Journal of the Chinese Chemical Society, **2001**, *48*, 997-1002

Cationic Phosphine-imine Rhodium(I) Complexes and Their Activity on Catalysis of Phenylacetylene Polymerization

K. Rajender Reddy (雷笛卡路), Chi-Feng Lin (林祺峰), Gene-Hsiang Lee (李錦祥),
Shie-Ming Peng (彭旭明), Jwu-Ting Chen (陳竹亭) and Shiuh-Tzung Liu* (劉緒宗)
Department of Chemistry, National Taiwan University, Taipei, Taiwan, 106, R.O.C.

A series of phosphine-imine rhodium(I) complexes have been prepared and characterized by both spectroscopic and X-ray single crystal analyses. Their activity on catalytic polymerization of phenylacetylene is investigated. The study of the solvent effect on polymerization shows that aqueous medium can increase the productivity of polymer.

INTRODUCTION

Due to the high π-conjugation of the carbon chain, the substituted polyacetylenes have been found many applications in various materials.[1-7] Thus, development of new transition metal complexes for catalysis of polymerization has been drawing much attention.[2-9] The rhodium(I) complexes appear to be reactive in polymerization of alkynes. Noyori and his coworkers clearly demonstrate that the mechanism contains migratory insertion of alkyne into Rh-C bond in the polymerization processes,[8] and ligand effect apparently can provide crucial role in such process.

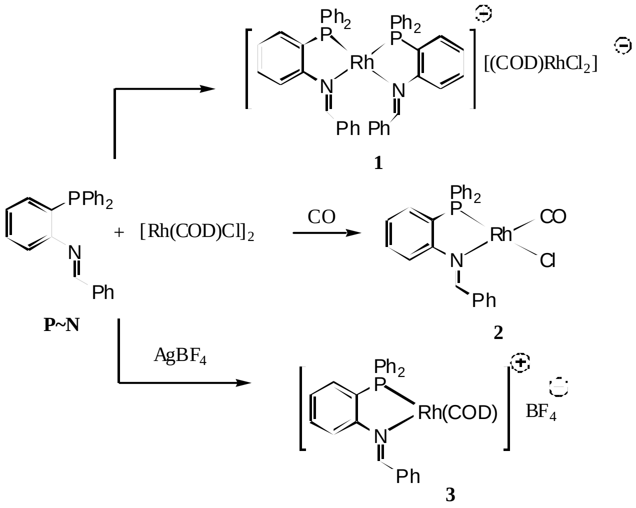
Recently, we have developed the phosphine-imine (**P~N**) ligand and its palladium complexes for catalytic coplymerization of CO and ethylene.[10] In this work, we reported the preparation of cationic phosphine-imine (**P~N**) rhodium complexes and their uses in the catalytic reaction of polyphenylacetylene formation.

RESULTS AND DISCUSSION

Phosphine-imine Rhodium(I) Complexes

The phosphine-imine ligand was prepared according to the procedure reported previously.[10] Preparation of the phosphine-imine rhodium(I) complexes is illustrated in Scheme I. The reaction of $[Rh(COD)Cl]_2$ with equimolar amount of phosphine-imine (**P~N**) ligand led to the ligand substitution *via* disproportionation at the metal center, giving the formation of the rhodium complex **1**.

Scheme I Preparation of phosphine-imine rhodium(I) complexes



While treating the above reaction mixture with silver tetrafluoroborate at the same time, the cationic phosphine-imine rhodium(I) **3** was obtained instead of having double chelation. Besides the ^{31}P NMR spectrum of complex **1** shows a signal at 51.8 with $J_{Rh\text{-}P} = 169$ Hz, indicating a four- coordinated rhodium species, the detailed molecular structure was also confirmed by its X-ray single crystallography. As to structural identification for **3**, it has been achieved mainly by spectral methods. The value of $J_{P=Rh} = 154$ Hz is in the typical range of a four-coordinated rhodium complex[11] as well as the ^{1}H NMR signals due to COD have evidenced the coordinating environment around the metal center.

In the presence of carbon monoxide, the reaction of the ligand **P~N** with $[Rh(COD)Cl]_2$ in THF yielded the rhodium(I) carbonyl complex **2**. Infrared absorption of **2** at 1986 and 1606 cm^{-1} clearly showed the coordination of a carbonyl

---

Dedicated to Professor Sheng-lieh Liu on the occasion of his ninetieth birthday.

