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Electronic Control of Regioselectivity in Coupling Reactions of $SiMe_3$-Substituted Alkenes with $Cp_2Zr(\eta^2(N,C^2)$-6-phenylpyridyl)(THF)$^+$

Anil S. Guram and Richard F. Jordan*

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242

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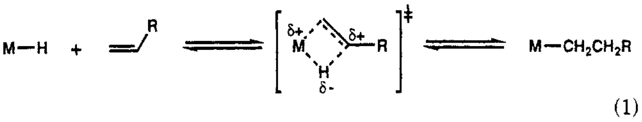
Summary: The reaction of [$Cp_2Zr(\eta^2(N,C^2)$-6-phenylpyridyl)(THF)][BPh_4] (**1**) with allyltrimethylsilane proceeds via 1,2-insertion to afford [$Cp_2Zr(\eta^2(C,N)$-$CH_2CH(CH_2SiMe_3)$(6-phenylpyrid-2-yl))][BPh_4] (**2**), in which the CH_2SiMe_3 substituent is placed at the β-carbon. In contrast, the reaction of **1** with vinyltrimethylsilane proceeds via 2,1-insertion to afford [$Cp_2Zr(\eta^2(C,N)$-$CH(SiMe_3)CH_2$-(6-phenylpyrid-2-yl))][BPh_4] (**4**), in which the $SiMe_3$ substituent is located on the α-carbon. These results are rationalized on the basis of electronic effects originating from the $SiMe_3$ group that dominate the steric effects and control the coupling/insertion regiochemistry in these systems.

The coupling/insertion reactions of terminal alkenes with Cp_2Zr(benzyne), $Cp_2Zr(\eta^2(N,C)$-$N(SiMe_3)CH(R))$-(THF), and related species proceed regioselectively to afford metallacycles in which the alkene substituent is placed at the β-carbon (1,2-insertion).[1] The same regioselectivity is observed for olefin insertions into early-transition-metal and lanthanide metal–alkyl and metal-hydride bonds.[2,3] Steric effects (Cp/alkene substituent interactions) strongly favor the transition states leading to, and the products of, 1,2-insertion. The 1,2-insertion products are also electronically more stable than the 2,1-isomers (primary vs secondary metal alkyl). Additionally, stabilization of the partial positive charge on the β-carbon in the insertion transition state (eq 1)[4] by the substituent provides a kinetic preference for 1,2-insertion. As a part of our efforts to develop synthetic organic applications of $Cp_2Zr(R)(L)^+$ complexes,[5] we are investigating the reactions of the cationic Zr pyridyl complex [$Cp_2Zr(\eta^2$-(N,C^2)-6-phenylpyridyl)(THF)][BPh_4] (1) (Scheme I) with unsaturated substrates.[5g,h] We report here that $SiMe_3$ substituents exert a strong electronic influence[6] on the regioselectivity of alkene coupling/insertion reactions of 1, which can override the normal steric preference for 1,2-insertion.



(1)

The reaction of 1 with allyltrimethylsilane at 65 °C (1.5 h) or room temperature (19 h) in dichloroethane proceeds via 1,2-insertion to afford 2 (93% NMR and 73% isolated yields, Scheme I). NMR data establish that the $SiMe_3$ group in 2 is located on the carbon β to zirconium.[7a] There is no evidence for the formation of the other regioisomer.

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[5] (a) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410. (b) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (c) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1041. (d) Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 778. (e) Jordan, R. F.; Taylor, D. F.; Baenziger, N. C. *Organometallics* **1990**, *9*, 1546. (f) Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; LaPointe, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1289. (g) Jordan, R. F.; Guram, A. S. *Organometallics*, in press. (h) Guram, A. S.; Jordan, R. F. Manuscript in preparation. (i) Jordan, R. F.; LaPointe, R. E.; Baenziger, N. C.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539.

