Inorganica Chimica Acta 366 (2011) 350-356

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

A new approach to coordination chemistry involving phosphorus-selenium based ligands. Ring opening, deselenation and phosphorus-phosphorus coupling of Woollins' Reagent

Richard C.S. Wong*, Mei Lee Ooi

Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

A R T I C L E I N F O

Article history: Received 19 August 2010 Received in revised form 12 November 2010 Accepted 18 November 2010 Available online 5 December 2010

Keywords: Woollins' Reagent Congener Ring-opening Bond cleavage Mechanistic pathway Thermolytic studies

ABSTRACT

The facile reaction of $[CpCr(CO)_3]_2$ (1) with an equivalent of 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide or Woollins' Reagent (WR) at ambient temperature gave mainly $[CpCr(CO)_2]_2$ Se (3) as the main product. A similar reaction with an excess of 1 gave 3 (58%) and *trans*- $[CpCr(CO)_2(SePPh)]_2$ (5, 25%). However reaction with an equivalent of the triply bonded congener Cp₂Cr₂(CO)₄ (2) at 60 °C took 3 h to complete and led to the isolation of *trans*- $[CpCr(CO)_2(SePPh)]_2$ (5, 3%), CpCr(CO)₂(SeP(H)Ph) (4, 18%) and $[CpCr(Se_2P(O)Ph)]_2$ (6, 2%). The ring-opening reaction of WR via an initial homolytic P–Se bond cleavage by CpCr(CO)_n. (*n* = 2 (2A) or 3 (1A)) depicts a new approach to coordination chemistry involving P–Se based ligands. A mechanistic pathway was proposed according to the evidences obtained from thermolysis, NMR and mass spectra studies. All the products of 4, 5 and 6 have been structurally characterized by single-crystal X-ray diffraction analysis.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

For the last two decades, mixed pnicogen-chalcogen ligands have attracted a lot of attention from organometallic chemists. Transition metals especially those at low oxidation states are stabilized by the presence of both pnicogen-chalcogen soft donors in these mixed ligands [1,2]. For example, ligands containing arsenic-sulfur [3-7], phosphorus-sulfur [8-14] and phosphorusselenium [15-22] have been associated with interesting chemistry due to their inherent potential liability and strong residual nucleophilicity. Mixed ligands especially organo-phosphorus-chalcogen heterocycles such as (*p*-methoxyphenyl)-thionophosphine sulfide (LR, Lawesson's reagent) [23,24] and 2,4-bis(p-tolylthio)1, 3-dithia-2,4-diphosphetane-2,4-disulfide (DR, Davy's Reagent) [25,26] have proven to be versatile ligands for novel metalcomplex formation. Another such ligand is Woollins' Reagent [27–32], whose reactivity with Group 6 organomolybdenum metal is relatively unexplored. With this background we embarked on the study of the reactivity of $[CpCr(CO)_n]_2$ (*n* = 2 or 3) towards Woollins' Reagent.

2. Experimental

2.1. General procedures

All reactions were carried out using conventional Schlenk techniques under an inert atmosphere of argon in a Vacuum Atmosphere Dribox equipped with a Model HE 493 Dri-train. ¹H, ¹³C and ³¹P NMR spectra were measured on JEOL Lambda and ECA 400 MHz spectrometers. ¹H and ¹³C chemical shifts were referenced to residual C₆H₆ in C₆D₆ and ³¹P chemical shifts to 85% aqueous H₃PO₄ (external standard) for ³¹P {¹H}. IR spectra in Nujol mulls were measured in the range of $4000-400 \text{ cm}^{-1}$ by means of a Perkin-Elmer 2000 FTIR instrument. Elemental analyses were performed by the in-house microanalytical laboratory using a Perkin-Elmer 2400 Series II CHNS/O System. Mass spectrometric measurements, performed by direct injection using electrospray ionization (ESI), were made on an Agilent 6230 LCMS instrument. Electrospray (high resolution) mass spectrometric measurements were obtained on an Accurate Mass Q-Tof spectrometer. All solvents were distilled of sodium/benzophenone under nitrogen prior to use. Silica gel (Merck Kieselgel 60, 35-70 mesh) and Celite (Fluka AG) were activated at 140 °C overnight before chromatographic use. 1,3,2,4-Dithiadiphosphetane 2,4-diselenides (Woollins' Reagent) was purchased from Sigma-Aldrich. [CpCr(CO)₃]₂ was synthesized as described by Manning and co-workers [33] from chromium hexacarbonyl (99% purity from Sigma).



