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Synthesis of Ruthenium(II) Complexes Containing Hydroxymethylphosphines and Their Catalytic Activities for Hydrogenation of Supercritical Carbon Dioxide

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Ligand substitution of $RuCl_2[P(C_6H_5)_3]_3$ and Cp*RuCl(isoprene) (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) complexes with hydroxymethylphosphines was investigated to develop new catalyst systems for CO_2 hydrogenation. A reaction of $P(C_6H_5)_2CH_2OH$ with $RuCl_2[P(C_6H_5)_3]_3$ in CH_2Cl_2 gave $Ru(H)Cl(CO)[P(C_6H_5)_2CH_2OH]_3$ (**1**), which was characterized by NMR spectroscopy and X-ray crystallographic analysis. An isotope labeling experiment using $P(C_6H_5)_2{}^{13}CH_2OH$ indicated that the carbonyl moiety in complex **1** originated from formaldehyde formed by degradation of the hydroxymethylphosphine. Elimination of formaldehyde from PCy_2CH_2OH (Cy = cyclohexyl) was also promoted by treatment of $RuCl_2[P(C_6H_5)_3]_3$ in ethanol to give $RuCl_2(PHCy_2)_4$ under mild conditions. On the other hand, the substitution reaction using Cp*RuCl(isoprene) with the hydroxymethylphosphine ligands proceeded smoothly with formation of $Cp^*RuCl(L)_2$ [**2a**–**2c**; L = $P(C_6H_5)_2CH_2OH$, $PCy(CH_2OH)_2$, and $P(CH_2OH)_3$] in good yields. The isolable hydroxymethylphosphine complexes **1** and **2** efficiently catalyzed the hydrogenative amidation of supercritical carbon dioxide ($scCO_2$) to *N*,*N*-dimethylformamide (DMF).

Introduction

Water-soluble tertiary phosphines have attracted considerable interest in the development of easily recoverable and reusable organometallic catalysts.[1] Structural modification of hydrophilic phosphorus ligands has been extensively studied, by practical works on aqueous biphasic catalysis with TPPTS (3,3′,3″-phosphinetriylbenzene sulfonic acid),[2] for aryl- and alkyl-phosphines with hydroxy, ammonium, phosphonium, or carboxylate groups.[3] Among them, tris(hydroxymethyl)phosphine, $P(CH_2OH)_3$, has been applied to the area of catalysis and biomedicine as a readily available and moderately air-stable compound.[4−6]

We have previously reported that $P(CH_2OH)_3$ was a beneficial supporting ligand of a highly efficient Ru catalyst for hydrogenation of $scCO_2$ to the formate salt, which transformed into DMF after its dehydration with dimethylamine (Scheme 1).[7] For the hydrogenation of CO_2, $scCO_2$ has been shown to be an advantageous reaction medium because of its unique physicochemical properties;[8] however,

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Scheme 1

$$CO_2 + H_2 + HN(CH_3)_2 \xrightarrow[scCO_2]{\text{Ru cat}} HCON(CH_3)_2 + H_2O$$

Scheme 2

$$RuCl_2[P(C_6H_5)_3]_3 + \underset{\text{4 equiv}}{P(C_6H_5)_2CH_2OH} \xrightarrow[\text{rt}]{CH_2Cl_2} \underset{\text{1 L= } P(C_6H_5)_2CH_2OH}{\text{L-Ru(H)(CO)(Cl)-L}}$$

45% yield

the catalyst performance may be altered by subtle phase behavior during the progress of reaction. In fact, compared with a Ru−$P(CH_3)_3$ system,[9] an analogous Ru−$P(CH_2OH)_3$ complex, $RuCl_2[PH(CH_2OH)_2]_2[P(CH_2OH)_3]_2$,[5] provided superior catalyst performance even at the later stage of the DMF synthesis, because the water-soluble catalyst could merge effectively with the reaction mixture including the coproduct water in $scCO_2$.[7] This finding of a marked ligand effect on the hydrogenation of $scCO_2$ prompted us to study other Ru catalyst precursors bearing OH-substituted phosphorus ligands with different polarity. We describe herein the synthesis of novel ruthenium(II) complexes by ligand substitution using several hydroxymethylphosphines and catalytic hydrogenative amidation of $scCO_2$ with these complexes.

Results and Discussion

Reaction of $RuCl_2[P(C_6H_5)_3]_3$ with Hydroxymethylphosphines. The ligand exchange of the Ru complex, $RuCl_2[P(C_6H_5)_3]_3$, with $P(C_6H_5)_2CH_2OH$ was examined according to the reported procedure for the reaction with $P(CH_2OH)_3$.[5] The reaction of $RuCl_2[P(C_6H_5)_3]_3$ with 4 molar equiv of $P(C_6H_5)_2CH_2OH$ at room temperature in CH_2Cl_2 for 24 h gave a colorless complex, Ru(H)Cl(CO)$[P(C_6H_5)_2CH_2OH]_3$ (**1**), bearing hydrido and carbonyl ligands in addition to $P(C_6H_5)_2CH_2OH$ ligands in 45% yield, as shown in Scheme 2. The ^{1}H NMR spectrum of **1** exhibits the hydrido resonance at −6.7 ppm as a doublet of triplets coupled to the phosphine ligands and two different sets of methylene protons at 4.54 and 4.25 ppm. The ^{31}P signals observed at 15.5 (t, $^2J_{PP}$ = 15.6 Hz) and 34.5 ppm (d, $^2J_{PP}$ = 15.6 Hz) correspond to an AX_2 pattern with no fluxional behavior. The IR spectrum of **1** displayed a strong CO stretching band around 1940 cm^{-1}, as well as absorption of the Ru−H group at 2359 cm^{-1}. Single crystals suitable for an X-ray diffraction study were obtained as solvates (**1**·CH_2Cl_2) from a concentrated CH_2Cl_2 solution at ambient temperature. The molecular structure of complex **1** was determined using the data collected at low temperature. The X-ray crystal structure of **1** is depicted in Figure 1, with selected bond lengths including the Ru−H bond and angles in the caption.

