Polyhedron 28 (2009) 322-326

Contents lists available at ScienceDirect

# Polyhedron

journal homepage: www.elsevier.com/locate/poly

# Heterobimetallic Re–Pd, Re–Au and Re–Cu complexes derived from diphenylphosphino cyrhetrene: Synthesis and X-ray structure

Diego Sierra<sup>a</sup>, Andres Muñoz<sup>a</sup>, Fernando Godoy<sup>a</sup>, A. Hugo Klahn<sup>a,\*</sup>, Andres Ibañez<sup>b</sup>, M. Teresa Garland<sup>b</sup>, Mauricio Fuentealba<sup>b</sup>

<sup>a</sup> Instituto de Quimica, Pontificia Universidad Catolica de Valparaíso, Casilla 4059, Valparaíso, Chile
<sup>b</sup> CIMAT, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 653, Santiago, Chile

## ARTICLE INFO

Article history: Received 3 September 2008 Accepted 27 October 2008 Available online 4 December 2008

Keywords: Cyrhetrenyldiphenylphosphine ligand Palladium Gold Copper Complexes

#### ABSTRACT

Diphenylphosphinecyrhetrene ligand  $(\eta^{5}-C_{5}H_{4}PPh_{2})Re(CO)_{3}$  (1) reacts with 1 equiv. of PdCl<sub>2</sub>(NCPh)<sub>2</sub> to form, after workup, the square-planar *trans*-[ $(\eta^{5}-C_{5}H_{4}PPh_{2})Re(CO)_{3}$ ]PdCl<sub>2</sub>(NCMe) (2). Similarly, reaction of **1** with (tetrahydrothiophene)AuCl produces, in excellent yield, the bimetallic complex [ $(\eta^{5}-C_{5}H_{4}PPh_{2})Re(CO)_{3}$ ]AuCl (3) with a linear P-Au-Cl moiety. From the reaction of 2 equiv. of **1** with CuBr(SMe<sub>2</sub>) the planar-trigonal complex [ $(\eta^{5}-C_{5}H_{4}PPh_{2})Re(CO)_{3}$ ]2CuBr (4) was obtained. <sup>31</sup>P NMR and X-ray crystallography demonstrate, for the three cases, that ( $\eta^{5}-C_{5}H_{4}PPh_{2})Re(CO)_{3}$  acts as a monodentate ligand. The structural parameters of the bimetallic complexes are compared with related diphenylphosphinoferrocene metal complexes, described in the literature.

© 2008 Elsevier Ltd. All rights reserved.

#### 1. Introduction

The diphenylphosphinocyclopentadienyl group  $\eta^5$ -coordinated to metal fragments has proved to be a versatile unsymmetrical mono- or bidentate ligand to form homo- and heterobimetallic complexes [1–3]. Complexes of this type include those which have two metal centers of a very different nature (for example, early and late transition metals) held together through a bridging ligand [4,5] or both a bridging ligand and a metal-metal bond [6-9]. The most common synthetic approach to form simple bridging bimetallic compounds has been to bind first the cyclopentadienyl moiety to one of the transition metals, thus producing a metallo ligand derivative, which may then act as a monodentate phosphorous ligand [4,5]. Several examples of metallo ligands of the type  $(\eta^5 C_5H_4PPh_2$ )MLn, M = Fe, Ti, Zr, Co, Mo, Rh, etc. have been used to prepare a large number of bimetallic complexes with interesting chemical, electrochemical and catalytic properties [1,2,10]. Nevertheless, examples of group 7 metallo ligands remain relatively unexplored.  $(\eta^5-C_5H_4PPh_2)M(CO)_3$  M = Mn and Re, were first reported by Rausch and Spink in 1989 [11] by reaction of diphenylphosphinocyclopentadienylthallium with BrM(CO)<sub>5</sub>. Much more recently, Gladysz and co-workers [12] prepared ( $\eta^5$ - $C_5H_4PR_2$ )Re(CO)<sub>3</sub>, R = Ph and tert-Bu, by direct reaction of (CpLi)R $e(CO)_3$  with PR<sub>2</sub>Cl. Although, the phenyl derivative was used in a

