Alkyne Insertion into the Pt−H Bond of Pt(H)(1-pentene)(β-diiminate) Initiates a Reaction Cascade That Results in C−H Activation or C−C Coupling

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The lability of the 1-pentene ligand in (Cl-nacnac)Pt(H)(1-pentene) (**1**; Cl-nacnac = bis(*N*-aryl)-β-diiminate), which has been synthesized from the reaction of $Me_4Pt_2(\mu\text{-}SMe_2)_2$ with Cl-nacnacH in pentane, allows the reactivity of the (Cl-nacnac)Pt(H) fragment to be probed. The reaction of **1** with alkynes was explored. Alkynes displace pentene and rapidly undergo insertion into the Pt−H bond of **1** to initiate a reaction cascade. The identity of the final platinum product depends on the substituents on the alkyne reagent. Reaction of **1** with 2-butyne results in hydrogen migration after insertion and yields an η^3-allyl product, (Cl-nacnac)Pt(η^3-C_3H_4Me) (**2**). When reacted with **1**, terminal silyl alkynes $R_3SiC{\equiv}CH$ (R_3Si = Me_3Si, Ph_3Si) undergo C−H activation of one of the silyl substituents after initial alkyne insertion into the Pt−H bond, resulting in net hydrogenation of the alkyne. The result is formation of (Cl-nacnac)Pt((*o*-C_6H_4)$SiPh_2$($CH{=}CH_2$)) (**3**) or (Cl-nacnac)Pt((CH_2)$SiMe_2$($CH{=}CH_2$)) (**5**), which contains either an aryl or an alkyl ligand with a chelated vinylsilane substituent; complex **3** was characterized by X-ray crystallography. These products are the result of 2,1-insertion of the alkyne into the Pt−H bond, thus placing the silyl group and Pt on the same carbon, which positions the substituents on the silicon proximal to Pt and ripe for C−H activation. In contrast to the silylalkyne reagents, terminal alkynes lacking propargylic hydrogens, PhC≡CH and *t*-BuC≡CH, insert into the Pt−H bond in a 1,2- rather than a 2,1-fashion, which places the alkyne substituent β to the metal and precludes facile C−H activation. Instead, a second alkyne enters the coordination sphere and couples with the adjacent vinyl group in a head-to-tail fashion to form (Cl-nacnac)Pt(η^1:η^2-C(H)=C(R)C(H)=C(H)(R)) (**7**), which has a chelated η^1:η^2-butadienyl ligand with R groups at the 2- and 4-positions.

Introduction

Dehydrogenation of *n*-pentane with a (nacnac)PtMe fragment formed in situ provides a convenient route to (nacnac)Pt(H)(1-pentene), and the pentene ligand is labile.[1,2] The β-diiminate ligands used here have phenyl rings on the nitrogens with no substituents at the ortho positions, and the absence of bulky ortho substituents allows facile ligand exchange. Similar compounds reported by Goldberg used bulky substituents in the ortho position on the phenyl rings of the β-diiminate ligands, which inhibited ligand exchange because the metal was too sterically crowded to readily undergo associative ligand exchange.[3] The simple synthesis of these olefin hydride complexes coupled with the ease of displacing the α-olefin ligand allowed access to a range of (nacnac)Pt(H)(L) complexes. Given the propensity for alkynes to insert into M−H bonds, we have undertaken a systematic study of alkyne reactions with (Cl-nacnac)Pt(H)(1-pentene).

Though many transition-metal complexes have been shown to dimerize terminal alkynes, few favor coupling in a head-to-tail fashion.[4−7] Reductive dimerization of terminal alkynes to yield 1,3-butadienes is somewhat less common, but once again head-to-tail coupling is rare.[8−10] Most couplings favor head-to-head coupling so that the R groups from RC≡CH reside at the 1- and 4-positions in the organic product.[8,9,11−19] Regardless

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(1) West, N. M.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **2007**, *129*, 12372.
(2) West, N. M.; Templeton, J. L. *Can. J. Chem.*, in press.
(3) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 15286.
(4) Trost, B. M.; Sorum, M. T.; Chan, C.; Harms, A. E.; Ruhter, G. *J. Am. Chem. Soc.* **1997**, *119*, 698.
(5) Schafer, M.; Wolf, J.; Werner, H. *Organometallics* **2004**, *23*, 5713.
(6) Gao, Y.; Puddephatt, R. J. *Inorg. Chim. Acta* **2003**, *350*, 101.
(7) Sans, V.; Trzeciak, A. M.; Luis, S.; Ziolkowski, J. J. *Catal. Lett.* **2006**, *109*, 37.
(8) Ananikov, V. P.; Mitchenko, S. A.; Beletskaya, I. P. *J. Organomet. Chem.* **2000**, *604*, 290.
(9) Ananikov, V. P.; Mitchenko, S. A.; Beletskaya, I. P. *Russ. J. Org. Chem.* **2002**, *38*, 636.
(10) Kong, J. R.; Krische, M. J. *J. Am. Chem. Soc.* **2006**, *128*, 16040.
(11) Bianchini, C.; Frediani, P.; Masi, D.; Peruzzini, M.; Zanobini, F. *Organometallics* **1994**, *13*, 4616.
(12) Weng, W.; Guo, C.; Celenligil-Cetin, R.; Foxman, B. M.; Ozerov, O. V. *Chem. Commun.* **2006**, *197*.
(13) Ciclosi, M.; Estevan, F.; Lahuerta, P.; Passarelli, V.; Perez-Prieto, J.; Sanau, M. *Adv. Synth. Catal.* **2008**, *350*, 234.
(14) Ghosh, R.; Zhang, X.; Achord, P.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2007**, *129*, 853.
(15) Ogoshi, S.; Ueta, M.; Oka, M.-A.; Kurosawa, H. *Chem. Commun.* **2004**, 2732.
(16) Slugovc, C.; Mereiter, K.; Zobetz, E.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 5275.
(17) Li, X.; Vogel, T.; Incarvito, C. D.; Crabtree, R. H. *Organometallics* **2005**, *24*, 62.
(18) Li, X.; Incarvito, C. D.; Crabtree, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 3698.

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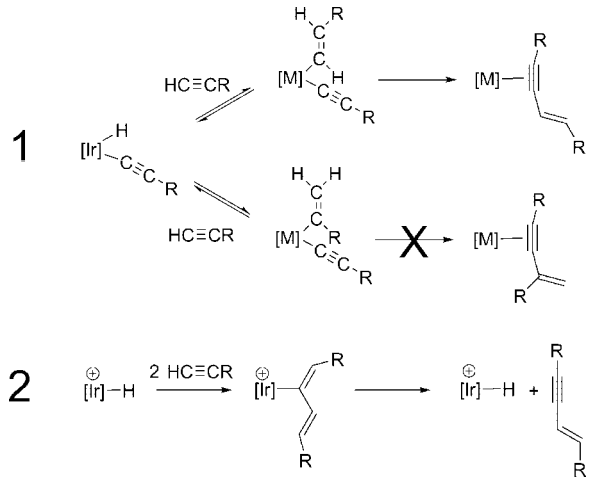
Scheme 1. Alkyne Coupling Pathways Favoring Head-to-Head Coupling Products



of whether the new C−C bond is formed via reductive elimination or alkyne insertion into an M−C bond, the head-to-head product is usually heavily favored due to the steric bulk of the R group on the tail carbon of the alkyne.

A recent report by Goldman showed that even though migration of hydride to the terminal carbon of phenylacetylene was favored, no reductive elimination with C−C bond formation occurred from the phenylacetylide intermediate due to the steric bulk at the C−C bond formation site (mechanism 1; Scheme 1).[14] Reductive elimination occurred only when the opposite alkyne insertion product was formed as an intermediate. Terminal alkyne dimerization has been accomplished with an Ir−H reagent, and it occurs by migration of the hydride to the most substituted alkyne position, yielding the less sterically hindered metal-bound vinyl group which then migrates to a second alkyne, but the second migration goes to the least substituted carbon and so the head-to-head product is formed upon β-H elimination (mechanism 2; Scheme 1).[13] Thus, 1,3-disubstituted 1,3-butadienes or enynes have proven far more elusive than than the 1,4-disubstituted analogues. As described in detail in this article, our results are particularly surprising, because we strongly favor coupling even with the bulky *tert*-butyl substituent on the alkyne. Aside from dimerization, alkynes can be used to synthesize more complex unsaturated compounds via reductive coupling to heteroatom containing unsaturated molecules.[10,20]

Alkynes react rapidly with the olefin hydride Pt(II) reagent, and they then undergo rapid insertion into the Pt−H bond. The fate of the unsaturated platinum vinyl intermediate depends on alkyne identity. Internal alkynes with protons on the carbons adjacent to the triple bond, such as 2-butyne, form Pt allyls. Terminal alkynes with no protons adjacent to the triple bond form one of two products, depending on the R group of the alkyne. Silylacetylenes, such as (triphenylsilyl)acetylene and (trimethylsilyl)acetylene, produce a cyclometalated vinylsilane where the alkyne has been reduced to an alkene and C−H activation of either the silyl methyl or phenyl has occurred. Carbon-substituted alkynes, such as phenylacetylene and *tert*-butylacetylene, couple in a head-to-tail fashion to form η^1:η^2-butadienyl complexes with substituents on the 2- and 4-carbons. The products of terminal alkyne addition reflect 1,2-insertion with C adjacent to the C≡C unit and 2,1-insertion into the Pt−H bond when a Si atom is adjacent to the C≡C triple bond. Multiple insertions of alkynes into metal−hydride bonds are rare because the second insertion, a C−C forming step, is usually significantly higher in energy than the first insertion, a C−H forming step; only a few examples of these multiple insertions have been reported.[17−19,21−24]

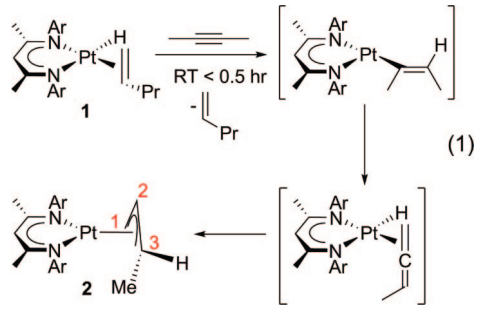
Results and Discussion

Reaction of (Cl-nacnac)Pt(H)(1-pentene) (1) with $CH_3C{\equiv}CCH_3$. We previously reported that olefin insertion into the Pt−H bond of (nacnac)Pt(H)(olefin) was surprisingly slow.[1,2] Use of aryl rings that are unsubstituted at the ortho position on the nacnac ligand allows access to the platinum center and promotes facile ligand displacement. Thus, reactivity patterns of ligands other than olefins can be explored. To further explore insertion chemistry accessible to the Pt−H bond, we report here reactions with alkynes. Alkynes tend to be much more reactive toward metal hydrides than alkenes; thus, we expect their insertion into the Pt−H bond to be rapid even though alkene insertion is slow.

