

Preliminary communication

H/D exchange reactions between C_6D_6 and $C_5Me_5Co(CH_2=CHR)_2$ ($R = H, SiMe_3$): evidence for oxidative addition of $C_{sp^2}-H$ bonds to the $[C_5Me_5(L)Co]$ moiety¹

Christian P. Lenges, Maurice Brookhart*, Brian E. Grant

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290, USA

Received 12 April 1996; accepted 14 June 1996

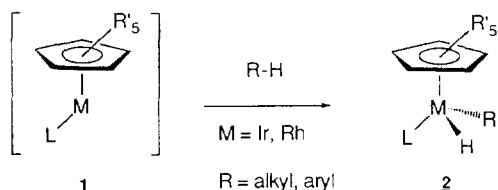
Abstract

Heating $C_5Me_5Co(CH_2=CHR)_2$ ($R = H, 60^\circ C$; $R = SiMe_3, 20^\circ C$) in C_6D_6 leads to deuterium incorporation in the vinylic sites of the olefin ligands. This observation is interpreted in terms of reversible oxidative addition of C_6D_6 to the 16-electron species $[C_5Me_5Co(CH_2=CHR)]$.

Keywords: C–H bond activation; Cobalt; Catalysis; Cyclopentadienyl

1. Introduction

Extensive studies by Bergman and coworkers [1], Jones and coworkers [2] and Graham and coworkers [3] have established that 16-electron species of the type $[C_5R_5ML]$ ($M = Rh, Ir$) (**1**), generated in situ, undergo facile oxidative addition reactions with the C–H bonds of saturated hydrocarbons and arenes to yield alkyl hydride and aryl hydride complexes of type **2**. The third-row iridium complexes are kinetically substantially more stable than the second-row rhodium complexes.



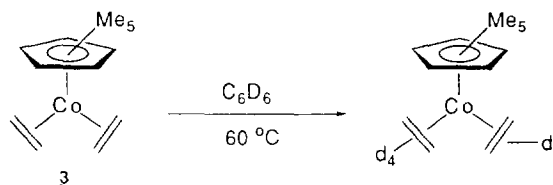
In this communication we describe experiments which suggest that first-row cobalt analogs also undergo facile oxidative addition reactions with the C–H bonds of

arenes. The experiments reported involve thermolysis of $C_5Me_5Co(olefin)_2$ complexes in C_6D_6 which results in H/D exchange between C_6D_6 and the vinylic hydrogens of the coordinated olefins. Similar observations have been described for $C_5R_5Rh(C_2H_4)_2$ as early as 1974 [4]. Wadepohl and coworkers [5] recently reported the C–H activation of simple alkenes in the course of the formation of polynuclear $[C_5H_5Co]$ -based clusters using the Jonas reagent $C_5H_5Co(C_2H_4)_2$ as the cobalt precursor.

2. Results and discussion

2.1. Thermolysis of $C_5Me_5Co(C_2H_4)_2$ in C_6D_6

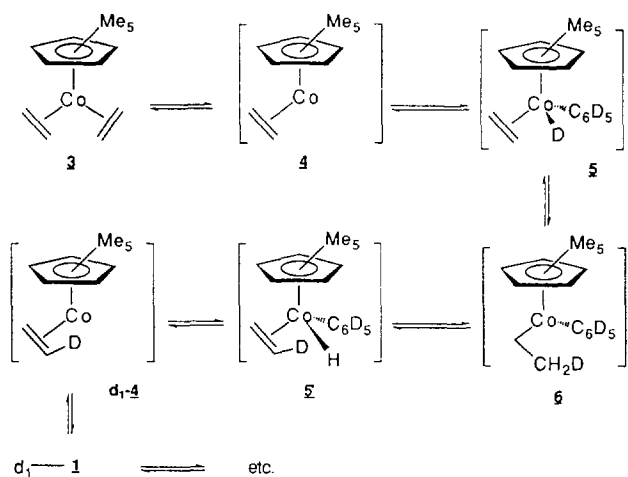
Heating $C_5Me_5Co(C_2H_4)_2$ (**3**) in C_6D_6 at $60^\circ C$ results in slow incorporation of deuterium into both the *syn* and *anti* sites of the bound ethylene:



As the 1H signals for the vinylic hydrogens decrease at $60^\circ C$, the signal for C_6D_5H correspondingly in-

* Corresponding author.