(C≡O) and an imine (-N=C) to the metal center. The coupling constant (167 Hz) of rhodium-phosphorus is also an indication of four-coordinate rhodium geometry.[11] The detail structure of **2** was determined by X-ray single-crystal analysis.

Discussion of Crystal Structures

Single crystals suitable for X-ray analysis of complexes **1**·1/2 CH_2Cl_2, **2**·CH_2Cl_2 and **3** were obtained in each case by slow evaporation of a dichloromethane/hexane solution under nitrogen atmosphere. The crystal data for these complexes are summarized in Table 1, and selected bond distances and angles are given in Table 2. ORTEP Plots of **1** ~ **3** are depicted in Figs. 1 ~ 3. In all instances, the rhodium atoms displays a square-planar geometry with a **P~N** chelation. All P-Rh and N-Rh distances in the range of 2.0 ~ 2.3 Å and 2.11 ~ 2.14 Å respectively lie within the normal range. The C=N distances are in a narrow range of 1.276(8) ~ 1.288(3) Å. The angles of P-Rh-N in the chelating ring of P-Rh-N-C9-C14 in all complexes lie in the range 78.6 ~ 81.9°, which is deviated form the standard square-planar geomerty, presumably due to the limitation of the *o*-phenylene backbone (C9-C14). In complex **2**, the carbonyl ligand is *trans* to the imine moiety. The formation of single isomer indicates that the **P~N** ligand exhibits a ground-state selectivity to the stereoselectivity. Similar selectivity is also observed in **1** of which only the *cis* form is obtained.

Table 2. Selected Bond Distances (Å) and Angles (deg)

Complex	1	2	3
Rh-P	2.204(2)	2.2111(8)	2.2716(7)
Rh-P1	2.206(2)		
Rh-N	2.134(5)	2.129(2)	2.111(2)
Rh-N1	2.143(5)		
Rh-C1	-	1.807(3)	-
N-C2	1.276(8)	1.286(4)	1.288(3)
C1-O	-	1.145(4)	-
P-Rh-N	81.9(2)	80.27(7)	78.63(6)
P-Rh-P1	102.26(6)	-	-
P-Rh-C1	-	94.4(1)	
N-Rh-C1	-	174.4(1)	

Polymerization of Phenylacetylene

The catalytic activity in phenylacetylene polymerization of the prepared phosphine-imine rhodium(I) complexes has been preliminarily examined. In a typical experiment, a round-bottom flask (25 mL) charged with catalyst (0.01

Table 1. Crystal Data of Rhodium Complexes **1** ~ **3**

	1	2	3
Formula	$C_{59.33}H_{54.67}Cl_{4.67}N_2P_2Rh_2$	$C_{27}H_{22}Cl_3NOPRh$	$C_{33}H_{32}BF_4NPRh$
Diffractometer	Bruker SMART	Nonius CAD4	Nonius CAD4
Fw	1228.91	616.69	663.29
T	295K	295K	295K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	monoclinic	triclinic	triclinic
Space group	C2/c	P1-	P1-
a, Å	40.593(1)	10.009(2)	9.926(1)
b, Å	21.4176(7)	10.724(2)	10.006(2)
c, Å	19.1768(6)	12.371(3)	15.587(2)
α,°	90	91.36(3)	92.68(1)
β,°	99.560(1)	102.24(3)	98.92(1)
γ,°	90	92.28(3)	106.61(1)
V, $Å^3$	16440.9(9)	1295.9(4)	1458.7(4)
Z	12	2	2
D_{calcd}, Mg/m^3	1.489	1.580	1.510
F(000)	7488	620	676
Crystal size	0.22 × 0.12 × 0.05	0.35 × 0.35 × 0.30	0.50 × 0.36 × 0.20
θ range	1.02 ~ 25.00	1.69 ~ 24.97	2.13 ~ 27.50
Refln Collected	36708	4551	6696
Independent refln.	14149 (R_{int} = 0.0645)	4551 (R_{int} = 0.0000)	6696 (R_{int} = 0.0000)
Refined method	Full-matrix least-squares on F^2		
R [I > 2σ(I)]	R_1 = 0.0807 wR_2 = 0.1227	R_1 = 0.0255 wR_2 = 0.0836	R_1 = 0.0319 wR_2 = 0.0915

mmol) was evacuated and flushed with nitrogen for several times, then phenylacetylene along with solvent was added. The reaction was carried out at 30 °C for 12 h and a polymer was isolated as an orange solid by filtration. It was found that only complex **3** shows its catalytic activity to the polymerization of phenylacetylene, whereas complexes **1** and **2** appear no activity at all.