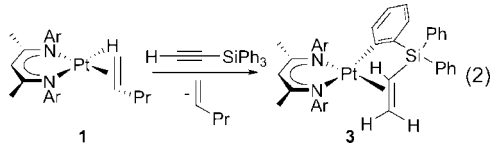
For this study we chose to use *p*-Cl-substituted aryl rings on the nacnac ligand, due to their slightly lower solubility in nonpolar solvents, making the compounds easier to isolate as solids than the previously reported phenyl nacnac complex.[1,2] The chlorine atoms at the para position do not appear to influence the reactivity dramatically relative to the unsubstituted phenyl. The chloride substituents are located far away from the metal, and they do not influence the steric environment. In addition the hydride resonance closely mimics the parent nacnac analogue: the chemical shift changes by only 0.17 ppm and the $^1J_{Pt-H}$ value changes by only 3 Hz out of 1200 Hz.

We first tested the reactivity of the pentene hydride complex **1** with 2-butyne; hydride migration was indeed rapid. Addition of 1 equiv of 2-butyne to a CD_2Cl_2 solution of **1** at room temperature resulted in a rapid color change from yellow to light orange. The ^{1}H NMR showed free 1-pentene, and no hydride signal remained. The product was identified as the 1-methylallyl adduct, (Cl-nacnac)Pt(anti-η^3-C_3H_4Me) (**2**) (eq 1). The ^{1}H NMR displayed signals indicative of one methylallyl isomer: a doublet of triplets at 4.6 ppm, a pseudo quintet at 2.4 ppm, and two doublets of doublets near 1.9 ppm, all with Pt satellites. These signals correspond to the central proton on C2, to the proton on C3, and to the two inequivalent protons on C1, respectively. The proton on C3 and one of the protons on C1 exhibit a syn coupling of 6.6 Hz to the central CH proton. The other proton on C1 exhibits an anti coupling of 10.8 Hz; therefore, the methyl on C3 must reside in the anti position. Typically only the anti isomer is observed when allyls are formed via alkyne insertion into a metal−hydride bond, since the alkyne insertion step is stereoselective for cis addition so that the vinyl geometry is poised to form the anti allyl product.[25] The 1,2-proton shift probably occurs by C−H activation of the methyl group adjacent to platinum to form an η^2-allene followed by hydride migration to the internal carbon to from the allyl ligand.

(19) Selnau, H. E.; Merola, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 4008.
(20) Ngai, M.-Y.; Barchuk, A.; Krische, M. J. *J. Am. Chem. Soc.* **2007**, *129*, 12644.
(21) Esteruelas, M. A.; Garcia-Yebra, C.; Olivan, M.; Onate, E.; Tajada, M. A. *Organometallics* **2000**, *19*, 5098.
(22) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Kainosho, M.; Ono, A.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1999**, *121*, 12035.
(23) Burrows, A. D.; Green, M.; Jeffery, J. C.; Lynam, J. M.; Mahon, M. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 3043.
(24) Chin, C. S.; Lee, H.; Park, H.; Kim, M. *Organometallics* **2002**, *21*, 3889.
(25) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; 3rd ed.; Wiley: New York, 2000.



Reaction of (Cl-nacnac)Pt(H)(1-pentene) (1) with $R_3SiC{\equiv}CH$ ($R_3 = Me_3, Ph_3, MePh_2$). Reactions with terminal alkynes lacking propargylic protons were also explored. Since silicon-containing alkynes lead to single platinum products following alkyne incorporation we consider $R_3SiC{\equiv}CH$ reagents before $R_3C{\equiv}CH$ reagents. Reaction of 1 equiv of $Ph_3SiC{\equiv}CH$ with a CD_2Cl_2 solution of **1** resulted in formation of complex **3**. The reaction was complete in less than 1 h and formed a single product quantitatively, as monitored by ^1H NMR. Complex **3** displayed diagnostic ^1H NMR signals characteristic of a Pt−bound vinyl group. Compound **3** has a doublet of doublets at 3.7 ppm (J = 10.8 and 14.4 Hz), a doublet at 3.2 ppm (J = 10.8 Hz), and a doublet at 3.1 ppm (J = 14.4 Hz); each signal displays a $^2J_{Pt-H}$ coupling in the 50−70 Hz range. The $^3J_{H-H}$ values are indicative of cis and trans couplings. This classic terminal olefin pattern reflects addition of another hydrogen in addition to the original Pt−H in order to generate (R_3Si)-$CH{=}CH_2$ from $R_3SiC{\equiv}CH$. The hydrogen does not originate in another 1 equiv of alkyne, as only 1 equiv of alkyne was consumed in the reaction. The platinum complex was purified by silica gel chromatography, yielding a yellow solid of pure **3**. After purification the aromatic region of the ^1H NMR was clean, and it was clear that the three phenyl rings on the $SiPh_3$ group had been desymmetrized. In addition to the aromatic Cl-nacnac *p*-C_6H_4Cl signals, two distinct C_6H_5 groups were observed, and there were also two doublets and two triplets in this region with each of the signals integrated for one proton. This indicates that one of the phenyls lost an ortho proton and each of the four remaining protons is unique in the product. Fitting these pieces together, it appeared that after alkyne insertion into the Pt−H bond the Pt activated an aromatic C−H bond on one of the $SiPh_3$ phenyl groups and then reductively eliminated the vinyl group to form a complex having a phenyl ligand with an *o*-diphenylvinylsilyl substituent chelating the Pt atom (eq 2).



Recrystallization of **3** from pentane at −30 °C yielded yellow crystals suitable for X-ray crystallography, and the resulting structure confirms the proposed geometry of **3** (Figure 1). The structure of (Cl-nacnac)Pt((*o*-C_6H_4)Si(Ph)$_2$($CH{=}CH_2$)) (**3**) shows that the Pt geometry deviates only slightly from an ideal square -planar geometry. The olefin is aligned virtually orthogonal to the square plane, as is typical for such Pt(II) complexes, but the olefin is not centered along the *z* axis. The olefin location is constrained by ring limitations, as evinced by the N1−Pt1−C21 and N1−Pt−C20 angles of 151.0 and 169.3°; if the olefin was orthogonal to the square plane with its midpoint in the N_2CPt plane, these two angles would be the same. The C34−Si1−C21 bond angle is compressed to 100.2°, reflecting a small amount of ring strain. The Pt1−C39−C34−Si1−C21 ring exhibits a classic envelope structure with the Pt1, C39, C34, and Si1 atoms virtually coplanar and C21 out of the plane. The Cl-nacnac ligand is somewhat twisted to place the nitrogens as close to directly trans to the aryl and olefin ligands as possible; this is evidenced by a torsion angle of 19.2° between the two Cl-nacnac methyl bonds (C6−C2 and C4−C7). The aryl−Pt bond distance, C39−Pt1, is 2.03 Å and the olefin−Pt bond lengths, C21−Pt1 and C20−Pt1, are both 2.14 Å. The Pt1−N5 bond trans to the phenyl is 2.12 Å, while the Pt1−N1 bond trans to the olefin is only 2.04 Å, indicating the stronger trans influence of the aryl group relative to the olefin. The Cl-nacnac Ar and the Pt-bound aryl adjacent to each other are stacked parallel to one another, and the distance between the two ipso carbons is only 2.94 Å, which rationalizes the hindered rotation of one Cl-nacnac Ar group evident in the ^1H NMR.

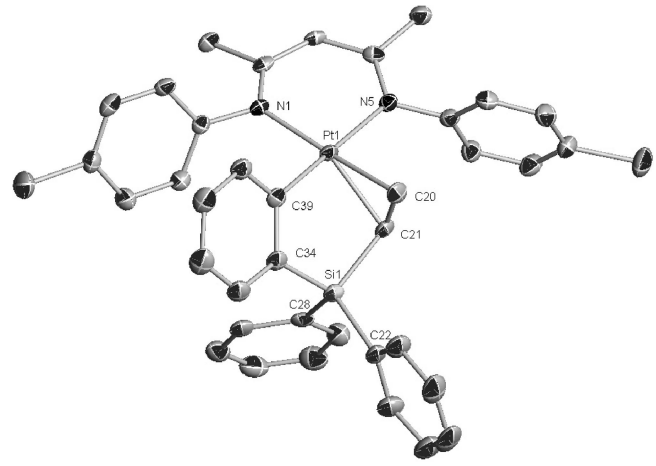
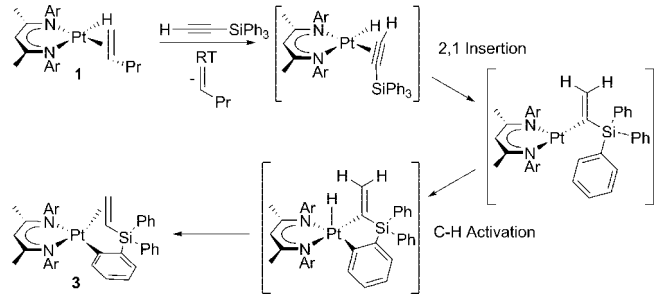


Figure 1. X-ray crystal structure of (Cl-nacnac)Pt((*o*-C_6H_4)-Si(Ph)$_2$($CH{=}CH_2$)) (**3**). Selected bond distances (Å) and angles (deg): Pt1−C39 = 2.031; Pt1−C20 = 2.142; Pt1−C21 = 2.140; Pt1−N1 = 2.044; Pt1−N5 = 2.120; C20−C21 = 1.404; C39−Pt1−C20 = 82.62; C39−Pt1−C21 = 86.12; C34−Si1−C21 = 100.2; N1−Pt1−C20 = 150.97; N1−Pt1−C21 = 169.33; N1−Pt1−N5 = 91.02.

