NMR Observation of Trialkylphosphite-Palladium(II) and Ruthenium(II) Complexes in Supercritical Carbon Dioxide

Yoshihito Kayaki, Tomoyuki Suzuki, Yushi Noguchi, Satoshi Sakurai,[†] Mamoru Imanari,[†] and Takao Ikariya^{*} Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology and CREST, JST, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552 [†]JEOL Ltd., 3-1-2 Musashino, Akishima, Tokyo 196-8558

(Received January 7, 2002; CL-020009)

A supercritical fluid nuclear magnetic resonance (scNMR) spectroscopic method has been developed using a commercially available NMR spectrometer equipped with a high-pressure zirconia cell, revealing that trialkylphosphite ligands are highly effective for increasing the solubility of dichloropalladium(II) and dichlororuthenium(II) complexes in supercritical carbon dioxide (scCO₂).

Supercritical fluids (SCFs) have attracted much scientific and industrial attention as reaction media because of their unique properties including pressure tunable density, dielectric constant, viscosity, and cage effect.¹ For homogeneous catalysis in scCO₂, the solubility of molecular catalysts in the CO₂ phase strongly affects the outcome of the reactions, and hence much attention has been paid to preparing CO₂-soluble metal complexes for the development of efficient catalysts.² The solubility of the catalysts as well as the phase behavior of the reaction system under supercritical conditions is sometimes examined by a visual inspection of the interior of a sapphire window-equipped reactor vessel. However, the spectroscopic verification of the homogeneity of the reaction mixture is almost never used. This paper presents the results of an NMR spectroscopic investigation of trialkylphosphite coordinated Pd(II) and Ru(II) complexes under scCO₂ conditions and catalytic use of the Ru–phosphite system for vinyl carbamate synthesis from terminal alkyne, diethylamine, and $scCO_2$.

Since the pioneering work on scNMR analysis was reported by Rathke et al.,³ several research groups have used NMR method to study transition metal complexes. On the basis of the narrowing effect on quadrupole nuclei under supercritical conditions, they investigated the chemical behavior of homogeneous cobalt hydroformylation catalysts in scCO₂ by using a toroid NMR system⁴ as a high-pressure probe technique.⁵ However, to date, the direct NMR observation of transition metal complexes in SCFs has been limited because of a lack of more versatile highpressure NMR instruments for SCFs. Although capillary NMR tube-cells⁶ have been used in commercially available NMR systems, severe limitation on the detection of the small amount of compounds or insensitive nuclei has still remained for practical measurement. It has been reported that high pressure cells made of sapphire,⁷ or ceramics⁸ can be used in commercial probes fitted within without special modifications of the spectrometer.

In this study, we used a zirconia NMR cell modified for routine operation under supercritical conditions as depicted in Figure 1. The high pressure cell assembly consists of a nonmagnetic Ti–Al alloy valve and a ceramic tube having a 9.0 mm o.d., 5.4 mm i.d., and a 152 mm length. The valves can be attached



Figure 1. Schematic diagram of the NMR cell for SCF. (a) Outside view. (b) Vertical sectional view.

to the top of the ceramic tube and fixed with Kalrez[®] perfluoroelastomer O-rings. Pressurized fluids can be introduced using a syringe pump (ISCO, model 260D) and monitored by a pressure gauge integrated into a back-pressure regulator (JASCO, 880–81). The temperature is controlled by a variable temperature (VT) spectrometer system. In order to minimize undesired convection of the fluids mixture arising from temperature differences between the top and the bottom of the cell, a sealed Pyrex tube containing dimethylsulfoxide- d_6 was placed into the cell as shown in Figure 1(b). This deuterated reference enables one to adjust the shim coil with the guidance of the deuterium lock signal providing high resolution spectra. The assembly is operated at pressures up to 20 MPa in the NMR spectrometer (JEOL, LA-300) in the non-spinning mode.⁹

We examined the solubility of the transition metal complexes bearing a fluorinated phosphorus ligand, 2,2,2-trifluoro-ethylphosphite, (P(OCH₂CF₃)₃), because the incorporation of fluorous groups into the ligands and/or counter ions is well known to increase the solubility of metal complexes in scCO₂.² The phosphite complexes, *trans*-[PdCl₂{P(OCH₂CF₃)₃}₂] (**1a**) and *trans*-[RuCl₂{P(OCH₂CF₃)₃}₄] (**2a**) can be easily prepared by ligand exchange reactions from known compounds.^{10,11}

