794 *Organometallics* **2001,** *20,* 794−797

Catalytic Hydrogenation of Alkenes by the Ruthenium−Carbene Complex HRu(CO)Cl(PCy$_3$)(IMes) (IMes = Bis(1,3-(2,4,6-trimethylphenyl)imidazol-2-ylidene)

Hon Man Lee,[†] Dale C. Smith, Jr.,[†] Zhengjie He,[‡] Edwin D. Stevens,[†]
Chae S. Yi,*,[‡] and Steven P. Nolan*,[†]

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148, and
Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53201-1881

Received October 16, 2000

*Summary: Using an exchange reaction involving one PCy$_3$ ligand in HRu(CO)Cl(PCy$_3$)$_2$ (**1**) for one IMes, a ruthenium−hydride complex HRu(CO)Cl(PCy$_3$)(IMes) (**2**) has been prepared. Complex **2** is an active catalyst in the hydrogenation of alkenes. A TON of 24 000 h^{-1} has been obtained at 100 °C under 4 atm of hydrogen. Addition of HBF$_4$·OEt$_2$ as cocatalyst enhanced the catalytic activity.*

Introduction

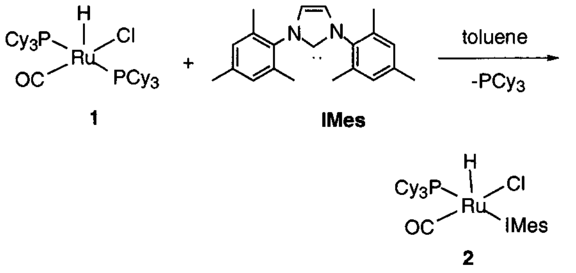
Five-coordinate hydrido(carbonyl) complexes of the type HM(CO)Cl(L)$_2$ (M = Ru, Os; L = PPr$^i_3$, PBu$^t_2$Me) are very efficient catalysts in the hydrogenation and hydrosilylation of alkenes and alkynes.[1] Recently, it was found that the replacement of PPr$^i_3$ in HRu(CO)Cl(PPr$^i_3$)$_2$ with the sterically demanding PCy$_3$ led to the catalyst HRu(CO)Cl(PCy$_3$)$_2$ (**1**), which displayed high activity in alkene hydrogenation.[2]

Nucleophilic N-heterocyclic carbenes, so-called “phosphine mimics”, have attracted considerable attention as possible alternatives for the widely used phosphine ligands in homogeneous catalysis.[3] Indeed, we and others found that the replacement of bulky phosphines with IMes (IMes = bis(1,3-(2,4,6-trimethylphenyl)imidazol-2-ylidene) or IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) can result in enhanced catalytic performances in olefin metathesis,[4] C−C bond formation reaction,[5] aryl amination,[6] and hydrogenation.[7]

In view of these findings, we wished to examine whether the replacement of PCy$_3$ with IMes in HRu(CO)Cl(PCy$_3$)$_2$ (**1**) could result in hydrogenation catalysts with enhanced properties, such as increased catalytic activity or thermal stability. We now report the synthesis of a new ruthenium carbene complex, HRu(CO)Cl(PCy$_3$)(IMes*)* (**2**), and its catalytic activity in the hydrogenation of alkenes.

Results and Discussion

Synthesis and Characterization of HRu(CO)Cl(PCy$_3$)(IMes) (2). A simple ligand exchange such as the one used in the preparation of the olefin metathesis catalyst RuCl$_2$(=C(H)Ph)(PCy$_3$)(IMes) from Grubbs' catalyst RuCl$_2$(=C(H)Ph)(PCy$_3$)$_2$ was employed to synthesize complex **2**.[4a] An excess of IMes was stirred with HRu(CO)Cl(PCy$_3$)$_2$ (**1**) in toluene at 80 °C for 2 h and for an additional 18 h at room temperature (eq 1). Subsequent reduction of the solvent volume and precipitation with ethanol gave **2** as an orange-yellow solid in 69% yield. Complex **2** was characterized by both ^{1}H and ^{31}P NMR spectroscopy. The ^{31}P{^{1}H} NMR spectrum showed a singlet at δ 47.5, indicating the presence of the PCy$_3$ ligand. In the ^{1}H NMR spectrum, the methyl signals of the IMes ligand were observed at δ 2.12, 2.37, and 2.48, respectively, and the signal for the imidazolyl ring protons was observed at δ 6.23. The metal−hydride signal was observed at δ −24.83 as a doublet with ^2J(HP) = 21.2 Hz. The upfield chemical shift suggested a cis disposition of the hydride and CO. The relatively



(1)

---

* To whom correspondence should be addressed. E-mail: snolan@uno.edu, chae.yi@marquette.edu.