Scheme 2. Formation of 3 via 2,1-Insertion of $Ph_3SiC{\equiv}CH$ into the Pt−H Bond of 1



Regarding the mechanism of the formation of **3** (Scheme 2), an attractive hypothesis is that reaction of **1** with $Ph_3SiC{\equiv}CH$ leads to 2,1-insertion of the alkyne into the Pt−H bond, affording a Pt−vinyl intermediate in which a $SiPh_3$ substituent is bound to the same carbon as the Pt atom. This positions a phenyl group close to the metal and allows for facile arene *o*-C−H activation. When the resulting platinum hydride ligand migrates to the vinyl substituent, the result is a Pt−aryl bearing an *o*-diphenylvinylsilyl substituent. In constrast, 1,2-insertion

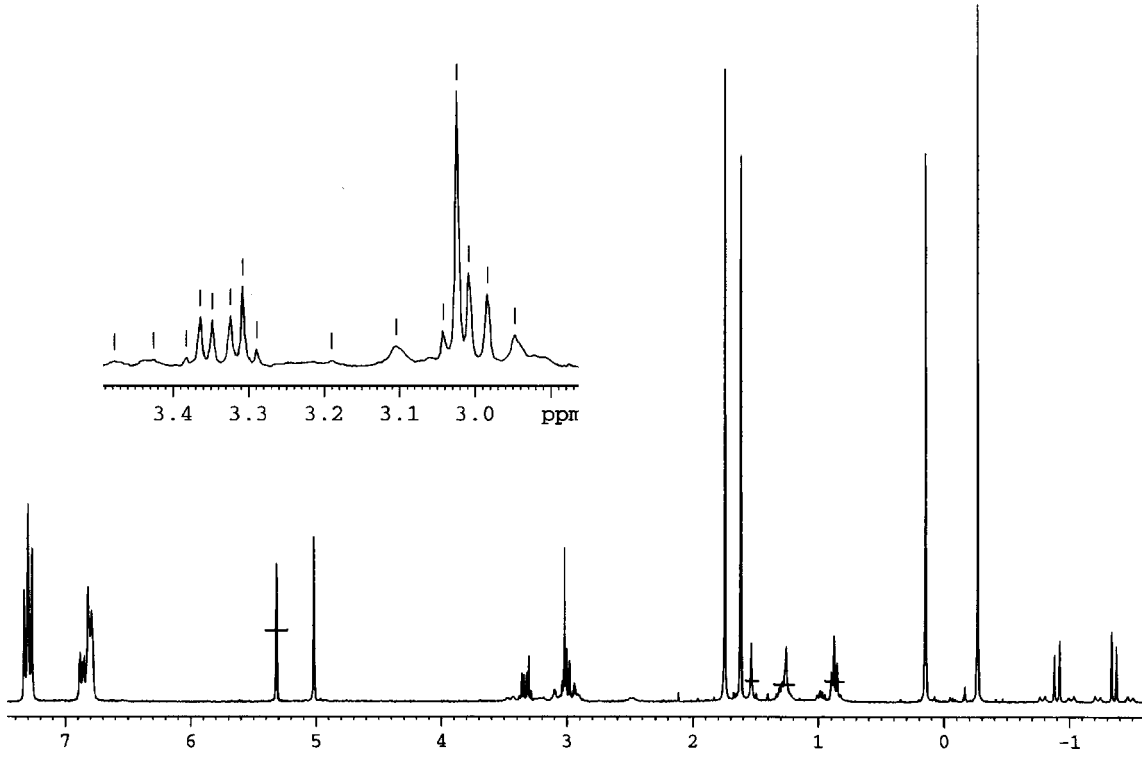
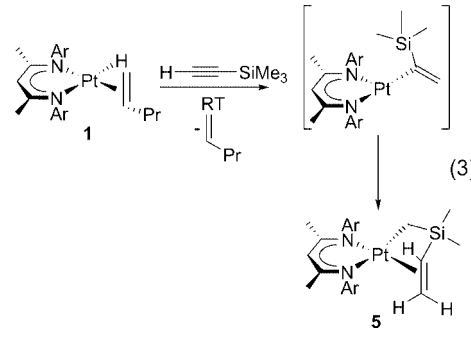


Figure 2. ^{1}H NMR of (Cl-nacnac)Pt($CH_2SiMe_2CH{=}CH_2$) (**5**) (CD_2Cl_2, 300 MHz, room temperature).

of the alkyne into the Pt−H bond would leave Pt bound to the terminal carbon of the vinyl group and place the $SiPh_3$ group γ to the metal, rendering arene C−H activation less likely.

If CO is bubbled into a solution of **3**, the coordinated olefin tail is rapidly displaced by CO. The reaction proceeds quantitatively by ^{1}H NMR in less than 5 min to produce (Cl-nacnac)Pt(CO)((*o*-C_6H_4)Si(Ph)$_2$($CH{=}CH_2$)) (**4**). The dechelated vinylsilane olefinic protons appear at 7.2, 6.2, and 5.6 ppm and display trans, cis, and geminal coupling constants of 20.0, 14.4, and 3.6 Hz, respectively. The Pt-bound aryl resonances shift only slightly and still appear as four distinct signals: two doublets and two triplets. The CO stretch for **4** appears at 2080 cm^{-1} in hexanes.

Addition of $Me_3SiC{\equiv}CH$ to a CD_2Cl_2 solution of **1** resulted in a reaction that formed a new product, **5**, quantitatively in less than 1 h, as monitored by ^{1}H NMR. Only 1 equiv of alkyne was consumed in the reaction. The product contained several signals integrating for a total of three protons in the chemical shift region indicative of bound olefins; the protons show a second-order coupling pattern. Simulated ^{1}H NMR matched the experimental data well and yielded coupling constants of 15.2, 10.2, and 3.2 Hz for the trans, cis, and geminal couplings, respectively. Surprisingly, the ^{1}H NMR spectrum also displays four inequivalent methyl signals: two due to the Cl-nacnac ligand and another two upfield at 0.16 and −0.26 ppm for diastereotopic Me groups at Si. In addition, roofed doublets appeared at −0.89 and −1.34 ppm with 12.4 Hz coupling to each other, and they exhibit 68 and 78 Hz Pt coupling, respectively (Figure 2). These Pt coupling constants are typical for two-bond coupling values, and these unique signals were assigned to diastereotopic protons on a Pt-bound methylene group. This assignment was consistent with both the chemical shifts and the magnitude of the H−H coupling constant. It appeared that the alkyne had inserted into the Pt−H bond and then activated a C−H bond of one of the silyl methyl groups to form a chelated alkyl olefin complex, (Cl-nacnac)Pt($CH_2SiMe_2CH{=}CH_2$) (**5**). The methylene residue of the activated methyl group displays high-field signals for the diastereotopic protons due to coordination to platinum and to shielding from the Cl-nacnac Ar group. Like the $SiPh_3$ analogue, $Me_3SiC{\equiv}CH$ must undergo 2,1-insertion prior to C−H activation of one of the silyl methyl groups (eq 3); a 1,2-insertion would place the methyl hydrogens far from the metal. Related chelated dimethylvinylsilane complexes of Pt(II) have been made by Young via metathesis of the Grignard reagent $ClMgCH_2SiMe_2CH{=}CH_2$ with Pt(II) chlorides; they exhibit similar ^{1}H NMR signals.[26,27]



Addition of CO to a solution of **5** resulted in displacement of the chelating olefin and replacement by CO to form (Cl-nacnac)Pt(CO)($CH_2SiMe_2CH{=}CH_2$) (**6**) quantitatively by ^{1}H NMR in less than 5 min (eq 4). The ^{1}H NMR of **6** displays terminal olefin signals at 6.10, 5.82, and 5.51 ppm with trans, cis, and geminal coupling constants of 20.1, 14.6, and 3.9 Hz, respectively. As a result of dechelation, the two silyl methyl groups (δ −0.10 ppm) are equivalent, since they are related by the mirror plane of the C_s-symmetrical complex, as are the two $PtCH_2$ protons (δ −0.08 ppm, $^2J_{Pt-H}$ = 78 Hz). The CO stretch

(26) Kelly, R. D.; Young, G. B. *J. Organomet. Chem.* **1989**, *361*, 123.
(27) Kelly, R. D.; Young, G. B. *Polyhedron* **1989**, *8*, 433.

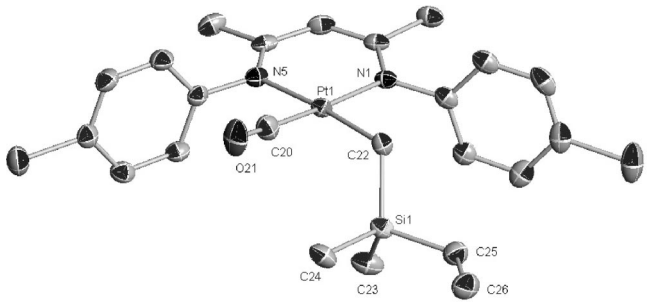
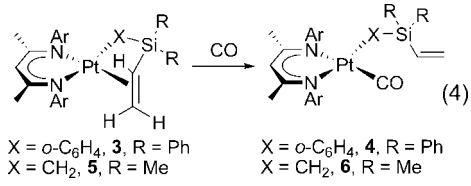


Figure 3. X-ray crystal structure of (Cl-nacnac)Pt(CH_2SiMe_2-$CH{=}CH_2$)(CO) (**6**). Selected bond distances (Å) and angles (deg): Pt1−C22 = 2.104; Pt1−C20 = 1.844; Pt1−N1 = 2.048; Pt1−N5 = 2.096; C20−O21 = 1.131; C25−C26 = 1.324; C20−Pt1−C22 = 82.79; C34−Si1−C21 = 100.2; N1−Pt1−C20 = 173.95; N5−Pt1−C22 = 175.23; N1−Pt1−N5 = 89.63.

appears at 2072 cm^{-1} in hexanes, indicating that the chelated alkyl group donates more electron density to the metal than the chelated arene in **4**, where the CO stretch is slightly higher at 2080 cm^{-1}. The complex was characterized by X-ray crystallography, and the Pt−$CH_2(SiR_3)$ bond length of 2.104 Å is noticeably longer than the Pt−C_{aryl} bond length of 2.031 Å in complex **3** and the Pt−CH_3 bond length of 2.082 Å in (nacnac)Pt(CH_3)(CO) (Figure 3).[1]



We hoped to compare phenyl activation and methyl activation processes by employing $Ph_2MeSiC{\equiv}CH$ as a reagent. Reaction of $Ph_2MeSiC{\equiv}CH$ with the labile Pt(II) pentene reagent **1** results in formation of a mixture of all three possible products: the methyl activation product and both diastereomers of the phenyl activation products. The two diastereomers resulting from phenyl activation are present in equal amounts, indicating that there is no preference for one phenyl relative to the other. Unexpectedly, the complex reflecting methyl activation is present in about a 1:1 ratio with the two phenyl activation isomers combined. This product ratio indicates that methyl C−H activation is about 1.33 times more likely than phenyl C−H activation, since if there were no preference, the number of *o*-phenyl (4) and methyl protons (3) would lead to the ratio 4/3 in favor of phenyl activation. We expected that the five-membered chelate structure would be significantly more stable than the four-membered ring and that this would thermodynamically favor phenyl activation. Platinum(II)−aryl bonds have been reported to be stronger than platinum(II)−methyl bonds, which would add further thermodynamic stability to the arene activation product.[28] The reaction products are probably determined kinetically, in which case the methyl activation may be favored because this conformer would have the large phenyl groups rotated away from the metal and avoid unfavorable steric interactions with the Cl-nacnac Ar groups. It should be noted that in most cases d^8 transition metals strongly favor arene C−H activation over sp^3 C−H activation; there are only a few cases in which sp^3 C−H activation is competitive with or favored over arene C−H activation.[29−32] While the present case is admittedly special, due to the silicon substituent on the methyl/phenyl groups it is noteworthy nonetheless.

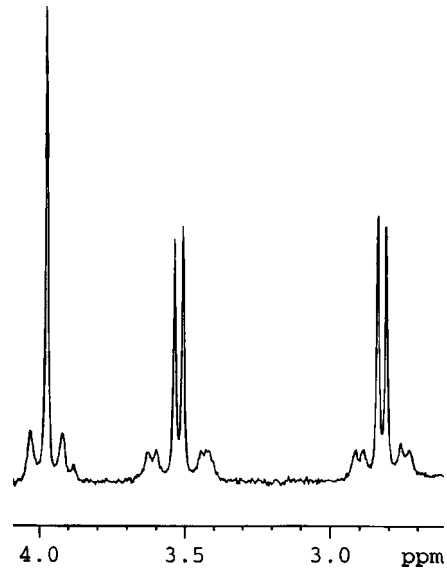


Figure 4. Olefinic region of the ^1H NMR of **7a**.

