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Preparation of a palladium dimer with a cobalt-containing bulky phosphine ligand: Its application in palladium catalyzed Suzuki reactions

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Abstract

A palladium dimer with a cobalt-containing phosphine ligand, $\{(\mu-PPh_2CH_2PPh_2)Co_2(CO)_4(\mu,\eta-(tBu)_2PC\equiv CC_6H_4-\kappa C^1)Pd(\mu-Cl)\}_2$ (3), was prepared from the reaction of its monomer precursor, $(\mu-PPh_2CH_2PPh_2)Co_2(CO)_4(\mu,\eta-(tBu)_2PC\equiv CC_6H_4-\kappa C^1)Pd(\mu-OAc)$ (2), with LiCl. The crystal structure of 3, determined by X-ray diffraction methods, revealed a doubly chloride-bridged palladium dimeric conformation. Suzuki coupling reactions of bromobenzene with phenylboronic acid were carried out catalytically using these two novel palladium complexes 2 and 3 as catalyst precursors. Factors such as the molar ratio of substrate/catalyst, reaction temperature, base and solvent that might affect the catalytic efficiencies were investigated. As a general rule, the performance is much better by employing 3 than 2 as the catalyst precursor.

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Keywords: Palladium dimer; Suzuki reaction; Transition-metal containing phosphine ligand; Orthometallation

1. Introduction

For the past few decades, phosphines have been proven to be the most versatile and commonly employed ligands in transition metal-catalyzed reactions [1]. Lately, due to their bulkiness, metal-containing phosphines, rather than the conventional organic phosphines, have received increasing interest from experimentalists [2]. Among all the metal-containing bidentate phosphine ligands, bis(diphenylphosphino)ferrocene (dppf) and its derivatives are probably the most well known [3]. Recently, the authors have been involved in developing a new category of metal-containing phosphine ligands. A series of cobalt-containing (mono- or bidentate) phosphine ligands (μ -PPh₂-CH₂PPh₂)Co₂(CO)₄(μ , η -R¹C \equiv CR²) {R¹, R²: P(*t*-Bu)₂, P(*i*-Pr)₂, PCy₂, PPh₂, Ph, py} were prepared (Scheme 1). These types of ligands lead directly to a class of phosphines having bulky and hopefully electron-rich character. Their efficiencies as assisting ligands in palladium-catalyzed Suzuki and amination reactions have been carefully evaluated [4,5]. Generally speaking, the catalytic efficiencies with monodentate phosphines are higher than with bidentate ones.

Our previous work had demonstrated that amination reactions of arylbromides and morpholine could be carried employing $(\mu$ -PPh₂CH₂PPh₂)Co₂(CO)₄(μ , η out by $(tBu)_2PC \equiv CPh)$ (1)-modified Pd(OAc)₂ complex as catalyst precursor. The reactions were carried out at various conditions and with satisfactory results. Meanwhile, a unique palladium complex 2, $(\mu - PPh_2CH_2PPh_2)Co_2(CO)_4$ - $(\mu, \eta - (tBu)_2 PC \equiv CC_6 H_4 - \kappa C^1) Pd(\mu - OAc)$, was prepared from the reaction of the cobalt-containing bulky phosphine 1 with Pd(OAc)₂ (Scheme 2) [5]. As disclosed by its crystal structure, during the formation of 2 a process of orthometallation occurred accompanied by the release of one equivalent of acetic acid. For comparison, amination reactions of aryl bromides and morpholine employing in situ

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Scheme 2.

Table 1 Crystal data of 3

prepared $1/Pd(OAc)_2$ and 2 were carried out. In general, complex 2 results in lower efficiency compared with that of in situ prepared $1/Pd(OAc)_2$.

It is well-known that halide-coordinated palladium complexes such as $[(\eta^4 - C_4 Ph_4)PdBr_2]_2$ are always present in dimeric form with two bridging halides [6]. The bonding of the chelating acetate toward palladium atom in 2 is seemingly weak resulting in replacement by a stronger ligand such as halide. It leads naturally to an energetically favorable form, a dimeric complex. Herein, we report the preparation of a new unusually large sized palladium dimeric compound and its catalytic activity in Suzuki reactions.