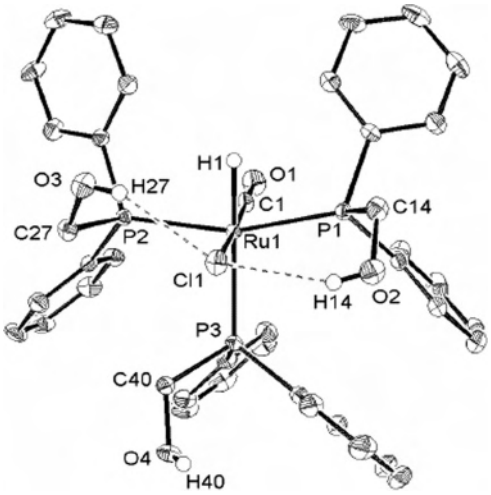

Figure 1. Molecular structure of Ru(H)Cl(CO)$[P(C_6H_5)_2CH_2OH]_3$·CH_2Cl_2 (**1**). The solvent molecule and hydrogen atoms, other than H(1), H(14), H(27), and H(40), are omitted for clarity, and the ellipsoids represent 50% probability. The dashed lines indicate the hydrogen bonds. Selected bond lengths (Å) and angles (deg): Ru(1)−H(1) = 1.57(3), Ru(1)−Cl(1) = 2.5133(6), Ru(1)−P(1) = 2.3497(7), Ru(1)−P(2) = 2.3632(6), Ru(1)−P(2) = 2.4453(6), Ru(1)−C(1) = 1.827(3), C(1)−O(1) = 1.149(3), P(1)−Ru(1)−Cl(1) = 92.01(2), P(2)−Ru(1)−Cl(1) = 92.01(2), P(3)−Ru(1)−Cl(1) = 87.85(2), C(1)−Ru(1)−P(1) = 85.90(8), C(1)−Ru(1)−P(3) = 98.46(8), P(1)−Ru(1)−P(3) = 101.71(2), P(2)−Ru(1)−P(3) = 95.53(2).

Complex **1** has an octahedral geometry with a meridional arrangement of three phosphines and a trans configuration of the carbonyl and chloro ligands. The hydrido ligand is in a cis position to Cl and CO ligands; the Ru−H distance is 1.57 Å and the H−Ru−Cl and H−Ru−C angles are 84 and 89°, respectively. Although the lengths of the Ru−P, Ru−C, and C−O bonds in **1** resemble the values observed for a related OH-free complex, Ru(H)Cl(CO)$[P(C_6H_5)_2CH_3]_3$, the Ru−Cl distance of 2.5133 Å in **1** is somewhat longer than that of 2.486 Å in the $P(C_6H_5)_2CH_3$ complex.[10] Notably, an intramolecular hydrogen bond between the chloro ligand and hydroxy tails of two phosphine ligands adjacent to the hydrido ligand was observed, while no marked interactions with the hydroxy group of neighboring molecules were found. The O(H)···Cl contacts (3.061 and 3.080 Å)[11] are shorter than those observed for $RuCl_2[PH(CH_2OH)_2]_2[P(CH_2OH)_3]_2$ (3.142 and 3.226 Å).[5a] The Ru−Cl bond elongation of **1** compared to the $P(C_6H_5)_2CH_3$ complex would be ascribed to the bifurcate hydrogen-bonding interaction of the chloro ligand.

To clarify the origin of the carbonyl moieties in the complex **1**, we prepared a ^{13}C-labeled phosphine, $P(C_6H_5)_2{}^{13}CH_2OH$, from H^{13}CHO and $PH(C_6H_5)_2$ and examined the ligand-exchange reaction using $RuCl_2[P(C_6H_5)_3]_3$ (Scheme 3). In the ^{13}C{^{1}H} NMR spectrum of the resulting complex, an

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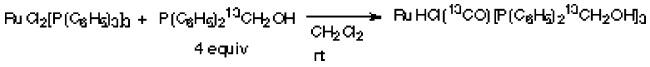
(11) The Cl(1)−H(14) and Cl(1)−H(27) distances are 2.36 and 2.37 Å, respectively.

Scheme 3



enhanced signal from the carbonyl carbon was observed at 200.1 ppm with $^2J_{CP}$ = 15.6 and 7.6 Hz, indicating the formation of the ^{13}C-enriched carbonyl complex. The coordination of ^{13}CO was further evidenced by the ^{13}C-coupled ^{31}P{^{1}H} NMR signals at 15.5 ($^2J_{CP}$ = 7.6 Hz) and 34.5 ppm ($^2J_{CP}$ = 15.3 Hz). On the basis of a well-known synthetic procedure for hydrido(carbonyl)ruthenium complexes Ru(H)Cl(CO)L_3 (L = $P(C_6H_5)_3$ and $P(C_6H_5)_2CH_3$) from formaldehyde and dichlororuthenium(II) complexes $RuCl_2L_3$,[12] the carbonyl and hydrido ligands in **1** would be introduced via the reverse process of the hydroxymethylphosphine formation from formaldehyde and $PH(C_6H_5)_2$. In fact, elimination of a formaldehyde unit from hydroxymethylphosphine ligands has already been reported in synthetic procedures of the [Pt{$P(CH_2OH)_2CH_2OP(CH_2OH)_2$}$_2$]$Cl_2$, $RuCl_2[PH(CH_2OH)_2]_2[P(CH_2OH)_3]_2$, and $RuCl_2[PH(C_6H_5)(CH_2OH)]_2[P(C_6H_5)(CH_2OH)_2]_2$ complexes.[4e,5]

The hydrido(carbonyl) complex **1** was also successfully synthesized in 56% yield from the reaction of *trans*-$RuCl_2(DMSO)_4$ with $P(C_6H_5)_2CH_2OH$ in a 1:10 molar ratio in CH_2Cl_2 for 3 h at room temperature (Scheme 4). Monitoring the progress of this reaction at 0 °C by ^{31}P{^{1}H} NMR spectroscopy showed an initially formed complex, $RuCl_2[P(C_6H_5)_2CH_2OH]_3$ (14.1 ppm), which gradually converted into the carbonyl complex **1**, indicating that the reaction proceeds through the coordination of $P(C_6H_5)_2CH_2OH$ to a ruthenium(II) center, followed by its degradation and incorporation of the hydrido and carbonyl ligands.

