Novel Ruthenium-Complex-Catalyzed Synthesis of Ureas from Formamides and Amines

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Various N,N′-disubstituted and trisubstituted ureas were obtained in high yields by the ruthenium-complex-catalyzed dehydrogenation of N-substituted formamides and amines under reflux in mesitylene for 12 h under an argon atmosphere. From formanilide (**1a**) and aniline (**2a**), *N,N′*-diphenylurea (**3a**) was obtained in 92% yield. During this reaction, a stoichiometric amount of gaseous hydrogen was spontaneously evolved; thus, the addition of a hydrogen acceptor was not required. Formamide itself, *i.e.*, $HCONH_2$ (**4**), can also be used as a versatile carbonyl source. From $HCONH_2$ (**4**) and primary amines, the corresponding N,N′-disubstituted ureas were obtained in high yields together with the evolution of hydrogen and ammonia. To identify a catalytically active species, the stoichiometric reaction of $RuCl_2(PPh_3)_3$ with formanilide (**1a**) was carried out in CH_2Cl_2 at room temperature to give a novel oxygen-atom-bridged dinuclear ruthenium complex, $Ru_2(\mu\text{-}Cl)_2Cl_2(\mu\text{-}PhNHCHO\text{-}O,O)(PPh_3)_4$ (**5**), in 87% yield. Complex **5** showed a high catalytic activity for the synthesis of *N,N′*-diphenylurea from formanilide (**1a**) and aniline (**2a**), and the stoichiometric reaction of **5** with aniline gave *N,N′*-diphenylurea, which strongly suggests that complex **5** is the key intermediate in the $RuCl_2(PPh_3)_3$-catalyzed synthesis of ureas using formamides as a versatile carbonyl source.

Introduction

Since Wöhler first synthesized urea from ammonia and a salt of isocyanic acid in 1828,[1] the use of various ureas in organic synthesis has been studied extensively.[2] Since both linear and cyclic ureas are found in many biologically important compounds,[3] several pesticides, herbicides, and medicines which have a urea structure have been synthesized. Interest in urea and its derivatives has recently increased because they are also important in the chemical industry as precursors of pigments[4] and resins.[5] Recently, a method for converting ureas to the corresponding carbamates using a palladium catalyst was established,[6] and ureas are now as chemically important as carbamates[7] and isocyanates.[8]

The traditional methods for preparing ureas involve the reaction of amines with either phosgene or the appropriate isocyanate. Although the yields are generally high, there are concerns regarding toxicity and reagent availability. Recently, alternative methods for synthesizing urea derivatives without phosgene have been developed. In particular, the synthesis of ureas by transition-metal-complex-catalyzed N-carbonylations of nitro compounds[9] and amines[10] has been widely studied. However, there still remains a problem with toxicity, and these reactions often require high carbon monoxide pressure.[11]

On the other hand, formyl compounds such as formic acid, alkyl formates, and formamides offer a promising C═O unit. However, the high stability of formyl compounds and the lack of reliable activation methods considerably limit their effective use. In our study on ruthenium catalysis,[12] we found that low-valence ru-

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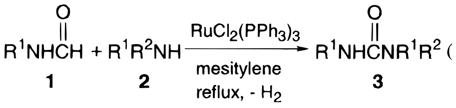
thenium complexes showed high catalytic activities for the hydroacylation,[13] hydroesterification,[14] and hydroamidation[15] of olefins via formyl C−H bond activation.

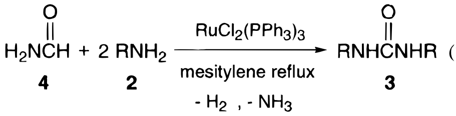
In this paper, we describe in detail an extremely simple, efficient, and highly selective ruthenium-complex-catalyzed *non phosgene* and *non carbon monoxide* route to N,N′-disubstituted and trisubstituted ureas (**3**) from N-substituted formamides (**1**) and amines (**2**) (eq 1).[16]



$$\underset{\mathbf{1}}{\mathrm{R^1NH\overset{\overset{O}{\|}}{C}H}} + \underset{\mathbf{2}}{\mathrm{R^1R^2NH}} \xrightarrow[\text{mesitylene reflux, - }\mathrm{H_2}]{\mathrm{RuCl_2(PPh_3)_3}} \underset{\mathbf{3}}{\mathrm{R^1NH\overset{\overset{O}{\|}}{C}NR^1R^2}} \quad (1)$$

Since this reaction proceeds under an argon atmosphere with spontaneous hydrogen evolution, no hydrogen acceptor is required.

The results of the ruthenium-complex-catalyzed reaction of readily available $\mathrm{HCONH_2}$ (**4**) with various amines (**2**) are also provided. Using this method, N,N′-symmetrically substituted ureas were obtained in high yields with the simultaneous evolution of hydrogen and ammonia (eq 2).



$$\underset{\mathbf{4}}{\mathrm{H_2N\overset{\overset{O}{\|}}{C}H}} + 2\ \underset{\mathbf{2}}{\mathrm{RNH_2}} \xrightarrow[\text{mesitylene reflux, - }\mathrm{H_2}\text{, - }\mathrm{NH_3}]{\mathrm{RuCl_2(PPh_3)_3}} \underset{\mathbf{3}}{\mathrm{RNH\overset{\overset{O}{\|}}{C}NHR}} \quad (2)$$

To investigate the mechanism for the activation of the formyl C−H bond, the stoichiometric reaction of $\mathrm{RuCl_2(PPh_3)_3}$ with formanilide (**1a**) was carried out to give a novel oxygen-bridged dinuclear ruthenium complex, $\mathrm{Ru_2(\mu\text{-}Cl)_2Cl_2(\mu\text{-}PhNHCHO\text{-}}O,O\mathrm{)(PPh_3)_4}$ (**5**), in high yield. Carboxylic acid amides are "hard" ligands, and most research has focused on their complexes with main-group, first-transition-series, and lanthanide elements,[17] since these metals are highly oxophilic. The oxygen-atom-coordinated complexes are more stable than the nitrogen-atom-coordinated complexes.[18] Since the late transition metals, especially platinum metals, are not particularly good receptors for O-donors,[17a] relatively few group 8−10 metal complexes with amide ligands have been isolated.[19−21]

To our knowledge, complex **5**, in which the oxygen atom bridges equally to the two ruthenium metals, is the first example of a group 8−10 metal dinuclear complex containing a carboxylic acid amide ligand. Considering the solution NMR and the X-ray crystal structure of **5**, we propose the most plausible mechanism of the present urea synthesis, including the activation of formamides.