2. Results and discussion

2.1. Preparation and characterization of a palladium dimer 3

A new and unusually large-sized palladium dimeric compound, {(μ -PPh₂CH₂PPh₂)Co₂(CO)₄(μ ,n-(*t*Bu)₂PC= $CC_6H_4-\kappa C^1)Pd(\mu-Cl)$ (3), was obtained in good yield from the treatment of 2 with LiCl in toluene at 25 °C for 72 h (Scheme 3).

The identity of **3** was confirmed by spectroscopic means as well as X-ray diffraction methods (Table 1). Interestingly, the spectroscopic data of 3 exhibit two distinct sets of signals for its constructed units, (µ-PPh₂CH₂PPh₂)Co₂- $(CO)_4(\mu,\eta-(tBu)_2PC \equiv CC_6H_4-\kappa C^1)$. These two components are not magnetically equivalent. In ¹H NMR, two sets of doublets appear at 8.52 and 8.69 ppm, which correspond to the adjacent protons of the orthomatallated arene. Another two sets of multiplets signals observed at 3.34



•	
Compound	3
Formula	C45H44ClCo2O4P3Pd
Formula weight	1001.42
Crystal system	monoclinic
Space group	C2/c
a (Å)	28.1956(18)
b (Å)	26.0181(16)
<i>c</i> (Å)	18.2245(11)
α (°)	
β (°)	128.0030(10)
γ (°)	
$V(\text{\AA}^3)$	10534.8(11)
Ζ	8
$D_{\rm c} ({\rm Mg/m^3})$	1.263
λ (Mo Kα, Å)	0.71073
$\mu (\mathrm{mm}^{-1})$	1.136
θ Range (°)	1.36-26.05
Observed reflections $(F \ge 4\sigma(F))$	10370
Number of refined parameters	485
$R_1^{\rm a}$ for significant reflections	0.0526
$wR_2^{\rm b}$ for significant reflections	0.1624

^a $R_1 = |\sum (|F_o| - |F_c|)/|\sum F_o||.$

Goodness-of-fit^c

0.997

^b $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2 / \sum [w(F_o^2)^2]\}^{1/2}; w = 0.1015 \text{ for } 3.$ ^c Goodness-of-fit = $[\sum w(F_o^2 - F_c^2)^2 / (N_{\text{reflections}} - N_{\text{parameters}})]^{1/2}.$

and 3.50 ppm are assigned to two distinct sets of methylene protons of **3**. The ³¹P NMR spectrum displays two sets of singlets at 82.87 and 84.40 ppm assigned to two phosphorous atoms coordinated to Pd. In addition, two sets of multiplets at 38.00 and 41.43 ppm correspond to the coordinated dppm ligand. The ¹³C NMR data also support the account that the two constructed components of 3 are not in the same magnetical environment. The ORTEP diagram for 3 is depicted in Fig. 1. As shown, it is a doubly chloridebridged palladium dimer. The original chelating acetate ligand was removed from 2. The four atoms, Pd_2Cl_2 , are arranged in a diamond shape and almost coplanar. The conformation of the rest of the dimer is almost unaltered from its counterpart in 2. Two isomeric forms of 3 might



