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Highly efficient and regioselective couplings of aryl halides to olefins catalyzed by a palladium complex with a hybrid phosphorus-sulfur ligand

David Morales-Morales^{a,*}, Rocío Redón^b, Yifan Zheng^c, Jonathan R. Dilworth^c

^a Instituto de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, Circuito Exterior, Coyoacán, 04510 México ^b Department of Chemistry, University of Hawaii, Honolulu, HI 96822, USA

^c Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK

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Abstract

The novel palladium phosphino-thioether P–S chelate complex, $[PdCl_2{MeSC_6H_4-2-(CH_2PPh_2)}]$ (3) is a highly efficient catalyst for the olefinic coupling of aryl bromo and iodo compounds to olefins under aerobic conditions, leading to more than 10⁶ turnovers for the reactions with bromo and iodo benzenes. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The formation of vinylic C-C bonds from the palladium catalyzed coupling of aryl bromides, iodides, and triflates with alkenes (the Heck reaction) is one of the 'true power tools of contemporary organic synthesis' [1]. However, the reaction has been little utilized industrially due to the instability of the palladium catalysts and the high cost of the aryl starting materials. In hope of expanding the scope of the Heck reaction, a number of recent studies have focused on the development of improved catalysts [2]. Among those, authors have agreed that the structure of the catalyst should be known in order to better understand the effects of the different substituents and chelating ligands have become the standard for several thermally stable complexes [2a,2b,2c,2d,2e,2f,2g]. The same species have also generated a debate, which renders the traditional Pd(0)/Pd(II) cycle to be unlikely in these cases and a new

mechanism involving Pd(IV) intermediates has been suggested [3,2e,2f,2g].

Sulfur containing complexes have not been widely used in catalysis due in part to the assumed tendency of sulfur to act as catalyst poison. This is certainly not the case and recently sulfur-containing species have found application in different catalytic processes such as allylic alkylation, hydroformylation, etc. [4]. Notably the complexes $[PdX{C_6H_3(CH_2SR)_2-2,6}]$ [5] $(X = Cl^-,$ $CF_3CO_2^-$, $R = Bu^t$, Ph) and $[PdCl{C_6H_4(CH_3CHSR)-$ 2]₂ [6] (R = Bu^t, Me) are efficient catalysts for the Heck couplings of iodobenzenes. In recent years hybrid ligands have received much attention due to the possibility of enhanced reactivity by cooperative effects. Thus P-N [7] and P-O [8] ligands have been tested and proved useful for some catalytic transformations. Interestingly, however, P-S hybrid ligands have not been extensively used in catalysis [9]. This is particularly true in the case of the Heck reaction.

We report here that the phosphino-thioether palladium complex **3** is an outstanding catalyst for the Heck reaction under aerobic conditions with turnover numbers of 10^6 even for those cases where aryl bromides are used.

^{*} Corresponding author. Tel.: +52-56-224514; fax: +52-56-162 217.

E-mail address: damor@servidor.unam.mx (D. Morales-Morales).

2. Experimental

2.1. General

All manipulations were carried out using standard Schlenk and glovebox techniques under purified argon. Solvents were degassed and dried using standard procedures. The following were purchased and used without further purification; PdCl₂, 2-bromobenzylbromide, dimethyldisulphide, LiAlH₄, n-BuLi and CDCl₃ (Aldrich). The complex [PdCl₂(COD)] [10] was synthesized by the literature methods. The ¹H NMR spectra were recorded on a Varian Unity Inova 400 spectrometer. Chemical shifts are reported in ppm down field of TMS using the solvent as internal standard (CDCl₃, δ 7.26). ¹³C and ³¹P NMR spectra were recorded with complete proton decoupling and are reported in ppm downfield of TMS with solvent as internal standard (CDCl₃, δ 77.0) and external 85% H₃PO₄, respectively. GC analyzes were carried out in a HP 5890A flame ionization detector (FID) and HP 5890 SERIES II with a 5971A mass selective detector gas chromatographs, and an HP-1 capillary column (25.0 m) from Hewlett-Packard.