^{*} Corresponding author. Tel.: +60 379674260; fax: +60 379674193.

E-mail addresses: richard@um.edu.my, richardwongcheeseng@gmail.com (R.C.S. Wong).

^{0020-1693/\$ -} see front matter \circledcirc 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2010.11.034

2.2. Reaction of $Cp_2Cr_2(CO)_6$ (1) with an equivalent of Woollins' reagent at ambient temperature

A deep green suspension of $Cp_2Cr_2(CO)_6$ (1) (200 mg, 0.497 mmol) in toluene (~15 mL) was added WR (264 mg, 0.497 mmol) and the mixture stirred at ambient temperature. A dark orange brown suspension was obtained after *ca*. 5 min. The reaction mixture was allowed to continue stirring for 0.5 h. The resultant dark orange brown solution was filtered through celite and the filtrate was concentrated to *ca*. 3–4 mL before loading onto a silica gel column (2 cm × 9 cm) prepared in *n*-hexane. Elution gave three fractions:

- (i) A dark purplish orange fraction was eluted with *n*-hexane (65 mL) which when concentrated to dryness gave fine dark orange brown crystalline solids of $[CpCr(CO)_2]_2Se$ (**3**) (70 mg, 0.165 mmol, 33.2% yield) [34,35], identified its ¹H NMR in benzene-*d*₆ [δ (Cp) 4.36] and TLC against an authentic sample [*R*_f = 0.64 in 6:3:1 *n*-hexane/toluene/ether as eluent] together with a trace amount of CpCr(CO)₂(SeP(H)Ph) (**4**).
- (ii) A dark orange brown fraction was eluted with toluene (48 mL) which when concentrated to dryness gave a dark brown oily precipitate (189 mg, 60%). Analyses *via* TLC showed it consisted of a mixture of [CpCr(CO)₂]₂Se (**3**), *trans*-[CpCr(CO)₂(SePPh)]₂ (**5**) and CpCr(CO)₂(SeP(H)Ph) (**4**) in ratio of 8:1:1. Attempts to separate the mixture resulted in failure.
- (iii) An uncharacterized green fraction was eluted with THF (60 mL) which when concentrated to dryness gave a green residue (162 mg).

A deep bluish green ring was remained unmoved on top of the column.

2.3. Reaction of excess $Cp_2Cr_2(CO)_6$ (1) with Woollins' Reagent at ambient temperature

A deep green suspension of $Cp_2Cr_2(CO)_6$ (1) (101 mg, 0.251 mmol) in toluene (~10 mL) was added in 0.125 equivalent of WR (16 mg, 0.031 mmol). The color of the reaction mixture changed to orange brown immediately. The reaction mixture was stirred at ambient temperature. After 1 h, no more color change was observed and the resultant dark orange brown reaction mixture was filtered through a sintered-glass funnel. The filtrate was concentrated to *ca*. 3 mL and loaded onto a silica gel column prepared in *n*-hexane (1.5 cm × 11.5 cm). Three fractions were eluted:

- (i) A dark orange brown fraction with *n*-hexane (10 mL) which upon evaporation to dryness gave a black crystalline solid **3** (62 mg, 0.146 mmol, 58.2% yield).
- (ii) A dirty green fraction was eluted with *n*-hexane/toluene mixture (4: 1) (18 mL) which upon evaporation to dryness gave green crystalline solids of unreacted $Cp_2Cr_2(CO)_6$ (1) (17 mg, 0.042 mmol, 16.7% recovery).
- (iii) A greyish brown fraction was eluted with toluene (36 mL) which upon evaporation to dryness gave the dark brown crystalline solids of *trans*-[CpCr(CO)₂(SePPh)]₂ (**5**) (45 mg, 0.062 mmol, 24.7% yield). Anal. Found: ¹H NMR (benzene- d_6): δ 4.01 (s, Cp); δ 7.02–7.72 (m, C₆H₅). ¹³CNMR (benzene- d_6): δ 90.4 (Cp), δ 126.02, 128.89, 129.65, 130.56, 138.23 and 138.65 (C₆H₅), δ 249.79, 254.22 (CO). IR: *v*(CO) at 1962.47vs, 1951.77vs, 1899.03vs cm⁻¹; other peaks at 1086.72m, 1063.01m, 1016.07m, 860.22vw, 844.94vw, 828.13w, 803.69w, 741.04w, 690.62w, 664.64vw cm⁻¹ (nujol). HR-MS ESI⁺ (*m*/*z*): (⁵²Cr, ⁸⁰Se): 722.4748