¹ Dedicated to M.L.H. Green on the occasion of his 60th birthday.



Scheme 1.

creases. No decomposition of **3** is observed. Using C_6Me_6 as an internal standard, the rate of deuterium incorporation into the ethylene ligand was found to obey first-order kinetics, $k = 4.0 \times 10^{-6} s^{-1}$ at $60^\circ C$. Under one atmosphere of ethylene, the exchange reaction is almost completely suppressed and after one week at $65^\circ C$ only traces of H/D exchange are noted, together with thermolysis products of **3** (thermolysis products were not identified; see for example, for complex **3**, Ref. [6]). Scheme 1 presents a mechanism consistent with these results.² Since excess ethylene suppresses exchange, the transition state for exchange must occur following a reversible step; that is, C_2H_4 dissociation is not rate-determining. Based on the work of Jones and

coworkers [2] on rhodium analogs, an η^2 -arene intermediate may intervene in the interconversion of **4** and **5**, but no evidence is available to support this notion.

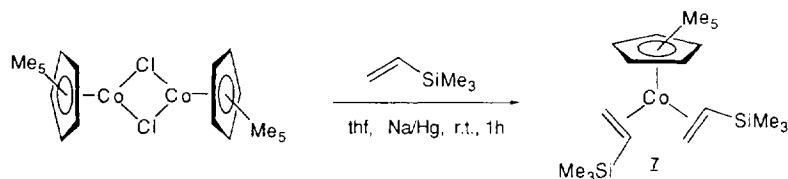
2.2. Thermolysis of $C_5Me_5Co(C_2H_3SiMe_3)_2$ (**7**)

Since olefin dissociation is required to generate the active intermediate **4**, a more labile olefin complex $C_5Me_5Co(C_2H_3SiMe_3)_2$ (**7**) was examined. Complex **7** was prepared using the method reported by Koelle et al. [8] for the synthesis of the parent bis-ethylene complex **3**. (C_5Me_5CoCl)₂ was reduced in the presence of vinyl trimethylsilane as shown in Eq. (1). Only a single isomer of **7** is observed.³ No dynamic behavior in the temperature range $+50$ to $-80^\circ C$ is detected. The similar rhodium complex $C_5H_5Rh(C_2H_3SiMe_3)_2$ has previously been reported. In contrast to **7**, two isomers are observed for this rhodium complex [9].⁴ For a report of isomers in similar Rh complexes see Ref. [11].

³ **7** was isolated as red crystalline material from pentane (75% isolated yield). NMR spectroscopic data for **7**: 1H (400 MHz, C_6D_{12} , $20^\circ C$): δ 1.51 (s, 15H, C_5Me_5), 0.10 (s, 18H, $SiMe_3$), 0.36 (d, 2H, CH_2 , *syn*), 1.84 (d, 2H, CH_2 , *anti*), 0.87 (dd, 2H, $CHSi$, *syn*); $^{13}C\{^1H\}$ (75 MHz, C_6D_6 , $20^\circ C$): δ 2.43 ($SiMe_3$), 9.67 (C_5Me_5), 93.5 (C_5Me_5), 43.7 ($CHSi$), 47.4 (CH_2).

⁴ The analogous cobalt complex $C_5H_5Co(C_2H_3SiMe_3)_2$ (**7'**) has been prepared in a modification of a procedure by Jonas for the parent cobalt bis-ethylene complex. Only one isomer is observed, in agreement with the characteristics for complex **7** [10]. **7'** was isolated as red crystalline material from pentane (45% isolated yield). NMR spectroscopic data: 1H (400 MHz, C_6D_6 , $24^\circ C$): δ -1.51 (dd, $CHSi$), 2.38 (d, CH_2 , *syn*), 2.48 (d, CH_2 , *anti*), 4.52 (s, C_5H_5), 0.13 (s, $SiMe_3$); $^{13}C\{^1H\}$ (75 MHz, C_6D_6 , $20^\circ C$): δ 0.29 ($SiMe_3$), 50.38 (CH_2), 41.21 ($CHSi$), 83.7 (C_5H_5); the reactivity of this species is under investigation.