Table 1. Catalytic Activities of Several Transition-Metal Complexes in *N,N*′-Diphenylurea (3a) Synthesis from Formanilide (1a) and Aniline (2a)[a]

catalyst	yield of **3a**/%[b]	catalyst	yield of **3a**/%[b]
$\mathrm{RuCl_2(PPh_3)_3}$	92 (90)	Ru(cod)(cot) + $\mathrm{PPh_3}$[f]	26
$\mathrm{RuHCl(PPh_3)_3}$	18	$\mathrm{PdCl_2(PPh_3)_2}$	trace
$\mathrm{RuH_2(PPh_3)_4}$	34	$\mathrm{RhCl(PPh_3)_3}$	0
$\mathrm{Ru_3(CO)_{12}}$[c]	0	$\mathrm{CoCl_2(PPh_3)_2}$	0
$\mathrm{Ru_3(CO)_{12}}$ + $\mathrm{PPh_3}$[d]	26	$\mathrm{CoCl(PPh_3)_3}$	0
$\mathrm{RuCl_3 \cdot }n\mathrm{H_2O}$	4	*cis*-$\mathrm{PtCl_2(PPh_3)_2}$	0
$\mathrm{RuCl_3 \cdot }n\mathrm{H_2O}$ + $\mathrm{PPh_3}$[e]	30		

[a] A mixture of formanilide (**1a**; 4.0 mmol), aniline (**2a**; 4.0 mmol), catalyst (0.20 mmol), and mesitylene (5.0 mL) was treated under reflux for 12 h. [b] Determined by HPLC. The value in parentheses gives an isolated yield. [c] $\mathrm{Ru_3(CO)_{12}}$ (0.07 mmol). [d] $\mathrm{Ru_3(CO)_{12}}$ (0.07 mmol) and $\mathrm{PPh_3}$ (0.60 mmol). [e] $\mathrm{RuCl_3 \cdot }n\mathrm{H_2O}$ (0.20 mmol) and $\mathrm{PPh_3}$ (0.60 mmol). [f] Ru(η^4-cyclooctadiene)(η^6-cyclooctatriene) (0.20 mmol) and $\mathrm{PPh_3}$ (0.60 mmol).

Results and Discussion

Synthesis of Ureas from N-Substituted Formamides and Amines. In the presence of a catalytic amount of $\mathrm{RuCl_2(PPh_3)_3}$, *N,N*′-diphenylurea (**3a**) was obtained in 92% yield by the dehydrogenation of formanilide (**1a**) with aniline (**2a**) under reflux in mesitylene for 12 h (Table 1). During this reaction, spontaneous hydrogen evolution was observed. After the reaction, the amount of hydrogen was 90%, based on the amount of formanilide (**1a**) used. Among the catalysts used, $\mathrm{RuCl_2(PPh_3)_3}$ showed the highest catalytic activity. The catalytic activities of other divalent ruthenium complexes containing a triphenylphosphine ligand, such as $\mathrm{RuHCl(PPh_3)_3}$ and $\mathrm{RuH_2(PPh_3)_4}$, were much lower than that of $\mathrm{RuCl_2(PPh_3)_3}$. Although $\mathrm{Ru_3(CO)_{12}}$, $\mathrm{RuCl_3 \cdot }n\mathrm{H_2O}$, and Ru(cod)(cot) (cod = cycloocta-1,5-diene, cot=cycloocta-1,3,5-triene) combined with triphenylphosphine showed some catalytic activity, they had almost no catalytic activity in the absence of the triphenylphosphine ligand. Furthermore, other group 8−10 transition-metal complexes, such as $\mathrm{PdCl_2(PPh_3)_2}$, $\mathrm{RhCl(PPh_3)_3}$, $\mathrm{CoCl_2(PPh_3)_2}$, $\mathrm{CoCl(PPh_3)_3}$, and *cis*-$\mathrm{PtCl_2(PPh_3)_2}$, did not catalyze the reaction at all.

The results of the $\mathrm{RuCl_2(PPh_3)_3}$-catalyzed reaction of formanilide (**1a**) with aniline (**2a**) under reflux in

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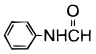
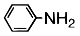
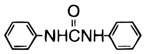
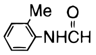
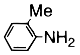
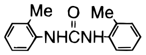
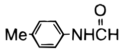
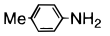
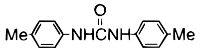
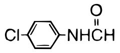
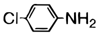
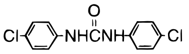
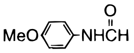
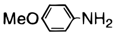
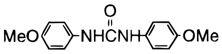
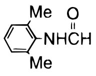
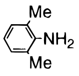
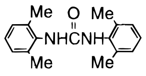
Table 2. Effect of Solvents on $RuCl_2(PPh_3)_3$-Catalyzed *N,N′*-Diphenylurea (3a) Synthesis from Formanilide (1a) and Aniline (2a)[a]

solvent	bp_{760}/°C	yield of **3a**/%[b]
mesitylene	164.7	91
decane	174.1	80
diglyme	162	42
DMSO[c]	189	0
o-xylene	144	33
m-xylene	139.3	14
toluene	110.6	trace
1,4-dioxane	101.1	0

[a] A mixture of formanilide (**1a**; 2.0 mmol), aniline (**2a**; 2.0 mmol), $RuCl_2(PPh_3)_3$ (0.10 mmol), and solvent (5.0 mL) was treated under reflux for 6 h. [b] Determined by HPLC. [c] Dimethyl sulfoxide.

Table 3. Synthesis of Ureas from N-Aryl-Substituted Formamides and Aminoarenes[a]

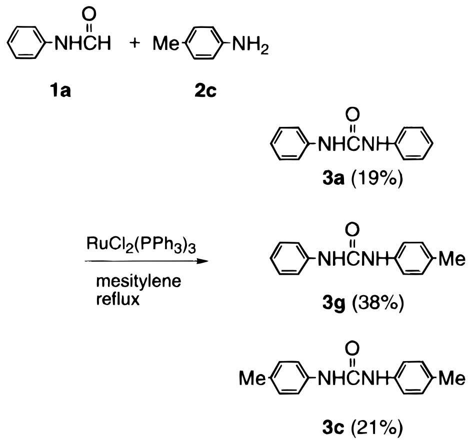
formamide	aminoarene	product	yield/%[b]
 **1a**	 **2a**	 **3a**	90 (92)
 **1b**	 **2b**	 **3b**	93
 **1c**	 **2c**	 **3c**	76
 **1d**	 **2d**	 **3d**	78
 **1e**	 **2e**	 **3e**	85
 **1f**	 **2f**	 **3f**	88

[a] A mixture of N-aryl-substituted formamide (**1**; 4.0 mmol), aminoarene (**2**; 4.0 mmol), $RuCl_2(PPh_3)_3$ (0.20 mmol), and mesitylene (5.0 mL) was treated under reflux for 12 h. [b] Isolated yields. The value in parentheses gives an HPLC yield.

various solvents are summarized in Table 2. *N,N′*-Diphenylurea (**3a**) was obtained in the best yield (92%) in mesitylene. Although this urea (**3a**) was also obtained in high yield in decane (80%), diglyme and dimethyl sulfoxide (DMSO) were not suitable solvents for the present reaction, probably due to their high coordination ability. Reactions were also carried out under reflux in other aromatic hydrocarbon solvents. The yield of **3a** decreased as their boiling points decreased (*o*-xylene to toluene). Therefore, mesitylene was used as the most suitable solvent for the following synthesis of various ureas.

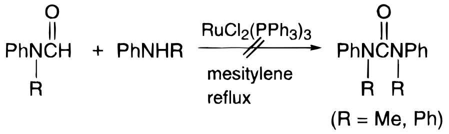
As shown in Table 3, symmetric *N,N′*-diarylureas bearing various substituents on phenyl rings were easily prepared in high yields by the $RuCl_2(PPh_3)_3$-catalyzed reaction of N-aryl-substituted formamides with aminoarenes. In addition to alkyl and alkoxy substituents, a chloro substituent was tolerated, and *N,N′*-bis(4-chlorophenyl)urea (**3d**) was obtained in 78% yield. Even sterically hindered *N,N′*-bis(2,6-dimethylphenyl)urea (**3f**) was obtained in high yield (88%).

