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Note

Synthesis of a neutral S–P–S pincer Pd(II) complex with the proligand PhP(C_6H_4–SH-2)$_2$ [*ph*PS$_2$H$_2$]. The X-ray crystal structure of [Pd(*ph*PS$_2$)(PPh$_3$)][☆]

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Abstract

The reactivity of the hybrid phosphorus–sulfur proligand *ph*PS$_2$H$_2$ with the *trans*-[Pd(Cl)$_2$(PPh$_3$)$_2$] precursor has been explored. By reacting *trans*-[Pd(Cl)$_2$(PPh$_3$)$_2$] with *ph*PS$_2$H$_2$ in the presence of NEt$_3$ as base, the complex [Pd(*ph*PS$_2$)(PPh$_3$)] was obtained. A single crystal X-ray structure determination for [Pd(*ph*PS$_2$)(PPh$_3$)] shown the compound to be square planar with the ligand *ph*PS$_2$ behaving as a S–P–S pincer ligand.

Keywords: Crystal structures; Palladium complexes; P,S-Proligands complexes; Pincer ligands complexes

1. Introduction

The chemistry of metal complexes of both simple and bulky thiolate ligands has been well documented [1]. Recently, attention has increasingly been paid to the coordination chemistry of polydentate ligands incorporating both thiolate and tertiary phosphine donor ligands, as their combination is likely to confer unusual structures and reactivities on their metal complexes [2]. Some of these complexes have been used as models of biologically active centres in metalloproteins such as ferredoxins, nitrogenase, blue copper proteins and metallothioneins [3] or as models for the design of complexes with potential application as radiopharmaceuticals [4]. These complexes have shown an intriguing variety of structures [5] or unusual oxidation states and enhanced solubility [6], making these species excellent candidates for further studies in reactivity. In the specific case of compounds with elements of the Groups 8–10 these may be suitable species for catalytic screening. Moreover, the presence of these ligands in the coordination sphere of transition metal-complexes may render interesting behaviours in solution as these ligands can be capable of full or partial de-ligation (hemilability) [7] being able to provide important extra coordination sites for incoming substrates during a catalytic process [8]. To date, most studies have focused on bidentate ligands such as R$_2$PCH$_2$CH$_2$SH [9] and R$_2$P(C$_6$H$_4$–SH-2) [10], while the potentially tridentate proligands *R*P(CH$_2$CH$_2$SH)$_2$ and *R*P(C$_6$H$_4$–SH-2)$_2$ have received much less attention [11]. Following our current interest in the design and synthesis of new pincer complexes with high thermal stability for potential application in catalytic reactions we have turn our attention to the potentially tridentated S–P–S ligand PhP(C$_6$H$_4$–SH-2)$_2$ as it may render analogous species to those obtained with the previously explored P–C–P pincer type ligands [12].

2. Experimental

2.1. Materials and methods

Unless stated otherwise, all reactions were carried out under an atmosphere of dinitrogen using conventional

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Schlenk glassware, solvents were dried using established procedures and distilled under dinitrogen immediately prior to use. The IR spectra were recorded on a Nicolet-Magna 750 FT-IR spectrometer as Nujol mulls. The ^1H NMR spectra were recorded on a JEOL GX300 spectrometer. Chemical shifts are reported in ppm down field of TMS using the solvent ($CDCl_3$, $\delta = 7.27$) as internal standard. ^{31}P NMR spectra were recorded with complete proton decoupling and are reported in ppm using 85% H_3PO_4 as external standard. Elemental analyses were determined on a Perkin–Elmer 240. Positive-ion FAB mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operated at an accelerating voltage of 10 kV. Samples were desorbed from a nitrobenzyl alcohol (NOBA) matrix using 3 kev xenon atoms. Mass measurements in FAB are performed at a resolution of 3000 using magnetic field scans and the matrix ions as the reference material or, alternatively, by electric field scans with the sample peak bracketed by two (polyethylene glycol or cesium iodide) reference ions. The $PdCl_2$ was obtained from Aldrich Chemical Co. and used without further purification. The proligand *ph*PS_2H_2 [13] and the starting material *trans*-[$Pd(Cl)_2(PPh_3)_2$] [14] were prepared according to published procedures.