palladium-base catalytic system for Suzuki coupling reactions, the bimetallic Re–Pd complex, which is probably involved in the catalytic system, was neither isolated nor characterized *in situ*. The lack of information about the coordination chemistry of  $(\eta^5-C_5H_4PPh_2)Re(CO)_3$  (1) and the unknown structural data for bimetallic complexes containing this metallo ligand, encouraged us to prepare and fully characterize by spectroscopic and crystallographic techniques the square-planar *trans*-[ $(\eta^5-C_5H_4PPh_2)Re(-CO)_3$ ]PdCl<sub>2</sub>(NCMe) (2), linear [ $(\eta^5-C_5H_4PPh_2)Re(CO)_3$ ]AuCl (3) and trigonal [ $(\eta^5-C_5H_4PPh_2)Re(CO)_3$ ]<sub>2</sub>CuBr (4) complexes.

#### 2. Results and discussion

The preparation of diphenylphosphinocyclopentadienyl rhenium tricarbonyl (1) was carried out according to the Gladysz procedure [12]. Bimetallic complex (2) is formed by the reaction of ( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)Re(CO)<sub>3</sub> with commercially available PdCl<sub>2</sub>(NCPh)<sub>2</sub> (1:1 molar ratio) in CHCl<sub>3</sub> under reflux for 4 h. Upon cooling the mixture to room temperature, a red solid is formed which was slightly soluble in chloroform but soluble in MeCN. Crystallization from MeCN–Et<sub>2</sub>O yielded orange-red microcrystals of **2** (Scheme 1).

This reaction probably involves in a first step, the formation of the chloro-bridged dimeric complex  $[Pd(\mu-Cl)Cl(\eta^5-C_5H_4PPh_2)-Re(CO)_3]_2$  which then, in the crystallization step, reacts with MeCN to form the observed product. We were unable to characterize the red solid in solution; nevertheless, the elemental analysis is consistent with the proposed formula. Similar palladium chloro-bridged





<sup>\*</sup> Corresponding author. Tel.: +56 32 2273174; fax: +56 32 2273422. *E-mail address*: hklahn@ucv.cl (A. Hugo Klahn).

<sup>0277-5387/\$ -</sup> see front matter @ 2008 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2008.10.038



Scheme 1.

complexes containing the phosphinoferrocene ligand have been reported [13–15].

Compound **2** is air and moisture stable and moderately soluble in polar organic solvents and insoluble in non polar solvents. The elemental analysis of this compound is in good agreement with the proposed structure. The <sup>1</sup>H NMR spectrum (in CD<sub>3</sub>CN) of **2** showed in addition to the resonances of the metallo ligand, the presence of coordinated MeCN as a singlet at  $\delta$  1.98. The  $\nu$ (CN) absorption band observed at 2297 cm<sup>-1</sup> (KBr disc) in the IR spectrum is further evidence for coordinated MeCN. A single resonance in the <sup>31</sup>P NMR spectrum indicates a single phosphorous environment due to the presence of the metallo ligand. This resonance is shifted to lower field when compared to the free ligand ( $\Delta \delta$  = 38.3). Similar shift have been observed in analogous palladium complexes possessing the diphenylphosphinoferrocene ligand [14].

The Re–Au bimetallic complex (**3**) was formed by reacting the ligand **1** with the recommended gold precursor chloro(tetrahydro-thiophene)gold(I) [16] in  $CH_2Cl_2$ , at room temperature (Scheme 1). It was isolated as white crystals in 90% yield. The mass spectrum and elemental analysis of this compound agrees well with the presence of a single cyrhetrenylphosphine.

