

# One-step Transformation of Coordinated CO into CH<sub>2</sub> on Diruthenium Complexes by the Action of Hydrosilanes: a Model System for the Fischer–Tropsch Mechanism

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By treatment with dihydrosilanes at 150 °C a diruthenium carbonyl complex Ru<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-CO)<sub>2</sub>(CO)<sub>2</sub> is sequentially transformed into a μ-methylene complex Ru<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-CH<sub>2</sub>)(μ-CO)(CO)<sub>2</sub> and a di(μ-methylene) complex Ru<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-CH<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>.

Transformation of coordinated CO into CH<sub>x</sub> and CH<sub>x</sub>O species is regarded as an elementary step of catalysed syngas reactions.<sup>1</sup> Of numerous examples of model reactions reported so far, reduction of cationic carbonyl complexes with borohydrides such as NaBH<sub>4</sub> and LiHBET<sub>3</sub> is the most frequently and thoroughly studied one.<sup>2</sup> 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.<sup>3</sup> 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.<sup>4</sup>

Heating a benzene solution of a diruthenium μ-methylene complex Ru<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-CH<sub>2</sub>)(μ-CO)(CO)<sub>2</sub> **1**<sup>4,5</sup> 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 Ru<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-CH<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub> **2** along with siloxane [(HR<sub>2</sub>Si)<sub>2</sub>O], 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-CH<sub>2</sub> signals (<sup>1</sup>H and <sup>13</sup>C NMR),<sup>†</sup> 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 (HSiR<sub>3</sub>) resulted in degradation of the dimetallic structure to give Ru(C<sub>5</sub>H<sub>5</sub>)(H)(CO)(SiR<sub>3</sub>)<sub>2</sub> **3** together with methane after prolonged heating.<sup>6</sup>

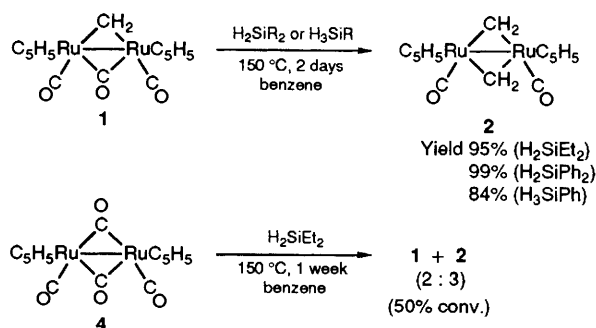
The formal reduction of the bridging carbonyl group in **1** to the μ-methylene ligand in **2** prompted us to apply the methylenation to a carbonyl complex Ru<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-

CO)<sub>2</sub>(CO)<sub>2</sub> **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 <sup>1</sup>H 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 Ru<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-CH<sub>2</sub>)(μ-CO)(CO)(MeCN)<sup>7</sup> with hydrosilanes does not afford **2** but **3**, methane, and so on under milder reaction conditions.<sup>6</sup> (ii) Intermolecular reaction mechanisms (CH<sub>2</sub> transfer and Ru–Ru bond scission) are neglected, since reaction of **1** with D<sub>2</sub>SiPh<sub>2</sub> gives Ru<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-CH<sub>2</sub>)(μ-CD<sub>2</sub>)(CO)<sub>2</sub> as a sole product and reaction of a mixture of **1** and Ru<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)<sub>2</sub>(μ-CH<sub>2</sub>)(μ-CO)(CO)<sub>2</sub> with H<sub>2</sub>SiEt<sub>2</sub> affords **2** and Ru<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)<sub>2</sub>(μ-CH<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub> in place of the crossover product Ru<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)(μ-CH<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>. (iii) Ionic hydrosilylation applied to reduction of ketones<sup>8</sup> turns out not to be a viable route, since treatment of the protonated product of **1** {[Ru<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-CH<sub>3</sub>)(μ-CO)(CO)<sub>2</sub>]<sup>+</sup>CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>}<sup>9</sup> 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<sup>3c,d,10</sup> is not effective. Hydrosilylation of **1**, at first, may give a μ-siloxymethylene intermediate Ru<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>[μ-CH(OSiHR<sub>2</sub>)](μ-CO)(CO)<sub>2</sub>, 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 Fe<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>[μ-CH(OMe)](μ-CO)(CO)<sub>2</sub> was readily reduced to Fe<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(μ-CH<sub>2</sub>)(μ-CO)(CO)<sub>2</sub> by the Rh-catalysed hydrosilylation.<sup>3d</sup> 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.<sup>3d</sup>

Finally, we examined pyrolysis of the resultant di(μ-methylene) complex **2**.<sup>11</sup> 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 C<sub>3</sub> and C<sub>4</sub> hydrocarbons were detected at all as reported for analogous di(μ-alkylidene) complexes by Knox *et al.*<sup>11</sup> 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,<sup>12</sup> 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**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 4.87 [10H, s, (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>], 8.03 (2H, s, μ-CH<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 90.1 [d, J 177 Hz, (C<sub>5</sub>H<sub>5</sub>)], 109.3 (t, J 148 Hz, μ-CH<sub>2</sub>), 201.8 (s, CO). IR (CH<sub>2</sub>Cl<sub>2</sub>) ν(C=O) 1920 cm<sup>-1</sup>. *cis*-**2**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 4.61 [10H, s, (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>], 7.41, 8.08 (1H × 2, d, J 0.44 Hz, μ-CH<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 88.0 [d, J 176 Hz, (C<sub>5</sub>H<sub>5</sub>)], 108.0 (dd, J 140 and 142 Hz, μ-CH<sub>2</sub>), 202.0 (s, CO). IR (CH<sub>2</sub>Cl<sub>2</sub>) ν(C=O) 1963 cm<sup>-1</sup>.

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  $\mu$ -methylene complexes in a quite selective and quantitative manner.

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