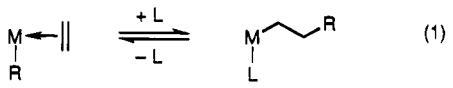
Interconversion of a 3,3-Dimethylruthenacyclobutane and a Methyl(2-methallyl)ruthenium Complex: The First Direct Observation of Reversible β-Methyl Elimination/Migratory Insertion

Kristopher McNeill, Richard A. Andersen,* and Robert G. Bergman*

Materials and Chemical Sciences Division Lawrence Berkeley Laboratory, and Department of Chemistry, University of California Berkeley, California 94720

Received November 28, 1994

The β-migratory insertion of olefins into metal–carbon bonds is recognized as a fundamental carbon–carbon bond forming process that is central to metal-catalyzed dimerization, oligomerization, and polymerization reactions (eq 1).[1] Model

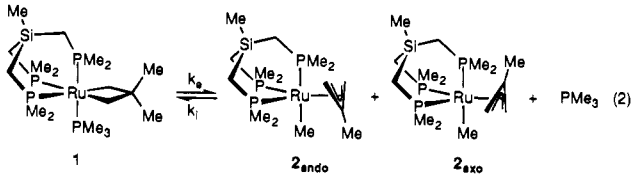


(1)

systems that provide direct evidence for the β-migratory insertion reaction remain few in number.[2-6] The microscopic reverse of β-insertion, C–C cleavage via β-alkyl elimination, has been observed even more rarely (eq 1). Only in the past 15 years has β-methyl elimination become recognized as an important chain termination step in early transition metal-based, model Ziegler–Natta polymerization systems.[7-16] In late transition metal systems, there are few reports in which β-alkyl elimination has even been proposed.[17-22] Herein we report the first direct observation of reversible β-methyl elimination and insertion, as well as the first direct observation of β-alkyl elimination at a late transition metal center.

The ruthenacyclobutane $(SiP_3)(PMe_3)Ru(\eta^2\text{-}CH_2CMe_2CH_2)$ (**1**) (SiP_3 = $MeSi(CH_2PMe_2)_3$) was synthesized in 72% yield from treatment of $(SiP_3)(PMe_3)RuCl_2$[23] with 2 equiv of Me_3CCH_2MgCl (0.66 M, Et_2O) in THF solvent. In addition to full spectroscopic and analytical characterization, the solid state structure of **1** was determined by single-crystal X-ray diffraction.[24] An ORTEP diagram of the molecule is shown in Scheme 1. The most notable feature of the structure is that the four-membered metallacyclic ring is planar and no close contacts between the metal center and the ring-bound methyl groups exist. Metallacycle **1** is closely related to $(PMe_3)_4Ru(\eta^2\text{-}CH_2CMe_2CH_2)$, which was synthesized from $(Me_3CCH_2)_2Mg$ and $Ru_2(OAc)_4Cl$ in the presence of PMe_3.[25]

Thermolysis of **1** (0.020 M, C_6D_6, 75 °C, 12 h) produces $(SiP_3)Ru(Me)(\eta^3\text{-}CH_2CMeCH_2)$ (**2**) in >98% yield as measured by ^1H NMR spectroscopy (integration against *p*-$MeOC_6H_4OMe$ internal standard) (eq 2). Complex **2** is isolated as a mixture of *endo* and *exo* isomers (6:1 *endo:exo*) from thermolysis of **1** in 42% yield after crystallization from $(Me_3Si)_2O$.[26] Complex



2 can also be synthesized independently by treatment of $(SiP_3)(PMe_3)Ru(Me)(Cl)$ with $CH_2{=}CMeCH_2MgBr$ (0.2 M, Et_2O) in THF. Complex **2** was recognized as the formal β-methyl migration product, and an investigation into the mechanism of the rearrangement was undertaken.[27]