The <sup>1</sup>H NMR spectrum of this complex showed, apart from the multiplet from the phenyl protons, the signal of the cyrhetrenyl unit as two multiplets for the cyclopentadienyl protons ring. Like the previous case, the phosphorous resonance (observed at  $\delta$  25.7) in the <sup>31</sup>P NMR spectrum is shifted to lower field upon coordination to Au(I).  $\Delta \delta$  = 42.7, this value is comparable to those observed in diphenylphosphinoferrocenes coordinated to the Au–Cl fragment [17,18].

With regard to the complex (4) and considering that the reaction of copper(I) halide, with tertiary organo-phosphines gives a wide range of products of variable stoichiometry and molecular structure [19], we decided to carry out the reaction of CuBr(SMe<sub>2</sub>) with an excess of ligand 1 (1:4 molar ratio) (Scheme 1). After overnight stirring (in CH<sub>2</sub>Cl<sub>2</sub> at room temperature) followed by solvent evaporation, a white solid was obtained, which showed two resonances in the <sup>31</sup>P NMR spectrum ( $\delta$  –17.0 and  $\delta$  –13.5) due to the presence of uncoordinated 1 and a new compound. Column chromatography allowed the separation of the two compounds; a mixture of CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1) moved unreacted 1 whereas the new complex was eluted with acetone. The solid obtained after evaporation of acetone showed the same spectroscopic parameters as the one isolated from the direct reaction of 1 and CuBr(SMe<sub>2</sub>) in a 2:1 molar ratio. From the latter procedure, complex 4, was isolated as white crystals in 81% yield, after crystallization from  $CH_2Cl_2$ /hexane. The elemental analysis of **4** is in good agreement with the proposed structure. The <sup>31</sup>P NMR spectrum of **4** is consistent with the presence of a single compound in solution ( $\delta$  –13.5). The small downfield shift from that of the parent ligand ( $\Delta \delta$  = 3.5) is comparable to those found in other three-coordinated complexes of copper(I) [20,21].

# 3. X-ray crystallography

The numbering scheme of the bimetallic Re–Pd complex 2 is presented in Fig. 1. Crystallographic data are presented in Table 1. whereas selected bond lengths and angles are shown in Table 2. In complex **2** the palladium atom exhibits a slightly distorted square-planar geometry which is supported by (i) the displacement of palladium atom by 0.06 Å away from the PNCl<sub>2</sub> leastsquares plane and (ii) the sum of the four angles around the palladium atom which is 361°. The phosphine and the acetonitrile ligand are found in a trans orientation with angles P(1)-Pd-N(1) 175.71°(15), Cl(1)-Pd-Cl(2) 171.25°(9). In the phosphine ligand the phosphorous atom is tetrahedrally surrounded by the two phenyl rings (P-C(14) = 1.808(5) Å and P-C(15) = 1.827(6) Å), and the cyrhetrenyl ligand (P-C(1) = 1.807(5) Å). The latter distance compares well to 1.803(3) Å found in (*trans*-[PdMeCl(PPh<sub>2</sub>Fc)<sub>2</sub>],  $(PPh_2Fc = ferrocenyldiphenylphosphine)$  [14]. The bond length Pd-P (2.2217(13) Å) is quite short when compare to the similar distance measured in related phosphinoferrocene complexes (*trans*-[PdMeCl(PPh<sub>2</sub>Fc)<sub>2</sub>], Pd-P = 2.3328(10) Å [14] *trans*-[PdCl<sub>2</sub>- $(PPh_3)_2$ ] Pd-P = 2.337(1) Å [22] but it resembles to the one observed in the dimer trans-[Pd(µ-Cl)Me(PPh<sub>2</sub>Fc)]<sub>2</sub> (avg. 2.223(9)Å) [13]. The Pd–N bond length (2.085(5)Å) compares well with those obtained for other square-planar Pd(II) complexes containing coordinated acetonitrile with a trans P-Pd-N moiety, such as (MeCN)PdCl<sub>2</sub>(µ-dpmp)PdCl<sub>2</sub> [23].

