

Tetrahedron Letters 42 (2001) 2169-2171

TETRAHEDRON LETTERS

## Hydrosilation of polyfluoroolefin in dense carbon dioxide

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Abstract—Ruthenium and rhodium phosphine complexes catalyze the hydrosilation of olefins in dense carbon dioxide. The incorporation of polyfluorinated phosphine ligands in the conventional hydrosilation catalysts provides enhanced solubility in dense carbon dioxide resulting in a higher catalytic activity and selectivity; the best result was obtained using  $RuCl_2[P(C_6H_4-p-CF_3)_3]_3$ . The reaction is applicable to the synthesis of a fluorous silane coupling agent. © 2001 Elsevier Science Ltd. All rights reserved.

Considerable attention has recently been directed toward dense carbon dioxide as a 'green' reaction media because carbon dioxide is nontoxic, noncorrosive, nonflammable, and inexpensive. Especially, homogeneous catalysis in dense carbon dioxide often displays improved selectivities as well as accelerated reaction rates.<sup>1</sup> On the other hand, polyfluoro compounds are materials with various functions due to their unique physical and chemical properties, such as thermal stability, water- and oil-repellency, and chemical stability against oxidants, acids, bases, etc. For example, polyfluoroalkyl(dimethoxy)silanes such as CF<sub>3</sub>(CF<sub>2</sub>)<sub>5</sub>- $CH_2CH_2SiCH_3(OCH_3)_2$  (1) are attractive silane-coupling agents for modifying the physical and chemical nature of glass surfaces.<sup>2</sup> Herein, we report the efficient synthesis of 1 from  $CF_3(CF_2)_5CH_2=CH_2$  via the complex-catalyzed hydrosilation in carbon dioxide,<sup>3,4</sup> a further example of the application of dense carbon dioxide to homogeneous catalysis. Although some papers reported the hydrosilation of carbon dioxide itself,<sup>1a,5</sup> hydrosilation of carbon–carbon multiple bonds in dense carbon dioxide has not yet been reported.

The catalytic hydrosilation of 3,3,4,4,5,5,6,6,7,7,8,8,8tridecafluoro-1-octene with dimethoxymethylsilane proceeded in dense carbon dioxide to yield a mixture of alkylsilanes (hydrosilation products, **1** and **2**) and alkenylsilanes (dehydrogenative silation products, **3** and **4**) as shown in Scheme 1. A typical reaction was carried out as follows. In a stainless steel autoclave (20 ml inner volume), carbon dioxide (liquid, 60 atm) was added to a mixture of catalyst (0.005 mmol),<sup>6</sup> polyfluoroolefin (1.0 mmol), and dimethoxymethylsilane (1.2 mmol) at room temperature. The autoclave was then heated in an oil bath and the initial pressure was adjusted to 300 atm at 90°C.<sup>7</sup> After cooling, 1,3,5trimethylbenzene was added to the reaction mixture as the internal standard for the GC analysis. The reaction



## Scheme 1.

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Keywords: hydrosilation; olefin; carbon dioxide; ruthenium; rhodium.

Table 1. Hydrosilation of polyfluoroolefin in dense  $CO_2$  using various rhodium and ruthenium complexes<sup>a</sup>

| Entry | Catalyst  | Total yield (%) <sup>b</sup> | Selectivity (%) |    |    |    |  |
|-------|---|------------------------------|-----------------|----|----|----|--|
|       |   |                              | 1               | 2  | 3  | 4  |  |
| 1     | $RhCl[P(C_6H_5)_3]_3$   | 1                            | Major           | _  | _  | _  |  |
| 2     | RhCl[P( $C_6H_4$ -p-CF <sub>3</sub> ) <sub>3</sub> ] <sub>3</sub> | 72                           | 55              | 3  | 17 | 25 |  |
| 3     | $RuCl_{2}[P(C_{6}H_{5})_{3}]_{3}$                                 | 11                           | 10              | 49 | 41 | _  |  |
| 4     | $RuCl_{2}[P(C_{6}H_{4}-p-CF_{3})_{3}]_{3}$                        | 74                           | 98              | _  | 2  | _  |  |
| 5     | $RhCl(CO)[P(CH_3)_3]_2$   | 32                           | 39              | 11 | 33 | 17 |  |
| 6     | $RhCl(CO)[P(CH_2CH_2C_6F_{13})_3]_2$                              | 50                           | 76              | 9  | 9  | 6  |  |
| 7°    | $RuCl_{2}[P(C_{6}H_{4}-p-CF_{3})_{3}]_{3}$                        | 70                           | 93              | _  | 7  | -  |  |

<sup>a</sup> Reaction conditions: catalyst (0.005 mmol), olefin (1.0 mmol), silane (1.2 mmol), CO<sub>2</sub> 300 atm, 90°C, 24 h.

<sup>b</sup> Total yield of **1** to **4**.

<sup>c</sup> Reaction at 230 atm.

 Table 2. Ruthenium-catalyzed hydrosilation of polyfluoroolefin in various solvents<sup>a</sup>

| Entry          | Catalyst                        | Total yield (%) <sup>b</sup> | Selectivity (%) |   |     |   |   |
|----------------|---------------------------------|------------------------------|-----------------|---|-----|---|---|
|                |                                 |                              | 1               | 2 | 3   | 4 | _ |
| 1              | scCO <sub>2</sub>               | 74                           | 98              | _ | 2   | _ |   |
| 2              | CH <sub>2</sub> Cl <sub>2</sub> | 60                           | 94              | 3 | 3   | _ |   |
| 3              | Benzene                         | 11                           | 75              | _ | 25  | _ |   |
| 4 <sup>c</sup> | n-PrOH                          | 11                           | _               | _ | 100 | _ |   |
| 5              | THF                             | 6                            | 51              | _ | 49  | _ |   |
| 6              | Hexane                          | 5                            | 87              | _ | 13  | _ |   |

<sup>a</sup> Reaction conditions: RuCl<sub>2</sub>[P(C<sub>6</sub>H<sub>4</sub>-*p*-CF<sub>3</sub>)<sub>3</sub>]<sub>3</sub> (0.005 mmol), olefin (1.0 mmol), silane (1.2 mmol), 90°C, 24 h, solvent 5 ml (entries 2–6) or CO<sub>2</sub> 300 atm (entry 1).