 $[CpCr(CO)_2(SePPh)]_2, 691 [Cp_2Cr_2(CO)_3(SePPh)_2], 664$ $[Cp_2Cr_2(CO)_2(SePPh)_2], 633 [Cp_2Cr_2(CO)(SePPh)_2)], 589$ $[Cp_2Cr_2(CO)_2(SePPh)(SeP)], 533 [Cp_2Cr_2(SePPh)(SeP)],$ $502 [Cp_2Cr_2(Se_2PPh)(Se)], 451 [Cp_2Cr_2(CO)(SePPh)], 413$ $[CpCr(Se_2(O)PPh)(O)], 401 [CpCr(Se_2(O)PPh)], 385$ $[CpCr(Se_2(O)PPh)], 359 [CpCr(CO)2(SePPh)], 331 [CpCr(CO)(SeP-Ph)], 303 [CpCr(SePPh)], 273 [CpCrSe_2], 228 [CpCrSeP]. Anal.$ $Calc. for <math>C_{26}H_{20}Cr_2O_4P_2Se_2$: C, 43.21; H, 2.77; Cr, 14.40; O, 8.86; P, 8.59; Se, 22.16. Found: C, 43.37; H, 2.89; Cr, 14.67; O, 8.45; P, 8.62; Se, 22.45%.

A deep bluish green ring was remained unmoved on top of the column.

2.4. Reaction of $Cp_2Cr_2(CO)_4$ (2) with Woollins' reagent at 60 °C

A deep green suspension of $Cp_2Cr_2(CO)_4$ (2) (300 mg, 0.867 mmol) in toluene (~15 mL) was added WR (461 mg, 0.867 mmol) and stirred at 60 °C for 3 h. The resultant dark brownish green reaction mixture was concentrated to *ca*. 10 mL left and was filtered through a sintered-glass funnel to remove a deep green residue (361 mg). The filtrate was concentrated to *ca*. 3 mL left and absorbed onto silica gel (~1 g). The dark brownish green slurry was evacuated to dryness under *vacuo* and chromatographed onto a silica gel column (1.5 cm × 9 cm) prepared in *n*-hexane. Elution under slight pressure gave four fractions:

- (i) A greyish brown eluant in *n*-hexane-toluene (1:2) (45 mL) when which was concentrated to dryness gave dark brown crystalline solids of **5** (18 mg, 0.022 mmol, 3% yield).
- (ii) A dark pinkish purple eluant in *n*-hexane-toluene (1:1, 15 mL) and when concentrated to dryness, gave dark pinkish purple crystalline solids of CpCr(CO)₂(SeP(H)Ph) (4) (55 mg, 0.152 mmol, 18% yield). Anal. Found: ¹H NMR (benzene- d_6): δ 4.26 (s, Cp); δ 5.72 (s, P-H); δ 6.68–7.37 (m, C₆H₅); ¹³C NMR (benzene- d_6): δ 89.53 (Cp), δ 132.71, 132.59, 131.37, 129.67, 129.62 and 129.50 (C₆H₅), 249.79, 254.22 (CO). ³¹P NMR (benzene- d_6 : proton coupled): δ 45.84, 48.26 (d. *J* = 387.6 Hz). IR: *v*(CO) at 1954.93vs, 1942.23vs, 1871.60vs, 1853.25sh, and 1847.43sh cm^{-1} and other peaks at 1159.72m, 1110.70m, 1093.53m, 1067.03m, 1055.44m, 1014.44m, 921.75m, 912.90m, 846.61m. 823.99m 748.56m. 727.74w. 706.84vw, 690.43m. 685.54m. 639.48m, 590.79m, 550.25 m cm⁻¹ (nujol). HR-MS ESI⁺ (*m/z*): (⁵²Cr, ⁸⁰Se): 362.2380 [CpCr(CO)₂(SeP(H)Ph)], 723 $[Cp_2Cr_2(CO)_4(SePPh)_2], 695 [Cp_2Cr_2(CO)_3(SePPh)_2], 666$ $[Cp_2Cr_2(CO)_2(SePPh)_2], 633$ $[Cp_2Cr_2(CO)(SePPh)_2],$ 451 $[Cp_2Cr_2(CO)(SePPh)],$ 413 [CpCr(Se(O)PPh)(O)],401 [CpCr(SePPh)(O)], 362 [CpCr(CO)2(SeP(H)Ph)], 331 [CpCr(CO)(SePPh)], 303 [CpCr(SePPh)], 273 [CpCrSe₂]. Anal. Calc. for C₁₃H₁₀CrO₂PSe: C, 43.09; H, 2.76; Cr, 14.36; O, 8.84; P, 8.56; Se, 22.10. Found: C, 43.37; H, 2.58; Cr, 14.39; O, 8.68; P, 8.47; Se, 22.54%.
- (iii) A dark green eluant in ether (9 mL) which when concentrated to dryness gave dark brownish green crystalline solids of Cp₂Cr₂(Se₂P(O)Ph)₂ (**6**) (14 mg, 0.018 mmol, 2% yield). Anal. Found: ¹H NMR (toluene- d_8): δ 5.04 (s, Cp); δ 6.82– 7.08 (m, C_6H_5). ¹³C NMR (benzene- d_6): δ 126.02 (Cp), δ 129.67, 130.56, 132.46, 138.20 and 138.63 (C₆H₅); ³¹P NMR (benzene- d_6): δ –123.34. I.R: v at 1157.67w, 1106.17m, 1084.11m, 1058.96m, 1026.21m, 998.64m, 815.55m, 741.12w, 728.43sh, 686.71w cm⁻¹ (nujol). HR-MS ESI⁺ (m/ z): $({}^{52}Cr, {}^{80}Se)$: 801.5744 [Cp₂Cr₂(Se₂P(O)Ph)₂], 413 $[CpCr(Se_2(O)PPh)(O)],$ 401 $[CpCr(Se_2P(O)Ph)],$ 385 [CpCr(Se₂PPh)], 303 [CpCr(Se₂P)], 273 [CpCrSe₂]. Anal. Calc. for C₂₀H₂₀Cr₂O₂P₂Se₄: C, 29.93; H, 2.49; Cr, 12.97; O, 3.99;

P, 7.73; Se, 39.90. Found: C, 29.62; H, 2.54; Cr, 12.88; O, 3.96; P, 7.45; Se, 39.46%.

(iv) A green eluant in THF (25 mL) which when concentrated to dryness gave an uncharacterized deep green crystalline precipitate (361 mg).

2.5. NMR tube reactions

The following thermolysis experiments were carried out in toluene- d_8 (~0.6 mL) in a 5 mm septum-capped NMR tube at 110 °C and monitored *via* ¹H NMR at specified time intervals for 14 h or otherwise stated. The final product composition from each thermolysis study is tabulated in Table 1.

2.5.1. Thermolysis of CpCr(CO)₂(SeP(H)Ph) (4)

A purple solution of **4** (20 mg, 0.055 mmol) was thermolyzed for 14 h. The resultant dark brown solution consists of **5** (38%) and **6** (11%) together with some uncharacterized dark brown precipitates.

2.5.2. Thermolysis of trans- $[CpCr(CO)_2(SePPh)]_2$ (5)

A greyish brown solution of **5** (13 mg, 0.018 mmol) was thermolyzed for 5 h. The resultant dark green solution consists of **4A** (10%) and **6** (70%) together with some uncharacterized dark brown precipitates.

Table 1

Time dependent variation of product composition.^a

Reaction	Products (% yield)			
	4 A	4	5	6
Thermolysis of 4 /14 h	-	-	38	11
Thermolysis of 5 /5 h	10	-	-	70
Co-thermolysis of 4 and Woollins' reagent/14 h	-	19	6	31

^a Product yields obtained by integration of Cp resonances in ¹H NMR spectrum of product mixture.