The ³¹P NMR spectrum of the Pd(II) complex **1a** (16.0 mg, 1.9×10^{-2} mmol) in scCO₂ (10.0 MPa, 50 °C) was successfully obtained as a sharp singlet signal at 96.4 ppm analogously to the spectra in liquid solvents. Its ¹⁹F NMR spectrum displayed a triplet coupled with the adjacent methylene protons at -78.0 ppm (³*J*_{FH} = 7.0 Hz). Similarly, NMR spectra of **2a** (20.0 mg, 1.3×10^{-2} mmol) in scCO₂ under the conditions of 15.0 MPa and 50 °C showed a singlet at 129.2 ppm in ³¹P NMR and a triplet at -77.7 ppm with ³*J*_{FH} = 7.7 Hz in ¹⁹F NMR. These results indicated that the phosphite complexes **1a** and **2a** apparently



Figure 2. ³¹P NMR spectrum (number of scans = 256) of **2a** and **2b** in scCO₂ (50 °C, 15 MPa). Chemical shifts of the spectra were refereced to an external 85% H₃PO₄ (δ 0).

dissolved into the CO_2 phase and that the complex **2a** has two chlorine atoms in a trans configuration.

The advantage of scNMR spectroscopy was further confirmed by successfully measuring the ³¹P NMR spectrum of a fluorine-free triethylphosphite complexes, *trans*-[PdCl₂{P(OC₂H₅)₃}₂] (**1b**)¹² and *trans*-[RuCl₂{P(OC₂H₅)₃}₄] (**2b**).¹³ The Pd complex **1b** was proved to be soluble in scCO₂ (15.0 MPa, 80 °C), whereas a triphenylphosphine complex, *trans*-[PdCl₂{P(C₆H₅)₃}₂] gave no signal under similar conditions because of its low solubility in scCO₂.

Thanks to the high solubility of the phosphite complexes, we tested the phosphite-Ru complex 2b on the catalytic reaction of phenylacetylene with diethylamine and CO₂.¹⁴ Dixneuf et al. has reported that the reaction proceeds via a vinylidene-Ru intermediate, which reacts with N, N-diethylcarbamate anion (or N, N-diethylcarbamic acid) derived from the amine and CO_2 or acetylene to give vinyl carbamates (3) and enynes (4), respectively. In fact, the reaction with 2b in acetonitrile proceeded with a poor selectivity as shown in Scheme 1. However, changing the reaction medium to $scCO_2$ caused a significant improvement in the reaction rate and the yield of (Z)vinyl carbamate 3, possibly due to the increase in the concentration of the carbamate ion.¹⁵ The scNMR investigation on a dynamic behavior of diethylamine in scCO₂ revealed that formation of N, N-diethylcarbamic acid was reversible and the concentration of the carbamic acid was highly influenced by the pressure and temperature.¹⁶



The results obtained here on the phosphite-coordinated complexes **1** and **2** confirm that the use of phosphite ligands has proven to be a practical ligand modification for preparing CO_2 -soluble transition metal complexes and that scNMR methods are now widely applicable to measuring the solubility and dynamic behavior of catalysts in scCO₂.

Dedicated to Professor Teruaki Mukaiyama on the occasion of his 75th birthday.