Fig. 1. ORTEP drawing of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)-C(3) 2.013(7); Pd(1)-P(1) 2.2690(19); Pd(1)-C(1) 2.4329(18); Pd(1)-Cl(1)#1 2.4512(19); Co(1)-C(2) 1.960(6); Co(1)-C(1) 1.998(7); Co(1)-P(2) 2.239(2); Co(1)-Co(2) 2.4770(13); Co(2)-C(2) 1.956(7); Co(2)-C(1) 1.959(7); Co(2)-P(3) 2.208(2); P(1)-C(1) 1.793(8); P(2)-C(45) 1.827(7); P(3)-C(45) 1.831(7); Cl(1)-Pd(1)#1 2.4512(19); C(1)-C(2) 1.362(9); C(2)-C(4) 1.461(10); C(3)-Pd(1)-P(1) 89.41(19); C(3)-Pd(1)-Cl(1) 90.42(19); P(1)-Pd(1)-Cl(1) 170.10(8); C(3)-Pd(1)-Cl(1)#1 164.9(2); P(1)-Pd(1)-Cl(1)#1 100.45(7); Cl(1)-Pd(1)-Cl(1)#1 81.83(7) and C(2)-Co(1)-C(1) 40.3(3); C(2)-Co(2)-C(1) 40.7(3); C(1)-P(1)-Pd(1) 104.3(2); Pd(1)-Cl(1)-Pd(1)#1 96.60(7); C(2)-C(1)-P(1) 123.2(5); C(2)-C(1)-Co(2) 69.5(4); C(2)-C(1)-Co(1) 68.4(4); Co(2)-C(1)-Co(1) 77.5(3); C(1)-C(2)-C(4) 128.8(7); Co(2)-C(2)-Co(1) 78.5(3); P(2)-C(45)-P(3) 110.8(4).

be presented in solution. Crystal structure of **3** only represents one of the two isomeric forms.

The authors have previously reported the preparation of a novel palladium complex *cis*-dichloride(1,2-bis(diphenylphosphino)vinyl-P,P',C)palladium(II)–(bis(diphenylphosphino)methane-P,P')cobaltacarbonyl (5). It was obtained from the treatment of $(\mu$ -Ph₂PCH₂PPh₂)Co₂(CO)₄-((μ , η -Ph₂PC \equiv CPPh₂)- κ^2 P,P')PdCl₂ (4) with hydrochloric acid (Scheme 4) [7]. This complex can be regarded as an unique derivative of the well known compound, PdCl₂(dppe) [8]. Nevertheless, there was no sign of forming a doubly chloride-bridged palladium dimer **6** from the reaction of **4** with LiCl.

2.2. Suzuki reactions using 2

Palladium-catalyzed Suzuki reactions of bromobenzenes with phenylboronic acid were carried out by employing **2** as a catalyst precursor (Scheme 5). The general procedures for the catalytic reactions under investigation are described as follows. A suitable Schlenk tube was charged with 1.0 mmol of bromobenzene, 1.5 mmol of phenylboronic acid, 1.0 ml THF, 3.0 mmol KF and 1.0 mol% of **2**. The reaction mixture was stirred at $60 \,^{\circ}\text{C}$ for 3–19 h followed by a work-up (Diagram 1). A satisfactory result was obtained only when the reaction time was 19 h.







Subsequently, the impact of various solvents used in the reaction was evaluated. As shown, the reaction rate is greatly affected by the kind of solvent used (Table 2). For instance, the coupling reaction was ineffective when DMF was used (entry 4). However, the yield was greatly improved when 1,4-dioxane was employed as solvent (entry 5).

It is well-known that the choice of a base is crucial to the success of a palladium-catalyzed Suzuki reaction [9]. Therefore, the influences of the bases used on the reactions were examined (Table 3). As shown, excellent yields were observed when alkaline metal fluorides such as KF and CsF (entries 1and 2) as well as NaO'Bu and K₃PO₄ (entries 4 and 6) were used as bases. The yields were lower when NaOH and K₂CO₃ were employed as bases under the same reaction condition (entries 3 and 5). Amine derived bases such as morpholine, NEt₃ and piperidine failed to promote the reactions resulting in very low yields (entries 7–9).

Table 2		
Suzuki coupling reactions	employing 2 in	various solvents ^a

Entry	ntry Solvent	
1	THF	82.7°
2	toluene	43.1 ^b
3	DME	78.2 ^b
4	DMF	25.9 ^b
5	1,4-dioxane	93.7 ^b
6	CH ₃ CN	68.4 ^b
7	H ₂ O	48.3 ^{b,e}

^a Condition: 1.0 mmol bromobenzene, 1.5 mmol phenylboronic acid, 1.0 mol% 2, 1.0 ml solvent, 3.0 mmol KF, 60 °C, 19 h.