As summarized in the Table 3, the catalytic activity of complex **3** depends on the solvent. In tetrahydrofuran or methanol, polymerization undergoes with moderate conversion. In contrast, no polymerization occurs in dichloromethane and acetonitrile, which are good solvents for dissolving the catalyst. It is noticed that the water can also serve as the medium for polymerization, giving moderate yield, although the complex and the polymer are not soluble in water. The mixed solvent of methanol/water or dimethylformamide/water provides moderate to excellent conversion to the polymers (entry 11 and 17). It has been reported that water-soluble rhodium complexes can be excellent catalysts for polymerization of phenylacetylene in water.[9] The mixed solvent for a better conversion is presumably that the dissolved rhodium complexes could be feasibly activated. The selectivity of *cis*-stereochemistry inclined to the polymers is observed in all instances. It seems that there is no obvious correlation of the stereo-regularity of polyphenylacetylene with the solvent systems. In mixed solvents, the selectivity of stereo-regularity for the polymer is generally lower than the selectivity run in a single solvent. It suggests that the true catalysts might be different in different solvents.

In this work, we have reported the synthesis and structural characterization of the phosphine-imine (**P~N**) rhodium(I) complexes. One of the rhodium(I) complexes, that contains a **P~N** and a COD ligands is an effective catalyst for polyphenylacetylene formation. Aqueous medium serves a good reaction enviornment and provides a convenient way of separation for the polymers from the reaction mixture.

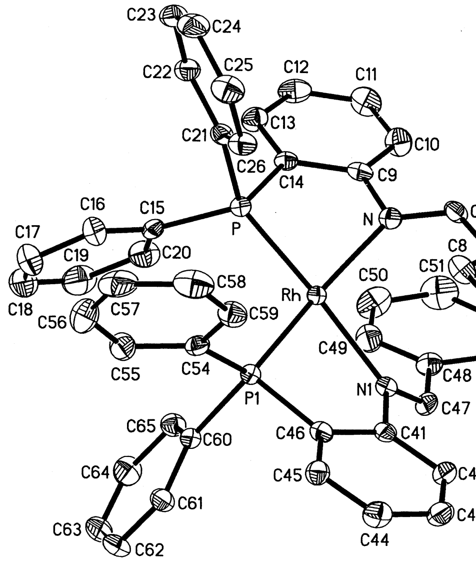


Fig. 1. ORTEP plot of the cationic portion of **1.**

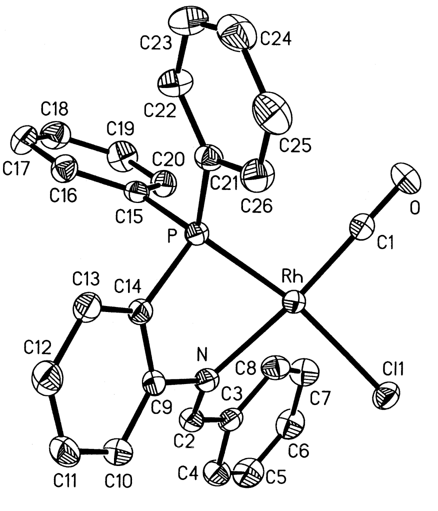


Fig. 2. ORTEP plot of **2**.