Reaction of (Cl-nacnac)Pt(H)(1-pentene) (1) with RC≡CH (R = *t*-Bu, Ph). Addition of 1 equiv of *t*-BuC≡CH to a CD_2Cl_2 solution of the pentene hydride complex **1** at room temperature resulted in a color change from yellow to light orange. After about 1 h the ^1H NMR spectrum showed a 1:1 ratio of unreacted **1** and a (Cl-nacnac)Pt product that contained no hydride ligand. Addition of another 1 equiv of *tert*-butylacetylene promotes complete conversion of **1** to the new Pt product **7a**. Note that 1-pentene was displaced during the reaction and did not react with the product. The ^1H NMR spectrum for **7a** exhibits a singlet at 4.01 ppm with 32 Hz Pt coupling in addition to two coupled doublets, one at 3.50 ppm and the other at 2.89 ppm with 53 and 47 Hz Pt coupling, respectively, as well as 8.8 Hz $^3J_{H-H}$ coupling (Figure 4). The ^1H NMR spectrum also displayed two distinct *tert*-butyl groups, confirming that 2 equiv of alkyne is incorporated into **7a**. We postulated that the vinyl fragment formed by 1,2-insertion into the Pt−H bond has coupled in a head-to-tail fashion to a second equivalent of alkyne to yield an η^1-butadienyl ligand which could then chelate to Pt through the second double bond to form an $\eta^1{:}\eta^2$-butadienyl complex (Scheme 3). A similar $\eta^1{:}\eta^2$-butadienyl complex was observed for the insertion of diphenylacetylene into a Pt−H bond followed by migration of the resulting vinyl to another 1 equiv of diphenylacetylene; this complex was characterized crystallographically.[33] Complex **7a,** (Cl-nacnac)Pt((H)C=C(*t*-Bu)(H)C=C(H)(*t*-Bu)), would contain three olefinic hydrogens for the $\eta^1{:}\eta^2$-butadienyl ligand, two of which would couple to one another and one that would stand alone, as observed. To confirm the identity of the product, $^{13}C\{^1H\}$, HMQC, and HMBC ^{13}C

(28) Al Takhin, G.; Skinner, H. A.; Zaki, A. A. *J. Chem. Soc., Dalton Trans.* **1984**, *371*.

(29) Zhu, Y.; Fan, L.; Chen, C.-H.; Finnell, S. R.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2007**, *26*, 6701.

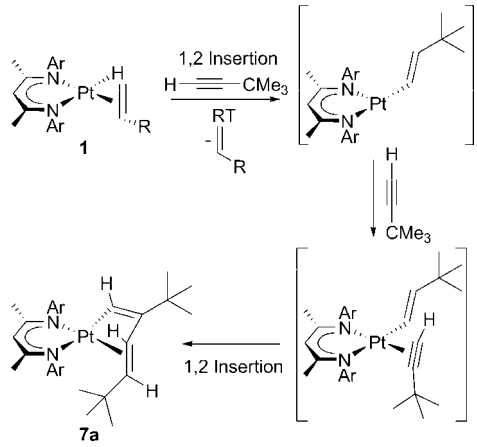
(30) Hofmann, P.; Heiss, H.; Neiteler, P.; Muller, G.; Lachmann, J. *Angew. Chem., Int. Ed.* **1990**, *29*, 880.

(31) Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378.

(32) Rybtchinski, B.; Cohen, R.; Ben-David, Y.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2003**, *125*, 11041.

(33) Tagge, C. D.; Simpson, R. D.; Bergman, R. G.; Hostetler, M. J.; Girolami, G. S.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 2634.

Scheme 3. Reductive Coupling of 2 Equiv of *t*-BuC≡CH

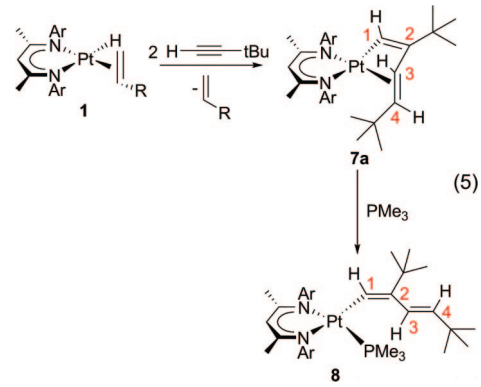


experiments were conducted. The olefinic signals at 4.0, 3.5, and 2.9 ppm correlated with carbons at 114, 64, and 104 ppm; the ^{13}C signal at 114 ppm had a Pt coupling of 740 Hz, and the signal at 104 ppm had a Pt coupling of 248 Hz. A $^{1}J_{Pt-C}$ coupling constant of 740 Hz is typical of a Pt−C σ bond and is consistent with an η^1-vinyl ligand;[1,34−41] the coupling of 248 Hz is typical of $^{1}J_{Pt-C}$ for a Pt-(η^2-olefin),[1,36,37] further supporting the proposed η^1:η^2-butadienyl structure. The ^{13}C resonance at 64 ppm had a Pt coupling constant of only 24 Hz, indicating that coordination of the η^2-olefin is not symmetrical because it is constrained by the ring size. The remaining vinyl carbon, with no protons attached, was found via HMBC to resonate at 151 ppm, compatible with our formulation of this product.

The *tert*-butyl alkyne is sterically similar to $Me_3SiC{\equiv}CH$; thus, the regiochemistry of the insertion appears to be dominated by the electronic effect of the atom bound to the C≡CH fragment atom. The silicon atom makes the adjacent Pt−C bond stronger and thus the insertion selectivity reverses from 1,2 with carbon to 2,1 with silicon, just as observed by Trost.[4] Such a reversal in insertion regioselectivity indicates that there is a subtle balance between the two pathways, and the stability of the vinyl intermediates formed from the initial insertion into the Pt−H bond likely determines the regiochemistry of insertion. This simple insertion guideline may be useful for alkyne coupling, since replacement of C by Si would reverse the C−C linkage in the product. Few catalyst systems can be modified to yield either 1,4- or 1,3-disubstituted alkynes, and those that can usually produce a mixture of isomers.[42−44]

When phenylacetylene was reacted with **1**, the analogous coupled product, **7b**, was observed. The three olefinic protons displayed the same pattern, with two doublets and one singlet (all with Pt satellites), but they were shifted about 1 ppm downfield relative to **7a**. This complex was less stable than the *tert*-butyl analogue and degraded over 1 day in solution to an unidentified product. The *tert*-butyl analogue, on the other hand, was stable in solution and was purified via silica gel chromatography, yielding a yellow solid.

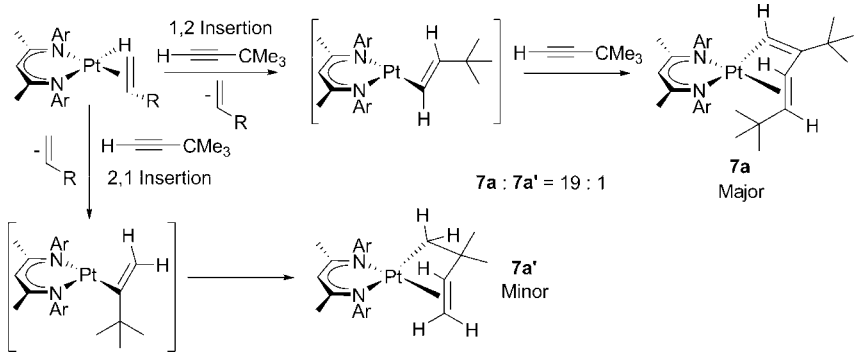
For further proof of the compound's identity and to explore its reactivity, we attempted to displace the η^2-olefin tail by addition of another ligand, thereby forming an η^1-butadienyl complex. Compound **7a** was found to be unreactive toward most ligands, including CO, which usually displaces olefins rapidly and irreversibly, but trimethylphosphine did displace the olefin and yielded (Cl-nacnac)Pt(PMe_3)(η^1-butadienyl) (**8**) quantitatively by NMR spectroscopy (eq 5). The vinyl proton on C1 in **8** shifted down 1.4 ppm from 4.0 ppm in **7a** to 5.4 ppm but retained an almost identical $^{2}J_{Pt-H}$ coupling of 34 Hz. The downfield shift of this proton was probably due to the fact that in the chelated species this proton would be oriented directly toward the Cl-nacnac aryl ring and thus was heavily shielded, resulting in the high field signal at 4 ppm (anisotropic chemical shifts reflecting shielding effects due to aryl substituents on nacnac ligands have been reported by Porschke[45]); once the ligand was dechelated, it could rotate away from the aryl and out of the shielding cone. The olefinic hydrogens on C3 and C4 shifted down to 5.2 and 5.5 ppm, respectively, and they no longer exhibited Pt coupling. The coupling between these two protons increased to 13.2 Hz, indicative of a trans geometry in accord with Pt−H addition to the triple bond. The carbon signals for C3 and C4 shifted downfield to 130 and 140 ppm, respectively, again with loss of Pt coupling; they were no longer coordinated to the metal. The resonance for C1 shifted only slightly downfield to 120 ppm, and now phosphorus coupling of 15 Hz was evident; C2 also underwent a small shift (to 144 ppm) and exhibited a 3 Hz $^{3}J_{P-C}$ coupling. The ^{1}H NMR for the butadienyl ligand resembles that of the free 1,3-di-*tert*-butyl-1,3-butadiene.[46]



We noticed that during the synthesis of the *t*-BuC≡CH coupled product **7a** a minor product formed in about 5% yield, as assessed by ^{1}H NMR. This minor product displayed Pt-coupled doublets at −0.22 and −0.74 ppm with 8 Hz J_{H-H} coupling and Pt satellites with approximately 70 Hz coupling. We were not able to isolate this compound for further characterization, but it was clear that these doublets were due to the same type of species as the $Me_3SiC{\equiv}CH$ product **5**. Thus,

(34) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 6423.
(35) Ananikov, V. P.; Mitchenko, S. A.; Beletskaya, I. P. *J. Organomet. Chem.* **2001**, *636*, 175.
(36) Iwayanagi, T.; Saito, Y. *Chem. Lett.* **1976**, *5*, 1193.
(37) Shiotsuki, M.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2007**, *129*, 4058.
(38) MacDonald, M. G.; Kostelansky, C. N.; White, P. S.; Templeton, J. L. *Organometallics* **2006**, *25*, 4560.
(39) Reinartz, S.; Baik, M. H.; White, P. S.; Brookhart, M.; Templeton, J. L. *Inorg. Chem.* **2001**, *40*, 4726.
(40) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2000**, *19*, 3854.
(41) Kostelansky, C. N.; MacDonald, M. G.; White, P. S.; Templeton, J. L. *Organometallics* **2006**, *25*, 2993.
(42) Yi, C. S.; Liu, N. *Organometallics* **1996**, *15*, 3968.
(43) Baratta, W.; Herrmann, W. A.; Rigo, P.; Schwarz, J. *J. Organomet. Chem.* **2000**, *593-594*, 489.
(44) Yang, C.; Nolan, S. P. *J. Org. Chem.* **2002**, *67*, 591.
(45) Tian, X.; Goddard, R.; Porschke, K.-R. *Organometallics* **2006**, *25*, 5854.
(46) Hopf, H.; Lipka, H.; Traetteberg, M. *Angew. Chem., Int. Ed.* **1994**, *33*, 204.

