

One-step Transformation of Coordinated CO into CH₂ on Diruthenium Complexes by the Action of Hydrosilanes: a Model System for the Fischer–Tropsch Mechanism

Munetaka Akita,* Tomoharu Oku and Yoshihiko Moro-oka*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

By treatment with dihydrosilanes at 150 °C a diruthenium carbonyl complex Ru₂(C₅H₅)₂(μ-CO)₂(CO)₂ is sequentially transformed into a μ-methylene complex Ru₂(C₅H₅)₂(μ-CH₂)(μ-CO)(CO)₂ and a di(μ-methylene) complex Ru₂(C₅H₅)₂(μ-CH₂)₂(CO)₂.

Transformation of coordinated CO into CH_x and CH_xO species is regarded as an elementary step of catalysed syngas reactions.¹ Of numerous examples of model reactions reported so far, reduction of cationic carbonyl complexes with borohydrides such as NaBH₄ and LiHBET₃ is the most frequently and thoroughly studied one.² In previous papers we demonstrated that metal-bound alkyl and acyl groups were successfully converted into hydrocarbons and oxygenates by employing hydrosilanes and hydrostannanes as an equivalent for dihydrogen.³ Group 14 metal hydrides have been known to exhibit reactivities similar to dihydrogen as well as a remarkable affinity towards an oxygen-containing functional group in a molecule. As an extension, we examined reduction of a diruthenium μ-methylene complex with hydrosilanes to find an unexpected one-step transformation of a bridging carbonyl group into a μ-methylene ligand.⁴

Heating a benzene solution of a diruthenium μ-methylene complex Ru₂(C₅H₅)₂(μ-CH₂)(μ-CO)(CO)₂ **1**^{4,5} with di- or tri-hydrosilanes in a sealed glass tube at 150 °C for 2 days (Scheme 1) resulted in a quantitative formation of a *cis* and *trans* mixture of a di(μ-methylene) complex Ru₂(C₅H₅)₂(μ-CH₂)₂(CO)₂ **2** along with siloxane [(HR₂Si)₂O], which was confirmed by a GC–MS analysis of the reaction mixture. Compound **2** was readily characterized on the basis of the diagnostic deshielded μ-CH₂ signals (¹H and ¹³C NMR),[†] disappearance of the bridging carbonyl ligand and the FD MS (field desorption mass spectrometry) spectra. In marked contrast to the present methylenation, reaction with monohydrosilanes (HSiR₃) resulted in degradation of the dimetallic structure to give Ru(C₅H₅)(H)(CO)(SiR₃)₂ **3** together with methane after prolonged heating.⁶

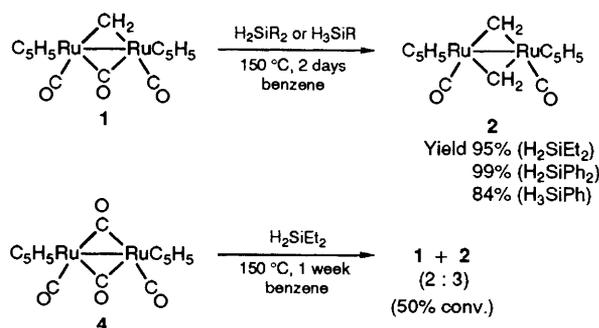
The formal reduction of the bridging carbonyl group in **1** to the μ-methylene ligand in **2** prompted us to apply the methylenation to a carbonyl complex Ru₂(C₅H₅)₂(μ-

CO)₂(CO)₂ **4**. As a result, **4** was also transformed to **2** by way of **1**, although the reaction was extremely slow. After heating at 150 °C for 1 week a 2 : 3 mixture of **1** and **2** was formed with the consumption of *ca.* 50% of **4**. Thus the methylenation of **1** appeared to be faster than that of **4**.

The reaction mechanism is not clear at the present time since the reaction is very clean and no intermediate and byproducts have been detected by ¹H NMR experiments. However, the following reaction mechanisms may be eliminated on the basis of the results of control experiments. (i) Initial CO dissociation is not involved, because reaction of Knox's labile μ-methylene complex Ru₂(C₅H₅)₂(μ-CH₂)(μ-CO)(CO)(MeCN)⁷ with hydrosilanes does not afford **2** but **3**, methane, and so on under milder reaction conditions.⁶ (ii) Inter-molecular reaction mechanisms (CH₂ transfer and Ru–Ru bond scission) are neglected, since reaction of **1** with D₂SiPh₂ gives Ru₂(C₅H₅)₂(μ-CH₂)(μ-CD₂)(CO)₂ as a sole product and reaction of a mixture of **1** and Ru₂(η⁵-C₅H₄Me)₂(μ-CH₂)(μ-CO)(CO)₂ with H₂SiEt₂ affords **2** and Ru₂(η⁵-C₅H₄Me)₂(μ-CH₂)₂(CO)₂ in place of the crossover product Ru₂(C₅H₅)(η⁵-C₅H₄Me)(μ-CH₂)₂(CO)₂. (iii) Ionic hydrosilylation applied to reduction of ketones⁸ turns out not to be a viable route, since treatment of the protonated product of **1** {[Ru₂(C₅H₅)₂(μ-CH₃)(μ-CO)(CO)₂]⁺CF₃CO₂⁻}⁹ with hydrosilane affords unknown products in low yields. (iv) Radical mechanism is also excluded, since no apparent effect is observed on addition of an initiator (azobisisobutyronitrile, AIBN) and an inhibitor (hydroquinone).

