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

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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 ($scCO_2$).

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 $scCO_2$, the solubility of molecular catalysts in the CO_2 phase strongly affects the outcome of the reactions, and hence much attention has been paid to preparing CO_2-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 $scCO_2$ 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 $scCO_2$ by using a toroid NMR system[4] 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 high-pressure NMR instruments for SCFs. Although capillary NMR tube-cells[6] 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 ceramics[8] 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 non-magnetic 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 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]

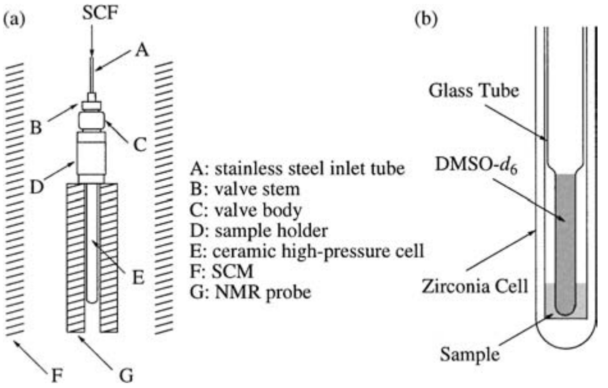


Figure 1. Schematic diagram of the NMR cell for SCF. (a) Outside view. (b) Vertical sectional view.

We examined the solubility of the transition metal complexes bearing a fluorinated phosphorus ligand, 2,2,2-trifluoro-ethylphosphite, ($P(OCH_2CF_3)_3$), because the incorporation of fluorous groups into the ligands and/or counter ions is well known to increase the solubility of metal complexes in $scCO_2$.[2] The phosphite complexes, *trans*-$[PdCl_2\{P(OCH_2CF_3)_3\}_2]$ (**1a**) and *trans*-$[RuCl_2\{P(OCH_2CF_3)_3\}_4]$ (**2a**) can be easily prepared by ligand exchange reactions from known compounds.[10,11]

The ^{31}P NMR spectrum of the Pd(II) complex **1a** (16.0 mg, 1.9×10^{-2} mmol) in $scCO_2$ (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 ^{19}F NMR spectrum displayed a triplet coupled with the adjacent methylene protons at -78.0 ppm ($^3J_{FH} = 7.0$ Hz). Similarly, NMR spectra of **2a** (20.0 mg, 1.3×10^{-2} mmol) in $scCO_2$ under the conditions of 15.0 MPa and 50 °C showed a singlet at 129.2 ppm in ^{31}P NMR and a triplet at -77.7 ppm with $^3J_{FH} = 7.7$ Hz in ^{19}F NMR. These results indicated that the phosphite complexes **1a** and **2a** apparently

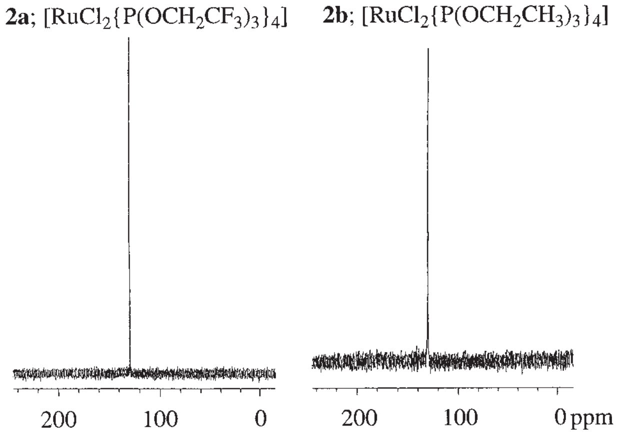
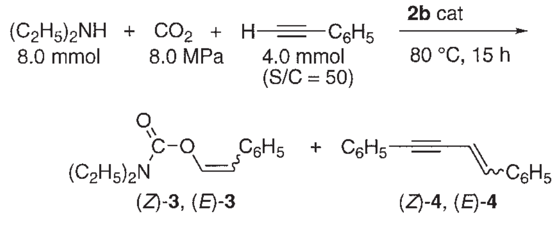


Figure 2. ^{31}P NMR spectrum (number of scans = 256) of **2a** and **2b** in $scCO_2$ (50 °C, 15 MPa). Chemical shifts of the spectra were refereced to an external 85% H_3PO_4 (δ 0).

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 ^{31}P NMR spectrum of a fluorine-free triethylphosphite complexes, *trans*-$[PdCl_2\{P(OC_2H_5)_3\}_2]$ (**1b**)[12] and *trans*-$[RuCl_2\{P(OC_2H_5)_3\}_4]$ (**2b**).[13] The Pd complex **1b** was proved to be soluble in $scCO_2$ (15.0 MPa, 80 °C), whereas a triphenylphosphine complex, *trans*-$[PdCl_2\{P(C_6H_5)_3\}_2]$ gave no signal under similar conditions because of its low solubility in $scCO_2$.

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 CO_2.[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 $scCO_2$ 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]



	conv	(*Z*)-**3**	(*E*)-**3**	(*Z*)-**4**	(*E*)-**4**
CH_3CN (10 mL)	15%	6%	< 1%	4%	5%
$scCO_2$ (8.0 MPa)	99%	74%	< 1%	6%	17%

Scheme 1.

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 $scCO_2$.

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

References and Notes

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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 $[PdCl_2(CH_3CN)_2]$ with 2 mol amount of $P(OCH_2CF_3)_3$ in THF at room temperature gave **1a** in 76% yield. The Ru complex **2a** was prepared in 84% yield from the reaction of $[RuCl_2\{P(C_6H_5)_3\}_3]$ and the phosphite ligand. Selected analytical data for **1a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.65 (m); ^{19}F NMR (283 MHz, $CDCl_3$): δ −75.8 (t, $^3J_{FH} = 7.77$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 65.0 (vtq, $J_{CP} =$ 38.5 Hz, $^2J_{CF} = 154.5$ Hz, OCH_2CF_3), 121.8 (q, $^1J_{CF} = 276.1$ Hz, OCH_2CF_3); ^{31}P NMR (122 MHz, $CDCl_3$): δ 96.9 (s); mp 113–114 °C; Anal. Calcd for $C_{12}H_{12}O_6P_2Cl_2F_{18}Pd$: C, 17.29; H, 1.45%. Found: C, 17.26; H, 1.44%. **2a**: ^{1}H NMR (300 MHz, CD_3OD): δ 4.76 (q, $^3J_{HF} = 8.3$ Hz); ^{19}F NMR (283 MHz, CD_3OD): $\delta - 77.0$ (t, $^3J_{FH} =$ 8.1 Hz); ^{31}P NMR (122 MHz, CD_3OD): δ 127.5 (s); Anal. Calcd for $C_{24}H_{24}O_{12}P_4Cl_2F_{36}Ru$: C, 19.42; H, 1.63%. Found: C, 19.77; H, 1.79%.

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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 $scCO_2$ (15.0 MPa, 80 °C).

13 The ^{31}P NMR spectrum of **2b** (12.0 mg, 1.4×10^{-2} mmol) displayed a sharp singlet at 130.1 ppm in $scCO_2$ (15.0 MPa, 50 °C).

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