stirred toluene solution of **1** (150 mg, 0.28 mmol in 5 mL) elicited an immediate color change to bright orange. After stirring at room temperature for 3 h, volatiles were removed under reduced pressure to afford an orange residue (196 mg), which was dissolved in warm toluene (3 mL) and stored for 4 days at −30 °C. A pale yellow solid formed, which was isolated from solution by decantation of the mother liquor, washed in cold hexane (2 mL), and dried under reduced pressure (62 mg). A second crop of solid (38 mg) was isolated after storing the mother liquor at −30 °C overnight (combined yield of **7**: 100 mg, 51%). $^1$H NMR (C$_6$D$_6$): δ 7.62 (d, 2H, $^3J_{HH}$ = 7.0 Hz, *Ph*), 7.15−6.80 (m, 13H, *Ph*), 6.75 (s, 1H, C*H*), 4.84 (s, 1H, N*H*), 3.50 (s, 2H, C*H*$_2$), 1.93 (s, 30H, C$_5$*Me*$_5$). $^{13}$C NMR (C$_6$D$_6$): δ 182.6 (d, $^2J_{CY}$ = 2.5 Hz, *C*≡N), 141.0, 138.3, 136.8, 136.3 (*q*-Ph/C═C) the remaining two phenyl or alkene quaternary carbons could not be resolved, 130.6, 130.3, 130.2, 129.4, 129.2, 129.1, 128.7, 128.6, 128.5, 128.2, 128.0, 127.8, 127.1, 126.9 (*o*-, *m*-, *p*-Ph), 124.1 (C═*C*H), 117.7 (C$_5$Me$_5$), 43.3 (*C*H$_2$), 10.7 (C$_5$*Me*$_5$). IR: 3430 w, 3378 w, 3325 w, 3058 w, 3023 w, 2902 m, 2857 m, 2725 w, 2122 s, 1599 w, 1501 s, 1444 m, 1378 m, 1256 w, 1180 m, 1156 m, 1077 w, 1022 w, 949 w, 925 w, 774 m, 756 m, 730 m, 697 s, 605 w, 560 w, 538 w, 464 w cm$^{-1}$. Anal. Calcd for $C_{44}H_{47}N_2Y$: C, 76.05; H, 6.83; N, 4.03. Found: C, 75.72; H, 7.23; N, 3.88.

**X-ray Crystallographic Data.** Information on X-ray data collection, structure determination, and refinement for **1**−**3** and **5**−**7** are given in the Supporting Information.

## RESULTS

**Reactivity of (C$_5$Me$_5$)$_2$Y(η$^3$-CH$_2$CHCH$_2$)(THF) and HC≡CPh.** Complex **1** was made by a variation of the syntheses of (C$_5$Me$_5$)$_2$Y(C≡CPh)(Et$_2$O)[21] and {[Me$_2$Si(C$_5$Me$_4$)(NPh)]Y(μ-C≡CPh)(THF)}$_2$[18] from phenylacetylene with (C$_5$Me$_5$)$_2$Y[CH(SiMe$_3$)$_2$] and [Me$_2$Si(C$_5$Me$_4$)(NPh)]Y[CH$_2$SiMe$_3$], respectively, using the allyl precursor (C$_5$Me$_5$)$_2$Y(η$^3$-CH$_2$CHCH$_2$)(THF). Bis(pentamethylcyclopentadienyl) rare earth allyl complexes have previously been shown to be convenient reagents to deliver the reactivity of a metal alkyl bond.[11,25,26]

Addition of 1 equiv of phenylacetylene to a bright yellow THF solution of (C$_5$Me$_5$)$_2$Y(η$^3$-CH$_2$CHCH$_2$)(THF) resulted in fast evolution of propene and fading of the color to pale yellow. The monomeric terminal alkynide (C$_5$Me$_5$)$_2$Y(C≡CPh)(THF), **1**, was isolated in 76% yield (Scheme 3).

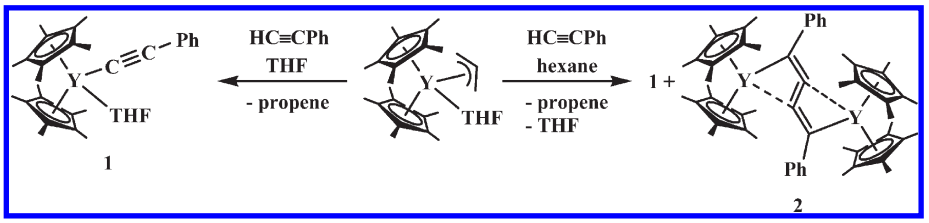
The NMR and IR spectra of **1** were consistent with those of (C$_5$Me$_5$)$_2$Y(C≡CPh)(Et$_2$O).[21] Because the latter complex had not been characterized by X-ray crystallography, complete structural data were obtained for **1**; see Figure 1 and Table S2 in the Supporting Information.

In contrast to the formation of **1** in THF, treatment of (C$_5$Me$_5$)$_2$Y(η$^3$-CH$_2$CHCH$_2$)(THF) with 1 equiv of phenylacetylene in hexane results in transient formation of a colorless solution that became dark orange with overnight stirring. Crystallization from hot benzene affords trienediyl complex [(C$_5$Me$_5$)$_2$Y]$_2$(μ-η$^2$:η$^2$-PhC═C═C═CPh), **2**, as orange crystals in low yield (Scheme 3) (Figure 2 and Table S3 in the Supporting Information). This complex arises from the formal coupling of two unsolvated (C$_5$Me$_5$)$_2$Y(C≡CPh) units. Similar complexes have been previously reported and structurally characterized.[23,28−31] NMR studies show that **1** is also a product of this reaction and the less soluble **2** is readily separated by precipitation from benzene.