^b Isolated vield.

^c Determined by GC.

^d Average of two runs.

e 0.2 mmol TBAB added.

Table 3	
Suzuki coupling reactions employing 2 with various bases	s ^a

Entry	Base	Yield (%) ^b
1	KF	93.7
2	CsF	99.7
3	NaOH	75.9
4	NaO'Bu	99.2
5	K ₂ CO ₃	82.7
6	K ₃ PO ₄	96.7
7	morpholine	3.1
8	NEt ₃	31.5
9	piperidine	7.2

^a Condition: 1.0 mmol bromobenzene, 1.5 mmol phenylboronic acid, 1.0 mol% 2, 1.0 ml 1,4-dioxane, 3.0 mmol base, 60 °C, 19 h.

^b Isolated yield; average of two runs.

2.3. Suzuki reactions using 3

For comparison, the same Suzuki reactions were carried out by employing 3 as the catalyst precursor. The general procedures for the catalytic reactions under investigation are described as follows. A suitable Schlenk tube was charged with 1.0 mmol of bromobenzene, 1.5 mmol of phenylboronic acid, 1.0 ml THF, 3.0 mmol KF and 0.5 mol% of **3**. The reaction mixture was stirred at 60 °C for 3–9 h followed by a work-up. As shown in Diagram 1, the catalytic efficiencies were much better than in the

Table 4

a 1.		•			•	-	•	•			
Suzuki	cound	ınσ	reactions	empl	oving	- 4	1n	various	SO	vent	í S
Juluni	coup		reactions	empi	io jing	-		(arroub	50		~~

Entry	Solvent	Yield (%) ^d
1	THF	85.1 ^b
2	toluene	62.5 ^c
3	DME	16.2 ^c
4	DMF	31.0 ^c
5	1,4-dioxane	94.8 ^c
6	CH ₃ CN	38.9 ^c
7	H ₂ O	52.9 ^{c,e}

^a Condition: 1.0 mmol bromobenzene, 1.5 mmol phenylboronic acid, 0.5 mol% 3, 3.0 mmol KF, 60 °C, 1.0 ml solvent, 6 h.

^b Determined by GC.

^c Isolated yield.

^d Average of two runs.

^e 0.2 mmol TBAB added.

Table 5	
Suzuki coupling reaction employing 3 with various bases ^a	

Entry	Base	Yield ^b
1	KF	94.8
2	CsF	99.1
3	K ₃ PO ₄	25.9
4	K ₂ CO ₃	30.1
5	NaOH	36.6
6	NaOt-Bu	55.9
7	morpholine	23.3
8	NEt ₃	19.8
9	piperidine	4.1

^a Condition: 1.0 mmol bromobenzene, 1.5 mmol phenylboronic acid,

0.5 mol% 3, 3.0 mmol base, 60 °C, 1.0 ml 1,4-dioxane, 6 h.

^b Isolated yield; average of two runs.

Table 6 Suzuki coupling reactions under various substrate/3 ratios^a

Entry	3 (mmol%)	Yield (%) ^b
1	0.5	99.1
2	0.25	97.3
3	0.1	91.2
4	0.05	85.9

 $^{\rm a}$ Condition: 1.0 mmol bromobenzene, 1.5 mmol phenylboronic acid, 3.0 mmol CsF, 60 °C, 1.0 ml 1,4-dioxane, 6 h.

^b Isolated yield; average of two runs.

previous case when 2 was employed. With 3 it takes a shorter reaction time to reach the same conversion. As known, the halide bridging bond is intrinsically weak in dimer. It is ready to break and form an unsaturated palladium monomer. The latter is presumably an active species that promptly accepts the oncoming substrate(s) for further catalytic reaction.