Scheme 4. Two Possible Insertion Pathways for *t*-BuC≡CH



it appears that a small amount of the $Me_3CC{\equiv}CH$ underwent 2,1-insertion before C−H activation of one of the *tert*-butyl methyl groups to form the chelated neohexenyl compound **7a′** (Scheme 4). It appears that when 2,1-insertion occurs, C−H activation of the R group, either methyl or phenyl, is faster than coordination and insertion of a second alkyne. When 1,2-insertion occurs, there is no alkyne substituent in position to be easily activated, and so the unsaturated vinyl intermediate binds a second alkyne and C−C coupling occurs. A similar mechanism is probably operative for the insertion of internal alkynes such as 2-butyne; once insertion occurs, the metal can rapidly activate the C−H bonds of the methyl group. This would yield a Pt allene hydride intermediate which would rapidly undergo hydride migration to the central carbon to form the observed Pt allyl complex.

It is worth noting that the structures of **7a′** and **5** are similar to the geometry of the vinyl−alkyne coupling products **7**. Both products link the internal olefin carbon to the metal through four-membered chelate rings. Also, both products are bound in an $\eta^1{:}\eta^2$ fashion through one Pt−C σ bond and one η^2-olefin. The only difference between the four-atom skeleton of the ligands, equating Si and C, is the double bond between C1 and C2 in **7**. The sp^2-hybridized carbons in **7** are more rigid than the sp^3 atoms in **7a′** and **5**. This rigidity probably increases the ring strain in **7** somewhat. While it seems like the four-membered rings would have substantial ring strain, the experimental evidence indicates that it is quite stable. All of the alkynes lead to chelated σ and π ligands after insertion into the Pt−H bond. These products appear to be a thermodynamic sink, as different reaction mechanisms and stoichiometries converge to remarkably similar structures.

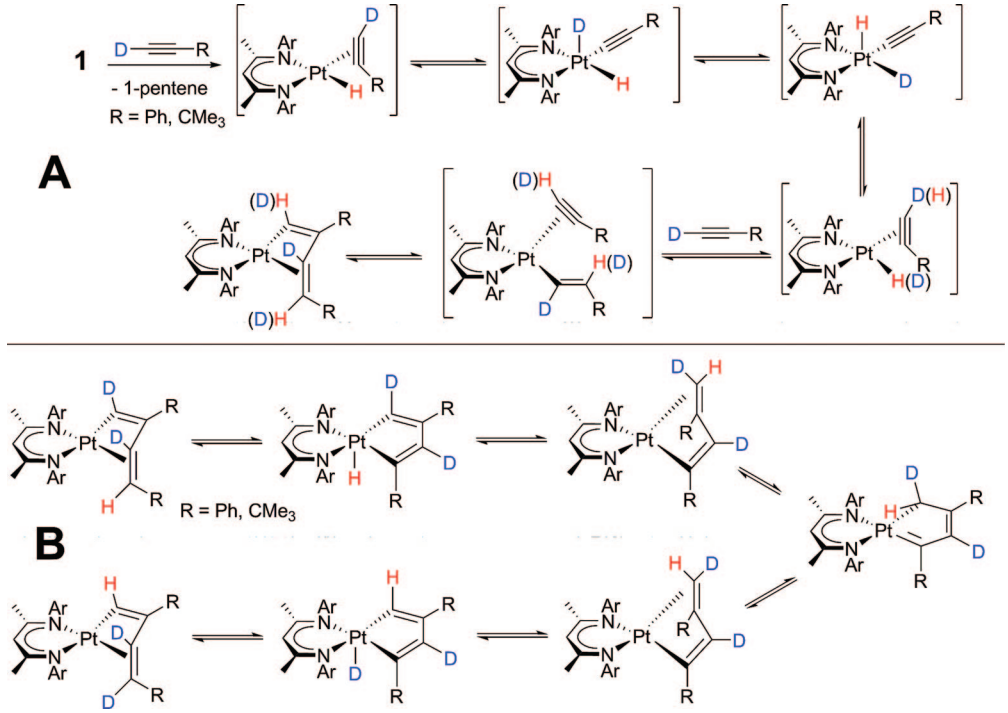
Mechanistic Considerations for Head-to-Tail Coupling of RC≡CH (R = *t*-Bu, Ph). To form the observed head-to-tail coupled product, the first alkyne must insert into the Pt−H bond in a 1,2-fashion, giving a Pt vinyl intermediate in which the R group is distal from the metal. Not only is a 1,2-insertion required to yield the observed head-to-tail coupling but it also prohibits C−H activation of the *t*-Bu substituent, indirectly allowing alkyne coupling to occur. We believe that the electropositive nature of the Si atom is the cause for the reversal between 2,1- and 1,2-insertion. Steric factors are not likely to dictate 2,1-insertion of the silyl alkynes, because the $SiMe_3$ group on the 2-carbon is sterically similar to the CMe_3 group of *t*-BuC≡CH, an alkyne that favors 1,2-insertion. The silyl group will stabilize the Pt−C bond formed by 2,1-insertion of the alkyne into the Pt−H, favoring this product thermodynamically even though it is more sterically crowded relative to the 1,2-insertion product. There is no significant electronic stabilization of the Pt−C bond from C-based groups such as *t*-Bu or Ph; thus, in those cases the most stable Pt−C bond is the one with the bulky group away from the metal. A switch from 1,2-insertion to 2,1-insertion on moving from CMe_3 to $SiMe_3$ was observed for the $Pd(OAc)_2$-catalyzed alkyne dimerization reaction reported by Trost.[4]

Once the alkyne has inserted into the Pt−H bond, a second alkyne coordinates to the metal and a 1,2-insertion of the alkyne into the Pt−C bond of the vinyl group occurs, yielding the complex that places the R group of the alkyne farther from the metal. It is notable that, while 1-pentene was available to trap the vinyl intermediate, we did not observe any pentene binding. Attempts to observe reaction intermediates via low-temperature ^{1}H NMR failed. The reaction of the phenylacetylene with **1** was monitored by VT ^{1}H NMR, but only loss of **1** and appearance of **7b** and 1-pentene were observed. This indicates that displacement of 1-pentene is rate limiting. We observed earlier (vide supra) that the second alkyne addition is faster than the first by adding 1 equiv of alkyne to **1** and getting a 1:1 ratio of **1** to **7**; thus, rate-limiting olefin displacement is not surprising because hydride migration should be rapid. Considering that olefin displacement is fairly rapid, the barrier to C−C bond formation in this system is quite low for a Pt species.

Deuterium labeling studies were conducted to test for scrambling between the Pt−H and the acetylenic protons. Two equivalents of PhCCH was added to a CD_2Cl_2 solution of (Cl-nacnac)Pt(D)(1-pentene-d_{10}) (**1-*d*$_{11}$**) and the resulting $\eta^1{:}\eta^2$-butadienyl complex exhibited integrations for the protons on C1, C3, and C4 as follows: singlet, ∼0.5 H; doublet over singlet, ∼1 H; doublet, ∼0.5 H. This indicates that the Pt−D is scrambled between the C1 and C4 positions. When PhCCD was reacted with (Cl-nacnac)Pt(H)(1-pentene) (**1**), the ^{1}H NMR spectrum showed a singlet integrating for about half a proton for the C1 and C4 signals and no signal was seen for the C3 proton. This again shows that the original Pt−H is ultimately scrambled between the C1 and C4 sites. Reaction of *t*-BuCCD with **1** yielded slightly different results. In this case the initial ^{1}H NMR showed only a small amount of scrambling between the positions on C1 and C4: ∼20% H at C1 and ∼20% D at C4. Upon standing in solution for several hours the spectrum showed complete scrambling: ∼50% H at C1 and ∼50% D at C4.

The labeling results indicate that the protons do not have to scramble along the reaction path forming **7** but rather that they can scramble once the product is formed. This is probably true for the phenylacetylene product as well; in that case the scrambling just happens too fast to catch it before completion. There are several plausible mechanisms for C1−C4 proton scrambling. The protons could be scrambled via acetylenic C−H activation before the alkynes are coupled, and if the coupling step is reversible, then scrambling after **7** is formed would occur.

Scheme 5. Possible Mechanisms for Proton Scrambling in 7



Alternatively, the protons could scramble after alkyne coupling via some type of vinylic C−H activation mechanism.

Mechanism A (Scheme 5) involves C−H activation of the first alkyne rather than insertion into the Pt−H bond. This yields a five-coordinate Pt(IV) dihydride which could rapidly equilibrate the hydrides. Reductive elimination of the alkyne will reform the Pt(II) hydride alkyne adduct with the hydride and acetylide protons scrambled. From here the *second* alkyne will insert into the Pt−H(D) bond to yield a Pt(II) vinyl alkyne intermediate. This Pt(II) vinyl alkyne species will then undergo migratory insertion to give the η^1:η^2-butadienyl product **7**. This mechanism would suffice if all of the scrambling occurred before formation of **7**, but since we observed scrambling of the protons in the already formed product when *t*-BuC≡CD is used, it does not seem sufficient. The alkyne coupling could conceivably be reversible, but that seems unlikely. Note that alkyne deinsertion from the Pt−H would be necessary to scramble the protons. There is a large thermodynamic driving force to reduce the alkyne; therefore, deinsertion seems unlikely. Though there are numerous reports of alkyne insertion into metal hydrides, there are few examples of alkyne deinsertion to generate a metal hydride.[14,47]

Mechanism B (Scheme 5) involves scrambling of the hydrogens on C1 and C4 in **7** via isomerization of the butadienyl ligand. Activation of the C4−H bond would yield a Pt(IV) hydride metallacyclopentadiene species. Hydride migration to C1 instead of C4 would form the opposite isomer of the η^1:η^2-butadienyl, in which C1 and C2 are now bound as the η^2-olefin. At this stage H,D exchange has not yet been accomplished, but isomerization of this intermediate to a carbene metallacyclopentadiene would create an sp^3-hybridized methylene group at C1. This complex is C_s symmetric with the mirror plane relating the protons on C1 to one another and thus equilibrating them. Isomerization back to the original geometry of **7** then results in scrambling of the original hydrogens attached to C1 and C4 in **7**. A possible variant of this mechanism is rehybridization to form the alkyl carbene metallacyclopentadiene with the proton and *t*-Bu group on the C4 methylene carbon and a 1,3-proton shift from C4 to C1, yielding the same C_s-symmetric intermediate for proton equilibration; it is not possible to distinguish between these two variants experimentally.

