JOC Article

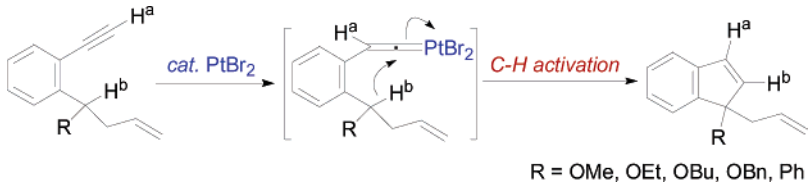
$PtBr_2$-Catalyzed Transformation of Allyl(*o*-ethynylaryl)carbinol Derivatives into Functionalized Indenes. Formal sp^3 C−H Bond Activation

Gan B. Bajracharya, Nirmal K. Pahadi, Ilya D. Gridnev, and Yoshinori Yamamoto*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

yoshi@mail.tains.tohoku.ac.jp

Received May 8, 2006



The $PtBr_2$-catalyzed reaction of 1-ethynyl-2-(1-alkoxybut-3-enyl)benzenes at 120 °C in CH_3CN gave functionalized indenes in good to allowable yields. Most probably, the hydrogen at the terminal alkyne is transferred to the adjacent internal β-carbon to form an (η^2-vinylidene)platinum carbene intermediate, which activates the sp^3 C−H bond at the benzylic carbon. This reaction pathway is supported by DFT calculations which suggest that the formation of the Pt−vinylidene complex is the rate-limiting stage for the whole transformation.

Introduction

Transition-metal-catalyzed cyclization of alkynes for the synthesis of carbo- and heterocycles has attracted great attention in recent years.[1] Although it is well established that terminal alkynes on treatment with transition metals lead to the formation of (η^2-vinylidene)metal complexes, we still await further development of synthetically useful transformations through these intermediates.[2] Depending upon the type of involved nucleophiles, mechanistically two distinct classes of intramolecular cycloisomerizations through metal vinylidene complexes exist in the literature: (1) intramolecular cyclization of dienylalkynes through 6π-electrocyclization (eq 1)[3] and (2) cyclization of terminal alkynes tethered to hetero- and carbonucleophiles (eq 2).[2e] In the latter case, a stoichiometric amount of a base is needed to remove a proton from YH. It is rather surprising that carbon nucleophiles have not been explored in the line of this strategy, except for in McDonald's paper.[4]

Herein, we report the $PtBr_2$-catalyzed transformation of 1-ethynyl-2-(1-alkoxybut-3-enyl)benzenes **1** into functionalized indenes **2** in which most probably a formal sp^3 C−H activation takes place by carbene insertion into the C−H bond of the Pt−vinylidene complex (eq 3).[2f,5] We recently reported formation of 1-vinylnaphthalenes **4** in the $PtBr_2$-catalyzed reaction of the internal alkyne analogues **3**, in which the cyclobutene intermediates are formed through Pt-catalyzed enyne metathesis (eq 4).[6] It is interesting that the terminal alkynes **1** behaved differently.

(1) For recent reviews see: (a) Nakamura, I.; Yamamoto, Y. *Chem. Rev.* **2004**, *104*, 2127. (b) Zeni, G.; Larock, R. C. *Chem. Rev.* **2004**, *104*, 2285. (c) Takacs, J. M.; Vayalakkada, S.; Jiang, X. *Science of Synthesis*; Thieme: Stuttgart, Germany, 2003; Vol. 1, pp 265−318.

(2) For reviews, see: (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (c) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311. Also see: (d) Weyerhausen, B.; Dotz, K. H. *Eur. J. Inorg. Chem.* **199**9, 1057. (e) McDonald, F. E. *Chem.—Eur. J.* **1999**, *5*, 3103 and references therein. (f) Nevado, C.; Echavarren, A. M. *Synthesis* **2005**, 167 and references therein. (g) Miki, K.; Uemura, S.; Ohe, K. *Chem. Lett.* **2005**, *34*, 1068 and references therein.

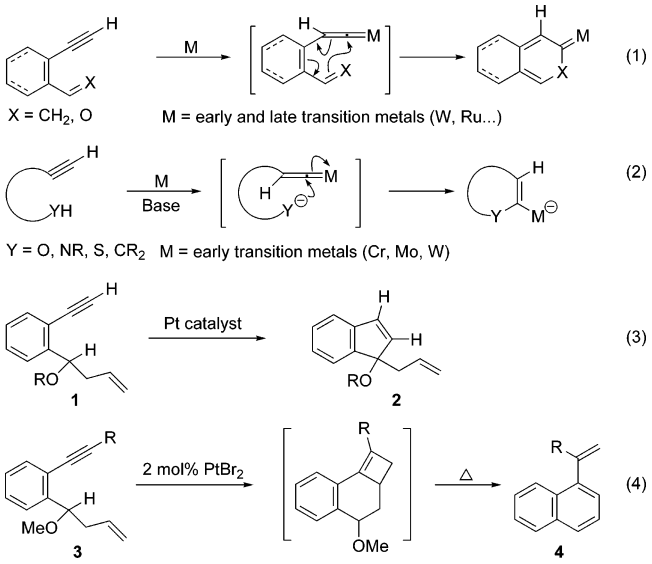
(3) (a) Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 11319. Also see: (b) Miura, T.; Iwasawa, N. *J. Am. Chem. Soc.* **2002**, *124*, 518 and references therein. (c) Dankwardt, J. W. *Tetrahedron Lett.* **2001**, *42*, 5809. (d) Martín-Matute, B.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2003**, *125*, 5757. (e) Madhushaw, R. J.; Lo, C.-Y.; Hwang, C.-W.; Su, M.-D.; Shen, H.-C.; Pal, S.; Shaikh, I. R.; Liu, R.-S. *J. Am. Chem. Soc.* **2004**, *126*, 15560 and references therein.

(4) McDonald, F. E.; Olson, T. C. *Tetrahedron Lett.* **1997**, *38*, 7691. NaH (0.5 equiv) was used as a base, and 0.5 equiv of $(Et_3N)Mo(CO)_5$ was needed to promote the carbocyclization.