The elimination of the formaldehyde unit from hydroxymethylphosphines was also observed in the ligand exchange with PCy_2CH_2OH. The reaction of $RuCl_2[P(C_6H_5)_3]_3$ with 4 molar equiv of PCy_2CH_2OH in ethanol at room temperature for 1 h gave rise to a yellow compound formulated as *trans*-$RuCl_2(PHCy_2)_4$ in 79% yield as outlined in Scheme 5. The ^{1}H NMR spectrum in $CDCl_3$ exhibits a doublet signal assigned to the secondary phosphine at 2.35 ppm with a large $^1J_{PH}$ coupling constant of 143.1 Hz. The hydroxymethyl moiety of PCy_2CH_2OH was lost to give $RuCl_2(PHCy_2)_4$, whereas partial elimination of formaldehyde from the ligand exchange with $P(CH_2OH)_3$ was observed and resulted in the formation of $RuCl_2[PH(CH_2OH)_2]_2[P(CH_2OH)_3]_2$.[5]

Coordination of Hydroxymethylphosphines to the Cp*Ru System. In contrast to the reaction chemistry of dichlororuthenium(II) complexes as discussed above, the reaction of Cp*RuCl(isoprene) with hydroxymethylphosphines such as $P(C_6H_5)_2CH_2OH$, $PCy(CH_2OH)_2$ and $P(CH_2OH)_3$ in a 1:2 molar ratio at room temperature gave bis(phosphine) complexes Cp*$RuClL_2$ (**2a**−**2c**) as shown in Scheme 6. In all cases, the ^{1}H and ^{31}P{^{1}H} NMR spectra of the reaction mixtures indicated formation of the corresponding bis(phosphine) complexes without loss of the hydroxymethyl moiety.[13]

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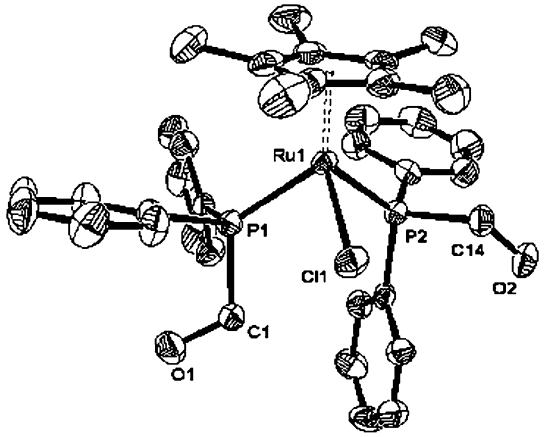


Figure 2. Molecular structure of Cp*$RuCl[P(C_6H_5)_2CH_2OH]_2 \cdot CH_2Cl_2$ (**2a**). Ellipsoids are shown at the 50% probability level for the non-hydrogen atoms, other than the solvent molecule.

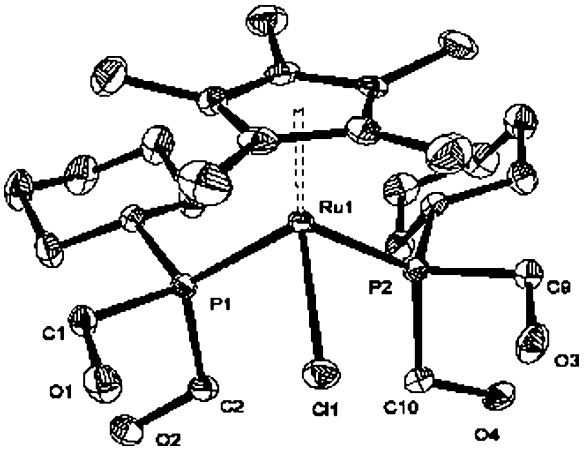


Figure 3. Molecular structure of Cp*$RuCl[PCy(CH_2OH)_2]_2$ (**2b**). Only one of the two independent molecules is shown. Ellipsoids are shown at the 50% probability level for the non-hydrogen atoms, other than the solvent molecule.

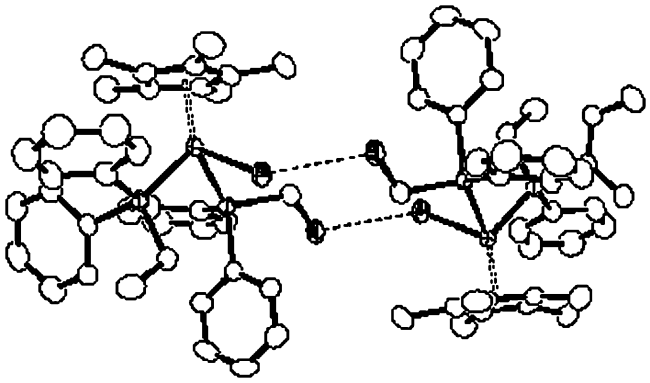
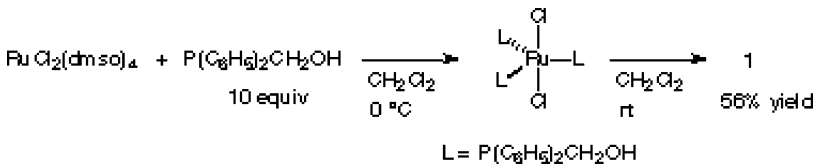


Figure 4. Schematic representation of the bimolecular interaction in Cp*$RuCl[P(C_6H_5)_2CH_2OH]_2$ (**2a**). The dashed lines indicate the hydrogen bonds.

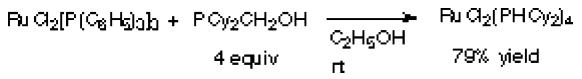
The molecular structures of complexes **2a** and **2b** were determined by X-ray crystallographic analysis. These ORTEP depictions are given in Figures 2 and 3, and selected bond lengths and angles are summarized in Table 1. Both complexes have a distorted octahedral geometry with Cp*,

(13) The loss of hydroxymethyl moiety was not observed similarly for coordination of $P(CH_2OH)_3$ to Cp*$RuCl(CO)_2$ under irradiation with UV light in ref 4k.