² Catalytic H/D exchange mediated by η^2 -coordination of arenes was first suggested by Parshall and coworkers [7].



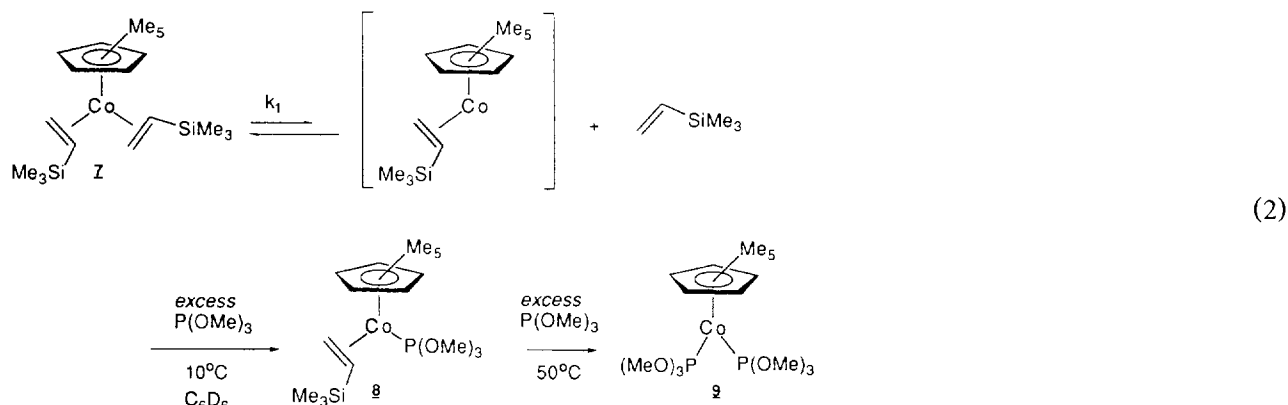
(1)

The high lability of **7** was established by a substitution reaction with $P(OMe)_3$. At $10^\circ C$ rapid displacement of olefin occurs to yield **8** as the sole product. **8** was isolated as dark red crystals from hexane (90%

yield). NMR spectroscopic data for **8**: 1H (400 MHz, C_6D_6 , $24^\circ C$): δ 1.68 (s, 15H, C_5Me_5), 0.35 (s, 9H, $SiMe_3$), 1.65 (d, 1H, CH_2 , *syn*), 2.09 (d, 1H, CH_2 , *anti*), 0.61 (ddd, 1H, $CHSi$, *syn*), 3.27 (d, 9H, $P(OMe)_3$);

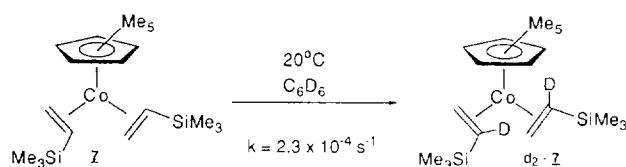
$^{13}\text{C}\{^1\text{H}\}$ (75 MHz, C_6D_6 , 20°C): δ 9.81 (s, C_5Me_5), 2.64 (s, SiMe_3), 91.2 (d, C_5Me_5), 50.9 (s, CH_2), 38.9 (d, $\text{P}(\text{OMe})_3$), 32.9 (s, CHSi .) The second equivalent of vinyl trimethylsilane is displaced at a convenient rate at

50°C ($k = 1.4 \times 10^{-4} \text{ s}^{-1}$, $\text{C}_6\text{D}_5\text{CD}_3$, 15 equiv. $\text{P}(\text{OMe})_3$) to yield the bis-phosphite complex **9** (Eq. (2)).