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[7] (a) A solution of 900 mg (1.18 mmol) of 1 and 803 mg (7.05 mmol) of allyltrimethylsilane in 20 mL of dichloroethane was heated at 60–65 °C for 1.5–2.0 h. The resulting yellow solution was cooled to room temperature, and hexane (20–25 mL) was added to induce precipitation (the product may precipitate in the form of a yellow oil). The precipitated product was washed with hexane (5 × 15 mL) and dried in vacuo. The crude solid was recrystallized from CH_2Cl_2/hexane to yield 694 mg (73%) of **2** as a yellow solid. ^1H and ^{13}C spectra of **2** contain normal BPh_4^- resonances. ^1H NMR (360 MHz, CD_2Cl_2): δ 7.93 (t, J = 7.8 Hz, 1 H, Ar H), 7.8 (t, J = 7.6 Hz, 1 H, Ar H), 7.69 (t, J = 7.6 Hz, 2 H, Ar H), 7.57 (d, J = 8.1 Hz, 1 H, Ar H), 7.4 (d, J = 8.1 Hz, 1 H, Ar H), 7.08 (obscured by BPh_4^-, 2 H, Ar H), 6.39 (s, 5 H, Cp), 5.36 (s, 5 H, Cp), 3.60 (m, 1 H, β-CH), 2.35 (t, J = 12.6 Hz, 1 H, α-CH), 1.6 (dd, J = 14.0 Hz, J = 3.8 Hz, 1 H, CH_2Si), 1.03 (dd, J = 12.6 Hz, J = 3.7 Hz, 1 H, α-CH), 0.74 (dd, J = 14.0 Hz, J = 10.2 Hz, 1 H, CH_2Si), 0.22 (s, 9 H, $SiMe_3$). ^{13}C NMR (90 MHz, CD_2Cl_2): δ 175.5, 158.6, 142.8, 139.7, 134.5, 133.3, 123.1, 122.3, 121.2, 113.3 (Cp), 112.7 (Cp), 57.1 ($ZrCH_2$), 44.8 ($ZrCH_2CH$), 26.0, 0.1. Anal. Calcd for $C_{51}H_{52}BNSiZr$: C, 75.71; H, 6.48; N, 1.73; Zr, 11.27. Found: C, 75.41; H, 6.46; N, 1.62; Zr, 11.10. (b) A solution of 100 mg (0.13 mmol) of 1 and 118 mg (1.04 mmol) of allyltrimethylsilane in 7 mL of $ClCH_2CH_2Cl$ was heated at 60–65 °C under N_2 for 2.0 h. The yellow reaction solution was cooled to room temperature, and 5 mL of H_2O (N_2 purged and degassed) was added. The resulting colorless slurry was stirred at room temperature for 5.0 h. The organics were extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with saturated $NaHCO_3$ solution (10 mL) and saturated NaCl solution (10 mL), dried with $MgSO_4$, and filtered. The solvents were removed by vacuum evaporation, and the crude yellowish oil was purified by column chromatography (alumina) with use of 8/1 hexane/CH_2Cl_2 as the eluent to yield 24 mg (73%) of **3** as a colorless oil. ^1H NMR (360 MHz, CD_2Cl_2): δ 8.05 (d, J = 6.9 Hz, 2 H, Ar H), 7.67 (t, J = 7.7 Hz, 1 H, Ar H), 7.55 (d, J = 7.8 Hz, 1 H, Ar H), 7.49–7.39 (m, 3 H, Ar H), 7.12 (d, J = 7.6 Hz, 1 H, Ar H), 3.15 (m, 1 H, $CH(Me)CH_2Si$), 1.37 (d, J = 6.8 Hz, 3 H, Me), 1.22 (dd, J = 14.5 Hz, J = 8.1 Hz, 1 H), 0.94 (dd, J = 14.5 Hz, J = 6.8 Hz, 1 H), −0.10 (s, 9 H, $SiMe_3$). ^{13}C NMR (90 MHz, CD_2Cl_2): δ 168.2, 156.4, 140.2, 137.3, 129.0, 128.9, 127.2, 119.9, 117.8, 39.0, 25.8, 25.0, −0.9. HRMS (EI) for $C_{17}H_{23}NSi$ (m/e): calcd, 269.1600; found, 269.1616.