The dark, intense color of **2** is unusual for an Y$^{3+}$ complex, but it is consistent with butatrienediyl formation.[28−31] The spectroscopic profile of **2** is similar to that of [(DAC)Y]$_2$(μ-PhC═C═C═CPh) (DAC = deprotonated 4,13-diaza-18-crown-6),[28] with the $^{13}$C NMR spectrum showing doublets at 197.9 ppm ($^1J_{CY}$ = 37.7 Hz, terminal carbon) and 155.2 ppm ($^2J_{CY}$ = 3.8 Hz, internal carbon) and an IR spectrum with ν(C═C) absorptions at 1588 and 1551 cm$^{-1}$. The facile formation of **2** contrasts with the analogous reaction with (C$_5$Me$_5$)$_2$Sm(C≡CPh)(THF), which required >120 °C for 3 days to get 40% of the coupled product.[23]

**Carbodiimide Reactivity.** Reactions of (C$_5$Me$_5$)$_2$Y(C≡CPh)(THF), **1**, with alkyl-substituted carbodiimides follow two different reaction pathways depending on the alkyl substituent. $^t$BuN═C═N$^t$Bu does not react at ambient temperature with **1**, but heating at 110 °C for 2 h affords the anticipated amidinate insertion product (C$_5$Me$_5$)$_2$Y[$^t$BuNC(C≡CPh)N$^t$Bu-κ$^2$*N,N*′], **3**, as a yellow solid in 68% yield (eq 1). The solid-state structure of **3** is shown in Figure 1, and the metrical parameters are listed in Table S2 (Supporting Information). The NMR spectra of **3** are consistent with its structure, and the IR spectrum displays a distinctive ν(C≡C)

**Scheme 3. Yttrium Allyl Reactivity with Phenylacetylene**



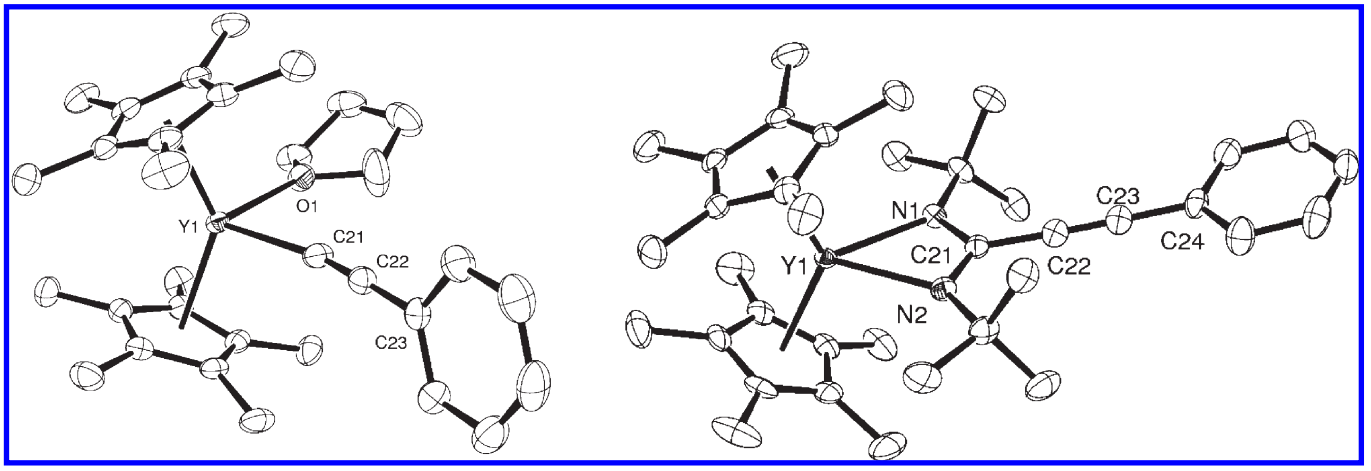




**Figure 1.** ORTEP[27] representation of $(C_5Me_5)_2Y(C{\equiv}CPh)(THF)$, **1**, (left) and $(C_5Me_5)_2Y[^tBuNC(C{\equiv}CPh)N^tBu\text{-}\kappa^2N,N']$, **3**, (right) drawn at the 50% probability level. Hydrogen atoms are omitted for clarity, and only one molecule of **3** present in the asymmetric unit is shown. Selected bond lengths (Å) and angles (deg): For **1**, Y1−O1 2.3988(12), Y1−C21 2.4071(18), C21−C22 1.206(2), (cnt)−Y1−(cnt) 137.7, O1−Y1−C21 91.10(5), Y1−C21−C22 169.04(15). For **3**, Y1−N1 2.3643(14), Y1−N2 2.3811(14), N1−C21 1.338(2), N2−C21 1.336(2), C21−C22 1.453(2), C22−C23 1.195(3), (cnt)−Y1−(cnt) 132.1, N1−Y1−N2 57.15(5), N1−C21−N2 116.20(15), C21−C22−C23 176.52(19).

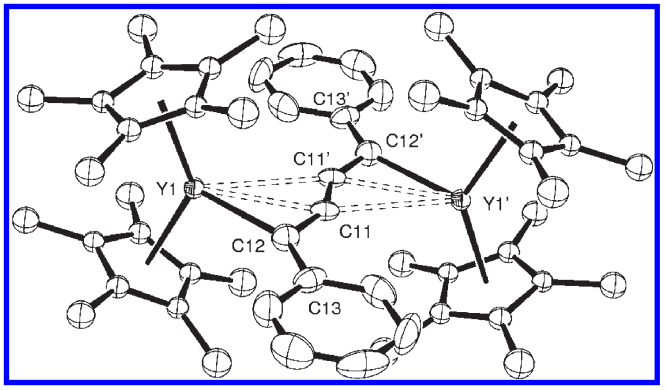
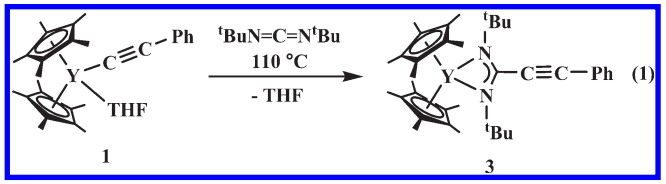