Scheme 1 illustrates two mechanistic possibilities that could provide the allyl product, both proceeding through a formal 16e⁻ intermediate, $(SiP_3)Ru(\eta^2\text{-}CH_2CMe_2CH_2)$ (**3**). The first involves β-transfer of the methyl group between the central carbon of the hydrocarbyl ligand and the metal center (path *a*), and the second is a three-step process that involves cycloreversion to give a methylidene intermediate (**4**), C–H activation, and finally α-hydride migration (path *b*). The two pathways predict different products from the thermolysis of labeled material. Path *a* requires that rearrangement of $(SiP_3)(PMe_3)Ru(\eta^2\text{-}CD_2C(CH_3)_2\text{-}CH_2)$ (**1**-d_2) yield no scrambling of deuterium into the Ru-bound methyl group; path *b* requires deuterium scrambling into the Rubound methyl group. The synthesis of **1**-d_2 is analogous to that of **1** employing instead the labeled Grignard reagent $(CH_3)_3\text{-}CCD_2MgBr$.[28] Thermolysis of **1**-d_2 yields one isotopomer for each of the *endo* and *exo* allyl species $(SiP_3)Ru(CH_3)(\eta^3\text{-}CD_2C\text{-}(CH_3)CH_2)$ (**2**-d_2) as confirmed by NMR spectroscopy (^1H and ^{13}C) and mass spectrometry. This result supports the β-methyl transfer pathway and rigorously excludes the cycloreversion pathway.

A kinetic investigation in the presence of excess phosphine also provided results consistent with β-methyl transfer, but revealed an additional feature: reversibility. We defined the observed phenomenological rate constants as k_i for the overall

(1) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980.
(2) Brookhart, M.; Hauptman, E.; Lincoln, D. M. *J. Am. Chem. Soc.* **1992**, *114*, 10394.
(3) Flood, T. C.; Wang, L. *J. Am. Chem. Soc.* **1992**, *114*, 3169.
(4) Lehmkuhl, H. *Pure Appl. Chem.* **1986**, *58*, 495.
(5) Pardy, R. B. A. *J. Organomet. Chem.* **1981**, *216*, C29.
(6) Bergman, R. G.; Evitt, E. R. *J. Am. Chem. Soc.* **1980**, *102*, 7003.
(7) Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147.
(8) Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H.; Renkema, J.; Evens, G. G. *Organometallics* **1992**, *11*, 362.
(9) Eshuis, J. J. W.; Tan, Y. Y.; Teuben, J. H.; Renkema, J. *J. Mol. Catal.* **1990**, *62*, 277.
(10) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025.
(11) Kesti, M. R.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 3565.
(12) Bercaw, J. E. *Pure Appl. Chem.* **1990**, *62*, 1151.
(13) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976.
(14) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51.
(15) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471.
(16) For an example in which β-alkyl elimination is used to effect polymerization: Yang, X.; Jia, L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3392.
(17) Ermer, S. P.; Struck, G. E.; Bitler, S. P.; Richards, R.; Bau, R.; Flood, T. C. *Organometallics* **1993**, *12*, 2634.
(18) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1991**, *10*, 3344.
(19) Thomson, S. K.; Young, G. B. *Organometallics* **1989**, *8*, 2068.
(20) Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076.
(21) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795.
(22) Ankianiec, B., C.; Christou, V.; Hardy, D. T.; Thompson, S. K.; Young, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 9963.
(23) Dahlenburg, L.; Kerstan, S.; Werner, D. *J. Organomet. Chem.* **1991**, *411*, 457.