2.2. Synthesis of [Pd(phPS$_2$)(PPh$_3$)] (1)

To a solution of *trans*-[$Pd(Cl)_2(PPh3)_2$] (428 mg, 0.613 mmol) in CH_2Cl_2 (10 cm^3) a solution (10 cm^3) of 1 equiv. of the phosphino-dithiol *ph*PS_2H_2 (200 mg, 0.613 mmol) and NEt_3 (0.116 mg, 1.227 mmol) was added. The solution was stirred for 24 h. Following the reaction time the solution was filtrated and the volume was then reduced in vacuum and the reddish–brown residue recrystallized from a double layer solvent system of CH_2Cl_2–MeOH. Yield 372 mg (87%).

2.3. Data collection and refinement for [Pd(phPS$_2$)(PPh$_3$)] (1)

A crystalline orange prism of [Pd(*ph*PS_2)(PPh_3)], grown from a CH_2Cl_2–MeOH solvent system was glued to a glass fiber. The X-ray intensity data were measured at 291 K on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å). The detector was placed at a distance of 4.837 cm. from the crystal. A total of 1800 frames were collected with a scan width of 0.3° in ω and an exposure time of 10 s/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a monoclinic unit cell yielded a total of 12 778 reflections to a maximum 2θ angle of 50.00° (0.93 Å resolution), of which 12 778 were independent ($R_{\text{int}} = 5.19\%$, $R_{\text{sig}} = 8.27\%$) and 4401 were greater than $2\sigma(F^2)$. Analysis of the data showed negligible decay during data collection. The structure was solved by Patterson method using SHELXS-97 [15] program. The remaining atoms were located via a few cycles of least-squares refinements and difference Fourier maps, using the space group *Pc*, with $Z = 2$. Hydrogen atoms were input at calculated positions, and allowed to ride on the atoms to which they are attached. Thermal parameters were refined for hydrogen atoms on the phenyl groups using a $U_{\text{eq}} = 1.2$ Å to precedent atom. The final cycle of refinement was carried out on all non-zero data using SHELXL-97 [16] and anisotropic thermal parameters for all non-hydrogen atoms. The details of the structure determination are given in Table 1 and selected bond lengths (Å) and angles (°) in Table 2. The numbering of the atoms is shown in Fig. 1 (ORTEP) [17].

Table 1
Summary of crystal structure data for complex [Pd(*ph*PS_2)(PPh_3)] (**1**)

Empirical formula	$C_{36}H_{28}P_2PdS_2$
Formula weight	693.04
Temperature (K)	291(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	*Pc*
Unit cell dimensions	
a (Å)	9.8375(5)
b (Å)	16.2918(9)
c (Å)	9.9065(5)
α (°)	90
β (°)	98.029(10)
γ (°)	90
Volume (Å^3)	1572.16(14)
Z	2
D_{calc} (g cm^{-3})	1.464
Absorption coefficient (mm^{-1})	0.849
F(000)	704
Crystal size (mm)	0.32 × 0.08 × 0.07
θ Range for data collection	2.09–24.99
Index ranges	$-11 \le h \le 11$, $-19 \le k \le 19$, $-11 \le l \le 11$
Reflections collected	12 778
Independent reflections	5499 [$R_{\text{int}} = 0.0519$]
Absorption correction	none
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	5499/2/370
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0413$, $wR_2 = 0.0579$ [b]
R indices (all data)	$R_1 = 0.0537$, $wR_2 = 0.0608$ [b]
Absolute structure parameter	−0.04(3)
Goodness-of-fit on F^2	0.895[a]
Largest difference peak and hole (e Å^{-3})	0.679 and −0.550

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

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

Table 2
Selected bond lengths and angles for [Pd(*ph*PS$_2$)(PPh$_3$)] (**1**)

Bond lengths (Å)	
Pd(1)–P(1)	2.2266(18)
Pd(1)–S(1)	2.2995(18)
Pd(1)–S(2)	2.3374(17)
Pd(1)–P(2)	2.3476(18)
Bond angles (°)	
P(1)–Pd(1)–S(1)	87.00(6)
P(1)–Pd(1)–S(2)	84.13(6)
S(1)–Pd(1)–S(2)	164.90(6)
P(1)–Pd(1)–P(2)	177.73(8)
S(1)–Pd(1)–P(2)	91.44(6)
S(2)–Pd(1)–P(2)	97.04(6)