**Figure 2.** ORTEP representation of $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PhC{=}C{=}C{=}CPh)$, **2**, drawn at the 50% probability level. Hydrogen atoms and solvent are omitted for clarity, and only one component of the $(C_5Me_5)^{1-}$ disorder is shown.

stretch at 2210 $cm^{-1}$, comparable to that observed by Hou at 2205 $cm^{-1}$ in $[Me_2Si(C_5Me_4)(NPh)]Y[^tBuNC(C{\equiv}CPh)N^tBu\text{-}\kappa^2N,N']$(THF).[18]




In contrast, the reaction of **1** with RN=C=NR, where R = $^i$Pr or cyclohexyl, occurs within minutes at ambient temperature to afford the iminovinyl complexes $(C_5Me_5)_2Y[C(=CHPh)C(N{=}CMe_2){=}N^iPr\text{-}\kappa^2C,N]$, **4**, and $(C_5Me_5)_2Y\{C(=CHPh)C[N{=}C(CH_2)_5]{=}N(Cy)\text{-}\kappa^2C,N\}$, **5**, respectively (Scheme 4).

Complex **5** was identified by X-ray crystallography (Figure 3 and Table S4 in the Supporting Information), and the identity of **4** was established by analytical and spectral means in comparison with **5**.

The IR spectra of **4** and **5** are consistent with reduction of the alkyne bond during the reaction. No absorptions are observed in the $\nu(C{\equiv}C)$ stretching region. Instead, absorptions at 1677 and 1509 $cm^{-1}$ for **4** and at 1670 and 1514 $cm^{-1}$ for **5** are observed and assigned to $\nu(C{=}N)$ and $\nu(C{=}C)$, respectively. These values are close to those observed in the cyclic iminiumazetidinylidenemethyl complex $[(C_5H_5)Ru\{CH{=}CCPh_2N(Cy)CN{=}C(CH_2)_4CH_2\}(CO)(P^iPr_3)][BF_4]$, which has similar functionality [$\nu(C{=}N)$ 1679 $cm^{-1}$ and $\nu(C{=}C)$ 1528 $cm^{-1}$][32] (Figure 4).

The NMR spectra of **4** and **5** are similar. Both have the expected phenyl and $(C_5Me_5)^{1-}$ resonances, as well as resonances for the two different substituents on the nitrogen atoms. Each $^1H$ NMR spectrum also contains a doublet with $J$ = 5.6 Hz attributable to the YC=C*H* vinyl proton: at 7.44 ppm in **4** and 7.55 ppm in **5**. Few rare earth vinyl complexes are available for comparison,[33] but $(C_5Me_5)_2Y[CH{=}CHCH(Me)Et]$ has an analogous vinyl resonance with $^3J_{HY}$ = 4 Hz.[34]

The 5.6 Hz $^3J_{HY}$ coupling in **4** and **5** was confirmed by a $^1H\{^{89}Y\}$ NMR experiment in which the YC=C*H* doublet collapsed to a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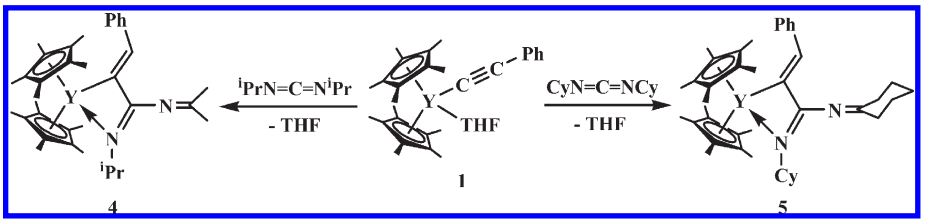
**Scheme 4. Alder-ene Reactivity With Carbodiimides**



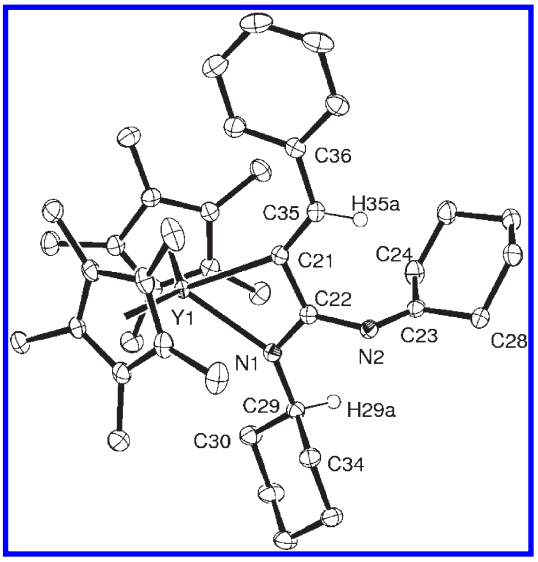




**Figure 3.** ORTEP representation of $(C_5Me_5)_2Y\{C(=CHPh)C[N=C(CH_2)_5]=NCH(CH_2)_5\text{-}\kappa^2C,N\}$, **5**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity, except H29a and H35a. Selected bond lengths (Å) and angles (deg): Y1−C21 2.4291(12), Y1−N1 2.4365(10), C21−C22 1.4782(17), C21−C35 1.3458(17), N1−C22 1.3063(16), N1−C29 1.4739(16), N2−C22 1.4003(16), N2−C23 1.2736(17), (cnt)−Y1−(cnt) 137.2, Y1−C21−C22 91.34(7), Y1−C21−C35 150.52(10), Y1−N1−C22 95.51(8), Y1−N1−C29 144.22(8), C22−C21−C35 118.11(11), C21−C22−N1 115.26(11), C21−C22−N2 121.12(11), N1−C22−N2 123.23(11), C22−N2−C23 124.43(11).