The C–P–Pd angles are all larger than the ideal  $109.5^{\circ}$ , and range from  $110.48(17)^{\circ}$  to  $118.25(18)^{\circ}$ , while all C–P–C are smaller than expected for normal tetrahedra, i.e. 101.3(2)– $104.5(2)^{\circ}$ . Similar deviation has been reported for related Pd-complexes and explained in term of the valence shell electron pair repulsion theory [14,24].

The molecular structure of complex **3** is shown in Fig. 2 and selected bond distances and angles are presented in Table 2. Taking into account the gold(I) environment this compound exhibits a very regular linear geometry, with a P–Au–Cl angle of  $178.24(4)^{\circ}$ 



Fig. 1. ORTEP's plots of complex 2 with displacement ellipsoids at the 30% probability level.

#### Table 1

Summary of crystallographic data and structure refinement for 2, 3 and 4.

	2	3	4
Empirical formula	C <sub>22</sub> H <sub>17</sub> Cl <sub>2</sub> NO <sub>3</sub> PPdRe	C <sub>20</sub> H <sub>14</sub> AuClO <sub>3</sub> PRe	C41H30BrCl2CuO6P2Re2
Formula mass (g mol <sup>-1</sup> )	737.84	751.90	1267.34
Collection T (K)	298(2)	150(2)	150(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 <sub>1</sub> /c	$P2_1/c$	C2/c
a (Å)	14.3454(11)	9.414(3)	15.8267(7)
b (Å)	8.9720(7)	22.808(7)	17.8010(7)
<i>c</i> (Å)	18.8294(15)	10.359(3)	14.8485(7)
β(°)	98.0260(10)	117.03	97.1780(10)
V (Å <sup>3</sup> )	2399.7(3)	1981.3(10)	4150.5(3)
Ζ	4	4	4
$D_{\text{calc}} (\text{g cm}^{-3})$	2.042	2.521	2.028
Crystal size (mm)	$0.29 \times 0.152 \times 0.13$	$0.20\times0.16\times0.10$	$0.43 \times 0.25 \times 0.17$
F(000)	1400	1376	2408
Absorption coefficient (mm <sup>-1</sup> )	semi-empirical from equivalents	full-matrix least-squares on F <sup>2</sup>	semi-empirical from equivalents
Maximum and minimum transmission	0.452 and 0.305	0.2653 and 0.0155	0.278 and 0.155
θ Range (°)	2.18-28.08	1.79–27.90	1.73-27.81
Range h, k, l	-18/18, -11/11, -23/24	-11/11, -28/29, -13/13	-20/20, -22/23, -19/18
Reflections collected	19649	20673	17275
Independent reflections (R <sub>int</sub> )	5417 (0.0365)	4432 (0.1052)	4730 (0.0369)
Data/restraints/parameters	5417/0/281	4432/0/244	4730/0/250
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0385, wR_2 = 0.0845$	$R_1 = 0.0261, wR_2 = 0.0655$	$R_1 = 0.0319, wR_2 = 0.0849$
R indices (all data)	$R_1 = 0.0478, wR_2 = 0.0885$	$R_1 = 0.0284, wR_2 = 0.0667$	$R_1 = 0.0379, wR_2 = 0.0889$
Goodness of fit on $F^2$	1.084	1.067	1.061
Largest difference in peak and hole ( $e A^{-3}$ )	1.729 and -0.554	1.657 and -2.174	2.662 and -1.396

#### Table 2

Select bond lengths (Å) and bond angles (°) for 2, 3 and 4.