There are a number of metallacyclopentadiene complexes of d^8 transition metals in the literature;[48−53] thus, postulating such a species as an intermediate has precedence. A Rh(I) catalyst was recently reported to C−H activate the terminal vinyl C−H bond in a η^1:η^2-eneiminyl ligand to form a Rh(III) metallapyrrole hydride species;[54] this transformation is analogous to the Pt(II) η^1:η^2-butadienyl to Pt(IV) metallacyclopentadiene transformation proposed here. A similar transformation has been proposed for a Rh(I) η^1-butadienyl complex.[22] One might hope to observe some of the other isomer in solution, but we believe that the isomer in which C1 and C2 form the η^2-olefin will be energetically less favorable than the observed isomer. Even though a terminal olefin typically binds more tightly to Pt than an internal olefin, here the *t*-Bu group on C4 would be forced to point directly toward the Cl-nacnac aryl ring and the result would be an unfavorable steric interaction. Mechanism B seems more attractive because, unlike A, it does not require either C−C bond cleavage or alkyne deinsertion.

(47) Gao, Y.; Jennings, M. C.; Puddephatt, R. J. *Dalton Trans.* **2003**, *261*.

(48) Muller, C.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **2002**, *21*, 1118.

(49) van Belzen, R.; Elsevier, C. J.; Dedieu, A.; Veldman, N.; Spek, A. L. *Organometallics* **2003**, *22*, 722.

(50) Eisch, J. J.; Ma, X.; Han, K. I.; Gitua, J. N.; Kruger, C. *Eur. J. Inorg. Chem.* **2001**, 77.

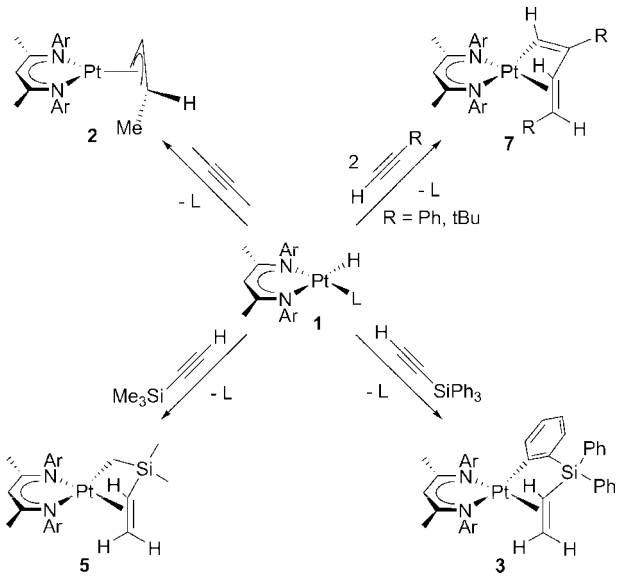
(51) Campora, J.; Palma, P.; Carmona, E. *Coord. Chem. Rev.* **1999**, *195*, 207.

(52) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245.

(53) Belluco, U.; Bertani, R.; Michelin, R. A.; Mozzon, M. *J. Organomet. Chem.* **2000**, *600*, 37.

(54) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2008**, *130*, 3645.

Scheme 6. Addition of Various Alkynes to (Cl-nacnac)Pt(H)(1-pentene) (1)



Conclusions

The (Cl-nacnac)Pt(H)(1-pentene) complex **1** is a useful starting material to assess the reactivity of the (Cl-nacnac)Pt(H) fragment, as the 1-pentene is easily displaced by other ligands. Complex **1** reacts with alkynes to displace 1-pentene, followed by rapid insertion of the alkyne into the Pt−H bond. Once insertion occurs, the electron-rich Pt reacts with alkyl or aryl C−H bonds on the newly formed vinyl group if they are in close proximity to the metal. This results in the formation of Pt allyls when alkynes with protons on the C adjacent to the triple bond, such as 2-butyne, are used. Alternatively, chelating alkyl/aryl olefins are formed when there are no protons adjacent to the triple bond, such as with $Ph_3SiC{\equiv}CH$ or $Me_3SiC{\equiv}CH$ (Scheme 6). These silyl alkynes insert into the Pt−H bond in a 2,1-manner, probably because the Si atom stabilizes the Pt−C bond when the silicon is β to the metal, placing the silyl substituents proximal to the Pt center for C−H activation. The 1,2-insertion of *t*-BuC≡CH places the alkyne substituents away from the metal such that C−H activation is disfavored and so the metal binds another alkyne and a second 1,2-insertion occurs, yielding an η^1:η^2-butadienyl complex. The product that results reflects head-to-tail reductive dimerization of two terminal alkynes.

Experimental Section

General Procedures. Unless otherwise stated, all reactions were performed under an atmosphere of dry nitrogen or argon using standard Schlenk and drybox techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieves. All glassware was flame-dried under vacuum and cooled under N_2 before use. Diethyl ether, methylene chloride, toluene, and pentane were purified under an argon atmosphere and passed through a column packed with activated alumina.[55] Tetrahydrofuran was distilled from sodium/benzophenone ketyl. Methylene chloride-d_2 was vacuum-transferred from calcium hydride and degassed by several freeze−pump−thaw cycles. $Me_4Pt_2(\mu\text{-}SMe_2)_2$[56] and Cl-nacnacH[57] (Cl-nacnacH = bis(*N*-(*p*-Cl-phenyl))-β-enamineimine) were synthesized via published procedures. Silylalkynes $Ph_3SiC{\equiv}CH$ and $Ph_2MeSiC{\equiv}CH$ were synthesized via published procedures.[58] The *t*-BuC≡CD was formed by stirring *t*-BuC≡CH with NaOD/D_2O for 2 days. All other reagents were used as received from Sigma Aldrich.

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AMX 300 MHz, Bruker Avance 400 MHz, and Bruker DRX 500 MHz spectrometers. ^{1}H NMR and ^{13}C NMR chemical shifts were referenced to residual ^{1}H and ^{13}C signals of the deuterated solvents. Infrared spectra were recorded on an ASI ReactIR 1000 instrument.

For clarity the NMR data for the Cl-nacnac ligand for all of the complexes has been omitted from the synthesis of each complex and given in Table 1.

Cl-nacnacPt(H)(1-pentene) (1). The complex was synthesized in a manner analogous to that for nacnacPt(H)(1-pentene). To a Schlenk flask was added 200 mg (0.348 mmol) of $Me_4Pt_2(\mu\text{-}SMe_2)_2$ and 245 mg (0.766 mmol, 2.2 equiv) of Cl-nacnacH. Methylene chloride and pentane were added, and the solution was stirred overnight. The bright yellow solution gradually changed to a darker orange color. The resulting oil was chromatographed on a silica column pretreated with a 3% NEt_3 in CH_2Cl_2 solution, using 80:20 hexanes−CH_2Cl_2 solution as the mobile phase. The first yellow band contains the product and free ligand; this product was collected and rotavapped to dryness. The product was chromatographed again using an untreated silica column and 100% CH_2Cl_2 to yield 106 mg (30%) of pure **1**. IR (CH_2Cl_2): ν_{Pt-H} 2217 cm^{-1}. ^{1}H NMR (δ, CD_2Cl_2, 400 MHz): 3.24 (1H, sextet, Pt−CH_2=C*H*Pr, $^3J_{H-H}$ = 6.8 Hz); 3.06 (1H, d, *cis*-Pt−CH_2=CHPr, $^3J_{H-H,trans}$ = 12.8 Hz, $^2J_{Pt-H}$ = 48 Hz); 2.75 (1H, d, *trans*-Pt−CH_2=CHPr, $^3J_{H-H,cis}$ = 7.6 Hz, $^2J_{Pt-H}$ = 62.4 Hz); 1.71, 1.58, 1.46, 1.33 (1H, m, Pt−CH_2=CHCH_2CH_2CH_3); 0.83 (3H, t, Pt−CH_2=CHCH_2CH_2CH_3, $^3J_{H-H}$ = 7.4 Hz); −21.57 (s, 1H, $^1J_{Pt-H}$ = 1216 Hz, Pt−H). Anal. Calcd for $C_{22}H_{26}N_2Cl_2Pt$: C, 45.21; H, 4.48; N, 4.79. Found: C, 45.31; H, 4.28; N, 4.68.

(Cl-nacnac)Pt(*anti*-η^3-C_3H_4Me) (2). In a vial was dissolved 30 mg (0.051 mmol) of **1** in 2 mL of pentane. To the solution was added 5.0 μL (3.5 mg, 0.065 mmol, 1.1 equiv) of 2-butyne. The vial was capped and shaken; after 30 min the solvent was evacuated, giving **2** as a yellow solid in quantitative yield. The product can be purified via liquid chromatography using silica gel treated with 97:3 CH_2Cl_2−NEt_3 and a mobile phase of 4:1 hexanes−CH_2Cl_2. ^{1}H NMR (δ, CD_2Cl_2, 400 MHz, room temperature): 4.63 (dt, 1H, $^3J_{H-H,syn}$ = 6.6 Hz, $^3J_{H-H,anti}$ = 10.8 Hz, $^2J_{Pt-H}$ = 78 Hz, H_2CC*H*C(H)(Me)); 2.46 (quin, 1H, $^3J_{H-H,syn}$ = $^3J_{H-H(Me)}$ = 6.6 Hz, $^2J_{Pt-H}$ = 40 Hz, H_2CCHC(*H*)(Me)); 1.93 (dd, 1H, $^3J_{H-H}$ = 6.6 Hz, $^2J_{H-H}$ = 2 Hz, $^2J_{Pt-H}$ = 24 Hz, *syn*-H_2CCHC(H)(Me)); 1.89 (dd, 1H, $^3J_{H-H}$ = 10.8 Hz, $^2J_{H-H}$ = 2 Hz, $^2J_{Pt-H}$ = 24 Hz, *anti*-H_2CCHC(H)(Me)); 0.60 (d, 3H, $^3J_{H-H}$ = 6.4 Hz, $^3J_{Pt-H}$ = 13.6 Hz, $H_2CCHC(H)(CH_3)$). ^{13}C NMR (δ, CD_2Cl_2, 100 MHz, room temperature): 98.1 ($^1J_{Pt-C}$ = 63 Hz, H_2CCHC(H)Me)); 59.3 ($^1J_{Pt-C}$ = 242 Hz, H_2CCHC(H)Me)); 40.1 ($^1J_{Pt-C}$ = 253 Hz, H_2CCHC(H)Me)); 14.0 ($^2J_{Pt-C}$ = 49 Hz, $H_2CCHC(H)(CH_3)$).