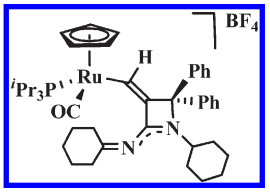



**Figure 4.** Comparison ruthenium complex.

singlet upon decoupling. A $^1H-^{89}Y$ HMQC experiment also showed coupling between yttrium and the vinyl proton and, in addition, revealed the presence of weak coupling with the "NC*H*" and $(C_5Me_5)^-$ protons. The $^{13}C$ NMR spectra of **4** and **5** are consistent with the formulation of these complexes, although the resonance assigned to the YC=CH vinyl carbon (confirmed by HMQC) does not appear as the expected yttrium coupled doublet, but rather as a singlet. The $^{89}Y$ NMR spectra of **4** and **5** are also similar, with resonances at −24.2 and −23.8 ppm, respectively. These are within the wide range of values observed for yttrium metallocenes.[35]

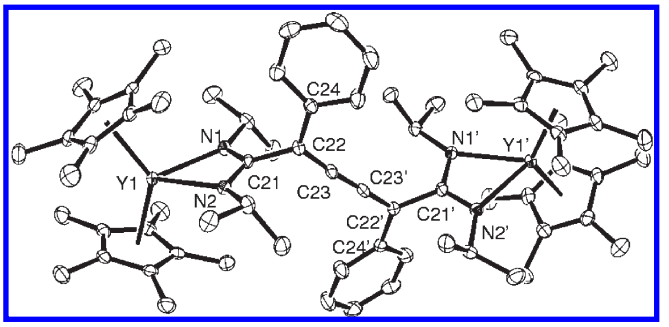
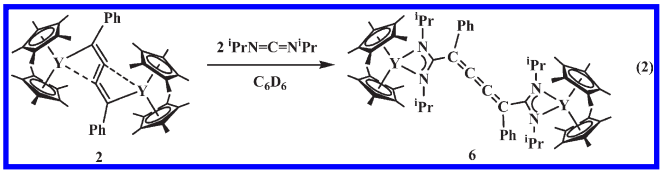



**Figure 5.** ORTEP drawing of $(C_5Me_5)_2Y[\mu\text{-}\kappa^2\text{-}(^iPrN)_2C-C(Ph)=C=C=C(Ph)-C(N^iPr)_2]Y(C_5Me_5)_2$, **6**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

In contrast to the reaction of $^i$PrN=C=N$^i$Pr with **1**, the trienediyl $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}PhC=C=C=CPh)$, **2**, reacts in a conventional way with the isopropyl carbodiimide (eq 2).




Carbodiimide insertion occurs at each Y−C bond to make a bimetallic complex containing a bridging ligand composed of two amidinates connected by a trienediyl linker $(C_5Me_5)_2Y[\mu\text{-}\kappa^2\text{-}(^iPrN)_2C-C(Ph)=C=C=C(Ph)-C(N^iPr)_2]Y(C_5Me_5)_2$, **6**. Crystals were obtained from an NMR scale reaction (Figure 5 and Table S5 in the Supporting Information).

The $^1H$ NMR spectrum of the solution showed a small amount of unreacted starting material and multiple aromatic and $(C_5Me_5)$ resonances that could not be satisfactorily assigned. Because only a small number of crystals formed and this indicated straightforward carbodiimide insertion, the system was not pursued further.

**Benzylnitrile Reactivity.** The reaction of **1** with 2 equiv of benzylnitrile did not give simple substitution of the THF, but instead led to the isolation of the amidonitrile complex $[(C_5Me_5)_2Y\{\mu\text{-}N(H)C(CH_2Ph)=C[C(Ph)=CHPh]C\equiv N\}]_2$, **7** (eq 3), identified by X-ray crystallography (Figure 6 and Table S6 in the Supporting Information). In this reaction, as in Scheme 4 above, insertion is accompanied by transfer of substitutents to the alkynide moiety in **1**.

Complex **7** is similar to the dimeric crotononitrileamido complex $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y[(\mu\text{-}N,N')\text{-}N(H)C(Me)=C(H)C\equiv N]\}_2$, prepared from $[Me_2Si(NCMe_3)(OCMe_3)]_2Y[CH(SiMe_3)_2]$ and MeCN.[36]


dx.doi.org/10.1021/om200419k |*Organometallics* 2011, 30, 4873–4881

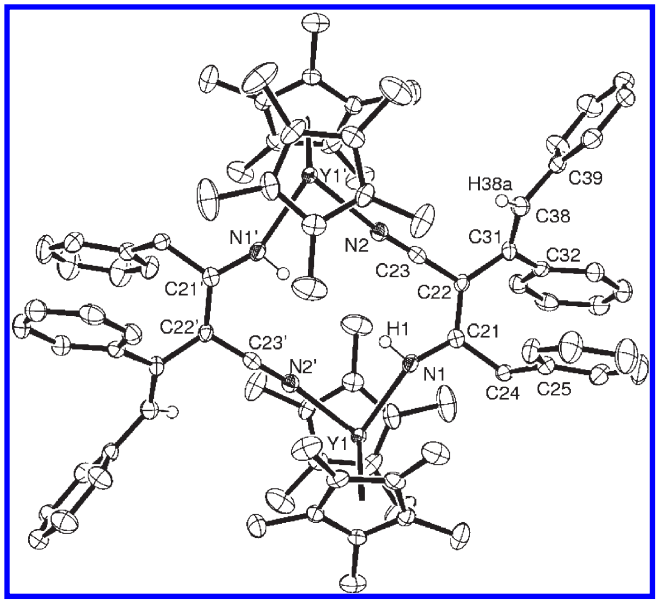
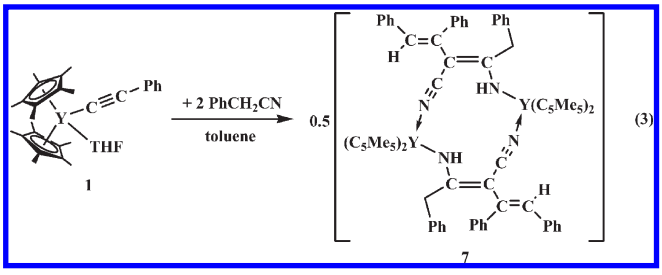