	2	3	4
Bond distances			
Re-C(6)	1.909(7)	1.918(5)	1.913(5)
Re-C(7)	1.914(7)	1.941(5)	1.918(5)
Re-C(8)	1.916(6)	1.895(5)	1.923(5)
Re-Cp(centroid)	1.952	1.956	1.961
C(1) - P(1)	1.807(5)	1.791(4)	1.802(4)
M-P(1)	2.2217(13)	2.2214(13)	2.2346(11
M-X(1)	2.2734(19)	2.2798(13)	2.3416(10
M-X(2)	2.2952(15)		
M–N	2.086(5)		
Bond angles			
Re-C(6)-O(1)	177.0(6)	177.5(4)	176.8(5)
Re-C(7)-O(2)	177.0(6)	176.6(4)	177.8(5)
Re-C(8)-O(3)	176.5(6)	177.5(4)	178.4(5)
C(1)-P(1)-M	116.56(17)	112.03(16)	114.44(15)
C(9)-P(1)-C(15)	110.40(16)	107.7(2)	103.7(2)
P(1)-M-X(1)	93.56(6)	178.24(4)	119.87(3)
P(1)-M-X(2)	88.36(5)		
P(1)-M-N(1)	175.67(14)		
P(1)-M-P(1)#			120.26(6)
M–N Bond angles Re–C(6)–O(1) Re–C(7)–O(2) Re–C(8)–O(3) C(1)–P(1)–M C(9)–P(1)–C(15) P(1)–M–X(1) P(1)–M–X(2) P(1)–M–N(1) P(1)–M–P(1)#	2.086(5) 177.0(6) 176.5(6) 116.56(17) 110.40(16) 93.56(6) 88.36(5) 175.67(14)	177.5(4) 176.6(4) 177.5(4) 112.03(16) 107.7(2) 178.24(4)	176.8(5) 177.8(5) 178.4(5) 114.44(15) 103.7(2) 119.87(3) 120.26(6)



Fig. 2. ORTEP's plots of complex 3 with displacement ellipsoids at the 30% probability level.

which is slightly larger to those found in related ferrocenyl phosphine derivatives, for example,  $177.12(10)^{\circ}$  in AuCl(PPh<sub>2</sub>Fc), [17] 176.1(1)^{\circ} in AuCl(PPhFc<sub>2</sub>) [25] and 176.01(7)^{\circ} in AuCl(PPh<sub>2</sub>CH<sub>2</sub>Fc) [26]. The Au–Cl and Au–P bond distances of 2.2798(13) Å and 2.2214(13) Å are similar to the ones measured in AuCl(PPh<sub>2</sub>Fc) and AuCl(PPhFc<sub>2</sub>) [17,25]. The shortest gold–gold distance in the lattice is 6.640 Å, which excludes the possibility of any bonding interaction between gold atoms.

Crystals of complex **4** were obtained from a of  $CH_2Cl_2$ /hexane mixture (1:5) at room temperature. A view of the molecular structure is presented in Fig. 3 with the relevant interatomic distances and angles summarized in Table 2. The coordination geometry about the copper atom is almost idealized trigonal planar according to (i) the negligible displacement of copper atom away from the P<sub>2</sub>Br plane and (ii) the sum of the three angles around the cop-

per atom which is  $360^{\circ}$ . These two last observations are consequences of symmetry operator ( $C_2$  axis) in the Cu–Br bond. The bulky cyrhetrenyl groups adopt an *anti* conformation respect to the trigonal plane. The Cu–Br distance of 2.3416(10) Å is comparable to those observed in other three-coordinated copper(I) compounds [20,21,27]. The Cu–P distance of 2.2346(11) Å is somewhat shorter than that measured previously in copper(I) bromide complexes containing tertiary organo-phosphines [20,21,27]. Within the cyrhetrenyl group the average Re–Cp (centroid) and Re–C(O) distances and Re–C–O angles are comparable to the one observed in complexes **2** and **3**, and are also concordant with the corresponding values reported for other complexes containing the cyrhetrenyl group [28–30].





C(12)

C(11)

C(10)

C(19)

Fig. 3. ORTEP's plots of complex 4 with displacement ellipsoids at the 30% probability level.