2.2. Preparation of BrC_6H_4 -2-(CH_2PPh_2) (1)

Approximately 150 ml of liquid ammonia were condensed into a 500 ml three-necked round bottom flask cooled to -78 °C (dry ice-acetone) and equipped with a dry ice condenser and N2 inlet. Small pieces of sodium (2.6 g) were added to give a deep blue solution. After stirring for 30 min, triphenylphosphine (15 g) was slowly added under vigorous stirring via the open neck of the flask. After 2 h stirring, the cool bath was removed, allowing the ammonia reflux gently turning the color of the solution to a dark orange. The cooling bath was replaced and dry NH₄Br (5.6 g) was slowly added. The stirring was continued for one extra hour to yield a pale orange solution. A degassed solution of BrC_6H_4 -2-(CH₂Br) (14.4 g) in 60 ml of dry, degassed THF was added dropwise discharging the orange coloration. The liquid ammonia was then allowed to evaporate. The resulting white solid was washed with 200 ml of distilled water (vigorously), and then with acetone. Yield 16 g (78%). NMR spectroscopy showed the product to be better than 98% pure and it was used in further steps without further purification. ¹H NMR (400.00 MHz, CDCl₃): $\delta = 7.6-6.50$ (m, 14H, arom.), 3.5 (s, 2H, CH₂PPh₂). ¹³C NMR (100.00 MHz, CDCl₃): $\delta = 127.13 - 138.81$ (m, ArC), 36.78 (d, ${}^{1}J_{PC} = 18.3$ Hz, CH_2PPh_2). ³¹P NMR (161.90 MHz, CDCl₃): $\delta =$ -12.43. Anal. Calc. for C₁₉H₁₆BrP (m/z = 355.21): C, 64.24; H, 4.54. Found: C, 64.32; H, 4.47%.

2.3. Preparation of $MeSC_6H_4$ -2-(CH_2PPh_2) (2)

To a solution of BrC_6H_4 -2-(CH₂PPh₂) (2 g) in 30 ml of dry THF, cooled to -78 °C, was added 2.25 ml of *n*-BuLi (2.5 M in *n*-hexane). The reaction mixture was stirred for 6 h. The resulting dark brown solution was reacted with 1.2 ml of MeS-SMe. The solvent was removed and the residue recrystallized from methanol. Yield 1.5 g (82%). NMR spectroscopy showed the product to be better than 98% pure and it was used in further steps without further purification. ¹H NMR (400.00 MHz, CDCl₃): $\delta = 6.73 - 7.44$ (m, 14H, arom.), 3.56 (s, 2H, CH₂PPh₂), 2.47 (s, 3H, SCH₃). ¹³C NMR (100.00 MHz, CDCl₃): $\delta = 124.71 - 138.33$ (m, ArC), 34.02 (d, ${}^{1}J_{PC} = 16.1$ Hz, CH_2PPh_2), 16.42 (s, SCH₃). ³¹P NMR (161.90 MHz, CDCl₃): $\delta = -13.65$. Anal. Calc. for $C_{20}H_{19}PS$ (m/z = 322.40): C, 74.51; H, 5.94. Found: C, 74.5; H, 6.10%.

2.4. Preparation of $[PdCl_2\{MeSC_6H_4-2-(CH_2PPh_2)\}]$ (3)

An acetone (50 ml) solution of MeSC₆H₄-2-(CH₂PPh₂) (500 mg, 1.46 mmol), and [PdCl₂(COD)] [10] (417 mg, 1.46 mmol) was heated under reflux for 2 h. The solvent was evaporated under vacuum and the crude product was extracted with acetone. Following recrystalization from CH₂Cl₂–MeOH, purified product was obtained as a bright yellow microcrystalline powder. Yield 630 mg (90%). ¹H NMR (400.00 MHz, CDCl₃) $\delta = 6.75-7.76$ (m, 14H, arom.), 3.59 (d, ²J_{PH} = 10.4 Hz, 2H, CH₂PPh₂), 3.17 (s, 3H, SCH₃). ¹³C NMR (100.00 MHz, CDCl₃) $\delta = 116.62-133.52$ (m, Ar*C*), 33.26 (d, J_{PC} = 24.14 Hz, CH₂PPh₂), 18.70 (s, SCH₃). ³¹P NMR (161.90 MHz, CDCl₃) $\delta = 64.2$ (s, 1P). Anal. Calc. for C₂₀H₁₉Cl₂PPdS (*m*/*z* = 499.73): C, 48.07; H, 3.83.C. Found: C 48.03; H 3.78%.