**Figure 6.** ORTEP representation of $[(C_5Me_5)_2Y\{\mu\text{-}N(H)C(CH_2Ph)=C[C(Ph)=CHPh]C\equiv N\}]_2$, **7**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity, except H1 and H38a. Selected bond lengths (Å) and angles (deg): Y1−N1 2.366(2), N1−C21 1.326(3), C21−C24 1.514(4), C21−C22 1.417(4), C22−C31 1.489(4), C31−C38 1.334(4), C22−C23 1.398(4), C23−N2 1.162(3), N2−Y1′ 2.351(2), (cnt)−Y1−(cnt) 138.7, N1−Y1−N2′ 82.05(8), Y1−N1−C21 149.9(2), N1−C21−C22 124.2(3), N1−C21−C24 115.9(2), C24−C21−C22 119.8(2), C21−C22−C31 128.4(2), C22−C23−N2 179.0(3), C22−C31−C38 121.3(3), C31−C22−C23 115.7(2), C23−N2−Y1′ 172.1(2).




The IR spectrum of **7** contains $\nu(C\equiv N)$ at 2122 $cm^{-1}$ and additional absorptions at 3300−3450 and 1500 $cm^{-1}$ due to the N−H and C=C stretches, respectively, similar to those observed for the crotononitrileamido complex above. The $^1H$ NMR spectrum shows single $(C_5Me_5)^{1-}$ and methylene resonances, as well as a complicated aromatic region consistent with the composition of **7**. Singlets at 6.75 and 4.84 ppm are assigned to the C=C*H* proton (confirmed by HMQC) and N*H* proton, respectively. The $^{13}C$ NMR spectrum is consistent with this and additionally shows a doublet at 182.6 ppm ($^2J_{CY}$ = 2.5 Hz) for the nitrile *C*≡N carbon.

**Structural Features.** Because most of the structural features in **1**−**3** and **5**−**7** are in the normal range (Tables S2−S6 in the Supporting Information), only a few select data will be discussed. For all of these complexes, the metallocene units have structural parameters within previously reported ranges.[37,38] For example, complex **1** (Figure 1) displays typical 2.367 and 2.377 Å Y−($C_5Me_5$ ring centroid) lengths and a 137.7° ($C_5Me_5$ ring centroid)−Y−($C_5Me_5$ ring centroid) bond angle.

The 2.407(2) Å Y1−C21(C≡CPh) length in eight coordinate $(C_5Me_5)_2Y(C\equiv CPh)(THF)$, **1**, can be compared to the 2.448(4) Å analogue in six coordinate $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(C\equiv CPh)(THF)$[39] and the 2.38(2) Å length in the eight coordinate "ate" complex $(C_5Me_5)_2Y(\mu\text{-}C\equiv CCMe_3)_2Li(THF)$.[40] The 1.206(2) Å C21−C22 bond distance in **1** is similar to the 1.217(5) and 1.24(2) Å lengths in these latter complexes.

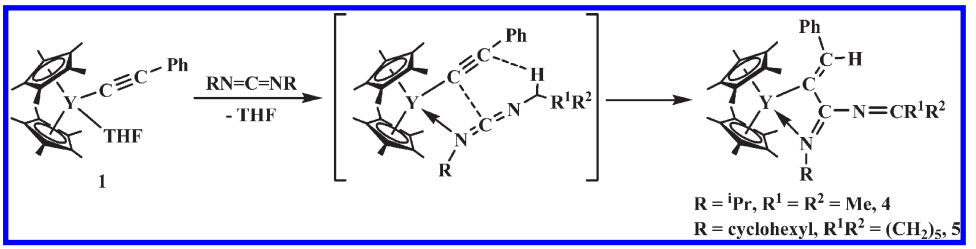
In the trienediyl $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}PhC=C=C=CPh)$, **2** (Figure 2), the 151.3(6)° C12−C11−C11′ angle (Table S3 in the Supporting Information) is similar to that in the analogous $[(C_5Me_5)_2Ln]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}PhC=C=C=CPh)$ (Ln = Sm,[41] La[29]) complexes of 146.9(10)° and 148.6(13)°, respectively. The 1.367(6) Å C11−C12 and 1.276(8) Å C11−C11′ distances are indicative of double bonds and are also similar to those in the other complexes, 1.363(17) and 1.298(19) Å for Sm and 1.36(2) and 1.26(2) Å for La. After insertion of diisopropylcarbodiimide into each of the Y−C bonds in **2**, the C22−C23−C23′ angle in $(C_5Me_5)_2Y[\mu\text{-}\kappa^2\text{-}(^iPrN)_2C-C(Ph)=C=C=C(Ph)-C(N^iPr)_2]Y(C_5Me_5)_2$, **6** (Figure 5), is now much closer to linear, 174.28(16)°. The carbon carbon multiple bonds in the trienediyl linker are 1.261(3) and 1.331(2) Å (Table S5, Supporting Information).