It is presumed that the methylenation consists of twice repeated hydrosilylation catalysed by a small amount of an unknown ruthenium species present in the reaction mixture, although the Rh-catalysed hydrosilylation^{3c,d,10} is not effective. Hydrosilylation of **1**, at first, may give a μ-siloxymethylene intermediate Ru₂(C₅H₅)₂[μ-CH(OSiHR₂)](μ-CO)(CO)₂, which, by the action of another molecule of hydrosilane, is further converted to **2** with liberation of siloxane. The second step is supported by our previous experiment that an iron analogue of the intermediate Fe₂(C₅H₅)₂[μ-CH(OMe)](μ-CO)(CO)₂ was readily reduced to Fe₂(C₅H₅)₂(μ-CH₂)(μ-CO)(CO)₂ by the Rh-catalysed hydrosilylation.^{3d} The feature that the reducing-ability of dihydrosilanes is by far superior to that of monohydrosilanes is common to the present methylenation and hydrosilylation of organic carbonyl compounds.^{3d}

Finally, we examined pyrolysis of the resultant di(μ-methylene) complex **2**.¹¹ On heating solid **2** above 200 °C, a mixture of small amounts of methane, ethene and ethane were produced (*in vacuo*: 0.4, 0.7 and 1.4%; under Ar: 0.3, 0.9 and 0.3%, respectively) and no C₃ and C₄ hydrocarbons were detected at all as reported for analogous di(μ-alkylidene) complexes by Knox *et al.*¹¹ While the yields of hydrocarbons are very low, a sequence of the present reactions (4 → 1 → 2 → ethene) serves as a model system for production of ethene following the Fischer–Tropsch mechanism,¹² that is, under catalysis of ruthenium ethene is produced *via* coupling of two methylene species which are formed by reduction of coordinated CO's with hydrosilane accompanied by liberation of siloxane (silylated water). In addition, the C and H atoms in ethene originate from CO and hydrosilane, respectively.



Scheme 1

[†] Selected spectroscopic data for *trans*-**2**: ¹H NMR (C₆D₆) δ 4.87 [10H, s, (C₅H₅)₂], 8.03 (2H, s, μ-CH₂). ¹³C NMR (C₆D₆) δ 90.1 [d, J 177 Hz, (C₅H₅)], 109.3 (t, J 148 Hz, μ-CH₂), 201.8 (s, CO). IR (CH₂Cl₂) ν(C=O) 1920 cm⁻¹. *cis*-**2**: ¹H NMR (C₆D₆) δ 4.61 [10H, s, (C₅H₅)₂], 7.41, 8.08 (1H × 2, d, J 0.44 Hz, μ-CH₂). ¹³C NMR (C₆D₆) δ 88.0 [d, J 176 Hz, (C₅H₅)], 108.0 (dd, J 140 and 142 Hz, μ-CH₂), 202.0 (s, CO). IR (CH₂Cl₂) ν(C=O) 1963 cm⁻¹.

Thus utilization of oxygenophilic hydrosilanes as a hydrogen-equivalent realized transfer of hydrogen atoms and removal of the CO's oxygen atom in one step to produce μ -methylene complexes in a quite selective and quantitative manner.

Received, 16th March 1992; Com. 2/01392D

References

- 1 J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry* University Science Book, Mill Valley, California, 2nd edn., 1987.
 - 2 J. R. Sweet and W. A. Graham, *J. Am. Chem. Soc.*, 1982, **104**, 2811; A. R. Cutler, P. K. Hanna and J. C. Vites, *Chem. Rev.*, 1988, **88**, 1363 and references cited therein.
 - 3 (a) M. Akita, O. Mitani and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, 1989, 527; (b) M. Akita, O. Mitani and Y. Moro-oka, *Organometallics*, 1991, **10**, 1394; (c) M. Akita, T. Oku and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, 1989, 1790; (d) M. Akita, T. Oku, M. Tanaka and Y. Moro-oka, *Organometallics*, 1991, **10**, 3081.
 - 4 One-step conversion of **4** to **1** by the action of LiHBEt_3 was already reported. See, D. H. Berry and J. E. Bercaw, *Polyhedron*, 1988, **7**, 759.
 - 5 S. A. R. Knox, *J. Organomet. Chem.*, 1990, **400**, 255 and references cited therein.
 - 6 M. Akita, T. Oku and Y. Moro-oka, unpublished results.
 - 7 N. M. Doherty, J. A. K. Howard, S. A. R. Knox, N. J. Terril and M. I. Yates, *J. Chem. Soc., Chem. Commun.*, 1989, 638.
 - 8 M. Fujita and T. Hiyama, *J. Am. Chem. Soc.*, 1985, **107**, 8294.
 - 9 D. L. Davies, B. P. Gracey, V. Guerchais, S. A. R. Knox and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1984, 841.
 - 10 E. J. Crawford, P. K. Hanna and A. R. Cutler, *J. Am. Chem. Soc.*, 1989, **111**, 6891.
 - 11 S. A. R. Knox, R. E. Colborn, D. L. Davies, A. F. Dyke, K. A. Mead, J. E. Guerchais and J. Roue, *J. Chem. Soc., Dalton Trans.*, 1989, 1799.
 - 12 F. Fischer and H. Tropsch, *Brennst. Chem.*, 1926, **7**, 97; R. C. Brady III and R. Pettit, *J. Am. Chem. Soc.*, 1980, **102**, 6181.
-