[†] University of New Orleans.

[‡] Marquette University.

(1) (a) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1563−1564. (b) Esteruelas, M. A.; Valero, C.; Oro, L. A.; Meyer, U.; Werner, H. *Inorg. Chem.* **1991**, *30*, 1159−1160. (c) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1992**, *11*, 3362−3369. (d) Esteruelas, M. A.; Herrero, J.; Oro, L. A. *Organometallics* **1993**, *12*, 2377−2379.

(2) Yi, C. S.; Lee, D. W. *Organometallics* **1999**, *18*, 5152−5156.

(3) (a) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 725−728. (b) Hermann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162−2187. (c) Adruengo, A. J., III; Krafczyk, R. *Chem. Z.* **1998**, *32*, 6−14. (d) Dullius, J. E. L.; Suarez, P. A. Z.; Einloft, S.; de Souza, R. F.; Dupont, J.; Fischer, J.; De Cian, A. *Organometallics* **1998**, *17*, 815−819. (e) Jafarpour, L.; Schanz, H. J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5416−5419. (f) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 336. (g) Chatterjee, A. K.; Grubbs, R. H. *Org. Lett.* **2000**, *1*, 1751−1753. (h) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39−91, and references therein.

(4) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674−2678.

(5) (a) Zhang, C.; Huang, J.; Trudell, M. L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804−3805. (b) Böhm, V. P. W.; Gstöttmayr, C. W. K.; Weskamp, T.; Hermann, W. A. *J. Organomet. Chem.* **2000**, *595*, 186−190. (c) Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 9889−9890. (c) Lee, H. M.; Nolan, S. P. *Org. Lett.* **2000**, *2*, 2053−2055.

(6) Huang, J.; Grasa, G.; Nolan, S. P. *Org. Lett.* **1999**, *1*, 1307−1309.

(7) Lee, H. M.; Jiang, T.; Stevens, E. D.; Nolan, S. P. *Organometallics*, in press.

10.1021/om000882a CCC: $20.00

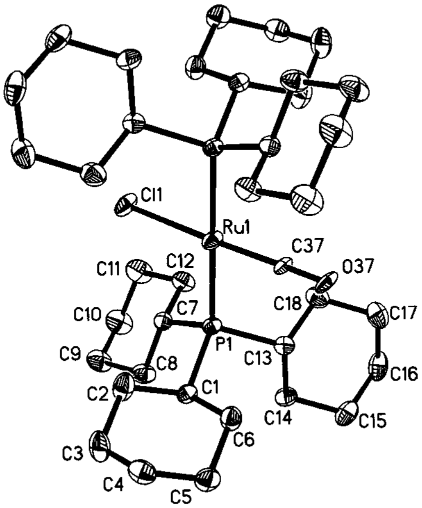


Figure 1. ORTEP of **1** with ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

small J_{HP} coupling constant was consistent with a hydride ligand cis to the PCy_3 ligand. Remarkably, the signal for the phenyl protons of the IMes ligand was observed as a doublet with a coupling constant of 17.6 Hz. Such a long-range coupling constant can only be possible if the IMes and the PCy_3 ligands are trans to each other. The IR spectrum of **2** showed a strong absorption of CO stretching vibration at 1896 cm^{-1}. The CO absorption of **1** was observed at 1901 cm^{-1}.[8] The lower frequency number of **2** indicated, in accord with our previous finding,[9] that IMes is more electron donating than PCy_3. To unequivocally establish the structure of **2**, a single-crystal X-ray diffraction study was performed on crystals grown from slow diffusion of diethyl ether into a saturated dichloromethane solution of **2**.