In $(C_5Me_5)_2Y[^tBuNC(C\equiv CPh)N^tBu\text{-}\kappa^2N,N']$, **3** (Figure 1), the 2.364(1) Å Y1−N1 and 2.381(1) Å Y1−N2 distances are similar and more symmetric than those in seven coordinate $[Me_2Si(C_5Me_4)(NPh)]Y[^tBuNC(C\equiv CPh)N^tBu\text{-}\kappa^2N,N'](THF)$[18] (2.393(5) and 2.339(5) Å), which has differing lengths presumably because it has an extra ligand in the metallocene wedge. The metrical parameters in the amidinate ligands in both complexes are similar, with 1.195(3) Å C22−C23 and 1.182(8) Å alkyne lengths, respectively. The trienediyl bis(amidinate) $(C_5Me_5)_2Y[\mu\text{-}\kappa^2\text{-}(^iPrN)_2C-C(Ph)=C=C=C(Ph)-C(N^iPr)_2]Y(C_5Me_5)_2$, **6**, has similar 2.378(1) and 2.385(2) Å Y−N distances; that is, the nature of the substituent on the central carbon does not seem to change the coordination to yttrium to a great extent.

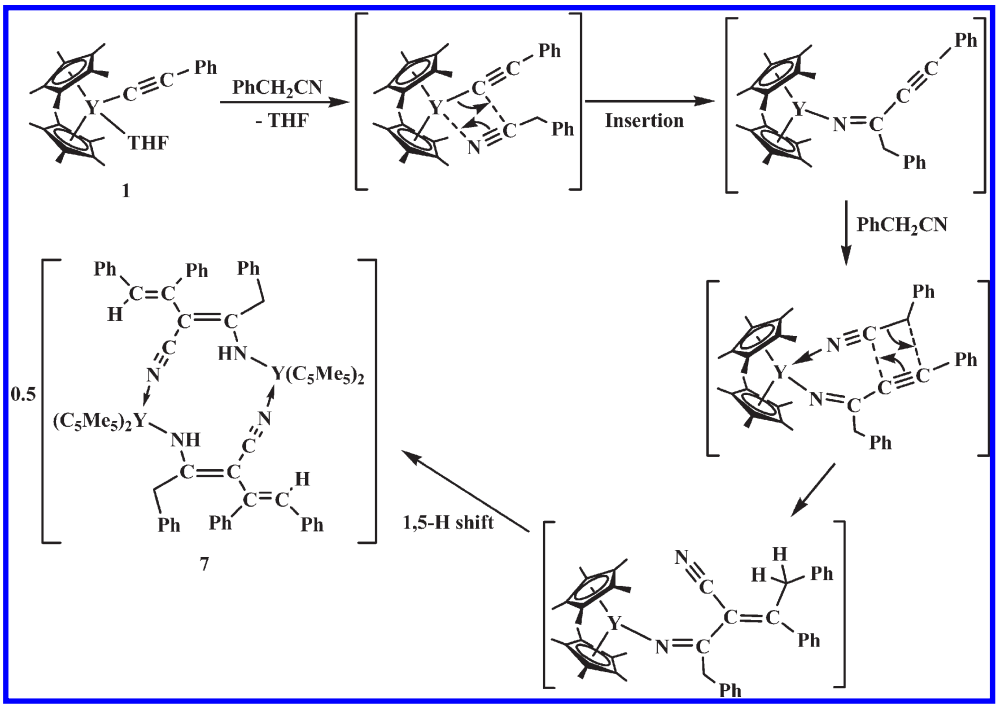
In eight coordinate $(C_5Me_5)_2Y\{C(=CHPh)C[N=C(CH_2)_5]=NCH(CH_2)_5\text{-}\kappa^2C,N\}$, **5** (Figure 3), the 2.429(1) Å yttrium−vinyl Y1−C21 bond length is identical to the 2.422(5) Å Lu−C(vinyl) length in $(C_5Me_5)_2Lu(CH=C_5Me_4)$.[33] Given the larger size of yttrium (8-coordinate ionic radius, $Y^{3+}$ = 1.019 Å; $Lu^{3+}$ = 0.977 Å)[42] and the larger coordination number in **5**, a longer distance would be expected. The 1.346(2) Å C21−C35 (alkene) length in **5** is also shorter than the 1.380(5) Å analogue in the lutetium complex, although both of these are longer than the typical 1.326 Å length for trisubstituted alkenes of the type $(C)_2-C=CH-C$.[43]

The central $YC_3N_2$ core in **5** has Y1/C35/C21/C22/N1/N2 bond angles within the range of 115.26(11)−124.43(11)° and a planar arrangement of these atoms, indicative of $sp^2$-hybridized carbon and nitrogen atoms. Along with the 1.346(2) Å C21−C35 and 1.306(2) Å C22−N1 double bonds, the 1.478(2) Å C21−C22 and 1.400(2) Å C22−N2 lengths are consistent with single bonds and are indicative of the localized structure shown in Scheme 4 for the iminovinyl ligand. The shorter than expected 2.429(1) Å Y1−C21 length and long 2.436(1) Å Y1−N1 value support this assignment and suggest that the negative charge of the ligand resides more on C21 than N1. This situation is in contrast to the delocalized azaallyl ligand in $(C_5H_5)_2Y[^tBuNC(Me)CHPh](THF)$,[44] which has a similar YCCN core motif with 2.366(4) Å Y−N and 2.613(6) Å Y−C bonds. These distances can also be compared with the Y−N lengths of the

**Scheme 5. One Possible Mechanism for the Formation of 4 and 5**




**Scheme 6. Possible Mechanism for the Formation of 7**




amidinate ligand in **3**, which are in the range of 2.364(1)−2.384(1) Å. The $C_6$ ring of **5** derived from deprotonation of the cyclohexyl group on the carbodiimide substrate now contains an $sp^2$-hybridized carbon atom bound to nitrogen, as evidenced by the 125.77(12)° and 119.69(12)° angles defined by N2−C23−C24 and N2−C23−C28, respectively, and the shorter 1.274(2) Å N2−C23 bond length, compared to the 1.474(2) Å N1−C29 length.