2.5. General procedure for the catalytic reactions

A DMF solution (5 ml) of 50.0 mmol of halogen benzene, 60.0 mmol of alkene, and the prescribed amount of **3** as catalyst was introduced into a Schlenk tube in the open air. The tube was charged with a magnetic stir bar and an equimolar amount of base, sealed, and fully immersed in a 120 °C silicon oil bath. After the prescribed reaction time (72 h), the mixture was cooled to room temperature (r.t.) and the organic phase was analyzed by gas chromatography (GC/FID, GC–MS). A Hewlett–Packard 5980A gas chromatograph with flame ionization detector (FID), and an HP-1 capillary column (25.0 m) was used for quantitative GC analysis.

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Table 1 Crystal data and structure refinement for complex $PdCl_2\{MeSC_6H_4-2-(CH_2PPh_2)\}$ (3)

$C_{20}H_{19}Cl_2PPdS$
499.68
293(2)
0.71073
monoclinic
$P2_1/n$
8.744(2)
14.841(5)
16.0310(10)
90
102.960(2)
90
2027.3(8)
4
250
$2.34 < \theta < 25.09$
1.637
1.361
1000
$0.7 \times 0.5 \times 0.5$
1.89-25.00
$-6 \le h \le 9, -16 \le k \le 14, -18 \le l \le 18$
5691
2799 $[R_{int} = 0.1072]$
SHELXL-97 (Sheldrick, 1997)
SHELXS-86 (Sheldrick, 1991)
Calc. $w = 1/[\sigma^2(F_0^2) + (0.0563P)^2]$
where $P = (F_{0}^{2} + 2F_{c}^{2})/3$
full-matrix least-squares on F^2
2799/0/226
0.927 ^a
$R_1 = 0.0527, wR_2 = 0.1244$ ^b
$R_1 = 0.0718, wR_2 = 0.1293$ ^b
1.251 and $-0.5\overline{75}$
< 0.001

^a $S = [w((F_o)^2 - (F_o)^2)^2/(n-p)]^{1/2}$ where *n*, number of reflections and *p*, total number of parameters.

^b $R_1 = |F_0 - F_c|/|F_0|$, $wR_2 = [w((F_0)^2 - (F_c)^2)^2/w(F_0)^2]^{1/2}$.

Table 2

1 aoic 2								
Selected 1	bond	distances	(Å)	and	angles	(°)	for	$PdCl_2\{MeSC_6H_4-2-$
(CH ₂ PPh	,)} (3)						

Bond distan	ces (°)	Bond angles (Å)			
Pd–P	2.232(2)	P–Pd–S	90.00(8)		
Pd–S	2.296(2)	P-Pd-Cl(2)	85.81(8)		
Pd–Cl(2)	2.321(2)	S-Pd-Cl(2)	175.64(8)		
Pd-Cl(1)	2.345(2)	P-Pd-Cl(1)	175.94(7)		
P-C(31)	1.806(8)	S-Pd-Cl(1)	92.70(8)		
P-C(21)	1.810(7)	Cl(2)-Pd-Cl(1)	91.42(8)		
P-C(1)	1.832(8)	C(1)–P–Pd	110.8(3)		
S-C(16)	1.759(8)	C(16)-S-Pd	106.1(3)		
S-C	1.797(9)	C–S–Pd	110.3(4)		



Fig. 1. A ZORTEP representation of the structure of $PdCl_2\{MeSC_6H_4-2-(CH_2PPh_2)\}$ (3). Showing the atom labeling scheme. Hydrogen atoms have been omitted for clarity. The thermal ellipsoids have been drawn at 50% probability.