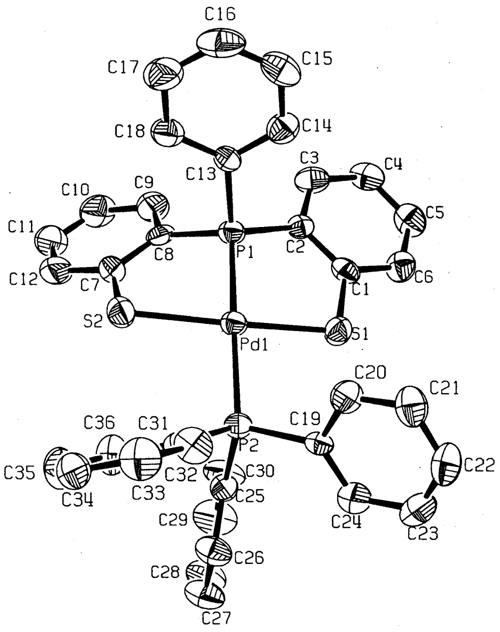


Fig. 1. An ORTEP representation of the structure of [Pd(*ph*PS$_2$)(PPh$_3$)] (**1**) at 50% of probability showing the atom labelling scheme.

3. Results and discussion

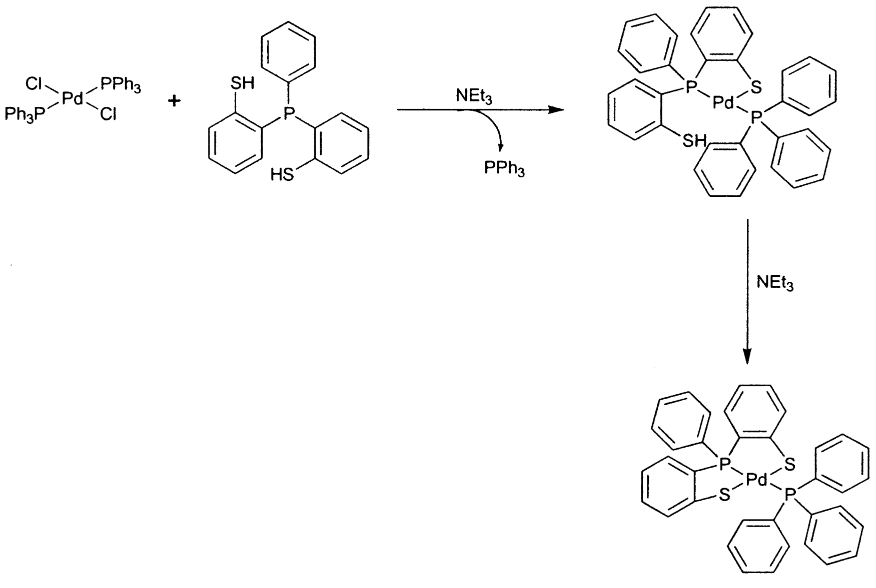
3.1. Synthesis and characterisation of [Pd(phPS$_2$)(PPh$_3$)] (1)

The reaction of the palladium starting material *trans*-[Pd(Cl)$_2$(PPh$_3$)$_2$] with half equivalent of the sulphur proligand *ph*PS$_2$H$_2$ in the presence of triethylamine as base yields complex [Pd(*ph*PS$_2$)(PPh$_3$)] (**1**) as red–orange powder in good yield. The infrared and ^{1}H NMR spectra of **1** are not very informative since both analysis only show absorptions and signals corresponding to the presence of the phenyl rings in the molecule. The ^{31}P NMR analysis is more informative, showing a couple of doublets in the spectrum, one at 85.33 ppm corresponding the tridentated ligand *ph*PS$_2$ and the other at 22.76 ppm which is assigned to the PPh$_3$ present in the molecule. The multiplicity of the signals is in agreement with a mutually *trans* configuration of the phosphorus ligands. The coupling constant of J_{P-P} 405.6 Hz is also in agreement with a *trans* configuration for the two phosphorus nuclei. Analysis by FAB-MS for **1** exhibits the molecular ion at $m/z = 692$ with the appropriate isotope distribution [18]. An additional peak corresponding to the lost of the fragment PPh$_3$ is observed at $m/z = 430$.