(Cl-nacnac)Pt(*o*-C_6H_4-$SiPh_2CH{=}CH_2$) (3). In a vial was dissolved 30 mg (0.058 mmol) of **1** in 2 mL of pentane. To the solution was added 1 equiv of $Ph_3SiC{\equiv}CH$. The vial was capped and shaken, and then after 1 h the solvent was evacuated, yielding compound **3**. The product can be purified via liquid chromatography using silica gel treated with 97:3 CH_2Cl_2−NEt_3 and a mobile phase of 4:1 hexanes−CH_2Cl_2. X-ray-quality crystals were formed by recrystallization from pentane at −30 °C. ^{1}H NMR (δ, CD_2Cl_2, 400 MHz, room temperature): 7.82 (m, 2H, *o*-SiPh); 7.54 (m, 3H, *m*,*p*-SiPh); 7.31 (m, 1H, *p*-SiPh′); 7.23 (m, 4H, *o*,*m*-SiPh′); 6.84 (d, 1H, $^3J_{H-H}$ = 6.8 Hz, C3-*H* Pt−PhSi); 6.74 (d, 1H, $^3J_{H-H}$ = 7.6

(55) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(56) Hill, G. S.; Irwin, M. J.; Levy, C. J.; Rendina, L. M.; Puddephatt, R. J. *Inorg. Synth.* **1998**, *32*, 149.

(57) Budzelaar, P. H. M.; de Gelder, R.; Gal, A. W. *Organometallics* **1998**, *17*, 4121.

(58) Ochida, A.; Ito, H.; Sawamura, M. *J. Am. Chem. Soc.* **2006**, *128*, 16486.

Table 1. ^{1}H and ^{13}C NMR Data for the Cl-nacnac Ligand of Complexes 1−8

complex	nacnac *p*-Cl-Ph (δ, ppm)	nacnac backbone (δ, ppm)
1	^{1}H: *m* 7.34 d, 2H, 8.4 Hz; *m* 7.23 d, 2H, 8.4 Hz; *o* 6.93 d, 2H, 8 Hz; *o* 6.83 d, 1H, 8.4 Hz; *o* 6.79 d, 1H, 8.4 Hz	^{1}H: C*H* 5.06 s, 1H; CH_3 1.74, 1.68 s, 3H
2	^{1}H: 7.30 m, 4H; 7.1−6.9 m, 4H ^{13}C: N−*C* 156.7, 156.3; *C*H/*C*Cl 128.3, 128.3, 128.3, 128.3, 124.8, 124.8, 124.6, 124.6, 124.3, 124.1	^{1}H: C*H* 4.92 s, 1H; CH_3 1.65, 1.64 s, 3H ^{13}C: *C*═N 158.5, 156.2; *C*H 98.7, $^3J_{Pt-H}$ = 61 Hz; *C*H_3 23.9, 23.6
3	^{1}H: *m* 7.34 br d, 2H; *o* 7.03 br, 1H; *o* 6.95 br, 1H; *m* 6.70 d, 2H, 8.4 Hz; *o* 6.28 d, 2H, 8.4 Hz ^{13}C: N−*C* 151.4, 148.4; *C*H/*C*Cl 139.2−122.4[a]	^{1}H: C*H* 5.08 s, 1H; CH_3 1.75, 1.72 s, 3H ^{13}C: *C*═N 160.9, 158.2; *C*H 100.8, $^3J_{Pt-H}$ = 48 Hz; *C*H_3 26.0, 25.7
4	^{1}H: *m* 7.23 d, 2H, 8.4 Hz; *m* 6.86 d, 2H, 8.4 Hz; *m* 6.62 br, 2H; *o* 6.20 br, 2H	^{1}H: C*H* 5.07 s, 1H; CH_3 1.81, 1.62 s, 3H
5	^{1}H: 7.30 m, 4H; 6.87 m, 1H; 6.81 m, 3H ^{13}C: N−*C* 152.4, 148.1; *C*H/*C*Cl 130.6, 129.8, 128.2, 128.2, 128.1, 128.1, 127.6, 127.6, 127.2, 127.2	^{1}H: C*H* 5.02 s, 1H; CH_3 1.75, 1.63 s, 3H ^{13}C: *C*═N 159.6, 156.9; *C*H 99.4, $^3J_{Pt-H}$ = 48 Hz; *C*H_3 26.0, 25.7
6	^{1}H: 7.35 d, 2H, 8.4 Hz; 7.31 d, 2H, 8.4 Hz; 7.02 d, 2H, 8.7 Hz; 6.86 d, 2H, 8.7 Hz	^{1}H: C*H* 5.01 s, 1H; CH_3 1.78, 1.71
7a	^{1}H: 7.32 d, 2H, 8 Hz; 7.30 d, 2H, 8 Hz; 6.86 br d, 2H; 6.80 d, 2H, 8.1 Hz ^{13}C: N−*C* 152.2, 151.2; *C*H/*C*Cl 130.2, 129.9, 128.5, 128.5, 128.5, 128.5, 128.2, 128.2, 127.3, 127.3	^{1}H: C*H* 4.91 s, 1H; CH_3 1.73, 1.67 ^{13}C: *C*═N 160.0, 156.2; *C*H 98.9, $^3J_{Pt-H}$ = 50 Hz; *C*H_3 25.3, 25.0
7b	^{1}H: 7.6−6.9[b] ^{13}C: N−*C* 153.6, 152.6; *C*H/*C*Cl 129−122[c]	^{1}H: C*H* 5.10 s, 1H; CH_3 1.85, 1.84 s, 3H ^{13}C: *C*═N 160.1, 156.4; *C*H 99.0; *C*H_3 25.3, 24.9
8	^{1}H: 7.24 d, 2H, 8.8 Hz; 7.22 d, 2H, 8.8 Hz; 7.03 d, 2H, 8 Hz; 6.96 d, 2H, 8 Hz ^{13}C: N−*C* 155.0, 150.1; *C*H/*C*Cl 129.3, 129.1, 129.1, 129.0, 129.0, 128.1, 128.1, 127.6, 127.6, 124.1	^{1}H: C*H* 4.70 s, 1H; CH_3 1.59, 1.57 s, 3H ^{13}C: *C*═N 158.2, 157.5; *C*H 99.4, $^3J_{Pt-H}$ = 43 Hz; *C*H_3 25.0, 25.0

[a] *p*-Cl-Ph carbons are indistinguishable from $SiPh_3$ carbons; all are given in the Experimental Section. [b] *p*-Cl-Ph protons are indistinguishable from aromatic phenylacetylene protons. [c] *p*-Cl-Ph carbons and aromatic phenylacetylene carbons were not individually identified.

Hz, C6-*H* Pt−PhSi); 6.61 (t, 1H, $^3J_{H-H}$ = 7.2 Hz, C5-*H* Pt−PhSi); 6.54 (t, 1H, $^3J_{H-H}$ = 7.2 Hz, C4-*H* Pt−PhSi); 3.70 (dd, 1H, $^3J_{H-H,cis}$ = 10.8 Hz, $^3J_{H-H,trans}$ = 14.8 Hz, (SiR_3)*H*C═CH_2); 3.24 (d, 1H, $^3J_{H-H,cis}$ = 10.8 Hz, (SiR_3)HC═C*H*$_2$); 3.07 (d, 1H, $^3J_{H-H,trans}$ = 14.8 Hz, (SiR_3)HC═C*H*$_2$). ^{13}C NMR (δ, CD_2Cl_2, 125 MHz, RT): 139.2, 136.5, 135.8, 135.8, 135.8, 135.5, 135.5, 135.5, 133.2, 133.1, 133.1, 131.2, 130.3, 130.2, 130.0, 129.9, 129.1, 128.4, 128.4, 128.4, 128.1, 128.1, 128.1, 126.6, 126.6, 124.1, 122.4 (28C, Ar/Ph *C*); 80.8 ($SiPh_2$CH═*C*H$_2$, $^1J_{Pt-C}$ = 193 Hz); 66.8 ($SiPh_2$*C*H═CH$_2$, $^1J_{Pt-C}$ = 198 Hz). Anal. Calcd for $C_{37}H_{32}N_2Cl_2PtSi$: C, 55.64; H, 4.04; N, 3.51. Found: C, 55.92; H, 3.92; N, 3.29.

(Cl-nacnac)Pt(CO)(*o*-C$_6$H$_4$-SiPh$_2$CH═CH$_2$) (4). In an NMR tube was dissolved 10 mg (0.013 mmol) of **3** in 2 mL of pentane. CO gas was bubbled into the solution, and then the tube was shaken, giving compound **4** in quantitative yield by ^{1}H NMR. IR (hexanes, room temperature): ν_{CO} 2080 cm^{-1}. ^{1}H NMR (δ, CD_2Cl_2, 400 MHz, room temperature): 7.46 (d, 4H, $^3J_{H-H}$ = 6.8 Hz, *o*-$SiPh_2$); 7.38 (m, 4H, *m*-$SiPh_2$); 7.30 (m, 2H, *p*-$SiPh_2$); 7.24 (dd, 1H, $^3J_{H-H,cis}$ = 14.4 Hz, $^3J_{H-H,trans}$ = 20.0 Hz, (SiR_3)*H*C═CH$_2$); 7.03 (d, 1H, $^3J_{H-H}$ = 6.8 Hz, C6-*H* Pt−PhSi); 6.74 (d, 1H, $^3J_{H-H}$ = 7.2 Hz, C3-*H* Pt−PhSi); 6.69 (t, 1H, $^3J_{H-H}$ = 7.2 Hz, C5-*H* Pt−PhSi); 6.51 (t, 1H, $^3J_{H-H}$ = 7.0 Hz, C4-*H* Pt−PhSi); 6.23 (dd, 1H, $^3J_{H-H,cis}$ = 14.4 Hz, $^3J_{H-H,gem}$ = 3.6 Hz, (SiR_3)HC═C*H*$_2$); 5.57 (dd, 1H, $^3J_{H-H,trans}$ = 20.0 Hz, $^3J_{H-H,gem}$ = 3.6 Hz, (SiR_3)HC═C*H*$_2$). Anal. Calcd for $C_{38}H_{32}N_2Cl_2OPtSi$: C, 55.21; H, 3.90; N, 3.39. Found: C, 55.42; H, 3.83; N, 3.11.

(Cl-nacnac)Pt(CH$_2$SiMe$_2$CH═CH$_2$) (5). In a vial was dissolved 30 mg (0.058 mmol) of **1** in 2 mL of pentane. To the solution was added 1 equiv of $Me_3SiC{\equiv}CH$. The vial was capped and shaken, and then after 1 h the solvent was evacuated, yielding compound **5**. The product can be purified via liquid chromatography using silica gel treated with 97:3 CH_2Cl_2−NEt_3 and a mobile phase of 4:1 hexanes−CH_2Cl_2. ^{1}H NMR (δ, CD_2Cl_2, 400 MHz, room temperature): 3.34 (m, 1H, $^2J_{Pt-H}$ = 68 Hz, (SiR_3)HC═C*H*$_2$ cis); 3.02 (m, 2H, (SiR_3)*H*C═C*H*$_2$ trans (simulated *J* values: $^3J_{H-H,trans}$ = 15.2 Hz, $^3J_{H-H,cis}$ = 10.2 Hz, $^2J_{H-H}$ = 3.2 Hz)); 0.16, (s, 3H, Si(Me$_2$)$_{up}$); −0.26 (s, 3H, Si(Me$_2$)$_{down}$); −0.89 (d, 1H, $^2J_{H-H}$ = 12.4 Hz, $^2J_{Pt-H}$ = 67.6 Hz, Pt−(C*H*$_2$)$_{down}$Si); −1.34 (d, 1H, $^2J_{H-H}$ = 12.4 Hz, $^2J_{Pt-H}$ = 77.6 Hz, Pt−(C*H*$_2$)$_{up}$Si). ^{13}C NMR (δ, CD_2Cl_2, 125 MHz, room temperature): 75.3 (SiMe$_2$CH═*C*H$_2$, $^1J_{Pt-C}$ = 242 Hz); 63.9 (SiMe$_2$*C*H═CH$_2$, $^1J_{Pt-C}$ = 75 Hz); 7.6 (SiMe(*C*H$_3$)$_{down}$); −2.3 (SiMe(*C*H$_3$)$_{up}$); −14.1 ((CH$_2$)SiMe$_2$, $^1J_{Pt-C}$ = 504 Hz). Anal. Calcd for $C_{22}H_{26}N_2Cl_2PtSi$: C, 43.14; H, 4.28; N, 4.57. Found: C, 43.50; H, 3.93; N, 4.33.