Scheme 4



Scheme 5



Scheme 6

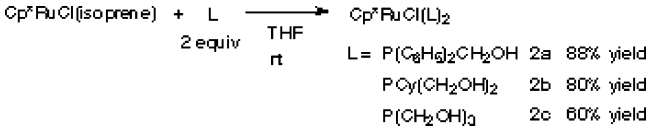


Table 1. Selected Bond Lengths (Å) and Angles (deg) for **2a** and **2b**

	2a·CH_2Cl_2	**2b**[a]	
Ru−P	2.3247(9)	2.3340(6)	2.3315(6)
	2.3136(9)	2.3256(6)	2.3297(6)
Ru−Cl	2.4778(7)	2.4940(7)	2.4918(7)
P−Ru−P	94.54(3)	99.13(2)	99.13(2)
P−Ru−Cl	88.37(3)	89.44(2)	89.84(2)
	88.11(3)	87.57(2)	87.49(2)

[a] Two independent molecules were observed.

two phosphines, and chloro ligands. The structure of **2a** is similar to that of a related OH-free bis(phosphine) complex, Cp*RuCl[$P(C_6H_5)_2CH_3$]$_3$: both complexes are monoclinic with the same space group (No. 14), although with different settings ($P2_1/n$ and $P2_1/c$, respectively).[14] A slight increase in the average Ru−P bond length of **2a** (av 2.319 Å) compared to that of the OH-free bis(phosphine) complex (av 2.310 Å) may reflect the greater steric effect or lower electron-donating property of $P(C_6H_5)_2CH_2OH$ compared to that of $P(C_6H_5)_2CH_3$. The increased steric demands can also be seen in the P−Ru−P bite angle of the $P(C_6H_5)_2CH_2OH$ complex (94.54°), being larger than that of the $P(C_6H_5)_2CH_3$ complex (93.02°).

In contrast to the complex **1**, the X-ray crystallography of **2a** does not show the presence of intramolecular hydrogen bond interactions through the hydroxy group, but each molecule has a connected neighbor, as shown in Figure 4. A distance of 3.142 Å for the O(H)···Cl motif indicates the presence of intermolecular hydrogen bonding, and therefore the Ru−Cl bond in **2a** may display a slightly longer distance (2.4778 Å) than that in the $P(C_6H_5)_2CH_3$ complex (2.4522 Å). On the other hand, it is also found that the hydroxyl moieties of **2b** participate in intramolecular O(H)···Cl contacts (O···Cl = 3.035−3.078 Å) and partly contact with two distinct adjacent hydroxy units (O···O = 2.819−3.083 Å), as shown in Figure 5.

The number of hydroxymethyl groups on the phosphine ligands in complexes **2a**−**2c** was found to influence the solubility of the complexes in water. For example, ^{1}H and ^{31}P{^{1}H}-NMR experiments at 25 °C revealed that the $P(CH_2OH)_3$ complex **2c** is more soluble in D_2O (>4.4 × 10^{-2} mol L^{-1}) than in C_6D_6 (∼1.6 × 10^{-4} mol L^{-1}), whereas the $P(C_6H_5)_2CH_2OH$ complex **2a** has appreciable solubility in C_6D_6 (>0.11 mol L^{-1}) and is sparingly soluble in D_2O (∼6.3 × 10^{-5} mol L^{-1}). Notably, the $PCy(CH_2OH)_2$ complex **2b** has amphiphilic nature in solution. Although it is hardly soluble in D_2O at 25 °C, an increase in the solution temperature caused a significant improvement in the solubility up to 2.2 × 10^{-2} mol L^{-1} in D_2O at 70 °C. The solid-state structure of **2b** as shown in Figure 5 implies that formation of the intra- and intermolecular hydrogen bond networks using all of the hydroxyl groups would contribute to formation of a rigid bimolecular pair, thereby preventing water molecules from approaching. Thus, the amphiphilic property of the complex **2b** was demonstrated by a comparable solubility (1.5 × 10^{-2} mol L^{-1}) in C_6D_6 at 70 °C.

Catalysis for Hydrogenative DMF Formation Using scCO$_2$. Synthesis of formic acid derivatives by hydrogenation of CO_2 using molecular catalysts represents one of the promising methods for CO_2 fixation into useful commodity chemicals.[15] In a number of experimental[9b,16] and theoretical[17] studies, it has been recognized that the ligand modulation and the presence of protic cocatalysts such as water, alcohols, and amines significantly influence the reaction profiles. The presence of hydroxy moiety on the alkylphosphines may provide positive effect on the CO_2 hydrogenation catalyzed by the Ru complexes.

The isolable hydroxymethylphosphine-ruthenium(II) complexes were tested for the catalytic hydrogenative amidation

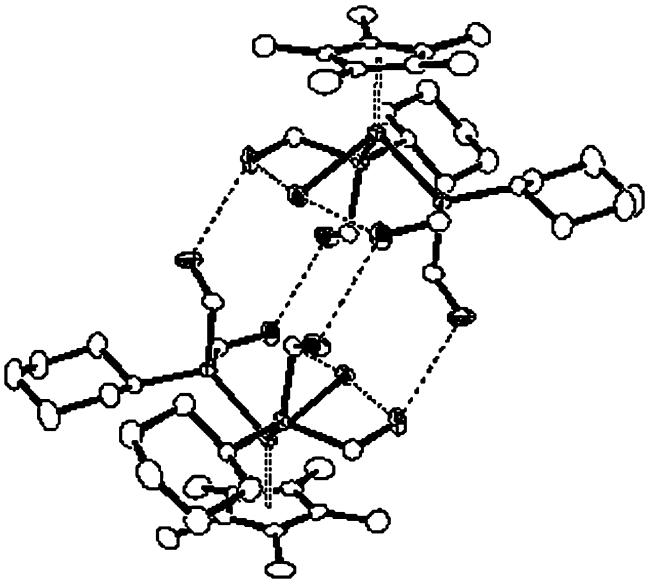


Figure 5. Schematic representation of the bimolecular interaction in Cp*RuCl[$PCy(CH_2OH)_2$]$_2$ (**2b**). The dashed lines indicate the hydrogen bonds.