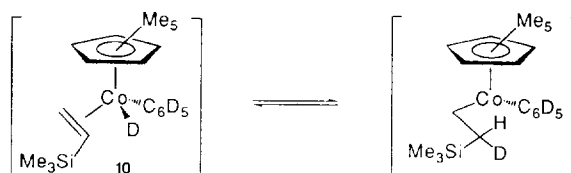
The rate of conversion of **7** to **8** was measured at several concentrations of $\text{P}(\text{OMe})_3$. With the concentration of **7** held at 0.018 mol l^{-1} , essentially identical first-order rate constants were observed at all concentrations of $\text{P}(\text{OMe})_3$ (0.04 mol l^{-1} , $k = 0.0012 \text{ s}^{-1}$; 0.18 mol l^{-1} , $k = 0.0012 \text{ s}^{-1}$; 0.48 mol l^{-1} , $k = 0.0012 \text{ s}^{-1}$; 0.76 mol l^{-1} , $k = 0.0011 \text{ s}^{-1}$; 1.21 mol l^{-1} , $k = 0.0013 \text{ s}^{-1}$). A typical rate plot is shown in Fig. 1. These results indicate that substitution occurs by a dissociative process with the observed rate constant, 0.0012 s^{-1} , equal to k_1 in Eq. (2) at 10°C . Furthermore, the high lability of **7** demonstrates it as an excellent source for the 14-electron building block $[\text{C}_5\text{Me}_5\text{Co}]$ and allows the introduction of a wide range of ligands **L** under mild conditions.

Thermolysis of **7** at 20°C in C_6D_6 led to the incorporation of deuterium into the α -position of the bound $\text{CH}_2=\text{CHSiMe}_3$:



The rate of deuterium incorporation follows first-order kinetics with $k = 2.3 \times 10^{-4} \text{ s}^{-1}$ (20°C) in C_6D_6 and is an order of magnitude slower than olefin dissociation. [The reaction of **7** with $\text{P}(\text{OMe})_3$ at 20°C was found to result in a first order rate constant k_1 for olefin dissociation of 0.006 s^{-1} .] A sample plot for this kinetic experiment presented in Fig. 2 illustrates the first-order deuterium incorporation. The temperature dependence

of this process was determined and the resulting Eyring plot yielded activation parameters for this H/D exchange reaction of $\Delta H^\ddagger = 23.6 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = 5.0 \text{ e.u.}$ (Fig. 3). No deuterium incorporation into the β -positions occurs under these conditions.⁵ Thermolysis of **7** longer than 2 h in aromatic solvents at temperatures higher than 40°C results in partial decomposition. Incorporation of a deuterium label into the $[\text{C}_5\text{Me}_5]$ proton sites of complex **7** or the parent bis-ethylene complex **3** during catalytic H/D exchange was never observed. A similar mechanism to that shown in Scheme 1 must apply, except the migratory insertion of the olefin deuteride intermediate, **10**, must be regioselective:



The rate of H/D exchange in complex **7** was also determined in the solvents $\text{C}_6\text{D}_5\text{CD}_3$ ($k = 1.3 \times 10^{-5} \text{ s}^{-1}$, 20°C) and $\text{C}_6\text{D}_5\text{Cl}$ ($k = 2.0 \times 10^{-4} \text{ s}^{-1}$, 20°C). The olefin complex **7** decomposed to unidentified products in $\text{C}_6\text{D}_5\text{Br}$ and $\text{C}_6\text{D}_5\text{NO}_2$ upon mixing. With $\text{C}_6\text{D}_5\text{CD}_3$ as a solvent regioselective H/D ex-

⁵ $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy of a reaction mixture of **7** in C_6D_6 after H/D exchange at 20°C , 2 h, reveals only one resonance coupled to deuterium at δ 43.7 (75 MHz, C_6D_6 , 20°C , t, CDSi).

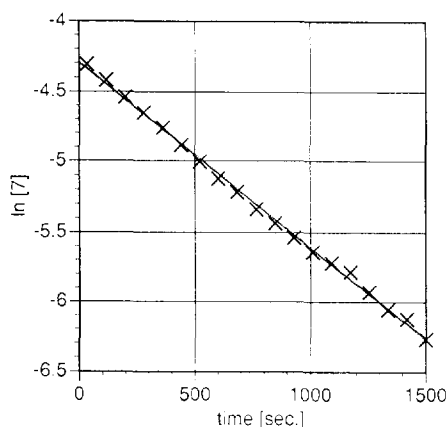


Fig. 1. Reaction of **7** ($0.0018 \text{ mol l}^{-1}$) with P(OMe)_3 (1.21 mol l^{-1}) to **8** in C_6D_6 at 10°C . Observed first-order rate constant $k_{\text{obs}} = 0.00131 \text{ s}^{-1}$. The reaction was followed by ^1H NMR and rate data extracted from changing C_5Me_5 resonances for **7** or **8**.