2.5.3. Thermolysis of $Cp_2Cr_2(Se_2P(O)Ph)_2$ (6)

A green solution of **6** (22 mg, 0.013 mmol) was thermolyzed for 14 h. The resultant dark green solution consists of some uncharacterized dark brown precipitates.

2.5.4. Co-thermolysis of CpCr(CO)₂(SeP(H)Ph) (**4**) and Woollins' reagent

A purple mixture of $CpCr(CO)_2(SeP(H)Ph)$ (4) (20 mg, 0.055 mmol) with an equivalent of WR (29 mg, 0.055 mmol) was thermolyzed for 14 h. The resultant dark brown solution consists of 4 (19%), 5 (6%) and 6 (31%) together with some uncharacterized dark brown precipitates.

2.6. Structural studies of 4, 5 and 6

Diffraction-quality single crystals were obtained from the solution at ambient temperature. Compound **4** was obtained as dark purple crystals from *n*-hexane/THF at room temperature after 2–3 days. Complexes **5** was obtained as dark brown crystals and **6** as dark brownish green crystals in THF at -28 °C after 1 week and 2 weeks, respectively. The crystals are mounted on quartz fibers. Details of crystal parameters, data collection and structure refinement are tabulated in Table 2. The data were corrected for Lorentz and polarization effects with SMART suite of programs [36] and for absorption effects with the SHELXTL suite of programs [37].

3. Results and discussion

3.1. Products isolation

The facile reaction of $[CpCr(CO)_3]_2$ (**1**) with one mole equivalent of WR at ambient temperature completed in 0.5 h had led to the isolation of $Cp_2Cr_2(CO)_4Se$ (**3**) as main product together with a trace amount of $[CpCr(CO)_2(SePPh)]_2$ (**5**), $CpCr(CO)_2(SeP(H)Ph)$

Table 2

Data collection and processing parameters of trans-[CpCr(CO)₂(SePPh)]₂ (5), CpCr(CO)₂(SeP(H)Ph) (4) and Cp₂Cr₂(Se₂P(O)Ph)₂ (6).

Complexes	trans-[CpCr(CO) ₂ (SePPh)] ₂ (5)	CpCr(CO) ₂ {SeP(H)Ph} (4)	$[CpCr(Se_2P(O)Ph)]_2$ (6)
Empirical formula	$C_{26}H_{20}Cr_2O_4P_2Se_2$	C ₁₃ H ₁₀ CrO ₂ PSe	C22H20Cr2O2P2Se4
Formula weight	720.28	360.14	399.08
Т (К)	223(2)	243(2)	223 (2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2(1)/c	$P2_1/n$	$P2_1/n$
Unit cell dimensions			
a (Å)	7.9095(8)	6.3855(6)	9.6596(6)
b (Å)	18.688(2)	18.3404(17)	8.0501(5)
<i>c</i> (Å)	9.2154(10)	11.3791(11)	17.2372(11)
α (°)	90	90	90
β (°)	104.246(2)	95.489(2)	103.2300(10)
γ (°)	90	90	90
$V(Å^3)$	1320.3(2)	1326.5(2)	1304.80(14)
Z	2	4	4
$D_{\text{calc}} (\text{Mg m}^{-3})$	1.812	1.803	2.032
Absorption coefficient (mm ⁻¹)	3.733	3.715	6.553
F(000)	708	708	764
Crystal size (mm)	$\textbf{0.16} \times \textbf{0.10} \times \textbf{0.10}$	$0.12 \times 0.06 \times 0.03$	$0.64 \times 0.18 \times 0.14$
θ range for data collection	2.18-25.00	2.11-27.50	2.17-27.50
Limiting indices	$-9 \leqslant h \leqslant 9$	$-7 \leqslant h \leqslant 8$	$-11 \leqslant h \leqslant 12$
	$-22 \leqslant k \leqslant 21$	$-22 \leqslant k \leqslant 23$	$-10 \leqslant k \leqslant 9$
	$-10 \leqslant l \leqslant 10$	$-14 \leqslant l \leqslant 14$	$-22 \leqslant l \leqslant 20$
Reflections collected/unique	7378/2329 [R(int) = 0.0452]	9213/3048 [R(int) = 0.0531]	9000/3002 [R(int) = 0.0316]
Data/restraints/parameters	2329/0/163	3048/0/163	3002/0/145
Goodness-of-fit on F^2	1.165	1.159	1.026
Final R indices $(I > 2\sigma(I))$	$R_1 = 0.0561$	$R_1 = 0.0592$	$R_1 = 0.0321$
	$wR_2 = 0.1268$	$wR_2 = 0.1152$	$wR_2 = 0.0791$
R indices (all data)	$R_1 = 0.0720$	R1 = 0.0785	$R_1 = 0.0395$
	$wR_2 = 0.1317$	$wR_2 = 0.2105$	$wR_2 = 0.0820$
Largest different peak and hole ($e A^{-3}$)	1.828 and -0.533	0.676 and -0.472	0.658 and -0.372