# 4. Experimental

All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. Solvents were purified as follow: hexane and tetrahydrofuran by distillation from sodium/ benzophenone ketyl; dichloromethane, chloroform and acetonitrile by distillation from P2O5. PdCl2(NCPh)2 and CuBr(SMe2) (Aldrich) were use as received.  $(\eta^5-C_5H_4PPh_2)Re(CO)_3$  (1) [12] and (tht)AuCl (tht = tetrahydrothiophene) [16] were prepared following published procedures. Infrared spectra were recorded with a Perkin-Elmer FT-IR Spectrum One spectrophotometer. NMR spectra were recorded with a Bruker Avance 400 spectrometer. <sup>1</sup>H NMR chemical shifts were referenced using the chemicals shifts of residual solvent resonances, and <sup>31</sup>P{<sup>1</sup>H}NMR chemical shifts were referenced to 85% H<sub>3</sub>PO<sub>4</sub> as external standard. The mass spectrum of 3 was obtained on a Thermo-Finnigan MAT 900XP, at the Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile.

## 4.1. trans- $[(\eta^5 - C_5 H_4 PPh_2)Re(CO)_3]PdCl_2(NCMe)$ (2)

To 60 mg (0.116 mmol) of  $(\eta^{5}-C_{5}H_{4}PPh_{2})Re(CO)_{3}$  (1) dissolved in 15 mL of chloroform were added 44 mg (0.115 mmol) of solid PdCl<sub>2</sub>(NCPh)<sub>2</sub> and the mixture was refluxed for 4 h. After cooling at room temperature a red precipitate was formed, this was filtered out and washed with chloroform. The elemental analysis of this material reveals a dimeric nature (*Anal.* Calc. for [ $C_{20}H_{14}O_{3}PCl_{2}$ -RePd]<sub>2</sub> · CHCl<sub>3</sub>: C, 32.52; H, 1.91. Found: C, 32,49; H, 1.89%). Crystallization from acetonitrile/diethylether (1:3) yielded orange-red microcrystals (suitable for analysis of X-ray diffraction) of **2** (62 mg, 0,084 mmol, 73%).

IR (cm<sup>-1</sup>, CH<sub>3</sub>CN)  $\nu_{(CO)}$  2029 (s); 1936 (vs). IR (cm<sup>-1</sup>, KBr)  $\nu_{(CN)}$  2297  $\nu_{(CO)}$  2032 (s); 1943 (vs); 1933 (vs). <sup>1</sup>H NMR (CD<sub>3</sub>CN)  $\delta$ : 1.98 (s, 3H, CH<sub>3</sub>CN), 5.60 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 5.81 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 7.50–7.74 (m, 10H, C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN)  $\delta$ : 21,3 (s, PPh<sub>2</sub>). Elemental *Anal.* Calc. for C<sub>22</sub>H<sub>17</sub>O<sub>3</sub>NPCl<sub>2</sub>RePd: C, 35.87; H, 2.31. Found: C, 35.79; H, 2.30%.

#### 4.2. $[(\eta^5 - C_5 H_4 PPh_2)Re(CO)_3]AuCl(3)$

To a solution of **1** (100 mg, 0.193 mmol) dissolved in 10 mL of  $CH_2Cl_2$  were slowly added 61 mg (0.193 mmol) of (tht)AuCl dissolved in 5 mL of  $CH_2Cl_2$ . The transparent mixture was stirred at room temperature for 4 h. Solvent was pumped off and the colorless oil produced was crystallized from  $CH_2Cl_2$ /hexane (1.5) to give white crystals of **3** (130 mg, 0.173 mmol, 90%).

IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>)  $v_{(CO)}$  2032 (s); 1942 (vs). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 5,56 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 5,69 (m, 2H, C<sub>5</sub>H<sub>4</sub>), 7.48–7.62 (m, 10H, C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$ : 25.7 (s, PPh<sub>2</sub>). Mass spectrum (<sup>187</sup>Re and <sup>35</sup>Cl) *m*/*z*: 752 [M<sup>+</sup>], 520 [M<sup>+</sup>–AuCl], 492 [M<sup>+</sup>–AuCl–CO], 435 [M<sup>+</sup>–AuCl–3CO]. Elemental *Anal.* Calc. for C<sub>20</sub>H<sub>14</sub>O<sub>3</sub>PCIReAu: C, 31.87; H, 1.86. Found: C, 31.92; H, 1.90%.