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Table 2. DMF Synthesis by Ruthenium Catalysts with Hydroxymethylphosphines[a]

run	Ru cat	TON
1	$Ru(H)Cl(CO)[P(C_6H_5)_2CH_2OH]_3$, **1**	4800
2	$RuCl_2[PH(CH_2OH)_2]_2[P(CH_2OH)_3]_2$[b]	9000
3	$Cp^*RuCl[P(C_6H_5)_2CH_2OH]_2$, **2a**	4100
4	$Cp^*RuCl[PCy(CH_2OH)_2]_2$, **2b**	3300
5	$Cp^*RuCl[P(CH_2OH)_3]_2$, **2c**	2100

[a] The reaction was conducted at 100 °C for 15 h, in a 50-mL reaction vessel: Ru catalyst = $4.7-5.3 \times 10^{-3}$ mmol, $[(CH_3)_2NH_2]^+[OCON(CH_3)_2]^-$ = 24 mmol, P_{H_2} = 8.4−8.6 MPa, total initial pressure = 21.6−22.0 MPa. [b] Ru catalyst = 3.1×10^{-3} mmol, $[(CH_3)_2NH_2]^+[OCON(CH_3)_2]^-$ = 15.5 mmol.

of $scCO_2$ (Scheme 1). The reaction with the catalysts **1** and **2** was conducted under the standard conditions (T = 100 °C, P_{total} = 21.0−21.4 MPa, P_{CO_2} = 12.8−13.0 MPa, with amine/catalyst molar ratio of 10 000:1) for comparison with our previous results obtained with $RuCl_2[PH(CH_2OH)_2]_2$-$[P(CH_2OH)_3]_2$.[7,18] The turnover numbers (TON) of the reaction are summarized in Table 2. The catalyst performance of new complexes **1** and **2** proved to be reliable for selective DMF formation analogously to $RuCl_2[PH(CH_2OH)_2]_2[P(CH_2$-$OH)_3]_2$. It should be noted that the reaction using the hydrido(carbonyl) complex **1** resulted in a TON of 4800 after 15 h, even though the presence of CO bound to ruthenium center might suppress the catalysis.[19] The intrinsic effect of hydroxymethylphosphines was also observed for the Cp*Ru complexes. Although limited catalyst activity of cyclopentadienyl−Ru complexes has been reported for the hydrogenation of CO_2,[20] the TON in the DMF formation using $Cp^*RuCl(L)_2$ **2a**−**2c** ranged from 2100 to 4100, increasing in the order of L = $P(CH_2OH)_3$ < $PCy(CH_2OH)_2$ < $P(C_6H_5)_2CH_2OH$.

Conclusions

A range of the novel ruthenium(II) complexes bearing hydroxymethylphosphines, $Ru(H)Cl(CO)[P(C_6H_5)_2CH_2OH]_3$ **1** and $Cp^*RuCl(L)_2$ **2** (L = $P(C_6H_5)_2CH_2OH$, $PCy(CH_2OH)_2$, and $P(CH_2OH)_3$), have been prepared and characterized by NMR spectroscopy and X-ray crystallographic analysis. The elimination of the formaldehyde unit from hydroxymethylphosphines, $P(C_6H_5)_2CH_2OH$ and PCy_2CH_2OH, proceeded during the ligand exchange reaction with dichlororuthenium(II) species, $RuCl_2[P(C_6H_5)_3]_3$ or *trans*-$RuCl_2(DMSO)_4$ to give **1** and *trans*-$RuCl_2(PHCy_2)_4$, respectively. The ^{13}C-labeling experiments revealed that the carbonyl moiety in **1** was originated from formaldehyde released from the hydroxymethylphosphine. On the other hand, degradation of the hydroxymethyl moiety was not observed in the ligand substitution of Cp*RuCl(isoprene) complex. Our current study also demonstrates that the hydroxymethylphosphine complexes, **1** and **2**, serve as useful catalyst precursors for hydrogenative amidation of $scCO_2$ to afford DMF efficiently.

Experimental Section

General Procedures. All reactions and manipulations were carried out under atmosphere of argon by using Schlenk techniques. Solvents were freshly distilled under argon after they were dried over an appropriate drying agent. Special grade liquefied carbon dioxide (99.999% purity) was used as received without purification. Diphenylphosphine was purchased from Tokyo Kasei Co., Ltd., and distilled before use. Other reagents were used as delivered unless otherwise noted. $RuCl_2[P(C_6H_5)_3]_3$,[21] *trans*-$RuCl_2(DMSO)_4$,[22] and $Cp^*RuCl(isoprene)$[23] were prepared according to the literature. NMR spectra were recorded on a JEOL Lambda 300 spectrometer for ^1H (300.5 MHz, referenced to $SiMe_4$ via residual solvent protons), $^{13}C\{^1H\}$ (75.5 MHz, referenced to $SiMe_4$ via the solvent resonance), and $^{31}P\{^1H\}$ (121.7 MHz, referenced to 85% H_3PO_4 as an external standard) NMR. IR spectra were recorded on a Jasco FT/IR-600 spectrometer. Elemental analyses were carried out using a CHNS-932 (LECO) and SX-Elements Micro Analyzer VS-10 (Yanaco).

Synthesis of Hydroxymethylphosphines. ***Caution:*** *For safe handling of the phosphine compounds, well-ventilated laboratory space and good fume hoods are required.* $P(C_6H_5)_2CH_2OH$, PCy_2-CH_2OH, and $PCy(CH_2OH)_2$ were prepared by reactions of the corresponding secondary and primary phosphines with paraformaldehyde or aqueous formaldehyde according to the literature methods.[24] $P(CH_2OH)_3$ was prepared from $P(CH_2OH)_4Cl$ following the method reported in the literature.[4d]

$P(C_6H_5)_2{}^{13}CH_2OH$. Hydroxymethyldiphenylphosphine labeled with ^{13}C on the hydroxymethyl carbon was prepared from the reaction of formaldehyde-^{13}C. $PH(C_6H_5)_2$ (0.562 g, 3.02 mmol) was added to an aqueous solution of formaldehyde-^{13}C (20% in H_2O, 99 atom % ^{13}C; 2.99 g, 3.85 mmol), and the mixture was stirred at 110 °C for 10 min. The reaction mixture was allowed to cool to room temperature and was evaporated under reduced pressure to give a colorless liquid as an analytically pure compound, quantitatively (0.654 g, 3.01 mmol). The $^{13}C\{^1H\}$ NMR spectrum was

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identical to that of the unlabeled $P(C_6H_5)_2CH_2OH$, except that the peak at 63.0 ppm was greatly increased in intensity, consistent with ^{13}C labeling of the hydroxymethyl carbon. The doublet signal at −10.2 ppm ($^1J_{CP}$ = 14.7 Hz) in ^{31}P NMR was consistent with the phosphorus atom attached to the labeled carbon. ^1H NMR (CD_2Cl_2): δ 1.64 (brs, O*H*, 1 H), 4.40 (ddd, CH_2, $^2J_{HC}$ = 145.8 Hz, $^2J_{HP}$ = 8.3 Hz, $^3J_{HH}$ = 5.6 Hz, 2 H), 7.32−7.40 (m, C_6H_5, 6 H), 7.44−7.51 (m, C_6H_5, 4 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 63.0 (d, $^1J_{CP}$ = 14.5 Hz), 129.0 (d, J_{CP} = 6.5 Hz), 129.3, 133.5 (dd, J_{CP} = 17.9, J_{CC} = 2.3 Hz), 135.6 (d, J_{CP} = 11.7 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −10.2 (d, $^1J_{CP}$ = 14.7 Hz).