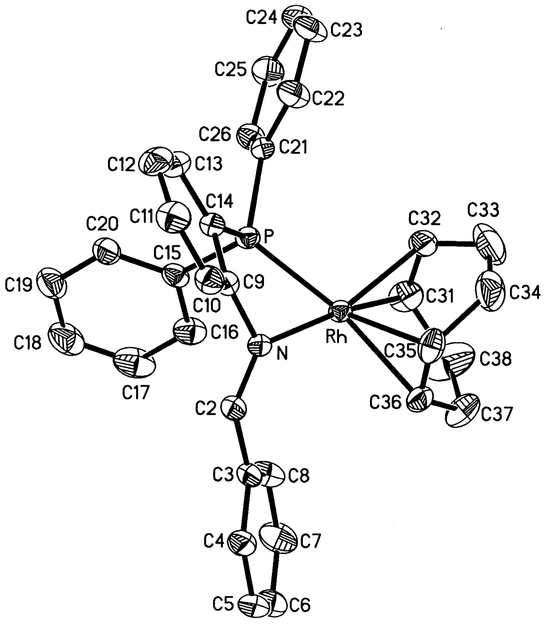


Fig. 3. ORTEP drawing of cationic portion of **3**.

Table 3. Polymerization of Phenylacetylene Catalyzed by Rhodium(I) Complex **3**

Entry	monomer	solvent	time	Conv.	M_N	PDI	Ratio of *cis*
1	10 mmol	THF	12 h	30%	26318	2.24	98
2	10 mmol	CH_2Cl_2	12 h	trace	-	-	-
3	10 mmol	CH_3CN	12 h	trace	-	-	-
4	10 mmol	MeOH	12 h	27%	29765	2.10	96
5	10 mmol	MeOH	72 h	37%	26851	2.04	80
6	10 mmol	Neat	24 h	20%	1800	2.57	41
7	10 mmol	H_2O	12 h	40%	16434	2.54	82
8	10 mmol	H_2O	24 h	47%	18882	2.41	91
9	20 mmol	H_2O	24 h	42%	10542	2.25	66
10	10 mmol	MeOH/ H_2O (9/1)	24 h	46%	26318	2.24	98
11	10 mmol	MeOH/ H_2O (1/1)	24 h	80%	27624	2.76	80
12	10 mmol	MeOH/ H_2O (3/7)	24 h	49%	13646	2.54	67
13	10 mmol	^{i}PrOH/ H_2O (1/1)	24 h	21%	19816	3.64	61
14	10 mmol	^{t}BuOH/ H_2O (1/1)	24 h	51%	27286	2.91	58
15	10 mmol	^{t}BuOH/ H_2O (1/1)	12 h	50%	18880	4.43	70
16	10 mmol	DMF/ H_2O (2/3)	24 h	70%	29938	1.99	74
17	10 mmol	DMF/ H_2O (1/1)	24 h	72%	39388	2.15	91
18	10 mmol	DEA/ H_2O (1/1)	24 h	20%	33269	2.47	50

PDI = M_w/M_N; DEA = diethylamine.

EXPERIMENTAL SECTION

General Information

Solvents were dried by standard procedures. IR spectra were recorded on a Bio-Rad FTS-40 spectrophotometer. The NMR spectra were recorded on a Bruker ACE-200 or a ACE-300 spectrometer. For the ^{31}P NMR spectra, the spectrometer frequency at 81.015 MHz or 121.49 MHz was employed and chemical shifts are given in ppm relative to 85% H_3PO_4 in $CDCl_3$. Values upfield of the standard are defined as negative. The corresponding frequencies for ^{13}C NMR spectra were at 50.32 MHz or 75.47 MHz for respective spectrometers.

Complex 1

$[Rh(COD)Cl]_2$ (100 mg, 0.2 mmol) and **P~N** ligand (150 mg, 0.41 mmol) were dissolved in 5 mL of THF and the resulting yellow-orange solution stirred under nitrogen at room temperature. After 10 min there was an orange-red suspension formed. Stirring continued for 1 h, whereupon more solid formation was observed. The resulting mixture was evaporated and washed with ether and dried under vacuum (180 mg, 90%). ^{1}H NMR ($CDCl_3$): δ 1.15 (s, 4H), 2.36 (s, 4H), 4.19 (s, 4H), 6.93-7.51 (m, 34H), 8.40 (s, 2H), 8.60 (d, 4H, *J* = 7.3 Hz); ^{31}P NMR ($CDCl_3$): δ 51.8 ($J_{Rh\text{-}P}$ = 169 Hz). Anal. Calcd for $C_{58}H_{52}N_2Cl_2P_2Rh_2$ (1115.74): C, 62.43; H, 4.70; N, 2.51. Found: C, 62.23; H, 4.59; N, 2.56.