Scheme 1



On the other hand, unsymmetrically substituted *N*-phenyl-*N′*-*p*-tolylurea (**3g**) was not obtained selectively from the reaction of formanilide (**1a**) with *p*-toluidine (**2c**) under the same reaction conditions, and this reaction gave a mixture of *N,N′*-diphenylurea (**3a**; 19%), *N*-phenyl-*N′*-*p*-tolylurea (**3g**; 38%), and *N,N′*-di-*p*-tolylurea (**3c**; 21%) (Scheme 1). Heck and co-workers reported that *N*-phenyl-*N′*-*p*-tolylurea (**3g**) did not react with *p*-toluidine (**2c**) at 90 °C.[9c] On the other hand, the thermal dissociation of ureas to the corresponding isocyanates and amines is well-known.[22] In our control experiment, treatment of *N*-phenyl-*N′*-*p*-tolylurea (**3g**) under mesitylene reflux in the absence of $RuCl_2(PPh_3)_3$ also gave the same 1:2:1 mixture of *N,N′*-diphenylurea (**3a**), *N*-phenyl-*N′*-*p*-tolylurea (**3g**), and *N,N′*-di-*p*-tolylurea (**3c**). This suggests that the initially generated *N*-phenyl-*N′*-*p*-tolylurea (**3g**) underwent thermal disproportionation under the present reaction conditions to give *N,N′*-diphenylurea (**3a**) and *N,N′*-di-*p*-tolylurea (**3c**).

Reactions of N,N-disubstituted formamides, such as *N*-methylformanilide and *N,N*-diphenylformamide, with N,N-disubstituted amines were attempted under the same reaction conditions. However, these reactions did not proceed at all, and the corresponding N,N,N′,N′-tetrasubstituted ureas were not obtained (eq 3).



$$\mathrm{Ph}\underset{\mathrm{R}}{\mathrm{N}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H} + \mathrm{PhNHR} \;\not\xrightarrow[\text{mesitylene reflux}]{\mathrm{RuCl_2(PPh_3)_3}}\; \mathrm{Ph}\underset{\mathrm{R}}{\mathrm{N}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\underset{\mathrm{R}}{\mathrm{N}}\mathrm{Ph} \quad (\mathrm{R} = \mathrm{Me, Ph}) \tag{3}$$

The synthesis of *N,N′*-diphenyl-*N*-methylurea (**3h**) from *N*-methylformanilide (**1g**) and aniline (**2a**) also failed (method A in Scheme 2). However, *N,N′*-diphenyl-*N*-methylurea (**3h**) was obtained in 59% yield, along with *N,N′*-diphenylurea (**3a**) (yield 16%), by reacting formanilide (**1a**) with *N*-methylaniline (**2g**) (method B in Scheme 2). In this reaction, *N,N′*-diphenylurea (**3a**) would be formed by the reaction of formanilide (**1a**) with aniline (**2a**) which was generated by the decarbonylation of formanilide (**1a**).

Similarly, the unsymmetrically N-alkyl-N′-aryl-substituted urea *N*-*tert*-octyl-*N′*-phenylurea (**3i**) was obtained in 31% yield from the reaction of formanilide (**1a**)

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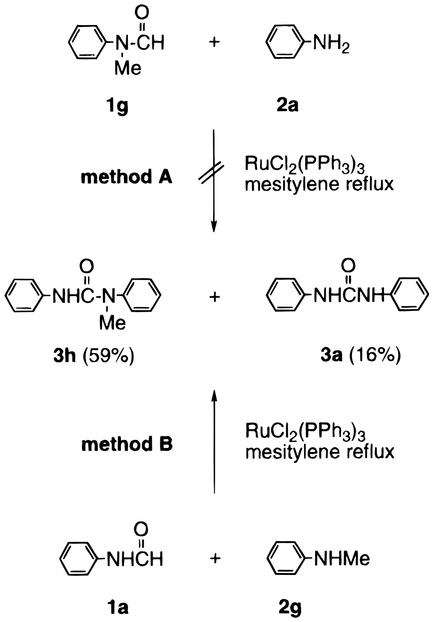
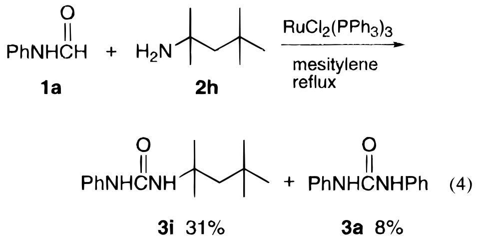
(22) (a) Davis, T. L.; Blanchard, K. C. *J. Am. Chem. Soc.* **1923**, *45*, 1816. (b) Hoshino, T.; Mukaiyama, T.; Hoshino, H. *J. Am. Chem. Soc.* **1952**, *74*, 3097.

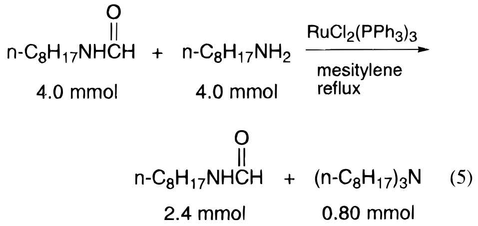
Scheme 2



with 1,1,3,3-tetramethylbutylamine (*tert*-octylamine; **2h**), which lacks an α-hydrogen (eq 4).

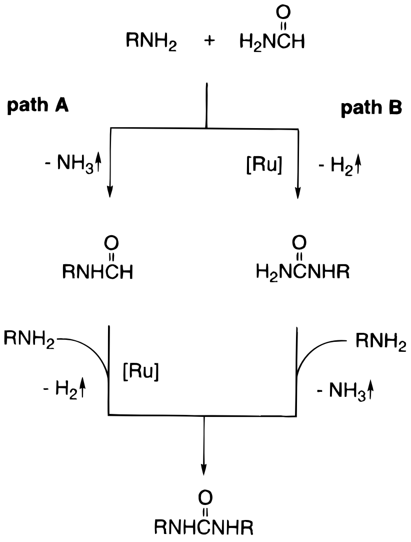


Finally, the synthesis of *N*,*N*′-dialkylureas was attempted by reacting *N*-octylformamide with octylamine (eq 5). However, the corresponding *N*,*N*′-dialkylurea was not obtained, and 60% of the starting *N*-octylformamide was recovered intact together with the generation of trioctylamine. It has been previously reported that several ruthenium complexes catalyze the alkyl group transfer reaction between aliphatic tertiary amines via an iminium ion or metallaazacyclopropane intermediate which is generated by the abstraction of an α-hydrogen of the aliphatic amines by an active metal center.[23] Thus, the trioctylamine obtained in this reaction would be formed by the ruthenium-complex-catalyzed decarbonylation of *N*-octylformamide to octylamine and a subsequent alkyl group transfer reaction.