(24) For **1** $[C_{18}H_{46}P_4RuSi]$ (FW = 515.62): orthorhombic *Pnma*, a = 14.2166(53) Å, b = 11.5874(39) Å, and c = 15.3374(76) Å; D_{calc} = 1.36 g/cm³ (Z = 4). A total of 1930 reflections were collected on an Enraf-Nonius CAD-4 diffractometer at −92 °C with use of graphite-monochromated Mo Kα radiation. The final residuals were R_F = 0.078, R_{wF} = 0.104 for 1465 reflections observed with $F_o > 3\sigma(F_o)$. All other details regarding the structure of **1** are reported in the supplementary material.
(25) Andersen, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 446.
(26) The mixture of $\mathbf{2}_{endo}$ and $\mathbf{2}_{exo}$ represents the thermodynamic ratio since these complexes interconvert rapidly under the reaction conditions as determined by variable temperature NMR and EXSY experiments. McNeill, K.; Andersen, R. A.; Bergman, R. G. Manuscript in preparation.
(27) The observed rearrangement is most similar to that documented for the intramolecular transfer of allylic and benzylic groups from Zr to the central carbon of an allyl ligand in $Cp_2Zr(\eta^3\text{-}C_3H_5)(\eta^1\text{-}R)$ (R = allyl or benzyl). In the Cp_2Zr system, a radical mechanism is favored although a concerted mechanism is considered possible; see: Tjaden, E. B.; Styker, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 2083.
(28) Caulton, K. G.; Chisholm, M. H.; Streib, W. E.; Xue, Z. *J. Am. Chem. Soc.* **1991**, *113*, 6082.

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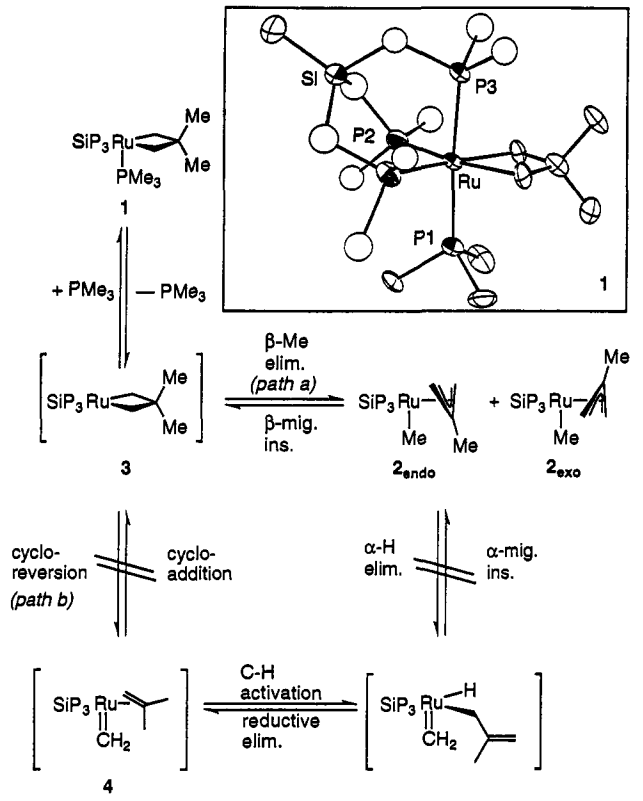
Scheme 1



migratory insertion reaction and k_e for its reverse, the β-elimination (eq 2). In order to establish the reaction order in both **1** and phosphine, the absolute concentration of PMe_3 must be known. It is convenient to control this quantity, and to simplify the kinetic behavior of the system, by operating under conditions that assure pseudo-first-order rate behavior in **1**. Conversion of **1** to **2** was therefore studied in the presence of excess PMe_3 while the progress was monitored by $^1H\{^{31}P\}$ NMR spectroscopy. Appearance of **2** as measured by integration of the Ru−Me resonance against p-$MeOC_6H_4OMe$ internal standard and disappearance of **1** as measured by the Si−Me resonance followed pseudo-first-order behavior over 5 half-lives. In each case the rates of appearance of **2** and disappearance of **1** were the same within error; however, the appearance data were used in subsequent calculations, as the Ru−Me resonance (δ −0.85) is well separated from the other resonances.

Under the high PMe_3 concentration conditions, the rearrangement of **1** to **2** did not proceed to completion. Instead, the reaction proceeded until measurable equilibrium concentrations of **1**, **2**, and PMe_3 were obtained. The fortuitously small ΔG_{rxn} allowed the measurement of both the observed rate and the equilibrium ratio of **1** and **2**. The fact that an equilibrium was observed was further confirmed by reconversion of an isolated mixture of $\mathbf{2}_{endo}$ and $\mathbf{2}_{exo}$ to an equilibrium mixture of **1** and **2** by the addition of PMe_3.