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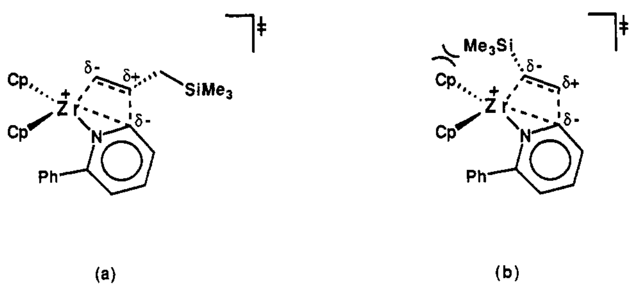
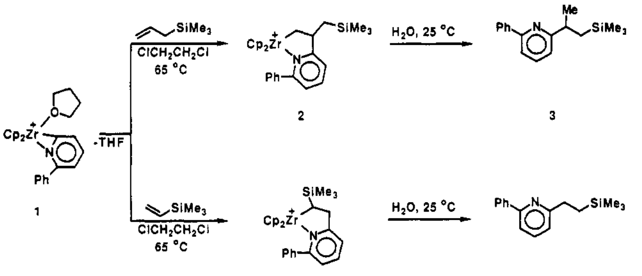


Figure 1. Proposed transition states for insertion of allyltrimethylsilane (a) and vinyltrimethylsilane (b) into the Zr–C bond of pyridyl complex 1.

Scheme I



The ${}^1H$ NMR spectrum of 2 includes a broad multiplet at δ 3.60 for the β-CH and a triplet at δ 2.35 and a doublet of doublets at δ 1.03 for the α-CH's. This pattern is most consistent with the assigned structure when compared to ${}^1H$ NMR data for related insertion complexes.[5e] Hydrolysis of 2 prior to isolation yields 2-phenyl-6-(1-methyl-2-(trimethylsilyl)ethyl)pyridine (3).[7b] The ${}^1H$ NMR spectrum of 3 includes doublets of doublets at δ 1.22 and 0.94 for the two diastereotopic hydrogens α to silicon, a doublet at δ 1.37 for the Me group, and a multiplet at δ 3.15 for $CH(Me)CH_2SiMe_3$ and confirms the insertion regiochemistry.

In contrast, the reaction of 1 with vinyltrimethylsilane at 65 °C (1.5 h) or room temperature (>120 h) in dichloromethane proceeds via 2,1-insertion to afford 4 (90% NMR and 69% isolated yields, Scheme I).[8a] Formation of the other regioisomer is not evident from the ${}^1H$ NMR spectrum of the reaction mixture. The ${}^1H$ NMR spectrum of 4 includes doublets of doublets at δ 3.72 and 3.40 for the β-CH's and a doublet of doublets at δ 3.32 for the α-CH. Hydrolysis of 4 prior to isolation yields 2-phenyl-6-(2-(trimethylsilyl)ethyl)pyridine (5).[8b] The ${}^1H$ NMR spectrum of 5 exhibits an AA′XX′ pattern for the $-CH_2CH_2Si-$ side chain, which confirms the insertion regiochemistry.

As their regioisomers are not available, it is not possible to rigorously establish if 2 and 4 are kinetic products, thermodynamic products, or both. However, we currently favor the third possibility on the basis of observations that (i) the alternate regioisomers are not observed when these reactions are monitored by ${}^1H$ NMR spectroscopy at room temperature, (ii) no isomerization of 2 or 4 is observed under conditions where the coupling/insertion reactions are reversible (65 °C for 2 and 110 °C for 4),[9] and (iii) thermolysis of 2 and 4 under severe conditions (chlorobenzene, 120 °C) does not induce isomerization.