(5) (a) Recently, ruthenium vinylidene complex-mediated alkenylation of pyridine at the α-C−H bond via [2 + 2] heterocycloaddition was reported: Murakami, M.; Hori, S. *J. Am. Chem. Soc.* **2003**, *125*, 4720. For recent advances in C−H activation, see: (b) *Handbook of C−H Transformation, Applications in Organic Synthesis*; Dyker, G., Ed.; Wiley-VCH: Weinheim, 2005; Vols. 1 and 2.

(6) Bajracharya, G. B.; Nakamura, I.; Yamamoto, Y. *J. Org. Chem.* **2005**, *70*, 892.

10.1021/jo060951g CCC: $33.50
Published on Web 07/14/2006



(1) (2) (3) (4)

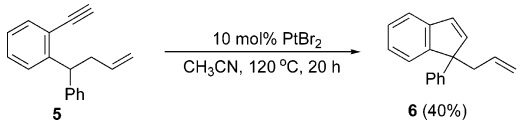
1 **2** **3** **4**

Results and Discussion

In our initial experimental setup, when 1-ethynyl-2-(1-methoxybut-3-enyl)benzene (**1a)** was heated with 2 mol % $PtBr_2$ in 1,4-dioxane at 120 °C for 42 h, 1-allyl-1-methoxy-1*H*-indene (**2a**) was isolated in 42% yield as the major product together with 24% 1-vinylnaphthalene (**4a)** (R = H). Encouraged by this result, we further optimized the reaction conditions. When *CH_3CN* was used as solvent, the selectivity for the formation of **2a** was improved. Increasing the amount of catalyst loading (5 mol %) was proved worthy, and **2a** was isolated in 55% yield in 12 h (65% NMR yield) (Table 1, entry 1). Besides platinum halides, $[RuCl_2(CO)_3]_2$ could be used as an alternative catalyst,[7] but it requires a longer reaction time. Other catalysts, such as $NiBr_2$, $PdCl_2(CH_3CN)_2$, $Pd(PPh_3)_4$, $Rh_6(CO)_{16}$, $CoCl_2$, $W(CO)_6$, $AuCl_3$, etc., did not promote the reaction at all. This reaction was not sensitive to moisture and was unaffected by addition of 50 mol % H_2O. The reaction was completely halted on treatment with an additional base (e.g., K_2CO_3 and Et_3N). Olefin additives, such as β-pinene (which can activate the platinum catalyst through π-coordination),[8] produced a comparable yield.

The scope of this reaction is summarized in Table 1. The reaction of substrates **1b**−**d** proceeded smoothly, affording the corresponding indene derivatives **2b**−**d** with a high selectivity over the formation of **4a** (entries 2−4). No significant effect was observed with the bulkiness of the alkoxide moiety. The reaction of **1e,f** bearing an electron-donating substituent (OMe) at the aromatic ring proceeded with perfect selectivity and produced the corresponding products **2e,f** (entries 5 and 6). Similarly, an excellent selectivity was observed with the substrate **1g** bearing a poor electron-withdrawing group (F) under the standard conditions, and product **2g** was isolated in a moderate yield (entry 7). On the other hand, the presence of a strong electron-withdrawing group (CF_3) reduced both the chemical yield and selectivity (entries 8 and 9).

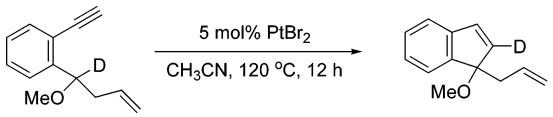
We tested the effect of the R^1 group in **1** on the present carbocyclization. The saturated analogue **1j**, the vinyl derivative **1k** bearing a shorter carbon chain, and **1l** having a longer carbon chain did not give **2** at all under the standard conditions; decomposition of the substrates took place, and a complex mixture of products was obtained. This observation suggests that the coordination of olefin to Pt at a right position/geometry might be essential for the indene formation. External olefin additives did not exert an influence on the reaction, but the internal olefin was needed to induce the reaction. On the other hand, replacing the methoxy substituent with the phenyl group proved to be possible. Thus, the phenyl-substituted analogue 1-ethynyl-2-(1-phenylbut-3-enyl)benzene **(5)** gave 1-allyl-1-phenyl-1*H*-indene (**6**) in 40% isolated yield (eq 5).



(5)

5 **6** (40%)

A deuterium-labeling experiment was carried out to get additional data for the elucidation of the reaction mechanism. When the substrate **1a**-*d* was treated with 5 mol % $PtBr_2$ under the standard conditions, the corresponding product **2a**-*d* (labeled with 100% deuterium at C-2 position) was obtained in 50% yield (eq 6). The deuterium labeling at another position was



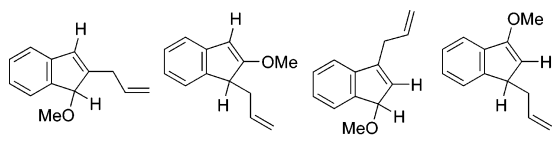
(6)

1a-*d* (100% *d*) **2a**-*d* (100% *d*) 50%

not observed. The structure of **2a**-*d*, as well as perfect selectivity of the position of deuterium incorporation, strongly suggests the intermediate formation of a vinylidene intermediate similar to those shown in eqs 1 and 2. In the case of a cationic pathway similar to the cyclization reactions of *o*-alkynylbenzaldehyde acetals and thioacetals,[8] one would expect some randomness in the distribution of deuterium. Moreover, the cationic mechanism would open the door to the migration of the methoxy group, actually observed in the corresponding reactions but not in the reaction under study. This observation corresponds well to the mechanism involving vinylidene insertion into the C−H bond, since it implies the conservation of the C−OMe bond throughout the whole transformation (Scheme 1). Another argument for the intermediate vinylidene formation in the case of terminal acetylenes is the completely different structure of the products yielded by the alkyl-substituted substrates under the same conditions (eq 4).[6] Although we are unaware of known examples

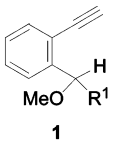
(7) More recently, two papers on cycloisomerization via Ru− and Rh−vinylidene intermediates appeared: (a) Datta, S.; Odedra, A.; Liu, R.-S. *J. Am. Chem. Soc.* **2005**, *127*, 11606. (b) Kim, H.; Lee, C. *J. Am. Chem. Soc.* **2005**, *127*, 10180.