The reaction of the proligand *ph*PS$_2$H$_2$ with *trans*-[Pd(Cl)$_2$(PPh$_3$)$_2$] it is likely to proceed in two steps (Scheme 1), the first one which would involve the addition of the proligand to the Pd metal center in a bidentate manner with the concomitant elimination of PPh$_3$, further reaction would involve the addition of the second S group to the metal to afford complex **1**.

3.2. X-ray crystal structure of [Pd(phPS$_2$)(PPh$_3$)] (1)

Crystals of complex **1** were obtained from a double layer solvent system of CH$_2$Cl$_2$–MeOH as orange prisms. The X-ray crystal structure analysis shows the Pd center to be in a slightly distorted square planar environment (Fig. 1). The coordination sphere of **1** is constituted by the ligand *phPS$_2$* coordinated in a tridentated S–P–S pincer like fashion and completed by a PPh$_3$ group located *trans* to the phosphorus atom of the ligand *phPS$_2$*. The main distortion from the square planar geometry is caused by the rigidity of the ligand and reflected in the angle S(1)–Pd(1)–S(2) to be 164.90(6), a less pronounced distortion is observed in the vector P(1)–Pd(1)–P(2) with and angle value of 177.73(8). The Pd–S distances are slightly different [Pd(1)–S(1) = 2.2995(18) and Pd(1)–S(2) = 2.3374(17) Å] and comparable to those found in other palladium complexes like [Pd(Ph$_2$PC$_6$H$_4$–S-2)$_2$] [Pd–S = 2.308(2) Å] [19] and [Pd(Cl)(Ph$_2$PC$_2$H$_4$S)(PPh$_3$)] [Pd–S = 2.270(2) Å] [20], the difference in bond distances can be attributed to the strains imposed by the geometry of the *phPS$_2$* ligand. A more marked difference is observed for the Pd–P bond distances [Pd(1)–P(1) = 2.2266(18) and Pd(1)–P(2) = 2.3476(18) Å] once again these differences are the result of the constrains imposed by the S–P–S ligand. The Pd(1)–P(1) distance is shorter to those observed in [Pd(Ph$_2$PC$_6$H$_4$–S-2)$_2$] [Pd–P = 2.291(1) Å] [19] and [Pd(Cl)(Ph$_2$PC$_2$H$_4$S)(PPh$_3$)] [Pd–P = 2.288(2) Å] [20], while the distance Pd(1)–P(2) is comparable to that found in [Pd(Cl)(Ph$_2$PC$_2$H$_4$S)(PPh$_3$)] [Pd–PPh$_3$ = 2.343(2) Å] [20]. The shorter distance in Pd(1)–P(1) reflects the strain exerted by both S moieties, bringing the phosphorus atom closer to the metal center, this bond robustness may suggest this specie to be suitable for testing in catalytic reactions, were the tridentated *ph*PS$_2$ ligand should behave as its bidentated counterpart (Ph$_2$PC$_6$H$_4$–S-2), however the fact that the ligand *ph*PS$_2$ contains an extra S arm may render in higher activity without the lost of the hemilabile properties,



(1)

Scheme 1. Proposed mechanism for the formation of complex [Pd(*ph*PS$_2$)(PPh$_3$)] (**1**).

characteristic of this kind of systems [21]. Efforts directed to explored this possibility are currently under investigation.

4. Supplementary material

Supplementary data have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 186027 for complex **1**. Copies of this information are available free of charge on request 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

[1] (a) P.J. Blower, J.R. Dilworth, Coord. Chem. Rev. 76 (1987) 121;
(b) J.R. Dilworth, J. Hu, Adv. Inorg. Chem. 40 (1993) 411;
(c) J.R. Dilworth, P. Arnold, D. Morales, Y.L. Wong, Y. Zheng. The Chemistry and Applications of Complexes with Sulphur Ligands, Pag. 217, in: G.J. Leigh, N. Winterton (Eds.), Modern Coordination Chemistry, The Legacy of Joseph Chatt, Royal Society of Chemistry, Cambridge, UK, 2002.

