A Highly Active Well-Defined Rhenium Heterogeneous Catalyst for Olefin Metathesis Prepared via Surface Organometallic Chemistry

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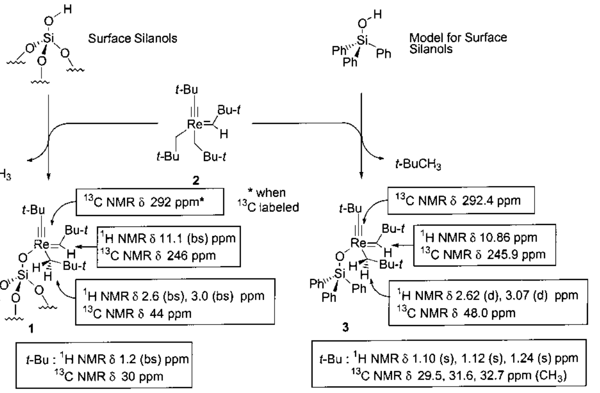
Received March 14, 2000

We report herein the synthesis and the characterization of $\equiv$SiO−Re($\equiv$C−Bu-*t*)(=CH−Bu-*t*)(CH_2Bu-*t*), **1**, a highly active "well-defined" heterogeneous catalyst supported on silica for olefin metathesis.

Some of the first olefin metathesis catalysts were prepared by impregnating γ-Al_2O_3 typically with aqueous solution of NH_4ReO_4 or $HReO_4$ followed by drying and calcination steps. These catalysts referred to as Re_2O_7/Al_2O_3 have been extensively studied because of their high activity and selectivity at low temperatures (273−373 K) as well as their ability to tolerate some functionalized olefins (especially when activated by organotin reagents).[1] In particular, it has been shown that during catalysis less than 2% of the Re is actually active,[2] and this has been associated with Re centers in proximity to some highly active acidic sites of alumina. More recently, methyltrioxorhenium supported on silica alumina or niobia have also shown good activity in olefin metathesis of functionalized olefins at room temperature without the use of additives.[3] All of these studies have related the activity with the acidity of the support, and usually no or low activity has been found for rhenium compounds supported on silica, a rather nonacidic support.[4]

Our strategy uses a different approach which stems from the concept of surface organometallic chemistry, and whose goal is to generate a well-defined coordination sphere around a metal grafted on a support usually via a direct covalent bond between the metal and the metal oxide such as silica or alumina.[5] In homogeneous systems, the best rhenium systems have been those having a d^0-configuration[6] and containing alkylidene ligands.[7,8] This led us to investigate the preparation of a well-defined carbene of rhenium supported on silica with a d^0-configuration. The complex Re($\equiv$CBu-*t*)(=CH Bu-*t*)(CH_2Bu-*t*)$_2$, **2**,[8] a d^0-Re(VII) hydrocarbyl complex was a promising molecular precursor, and its grafting was therefore studied.

Scheme 1



Typically, when a mixture of 1.00 g of $SiO_{2-(700)}$ (0.23−0.26 mmol of surface $\equiv$SiOH)[9] and 0.20 g of **2** (0.43 mmol) in pentane is stirred for 2 h at 20 °C, 0.24 mmol of neopentane is liberated.[10] This corresponds to 0.92−1.04 neopentane formed/available surface $\equiv$SiOH. The corresponding yellow surface organometallic compound **1** obtained—after washing the excess of **2** and drying under high vacuum at 25 °C—contains 14.9 C/grafted Re (4.75 and 4.55 wt % of Re and C, respectively).[11] The microanalysis is in agreement with the formation of 0.94 equiv of neopentane/Re during the grafting process[12] and the grafting of one Re per silanol available on $SiO_{2-(700)}$.[9] These numbers are further confirmed by the hydrogenolysis of **1** at 250 °C which produces 14.1 equiv of methane per Re. Therefore, the surface complex **1** is a rhenium complex monografted to the silica surface and surrounded by 3 "neopentyl-like ligands ($Np^{\#}$)": $\equiv$Si−O−Re($Np^{\#}$)$_3$. Moreover, spectroscopic data (vide infra, comments and Scheme 1) support the following structure for **1**: $\equiv$Si−O−Re($\equiv$CBu-*t*)(=CH Bu-*t*)(CH_2Bu-*t*).[13] First, the solid-state ^1H NMR spectrum of **1** has two distinct signals at 11.0 ± 0.5 (=C***H***Bu-*t*, 1H) and 1.0 ± 0.5 (C***H***$_3$, Bu-*t*, 27H) ppm (Figure 1a). Two other signals of weak intensity at 3.0 and 2.6 ppm are assigned to the two diastereotopic protons of the methylene fragment of the neopentyl ligand (C***HaHb***Bu-*t*, 2H). Second, the CP MAS ^{13}C NMR gives three

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(1) For a review on olefin metathesis, see: Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, 1997.