## 4.3. $[(\eta^5 - C_5 H_4 PPh_2)Re(CO)_3]_2CuBr(\mathbf{4})$

To a solution of ligand **1** (120 mg, 0.231 mmol) in 15 mL of  $CH_2Cl_2$  were added 24 mg (0.115 mmol) of solid  $CuBr(Sme_2)$ . The pale purple suspension formed was stirred overnight at room temperature. After this time the mixture became a colorless solution. Solvent evaporation to dryness produced a white solid which was crystallized from  $CH_2Cl_2$ /hexane (1:5) generating transparent crystals of complex **4** (112 mg, 0.095 mmol, 81%).

IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>)  $v_{(CO)}$  2028 (s); 1933 (vs). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 5.36 (broad signal, 2H, C<sub>5</sub>H<sub>4</sub>), 5.86 (broad signal, 2H, C<sub>5</sub>H<sub>4</sub>), 7.28–7.40 (m, 10H, C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$ : –13.5 (broad signal, *P*Ph<sub>2</sub>). Elemental *Anal.* Calc. for C<sub>40</sub>H<sub>28</sub>O<sub>6</sub>P<sub>2</sub>BrReCu: C, 40.54; H, 2.36. Found: C, 40.39; H, 2.35.

#### 4.4. X-ray crystal structure determination of complexes 2, 3 and 4

Single crystals of complexes 2, 3 and 4, obtained as mentioned above, were mounted on the tip of a glass fiber in a random orientation. Intensity data were collected on a Bruker Smart Apex diffractometer equipped with a bidimensional CCD detector using graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Semiempirical corrections, via  $\psi$ -scans, were applied for absorption for complexes 2 and 3, and face indexing absorption correction was applied to complex 4. The diffraction frames were integrated using the SAINT package [31] and corrected for absorption with XPREP in SHELXTL-PC [32] and sadabs [33]. The structures were solved using XS in SHELXTL-PC [32] by direct methods and completed (non-H atoms) by difference Fourier techniques. Refinement was performed by the full-matrix least-squares method based on  $F^2$ . All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed in their calculated positions, assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. A summary of the data collection and structure refinement parameters is given in Table 1. ORTEP plots of complexes 2, 3 and 4 with displacement ellipsoids at the 30% probability level were generated with XP in SHELXTL-PC [32].

#### Acknowledgements

A.H.K. acknowledges FONDECYT (Project 1060487) and D.I. Pontificia Universidad Catolica de Valparaiso. D.S. acknowledges MECESUP and FONDECYT for a Doctoral scholarship. We also appreciate the financial support of MECESUP (Project UCH 0116) for a MS instrument. The loan of NH<sub>4</sub>ReO<sub>4</sub> from MOLYMET-Chile is also much appreciated.

## Appendix A. Supplementary data

CCDC 692241, 692242 and 692243 contain the supplementary crystallographic data for complexes **2**, **3** and **4**. These data can be

obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.10.038.

#### References

- M. Herberhold, Ferrocene Compounds Containing Heteroelements, Ferrocenes: Homogeneous Catalysis-Organic Synthesis-Materials Science, VCH, Weinheim, 1995. p. 22.
- [2] R.C.J. Atkinson, N.J. Long, Monodentate Ferrocene Donor Ligands in Ferrocenes: Ligands, Materials and Biomolecules, John Wiley & Sons Ltd., 2008. p. 3.
- X.D. He, A. Maisonnat, F. Dahan, R. Poliblanc, Organometallics 8 (1989) 2618.
   M.D. Rausch, B.H. Edwards, R.D. Rogers, J.L. Atwood, J. Am. Chem. Soc. 105 (1983) 3882.
- [5] M.S. Blais, R.D. Rogers, M.D. Rausch, J. Organomet. Chem. 593 (2000) 142.
- [6] R.M. Bullock, C.P. Casey, Acc. Chem. Res. 20 (1987) 167.
- [7] C. Corneliben, G. Erker, G. Kehr, R. Fröhlich, Dalton Trans. (2004) 4059.
- [8] L.-Ch. Song, G.-A. Yu, Y. Liu, B.-S. Yin, X.-G. Zhang, Q.-M. Hu, Organometallics 26 (2007) 1966.
- [9] B. Brumas-Soula, F. Dahan, R. Poilblanc, New J. Chem. (1998) 15.
- [10] R.C.J. Atkinson, V.C. Gibson, N.J. Long, Chem. Soc. Rev. 33 (2004) 313.
- [11] M.D. Rausch, W.C. Spink, Synth. React. Inorg. Metal-Org. Chem. 19 (1989) 1093.
- [12] S. Eichenseher, O. Delacroix, K. Kromm, F. Hampel, J.A. Gladysz, Organometallics 24 (2005) 245.
- [13] S. Otto, J. Chem. Crystallogr. 31 (2001) 185.
- [14] S. Otto, A. Roodt, J. Smith, Inorg. Chim. Acta 303 (2000) 295.