Complex 2

$[Rh(COD)Cl]_2$ (100 mg, 0.2 mmol) and **P~N** ligand (150 mg, 0.41 mmol) were dissolved in 5 mL of THF under CO atmosphere. The resulting light yellow-orange solution was stirred at room temperature. After 10 min there was a yellow solid formation. Stirring continued for 1 h, whereupon more solid formation was observed. The resulting mixture was evaporated and washed with ether and dried under vacuum (200 mg, 92%). IR (KBr): 1986 (C≡O), 1606 (C=N); ^{1}H NMR ($CDCl_3$): δ 7.11-7.69 (m, 17H), 8.62 (m, 3H); ^{31}P NMR ($CDCl_3$): δ 54.2 ($J_{Rh\text{-}P}$ = 167 Hz). Anal. Calcd for $C_{26}H_{20}NClOPRh$: C, 58.72; H, 3.79; N, 2.63. Found: C, 58.58; H, 3.92; N, 2.49.

Complex 3

$[Rh(COD)Cl]_2$ (100 mg, 0.2 mmol) and **P~N** ligand (150 mg, 0.41 mmol) were dissolved in 5 mL of THF under nitrogen atmosphere. 76 mg (0.2 mmol) of $AgBF_4$ dissolved in 2 mL of acetonitrile was added immediately to the above reaction mixture and stirred at room temperature for 30 min. AgCl precipitate was filtered and the orange-yellow solution was evaporated to dryness and washed with ether, which resulted in a yellow solid (220 mg, 83%). IR (KBr): 1606 (C=N). ^{1}H NMR ($CDCl_3$); δ 1.94 (s, 2H), 2.13 (s, 4H), 2.42 (s, 2H), 4.17 (s, 2H), 4.64 (s, 2H), 7.20-8.04 (m, 17H), 8.69 (d, 2H), 8.87 (s, 1H); ^{31}P NMR ($CDCl_3$): δ 34.7 ($J_{Rh\text{-}P}$ = 154 Hz). Anal. Calcd for $C_{33}H_{32}NPBF_4Rh$ (663.3): C, 59.75; H, 4.86;

N, 2.11. Found: C, 59.68; H, 4.91; N, 2.06. FABMS: 576.1 (M^+).

Polymerization of Phenylacetylene

To a 25 mL round-bottom flask was charged with rhodium catalyst (0.01 mmol), which was evacuated and flashed with nitrogen three times. Solvent (10 mL) was added with stirring to dissolve the catalyst and then phenylacetylene (1.1 mL, 10 mml) was injected through septum. The reaction flask was immersed into a water bath, which was kept at 30 °C. After reaction was stopped, the polymer was filtered and re-dissolved in dichloromethane and precipitated by addition into methanol. All results are summarized in Table 3.

ACKNOWLEDGMENT

We thank the National Science Council, Taiwan, R.O.C. for the financial support (NSC89-2113-M002-070).

Supporting Information Available

Complete description of the X-ray crystallographic structure determination of **1**, **2**, and **3** including ORTEP plot of all complexes, atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles (27 pages) are available from the corresponding authors.

Received September 6, 2001.

Key Words

Rhodium; Polymerization; Phenylacetylene; Alkyne; Aqueous medium.