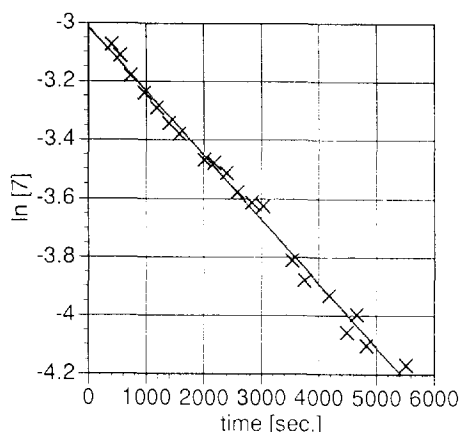
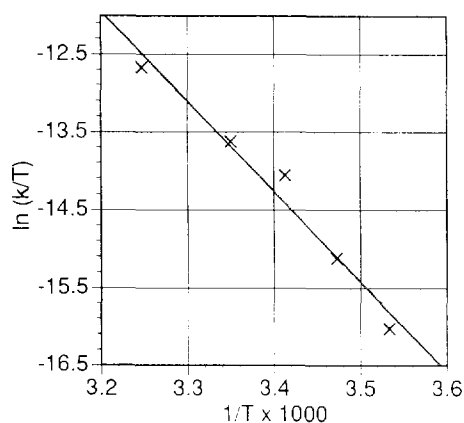


Fig. 2. First-order plot for deuterium incorporation into the α -olefinic sites of **7** in C_6D_6 at 20.1°C . $k_{\text{obs}} = 2.2 \times 10^{-4} \text{ s}^{-1}$.



Temp. [K]	k_{obs} [s^{-1}]
283	$3.1 \cdot 10^{-5}$
288	$7.8 \cdot 10^{-5}$
293	$2.3 \cdot 10^{-4}$
298.5	$3.6 \cdot 10^{-4}$
308	$9.7 \cdot 10^{-4}$

Fig. 3. Temperature dependence of the first-order rate constant for H/D exchange into the α -olefinic sites of **7** in C_6D_6 – Eyring plot and observed rate data.

change into the *meta* and *para* sites of the arene is observed (the *para* site is slightly preferred). The residual resonance of the toluene methyl group was not changed in integration over the reaction period investigated.

Addition of excess vinyl trimethylsilane to a solution of **7** in C_6D_6 inhibits the observed deuterium incorporation into coordinated olefin at 20°C . This confirms the mechanistic proposal of a dissociative first step. However, in a reaction of complex **7** with 5 equiv. vinyl trimethylsilane in C_6D_6 at 50°C , deuterium incorporation into all vinylic sites of coordinated as well as uncoordinated olefin in solution is observed after 5 h.⁶ At this temperature complex **7** decomposes without excess olefin in solution. The deuteration of free vinyl trimethylsilane clearly results from H/D exchange in the bound vinyl silane followed by olefin exchange.

3. Summary

The H/D exchange reactions described here establish that the 16-electron species $[\text{C}_5\text{Me}_5\text{Co(L)}]$ can activate sp^2 C–H bonds via oxidative addition under mild conditions. While this is a well-established reaction for Ir(I) and Rh(I) analogs, the ability of the first-row cobalt systems to participate in such C–H activation reactions has been unresolved, see for example Ref. [12]. Similar H/D exchange reactions have been described for $\text{C}_5\text{R}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ [4], but high temperatures (130°C) were required due to the high barrier for loss of C_2H_4 from these species. A key to observing H/D exchange at much lower temperatures in the present cobalt system was the synthesis of the stable but very labile bulky bis-olefin complex $\text{C}_5\text{Me}_5\text{Co}(\text{C}_2\text{H}_3\text{-SiMe}_3)_2$, **7**. The high lability of the vinyl trimethylsilane ligands in this complex make it an excellent source of the 14-electron fragment $[\text{C}_5\text{Me}_5\text{Co}]$ and we are currently developing new catalytic reactions based on **7**.⁷

⁶ The resonance of the α -proton of vinyl trimethylsilane in solution is reduced to 33% after 3 h at 50°C . The resonance for the β -protons of vinyl trimethylsilane is reduced to 70% in the same time period (^1H NMR spectroscopy). $^{13}\text{C}\{^1\text{H}\}$ NMR of a typical reaction mixture after thermolysis at 50°C for 8 h demonstrates deuterium incorporation into free olefin (δ 140.2, qi, CD_2 ; 131.1, t, CDSi; 75 MHz, C_6D_6 , 20°C).