The X-ray structure of $[(C_5Me_5)_2Y\{\mu\text{-}N(H)C(CH_2Ph)=C\text{-}[C(Ph)=CHPh]C\equiv N\}]_2$, **7** (Figure 6), revealed that the newly formed amidonitrile ligand bridged two yttrium metallocene units to form a dimer with a crystallographically imposed inversion center. The $YC_3N_2$ core bears the hallmarks of the crotononitrile ligand in the yttrium complex $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y[(\mu\text{-}N,N')\text{-}N(H)C(Me)=C(H)C\equiv N]\}_2$.[36] The short 1.326(3) Å N1−C21 and 1.398(4) Å C22−C23 (typical $Csp^2$−N and $Csp^2$−Csp lengths are 1.36−1.38 and 1.43 Å, respectively) and long 1.417(4) Å C21−C22 bond lengths (a typical $Csp^2$=$Csp^2$ length is 1.33 Å)[43] are indicative of charge delocalization across the central ligand core. This is similar to the crotononitrile complex, which displays comparable lengths of 1.331(6), 1.393(7), and 1.375(7) Å, respectively. The 2.366(2) Å Y1−N1 amido and 1.162(3) Å C23−N2 nitrile lengths in **7** are similar to those in the crotononitrile complex (2.344(4) and 1.156(6) Å). In **7**, the 2.351(2) Å N2−Y1′ length is shorter and the 149.9° Y1−N1−C21 angle larger than those observed in the crotononitrile complex of 2.460(4) Å and 143.1(3)°, respectively, which could be due to the differing steric bulk of the ligands in the two complexes.

## DISCUSSION

The allyl complex $(C_5Me_5)_2Y(\eta^3\text{-}CH_2CHCH_2)(THF)$ functions as an effective alkyl synthon in Scheme 3 to deprotonate HC≡CPh to make the alkynide $(C_5Me_5)_2Y(C\equiv CPh)(THF)$, **1**. Surprisingly, when the reaction is done in hexane, the unsolvated trienediyl, $[(C_5Me_5)_2Y]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}PhC=C=C=CPh)$, **2**, can be isolated, despite the presence of THF. Formation of trienediyl complexes from unsolvated "$[(C_5Me_5)_2LnC\equiv CPh]$" precursors is well-known, but usually the presence of an equivalent of THF inhibits this conversion.[23]

The reactions of $^t$BuN=C=N$^t$Bu with **1** and $^i$PrN=C=N$^i$Pr with **2**, eqs 1 and 2, respectively, involve conventional insertions to form amidinates, which require heating as previously reported.[18]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However, in the case of isopropyl and cyclohexyl carbodiimide reactions with **1** (Scheme 4), an unexpected C−H activation occurs upon mixing at room temperature and the iminovinyl products $(C_5Me_5)_2Y[C(=CHPh)C(N=CMe_2)=N^iPr\text{-}\kappa^2C,N]$, **4**, and $(C_5Me_5)_2Y\{C(=CHPh)C[N=C(CH_2)_5]=N(Cy)\text{-}\kappa^2C,N\}$, **5**, are obtained. The reaction is formally an organometallic version of the Alder-ene reaction (Scheme 2). Because typical C=N insertion has been observed with less substituted cyclopentadienyl complexes, it is possible that the steric profile of the pentamethylcyclopentadienyl auxiliary ligands allows the observed C−H activation to occur.

One scenario by which the product could form is shown in Scheme 5. Initial displacement of the coordinated THF in **1** by the carbodiimide seems plausible. If the carbodiimide aligns with the alkynide as shown, the intermediate is set up for an Alder-ene reaction to give the observed vinyl−amide products. $^t$BuN=C=N$^t$Bu reacts differently from $^i$PrN=C=N$^i$Pr and CyN=C=NCy because the latter carbodiimides have a hydrogen available for transfer.

The formation of $[(C_5Me_5)_2Y\{\mu\text{-}N(H)C(CH_2Ph)=C[C(Ph)=CHPh]C\equiv N\}]_2$, **7**, from the reaction of **1** with benzylnitrile (eq 3) can be explained along similar lines, and one possible mechanism is shown in Scheme 6. Although there are many pathways by which complex **7** could be formed in this fast reaction, displacement of THF by the nitrile and insertion seem most likely for the initial steps. Subsequent alignment of a second benzylnitrile with the iminoalkyne ligand formed by the initial insertion could lead to benzylcyanide addition across the alkyne. A subsequent 1,5-hydrogen shift and dimerization would give the observed product. The insertion step and a 1,3-H shift are components in the previously observed formation of the crotononitrile-containing complex $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y[(\mu\text{-}N,N')\text{-}N(H)C(Me)=C(H)C\equiv N]\}_2$.[36]

## CONCLUSIONS

Carbodiimide insertion into rare earth−carbon bonds of rare earth metallocene alkynide complexes can take an unexpected turn when reagents with secondary alkyl groups are present. As shown with $(C_5Me_5)_2Y(C\equiv CPh)(THF)$, **1**, C−H activation can occur in an organometallic Alder-ene reaction to make iminovinyl products. Alkynide **1** can also display reactivity beyond conventional insertion with nitriles, as shown by the formation of the amido nitrile, $[(C_5Me_5)_2Y\{\mu\text{-}N(H)C(CH_2Ph)=C[C(Ph)=CHPh]C\equiv N\}]_2$, **7**. In each of these reactions, the yttrium metallocene unit functions as an anchor point to facilitate the reactivity between the unsaturated organic ligands.