(8) Recently, we reported the Pd-catalyzed carbocyclization of alkynylacetals in which the cleavage of the C−O bond of *o*-alkynylbenzaldehyde acetal produces the cationic intermediate and both the triple bond and the acetal group are bonded to the metal. Ring closure of the cationic intermediates leads to the cyclic vinyl cations, which are trapped by Pd−OR. (a) Nakamura, I.; Bajracharya, G. B.; Wu, H.; Oishi, K.; Mizushima, Y.; Gridnev, I. D.; Yamamoto, Y. *J. Am. Chem. Soc.* **2004**, *126*, 15423. (b) Nakamura, I.; Bajracharya, G. B.; Yamamoto, Y. *Chem. Lett.* **2005**, *34*, 174. (c) Nakamura, I.; Mizushima, Y.; Gridnev, I. D.; Yamamoto, Y. *J. Am. Chem. Soc.* **2005**, *127*, 9844. We were aware that if the present reaction proceeds through a similar mechanistic fashion, **7a**, **7b**, **7c**, or **7d** should be obtained. None of them were obtained.



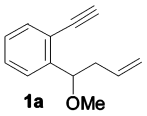
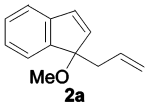
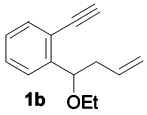
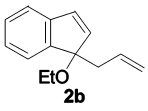
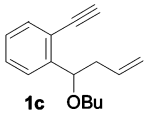
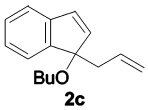
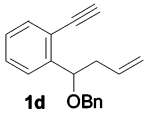
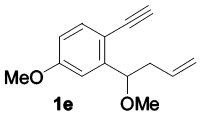
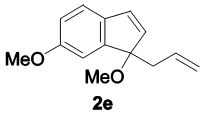
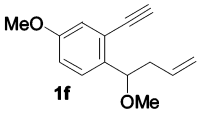
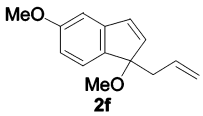
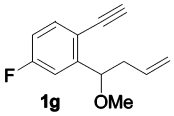
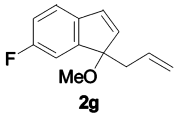
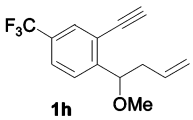
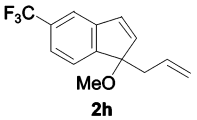
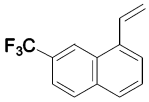
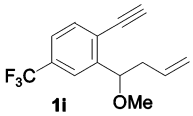
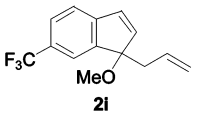
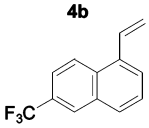
7a **7b** **7c** **7d**

TABLE 1. $PtBr_2$-Catalyzed *endo*-Carbocyclization of Terminal Alkynes[a]



1

1j; R^1 = $CH_2CH_2CH_3$
1k; R^1 = $HC{=}CH_2$
1l; R^1 = $CH_2CH_2CH{=}CH_2$

entry	substrate **1**	product(s)	yield/%[b]	**2**:**4**[c]
1	 **1a**	 **2a**	75 (61)	90:10
2	 **1b**	 **2b**	69 (59)	89:11
3	 **1c**	 **2c**	60 (52)	97:3
4[d]	 **1d**	 **2d**	56 (52)	95:5
5	 **1e**	 **2e**	70 (65)	100:0
6[d]	 **1f**	 **2f**	22 (20)	100:0
7	 **1g**	 **2g**	65 (50)	100:0
8	 **1h**	 **2h** +  **4b**	38 (36)	59:41
9	 **1i**	 **2i** +  **4c**	26 (25)	37:63

[a] Conditions: 5 mol % $PtBr_2$, CH_3CN, 120 °C, 12 h. [b] Combined yields of **2** + **4** based on ^1H NMR analysis; isolated yields are in parentheses. [c] Ratio based on isolated yield. [d] Reaction time was 24 h.

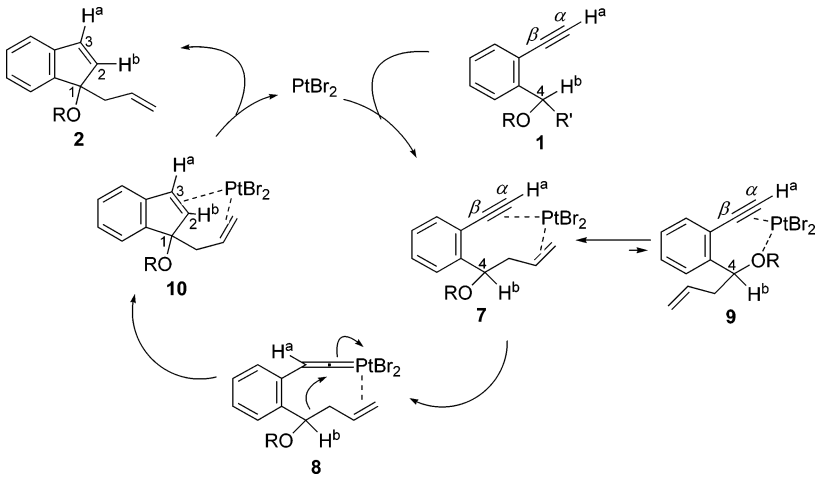
of platinum vinylidene intermediates, recent results demonstrate that the pincer vinylidene complexes of Pt(IV) can be isolated.[9]

To get more support for the mechanism of Pt−vinylidene insertion, we have followed the reaction pathway (Scheme 1) computationally (Figures 1 and 2).We have located the structures of three different complexes of $PtBr_2$ with the starting compound **1a**, viz., alkyne−$PtBr_2$−alkene complex **7**, $PtBr_2$−vinylidene complex **8**, alkyne−$PtBr_2$−OMe complex **9**, and $PtBr_2$−product complex **10** (Scheme 1, Figure 2).