The effect of the solvent used was evaluated as well (Table 4). The procedures for Suzuki reactions were the

Table 7 Suzuki coupling reactions employing **3** under various substrate^a

Entry	Subtract	Temperatue (°C)	Yield (%) ^b
1		50	83.9
	Br	60	89.7
2		50	14.7
	H ₃ CO—Br	60	62.8
3		50	17.7
	H ₃ C—Br	60	71.5
4	СЦ	50	2.5
•	CH ₃	60	50.3
	Br		
5		50	4.4
	N Br	60	40.1
6	0	50	83.1
	Br	60	91.2
7	0	50	87.3
	Br	60	95.1
8	0	50	87.9
0	l l	60	96.8
	Br		

^a Conditions: 1.00 mmol phenylbromide, 1.50 mmol phenylboronic acid, 3.00 equiv. CsF, 0.05 mol% 3, 1.0 mL 1,4-dioxane, 5 h, 50 °C.

^b Averaged by two runs; isolated yield.

same as previously mentioned. Again, the best yield was observed using 1,4-dioxane as a solvent (entry 5). It is in accord with the previous case (Table 2).

The influences of the bases used on the reactions were examined next (Table 5). As shown, excellent yields were observed when alkaline metal fluorides KF and CsF were used as bases (entries 1 and 2). Other bases, especially amines, were much less effective (entries 3–9).

The Suzuki coupling reactions with various substrate/ catalyst loading ratios (0.5-0.05 mol% 3) were also examined (Table 6). A reasonable yield was achieved even when 0.05 mol% 3 was employed.

The following table shows the results from the 3-assisted Suzuki cross-coupling reactions (Table 7). The catalytic performance was good for the substrate with electron-with-drawing group (entries 6–8). Nevertheless, the efficiency was low for the substrate with electron-donating group (entries 2 and 3). It is consistent with the general observation for the palladium-catalyzed Suzuki reaction.

3. Concluding remarks

We have demonstrated that the Suzuki reactions of aryl bromides with phenylboronic acid could be carried out catalytically with two novel palladium complexes 2 and 3. The catalytic performance is better with 3 probably due to its readiness to form the unsaturated active monomer.

4. Experimental

4.1. General

All manipulations were carried out under a dry nitrogen atmosphere. All solvents including deuterated solvents were purified before use. All separations of the products were performed by Centrifugal Thin Layer Chromatography (CTLC, Chromatotron, Harrison model 8924). ¹H NMR spectra were recorded (Varian VXR-300S spectrometer) at 300.00 MHz; chemical shifts are reported in ppm relative to internal CHCl₃ or CH₂Cl₂. ³¹P and ¹³C NMR spectra were recorded at 121.44 and 75.46 MHz, respectively. Some other routine ¹H NMR spectra were recorded on Gemini-200 spectrometer at 200.00 MHz or Varian-400 spectrometer at 400.00 MHz. Mass spectra were recorded on JOEL JMS-SX/SX 102A GC/MS/MS spectrometer. Elemental analyses were obtained on Heraeus CHN-O-S-Rapid.

4.2. Synthesis of 3

A 100 cm³ round-bottomed flask was charged with 1.00 mmol (1.025 g) (μ -PPh₂CH₂PPh₂)Co₂(CO)₄(μ , η -(*t*Bu)₂PC=CC₆H₄- κ C¹)Pd(μ -OAc) **2** and one molar equivalent of LiCl (0.0424 g) as well as 15 ml of toluene. The mixture was stirred at 25 °C for 72 h. Subsequently, purification of products using centrifugal thin-layer chromatography (CTLC) was carried out. The first band, brown in color, was eluted out by a mixture solvent of CH₂Cl₂/ethyl acetate (10/1). It was identified as the title compound { $(\mu$ -PPh₂CH₂PPh₂)Co₂(CO)₄(μ , η -(*t*Bu)₂PC \equiv CC₆H₄- κ C¹)Pd(μ -Cl) $_2$ (**3**). The yield of **3** is 75% (0.1503 g, 0.750 mmol).