2.6. Single crystal X-ray structure determination of $[PdCl_2\{MeSC_6H_4-2-(CH_2PPh_2)\}]$ (3)

Intensity data were collected at the EPSRC service, Cardiff on an Delft-Instruments FAST-TV Area detector diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å). Cell constants were obtained from least-squares refinement of the setting angles of 250 reflections having $\theta = 2.34 - 25.09^{\circ}$. The structure was solved via direct methods [11] and refined by F_{0}^{2} by full-matrix least-squares. All non-hydrogen atoms were anisotropic. The hydrogen atoms were included in idealized positions with U_{iso} free to refine. The weighting scheme gave satisfactory agreement analyzes. Final R indices [1940 $I > 2\sigma(I)$] R_1 (on F) = 0.0527, $wR_2 = 0.1244$. The largest difference peak and hole were 1.251 and -0.575 e Å⁻³, the highest peak in the final difference Fourier map was in the vicinity of metal atoms, the final map had no significant features. The maximum shift/esd was < 0.001. Sources of scattering factors were as in reference [12]. The details of the structure determination are given in Table 1, selected bond lengths (Å) and angles (°) in Table 2. The numbering of the atoms is shown in Fig. 1 (ZORTEP [13]).

3. Results and discussion

3.1. Synthesis of $[PdCl_2\{MeSC_6H_4-2-(CH_2PPh_2)\}]$ (3)

The synthesis of complex **3** is outlined in Scheme 1. The ligand precursor diphenylphosphinobenzyl-2methylthioether was conveniently prepared in two steps from the reaction of diphenylphosphine, 2-bromobenzylbromide and dimethyldisulphide. Reaction of the phosphino-thioether compound with [PdCl₂(COD)] [10] in acetone under reflux for 2 h yielded the palladium complex $[PdCl_2{MeSC_6H_4-2-(CH_2PPh_2)}]$ (3).

The purified compound was isolated in 90% yield as a yellow powder upon recrystallization from CH₂Cl₂-MeOH. ¹H and ³¹P NMR spectroscopic results are consistent with the formulation proposed. FAB mass spectrometry and elemental analysis results also agree with the proposed formulation. The ¹H NMR (CDCl₃) spectrum shows a set of signals between 7.8 and 6.8 ppm, (14H, arom.) which is assigned to the protons of the aromatic rings. A doublet at 3.6 ppm (2H) and a sharp singlet at 3.17 ppm (3H) are assigned to the protons on the CH_2PPh_2 and SCH_3 groups, respectively. Integration of these signals is in agreement with the proposed formulation. The ³¹P NMR (CDCl₃) spectrum exhibits a single peak at 64.2 ppm as expected for the proposed structure where a unique phosphorus nucleus is present in the complex. The FAB mass spectrum shows a peak at 465 m/z, which corresponds to the fragment $[M^+-Cl]$.

3.2. The molecular structure of $PdCl_{2}\{MeSC_{6}H_{4}-2-(CH_{2}PPh_{2})\}$ (3)

Crystals of complex (3) were obtained from a double layer system of CH_2Cl_2 –MeOH as orange–yellow square shaped crystals. The complex is monomeric, with a slightly distorted square planar coordination geometry comprising the S and P atoms of the bidentate-{MeSC₆H₄-2-(CH₂PPh₂)}-ligand and the two chlorine atoms. The Pd–Cl distance *trans* to P is 2.345(2) Å whereas that *trans* to S is 2.321(2) Å. The difference in bond lengths illustrates the greater structural *trans* influence of the phosphine compared to the thioether donor. The Pd–P and P–S distances of 2.232(2) and 2.296(2) Å, respectively, are within the expected values.

The distortion of the square planar structure is reflected in the deviations from 90° of the angles at Pd,



Scheme 1.

in particular P–Pd–Cl(2) $85.81(8)^{\circ}$ and S–Pd–Cl(1) 92.70(8)°. The closing of the P–Pd–Cl(2) is consistent with the steric effect exerted by the CH₂ adjacent to the phosphorus, whereas the opening of the S–Pd–Cl(1) is consistent with the steric hindrance due to the methyl of the thioether group. A ZORTEP [13] view of the crystal structure is shown in Fig. 1. The selected bond distances and bond angles are listed in Table 2.

3.3. Catalytic activity of **3** for the Heck coupling of aryl halides with olefins

The high thermal and air stability of the phosphinothioether complex **3** both in the solid state and in solution permitted the catalytic reactions to be carried out completely aerobically.

Preliminary experiments showed that the performance of the catalyst was enhanced by the use of inorganic bases such as Na_2CO_3 or NaOAc, whereas in the case of organic bases (amines) the yields were considerably reduced and the regioselectivity minimized. This may be due in part to steric effects exerted by competitive coordination of the amine to the Pd center.