[2] (a) M. Hiraoka, A. Nishikawa, T. Morimoto, K. Achiwa, Chem. Pharm. Bull. 46 (1998) 704;
(b) E. Hauptman, R. Shapiro, W. Marshall, Organometallics 17 (1998) 4976;
(c) E. Hauptman, P.J. Fagan, W. Marshall, Organometallics 18 (1999) 2061;
(d) H.-S. Lee, J.-Y. Bae, J. Ko, Y.S. Kang, H.S. Kim, S.O. Kang, Chem. Lett. (2000) 602;
(e) A.S. Abu-Surrah, K. Lappalainen, T. Repo, M. Klinga, M. Leskelä, H.A. Hodali, Polyhedron 19 (2000) 1601;
(f) D.A. Evans, K.R. Campos, J.S. Tedrow, F.E. Michael, M.R. Gagné, J. Am. Chem. Soc. 122 (2000) 7905;
(g) J.R. Dilworth, D. Morales, Y. Zheng, J. Chem. Soc., Dalton Trans. (2000) 3007.

[3] (a) J.D. Franolic, M. Millar, S.A. Koch, Inorg. Chem. 34 (1995) 1981;
(b) D.H. Nguyen, H.-F. Hsu, M. Millar, S.A. Koch, J. Am. Chem. Soc. 118 (1996) 8963;
(c) H.-F. Hsu, S.A. Koch, J. Am. Chem. Soc. 119 (1997) 8371;
(d) K.A. Clark, T.A. George, T.J. Brett, Ch.R. Ross, R.K. Shoemaker, Inorg. Chem. 39 (2000) 2252;
(e) J.D. Niemoth-Anderson, K.A. Clark, T.A. George, Ch.R. Ross, J. Am. Chem. Soc. 122 (2000) 3977.

[4] (a) N. De Vries, A. Davison, A.G. Jones, Inorg. Chim. Acta 165 (1989) 9;
(b) C. Bolzati, F. Refosco, F. Tisato, G. Bandoli, A. Dolmella, Inorg. Chim. Acta 201 (1992) 7;
(c) J.R. Dilworth, S.J. Parrot, Chem. Soc. Rev. 27 (1998) 43.

[5] (a) S.-T. Liu, D.-R. Hou, T.-Ch. Lin, M.-Ch. Cheng, S.-M. Peng, Organometallics 14 (1995) 1529;
(b) L. Dahlenburg, K. Herbst, M. Kühnlein, Z. Anorg. Allg. Chem. 623 (1997) 250;
(c) K. Kashiwabara, N. Taguchi, H.D. Tagaki, K. Nakajima, T. Suzuki, Polyhedron 17 (1998) 1817;
(d) L.V. Andreasen, O. Simonsen, O. Wernberg, Inorg. Chim. Acta 295 (1999) 153;
(e) N. Taguchi, K. Kashiwabara, K. Nakajima, H. Kawaguchi, K. Tatsumi, J. Organomet. Chem. 587 (1999) 290.

[6] (a) K. Ortner, L. Hilditch, Y. Zheng, J.R. Dilworth, U. Abram, Inorg. Chem. 39 (2000) 2801;
(b) N. Froelich, P.B. Hitchcock, J. Hu, M.F. Lappert, J.R. Dilworth, J. Chem. Soc., Dalton Trans. (1996) 1941;
(c) E.J. Fernandez, J.M. López-de-Luzuriaga, M. Monge, M.A. Rodríguez, O. Crespo, M.C. Gimeno, A. Laguna, P.G. Jones, Chem. Eur. J. 6 (2000) 636;
(d) J.S. Kim, J.H. Reibenspies, M.Y. Darensbourg, J. Am. Chem. Soc. 111 (1996) 4115.

[7] J.R. Dilworth, N. Weatley, Coord. Chem. Rev. 199 (2000) 89.

[8] (a) C.S. Stone, D.D. Weinberger, C.A. Mirkin, Prog. Inorg. Chem. 48 (1999) 233;
(b) P. Braunstein, F. Naud, Angew. Chem., Int. Ed. Engl. 40 (2001) 680.

[9] (a) L. Vaska, Jr., J. Peone, J. Chem. Soc., Sect. D (1971) 418;
(b) D.W. Stephan, Inorg. Chem. 23 (1984) 2207;
(c) J. Chatt, J.R. Dilworth, J.A. Schmutz, J.A. Zubieta, J. Chem. Soc., Dalton Trans. (1979) 1595.