(2) Chauvin, Y.; Commereuc, D. *J. Chem. Soc., Chem. Commun.*, **1992**, 462 and references cited therein.

(3) Herrmann, W. A.; Wagner, W.; Flessner, U. N.; Volkhardt, U.; Komber,H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1636. Buffon, R.; Auroux, A.; Lefebvre, F.; Leconte, M.; Choplin, A.; Basset, J.-M.; Herrmann, W. A. *J. Mol. Catal.* **1992**, *76*, 287. Buffon, R.; Choplin, A.; Leconte, M.; Basset, J.-M.; Touroude, R.; Herrmann, W. A. *J. Mol. Catal.* **1992**, *72*, L7.

(4) The activity of rhenium oxides supported on silica is usually poor under 120 °C. For some examples, see: Aldag, A. W.; Lin, C. J.; Clark, A. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, M27; Tsuda, N.; Fujimori, A. *J. Catal.* **1981**, *69*, 410; Duquette, L. G.; Cieslinski, R. C.; Jung, C. H.; Garrou, P. E. *J. Catal.* **1984**, *90*, 362; Kirlin, P. S.; Gates, B. C. *J. Chem. Soc., Chem. Commun.* **1985**, 277; Edreva-Kardjieva, R. M.; Andreev, A. A. *J. Catal.* **1986**, *97*, 321.

(5) (a) For a review, see: Copéret, C.; Thivolle-Cazat, J.; Basset, J.-M. In *Fine Chemicals through Heterogeneous Catalysis*; Sheldon, R. A., van Bekkum, H., Eds.; Wiley-VCH: Weinheim 2001. (b) For seminal papers on group VI olefin metathesis catalysts prepared via SOMC, see: Weiss, K.; Loessel, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 62; Buffon, R.; Leconte, M.; Choplin, A.; Basset, J.-M. *J. Chem. Soc., Chem. Commun.*, **1993**, 361; Buffon, R.; Leconte, M.; Choplin, A.; Basset, J.-M. *J. Chem. Soc., Dalton Trans.*, **1994**, 1723; Herrmann, W. A.; Stumpf, A. W.; Priermeier, T.; Bogdanovic, S.; Dufaud, V.; Basset, J.-M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2803.

(6) Commereuc, D. *J. Chem. Soc., Chem. Commun.*, **1995**, 791.

(7) (a) Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2448. (b) Toreki, R.; Schrock, R. R.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 3610. (c) Schofield, M. H.; Schrock, R. R.; Park, L. Y. *Organometallics* **1991**, *10*, 1844. (d) Toreki, R.; Vaughan, G. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 127. (e) Vaughan, G. A.; Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 2980. (f) LaPointe, A. M.; Schrock, R. R. *Organometallics* **1995**, *14*, 1875. (g) Flatt, B. T.; Grubbs, R. H.; Blanski, R. L.; Calabrese, J. C.; Feldman, J. *Organometallics* **1994**, *13*, 2728.

(8) For the preparation of the first well-defined alkylidyne and alkylidene complexes of Re including **2**, see: (a) Edwards, D. S.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6806. (b) Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505. (c) Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 3367.

(9) For a 200 m^2/g aerosil silica (Degussa) treated at 700 °C under vacuum (12 h at 500 °C followed by 4 h at 700 °C), perhydrocarbyl complexes of Ti, Zr, Hf, Ta, and Mo have been grafted, yielding the corresponding monografted surface complexes and 1 equiv of neopentane per grafted metal. Microanalysis shows a 1.28, 2.30, 4.2, and 2.07 wt % of Ti, Zr, Hf, and Mo respectively in agreement with the presence of 0.7−0.8 reactive OH/nm^2. This value corresponds to 0.23−0.26 mmol of OH available/g of silica.