<sup>b</sup> Total yield of 1 to 4.

<sup>c</sup> The main product was methyltripropoxysilane.

products were analyzed by GC and further characterized using GC–MS. The phase behavior of the reaction mixture was visually examined through sapphire windows.

The structure of metal complexes dramatically influences the catalytic activity (Table 1). Although the use of a typical hydrosilation catalyst such as Wilkinson complex, RhCl(PPh<sub>3</sub>)<sub>3</sub>, resulted in a poor yield, incorporation of polyfluorinated ligands remarkably improved the catalytic activity (entries 1 and 2). Similar acceleration phenomena using fluorous ligands were also observed for other complexes (entries 3-6). In addition, the use of polyfluorinated phosphine ligands led to increasing product selectivities to afford 1. As for the central metal, ruthenium was more preferable than rhodium for achieving higher selectivity. Hence, the best result was obtained by  $RuCl_2[P(C_6H_4-p-CF_3)_3]_3$ .<sup>8</sup> In the reactions represented in Table 1, silyl formate, the hydrosilation product of carbon dioxide, was not observed. This contrasts with the recent paper reporting the facile hydrosilation of carbon dioxide catalyzed by ruthenium complexes.5a,9

The higher yield and selectivity achieved by fluorous phosphines is presumably assignable to the higher solubility in dense carbon dioxide to afford a single reaction phase. Indeed, the metal complexes with polyfluorinated substituents led to homogeneous solution in dense carbon dioxide under the stated reaction conditions (entries 2, 4, and 6) while the conventional complexes were not completely soluble. Phase behavior is also dependent on the reaction pressure. Thus, gas and liquid phases were observed at 60 atm. The gas phase became smaller with increasing  $CO_2$  pressure and the reaction mixture became completely homogeneous around 300 atm. The higher pressure was favorable for achieving higher activity and selectivity; the total yield and selectivity for 1 were lower at 230 atm (entry 7) compared with those at 300 atm.

Table 2 summarizes the effect of the reaction media. Obviously, the activity and selectivity in dense carbon dioxide are higher than those observed in organic solvents. This is presumably attributable to the high solubility of the polyfluoroolefins and the catalyst in dense carbon dioxide. As for reaction media other than  $CO_2$ , the use of a halogenated compound, such as dichloromethane, was necessary to achieve a high yield and selectivity.

In summary, the hydrosilation of perfluoroolefin in dense carbon dioxide proceeded smoothly with high regioselectivity using a ruthenium-based homogeneous catalyst with a commercially-available fluorous phosphine ligand. This catalytic system realizes a single-step and the atom-economical synthesis of the polyfluorinated silane-coupling agent utilizing an environmentally benign reaction medium.

## Acknowledgements

The authors are indebted to Professor Istvan Horvàth for generous information on the synthesis of fluorous phosphine ligands. The authors also thank NEDO for generous financial support to L.-N.H.

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- 3. The reported synthetic procedure of 1 requires the use of a fluorinated solvent, 1,1,2-trichloro-1,2,2-trifluoroethane, and gives the desired product in a relatively low yield (about 40% starting from CF<sub>3</sub>(CF<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>=CH<sub>2</sub>); see Ref. 2. Hence, the development of a more effective and environmentally friendly process is desirable.
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- 6. RhCl[P(C<sub>6</sub>H<sub>4</sub>-*p*-CF<sub>3</sub>)<sub>3</sub>]<sub>3</sub> was synthesized by the addition of the corresponding phosphine to [RhCl(cyclooctene)<sub>2</sub>]<sub>2</sub>. RuCl<sub>2</sub>[P(C<sub>6</sub>H<sub>4</sub>-CF<sub>3</sub>)<sub>3</sub>]<sub>3</sub> was synthesized by a modification of the literature method employed for producing RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>. RhCl(CO)[P(CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>F<sub>13</sub>)<sub>3</sub>]<sub>2</sub> was synthesized by the addition of the phosphine to [RhCl(cyclooctene)<sub>2</sub>]<sub>2</sub> followed by the treatment with excess carbon monoxide.
- 7. Reaction in the liquid phase before reaching the prescribed reaction conditions was avoided by separating the catalyst from the silane using a small glass vessel. However, the result was nearly the same as that without using the glass vessel.
- Erkey recently reported the catalysis in supercritical CO<sub>2</sub> using rhodium complexes with the P(C<sub>6</sub>H<sub>4</sub>-*p*-CF<sub>3</sub>)<sub>3</sub> ligand.
   See: Palo, D. R.; Erkey, C. *Organometallics* 2000, 19, 81–86 and references cited therein.
- 9. The use of PhMe<sub>2</sub>SiH in place of HSiMe(OMe)<sub>2</sub> led to hydrosilation of carbon dioxide to produce HCO<sub>2</sub>SiMe<sub>2</sub>Ph (see Refs. 1a and 5). On the other hand, the reaction of a typical olefin like 1-octene in place of the perfluoroolefin resulted in facile double bond isomerization to give internal olefins.