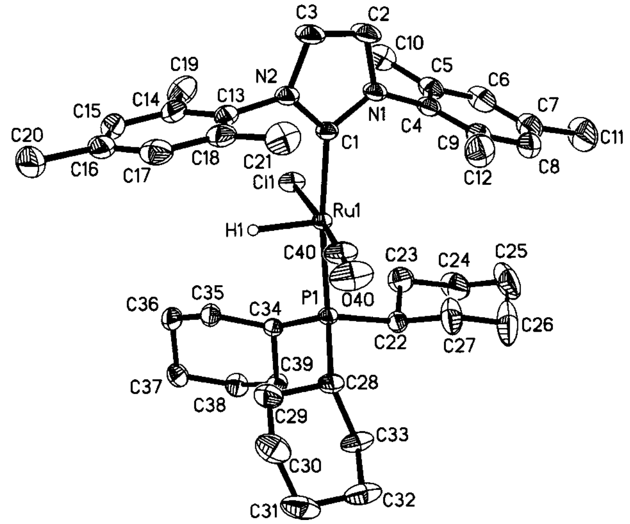


Figure 2. ORTEP of **2** with ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

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

	1	**2**
	Bond Lengths	
Ru−IMes		2.0826(14)
Ru−P	2.3865(5)	2.3669(4)
Ru−Cl	2.3968(15)	2.4217(11)
Ru−CO	1.822(6)	1.784(4)
CO	1.141(6)	1.180(4)
Ru−H	not located	1.57(2)
	Bond Angles	
CO−Ru−IMes		90.43(12)
P−Ru−CO	89.0(2)	90.82(12)
Cl−Ru−IMes		89.40(4)
P−Ru−Cl	88.12(4)	89.81(2)
P−Ru−IMes		173.44(4)
Cl−Ru−CO	177.9(3)	175.87(14)

Single X-ray Analysis of 1 and 2. As shown in the ORTEP (Figure 2), **2** adopts a square-pyramidal geometry around the ruthenium center, with the hydride ligand occupying the apical position. The chloride is trans to the CO (angle Cl−Ru−CO = 175.87°), while the PCy_3 and the IMes are in trans disposition to each other (angle P−Ru−IMes = 173.44°). The structure of **2** is very similar to that of **1**, which was also obtained for comparative purpose (Figure 1). Both structures are very similar to that of $HRu(CO)Cl(PPr^i_3)_2$, which has recently been reported by Caulton and co-workers.[10] Selected bond lengths and angles for **1** and **2** are given in Table 1. The Ru−CO bond distance in **2** (1.784 Å) is significantly shorter than that in **1** (1.822 Å), which we attribute to a better σ donation from IMes and PCy_3, which results in increased π-back-donation in the CO π^* orbital of **2**. Consistently, the CO bond distance is longer in **2** (1.180 Å) than in **1** (1.141 Å). Unexpectedly, the Ru−P bond distance in **2** (2.3669 Å) is shorter than that in **1** (2.3865 Å). The difference might be attributed to the π-back-donation to the IMes ligand trans to the PCy_3 in **2**, although photoelectron spectroscopy and density functional calculations for Pd and Pt bis(carbene) complexes suggest that N-heterocyclic carbenes behave predominantly as strong σ donor, their π acceptor property being negligible.[11] From this shorter Ru−P distance, it might be concluded that the PCy_3 in **2** is more strongly bonded to the ruthenium center. (vide infra). A comparison of structures **1** and **2** clearly shows that IMes is sterically more demanding than PCy_3.

Catalytic Hydrogenation. The catalytic performance of **2** for hydrogenation of 1-hexene was compared with the catalytic activity of **1** (Table 3). The catalytic reactions were performed with 0.1 mol % of catalyst in 4 mL of C_6H_6 and 4.0 atm of hydrogen. At ambient temperature, **2** with a turnover number (TON) of 3000 h^{-1} was less efficient than **1** (TON = 12 000 h^{-1}) (entries 1 and 2). However, when the catalytic reactions were conducted at 50 °C, a 4-fold increase in the activity of **2** with a TON of 12 600 h^{-1} was observed (entry 4). A further increase in temperature, to 100 °C, resulted in an even more efficient system with a TON as high as 24 000 h^{-1} (entry 6). In contrast, **1** gave only a marginal increase to a TON of 15 200 h^{-1} when the reaction was conducted at 50 °C (entry 3). Increasing the operating temperature to 100 °C leads to significant rate increases for both **1** and **2**, with **2** having a slightly higher activity (entries 5 and 6).