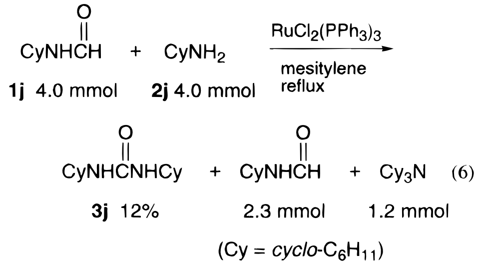


$$\underset{4.0\ \text{mmol}}{\text{n-C}_8\text{H}_{17}\text{NH}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{H}} + \underset{4.0\ \text{mmol}}{\text{n-C}_8\text{H}_{17}\text{NH}_2} \xrightarrow[\text{mesitylene reflux}]{\text{RuCl}_2(\text{PPh}_3)_3} \underset{2.4\ \text{mmol}}{\text{n-C}_8\text{H}_{17}\text{NH}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{H}} + \underset{0.80\ \text{mmol}}{(\text{n-C}_8\text{H}_{17})_3\text{N}} \quad (5)$$

Scheme 3



The reaction using *N*-cyclohexylformamide (**1j**) gave *N*,*N*′-dicyclohexylurea (**3j**) in 12% yield, while 57% of **1j** was recovered (eq 6). Consequently, the present catalyst system was less effective with N-alkyl-substituted formamides than with N-aryl-substituted ones.



$$\underset{\mathbf{1j}\ 4.0\ \text{mmol}}{\text{CyNH}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{H}} + \underset{\mathbf{2j}\ 4.0\ \text{mmol}}{\text{CyNH}_2} \xrightarrow[\text{mesitylene reflux}]{\text{RuCl}_2(\text{PPh}_3)_3} \underset{\mathbf{3j}\ 12\%}{\text{CyNH}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{NHCy}} + \underset{2.3\ \text{mmol}}{\text{CyNH}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{H}} + \underset{1.2\ \text{mmol}}{\text{Cy}_3\text{N}} \quad (6)$$

(Cy = *cyclo*-C_6H_{11})

Synthesis of N,N′-Disubstituted Ureas using $HCONH_2$ as a Versatile Carbonyl Source. We also examined the reaction of $HCONH_2$ (**4**) with amines (eq 2). When $HCONH_2$ (**4**) was treated with aniline (**2a**) in the presence of $RuCl_2(PPh_3)_3$ catalyst, the reaction proceeded smoothly with a simultaneous evolution of hydrogen and ammonia[24] to give *N*,*N*′-diphenylurea (**3a**) in 77% yield with high selectivity. Phenylurea was not obtained at all. It is well-known that alkyl group exchange readily occurs between carboxylic acid amides and aliphatic amines on heating, while the reaction barely proceeds with aminoarenes in the absence of a catalyst.[25] Our control reaction, in which we treated $HCONH_2$ (**4**; 6.0 mmol) with aniline (**2a**; 8.0 mmol) under reflux in mesitylene for 12 h in the absence of ruthenium catalyst, gave formanilide (**1a**) in only 24% yield. Therefore, *N*,*N*′-diphenylurea (**3a**) should be obtained by the two ruthenium-catalyzed pathways illustrated in Scheme 3. In path A, a ruthenium-catalyzed amide exchange reaction with amine occurs first to give the corresponding N-substituted formamide with the evolution of ammonia. Subsequently, the generated amide reacts with another molecule of amine due to ruthenium catalysis to give N,N′-disubstituted urea with the evolution of hydrogen. In path B, N-monosubstituted urea is primarily formed by the ru-

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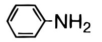
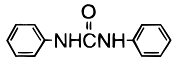
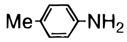
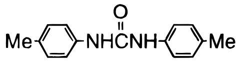
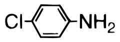
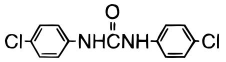
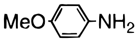
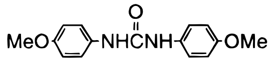
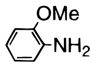
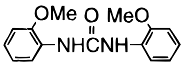
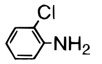
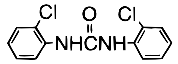
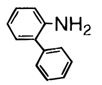
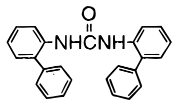
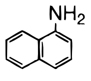
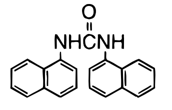
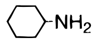
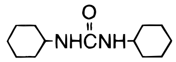
[23] (a) Benett, M. A.; Matheson, T. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K., 1982; Vol. 4, p 960. (b) Wilson, R. B.; Laine, R. M. *J. Am. Chem. Soc.* **1985**, *107*, 361.

[24] In the reaction of formamide (**4**) with aniline (**2a**) (Table 4), the evolved ammonia was collected by dissolving it in aqueous sulfuric acid, and the amount was measured by titration. The amount of evolved ammonia was 74% based on formamide (**4**).

[25] (a) Kraus, M. A. *Synthesis* **1973**, 361. (b) Pettit, G. R.; Thomas, E. G. *J. Org. Chem.* **1959**, *24*, 895.

Table 4. Synthesis of Ureas from $HCONH_2$ (4) and Amines[a]

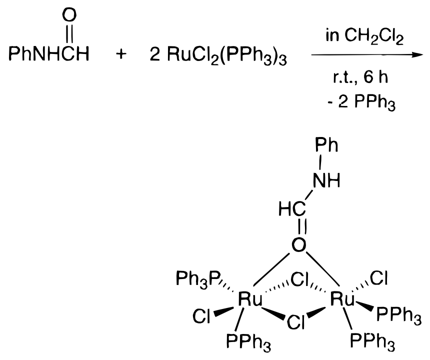
aminoarene	product	yield/%[b]
 **2a**	 **3a**	77
 **2c**	 **3c**	76
 **2d**	 **3d**	70
 **2e**	 **3e**	66
 **2k**	 **3k**	45
 **2l**	 **3l**	33
 **2m**	 **3m**	58
 **2n**	 **3n**	70
 **2j**	 **3j**	20

[a] A mixture of $HCONH_2$ (**4**; 6.0 mmol), aminoarene (**2**; 8.0 mmol), $RuCl_2(PPh_3)_3$ (0.20 mmol), and mesitylene (5.0 mL) was treated under reflux for 12 h. [b] Isolated yields.

thenium-complex-catalyzed reaction of formamide and amine with the evolution of hydrogen. This urea then thermally dissociates to the corresponding isocyanate and ammonia, and the isocyanate reacts with another molecule of amine to yield the N,N′-disubstituted urea.

The syntheses of various ureas from $HCONH_2$ (**4**) with amines are summarized in Table 4. From the reaction of $HCONH_2$ (**4**) with aniline (**2a**), *N,N′*-diphenylurea (**3a**) was obtained in 77% yield. Other various *N,N′*-diarylureas bearing substituents on aromatic rings were also obtained in fair to good yields. *N,N′*-Bis(1-naphthyl)urea (**3m**) was also prepared from the reaction of **4** with 1-aminonaphthalene (**2m**) in 70% yield. When cyclohexylamine (**2j**) was treated with **4**, *N,N′*-dicyclohexylurea (**3j**) was obtained, but the yield was only 20%, which is reminiscent of the low reactivities of N-*alkyl*-substituted formamides.