Synthesis of $Ru(H)Cl(CO)[P(C_6H_5)_2CH_2OH]_3$ (1). Method A. A solution of $P(C_6H_5)_2CH_2OH$ (0.796 g, 3.68 mmol) in 2 mL of CH_2Cl_2 was added to a stirred solution of $RuCl_2[P(C_6H_5)_3]_3$ (1.19 g, 1.24 mmol) in 10 mL of CH_2Cl_2. The resulting mixture was stirred at room temperature for 36 h. The product was formed as a white precipitate, which was collected by filtration, washed with ether (5 mL × 3), and dried under vacuum. Yield: 42% (0.427 g, 0.524 mmol). After recrystallization from CH_2Cl_2, colorless crystals formulated as $Ru(H)Cl(CO)[P(C_6H_5)_2CH_2OH]_3 \cdot CH_2Cl_2$ were obtained. **Method B.** $P(C_6H_5)_2CH_2OH$ (2.14 g, 9.91 mmol) was dissolved in CH_2Cl_2 (5 mL) and added slowly to a solution (30 mL) of *trans*-$RuCl_2(DMSO)_4$ (0.487 g, 1.01 mmol) in the same solvent. After the mixture was stirred for 18 h at room temperature, the white precipitate was collected by filtration and washed with ether (5 mL × 3) to give the analytically pure compound **1**. Yield: 56% (0.464 g, 0.570 mmol). mp: 176.3 °C (dec). ^1H NMR (300.5 MHz, CD_2Cl_2): δ −6.65 (dt, Ru*H*, $^2J_{HP}$ = 101.6, 20.6 Hz, 1 H), 1.97 (td, O*H*, $^3J_{HH}$ = 6.9 Hz, $^3J_{HP}$ = 2.7 Hz, 1 H), 3.75 (dd, O*H*, $^3J_{HH}$ = 6.9 Hz, 8.0 Hz, 2 H), 4.28 (dd, CH_2, $^3J_{HH}$ = 6.6 Hz, $^2J_{HP}$ = 4.8 Hz, 2 H), 4.54 (m, CH_2, 2 H), 4.75−4.89 (m, CH_2, 2 H), 7.09−7.44 (m, C_6H_5, 26 H), 7.74−7.85 (m, C_6H_5, 4 H). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): δ 61.2 (d, *C*H_2, $^1J_{CP}$ = 21.4 Hz), 64.6 (vt, *C*H_2, $^1J_{CP}$ + $^3J_{CP}$ = 15.6 Hz), 128.9−136.1 (m, *C*$_6H_5$), 201.7 (dt, $^2J_{CP}$ = 15.3, 7.3 Hz). $^{31}P\{^1H\}$ NMR (121.7 MHz, CD_2Cl_2): δ 15.5 (t, $^2J_{PP}$ = 15.6 Hz), 34.5 (d, $^2J_{PP}$ = 15.6 Hz). IR (cm^{-1}, KBr): ν 3390 (O−H), 3334 (O−H), 2359 (Ru−H), 1940 (C═O). Calcd for $C_{40}H_{40}ClO_4P_3Ru$: C, 59.01; H, 4.95. Found: C, 59.09; H, 4.85.

Reaction of $RuCl_2[P(C_6H_5)_3]_3$ with $P(C_6H_5)_2{}^{13}CH_2OH$. The reaction of $P(C_6H_5)_2{}^{13}CH_2OH$ (0.654 g, 3.01 mmol) with $RuCl_2[P(C_6H_5)_3]_3$ (0.936 g, 0.976 mmol) was performed in a manner similar to that given above for unlabeled $P(C_6H_5)_2CH_2OH$. Yield: 32% (0.259 g, 0.317 mmol). The $^{13}C\{^1H\}$ NMR spectrum of the product was identical to that obtained in the experiment using unlabeled phosphine, except that the signals at 61.2, 64.6, and 201.5 ppm were greatly increased in intensity. The ^{31}P resonances at 15.5 and 34.5 ppm were coupled with the labeled ^{13}C atoms of the carbonyl ligand and hydroxymethyl carbons. ^1H NMR (300.5 MHz, CD_2Cl_2): δ −6.69 (ddt, Ru*H*, $^2J_{HP}$ = 101.1 and 21.8 Hz, $^2J_{HC}$ = 6.59 Hz, 1 H), 1.93 (br, O*H*, 1 H), 3.74 (m, O*H*, 2 H), 4.25 (m, CH_2, $^1J_{HC} \approx$ 149 Hz, 2 H), 4.55 (m, CH_2, $^1J_{HC} \approx$ 148 Hz, 2 H), 4.76 (m, CH_2, $^1J_{HC} \approx$ 148 Hz, 2 H), 7.06−7.39 (m, C_6H_5, 26 H), 7.64−7.80 (m, C_6H_5, 4 H). $^{31}P\{^1H\}$ NMR (121.7 MHz, CD_2Cl_2): δ 15.5 (tdd, $^2J_{PP}$ = 15.6, $^1J_{CP}$ = 21.4 Hz, $^2J_{CP}$ = 7.6 Hz), 34.5 (ddd, $^2J_{PP}$ = 15.6, $^1J_{CP}$ = 15.6 Hz, $^2J_{CP}$ = 15.3 Hz).