General expressions for k_{obs} and K were obtained (eqs 4 and 5) for the mechanism involving reversible PMe_3 dissociation followed by reversible β-methyl transfer (eq 3). The pseudo-

$$\mathbf{1} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{3} + PMe_3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathbf{2} + PMe_3 \qquad (3)$$

$$k_{obs} = k_e + k_i = \frac{k_1 k_2}{k_{-1}[PMe_3] + k_2} + \frac{k_{-1}k_{-2}[PMe_3]}{k_{-1}[PMe_3] + k_2} \qquad (4)$$

$$K = \frac{k_1 k_2}{k_{-1}k_{-2}[PMe_3]} = \frac{K_{eq}}{[PMe_3]} \qquad (5)$$

first-order conditions employed were such that $k_{-1}[PMe_3] \gg k_2$, allowing simplification of the expression for k_{obs} (eq 6). Our data are consistent with the predictions arising from this expression for k_{obs}; namely, the rate is depressed by added PMe_3, and at very high PMe_3 concentrations k_{obs} approaches k_{-2}.

$$k_{obs} = k_e + k_i = \frac{k_1 k_2}{k_{-1}[PMe_3]} + k_{-2} \qquad (k_{-1}[PMe_3] \gg k_2) \qquad (6)$$

The rate constant for the β-methyl transfer step, k_{-2}, may be expressed in terms of the experimentally determined variables k_{obs} and K by linear reduction of eqs 5 and 6 (eq 7). A complete

$$k_{-2} = \frac{k_{obs}}{K + 1} \qquad (7)$$

study of the temperature dependence (346.8 K < T < 390.5 K) at high [PMe_3] of K_{eq}, k_e and k_i (=k_{-2} under these conditions) yielded the activation parameters associated with the β-methyl transfer step: $\Delta G^{\ddagger}_{363.7} = 28.6 \pm 0.7$ kcal mol^{-1}, $\Delta H^{\ddagger} = 26.0 \pm 1.2$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -10.5 \pm 0.9$ cal K^{-1} mol^{-1}. Values for the thermodynamic parameters associated with the interconversion of **1** with **2** + PMe_3 are ΔG_{rxn} (363.7 K, 1 M PMe_3) = -1.16 ± 0.07 kcal mol^{-1}, ΔH°_{rxn} (1 M PMe_3) = 14.3 ± 1.1 kcal mol^{-1}, and ΔS°_{rxn} (1 M PMe_3) = 41.3 ± 2.8 cal K^{-1} mol^{-1}. We estimate the rate of PMe_3 dissociation, k_1, to be >7 s^{-1} (<20 kcal mol^{-1}) primarily on the basis of NMR line-broadening at temperatures above 50 °C. We attribute the broadening to exchange of free and bound PMe_3 on the NMR time scale. Experiments designed to provide a more precise measurement of k_1 and k_{-1}/k_2 are currently underway.

In summary, we have directly observed the first reversible overall β-alkyl elimination/allyl migratory insertion reaction. On the basis of the results of the labeling study and the kinetic investigation, we favor a mechanism for this process that involves simple methyl transfer with the intermediacy of a 16e$^-$ unsaturated intermediate. Further studies on the mechanism and scope of the β-alkyl transfer are being pursued.

Acknowledgment. We acknowledge the National Science Foundation (Grant No. CHE-9113261) for generous financial support of this work and Dr. F. J. Hollander, Director of the University of California at Berkeley X-ray diffraction facility (CHEXRAY), for helpful discussions.

Supplementary Material Available: Spectroscopic and analytical data for compounds **1** and **2**, representative kinetics data and plots for the conversion of **1** to **2**, and additional structural data for **1** (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA943823V