Synthesis and Structure of $Ru_2(\mu\text{-}Cl)_2Cl_2(\mu\text{-}PhNHCHO\text{-}O,O)(PPh_3)_4$ (5). We have succeeded in preparing various N,N′-disubstituted or trisubstituted ureas by the reaction of formamides with amines in the presence of a catalytic amount of $RuCl_2(PPh_3)_3$. Although we believe that these reactions proceed via ruthenium-catalyzed formyl C−H bond activation, the detailed reaction sequences are not yet clear. To determine this mechanism, the stoichiometric reaction of $RuCl_2(PPh_3)_3$ with formanilide (**1a**) was carried out in CH_2Cl_2 at ambient temperature to yield a purple complex, $Ru_2(\mu\text{-}Cl)_2Cl_2(\mu\text{-}PhNHCHO\text{-}O,O)(PPh_3)_4$ (**5**), in 87% yield (eq 7). Further recrystallization of **5** from CH_2Cl_2/pentane gave single purple crystals of **5**, whose structure was determined by an X-ray diffraction study.



(7)

5

Table 5. Crystal and Intensity Collection Data for 5

composition	$C_{79}H_{67}Cl_4NOP_4Ru_2$
fw	1514.25
cryst color	purple, prismatic
cryst dimens, mm	0.10 × 0.10 × 0.30
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
cell const	
a, Å	21.21(4)
b, Å	15.03(4)
c, Å	22.16(2)
β, deg	95.4(1)
V, Å^3	7036(20)
Z	4
diffractometer	Rigaku AFC7R
radiation (λ, Å)	Mo Kα (av 0.710 69)
D_{calcd}, g cm^{-3}	1.429
μ(Mo Kα), cm^{-1}	7.18
$2\theta_{max}$ (deg)	55.1
no. of collected rflns	17099
no. of unique rflns	6007 ($I > 3.00\sigma(I)$)
goodness of fit	1.26
R^a	0.051
$R_w{}^b$	0.046

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$.

The results of the X-ray diffraction analysis of complex **5** are shown in Tables 5 and 6 and in Figure 1. Complex **5** is a novel dinuclear ruthenium complex coordinatively bridged by the oxygen atom of formanilide and two chloride ligands.

The distances of both Ru(1)−O(1) and Ru(2)−O(1) in complex **5** were almost the same (2.283(5) and 2.229(6) Å) and were apparently longer than the reported Ru−O bond distances (1.876[26]−2.182[27] Å). The Ru(1)−O(1)−Ru(2) angle of 95.7(2)° in complex **5** was much smaller than that reported for an oxo-bridged ruthenium complex (157.2°),[26] probably due to the doubly bridged chloride ligands. The lengths of the nonbridged Ru−Cl bonds in complex **5** were 2.382(5) Å (Ru(1)−Cl(3)) and

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[26] Phelps, D. W.; Kahn, E. M.; Hodgson, D. J. *Inorg. Chem.* **1975**, *14*, 2486.

[27] Voss, E. J.; Sabat, M.; Shriver, D. F. *Inorg. Chem.* **1991**, *30*, 2705.

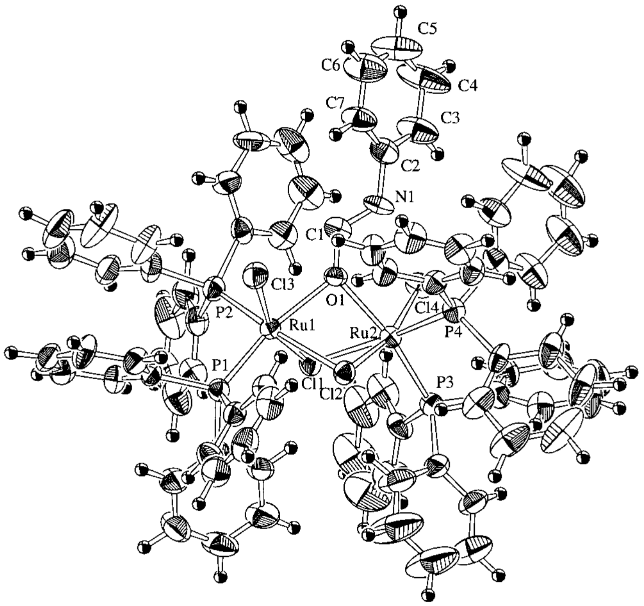

Figure 1. Molecular structure and labeling scheme for **5**.

Table 6. Selected Interatomic Distances (Å) and Angles (deg) for Non-Hydrogen Atoms in $Ru_2(\mu\text{-}Cl)_2Cl_2(\mu\text{-}PhNHCHO\text{-}O,O)(PPh_3)_4$ (5)

Ru(1)–Cl(1)	2.408(5)	Ru(1)–Cl(2)	2.539(2)
Ru(1)–Cl(3)	2.382(5)	Ru(1)–P(1)	2.277(2)
Ru(1)–P(2)	2.297(2)	Ru(1)–O(1)	2.283(5)
Ru(2)–Cl(1)	2.531(2)	Ru(2)–Cl(2)	2.412(2)
Ru(2)–Cl(4)	2.412(2)	Ru(2)–P(3)	2.292(4)
Ru(2)–P(4)	2.316(3)	Ru(2)–O(1)	2.229(6)
O(1)–C(1)	1.259(9)	N(1)–C(1)	1.334(10)
Cl(1)–Ru(1)–Cl(2)	78.32(7)	Cl(1)–Ru(1)–Cl(3)	159.61(9)
Cl(1)–Ru(1)–P(1)	106.37(8)	Cl(1)–Ru(1)–P(2)	89.49(8)
Cl(1)–Ru(1)–O(1)	75.8(1)	Cl(2)–Ru(1)–Cl(3)	94.95(8)
Cl(2)–Ru(1)–P(1)	90.71(7)	Cl(2)–Ru(1)–P(2)	166.75(8)
Cl(2)–Ru(1)–O(1)	74.5(1)	Cl(3)–Ru(1)–P(1)	92.89(9)
Cl(3)–Ru(1)–P(2)	94.78(9)	Cl(3)–Ru(1)–O(1)	83.9(1)
P(1)–Ru(1)–P(2)	97.77(9)	P(1)–Ru(1)–O(1)	164.5(1)
P(2)–Ru(1)–O(1)	97.6(1)	Cl(1)–Ru(2)–Cl(2)	78.42(8)
Cl(1)–Ru(2)–Cl(4)	95.69(8)	Cl(1)–Ru(2)–P(3)	90.75(9)
Cl(1)–Ru(2)–P(4)	167.57(8)	Cl(1)–Ru(2)–O(1)	74.2(2)
Cl(2)–Ru(2)–Cl(4)	165.14(8)	Cl(2)–Ru(2)–P(3)	104.2(1)
Cl(2)–Ru(2)–P(4)	90.97(9)	Cl(2)–Ru(2)–O(1)	78.1(2)
Cl(4)–Ru(2)–P(3)	89.4(1)	Cl(4)–Ru(2)–P(4)	93.03(9)
Cl(4)–Ru(2)–O(1)	87.2(2)	P(3)–Ru(2)–P(4)	98.2(1)
P(3)–Ru(2)–O(1)	164.2(1)	P(4)–Ru(2)–O(1)	97.4(2)
Ru(1)–Cl(1)–Ru(2)	85.28(8)	Ru(1)–Cl(2)–Ru(2)	85.00(7)
Ru(1)–O(1)–Ru(2)	95.7(2)	Ru(1)–O(1)–C(1)	129.3(6)
Ru(2)–O(1)–C(1)	134.9(6)	O(1)–C(1)–N(1)	119.3(8)