REFERENCES

1. For recent reviews: (a) Tang, B. Z.; Xu, K.; Sun, Q.; Lee, P. P. S.; Peng, H.; Salhi, F.; Dong, Y. In *Transition Metal Catalysis in Macromolecular Design*; Bofa, L. S.; Novak, B. M., Eds.; American Chemical Society: Washington, DC, 2000; Chapter 9, p 146. (b) Ehrlich, P.; Anderson, W. A. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1, Chapter 12, p 441.
2. Kreiter, C. G. *Adv. Organomet. Chem.* **1986**, *26*, 297.
3. (a) Shivasubramanian, V.; Sundarajan, G. *J. Mol. Catal.* **1991**, *65*, 205. (b) Ganasamoorthy, S.; Sundarajan, G. *Macromolecules* **1992**, *25*, 2060. (c) Anatharaj, T. A.; Sundarajan, G. *Organometallics* **1997**, *16*, 4940.
4. (a) Teraguchi, M.; Masuda, T.; Hachisuka, H. *J. Macromol. Sci., Pure Appl. Chem.* **2000**, *A37*, 1173. (b) Miyake, M.; Misumi, Y.; Masuda, T. *Macromolecules* **2000**, *33*, 6636. (c) Kwak, G.; Masuda, T. *Macromolecules* **2000**, *33*, 6633. (d) Hayano, S.; Masuda, T. *J. Macromol. Sci., Pure Appl. Chem.* **2000**, *A*37, 853, and references therein.
5. Recent examples of TM catalyzed polymerization of phenylacetylene (a) Mula, M. B.; Beaumont, A. J.; Doyle, K. O.; Gallagher, M. L.; Rooney, A. D. *J. Mol. Catal. A*: *Chem.* **1999**, *148*, 23. (b) Yao, J.; Wong, W. T.; Jia, G. *J. Organomet. Chem.* **2000**, *598*, 228. (c) Douglas, W. E. *J. Chem. Soc., Dalton Trans.* (*1*) **2000**, 57. (d) Matusiak, R.; Keller, A. *Polym. Bull. (Berlin)* **1999**, *43*, 199.
6. Rh complexes for polyemrization of alkynes: (a) Furlani, A.; Napoletano, C.; Russo, M. V.; Feast, W. *J. Polym. Bull.* **1986**, *16*, 311. (b) Furlani, A.; Licoccia, S.; Russo, M. V.; Camus, A.; Marsich, N. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 991. (c) Furlani, A.; Napoletano, C.; Russo, M. V.; Camus, A.; Marsich, N. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 75. (d) Tabata, M.; Yang, W.; Yokota, K. *Polym. J.* **1990**, *22*, 1105. (e) Haupt, H.-J.; Ortmann, U. Z. *Anorg. Allg. Chem.* **1993**, *619*, 1209. (f) Goldberg, Y.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1994**, 1209. (g) Lee, S.-I.; Shim, S.-C.; Kim, T.-J. *J. Polym. Sci. Part A, Polym. Chem.* **1996**, *24*, 2377.
7. (a) Schrock, R. R.; Luo, S.; Zanetti, N. C.; Fox, H. H. *Organometallics* **1994**, *13*, 3396. (b) Schrock, R. R.; Luo, S.; Lee, J. C., Jr.; Zanetti, N. C.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3883, and references therein.
8. Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Kainosho, M.; Ono, A.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1999**, *121*, 12035.
9. (a) Cheuk, K. K. L.; Lam, J. W. Y.; Cha, J. A. K.; Sun, Q.; Tang, B. Z. *Polym. Prepr.* **2000**, *41*, 981. (b) Xu, K.; Peng, H.; Lam, J. W. Y.; Poon, T. W. H.; Dong, Y.; Xu, H.; Sun, Q.; Cheuk, K. K. L.; Salhi, F.; Lee, P. P. S.; Tang, B. Z. *Macromolecules* **2000**, *33*, 6918. (c) Cheuk, K. K. L.; Lam, J. W. Y.; Tang, B. Z. *Polym. Mater. Sci. Eng.* **2000**, *82*, 56. (d) Sun, Q.; Xu, K.; Fouad, S.; Dong, Y.; Tang, B. Z. *Polym. Mater. Sci. Eng.* **2000**, *82*, 111. (e) Lam, J. W. Y.; Ngai, L. Y.; Poon, T. W. H.; Lin, Z.; Tang, B. Z. *Polym. Prepr.* **2000**, *41*, 289. (f) Tang, B. Z.; Poon, W. H.; Leung, S. M.; Leung, W. H.; Peng, H *Macromolecules* **1997**, *30*, 2209.

10. (a) Reddy, K. R.; Chen, C.-L.; Liu, Y.-H.; Peng, S.-M. Chen, J.-T.; Liu, S.-T. *Organometallic* **1999**, *18*, 2574. (b) Reddy, K. R.; Surekha, K.; Lee, G.-H.; Peng, S.-M.; Chen, J.-T.; Liu, S.-T. *Organometallics* **2001**, *20*, 1285.
11. (a) Wang, H.-E. Ph. D. Thesis, National Taiwan University, June 1991. (b) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397. (c) Messmer, G. G.; Amma, E. L.; Ibers, J. A. *Inorg. Chem.* **1980**, *19*, 2437.