⁷ The propene complex $\text{C}_5\text{Me}_5\text{Co}(\text{C}_2\text{H}_3\text{Me})_2$ **11** was reported by Spencer and coworkers [13] to be unstable and was not isolated after in situ generation. The intermediate position of vinyl trimethylsilane between ethylene and propene, considering steric requirements for olefin coordination, allows the synthesis of the highly labile olefin complex **7**.

Acknowledgements

We thank the National Institutes of Health for support of this work (Grant GM 28938). C.P.L. was supported in part by a fellowship of the German Academic Exchange Service.

References

- [1] R.G. Bergman and A.H. Janowicz, *J. Am. Chem. Soc.*, **104** (1982) 352–354; **105** (1983) 3929–3939; R.G. Bergman, J.M. Buchanan and J.M. Stryker, *J. Am. Chem. Soc.*, **107** (1985) 1537–1550; R.G. Bergman and R.A. Periana, *J. Am. Chem. Soc.*, **108** (1986) 7346–7355; R.G. Bergman, *Science*, **223** (1984) 902.
- [2] W.D. Jones and F.J. Feher, *Organometallics*, **2** (1983) 686–687; *J. Am. Chem. Soc.*, **106** (1984) 1650–1663; *Acc. Chem. Res.*, **22** (1989) 91–100; W.D. Jones, R. Perutz, R.M. Chin, L. Dong, S.B. Duckett and M.G. Partridge, *J. Am. Chem. Soc.*, **115** (1993) 7685–7695.
- [3] W.A.G. Graham and J.K. Hoyano, *J. Am. Chem. Soc.*, **104** (1982) 3723–3725; W.A.G. Graham, J.K. Hoyano and A.D. McMaster, *J. Am. Chem. Soc.*, **105** (1983) 7190–7191.
- [4] L.P. Seiwell, *J. Am. Chem. Soc.*, **96** (1974) 7134–7135.
- [5] H. Wadepohl, T. Borchert and H. Pritzkow, *J. Chem. Soc., Chem. Commun.*, (1995) 1447–1448; H. Wadepohl, T. Borchert, H. Büchner and H. Pritzkow, *Chem. Ber.*, **126** (1993) 1615–1618.
- [6] R. Pardy, G. Smith and M. Vickers, *J. Organomet. Chem.*, **252** (1983) 344; C. Casey, R. Widenhoefer and S. Hallenbeck, *Organometallics*, **12** (1993) 3788.
- [7] G. Parshall and U. Klabunde, *J. Am. Chem. Soc.*, **94** (1972) 9081; G. Parshall and F. Tebbe, *J. Am. Chem. Soc.*, **92** (1970) 5234; see also R.J. Hodges and J.L. Garnett, *J. Phys. Chem.*, **73** (1969) 1525–1532.
- [8] U. Koelle, B. Fuss, M. Belting and E. Raabe, *Organometallics*, **5** (1986) 980–987.
- [9] R.N. Perutz, D.M. Haddleton, S.B. Duckett and S.T. Belt, *Organometallics*, **8** (1989) 748–759.
- [10] K. Jonas and E.D. Deffense, *Angew. Chem. Suppl.*, (1983) 1005–1016.
- [11] R. Cramer and G.S. Reddy, *Inorg. Chem.*, **12** (1973) 346.
- [12] P.E.M. Siegbahn, *J. Am. Chem. Soc.*, **118** (1996) 1487–1496; A.A. Bengali, R.G. Bergman and C.B. Moore, *J. Am. Chem. Soc.*, **117** (1995) 3879–3880.
- [13] R.G. Beavor, S.A. Frith and J.L. Spencer, *J. Organomet. Chem.*, **221** (1981) C25–C27.