Interestingly, $PtBr_2$−vinylidene complex **8** is much more stable (about 8 kcal/mol) than alkyne−$PtBr_2$−OMe complex **9** and only 2.2 kcal/mol less stable than starting **7**. The geometry of the Pt atom in **8** is very close to square planar (angles Br−Pt−Br and Br−Pt−C are 91.6° and 82.5°, respectively). On the other hand, in the optimized structure of the intermediate **11** (analogue of **8** having a vinyl substituent instead of allyl) the square planar geometry of Pt atom is significantly distorted (angles Br−Pt−Br and Br−Pt−C are 104.5° and 49.1°, respectively). The less effective intramolecular coordination of the vinyl substituent might be one of the reasons why we failed to obtain the corresponding cyclization products, although one cannot exclude the possibility of just inferior stability of the vinyl-substituted product.

(9) Kubo, K.; Jones, D.; Ferguson, M. J.; McDonald, R.; Cavell, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 5314.

SCHEME 1. Formation of the $PtBr_2$−Vinylidene Complex into the C−H^b Bond



We have also located transition structures (Figure 3) connecting **7** and **8** (**TS1**) as well as **8** and **10** (**TS2**); their validity was confirmed with the frequency analysis (only one negative vibration for either **TS1** or **TS2**). In both transition structures the participation of the double bond in the Pt coordination is evident: the Pt atom keeps almost ideal square planar geometry, one of the four ligands being the double bond of the allylic substituent. The activation barrier for the isomerization of **7** to **8** is quite high (33.4 kcal/mol); this is the limiting stage of the whole transformation, since the activation barrier of the cyclization step is quite low (3.1 kcal/mol). Energy minimization using **TS2** as the input structure afforded **10**; therefore, no other intermediates are involved in the cyclization step.

A alternative transition state (**TS3**) for the limiting stage connecting **9** and **12** (analogue of **8** with Pt coordinated to OR rather than to the double bond) was also computed. It was 18.2 kcal/mol higher in energy than **TS1**. The geometry of the Pt atom in **TS3** strongly deviated from square planar. Hence, the computational results indicate that the uniqueness of the allyl-substituted substrates for the cyclization might be stipulated for the geometry of the allylic substituent which is appropriate to keep the square planar geometry on the Pt atom throughout the whole transformation.

Experimental Section

General Information. ^{1}H NMR spectra are reported as follows: chemical shift in parts per million (δ) relative to the chemical shift of $CDCl_3$ at 7.24 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra are reported in parts per million (δ) relative to the central line of the triplet for $CDCl_3$ at 77 ppm. IR bands are reported in inverse centimeters. Column chromatography was carried out employing silica gel 60 N (spherical, neutral, 100−210 μm). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F_{254}. All manipulations were conducted under an argon atmosphere using standard Schlenk techniques.

Materials. 2-[(Trimethylsilanyl)ethynyl]benzaldehyde derivatives were obtained from the coupling of the corresponding 2-bromoben-

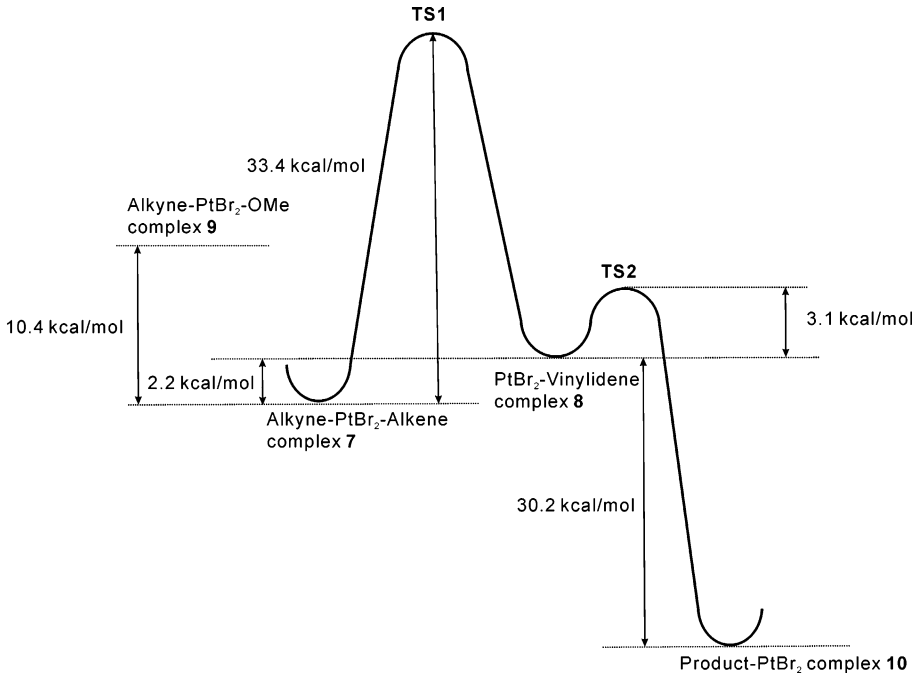


FIGURE 1. Energy profile for the transformation of the alkyne−Pt−alkene complex **7** to the product−$PtBr_2$ complex **10**.