It has been shown in the hydrogenation of alkenes catalyzed by **1** that the addition of protic acids with weakly coordinating anions, such as $HBF_4 \cdot OEt_2$ or

---

[8] The IR spectrum of **1** has not been reported previously. IR of **1** (toluene, cm^{-1}): ν(CO) 1901.

[9] Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5375−5380, and references therein.

[10] Huang, D.; Streib, W. E.; Bollinger, J. C.; Caulton, K. G.; Winter, R. F.; Scheiring, T. *J. Am. Chem. Soc.* **1999**, *121*, 8087−8097.

Table 2. Crystallographic Data for Complexes 1 and 2

	1	2
formula	$C_{37}H_{66}ClOP_2Ru$	$C_{40}H_{58}ClN_2OPRu$
fw	725.36	750.37
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a, Å	9.7838(6)	12.1956 (13)
b, Å	10.2458(6)	17.8010(18)
c, Å	10.8180(6)	18.3708(19)
α, deg	114.308(2)	90
β, deg	108.158(2)	103.223(2)
γ, deg	91.524(2)	90
V, Å^3	923.93(9)	3882.4(7)
Z	1	4
D_{calcd}, Mg/m^3	1.304	1.284
R	0.0372	0.0289
R_w	0.0632	0.0398
no.of refined params	336	675
no. of data collected	6984	63 772
no. of unique data, $I > 3\sigma$	5709	11 321
R_{merge}	0.0276	0.0663

Table 3. Hydrogenation of 1-Hexene to Hexane Catalyzed by 1 and 2[a]

entry	catalyst	temp (°C)	turnover rate[b]
1	**1**	20	12 000
2	**2**	20	3000
3	**1**	50	15 200
4	**2**	50	12 600
5	**1**	100	21 500
6	**2**	100	24 000

[a] Reaction conditions: 1-hexene, 5.7 mmol; catalyst, 0.69 μmol; C_6H_6, 4 mL; $P(H_2)$, 4.0 atm. [b] Turnover rate = (mol of product)(mol of catalyst)$^{-1}$ h^{-1}.

Table 4. Effect of HBF_4 on the Hydrogenation of Alkenes Catalyzed by 2[a]

entry	alkene	acid	turnover rate
1	1-hexene	none	313
2	1-hexene	HBF_4	1600
3	allylbenzene	none	100
4	allylbenzene	HBF_4	680
5	cyclooctene	none	520
6	cyclooctene	HBF_4	1185

[a] Reaction conditions: alkene, 5.7 mmol; catalyst, 0.69 μmol; acid, 1−2 equiv; C_6H_6, 4 mL; $P(H_2)$, 1.0 atm. [b] Turnover rate = (mol of product)(mol of catalyst)$^{-1}$ h^{-1}.

HOTf, could lead to substantial rate enhancements.[12] The increase in activity was attributed to the selective formation of $HPCy_3^+BF_4^-$ from **1**, which resulted in the formation of a 14-electron species. We applied this protocol to the IMes modified complex and found that **2**/HBF_4·OEt_2 also gave a 2−5-fold increase in activity for the hydrogenation of a 1-hexene, allybenzene, and cyclooctene at ambient temperature and pressure of hydrogen (Table 4, entries 1−6).

One of us had established the monohydride mechanistic pathway of **1** in which an alkene-induced dissociation of one PCy_3 from **1** was crucial to the formation of the active species.[2] The mechanism was further supported by the fact that addition of HBF_4·OEt_2 led to a more efficient catalytic system (vide supra).[12] Presumably, **2** follows the same mechanistic pathway. The lower activity of **2** at ambient temperature might be related to stronger ligand coordination and steric congestion around the ruthenium center. However, at elevated temperatures, ligand dissociation becomes more favorable. The rate enhancement induced by the addition of HBF_4·OEt_2 implied the involvement of an active 14-electron species. Since IMes is more electron donating than PCy_3,[4a] the addition of HBF_4 should preferentially result in the formation of $HPCy_3^+BF_4^-$ and the 14-electron complex [HRu(CO)Cl(IMes)], which is the active catalytic species in the hydrogenation reaction.