## ASSOCIATED CONTENT

**Supporting Information.** X-ray data collection (Table S1), selected metrical parameters (Tables S2−S6), and structure determination and refinement parameters for **1**−**3** and **5**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 824449-824454 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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## REFERENCES

(1) Ma, L.; Zhang, J.; Cai, R.; Chen, Z.; Weng, L.; Zhou, X. *J. Organomet. Chem.* **2005**, *690*, 4926.
(2) Shen, H.; Chan, H.-S.; Xie, Z. *Organometallics* **2006**, *25*, 5515.
(3) Zhang, J.; Ruan, R.; Shao, Z.; Cai, R.; Weng, L.; Zhou, X. *Organometallics* **2002**, *21*, 1420.
(4) Evans, W. J.; Walensky, J. R.; Ziller, J. W.; Rheingold, A. L. *Organometallics* **2009**, *28*, 3350.
(5) Zhang, J.; Ma, L.; Han, Y.; Zhang, F. H. Z.; Cai, R.; Chen, Z.; Zhou, X. *Dalton Trans.* **2009**, 3298.
(6) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219.
(7) Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Wang, J. *Inorg. Chem.* **2007**, *46*, 10022.
(8) Cole, M. L.; Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Ceron, D. P.; Wang, J. *Dalton Trans.* **2010**, *39*, 6732.
(9) Evans, W. J.; Seibel, C. A.; Ziller, J. W. *Inorg. Chem.* **1998**, *37*, 770.
(10) Evans, W. J.; Rego, D. B.; Ziller, J. W.; Dipasquale, A. G.; Rheingold, A. L. *Organometallics* **2007**, *26*, 4737.
(11) Evans, W. J.; Walensky, J. R.; Ziller, J. W. *Organometallics* **2010**, *29*, 945.
(12) Zhou, X.; Zhu, M. *J. Organomet. Chem.* **2002**, *647*, 28.
(13) Kirchbauer, F. G.; Pellny, P.-M.; Sun, H.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2001**, *20*, 5289.
(14) Davies, N. W.; Frey, A. S. P.; Gardiner, M. G.; Wang, J. *Chem. Commun.* **2006**, 4853.
(15) Evans, W. J.; Davis, B. L. *Chem. Rev.* **2002**, *102*, 2119.
(16) Brown, D. J.; Chisholm, M. H.; Gallucci, J. C. *Dalton Trans.* **2008**, 1615.
(17) Barrett, A. G. M.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B.; Lomas, S. L.; Mahon, M. F.; Procopiou, P. A.; Suntharalingam, K. *Organometallics* **2008**, *27*, 6300.
(18) Zhang, W.-X.; Nishiura, M.; Hou, Z. *J. Am. Chem. Soc.* **2005**, *127*, 16788.
(19) Zhang, W.-X.; Hou, Z. *Org. Biomol. Chem.* **2008**, *6*, 1720.
(20) Du, Z.; Li, W.; Zhu, X.; Xu, F.; Shen, Q. *J. Org. Chem.* **2008**, *73*, 8966.
(21) den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053.
(22) Kurti, L.; Czako, B. *Strategic Applications of Named Reactions in Organic Synthesis*; Elsevier Academic Press: Burlington, MA, 2005; pp 6−7.
(23) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1993**, *12*, 2618.
(24) Evans, W. J.; Kozimor, S. A.; Brady, J. C.; Davis, B. L.; Nyce, G. W.; Seibel, C. A.; Ziller, J. W.; Doedens, R. J. *Organometallics* **2005**, *24*, 2269.
(25) Evans, W. J.; Seibel, C. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1998**, *120*, 6745.
(26) Demir, S.; Montalvo, E.; Ziller, J. W.; Meyer, G.; Evans, W. J. *Organometallics* **2010**, *29*, 6608.
(27) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.
(28) Lee, L.; Berg, D. J.; Bushnell, G. W. *Organometallics* **1995**, *14*, 5021.
(29) Forsyth, C. M.; Nolan, S. P.; Stern, C. L.; Marks, T. J.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3618.
(30) Heeres, H. J.; Nijhoff, J.; Teuben, J. H.; Rogers, R. D. *Organometallics* **1993**, *12*, 2609.
(31) Saliu, K. O.; Cheng, J.; McDonald, R.; Ferguson, M. J.; Takats, J. *Organometallics* **2010**, *29*, 4950.

(32) Esteruelas, M. A.; Gomez, A. V.; Lopez, A. M.; Onate, E.; Ruiz, N. *Organometallics* **1999**, *18*, 1606.
(33) Evans, W. J.; Champagne, T. M.; Ziller, J. W. *J. Am. Chem. Soc.* **2006**, *128*, 14270.
(34) Casey, C. P.; Tunge, J. A.; Fagan, M. A. *J. Organomet. Chem.* **2002**, *663*, 91.
(35) Evans, W. J.; Meadows, J. H.; Kostka, A. G.; Closs, G. L. *Organometallics* **1985**, *4*, 324.
(36) Duchateau, R.; Tuinstra, T.; Brussee, E. A. C.; Meetsma, A.; van Duijnen, P. Th.; Teuben, J. H. *Organometallics* **1997**, *16*, 3511.
(37) Casely, I. J.; Suh, Y. S.; Ziller, J. W.; Evans, W. J. *Organometallics* **2010**, *29*, 5209.
(38) Evans, W. J.; Foster, S. E. *J. Organomet. Chem.* **1992**, *433*, 79.
(39) Duchateau, R.; Brussee, E. A. C.; Meetsma, A.; Teuben, J. H. *Organometallics* **1997**, *16*, 5506.
(40) Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; Olofson, J. M. *J. Organomet. Chem.* **1989**, *376*, 311.
(41) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1990**, *9*, 2628.
(42) Shannon, R. D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1976**, *32*, 751.
(43) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.
(44) Zhang, Z.; Bu, X.; Zhang, J.; Liu, R.; Zhou, X.; Weng, L. *Organometallics* **2010**, *29*, 2111.