- [15] N.J. Long, A.J.P. White, D.J. Williams, M. Younus, J. Organomet. Chem. 649 (2002) 94.
- [16] R. Uson, A. Lagunas, Organomet. Synth. 3 (1986) 322.
- [17] K. Robler, T. Ruffer, B. Walfort, R. Packheiser, R. Holze, M. Zharnikov, H. Lang, J. Organomet. Chem. 692 (2007) 1530.
- [18] J.E. Aguado, S. Canales, M.C. Gimeno, P.G. Jones, A. Lagunas, D. Villacampa, Dalton Trans. (2005) 3005.
- [19] D.J. Fife, W.M. Moore, K.W. Morse, Inorg. Chem. 23 (1984) 1684.
- [20] G.A. Bowmaker, L.M. Engelhardt, P.C. Healy, J.D. Kildea, R.I. Papasergio, A.H. White, Inorg. Chem. 26 (1987) 3533.
- [21] G.A. Bowmaker, S.E. Boyd, J.V. Hanna, R.D. Hart, P.C. Healy, B.W. Skelton, A.H. White, Dalton Trans. (2002) 2722.
- [22] F. Ferguson, R. McCrindle, A.J. McAlees, M. Parvez, Acta Crystallogr., Sect. B 38 (1992) 2679.
- [23] R.R. Guimerans, M.M. Olmstead, A.L. Balch, Inorg. Chem. 22 (1983) 2223.
- [24] A. Houlton, R.M.G. Roberts, J. Silver, M.G.B. Drew, Dalton Trans. (1990) 1543.
- [25] P.C. Jones, C. Freire Erdbrügger, R. Hohbein, E. Schwarzmann, Acta Crystallogr., Sect. C 44 (1988) 1302.
- [26] E.M. Barranco, O. Crespo, M. Concepcion Gimeno, A. Lagunas, P.G. Jones, B. Ahrens, Inorg. Chem. 39 (2000) 680.
- [27] P.H. Davis, R.L. Belford, I.C. Paul, Inorg. Chem. 12 (1973) 213.
- [28] P.J. Fitzpatrick, Y. LePage, I.A. Butler, Acta Crystallogr., Sect. B 37 (1981) 1052.
   [29] T. Cautivo, F. Godoy, A.H. Klahn, G.E. Buono-Core, D. Sierra, M. Fuentealba, M.T.
- Garland, Inorg. Chem. Commun. 10 (2007) 1031.
  [30] R. Arancibia, F. Godoy, G.E. Buono-Core, A.H. Klahn, E. Gutierrez-Puebla, A. Monge, Polyhedron 27 (2008) 2421.
- [31] SAINT-PLUS (Version 6.02), Bruker Analytical X-ray Systems Inc., Madison, WI, USA. 1999.
- [32] SHELXTL Reference Manual (Version 6.14), Bruker Analytical X-ray Systems Inc., Madison, WI, USA, 1998.
- [33] G.M. Sheldrick, sADABS (Version 2.05), Bruker Analytical X-ray Systems Inc., Madison, WI, USA, 1999.