[10] (a) J.R. Dilworth, Y. Zheng, L. Shaofang, W. Qiangjin, Transition Met. Chem. 17 (1992) 364;
(b) J.R. Dilworth, A.J. Hutson, J. Zubieta, Q. Chen, Transition Met. Chem. 19 (1994) 61;
(c) J.R. Dilworth, J.R. Miller, N. Wheatley, M.J. Baker, J.G. Sunley, J. Chem. Soc., Chem. Commun. (1995) 1579;
(d) P. Pérez-Lourido, J. Romero, J. García-Vázquez, A. Sousa, K.P. Maresca, D.J. Rose, J. Zubieta, Inorg. Chem. 37 (1998) 3331;
(e) P. Pérez-Lourido, J. Romero, J.A. García-Vázquez, A. Sousa, J. Zubieta, K. Maresca, Polyhedron 17 (1998) 4457;
(f) P. Pérez-Lourido, J. Romero, J.A. García-Vázquez, A. Sousa, K. Maresca, J. Zubieta, Inorg. Chem. 38 (1999) 1293;
(g) K. Ortner, L. Hilditch, J.R. Dilworth, U. Abram, Inorg. Chem. Commun. 1 (1998) 469;
(h) J. Real, E. Prat, A. Polo, A. Alvarez-Larena, J.F. Piniella, Inorg. Chem. Común. 3 (2000) 221.

[11] (a) G. Schwarzenbach, Chem. Zvesti. 19 (1965) 200;
(b) P.J. Blower, J.R. Dilworth, G.J. Leigh, B.D. Neaves, F.B. Normanton, J. Hutchinson, J.A. Zubieta, J. Chem. Soc., Dalton Trans. (1985) 2647;
(c) K. Jurkschat, W. Uhlig, C. Mügge, B. Schmidt, M. Dräger, Z. Anorg. Allg. Chem. 556 (1988) 161;
(d) J.R. Dilworth, Y. Zheng, J.R. Miller, J. Chem. Soc., Dalton Trans. (1992) 1757;
(e) R.J. Smith, A.K. Powell, N. Barnard, J.R. Dilworth, P.J. Blower, J. Chem. Soc., Chem. Commun. (1993) 54;
(f) D. Morales-Morales, S. Rodríguez-Morales, J.R. Dilworth, A. Sousa-Pedrares, Y. Zheng, Inorg. Chim. Acta 332 (2002) 101.

[12] (a) D. Morales-Morales, C. Grause, K. Kasaoka, R. Redón, R.E. Cramer, C.M. Jensen, Inorg. Chim. Acta 300–302 (2000) 958;
(b) D. Morales-Morales, R. Redón, C. Yung, C.M. Jensen, Chem. Commun. (2000) 1619;
(c) D. Morales-Morales, R. Redón, Z. Wang, D.W. Lee, C. Yung, K. Magnuson, C.M. Jensen, Can. J. Chem. 79 (2001) 823;
(d) D. Morales-Morales, R. Redón, D.W. Lee, Z. Wang, C.M. Jensen, Organometallics 20 (2001) 1144;
(e) D. Morales-Morales, R.E. Cramer, C.M. Jensen, J. Organomet. Chem. 654 (2002) 44;
(f) X. Gu, W. Chen, D. Morales-Morales, C.M. Jensen, J. Mol. Catal. A 189 (2002) 119.

[13] E. Bloch, V. Eswarakrishnan, M. Gernon, G. Ofori-Okai, C. Saha, K. Tang, J. Zubieta, J. Am. Chem. Soc. 111 (1989) 658.

[14] J. Chatt, F.G. Mann, J. Chem. Soc. (1939) 1622.

[15] G.M. Sheldrick, Acta Crystallogr., A 46 (1990) 467.

[16] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1998.

[17] L.J. Farrugia, ORTEP-3 for Windows, J. Appl. Crystallogr. 30 (1997) 565.

[18] J.J. Manura, D.J. Manura, Isotope Distribution Calculator, Scientific Instrument Service, Ringoes, NY, 1996.

[19] A. Benefiel, D.M. Roundhill, W.C. Fultz, A.L. Rheingold, Inorg. Chem. 23 (1984) 3316.

[20] N. Brugat, A. Polo, A. Álvarez-Larena, J.F. Piniella, J. Real, Inorg. Chem. 38 (1999) 4829.

[21] D. Morales-Morales, R. Redón, Y. Zheng, J.R. Dilworth, Inorg. Chim. Acta 328 (2002) 39.