(**4**) and an uncharacterized insoluble green residue believed to be decomposed WR.

This observation is comparable to the reaction of **1** with elemental selenium [34,35] and mixed ligand P₄Se₃ [15–17] affording **3** as the main product. It is envisaged that the labile monomeric species CpCr(CO)₃· (**1A**) or CpCr(CO)₂· (**2A**) [38–40] generated from the dissociation of **1** reacts with excess WR resulting in its cleavage and subsequent abstraction of Se atom to form **3** as depicted in route (i) in Scheme 1. However, a similar reaction of **1** with 0.125 equivalent of WR gave Cp₂Cr₂(CO)₄Se (58% yield), unreacted Cp₂Cr₂(CO)₆ (**1**) (17% recovery) and *trans*-[CpCr(CO)₂(SePPh)]₂ (**5**) (25% yield). Here we noticed that the WR was completely consumed since **1** was in excess and noticeably the uncharacterized insoluble green residue was not formed.

The reaction of the triply bonded congener $Cp_2Cr_2(CO)_4$ (2) with an equivalent of WR required a longer time of 3 h and at an elevated temperature of 60 °C to yield **4** (18%), **5** (3%), **6** (2%) and an uncharacterized insoluble green precipitate (361 mg). It is worthy to note that $Cp_2Cr_2(CO)_4Se$ (**3**) was not formed here which agrees with previous reports involving selenation agents such as Se_8 [34,35] and Ph₂Se₂ [41].

During the thermolysis of **5** which was monitored by ¹H NMR at 110 °C, we noticed the emergence of a species at δ 4.26 together with the formation of **6** (δ 5.04). We propose that this species (δ 4.26) to be CpCr(CO)₂(SePPh) (**4A**) resulting from the loss of a

hydrogen since the ¹H chemical shifts for **4** are δ 4.26 (Cp) and δ 5.72 (P–H) (route v). The formation of this phosphinoselenoylidene product. **4A**, is believed to be the common intermediate species which acts as a precursor to the formation of 5 and 6. This postulation agrees with the NMR tube thermolysis study of 4 at 110 °C for 14 h which gave 5 (38% yield) and 6 (11% yield) and also the ESI mass spectrum of 4 which shows the presence of trans- $[CpCr(CO)_2(SePPh)]_2$ (*m*/*e* = 722). These observations suggest that the thermally unstable **4** is likely to be the primary product which slowly converts to the secondary product 5 via 4A (route iv and vi). Under similar condition, cothermolysis of 4 with WR gave unreacted 4 (19% recovered), 5 (6% yield), 6 (31% yield) and some uncharacterized Cp-containing compounds. As expected, in the presence of WR more Se atoms will be available for the formation of **6**, hence prolonged thermolysis ultimately resulted in the isolation of the eight-membered ring complex $[CpCr(Se_2P(O)Ph)]_2$ (6) as the final thermolytic product (route vii).

3.2. Mechanistic pathways

Similar to its sulfur analogue of LR [23], WR also underwent P_2Se_2 ring opening mechanism with a propensity to give several types of fragments as detected by mass spectrometry [42] (Scheme 2). The molecular structure of **4** suggested that its formation is likely to result from the attack of $CpCr(CO)_n$. (n = 2 (**2A**) or 3



Scheme 1. Proposed synthetic pathway for the formation of products 3, 4, 5 and 6.



Scheme 2. Fragmentation of Woollins' Reagent as detected by mass spectrometry.