In summary, an active hydrogenation catalyst was prepared by the substitution of one PCy_3 ligand with IMes from **1**. At ambient temperature, the catalytic activity of **2** in the hydrogenation of alkenes was less efficient than **1**. But at elevated temperatures, a comparable activity to that of **1** could be obtained. Indeed, a TON of 24 000 h^{-1} was achieved at 100 °C. The addition of HBF_4·OEt_2 enhanced the activity, presumably due to the formation of the 14-electron active species, [HRu(CO)Cl(IMes)].

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry argon with standard Schlenk tube techniques or in an MBraun glovebox containing less than 1 ppm of oxygen and water. C_6H_6 was distilled from a purple solution of sodium and benzophenone immediately prior to use. Anhydrous solvents and HBF_4·OEt_2 were purchased from Aldrich and used as received. The NMR solvents were dried from activated molecular sieves (4 Å). All alkene substrates were purchased from commercial sources and vacuum-distilled from either molecular sieves or sodium prior to use. HRu(CO)Cl$(PCy_3)_2$[13] and IMes[14] (IMes.HCl is now commercially available from Strem) were prepared according to the literature procedure. NMR spectra were recorded using a Varian 400 MHz spectrometer, and elemental analyses were performed by Desert Analysis, Tucson, AZ. GC analyses were performed on a Hewlett-Packard HP 6890 GC spectrometer with an FID detector and an HP-5 column. IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer.

Synthesis of HRu(CO)Cl(PCy_3)(IMes) (2). In the glovebox, a Schlenk flask was charged with 510 mg of HRu(CO)Cl$(PCy_3)_2$ (0.70 mmol) and 302 mg of IMes (1.05 mmol). Then 20 mL of toluene was added via a syringe. The solution was heated to 80 °C for 2 h and then stirred for 18 h at room temperature. The solvent was removed under vacuum. The orange-yellow residue was taken up in 20 mL of ethanol, and the suspension was filtered. The precipitate was washed with ethanol (3 × 20 mL) and dried under vacuum. Yield: 365 mg (69%). Anal. Calcd for $C_{40}H_{58}N_2OClPRu$: C, 64.02; H, 7.79; N, 3.73. Found: C, 64.11; H, 7.99; N, 3.73. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1896. ^1H NMR (399.95 MHz, C_6D_6): δ −24.83 (d, ^2J(HP) = 21.2 Hz, HRu), 1.12−2.24 (m, 33 H, Cy); 2.12, 2.37, 2.48 (s, 18 H, CH_3); 6.23 (s, 2 H, NCHCHN), 6.81 (d, ^7J(HP) = 17.6 Hz, 4 H, Ar). $^{31}P\{^1H\}$ NMR (161.90 MHz, CD_2Cl_2): δ 47.5 (s). Crystals suitable for X-ray measurements were obtained by slow diffusion of ether into a saturated dichloromethane solution of **2**.

Catalytic Hydrogenation. In a glovebox, 1.0 mL of predissolved 0.69 mM C_6H_6 solution of catalyst (0.69 μmol) was placed in a 100 mL Fisher-Porter pressure bottle equipped with a pressure gauge and a stirring bar. In some cases, 1−2 equiv of HBF_4·OEt_2 was also added. The solution was diluted

---

(11) Green, J. C.; Scurr, R. G.; Arnold, P. L.; Cloke, F. G. N. *Chem. Commun.* **1997**, 1963−1964.

(12) Yi, C. S.; Lee, D. W.; He, Z. *Organometallics* **2000**, *19*, 2909−2915.

(13) Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043−2045.

(14) Arduengo, A. J., III. U.S. Patent No. 5 182 405, 1993.

with 4.0 mL of C_6H_6. Excess alkene (5.7 mmol) was added, and the bottle was attached to a vacuum line. The reaction bottle was evacuated while it was cooled in a liquid N_2 bath. The reaction bottle was allowed to warm to room temperature with stirring in a 20 min period. An appropriate amount of H_2 gas pressure was applied to the reaction bottle, and the reaction mixture was vigorously stirred at the temperature specified for 1−4 h. The product yields were determined by GC analyses. In all cases, less than 5% of isomerized olefin was detected by GC.

Acknowledgment. The National Science Foundation, the Petroleum Research Fund administrated by the ACS, the Louisiana Board of Regents, and DuPont are gratefully acknowledged for partial support of this work.

Supporting Information Available: Tables of crystal data and structure refinement details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000882A