3: ¹H NMR (C₆D₆, δ /ppm): 1.37 (t, $J_{P-H} = 30.0$, 36H, -C(CH₃)₃), 3.34, 3.50 (m, 2H, dppm), 6.71–7.46 (m, 46H, arene), 8.52 (d, $J_{H-H} = 6.8$, 1H, *o*-hydrogen of the orthometallated arene), 8.69 (d, $J_{H-H} = 7.2$, 1H, *o*-hydrogen of the orthometallated arene); ¹³C NMR (C₆D₆, δ /ppm): 30.5 (d, 12C, C(CH₃)₃), 39.0 (d, 4C, C(CH₃)₃), 40.8 (s, 2C, CH₂), 73.8 (d, 4C, PhC=CP(*t*-Bu)₂), 124.6–146.9 (m, 56C, arene), 146.0 (s, 2C, *ipso* of arene), 158.4 (d, 2C, *ipso* of arene), 202.8–207.0 (m, 8C, CO); ³¹P NMR (C₆D₆, δ /ppm): 38.0 (dd, $J_{P-P} = 109.9$, 2P, dppm), 41.4 (t, $J_{P-P} = 86.1$, 2P, dppm), 82.9 (s, 1P, P(*t*-Bu)₂), 84.4 (s, 1P, P(*t*-Bu)₂). *Anal*. Calc. for 3: C, 41.60; H, 4.07. Found: C, 41.59; H, 4.04%. M.S.: *m*/*z* 696 (M⁺).

4.3. General procedures for the Suzuki cross-coupling reactions

Suzuki cross-coupling reactions were performed according to the following procedures. Complex **3** (10.02 mg, 0.005 mmol), boronic acid (0.183 g, 1.500 mmol) and potassium fluoride (0.174 g, 3.0 mmol) were placed into a 20 ml Schlenk flask. The flask was evacuated and backfilled with nitrogen before adding THF (1 ml) and bromobenzene (0.11 ml, 1.000 mmol). The solution was stirred at 60 °C for 6 h. Subsequently, excess amount of water was added and the product was extracted with ether (2 × 30 ml). The combined organic extracts were dried over anhydrous MgSO₄ and concentrated under vacuum. The crude residue was purified by flash chromatography on silica gel or gas chromatography.

4.4. X-ray crystallographic studies

Suitable crystals of **3** were sealed in thin-walled glass capillaries under nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing ω (width of 0.3° per frame). The absorption correction was based on the symmetry equivalent reflections using sADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package [10]. All non-H atoms were located from successive Fourier maps and the hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms and fixed isotropic parameters were used for H atoms.¹ Crystallographic data of **3** are summarized in Table 1.

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Appendix A. Supplementary data

Crystallographic data for the structural analysis of compound **3** have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 293127. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.07.005.