The 1,2-insertion regioselectivity observed in the reaction of 1 with allyltrimethylsilane is expected on both steric and electronic grounds. Unfavorable steric interactions between the CH_2SiMe_3 substituent and the Cp ligands are expected to disfavor the transition state for, and the product of, 2,1-insertion. Additionally, a transition state (Figure 1a) similar to that proposed by Bercaw for 1,2-insertions of alkenes into M–H and M–R bonds,[4] containing a partial positive charge on the β-carbon, would be stabilized by the $SiMe_3$ group, which is β to this center. In contrast, the regioselectivity observed in the reaction of 1 with vinyltrimethylsilane is opposite to that expected on the basis of steric effects (destabilizing $Cp/SiMe_3$ interaction) and implies that electronic effects are dominant. It is likely that electronic stabilization of the electron-poor Zr^+ center and the electron-rich Zr–alkyl carbon of 4 by the $SiMe_3$ group (which is β and α, respectively, to these centers) favors 4 over its regioisomer.[6,10] Additionally, this regiochemistry can be rationalized on the basis of a polar transition state (Figure 1b) in which the α negative charge (developing Zr–C bond) and the β positive charges are stabilized by the $SiMe_3$ substituent.[6,10,11] The 2,1-insertion leading to 4 contrasts with the 1,2-insertion observed in reactions of vinyltrimethylsilane with $Cp'_2Zr(H)(THF)^+$ and Cp^*_2ScH.[5f,12] However, the formation of 4 is similar to the formation of α-Si-substituted products in coupling/insertion reactions of silylacetylenes at Cp_2Zr centers, though steric interactions are quite different in these cases.[5h,13]

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[8] (a) Complex 4 was isolated as a yellow solid in 69% (357 mg) yield from the reaction of 1 with vinyltrimethylsilane at 65 °C with use of the procedure described in ref 7a. ${}^1H$ and ${}^{13}C$ spectra of 4 contain normal BPh_4^- resonances. ${}^1H$ NMR (360 MHz, CD_2Cl_2): δ 7.87 (t, *J* = 7.8 Hz, 1 H, Ar H), 7.76 (t, *J* = 7.5 Hz, 1 H, Ar H), 7.64 (t, *J* = 7.8 Hz, 2 H, Ar H), 7.31 (obscured by BPh_4^-, 2 H, Ar H), 7.13 (d, *J* = 7.0 Hz, 2 H, Ar H), 6.54 (s, 5 H, Cp), 5.64 (s, 5 H, Cp), 3.72 (dd, *J* = 18.7 Hz, *J* = 12.9 Hz, 1 H, β-CH), 3.40 (dd, *J* = 18.7 Hz, *J* = 3.0 Hz, 1 H, β-CH), 3.32 (dd, *J* = 12.9 Hz, *J* = 3.0 Hz, 1 H, α-CH), 0.09 (s, 9 H, $SiMe_3$). ${}^{13}C$ NMR (90 MHz, CD_2Cl_2): δ 169.1, 160.4, 143.1, 137.9, 132.7, 131.4, 126.8, 124.9, 124.4, 115.4 (Cp), 114.1 (Cp), 69.2 (ZrCHSi), 38.6 (ZrCH(Si)CH_2), 0.8. Anal. Calcd for $C_{50}H_{50}BNSiZr$: C, 75.53; H, 6.34; N, 1.76; Zr, 11.47. Found: C, 75.27; H, 6.33; N, 1.62; Zr, 11.25. (b) Compound 5 was isolated in 80% (28 mg) yield from the hydrolysis of the reaction mixture of 1 and vinyltrimethylsilane with use of the procedure described in ref 7b. ${}^1H$ NMR (360 MHz, CD_2Cl_2): δ 8.04 (d, *J* = 6.9 Hz, 2 H, Ar H), 7.65 (t, *J* = 7.7 Hz, 1 H, Ar H), 7.55 (d, *J* = 7.2 Hz, 1 H, Ar H), 7.49–7.37 (m, 3 H, Ar H), 7.13 (d, *J* = 7.6 Hz, 1 H, Ar H), 2.86 (m, AA′XX′ pattern, 2 H), 1.03 (m, AA′XX′ pattern, 2 H), 0.05 (s, 9 H, $SiMe_3$). ${}^{13}C$ NMR (90 MHz, CD_2Cl_2): δ 164.7, 156.6, 140.1, 137.3, 129.0, 128.9, 127.2, 120.7, 117.6, 33.1, 17.1, −1.7. HRMS (EI) for $C_{16}H_{21}NSi$ (*m/e*): calcd, 225.1443; found, 255.1439.