The catalytic activity of **3** for the Heck reaction was probed through studies of the reactions of styrene with iodo and bromobenzenes. As seen in Table 3, quantitative conversion to the corresponding olefins was achieved under the conditions used. The observed catalytic behavior, in regard to both yield and turnover numbers (TON), is similar or higher to those obtained by Milstein [14] and Shaw [2d] using the amino palladacycles or phosphino imino complexes, respectively. However, the phosphino-thioether complex not only produces exclusively *trans*-stilbenes in quantitative yields, but surprisingly turnover numbers of 10^6 were observed for bromobenzenes. To our knowledge these are among the highest TON reported to date for the coupling reactions of styrene with bromobenzenes.

The reactivities of a variety of aryl halides were examined under the optimized conditions and uniformly showed > 99% selective for the *trans* configured product. The system is also one of the few reported systems to show high reactivity with electron-rich and sterically hindered aryl halides [15]. The practical utility of this catalytic system was probed by carrying out preparative scale couplings (Table 3). We uniformly obtained the corresponding *E*-stilbenes in > 95% isolated yields. To our knowledge, these yields are among the highest that have been achieved to date for the Heck coupling of these aryl halides with styrene.

The precise mechanism of the catalytic reaction remains to be elucidated. ³¹P analyzes of the reaction mixtures show that complex **3** persists essentially intact at the end of the reaction, with only halide exchange having occurred. There has been considerable debate in

Table 3

Heck couplings of halobenzenes with $[PdCl_2\{MeSC_6H_4\mathchar`eq. 2\mathchar`eq. 2\mathchar`eq. (CH_2PPh_2)\}]$ (3) as catalyst



Entry	X, R	Base	TON	Yield (%) ^a	Isolated yield (%) $^{\rm b\ c}$	$\mathbf{E}/\mathbf{Z}/\mathbf{T}$
1	I, H	Net ₃	1 214 219	>98		87.0/10.0/2.0
2	I, H	DIPEA	1 223 964	>99		87.0/11.0/1.4
3	I, H	NaOAc	1 235 832	>99		94.0/4.7/1.1
4	I, H	Na_2CO_3	1 249 325	>99	97	, ,
5	Br, H	NEt ₃	981 969	79		65.5/8.1/5.4
6	Br, H	DIPEA	1 179 363	95		88.3/5.5/1.2
7	Br, H	NaOAc	1 159 998	>99		98.1/1.4/0.2
8	Br, H	Na_2CO_3	1 249 325	>99	95	
9	Br, 4-Ome	Na ₂ CO ₃	1 249 325	>99	97	
10	Br, 4-COMe	Na ₂ CO ₃	1 249 325	>99	94	
11	Br, 4-COH	Na ₂ CO ₃	1 249 325	>99	96	
12	Br, 4-CH ₃	Na ₂ CO ₃	1 249 325	>99	97	
13	Br, 2-Cl	Na ₂ CO ₃	1 249 325	>99	96	

Reaction conditions 50 mmol of halobenzene, 60 mmol of styrene, 60 mmol of base, 4.0×10^{-5} mmol of catalyst and 5 ml of DMF, 72 h at 120 °C.

^a Yields obtained by GC are based on haloarene.

^b Only the *trans* configured product was detected.

^c Isolated yields are the average of two runs.

the literature about the oxidation states of the species involved in the cycle with Pd(IV)/Pd(II) and Pd(II)/Pd(0) both being suggested at various times [3]. As is the case in other examples of Heck catalyst employing hemilabile chelate ligands [16] we favor the Pd(0)/Pd(II) mechanism although participation of Pd(IV)/Pd(II) species cannot be ruled out.

In summary the phosphino-thioether palladium P–S complex, **3** is a highly efficient catalyst for the olefinic coupling of aryl bromides and iodides. Most significantly, turnover numbers of 10^6 can be obtained with bromobenzenes. It is also noteworthy that the attractive features of this catalytic system: high yields and air and water stability, approach those required for commercial viability and opens future perspectives for its use in other palladium-catalyzed reactions which are currently under research.

4. Supplementary material

Crystallographic data for the structural analysis and additional material comprising atomic coordinates, thermal parameters and remaining bond lengths (Å) and angles (°) have been deposited at the Cambridge Crystallographic Data Center (CCDC), CCDC no. 149905 for compound **3**. 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).