(10) Upon using 92% deuterated $SiO_{2-(700)}$, the neopentane liberated is typically 77% deuterated. The formation of both NpH and NpD during the grafting process shows that the grafting is more complex than a simple electrophilic cleavage of a Re−alkyl bond. For an example of the mechanism of grafting of Ta(=CHBu-*t*)(CH_2Bu-*t*)$_3$ on silica, see: Dufaud, V.; Niccolai, G. P.; Thivolle-Cazat, J.; Basset, J.-M. *J. Am. Chem. Soc.* **1995**, *117*, 4288; Lefort, L.; Chabanas, M.; Maury, O.; Meunier, D.; Copéret, C.; Thivolle-Cazat, J.; Basset, J.-M. *J. Organomet. Chem.* **2000**, *593*−*594*, 96.

(11) IR spectra can be found in the Supporting Information.

(12) The value of 0.94 equiv of neopentane/Re is an average value over several experiments, $\sigma = 0.10$.

(13) No signal was detected by ESR spectroscopy, which is consistent with a Re^{VII} species.

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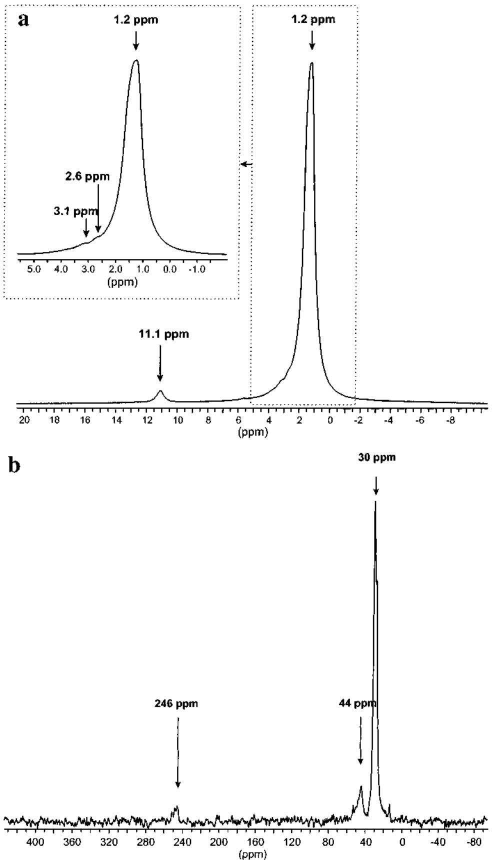

Figure 1. (a) Solid-state ^{1}H NMR spectrum of **1**. (b) Solid-state CP MAS ^{13}C NMR spectrum of **1**.

broad peaks at 246 (=***C***HBu-*t*), 44 (***C***H_2Bu-*t*) and 30 (***C***H_3, Bu-*t*) ppm (Figure 1b). The carbyne carbon of **1** has not been detected (it should appear around 300 ppm, vide infra).[14] This is not surprising since this carbon does not have hydrogen either in its α- or β-position and therefore no signal enhancement is achieved in CP MAS NMR.

To further understand the structure of the surface organorhenium complex, the corresponding molecular complex **3** with a triphenylsiloxy substituent in place of a siloxy group of the silica surface was prepared. The reaction of **2** with 1 equiv of triphenylsilanol in benzene at room temperature quantitatively gives **3** as a 10/1 mixture of its *syn*- and *anti*-rotamers (Scheme 1). The NMR data of the major isomer of **3** (*syn*) fully support the assignments of **1** (*See closely the proton and carbon chemical shifts of all of the ligands of the syn-rotamer of* **3**—molecular model—and **1**—supported complex—Scheme 1).[15] As compared to **1**, the model complex **3** does show a resonance characteristic of its carbyne ligand at 292 ppm, which unfortunately cannot be seen for **1** (for reasons aforementioned, vide supra). On the other hand, upon using a partially ^{13}C-labeled surface complex **1** on the carbons α to the metal center, the presence of the three different ligands was clearly established, and the chemical shifts of their corresponding α-carbon were close to identical to those of **3** (Figure 2).[16]

All of the data and their comparison with those of the model complex **3** are consistent with a Re-surface complex bearing four different ligands, that is a neopentyl, a neopentylidene, a neopentylidyne, and the siloxy group from the surface, like in the proposed structure of **1**. To our knowledge, this is the first example of a fully characterized silica-supported rhenium(VII) carbene and carbyne complex, which should be a metathesis catalyst for olefins and alkynes.