References and Notes

- a) P. G. Jessop, T. Ikariya, and R. Noyori, *Chem. Rev.*, 99, 475 (1999). b)
 "Chemical Synthesis using Supercritical Fluids," ed. by P. G. Jessop and W. Leitner, VCH/Wiley, Weinheim (1999). c) R. S. Oakes, A. A. Clifford, and C. M. Rayner, *J. Chem. Soc., Perkin Trans. 1*, 2001, 917.
- a) D. Koch and W. Leitner, J. Am. Chem. Soc., 120, 13398 (1998). b) S. Kaintz, A. Brinkmann, W. Leitner, and A. Pfaltz, J. Am. Chem. Soc., 121, 6421 (1999). c) M. A. Carroll and A. B. Holmes, Chem. Commun., 1998, 1395. d) C. A. G. Carter, R. T. Baker, S. P. Nolan, and W. Tumas, Chem. Commun., 2000, 347.
- 3 J. W. Rathke, R. J. Klingler, and T. R. Krause, *Organometallics*, **11**, 585 (1992).
- 4 J. W. Rathke, R. J. Klingler, R. E. Gerald, II, K. W. Kramarz, and K. Woelk, *Prog. Nucl. Magn. Reson. Spectrosc.*, **30**, 209 (1997).
- 5 B. T. Heaton, L. Strona, J. Jonas, T. Eguchi, and G. A. Hoffman, J. Chem. Soc., Dalton Trans., **1982**, 1159.
- 6 C. R. Yonker, T. S. Zemanian, S. L. Wallen, J. C. Linehan, and J. A. Franz, J. Magn. Reson., A, 113, 102 (1995).
- 7 a) S. Gaemers, H. Luyten, J. M. Ernsting, and C. J. Elsevier, *Magn. Reson. Chem.*, **37**, 25 (1999). b) S. Bai, C. L. Mayne, R. J. Pugmire, and D. M. Grant, *Rev. Sci. Instrum.*, **67**, 240 (1995). c) D. C. Roe, *J. Magn. Reson.*, **63**, 388 (1985).
- 8 T. Aizawa, O. Sato, Y. Ikushima, K. Hatakeda, and N. Saito, *Rev. High Pressure Sci. Technol.*, 7, 1426 (1998).
- 9 The ceramic cell achieved comparable resolution on protons (about 1.5 Hz of half-line width for measurements on chloroform in acetone- d_6 at 300 MHz) to a sapphire tube.
- 10 Treatment of [PdCl₂(CH₃CN)₂] with 2 mol amount of P(OCH₂CF₃)₃ in THF at room temperature gave **1a** in 76% yield. The Ru complex **2a** was prepared in 84% yield from the reaction of [RuCl₂{P(C₆H₅)₃}₃] and the phosphite ligand. Selected analytical data for **1a**: ¹H NMR (300 MHz, CDCl₃): δ 4.65 (m); ¹⁹F NMR (283 MHz, CDCl₃): δ -75.8 (t, ³*J*_{FH} = 7.77 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 65.0 (vtq, *J*_{CP} = 38.5 Hz, ²*J*_{CF} = 154.5 Hz, OCH₂CF₃), 121.8 (q, ¹*J*_{CF} = 276.1 Hz, OCH₂CF₃); ³¹P NMR (122 MHz, CDCl₃): δ 96.9 (s); mp 113–114 °C; Anal. Calcd for C₁₂H₁₂O₆P₂Cl₂F₁₈Pd: C, 17.29; H, 1.45%. Found: C, 17.26; H, 1.44%. **2a**: ¹H NMR (300 MHz, CD₃OD): δ 4.76 (q, ³*J*_{HF} = 8.3 Hz); ¹⁹F NMR (283 MHz, CD₃OD): δ -77.0 (t, ³*J*_{FH} = 8.1 Hz); ³¹P NMR (122 MHz, CD₃OD): δ 127.5 (s); Anal. Calcd for C₂₄H₂₄O₁₂P₄Cl₂F₃₆Ru: C, 19.42; H, 1.63%. Found: C, 19.77; H, 1.79%.
- 11 Y. Kayaki, Y. Noguchi, S. Iwasa, T. Ikariya, and R. Noyori, *Chem. Commun.*, **1999**, 1235.
- 12 The 31 P NMR spectrum of **1b** (34.2 mg, 6.7×10^{-2} mmol) showed a singlet signal at 95.0 ppm in scCO₂ (15.0 MPa, 80 °C).
- 13 The ³¹P NMR spectrum of **2b** (12.0 mg, 1.4×10^{-2} mmol) displayed a sharp singlet at 130.1 ppm in scCO₂ (15.0 MPa, 50 °C).
- 14 R. Mahé, Y. Sasaki, C. Bruneau, and P. H. Dixneuf, J. Org. Chem., 54, 1518 (1989).
- 15 During the preparation of this manuscript, a similar result on the vinyl carbamate formation using [RuCl₂(C₅H₅N)₄] and [RuCl₂(η⁶-C₆H₆){P(CH₃)₃] as catalysts was reported. M. Rohr, C. Geyer, R. Wandeler, M. S. Schneider, E. F. Murphy, and A. Baiker, *Green Chem.*, **3**, 123 (2001).
- 16 Further details of the carbamic acid formation in scCO₂ will be reported elsewhere.