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References

- (a) K.C. Nicolaou, E.J. Sorensen, Classics in Total Synthesis, VCH, Weinheim, 1996;
 (b) R.F. Heck, in: B.M. Trost, I. Flemming (Eds.), Comprehensive Organic Synthesis, vol. 4, Pergamon Press, Oxford, 1991, p. 833 Chapter 3.4;
 (c) A. de Meijere, F.E. Meyer, Angew. Chem., Int. Ed. Engl. 33 (1994) 2379;
 (d) W. Cabri, I. Candiani, Acc. Chem. Res. 28 (1995) 2;
 (e) T. Jeffery, Adv. Met. Org. Chem. 5 (1996) 153;
 (f) S. Bräse, A. de Meijere, in: P.J. Stang, F. Diederich (Eds.), Metal Catalyzed Cross-Coupling Reactions, Wiley, New York, 1998 Chapter 3;
 (g) I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009.
 (a) M. Beller, T.H. Riermeier, Tetrahedron Lett. 37 (1996) 6535;
- [2] (a) M. Beller, 1.H. Riermeier, Tetrahedron Lett. 37 (1996) 6555;
 (b) W.A. Herrmann, C. Brossmer, C.P. Reisinger, T.H. Riermeier, K. Öfele, M. Beller, Chem. Eur. J. 3 (1997) 1357;

(c) W.A Herrman, C. Brossmer, K. Öfele, C.P. Reisinger, T. Priermeier, M. Beller, H. Fischer, Angew. Chem., Int. Ed. Engl. 34 (1995) 1844;

(d) B.L. Shaw, S.D. Perera, Chem. Commun. (1998) 1863;

(e) M. Ohff, A. Ohff, M.E. van der Bomm, D. Milstein, J. Am. Chem. Soc. 119 (1997) 11687;

(f) D. Morales-Morales, R. Redón, C. Yung, C.M. Jensen, Chem. Commun. (2000) 1619;

(g) D. Morales-Morales, C. Grause, K. Kasaoka, R. Redón, R.E. Cramer, C.M. Jensen, Inorg. Chim. Acta 300–302 (2000) 958;

(h) K.H. Shaughnessy, P. Kim, J.F. Hartwig, J. Am. Chem. Soc. 121 (1999) 2123;

(i) J.P. Wolfe, S.L. Buchwald, Angew. Chem., Int. Ed. Engl. 38 (1999) 2413;

(j) M. Beller, A. Zapf, Synlett (1998) 792;

(k) D.A. Albisson, R.B. Bedford, P.N. Scully, Tetrahedron Lett. 39 (1998) 9793.

- [3] (a) B.L. Shaw, S.D. Perera, E.A. Staley, Chem. Commun. (1998) 1361;
 - (b) B.L. Shaw, New J. Chem. (1998) 77.
- [4] (a) J.C. Bayon, C. Claver, A.M. Masdeu-Bultó, Coord. Chem. Rev. 193–195 (1999) 73;

(b) J.R. Dilworth, D. Morales, Y. Zheng, J. Chem. Soc., Dalton Trans. (2000) 3007.

- [5] D.E. Bergbreiter, P.L. Osburn, Y.-S. Liu, J. Am. Chem. Soc. 121 (1999) 9531.
- [6] A.S. Gruber, D. Zim, G. Ebelling, A.L. Monteiro, J. Dupont Org. Lett. 2 (2000) 1287.
- [7] (a) G. Knuhl, P. Sennhenn, G. Helmchen, Chem. Commun. (1995) 1845;

(b) R. Kadyrov, J. Heinicke, M.K. Kindermann, D. Heller, C. Fischer, R. Selke, A.K. Fischer, P.G. Jones, Chem. Ber. 130 (1997) 1663;

(c) J. Heinicke, R. Kadyrov, M.K. Kindermann, M. Koesling, P.G. Jones, Chem. Ber. 129 (1996) 1547;

(d) J. Heinicke, U. Jux, R. Kadyrov, M. He, Heteroatom Chem. 8 (1997) 383;

(e) J. Heinicke, R. Kadyrov, M.K. Kindermann, M. Koesling, P.G. Jones, Chem. Ber. 130 (1997) 431;