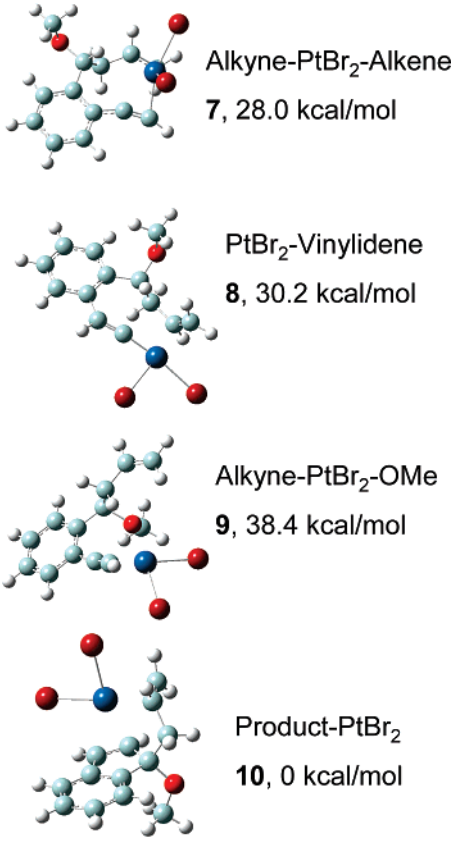


FIGURE 2. Structures of Pt complexes 7−**10** optimized at the B3LYP/SDD level of theory. The relative energies are given with respect to product−PtB_2 complex **10**.

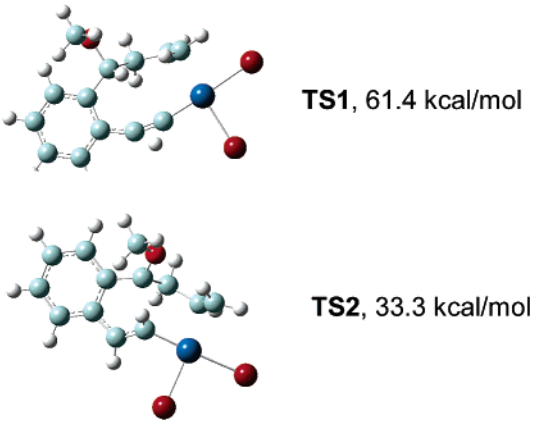
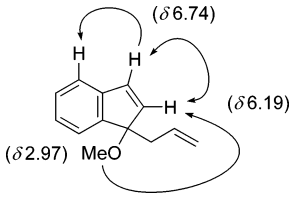


FIGURE 3. Transition structures **TS1** and **TS2** optimized at the B3LYP/SDD level of theory via the QST3 procedure. The relative energies are given with respect to product−PtB_2 complex **10**.

zaldehyde derivatives with (trimethylsilyl)acetylene by using the Sonogashira reaction.[10] 2-[(Trimethylsilanyl)ethynyl]benzaldehyde derivatives were then treated with KF in methanol for the deprotection of the trimethylsilyl group, producing the corresponding 2-ethynylbenzaldehydes. 2-Ethynylbenzaldehydes on treatment with allyltrimethylsilane in the presence of scandium triflate following the known protocol produced the desired 1-ethynyl-2-(1-alkoxybut-3-enyl)benzene.[11] 2-Bromobenzaldehyde, 2-bromo-5-fluorobenzaldehyde, (trimethylsilyl)acetylene, and allyltrimethylsilane were purchased and used as received. 2-Bromo-5-methoxybenzaldehyde,[12] 2-bromo-4-methoxybenzaldehyde,[13] 2-bromo-4-(trifluoromethyl)benzaldehyde,[14] and 2-bromo-5-(trifluoromethyl)-benzaldehyde[14] were prepared according to the reported procedures. 2-[(Trimethylsilanyl)ethynyl]benzaldehyde on treatment with phenylmagnesium bromide produced phenyl[2-[(trimethylsilanyl)ethynyl]phenyl]methanol, which after allylation[15] followed by deprotection of the trimethylsilyl group using KF afforded 1-ethynyl-2-(1-phenylbut-3-enyl)benzene. All the catalysts used were commercially available.

Representative Procedure for the *endo*-Carbocyclization. To a mixture of $PtBr_2$ (5.3 mg, 0.015 mmol, 5 mol %) and 1-ethynyl-2-(1-methoxybut-3-enyl)benzene (**1a**) (55.9 mg, 0.3 mmol) was added CH_3CN (5.0 mL, 0.06 M) under an argon atmosphere in a microreactor. The mixture was stirred for 20 min at room temperature and then heated at 120 °C for 12 h. The product was filtered through a short column of SiO_2 using ethyl acetate as an eluent, and the resulting filtrate was concentrated. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate, 100/1) to afford 1-allyl-1-methoxy-1*H*-indene (**2a**) in 55% yield (30.7 mg), and 1-vinylnaphthalene (**4a**) was obtained in 6% yield (2.8 mg).

Data for 1-allyl-1-methoxy-1*H*-indene (2a): R_f 0.52 (silica gel, hexane/EtOAc, 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.52 (dd, J = 7.0, 14.0 Hz, 1H), 2.71 (dd, J = 7.5, 14.0 Hz, 1H), 2.97 (s, 3H), 5.02−4.98 (m, 2H), 5.77−5.69 (m, 1H), 6.19 (d, J = 5.5 Hz, 1H), 6.74 (d, J = 5.5 Hz, 1H), 7.32−7.18 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.2, 51.7, 89.7, 117.7, 121.5, 122.6, 126.0, 128.5, 132.9, 133.7, 139.3, 143.0, 145.0; IR (neat) 3070−2824, 1640, 1464, 1315, 1101, 1074, 990, 920, 791, 758 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{13}H_{14}O$ (M^+) 186.1045, found 186.1039. Anal. Calcd for $C_{13}H_{14}O$ (186.25): C, 83.83; H, 7.58. Found: C, 83.54; H, 7.66. The structure of **2a** was confirmed by an NOE experiment:



Data for 1-allyl-1-ethoxy-1*H*-indene (2b): R_f 0.48 (silica gel, hexane/EtOAc, 10/1); yield 53%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (*t*, J = 7.2 Hz, 3H), 2.45 (dd, J = 7.2, 14.0 Hz, 1H), 2.64 (dd, J = 7.2, 14.0 Hz, 1H), 2.96−2.88 (m, 1H), 3.17−3.10 (m, 1H), 4.91−4.86 (m, 2H), 5.66−5.57 (m, 1H), 6.13 (d, J = 5.6 Hz, 1H), 6.62 (d, J = 5.6 Hz, 1H), 7.25−7.08 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.0, 42.3, 59.2, 89.2, 117.4, 121.2, 122.5, 125.8, 128.2, 132.1, 133.6, 139.9, 142.7, 145.7; IR (neat) 3070−2876, 1639, 1464, 1456, 1315, 1119, 1080, 995, 914, 789, 756 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{14}H_{16}O$ (M^+) 200.1201, found 200.1204. Anal. Calcd for $C_{14}H_{16}O$ (200.28): C, 83.96; H, 8.05. Found: C, 84.09; H, 7.72.