[9] Thermolysis of 2 in the presence of excess propene ($ClCD_2CD_2Cl$, 65 °C, 1.5 h) gives a mixture of allyltrimethylsilane, 2, and the propene insertion complex $Cp_2Zr(\eta^2(C,N)\text{-}CH_2CH(Me)(\text{6-phenylpyrid-2-yl}))^+$ (6),[5h] establishing that the reaction of allyltrimethylsilane with 1 is reversible. No reaction is observed in the thermolysis of 4 in the presence of excess propene or excess (trimethylsilyl)acetylene at 65 °C ($ClCD_2CD_2Cl$). However, thermolysis of 4 in the presence of excess propene at 110 °C ($ClCD_2CD_2Cl$) gives a mixture of vinyltrimethylsilane, 4, and 6, establishing that the reaction of vinyltrimethylsilane with 1 is reversible at elevated temperatures. Similar reversibility has been established for related coupling/insertion reactions at Cp_2M centers (see ref 1 and: Erker, G.; Dorf, U.; Rheingold, A. L. *Organometallics* **1988**, *7*, 138).

[10] Recent kinetic and theoretical studies show that the SiR_3 group stabilizes an α positive charge by ca. 12–14 kcal mol^{-1} relative to hydrogen. See ref 6f and: Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806. However, the observed regioselectivity in the formation of 4 indicates that this effect is insignificant compared to those discussed in the text.

[11] It is possible that $Cp/SiMe_3$ steric interactions force the $SiMe_3$ group toward the plane between the Cp ligands and enhance hyperconjugative stabilization of the Zr^+ center in 4 and/or the β positive charge in the transition state proposed in Figure 1b.

[12] See ref 4c and: Burger, B. J. Ph.D. Thesis, California Institute of Technology, 1987.

[13] For leading references see ref 1 and: (a) Hyla-Kryspin, I.; Gleiter, R.; Kruger, C.; Zwettler, R.; Erker, G. *Organometallics* **1990**, *9*, 517. (b) Erker, G.; Zwettler, R.; Kruger, C.; Hyla-Kryspin, I.; Gleiter, R. *Organometallics* **1990**, *9*, 524. (c) Buchwald, S. L.; Fang, Q. *J. Org. Chem.* **1989**, *54*, 2793. (d) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870. (e) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219. (f) Mattia, J.; Humphrey, M. B.; Rogers, R. D.; Atwood, J. L.; Rausch, M. D. *Inorg. Chem.* **1978**, *17*, 3257. (g) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952.

These results establish that electronic effects can dominate steric effects in determining the regiochemistry of coupling/insertion reactions of $Cp_2Zr(pyridyl)^+$ complexes. Our efforts to utilize this concept in the regioselective preparation of potentially interesting organic intermediates and our studies of the reactions of 1 with other unsaturated substrates will be discussed in subsequent reports.[5h]

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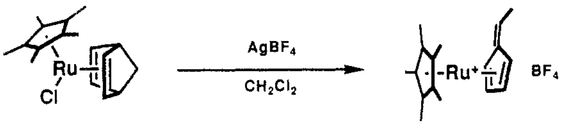
Preparation and Reactions of a Cationic (μ_3-Methylidyne)ruthenium Complex

Takeaki Kakigano, Hiroharu Suzuki,* Minoru Igarashi, and Yoshihiko Moro-oka
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Received March 21, 1990

Summary: The reaction of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ (**1**) with $AgBF_4$ in ethanol yields the cationic μ_3-methylidyne complex $[((\eta^5\text{-}C_5Me_5)Ru)_3(\mu_2\text{-}Cl)_2(\mu_2\text{-}H)(\mu_3\text{-}CH)](BF_4)$ (**2**), which undergoes reductive coupling between μ_3-methyne and μ_2-hydride ligands to give $[(\eta^5\text{-}C_5Me_5)Ru(CO)(\mu_2\text{-}CH_2)(\mu_2\text{-}Cl)Ru(CO)(\eta^5\text{-}C_5Me_5)](BF_4)$ (**4**) upon treatment with carbon monoxide. Molecular structures of **2** and **4** determined by X-ray diffraction studies are described.