2.412(2) Å (Ru(2)–Cl(4)). As for the bridging Cl ligands, the bond angles of Ru(1)–Cl(1)–Ru(2) and Ru(1)–Cl(2)–Ru(2) were 85.28(8) and 85.00(7)°, respectively, and the bond lengths of Ru–Cl–Ru ranged from 2.408(5) to 2.539(2) Å. These values are close to those previously reported for ruthenium complexes containing both bridged and nonbridged chloride ligands (Ru–Cl, 2.446–2.494 Å; Ru–Cl–Ru, 64–95°).[28] These results demonstrate that the oxygen atom in the formanilide ligand coordinates equally to the two ruthenium centers in the $Ru_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_4$ moiety.[29] The distance of C(1)–O(1) in complex **5** (derived from a carbon–oxygen double bond of the formyl group in formanilide) is 1.259(9) Å, which is relatively longer than the reported C=O bond distance of the coordinated DMF in iron(II) complexes (1.18(3) Å).[19b]

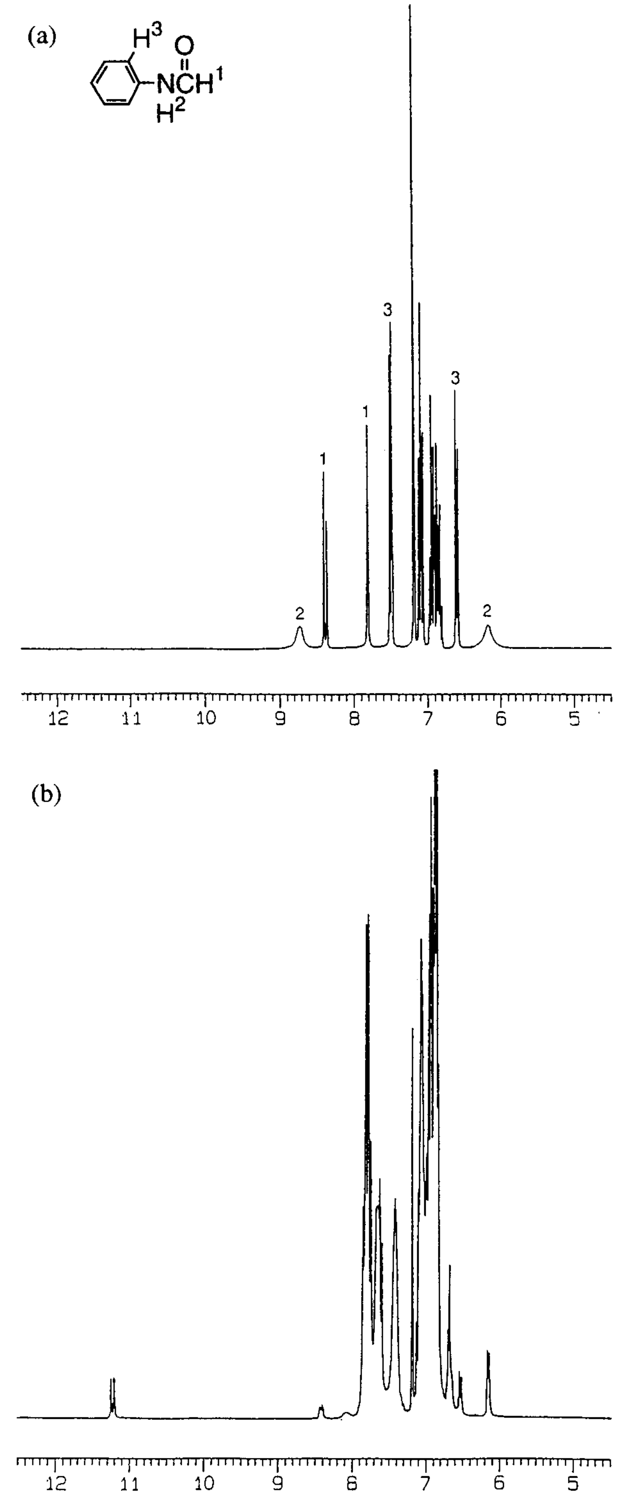

Figure 2. ^1H NMR spectra of formanilide and complex **5** in benzene-d_6: (a) formanilide; (b) complex **5**.

The ^1H NMR spectra of complex **5** and formanilide (**1a**) in benzene-d_6 are shown in Figure 2. The most

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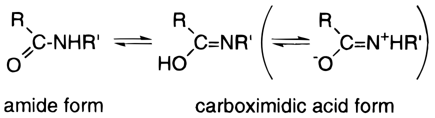
(28) (a) Southern, T. G.; Dixneuf, P. H.; Marouille, J. Y. L.; Grandjean, D. *Inorg. Chem.* **1979**, *18*, 2987. (b) Mason, R.; Thomas, K. M.; Gill, D. F.; Shaw, B. L. *J. Organomet. Chem.* **1972**, *40*, C67.

(29) The formation of $Ru_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_4$ by the dissociation of PPh_3 from $RuCl_2(PPh_3)_3$ in carboxylic acid amide solvents has been reported previously; see: (a) Scröder, M.; Stephenson, T. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K., 1987; Vol. 4, p 377. (b) Vriends, R. C. J.; van Koten, G.; Vrieze, K. *Inorg. Chim. Acta* **1978**, *26*, L29. (c) Hoffman, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 4221. (d) James, B. R.; Markham, L. D. *Inorg. Chem.* **1974**, *13*, 97.

Scheme 4



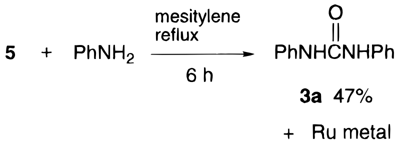
characteristic resonance observed in the ^{1}H NMR spectrum of complex **5** appeared at quite low field, 11.23 ppm, as a doublet signal ($J = 11.6$ Hz), while the resonances of two nonequivalent N−*H* protons of free formanilide (**1a**) at 6.18 (br) and 8.73 (br) ppm completely disappeared. This proton has no correlation with any carbons (in ^{1}H−^{13}C COSY) and was attributed to the N−*H* proton of the coordinated formanilide ligand. Resonance of the *ortho* protons of the phenyl ring was observed at a higher field, 6.15 (d) ppm (in free formanilide; 6.58 (d) and 7.50 (d) ppm), and 11.1% NOE was observed between the proton at 11.23 ppm and the *ortho* protons of the phenyl ring (6.15 ppm) in the DIFNOE spectrum of **5**, which also indicates that this proton is attached to the nitrogen atom.[30] Although the N−*H* proton of noncoordinated formanilide did not exchange with deuterium with the addition of D_2O, the proton observed at 11.23 ppm completely disappeared when D_2O was added to a solution of **5** in benzene-d_6, which clearly indicates that the coordination of formanilide to ruthenium increases the acidity of the N−*H* proton. Unfortunately, the resonance attributed to the C*H*═O proton of the coordinated formanilide ligand was hidden in the resonances of phenyl ring protons, and the effect of coordination on the C*H*═O proton could not be deduced.

In the ^{13}C NMR spectra of **5**, the signals of the −N*C*H═O carbon of free formanilide observed at 158.5 (d) and 162.2 (d) ppm almost completely disappeared, and a new signal appeared at a lower field, 169.2 (d) ppm. On the basis of ^{13}C{^{1}H} off-resonance and ^{1}H−^{13}C COSY NMR spectra, it was confirmed that formyl C−H bond cleavage did not occur at this stage.