Data for 1-allyl-1-butoxy-1*H*-indene (2c): R_f 0.44 (silica gel, hexane/EtOAc, 10/1); yield 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ

(10) For a review, see: Brandsma, L.; Vasilevsky, S. F.; Verkruijsse, H. D. *Application of Transition Metal Catalyst in Organic Synthesis*; Springer-Verlag: Berlin, Heidelberg, 1999; Chapter 10.

(11) Yadav, J. S.; Subba Reddy, B. V.; Srihari, P. *Synlett* **2001**, 673.

(12) Gies, A.-E.; Pfeffer, M. *J. Org. Chem.* **1999**, *64*, 3650.

(13) Stuffert, J.; Abraham, E.; Raeppel, S.; Brûckner, R. V. *Liebigs Ann.* **1996**, 447.

(14) (a) Šindelář, K.; Dlabač, A.; Metyšová, J.; Kakáč, B.; Holubek, J.; Svátek, E.; Sedivý, Z.; Protiva, M. *Collect. Czech. Chem. Commun.* **1975**, *40*, 1940. (b) Perchonock, C. D.; Uzinskas, I.; McCarthy, M. E.; Erhard, K. F.; Gleason, J. G.; Wasserman, M. A.; Muccitelli, R. M.; DeVan, J. F.; Tucker, S. S.; Vickery, L. M.; Kirchner, T.;. Weichman, B. M.; Mong, S.; Scott, M. O.; Chi-Rosso, G.; Wu, H.-L.; Croole, S. T.; Newton, J. F. *J. Med. Chem.* **1986**, *29*, 1442.

(15) Yasuda, M.; Saito, T.; Ueba, M.; Baba, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 1414.

0.82 (*t*, $J = 7.2$ Hz, 3H), 1.29−1.23 (m, 2H), 1.42−1.37 (m, 2H), 2.49 (dd, $J = 7.2$, 13.6 Hz, 1H), 2.69 (dd, $J = 7.2$, 13.6 Hz, 1H), 2.92 (td, $J = 6.8$, 8.8 Hz, 1H), 3.12 (td, $J = 6.4$, 9.2 Hz, 1H), 4.97−4.92 (m, 2H), 5.73−5.65 (m, 1H), 6.19 (d, $J = 6.0$ Hz, 1H), 6.68 (d, $J = 6.0$ Hz, 1H), 7.30−7.14 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 19.3, 32.5, 42.4, 63.4, 89.0, 117.3, 121.2, 122.5, 125.7, 128.2, 132.1, 133.7, 140.0, 142.7, 145.7; IR (neat) 3070−2870, 1639, 1464, 1315, 1281, 1094, 993, 914, 789, 756 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{16}H_{20}O$ (M^+) 228.1514, found 228.1514. Anal. Calcd for $C_{16}H_{20}O$ (228.33): C, 84.16; H, 8.83. Found: C, 84.29; H, 8.92.

Data for 1-allyl-1-benzyloxy-1*H*-indene (2d): R_f 0.38 (silica gel, hexane/EtOAc, 10/1); yield 49%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58 (dd, $J = 7.2$, 13.6 Hz, 1H), 2.79 (dd, $J = 7.2$, 13.6 Hz, 1H), 4.02 (d, $J = 11.6$ Hz, 1H), 4.18 (d, $J = 11.6$ Hz, 1H), 5.01−4.96 (m, 2H), 5.83−5.73 (m, 1H), 6.25 (d, $J = 5.6$ Hz, 1H), 6.74 (d, $J = 5.6$ Hz, 1H), 7.38−7.17 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.3, 65.7, 89.5, 117.6, 121.4, 122.7, 126.0, 127.1, 127.2, 128.1, 128.4, 132.6, 133.6, 139.3, 139.5, 142.8, 145.2; IR (neat) 3067−2860, 1637, 1558, 1497, 1456, 1379, 1317, 1097, 1063, 993, 916, 756 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{19}H_{18}O$ (M^+) 262.1358, found 262.1359. Anal. Calcd for $C_{19}H_{18}O$ (262.35): C, 86.99; H, 6.92. Found: C, 86.67; H, 7.15.

Data for 1-allyl-1,6-dimethoxy-1*H*-indene (2e): R_f 0.55 (silica gel, hexane/EtOAc, 8/2); yield 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (dd, $J = 7.2$, 14.0 Hz, 1H), 2.67 (dd, $J = 7.2$, 14.0 Hz, 1H), 2.96 (s, 3H), 3.81 (s, 3H), 5.03−4.97 (m, 2H), 5.76−5.66 (m, 1H), 6.06 (d, $J = 5.6$ Hz, 1H), 6.66 (d, $J = 5.6$ Hz, 1H), 6.76−6.74 (m, 1H), 6.91−6.89 (m, 1H), 7.09−7.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.6, 51.7, 55.5, 89.6, 109.7, 112.8, 117.6, 121.7, 132.4, 133.5, 135.6, 137.0, 147.0, 158.7; IR (neat) 3074−2825, 1599, 1475, 1429, 1364, 1313, 1279, 1161, 1101, 1068, 1030, 916, 816, 781 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{14}H_{16}O_2$ (M^+) 216.1150, found 216.1150. Anal. Calcd for $C_{14}H_{16}O_2$ (216.28): C, 77.75; H, 7.46. Found: C, 77.60; H, 7.35.