Formation of $RuCl_2[P(C_6H_5)_2CH_2OH]_3$ by the Ligand Exchange of $RuCl_2(dmso)_4$ with $P(C_6H_5)_2(CH_2OH)$. A solution of $P(C_6H_5)_2CH_2OH$ (2.10 g, 9.71 mmol) in 5 mL of CH_2Cl_2 was added to a stirred solution of *trans*-$RuCl_2(DMSO)_4$ (0.484 g, 1.00 mmol) in 25 mL of CH_2Cl_2. After the mixture was stirred at 0 °C for 10 min, the solvent was removed under a reduced pressure. The residue was dissolved in CD_2Cl_2 and transferred to a NMR tube under Ar. In the $^{31}P\{^1H\}$ NMR spectrum, the singlet signals for $RuCl_2[P(C_6H_5)_2CH_2OH]_3$ and free $P(C_6H_5)_2CH_2OH$ were observed at 14.1 and −10.4 ppm, respectively. Repeated recrystallization of the products from THF−ether at −20 °C yielded an orange solid formulated as $RuCl_2[P(C_6H_5)_2CH_2OH]_3 \cdot 2(C_4H_8O)$. Yield: 3% (0.027 g, 0.028 mmol). ^1H NMR (300.5 MHz, CD_2Cl_2): δ 2.46 (br, O*H*, 3 H), 4.95 (m, CH_2, 6 H), 7.0−7.8 (m, C_6H_5, 15 H). $^{31}P\{^1H\}$ NMR (121.7 MHz, CD_2Cl_2): δ 14.1 (s). Anal. Calcd for $C_{47}H_{55}Cl_2O_5P_3Ru$: C, 58.51; H, 5.75. Found: C, 59.06; H, 5.69.

Formation of $RuCl_2(PHCy_2)_4$ from $PCy_2(CH_2OH)$ and $RuCl_2(PPh_3)_3$. $PCy_2(CH_2OH)$ (1.97 g, 7.58 mmol) was dissolved in ethanol (10 mL) and slowly added to $RuCl_2[P(C_6H_5)_3]_3$ (1.82 g, 1.90 mmol) in ethanol (25 mL). After the mixture was stirred for 30 min at room temperature, the resultant precipitate was filtered off, washed with ether (10 mL × 3), and dried in vacuo to yield a bright yellow powder of $RuCl_2(PHCy_2)_4$. Yield: 79% (1.45 g, 1.50 mmol). ^1H NMR (300.5 MHz, $CDCl_3$): δ 1.18−1.82 (m, C_6H_{11}, 44 H), 2.35 (d, P*H*Cy_2, $^1J_{HP}$ = 143.1 Hz, 4 H). $^{31}P\{^1H\}$ NMR (121.7 MHz, $CDCl_3$): δ 12.8 (s). Anal. Calcd for $C_{48}H_{92}Cl_2P_4Ru$: C, 59.74; H, 9.61. Found: C, 59.46; H, 9.52. The analytical data is also in good agreement with that found in the literature.[25]

Synthesis of $Cp^*RuCl[P(C_6H_5)_2CH_2OH]_2$ (2a). $P(C_6H_5)_2CH_2OH$ (0.435 g, 2.01 mmol) was dissolved in THF (2 mL), and the mixture was added slowly to a THF solution (10 mL) of Cp*RuCl(isoprene) (0.345 g, 1.02 mmol). After the mixture was stirred for 36 h at room temperature, the solvent was removed under vacuum. The obtained residue was washed with *n*-hexane (5 mL) and ether (5 mL) to give the analytically pure compound **2a**. Yield: 88% (0.629 g, 0.893 mmol). Orange crystals suitable for X-ray crystallographic analysis were obtained as solvates, $Cp^*RuCl[P(C_6H_5)_2CH_2OH]_2 \cdot CH_2Cl_2$, by slow diffusion of hexane into their solutions of in CH_2Cl_2. mp: 189.6 °C (dec). ^1H NMR (300.5 MHz, CD_2Cl_2): δ 1.21 (t, CH_3, $^4J_{HP}$ = 1.5 Hz, 15 H), 3.01 (br, O*H*, 2 H), 4.04 (m, CH_2, 4 H), 7.18−7.46 (m, C_6H_5, 20 H). $^{13}C\{^1H\}$ NMR (75.6 MHz, CD_2Cl_2): δ 9.50 (s, *C*H_3), 64.6 (s, *C*H_2), 89.7 (t, *C*$_5(CH_3)_5$, $^2J_{CP}$ = 1.9 Hz), 127.9 (m, *C*$_6H_5$), 128.6 (m, *C*$_6H_5$), 129.6 (s, *C*$_6H_5$), 129.9 (s, *C*$_6H_5$), 132.7 (m, *C*$_6H_5$), 134.1 (m, *C*$_6H_5$), 136.0 (m, *C*$_6H_5$), 137.1 (m, *C*$_6H_5$). $^{31}P\{^1H\}$ NMR (121.7 MHz, CD_2Cl_2): δ 33.7 (s). Anal. Calcd for $C_{36}H_{41}ClO_2P_2Ru$: C, 61.40; H, 5.87; Cl, 5.03. Found: C, 60.99; H, 5.93; Cl, 5.12.

Synthesis of $Cp^*RuCl[PCy(CH_2OH)_2]_2$ (2b). PCy_2CH_2OH (0.353 g, 2.00 mmol) was dissolved in CH_2Cl_2 (2 mL), and it was added slowly to a solution (10 mL) of Cp*RuCl(isoprene) (0.333 g, 0.98 mmol) in the same solvent. After the mixture was stirred for 14 h at room temperature, the solvent was removed under vacuum. The residue was washed with ether (10 mL × 3) to give the analytically pure compound **2b**. Yield: 80% (0.490 g, 0.785 mmol). After recrystallization from CH_2Cl_2/hexane, red crystals were obtained. mp: 145.9 °C (dec). ^1H NMR (300.5 MHz, CD_2Cl_2): δ 1.13−2.07 (m, C_6H_{11}, 22 H), 1.61 (t, CH_3, $^4J_{HP}$ = 1.4 Hz, 15 H), 3.36 (br, O*H*, 2 H), 3.47 (br, O*H*, 2 H), 4.05−4.49 (m, CH_2, 8 H). $^{13}C\{^1H\}$ NMR (75.6 MHz, CD_2Cl_2): δ 10.2 (s, *C*H_3), 26.3 (s, *C*$_6H_{11}$), 27.8 (m, *C*$_6H_{11}$), 29.3 (s, *C*$_6H_{11}$), 40.0 (vt, *C*HOH, $^1J_{CP}$ + $^3J_{CP}$ = 9.9 Hz), 60.4 (m, *C*H_2), 88.2 (t, *C*$_5(CH_3)_5$, $^2J_{CP}$ = 1.9 Hz). $^{31}P\{^1H\}$ NMR (121.7 MHz, CD_2Cl_2): δ 34.3 (s). Anal. Calcd for $C_{26}H_{49}ClO_4P_2Ru$: C, 50.03; H, 7.91; Cl, 5.68. Found: C, 50.07; H, 7.30; Cl, 5.90.