(Cl-nacnac)Pt(CO)(CH$_2$SiMe$_2$CH═CH$_2$) (6). In an NMR tube was dissolved 10 mg (0.016 mmol) of **5** in 2 mL of pentane. CO gas was bubbled into the solution, and then the tube was shaken, giving compound **6** in quantitative yield by ^{1}H NMR. IR (hexanes, room temperature): ν_{CO} 2072 cm^{-1}. ^{1}H NMR (δ, CD_2Cl_2, 300 MHz, room temperature): 6.10 (dd, 1H, $^3J_{H-H,trans}$ = 20.1 Hz, $^3J_{H-H,cis}$ = 14.6 Hz, (SiR_3)*H*C═CH$_2$); 5.81 (dd, 1H, $^3J_{H-H,cis}$ = 14.6 Hz, $^3J_{H-H,gem}$ = 3.2 Hz, (SiR_3)HC═C*H*$_2$); 5.51 (dd, 1H, $^3J_{H-H,trans}$ = 20.1 Hz, $^3J_{H-H,gem}$ = 3.2 Hz, (SiR_3)HC═C*H*$_2$); −0.08 (s, 2H, $^2J_{Pt-H}$ = 78 Hz, Pt−C*H*$_2$Si); −0.10 (s, 6H, $SiMe_2$). Anal. Calcd for $C_{23}H_{26}N_2Cl_2OPtSi$: C, 43.13; H, 4.09; N, 4.37. Found: C, 43.40; H, 3.81; N, 4.10.

(Cl-nacnac)Pt(η^1:η^2-C(H)═C(*t*-Bu)C(H)═C(H)(*t*-Bu)) (7a). In a vial was dissolved 30 mg (0.058 mmol) of **1** in 2 mL of pentane. To the solution was added 21.4 μL (14.2 mg, 3 equiv) of 3,3-dimethyl-1-butyne. The vial was capped and shaken, and then after 3 h the solvent was evacuated, yielding compound **7a**. The product can be purified via liquid chromatography using silica gel treated with 97:3 CH_2Cl_2−NEt_3 and a mobile phase of 4:1 hexanes−CH_2Cl_2. ^{1}H NMR (δ, CD_2Cl_2, 300 MHz, room temperature): 4.01 (s, 1H, $^2J_{Pt-H}$ = 32 Hz, Pt−C(*H*)═C(*t*-Bu)−); 3.50 (d, 1H, $^3J_{H-H}$ = 8.8 Hz, $^2J_{Pt-H}$ = 53 Hz, −C(*H*)═C(H)(*t*-Bu)); 2.89 (d, 1H, $^3J_{H-H}$ = 8.8 Hz, $^2J_{Pt-H}$ = 47 Hz, −C(H)═C(*H*)(*t*-Bu)); 0.87 (s, 9H, −C(H)═C(H)(C(C*H*$_3$)$_3$)); 0.82 (s, 9H, −C(H)═C(C(C*H*$_3$)$_3$)−). ^{13}C NMR (δ, CD_2Cl_2, 100 MHz, room temperature): 151.2 (Pt−C(H)═*C*(*t*-Bu)−); 113.7 ($^1J_{Pt-C}$ = 740 Hz, Pt−*C*(H)═C(*t*-Bu)−); 104.0 ($^1J_{Pt-C}$ = 248 Hz, −C(H)═*C*(H)(*t*-Bu)); 63.7 ($^1J_{Pt-C}$ = 24 Hz, −*C*(H)═C(H)(*t*-Bu)); 37.3 ($^3J_{Pt-C}$ = 77 Hz, Pt−C(H)═C(*C*Me$_3$)−); 36.0 ($^2J_{Pt-C}$ = 21 Hz, −C(H)═C(H)-(*C*Me$_3$)); 32.0 ($^3J_{Pt-C}$ = 24 Hz, −C(H)═C(H)(C(C*H*$_3$)$_3$)−); 28.3 (Pt−C(H)═C(C(*C*H$_3$)$_3$)−). Anal. Calcd for $C_{29}H_{36}N_2Cl_2PtSi$: C, 51.33; H, 5.35; N, 4.13. Found: C, 51.41; H, 5.29; N, 3.99.

(Cl-nacnac)Pt(η^1:η^2-C(H)═C(Ph)C(H)═C(H)(Ph)) (7b). In an NMR tube was dissolved 10 mg (0.017 mmol) of **1** in 0.6 mL of CD_2Cl_2. To the solution was added 3.8 μL (3.5 mg, 2 equiv) of phenylacetylene. The tube was capped and shaken, and the ^{1}H NMR spectrum recorded after 20 min displayed complex **7b**. ^{1}H NMR (δ, CD_2Cl_2, 400 MHz, room temperature): 7.6−6.9 (18H, Ph); 5.22 (s,

Table 2. Crystal Data and Structure Refinement Details for 3 and 6

	3	**6**
empirical formula	$C_{37}H_{32}Cl_2N_2PtSi$	$C_{23}H_{26}Cl_2N_2OPtSi$
mol wt	798.73	640.54
temp, K	100(2)	100(2)
wavelength, Å	0.710 73	1.541 78
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	10.2345(2)	12.6224(5)
b, Å	11.6447(2)	9.5550(4)
c, Å	14.6854(3)	20.1223(8)
α, deg	97.484(1)	90
β, deg	90.520(1)	91.486(2)
γ, deg	91.588(1)	90
V, Å^3	1734.45(6)	2426.07(17)
Z	2	4
calcd density, Mg/m^3	1.529	1.754
μ, mm^{-1}	4.261	13.451
F(000)	788	1248
crystal size, mm^3	0.59 × 0.12 × 0.10	0.25 × 0.05 × 0.05
2θ range, deg	1.40−25.68	3.50−69.51
index ranges	$-12 \le h \le 12$, $-13 \le k \le 14$, $-17 \le l \le 11$	$-15 \le h \le 15$, $-11 \le k \le 11$, $-24 \le l \le 24$
no. of rflns collected	15 681	24 550
no. of indep rflns	6559 (R(int) = 0.0330)	4485 (R(int) = 0.0351)
no. of data/restraints/params	6559/0/390	4485/0/275
goodness of fit on F^2	1.101	1.139
final R indices ($I > 2\sigma(I)$)	R1 = 0.0274, wR2 = 0.0733	R1 = 0.0256, wR2 = 0.0615
R indices (all data)	R1 = 0.0314, wR2 = 0.0751	R1 = 0.0278, wR2 = 0.0626
largest diff peak and hole, e Å^{-3}	1.291 and −0.693	2.059 and −0.988

1H, $^2J_{Pt-H}$ = 34 Hz, Pt−C(*H*)═C(Ph)−); 4.41 (d, 1H, $^3J_{H-H}$ = 7.6 Hz, $^2J_{Pt-H}$ = 46 Hz, −C(H)═C(*H*)(Ph)); 4.29 (d, 1H, $^3J_{H-H}$ = 7.6 Hz, $^2J_{Pt-H}$ = 50 Hz, −C(*H*)═C(H)(Ph)). ^{13}C NMR (δ, CD_2Cl_2, 100 MHz, room temperature): 142.7 (Pt−C(H)═*C*(Ph)−); 140.0, 138.6 (C−Ph ipso *C*); 129−122 (15C, Ph *C*); 123.4 (Pt−*C*(H)═C(Ph)−); 92.5 (−C(H)═*C*(H)(Ph)); 63.7 (−*C*(H)═C(H)(Ph)).

(Cl-nacnac)Pt(η^1-C(H)═C(*t*-Bu)C(H)═C(H)(*t*-Bu))(PMe_3) (8). A CH_2Cl_2 solution of the butadienyl complex **7** was placed in a flask in the drybox. The flask was removed from the box and placed under positive N_2 pressure. Trimethylphosphine was added via microliter syringe; upon addition the light orange solution turned bright yellow. After 30 min the solvent was removed and the product triturated with pentane, giving **8** in quantitative yield. ^{1}H NMR (δ, CD_2Cl_2, 400 MHz, room temperature): 5.50 (d, 1H, $^3J_{H-H}$ = 13 Hz, −C(H)═C(*H*)(*t*-Bu)); 5.39 (s, 1H, $^2J_{Pt-H}$ = 34 Hz, Pt−C(*H*)═C(*t*-Bu)−); 5.23 (d, 1H, $^3J_{H-H}$ = 13 Hz, −C(*H*)═C(H)(*t*-Bu)); 1.21, (s, 9H, −C(H)═C(C(CH_3)$_3$)−); 0.87 (d, 9H, $^2J_{P-H}$ = 10.4 Hz, $^3J_{Pt-H}$ = 30 Hz, P(CH_3)$_3$); 0.73 (s, 9H, −C(H)═C(H)(C(CH_3)$_3$)). ^{31}P NMR (δ, CD_2Cl_2, 162 MHz, room temperature): −39.5 (s, $^1J_{Pt-P}$ = 4164 Hz, PMe_3). ^{13}C NMR (δ, CD_2Cl_2, 100 MHz, room temperature): 143.6 ($^3J_{P-C}$ = 3 Hz, Pt−C(H)═*C*(*t*-Bu)−); 140.4 (−C(H)═*C*(H)(*t*-Bu)); 129.9 (−*C*(H)═C(H)(*t*-Bu)); 120.1 ($^2J_{P-C}$ = 15 Hz, Pt−*C*(H)═C(*t*-Bu)−); 38.4 ($^3J_{Pt-C}$ = 70 Hz, Pt−C(H)═C(*C*Me_3)−); 32.6 (−C(H)═C(H)(*C*Me_3)); 30.9 (Pt−C(H)═C(C(*C*H_3)$_3$)−); 30.1 (−C(H)═C(H)(C(*C*H_3)$_3$)); 16.8 ($^1J_{P-C}$ = 40 Hz, $^2J_{Pt-C}$ = 53 Hz, P(*C*H_3)$_3$).

Crystallographic Data for 3 and 6. Crystal data and structure refinement details for **3** and **6** are given in Table 2.

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Supporting Information Available: CIF files giving structural data for complexes **3** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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