Data for 1-allyl-1,5-dimethoxy-1*H*-indene (2f): R_f 0.31 (silica gel, hexane/EtOAc, 10/1); yield 20%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (dd, $J = 7.2$, 14.0 Hz, 1H), 2.66 (dd, $J = 7.2$, 14.0 Hz, 1H), 2.94 (s, 3H), 3.80 (s, 3H), 5.01−4.96 (m, 2H), 5.76−5.66 (m, 1H), 6.19 (d, $J = 5.6$ Hz, 1H), 6.66 (d, $J = 5.6$ Hz, 1H), 6.70−6.68 (m, 1H), 6.77−6.75 (m, 1H), 7.19−7.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.3, 51.5, 55.4, 89.0, 108.0, 110.4, 117.6, 123.2, 132.5, 133.7, 136.6, 140.5, 144.5, 160.2; IR (neat) 3072−2833, 1610, 1508, 1473, 1431, 1279, 1257, 1232, 1032, 916, 831, 787 cm^{-1}; GC−MS *m*/*z* calcd for $C_{14}H_{16}O_2$ (M^+) 216.1, found 216.0. Anal. Calcd for $C_{14}H_{16}O_2$ (216.28): C, 77.75; H, 7.46. Found: C, 78.02; H, 7.07.

Data for 1-allyl-6-fluoro-1-methoxy-1*H*-indene (2g): R_f 0.40 (silica gel, hexane/EtOAc, 10/1); yield 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (dd, $J = 7.2$, 14.0 Hz, 1H), 2.65 (dd, $J = 7.2$, 14.0 Hz, 1H), 2.96 (s, 3H), 5.02−4.96 (m, 2H), 5.74−5.64 (m, 1H), 6.16 (d, $J = 5.6$ Hz, 1H), 6.67 (d, $J = 5.6$ Hz, 1H), 6.94−6.89 (m, 1H), 7.03−7.00 (m, 1H), 7.12−7.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.2, 51.8, 89.6, 110.8, 114.8, 118.0, 122.0, 132.0, 133.1, 138.7, 147.6, 160.8, 163.5; IR (neat) 3076−2825, 1641, 1603, 1472, 1427, 1362, 1257, 1101, 987, 912, 872, 825, 783, 739 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{13}H_{13}FO$ (M^+) 204.0950, found 204.0952. Anal. Calcd for $C_{13}H_{13}FO$ (204.24): C, 76.45; H, 6.42; F, 9.30. Found: C, 76.34; H, 6.64.

Data for 1-allyl-1-methoxy-5-(trifluoromethyl)-1*H*-indene (2h): R_f 0.42 (silica gel, hexane/EtOAc, 10/1); yield 21%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (dd, $J = 7.2$, 14.0 Hz, 1H), 2.67 (dd, $J = 7.2$, 14.0 Hz, 1H), 2.95 (s, 3H), 5.00−4.96 (m, 2H), 5.75−5.65 (m, 1H), 6.30 (d, $J = 5.6$ Hz, 1H), 6.75 (d, $J = 5.6$ Hz, 1H), 7.47−7.38 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.0, 52.0, 90.0, 118.2, 118.2, 122.7, 123.1, 130.7, 131.0, 131.9, 132.9, 141.1, 143.4, 148.8; IR (neat) 3078−2827, 1431, 1360, 1321, 1269, 1165, 1126, 1076, 1053, 920, 895, 837, 791, 746 cm^{-1}; GC−MS *m*/*z* calcd for $C_{14}H_{13}F_3O$ (M^+) 254.1, found 254.0. Anal. Calcd for $C_{14}H_{13}F_3O$ (254.25): C, 66.14; H, 5.15; F, 22.42. Found: C, 66.17; H, 5.36.

Data for 1-allyl-1-methoxy-6-(trifluoromethyl)-1*H*-indene (2i): R_f 0.42 (silica gel, hexane/EtOAc, 10/1); yield 9%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (dd, $J = 7.2$, 14.0 Hz, 1H), 2.68 (dd, $J = 7.2$, 14.0 Hz, 1H), 2.96 (s, 3H), 5.01−4.96 (m, 2H), 5.75−5.65 (m, 1H), 6.36 (d, $J = 5.6$ Hz, 1H), 6.75 (d, $J = 5.6$ Hz, 1H), 7.28−7.26 (m, 1H), 7.53−7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.0, 52.0, 90.0, 117.3, 118.3, 119.3, 121.4, 126.0, 126.1, 131.9, 132.9, 142.4, 145.7, 146.2; IR (neat) 3076−2827, 1431, 1331, 1267, 1165, 1122, 1076, 1053, 918, 839 cm^{-1}; GC−MS *m*/*z* calcd for $C_{14}H_{13}F_3O$ (M^+) 254.1, found 254.0. Anal. Calcd for $C_{14}H_{13}F_3O$ (254.25): C, 66.14; H, 5.15; F, 22.42. Found: C, 66.41; H, 5.28.

Data for 1-vinylnaphthalene (4a):[16] R_f 0.66 (silica gel, hexane/EtOAc, 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (dd, $J = 1.6$, 10.8 Hz, 1H), 5.80 (dd, $J = 1.6$, 17.2 Hz, 1H), 7.54−7.40 (m, 4H), 7.64−7.62 (m, 1H), 7.87−7.78 (m, 2H), 8.15−8.11 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 117.0, 123.5, 123.7, 125.5, 125.7, 126.0, 128.0, 128.4, 131.0, 133.5, 134.3, 135.5; IR (neat) 3085−2978, 1618, 1590, 1509, 1418, 1389, 1341, 1168, 1009, 986, 916, 861, 800, 777 cm^{-1}; GC−MS *m*/*z* calcd for $C_{12}H_{10}$ (M^+) 154.1, found 154.0.