(1A)) radical at the P₂Se₂ central ring of the WR to generate the PhPSe- fragment. Further interaction of 1A or 2A with a PhPSefragment followed by subsequent abstraction of H afforded 4 (route ii and iii). The source of hydrogen is believed to be the coordinated Cp, as proposed by Goh and co-workers in a similar reaction with LR [23] which explained the presence of several unassigned peaks in the Cp region encountered in the product solutions. Such observation was also present especially in reaction mixtures of 1 and 2 with WR and some chromatographed fractions as weak intensity Cp resonances between δ 4.07 and 5.55. However, the unstable 4 underwent thermolytic degradation with the loss of hydrogen to give 4A (route iv). From the thermolysis study, we concluded that the formation of 5 is reversible which proceeds with dimerization of **4A** via P–P bond coupling and decoupling (route v and vi). Similarities in both P-Se (2.1487(14) Å) and Cr-Se (2.6389(9) Å) bond lengths for CpCr(CO)₂(SeP(H)Ph) (**4**) as compared to those in **5** (2.1425(17) Å and 2.6309(12) Å, respectively) provides further supportive evidence.

Selenation of **5** from the WR ligand with concomitant bond forming and breaking followed by intramolecular bond rearrangements with dimerization, decarbonylation and oxygen abstraction has led to the formation of **6** (route vii). It was not possible for us to conclude experimentally the source of oxygen in **6** as all manipulations were performed in the absence of water and oxygen.

The ease of fragmentation of the P–Se heterocyclic ligand which leads to ring opening in WR resembles well with its P–S analogue, LR. Indeed, both ligands behaved showed similar patterns of reactivity which yielded some structurally identical products with **1** [23].

3.3. Molecular structures of 4, 5 and 6

The molecular structures of **4**, 5 and **6** are shown in Figs. 1–3. Selected bond lengths and angles are listed in Tables 3–5, respectively.

The structure of CpCr(CO)₂(SeP(H)Ph) (**4**) possesses a fourlegged piano-stool configuration at Cr. **4** contains a Cp moiety at the apical position while bonded to two CO groups and a η^2 arylselenaphosphetane ligand. The complex is isostructural to CpCr(CO)₂(SP(H)Ar) (Ar = C₆H₄OMe) obtained from the reaction of **1** with LR [23] and [MoCp{ κ^2 -OP(OC₆H₄OH)R^{*}](CO)₂] (R^{*} = 2,4,6-C₆H₂'Bu₃) from *p*-benzoquinone oxidation of [MoCp(CO)₂ {P(O)R^{*}]⁻ to [43].

The Cr–P bond is indicated as a single bond with bond distance of 2.2643(15) Å which is similar with some of the reported complexes such as CpCr(CO)₂(SP(H)Ar) (2.2607(8) Å) [23]; CpCr(CO)₂(SPR₂) (R = Me, 2.2704(6) Å; Et, 2.2738 (18) Å) [44]. The Cr–Se bond distance of 2.6389(9) Å possessed a single Cr–Se bond



Fig. 1. Molecular structure of $CpCr(CO)_2(SeP(H)Ph)$ (4). Thermal ellipsoids are shown at the 50% probability level.



Fig. 2. Molecular structure of trans-[CpCr(CO)₂(SePPh)]₂ (5). Thermal ellipsoids are shown at the 50% probability level.

which is longer than those observed in the $(\mu-\eta^2-Se_2)$ complexes of $[CpCr(CO)_2]_2Se_2$ (2.277 Å) [35] or $Cp_4Cr_4(CO)_8(P_2Se_2)$ (2.566(2) and



Fig. 3. Molecular structure of $[CpCr(Se_2P(O)Ph)]_2$ (6). Thermal ellipsoids are shown at the 50% probability level.

Table 3 Bond lengths (Å) and angles (°) for $CpCr(CO)_2(SeP(H)Ph)$ (4).

Bond lengths			
Cr(1) - C(7)	1.837(5)	Se(1)-P(1)	2.1487(14)
Cr(1) - C(6)	1.837(5)	P(1)-C(8)	1.802(5)
Cr(1) - P(1)	2.2643(15)	O(1)-C(6)	1.150(6)
Cr(1)-Se(1)	2.6389(9)	O(2)-C(7)	1.147(6)
Bond angles			
C(7)-Cr(1)-C(6)	81.0(2)	P(1)-Se(1)-Cr(1)	55.31(4)
C(7)-Cr(1)-P(1)	83.68(16)	Se(1)-P(1)-Cr(1)	73.40(5)
C(6)-Cr(1)-P(1)	112.14(16)	O(1)-C(6)-Cr(1)	177.2(5)
C(7)-Cr(1)-Se(1)	118.84(15)	O(2)-C(7)-Cr(1)	178.9(4)
C(6)-Cr(1)-Se(1)	81.36(16)	C(9)-C(8)-P(1)	119.9(4)
P(1)-Cr(1)-Se(1)	51.29(4)		

Table 4

Bond lengths (Å) and angles (°) for 5.