References

- [1] (a) T.E. Barder, S.D. Walker, J.R. Martinelli, S.L. Buchwald, J. Am. Chem. Soc. 127 (2005) 4685;
 - (b) S.D. Walker, T.E. Barder, J.R. Martinelli, S.L. Buchwald, Angew. Chem., Int. Ed. 43 (2004) 1871;
 - (c) W. Tang, X. Zhang, Chem. Rev. 103 (2003) 3029;
 - (d) Q.-S. Hu, Y. Lu, Z.-Y. Tang, H.-B. Yu, J. Am. Chem. Soc. 125 (2003) 2856;
 - (e) T.E. Pickett, F.X. Roca, C.J. Richards, J. Org. Chem. 68 (2003) 2592;
 - (f) Z.-Y. Tang, Y. Lu, Q.-S. Hu, Org. Lett. 5 (2003) 297;
 - (g) J. Hassan, M. Sévingnon, C. Gozzi, E. Schulz, M. Lemaire, Chem. Rev. 102 (2002) 1359;
 - (h) N. Kataoka, Q. Shelby, J.P. Stambuli, J.F. Hartwig, J. Org. Chem. 67 (2002) 5553;
 - (i) J.G. Planas, J.A. Gladysz, Inorg. Chem. 41 (2002) 6947;
 - (j) N.G. Andersen, B.A. Keay, Chem. Rev. 101 (2001) 997;
 - (k) C.A. Bessel, P. Aggarwal, A.C. Marschilok, K.J. Takeuchi, Chem. Rev. 101 (2001) 1031;
 - (1) A.F. Littke, C. Dai, G.C. Fu, J. Am. Chem. Soc. 122 (2000) 4020; (m) J.F. Hartwig, Angew. Chem., Int. Ed. 37 (1998) 2046;
 - (n) G. Mann, J.F. Hartwig, J. Am. Chem. Soc. 118 (1996) 13109.
- [2] (a) S. Eichenseher, O. Delacroix, K. Kromm, F. Hampel, J.A. Gladysz, Organometallics 24 (2005) 245;
 - (b) O. Delacroix, J.A. Gladysz, Chem. Commun. (2003) 665;
- (c) K. Kromm, F. Hampel, J.A. Gladysz, Organometallics 21 (2002) 4264.
- [3] (a) R.C.J. Atkinson, V.C. Gibson, N.J. Long, Chem. Soc. Rev. 33 (2004) 313;
- (b) T.J. Colacot, Chem. Rev. 103 (2003) 3101.
- [4] (a) F.-E. Hong, Y.-J. Ho, Y.-C. Chang, Y.-L. Huang, J. Organomet. Chem. 690 (2005) 1249;
 - (b) C.-P. Chang, Y.-L. Huang, F.-E. Hong, Tetrahedron 61 (2005) 3835;
 - (c) Y.-C. Chang, F.-E. Hong, Organometallics 24 (2005) 5686;
 - (d) F.-E. Hong, Y.-C. Chang, C.-P. Chang, Y.-L. Huang, Dalton Trans. (2004) 157;
 - (e) F.-E. Hong, Y.-J. Ho, Y.-C. Chang, Y.-C. Lai, Tetrahedron 60 (2004) 2639;
 - (f) F.-E. Hong, C.-P. Chang, Y.-C. Chang, Dalton Trans. (2003) 3892;
 - (g) F.-E. Hong, Y.-C. Lai, Y.-J. Ho, Y.-C. Chang, J. Organomet. Chem. 688 (2003) 161;
 - (h) F.-E. Hong, Y.-C. Chang, R.-E. Chang, S.-C. Chen, B.-T. Ko, Organometallics 21 (2002) 961.
- [5] J.-C. Lee, M.-G. Wang, F.-E. Hong, Eur. J. Inorg. Chem. (2005) 5011.

 $^{^1}$ The hydrogen atoms were ride on carbons or oxygen atoms in their idealized positions and held fixed with the C–H distances of 0.96 Å.

- [6] (a) A.T. Blomquist, P.M. Maitlis, J. Am. Chem. Soc. 84 (1962) 2329;
 (b) P.M. Maitlis, M.L. Games, Can. J. Chem. 42 (1964) 183;
 (c) J. Dupont, C.S. Consorti, J. Spencer, J. Chem. Rev. 105 (2005) 2527;
 (d) M. Prashad, X.Y. Mak, Y. Liu, O. Repic, J. Org. Chem. 68 (2003) 1163;
 - (e) K. Yuan, T.K. Zhang, X.L. Hou, J. Org. Chem. 70 (2005) 6085.
- [7] C.-P. Chang, F.-E. Hong, J. Chin. Chem. Soc. 52 (2005) 1105.
- [8] (a) P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University

Science Books, Mill Valley, CA, 1987 (Chapter 3); (b) R.J. Puddephatt, Chem. Soc. Rev. 12 (1983) 99.

- [9] (a) N. Miyaura, K. Yamada, H. Suginome, A. Suzuki, J. Am. Chem. Soc. 107 (1985) 972;
- (b) G.A. Grasa, A.C. Hillier, S.P. Nolan, Org. Lett. 3 (2001) 1077;
- (c) S.R. Dubbaka, P. Vogel, Org. Lett. 6 (2004) 95.
- [10] G.M. Sheldrick, SHELXTL PLUS User's Manual. Revision 4.1 Nicolet XRD Corporation, Madison, WI, USA, 1991.