(f) K.R. Dunbar, J.-S. Sun, A. Quillevere, Inorg. Chem. 33 (1994) 3598;

(g) K.R. Reddy, K. Surekha, G.-H. Lee, S.-M. Peng, S.-T. Liu, Organometallics 19 (2000) 2637;

- (h) G. Helmchen, A. Pfaltz, Acc. Chem. Res. 33 (2000) 336.
- [8] (a) J. Sprinz, M. Kiefer, G. Helmchen, M. Reggelin, G. Huttner, O. Walter, L. Zsolnai, Tetrahedron Lett. 35 (1994) 1523;

(b) A.K.H. Knöbel, I.H. Escher, A. Pfaltz, Synlett 12 (1997) 1429; (c) P. Braunstein, J. Pietsch, Y. Chauvin, A. DeCian, J. Fischer, J. Organomet. Chem. 529 (1997) 387: (d) U. Nagel, H.G. Nedden, Chem. Ber. 130 (1997) 535; (e) A. Schnyder, A. Togni, U. Wiesli, Organometallics 16 (1997) 255: (f) P.E. Blöchl, A. Togni, Organometallics 15 (1996) 4125; (g) H. Kubota, K. Koga, Heterocycles 42 (1996) 543; (h) J.-M. Valk, G.A. Whitlock, T.P. Layzell, J.M. Brown, Tetrahedron: Asymmetry 6 (1995) 2593; (i) C. Grazia, F. Nicolò, D. Drommi, G. Bruno, F. Faraone, Chem. Commun. (1994) 2251: (j) K.V. Katti, R.G. Cavell, Comm. Inorg. Chem. 10 (1990) 53. [9] (a) M. Bressan, C. Bonuzzi, F. Morandini, A. Morvillo, Inorg. Chim. Acta 182 (1991) 153; (b) M. Bressan, F. Morandini, A. Morvillo, P. Rigo, J. Organomet. Chem. 280 (1985) 139; (c) M. Bressan, F. Morandini, P. Rigo, J. Organomet. Chem. 247 (1983) C8; (d) P. Rigo, M. Bressan, M. Basato, Inorg. Chem. 18 (1979) 860; (e) M. Hiraoka, A. Nishikawa, T. Morimoto, K. Achiwa, Chem. Pharm. Bull. 46 (1998) 704; (f) E. Hauptman, R. Shapiro, W. Marshall, Organometallics 17 (1998) 4976; (g) P. Barbaro, A. Currao, J. Herrmann, R. Nesper, P.S. Pregosin, R. Salzmann, Organometallics 15 (1996) 1879; (h) S. Gladiali, A. Dore, D. Fabbri, Tetrahedron: Asymmetry 5 (1994) 1143; (i) E. Hauptman, P.J. Fagan, W. Marshall, Organometallics 18 (1999) 2061; (j) J.R. Dilworth, J.R. Miller, N. Wheatley, M.J. Baker, J.G. Sunley, Chem. Commun. (1995) 1579; (k) H.-S. Lee, J.-Y. Bae, J. Ko, Y.S. Kang, H.S. Kim, S.O. Kang, Chem. Lett. (2000) 602; (1) D.A. Evans, K.R. Campos, J.S. Tedrow, F.E. Michael, M.R. Gagné, J. Am. Chem. Soc. 122 (2000) 7905; (m) X. Verdaguer, A. Moyano, M.A. Pericàs, A. Riera, M.A. Maestro, J. Mahía, J. Am. Chem. Soc. 122 (2000) 10242.

- [10] D. Drew, J.R. Doyle, Inorg. Synth. 28 (1990) 348.
- [11] G.M. Sheldrick, SHELX-86, Program for Crystal Structure Determination. University of Göttingen, Germany, 1986.
- [12] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement. University of Göttingen, Germany, 1997.
- [13] L. Zsolnai, ZORTEP, an ellipsoid representation program, University of Heidelberg, 1994.
- [14] M. Ohff, A. Ohff, D. Milstein, Chem. Commun. (1999) 357.
- [15] A.F. Littke, G.C. Fu, J. Org. Chem. 64 (1999) 10.
- [16] M. Casey, J. Lawless, C. Shirran, Polyhedron 19 (2000) 517.