Synthesis of $Cp^*RuCl[P(CH_2OH)_3]_2$ (2c). A THF (15 mL) solution of Cp*RuCl(isoprene) (0.643 g, 1.89 mmol) was added to $P(CH_2OH)_3$ (0.473 g, 3.81 mmol) in THF (15 mL) and stirred at room temperature for 34 h. The solvent was removed under vacuum,

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and the obtained residue was washed with cold acetone (3 mL) and ether (10 mL) to give the analytically pure compound **2c**. Yield: 60% (0.586 g, 1.13 mmol). mp: 161.8 °C (dec).^{1}H NMR (300.5 MHz, CD_2Cl_2): δ 1.69 (t, CH_3, $^4J_{HP}$ = 1.5 Hz, 15 H), 3.84 (br, CH_2, 6 H), 4.24 (dd, J_{HP} = 14.4 and 15.7 Hz, 12 H). ^{13}C{^{1}H} NMR (75.6 MHz, acetone-d_6): δ 11.0 (s, CH_3), 59.1 (vt, CH_2OH, $^1J_{CP} + {}^3J_{CP}$ = 13.4 Hz), 89.9 (t, C_5(CH$_3$)$_5$, $^2J_{CP}$ = 2.1 Hz). ^{31}P{^{1}H} NMR (121.7 MHz, acetone-d_6): δ 36.0 (s). Anal. Calcd for $C_{16}H_{33}ClO_6P_2Ru$: C, 36.96; H, 6.40; Cl, 6.82. Found: C, 36.76; H, 6.26; Cl, 7.02.

X-ray Structure Determinations of 1, 2a, and 2b. All measurements were made on a Rigaku Saturn CCD area detector equipped with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) under a nitrogen stream at 193 K. Indexing was performed from seven images that were exposed for 3 s. The crystal-to-detector distance was 45.05 mm. The data were collected to a maximum 2θ value of 54.9°. A total of 720 oscillation images were collected. A sweep of data was carried out using ω scans from −110.0 to 70.0° in 0.5° steps, at χ = 45.0° and ϕ = 0.0°. A second sweep was performed using ω scans from −110.0 to 70.0° in 0.5° steps, at χ = 45.0° and ϕ = 90.0°. The exposure rate was 3.0 s/deg, and the detector swing angle was −19.86°. Intensity data were collected for Lorentz-polarization effects as well as absorption. Structure solution and refinements were performed with the CrystalStructure program package. The heavy atom positions were determined by a direct program method (SIR92), and the remaining non-hydrogen atoms were found by subsequent Fourier techniques (DIRDIF99). An empirical absorption correction based on equivalent reflections was applied to all data. All non-hydrogen atoms were refined anisotropically by full-matrix least-square techniques based on F^2. The low-temperature data collection enabled hydrogens attached to the oxygens and ruthenium center in **1** to be located from the Fourier difference map and refined isotropically. All other hydrogens either were not refined or were constrained to ride on their parent atom. Relevant crystallographic data are compiled in Table 3.

Catalytic Hydrogenative Amidation of CO_2. ***Caution:*** *Operators of high-pressure equipment should take proper precautions to minimize the risk of personal injury.* A stainless steel reactor was charged with argon gas and was placed in the oven at 100 °C before the introduction of reagents. A mixture of $[(CH_3)_2NH_2]^+[OCON(CH_3)_2]^-$ (24.0 mmol) and ruthenium catalyst ($4.7-5.3 \times 10^{-3}$ mmol) was transferred into the reactor with a syringe through an opening against the flow of CO_2. Subsequently, the reactor was charged with CO_2 to the pressure of 12.6−12.8 MPa through a valve with a syringe pump (ISCO model 260D), and the mixture was stirred for 30 min. After the mixture reached a steady state, H_2 gas was introduced with the syringe pump up to the total pressure of 21.0−21.4 MPa. After the mixture was stirred for 15 h, the reactor was cooled in a bath of methanol with dry ice. The gaseous matter was vented, and the reactor was slowly warmed to the room temperature. The yields of DMF were determined by ^{1}H NMR analyses using durene as an internal standard.

Table 3. Crystallographic Data for **1**, **2a**, and **2b**

	1·CH_2Cl_2	**2a**·CH_2Cl_2	**2b**
formula	$C_{41}H_{42}Cl_3O_4P_3Ru$	$C_{37}H_{43}Cl_3O_2P_2Ru$	$C_{26}H_{49}ClO_4P_2Ru$
fw	899.13	789.12	624.14
color	colorless	orange	orange
temp (K)	173	193	193
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	12.699(4)	11.901(6)	20.689(9)
b (Å)	20.240(6)	17.515(9)	13.894(6)
c (Å)	15.276(5)	17.487(8)	20.617(10)
β (deg)	96.060(3)	94.339(7)	102.489(6)
V (Å^3)	3904.6(20)	3634.6(30)	5786.3(45)
Z	4	4	8
D_{calcd} (g cm^{-3})	1.529	1.442	1.433
F_{000}	1840	1624	2624
μ(Mo Kα) (cm^{-1})	7.71	7.71	7.74
measured reflns	30 257	29 079	46 131
unique reflns	29 803 [R_{int} = 0.031]	28 562 [R_{int} = 0.071]	45 061 [R_{int} = 0.053]
variable params	523	449	711
$R1^a$ [$I > 2\sigma(I)$]	0.039	0.076	0.049
wR2^b (all data)	0.108	0.219	0.149
GOF on F^2	0.991	1.003	0.885

^{a} $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. ^{b} $wR2 = [\sum w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$.

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Supporting Information Available: Crystallographic data for **1**, **2a**, and **2b** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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