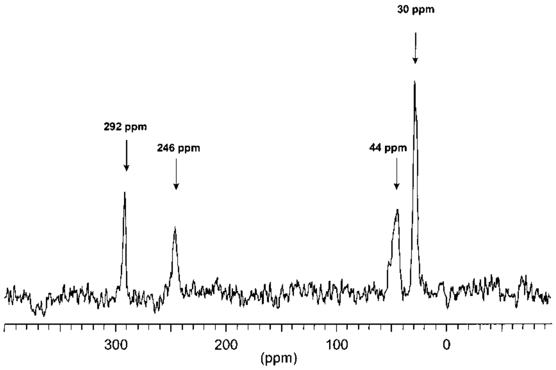

Figure 2. Solid-state HP DEC MAS ^{13}C NMR spectrum of partially ^{13}C-labeled **1**.

In fact, when 500 equiv of propene are contacted with **1** at 20 °C, the equilibrium is reached within less than 1 h.[17] The initial rate (TOF) is 0.25 mol/mol Re/s, which corresponds to one of the best for Re catalysts.[1,4,6,7] Moreover, the evolution of roughly 1 equiv of a 1:3 mixture of 3,3-dimethylbutene and 4,4-dimethyl-2-pentene is consistent with a cross-metathesis of the neopentylidene ligand of **1** and propene.[18] Additionally, this surface complex **1** is also able to catalyze alkyne metathesis, thus equilibrating in 20 min at room temperature 15 equiv of 2-pentyne into 2-butyne and 3-hexyne.[19] These data are also consistent with the structure of **1**. In conclusion, this study constitutes the first synthesis of a highly active well-defined rhenium heterogeneous catalyst supported on silica for olefin and alkyne metathesis.

Acknowledgment. Dedicated to Professor E. Negishi on the occasion of his 65th Birthday. We thank D. Alcor for the preparation of some starting materials, Dr. D. Bouchu (Centre de Spectrométrie de Masse, Université Claude Bernard, Lyon I) and Dr. B. Fenet (NMR services, ESCPE Lyon) for recording Mass spectrometry and 2D NMR spectroscopy, respectively. We are thankful to Dr. Y. Chauvin, A. Lesage and Professor L. Emsley for helpful discussions. We are also indebted to the CNRS and ESCPE Lyon for financial supports. M.C. is grateful to the French ministry of education, research and technology (MENRT) for a pre-doctoral fellowship.

Supporting Information Available: All data including IR spectra of **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] This type of carbon appears in the 280−310 ppm range; for a comprehensive data set on carbyne chemical shifts, see: ref 8c.

[15] Interestingly, when the surface complex is heated at 120 °C under Ar, a second carbenic C−H proton appears at 12.7 ppm in the ^{1}H NMR spectrum. This chemical shift corresponds to that of the *anti*-rotamer of the model compound **3**. This would mean that the surface complex **1** is present as the *syn*-rotamer only at low temperatures (<25 °C) and isomerize to a mixture of rotamers upon warming. The complete set of NMR data for *syn*-**3** and *anti*-**3** can be found in the Supporting Information.

[16] The surface complex **1**, 10% ^{13}C-labeled on the carbon α to the metal center was prepared by using ^{13}C-enriched *t*-BuCH_2MgCl in the synthesis of **2**, see ref 8. To observe the carbyne signal, it is better to use HP DEC MAS NMR in place of CP MAS NMR.

[17] At 25 °C, the $\Delta G°$ of this reaction is 1.7 kJ/mol, which corresponds to a 34.1% conversion of propene into a one-to-one mixture of ethene and 2-butenes (*trans*/*cis* = 3).

[18] In trying to characterize the surface complex arising from a cross-metathesis reaction, ^{13}C-dilabeled ethylene was used. Upon addition of 13.5 equiv of labeled ethylene in two cycles on **1,** the evolution of 0.5 equiv of 3,3-dimethylbutene, 100% ^{13}C-labeled at the methylene, was observed in agreement with a cross-metathesis between the neopentylidene ligand and ethylene. NMR spectroscopy on **1** treated with ethylene showed the disappearance of the signals corresponding to the neopentylidene ligand and the appearance of new signals at 230, 120−100, 50−30 ppm, consistent with the formation of both methylene rhenium and rhenacyclobutane surface complexes (see ref 7e). The data obtained for both the metathesis of propene and ethylene clearly shows that **1** is the olefin metathesis catalyst precursor, and further studies to characterize these new complexes and to understand the fate of **1** during catalysis are currently underway.

[19] For an example of alkyne metathesis with a Re^{VII}−alkylidyne complex, see: Weinstock, I. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1991**, *113*, 135.