In the IR spectrum, an original ν(C═O) absorption band of formanilide at 1684 cm^{-1} completely disappeared, and an alternative absorption band was observed at 1642 cm^{-1}, indicating that the carbon−oxygen double bond of the formyl group in **5** was weakened by the coordination of formanilide to ruthenium.

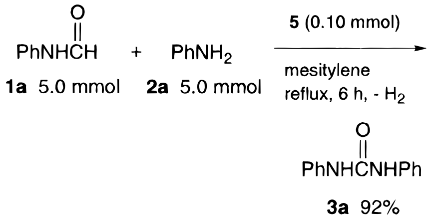
On the basis of this NMR study, formamide has been activated in solution, which leads to an increase in the acidity of the N−*H* proton. This was attributed to equilibrium between an amide form and a carboximidic acid form; in solution, the carboximidic acid form predominates due to coordination of formamide to Ru (Scheme 4).

Reactivity of $Ru_2(\mu\text{-}Cl)_2Cl_2(\mu\text{-}PhNHCHO\text{-}O,O)(PPh_3)_4$ (5). To clarify the intermediacy of complex **5** in the $RuCl_2(PPh_3)_3$-catalyzed synthesis of ureas from formamides and amines, complex **5** was reacted with an equimolar amount of aniline (**2a**) under reflux in mesitylene for 6 h (eq 8). The reaction proceeded smoothly, and *N,N′*-diphenylurea was obtained in 47% yield, together with the deposition of ruthenium metal.



$$\mathbf{5} + PhNH_2 \xrightarrow[6\ h]{\text{mesitylene reflux}} PhNH\overset{O}{\overset{\|}{C}}NHPh\ \ \mathbf{3a}\ 47\% \ + \text{Ru metal} \qquad (8)$$

Complex **5** was a highly effective catalyst for the synthesis of *N,N′*-diphenylurea (**3a**) from formanilide (**1a**) and aniline (**2a**). When a mixture of formanilide (**1a**; 5.0 mmol), aniline (**2a**; 5.0 mmol), and a catalytic amount of complex **5** (0.10 mmol, 4.0 mol %) was treated under reflux in mesitylene for 6 h, *N,N′*-diphenylurea was obtained in 92% yield (eq 9). This result was consistent with the $RuCl_2(PPh_3)_3$-catalyzed synthesis of *N,N′*-diphenylurea (**3a**) (Table 1). Consequently, complex **5** appears to be the key intermediate for the present reaction.



$$\underset{\mathbf{1a}\ 5.0\ \text{mmol}}{PhNH\overset{O}{\overset{\|}{C}}H} + \underset{\mathbf{2a}\ 5.0\ \text{mmol}}{PhNH_2} \xrightarrow[\text{mesitylene reflux, 6 h, - }H_2]{\mathbf{5}\ (0.10\ \text{mmol})} \underset{\mathbf{3a}\ 92\%}{PhNH\overset{O}{\overset{\|}{C}}NHPh} \qquad (9)$$

In comparison with the stoichiometric reaction, the deposition of ruthenium metal was not observed after catalytic reactions. This result suggests that the coordination of amines and/or formamides to ruthenium is essential for the catalytic cycle, and if the amount of amines and/or formamides is insufficient, deactivation of the ruthenium catalyst leading to deposition of ruthenium metal would occur.

Considering these results, a possible mechanism for the $RuCl_2(PPh_3)_3$-catalyzed synthesis of ureas from formamides and amines is illustrated in Scheme 5. This reaction starts from the coordination of the formamide to two molecules of $RuCl_2(PPh_3)_3$ through the carbonyl oxygen atom with the dissociation of two triphenylphosphine ligands, to give dinuclear ruthenium complex **5**. In solution, complex **5** will be converted smoothly into **6**, which has a formimidic acid ligand. Thus, the acidity of the N−*H* proton in **6** drastically increases, and the activated N−H bond oxidatively adds to the ruthenium center to give intermediate **7**. The interaction of β-C−H with both ruthenium centers facilitates the further oxidative addition of the formyl C−H bond to the ruthenium center to yield isocyanate-coordinated intermediate **8**.[31] After the reductive elimination of molecular hydrogen from **8**, the amine nucleophilically attacks the isocyanate ligand in **9**, to give the corresponding ureas with the regeneration of an active Ru(II) species, **5**. The result that N-substituted formamides react smoothly with amines to give the corresponding ureas, while N,N-disubstituted formamides do not react at all, demonstrates the necessity of a hydrogen atom on the amide nitrogen (*vide supra*). This suggests that the reaction proceeds via an isocyanate intermediate which can be generated from N-substituted formamides but not from N,N-disubstituted formamides.

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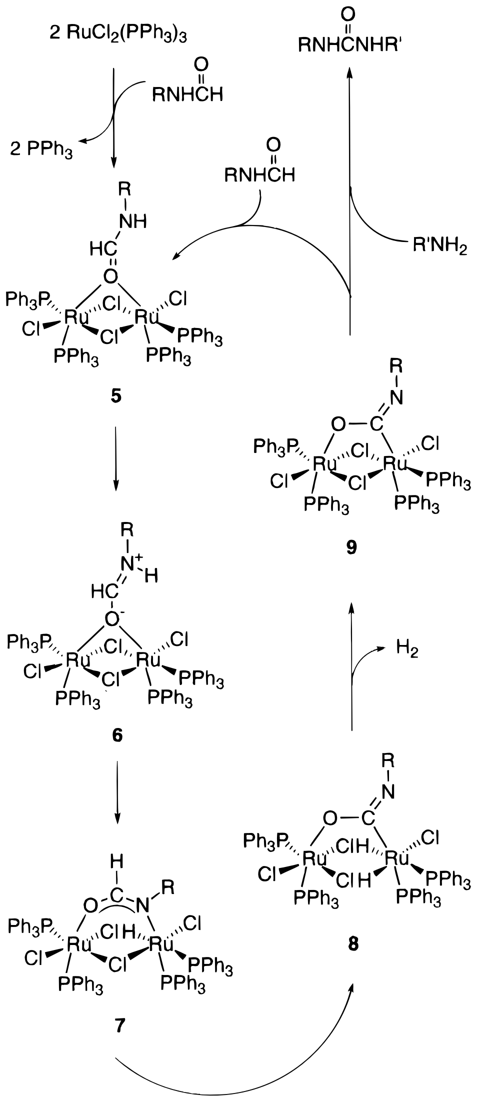
(30) Indeed, 14.4% NOE was observed between the N−*H* proton and protons in the *ortho* position of the phenyl ring by DIFNOE analysis of formanilide itself.

(31) We have been making an effort to observe these isocyanate-coordinated intermediates **8** and **9** by NMR etc., but at this stage we could not observe and isolate the intermediates **8** and **9**.

Scheme 5



Conclusion

In conclusion, the present reactions give various ureas using available formamides as a versatile carbonyl source. Hence, they offer a convenient method for the synthesis of ureas without the use of hazardous phosgene or carbon monoxide. Activation of the formyl C−H bond in formamides by the ruthenium catalyst is initially induced by the coordination of the formamide to the ruthenium through the formyl oxygen atom. Next, the oxidative addition of the activated N−H bond to the ruthenium, which leads to the activation of the β-C−H bond, facilitates the subsequent oxidative addition of the formyl C−H bond. Thus, complex **5** is the key intermediate for the catalytic activation of the formyl C−H bond in formamides by the ruthenium catalyst.