The activation of C–H and C–C bonds by soluble transition-metal complexes has been a focus of recent studies in the field of organometallic chemistry. In these studies, it has been shown that coordinatively unsaturated species formed by thermal and/or photochemical excitation of transition-metal polyhydride,[1] alkyl hydride,[2] or carbonyl[3] complexes play an important role as reactive intermediates. Abstraction of halogen atoms by Ag^+ ion from transition-metal halo complexes may also become an efficient method for the generation of coordinative unsaturation. We previously found that the norbornadiene–ruthenium complex $(\eta^5\text{-}C_5Me_5)Ru(norbornadiene)Cl$ could readily be converted to the cationic 6-methylfulvene–ruthenium complex $[(\eta^5\text{-}C_5Me_5)Ru(6\text{-}methylfulvene)](BF_4)$ by treatment with $AgBF_4$ in dichloromethane (eq 1).[4]



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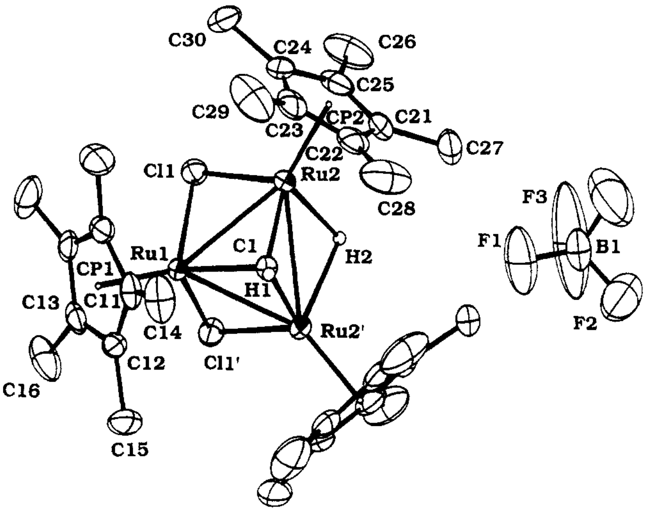

Figure 1. Molecular structure of $[((\eta^5\text{-}C_5Me_5)Ru)_3(\mu_2\text{-}Cl)_2(\mu_2\text{-}H)(\mu_3\text{-}CH)](BF_4)$ (**2**). Bond lengths (Å) and angles (deg) of interest are as follows: Ru(1)–CP(1), 1.859 (0); Ru(2)–CP(2), 1.846 (1); Ru(1)–Ru(2), 2.757 (1); Ru(2)–Ru(2′), 2.871 (1); Ru(1)–C(1), 2.089 (7); Ru(2)–C(1), 1.997 (5); Ru(1)–Cl(1), 2.416 (1); Ru(2)–Cl(1), 2.363 (1); Ru(2)–H(2), 2.18 (7); Ru(2)–Ru(1)–Ru(2′), 62.71 (2); Ru(1)–Ru(2)–Ru(2′), 58.68 (1); Ru(1)–C(1)–Ru(2), 84.9 (3); Ru(2)–C(1)–Ru(2′), 91.9 (3); Ru(1)–Ru(2)–C(1), 49.0 (2); Ru(2)–Ru(1)–C(1), 41.2 (2); Ru(2)–Ru(2′)–C(1), 44.1 (2); Ru(1)–Cl(1)–Ru(2), 70.46 (4). CP indicates the centroid of a C_5Me_5 ring.

Several observations suggested that the skeletal rearrangement of the coordinated norbornadiene proceeded via a C–C bond activation reaction induced by an intermediary coordinatively unsaturated ruthenium species, "$[(\eta^5\text{-}C_5Me_5)Ru(norbornadiene)]^+$". Motivated by these results, we investigated the generation and reactions of a coordinatively unsaturated cationic ruthenium complex having only the C_5Me_5 group as an auxiliary ligand. We describe herein the formation of a novel trinuclear μ_3-methylidyne complex by the reaction of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ (1) with $AgBF_4$ in ethanol via an activation of the primary C–H bond of ethanol.

Treatment of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ (1) with an equimolar amount of $AgBF_4$ in refluxing ethanol for 2 h followed by chromatographic separation on Al_2O_3 (Merck Art 1097) with CH_2Cl_2 gave a dark green solid. Crystallization from

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