Data for 7-(trifluoromethyl)-1-vinylnaphthalene (4b): R_f 0.58 (silica gel, hexane/EtOAc, 10/1); yield 15%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.55 (dd, $J = 1.2$, 10.8 Hz, 1H), 5.81 (dd, $J = 1.2$, 17.2 Hz, 1H), 7.48−7.41 (m, 1H), 7.58−7.54 (m, 1H), 7.70−7.63 (m, 2H), 7.83−7.81 (m, 1H), 7.95−7.93 (m, 1H), 8.43−8.37 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.4, 121.3, 121.7, 124.8, 125.8, 127.5, 127.8, 127.8, 129.5, 129.9, 133.5, 134.7, 136.6; IR (neat) 3090−2924, 1462, 1313, 1234, 1161, 1122, 1068, 837, 754, 739 cm^{-1}; GC−MS *m*/*z* calcd for $C_{13}H_9F_3$ (M^+) 122.1, found 122.0.

Data for 6-(trifluoromethyl)-1-vinylnaphthalene (4c): R_f 0.62 (silica gel, hexane/EtOAc, 10/1); yield 16%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (dd, $J = 1.2$, 11.2 Hz, 1H), 5.80 (dd, $J = 1.2$, 17.2 Hz, 1H), 7.73−7.40 (m, 4H), 7.86−7.84 (m, 1H), 8.22−8.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.1, 121.5, 121.5, 125.0, 125.7, 126.1, 126.9, 127.4, 128.1, 128.7, 132.3, 133.6, 135.8; IR (neat) 3088−2926, 1473, 1381, 1346, 1315, 1234, 1198, 1124, 1074, 918, 899, 831, 798, 758, 739 cm^{-1}; GC−MS *m*/*z* calcd for $C_{13}H_9F_3$ (M^+) 122.1, found 122.0.

Data for 1-allyl-1-phenyl-1*H*-indene (6): yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.84 (dd, $J = 6.8$, 14.0 Hz, 1H), 3.05 (dd, $J = 7.6$, 14.0 Hz, 1H), 4.99−4.94 (m, 1H), 4.89−4.85 (m, 1H), 5.49−5.42 (m, 1H), 6.55 (d, $J = 5.6$ Hz, 1H), 6.78 (d, $J = 5.6$ Hz, 1H), 7.32−7.12 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.0, 60.6, 117.3, 121.4, 123.3, 125.3, 126.3, 126.5, 126.8, 128.4, 130.0, 134.3, 141.6, 143.4, 144.2, 150.7; IR (neat) 3062−2923, 1654, 1496, 1461, 1033, 914 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{18}H_6$ (M^+) 232.1252, found 232.1250.

Deuterium-Labeling Experiment. To a mixture of $PtBr_2$ (5.3 mg, 0.015 mmol, 5 mol %) and 1-ethynyl-2-(1-deuterio-1-methoxybut-3-enyl)benzene (**1a**-*d*) (56.4 mg, 0.3 mmol) was added CH_3CN (5.0 mL, 0.06 M) under an argon atmosphere in a microreactor. The mixture was stirred for 20 min at room temperature and then heated at 120 °C for 12 h. The product was filtered through a short column of SiO_2 using ethyl acetate as an eluent, and the resulting filtrate was concentrated. The residue was purified by column chromatography (silica gel, hexane/ethyl acetate, 100/1) to afford **2a**-*d* in 50% yield (28.1 mg), and **4a**-*d* was obtained in 6% isolated yield (2.7 mg).

Computational Details. Geometries of all stationary points were optimized using analytical energy gradients of self-consistent-field theory and density functional theory (DFT).[17] The latter utilized Becke's three-parameter exchange-correlation functional[18] including the nonlocal gradient corrections described by Lee−Yang−Parr

(16) Littke, A. F.; Schwarz, L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 6343.

(LYP),[19] as implemented in the Gaussian 03 program package.[20] All geometry optimizations were performed using the SDD basis set.[21] This approach is widely used for the recent computational studies of transition-metal complexes and was shown to yield results conforming with experimental data in our work[8,22] and the work of others.[23]

Acknowledgment. The computational results in this research were obtained using supercomputing resources at the Information Synergy Center, Tohoku University.

Supporting Information Available: NMR charts, Cartesian Coordinates, and full Gaussian citation. This material is available free of charge via the Internet at http://pubs.acs.org.

JO060951G

(17) (a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989. (b) Cheeseman, J. R.; Frisch, M. J.; Devlin, F. J.; Stephens, P. J. *Chem. Phys. Lett. 2* **1996**, *52*, 211.

(18) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(19) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989,** *157*, 200.

(20) Gaussian 03, Revision B.05: M. J. Frisch et al., Gaussian, Inc., Pittsburgh PA, 2003 (full reference in the Supporting Information).

(21) (a) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1976; Vol. 3, p 1. (b) Leininger, T.; Nicklass, A.; Stoll, H.; Dolg, M.; Schwerdtfeger, P. *J. Chem. Phys.* **1996**, *105*, 1052.

(22) (a) Nishikata, T.; Yamamoto, Y.; Gridnev, I. D.; Miyaura, N. *Organometallics* **2005**, *25*, 5025. (b) Gridnev, I. D.; del Rosario, M. K. C.; Zhanpeisov, N. U. *J. Phys. Chem. B* **2005**, *109*, 12498. (c) Imamoto, T.; Yashio, K.; Crepy, K. V. L.; Katagiri, K.; Takahashi, H.; Kouchi, M.; Gridnev, I. D. *Organometallics* **2006**, *26*, 908. (d) Patil, N. T.; Lutete, L. M.; Wu, H.; Pahadi, N. K.; Gridnev, I. D.; Yamamoto, Y. *J. Org. Chem.* **2006**, *71*, 4270.

(23) (a) Bittner, M.; Koppel, H. *J. Phys. Chem. A* **2004**, *108*, 11116. (b) McKee, M. L.; Swart, M. *Inorg. Chem.* **2005**, *44*, 6975. (c) Kondo, T.; Tsunawaki, F.; Ura, Y.; Sadaoka, K.; Iwasa, T.; Wada, K.; Mitsudo, T. *Organometallics* **2005**, *24*, 905. (d) Nowroozi-Isfahani, T.; Musaev, D. G.; McDonald, F. E.; Morokuma, K. *Organometallics* **2005**, *24*, 2921.