Experimental Section

Materials. Amines, formamide, PPh$_3$, and solvents used in this study were purified by distillation or recrystallization before use. RuCl$_3$·nH$_2$O (mainly n = 3) and Ru$_3$(CO)$_{12}$ were obtained from commercial sources and used without further purification. The complexes RuCl$_2$(PPh$_3$)$_3$,[32] RuHCl(PPh$_3$)$_3$,[33] RuH$_2$(PPh$_3$)$_4$,[34] Ru(cod)(cot),[35] PdCl$_2$(PPh$_3$)$_2$,[36] RhCl(PPh$_3$)$_3$,[37] CoCl$_2$(PPh$_3$)$_2$,[38] CoCl(PPh$_3$)$_3$,[39] and *cis*-PtCl$_2$(PPh$_3$)$_2$[40] were prepared as described in the literature.

N-Substituted Formamides. N-Substituted formamides were prepared as described in the literature[41] and purified by recrystallization. A typical procedure for the preparation of *N*-(2-methylphenyl)formamide is as follows. To a mixture of *o*-toluidine (25 g, 233 mmol) and toluene (140 mL) was slowly added formic acid (19 mL, 504 mmol) with vigorous stirring. The slightly exothermic reaction occurred immediately, and a large amount of solid was simultaneously precipitated. The generated water was removed from the reaction mixture by azeotropic distillation with toluene to give a white solid. The solid was filtered and purified by recrystallization from xylene/ligroin. Finally, *N*-(2-methylphenyl)formamide was obtained in 92% yield.

Analytical Procedure. The products were identified by IR, ^{1}H and ^{13}C NMR, and elemental analysis.

The ^{1}H NMR spectra were recorded at 90 and/or 270 MHz. ^{13}C NMR spectra were recorded at 25.05 and/or 67.8 MHz. Samples were analyzed in dimethyl sulfoxide-d_6 (DMSO-d_6), and the chemical shift values were expressed relative to tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed at the Microanalytical Center of Kyoto University. HPLC analyses were performed on a Shimadzu LC-5A liquid chromatograph with a Shimadzu SPD-2A spectrophotometric detector at UV 254 nm. The columns consisted of a Hiber Lichrosorb RP-18 (5 μm) and a RP-Select B (5 μm), and the eluents were methanol/water (6/4 in volume) or acetonitrile/water (6/4 in volume). The yields were determined by HPLC with phenetole as an internal standard.

General Procedure. A mixture of N-substituted formamide **1** (4.0 mmol), amine **2** (4.0 mmol), RuCl$_2$(PPh$_3$)$_3$ (0.20 mmol), and mesitylene (5.0 mL) was placed in a two-necked 50 mL Pyrex flask equipped with a magnetic stirring bar and a reflux condenser under a flow of argon. The flask was immersed in a preheated silicone oil bath (*ca.* 170 °C), and the reaction was carried out under reflux for 12 h with stirring. After the reaction mixture was cooled to room temperature, the precipitated product was filtrated with a glass filter (G4) and washed with ether. If necessary, the precipitate was purified by recrystallization from suitable solvents (*e.g.* ethanol and dimethyl sulfoxide/methanol).

Ru$_2$(μ-Cl)$_2$Cl$_2$(μ-PhNHCHO-*O,O*)(PPh$_3$)$_4$ (5). RuCl$_2$(PPh$_3$)$_3$ (1.92 g, 2.0 mmol), formanilide (0.15 g, 1.2 mmol), and CH$_2$Cl$_2$ (10 mL) were placed in a 200 mL Schlenk flask under a stream of argon. After the reaction mixture was stirred at room temperature for 1 h, pentane (40 mL) and CH$_2$Cl$_2$ (10 mL) were added and the solution was stirred for another 30 min. After stirring was complete, the solution was allowed to stand for more than 30 min, and pentane (60 mL) was slowly poured into the solution to separate the solution into two layers. After the solution was allowed to stand for 2 days, purple crystals were precipitated. Separating the crystals from the solution, washing with pentane, and drying in vacuo gave 1.31 g (0.87 mmol, 87%) of Ru$_2$(μ-Cl)$_2$Cl$_2$(μ-PhNHCHO-*O,O*)(PPh$_3$)$_4$ (**5**).

Mp: 136.5 °C dec. IR (KBr): 1641.6 cm^{-1} (s, ν(CO)). ^{1}H NMR (270 MHz, CD$_2$Cl$_2$): δ 6.15 (d, 2H, NH-phenyl-2*H*, J= 7.1 Hz), 6.85−7.68 (m, 64H, PPh$_3$-*H*, NHC*H*O, and NH-phenyl-

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3,4*H*), 10.75 (d, 1H, N*H*, *J* = 11.4 Hz). ^{13}C NMR (67.8 MHz, CD_2Cl_2): δ 117.9 (d, NH-phenyl-*C*^{2}), 125.8 (d, NH-phenyl-*C*^{4}), 126.8, 126.9, 127.8, and 127.9 (d, PPh_3-*C*^{3} and -*C*^{4}), 129.0−129.8 (m, PPh_3-*C*^{2} and NH-phenyl-*C*^{3}), 135.4−136.2 (m, PPh_3-*C*^{1} and NH-phenyl-*C*^{1}), 169.2 (d, NH*C*HO). Anal. Calcd for $C_{79}H_{67}Cl_4NOP_4Ru_2$: C, 62.66; H, 4.46; Cl, 9.37; N, 0.92. Found: C, 62.65; H, 4.38; Cl, 9.42; N, 0.87.

X-ray Structure Determination of $Ru_2(\mu\text{-}Cl)_2Cl_2(\mu\text{-}PhNHCHO\text{-}O,O)(PPh_3)_4$ (5). Crystal data, data collection, and refinement parameters for $Ru_2(\mu\text{-}Cl)_2Cl_2(\mu\text{-}PhNHCHO\text{-}O,O)(PPh_3)_4$ are summarized in Table 5. A single crystal of $Ru_2(\mu\text{-}Cl)_2Cl_2(\mu\text{-}PhNHCHO\text{-}O,O)(PPh_3)_4$ was mounted and placed on a Rigaku AFC-7R diffractometer. The unit cell was determined by the automatic indexing of 25 centered reflections and confirmed by examination of axial photographs. Intensity data were collected using graphite-monochromated Mo Kα X-radiation (λ = 0.710 69 Å). Check reflections were measured every 150 reflections; the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects. The structure was determined using Patterson and standard difference map techniques on a IRIS computer using SHELX86.[42] Systematic absences were uniquely consistent with the space group $P2_1/c$ (No. 14). Selected bond lengths and angles for $Ru_2(\mu\text{-}Cl)_2Cl_2(\mu\text{-}PhNHCHO\text{-}O,O)(PPh_3)_4$ are given in Table 6. Atomic coordinates and B_{iso}/B_{eq} are given in the Supporting Information.

Acknowledgment. This work was supported in part by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science and Culture.

Supporting Information Available: Text and tables giving complete crystallographic data for **5** and text giving characterization data for all numbered compounds (44 pages). Ordering information is given on any current masthead page.

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