$\begin{array}{ccccccc} Cr(1)-C(13) & 1.833(7) & Se(1)-P(1) & 2.1425(17) \\ Cr(1)-C(12) & 1.854(7) & P(1)-C(6) & 1.823(6) \\ Cr(1)-P(1) & 2.2700(18) & P(1)-P(1)\#1 & 2.212(3) \\ Cr(1)-Se(1) & 2.6309(12) & O(1)-C(12) & 1.140(8) \\ Cr(1)-Cr(1)\#1 & 6.1018(19) & O(2)-C(13) & 1.148(8) \\ \hline & Bond angles \\ C(13)-Cr(1)-P(1) & 86.7(2) & P(1)-Se(1)-Cr(1) & 55.66(5) \\ C(12)-Cr(1)-P(1) & 110.7(2) & C(6)-P(1)-Se(1) & 114.2(2) \\ C(13)-Cr(1)-Se(1) & 124.4(2) & C(6)-P(1)-P(1)\#1 & 104.5(2) \\ C(12)-Cr(1)-Se(1) & 82.3(2) & Se(1)-P(1)-P(1)\#1 & 108.70(11) \\ \end{array}$	Bond lengths			
$\begin{array}{ccccc} Cr(1)-C(12) & 1.854(7) & P(1)-C(6) & 1.823(6) \\ Cr(1)-P(1) & 2.2700(18) & P(1)-P(1)\#1 & 2.212(3) \\ Cr(1)-Se(1) & 2.6309(12) & O(1)-C(12) & 1.140(8) \\ Cr(1)-Cr(1)\#1 & 6.1018(19) & O(2)-C(13) & 1.148(8) \\ \hline & Bond angles & & & \\ C(13)-Cr(1)-P(1) & 86.7(2) & P(1)-Se(1)-Cr(1) & 55.66(5) \\ C(12)-Cr(1)-P(1) & 110.7(2) & C(6)-P(1)-Se(1) & 114.2(2) \\ C(13)-Cr(1)-Se(1) & 124.4(2) & C(6)-P(1)-P(1)\#1 & 104.5(2) \\ C(12)-Cr(1)-Se(1) & 82.3(2) & Se(1)-P(1)-P(1)\#1 & 108.70(11) \\ \end{array}$	Cr(1)-C(13)	1.833(7)	Se(1)-P(1)	2.1425(17)
$\begin{array}{ccccc} Cr(1)-P(1) & 2.2700(18) & P(1)-P(1)\#1 & 2.212(3) \\ Cr(1)-Se(1) & 2.6309(12) & O(1)-C(12) & 1.140(8) \\ Cr(1)-Cr(1)\#1 & 6.1018(19) & O(2)-C(13) & 1.148(8) \\ \hline \end{angles} & & & & \\ C(13)-Cr(1)-P(1) & 86.7(2) & P(1)-Se(1)-Cr(1) & 55.66(5) \\ C(12)-Cr(1)-P(1) & 110.7(2) & C(6)-P(1)-Se(1) & 114.2(2) \\ C(13)-Cr(1)-Se(1) & 124.4(2) & C(6)-P(1)-P(1)\#1 & 104.5(2) \\ C(12)-Cr(1)-Se(1) & 82.3(2) & Se(1)-P(1)-P(1)\#1 & 108.70(11) \\ \end{array}$	Cr(1)-C(12)	1.854(7)	P(1)-C(6)	1.823(6)
$\begin{array}{cccc} Cr(1)-Se(1) & 2.6309(12) & O(1)-C(12) & 1.140(8) \\ Cr(1)-Cr(1)\#1 & 6.1018(19) & O(2)-C(13) & 1.148(8) \\ \hline & Bond \ angles \\ C(13)-Cr(1)-P(1) & 86.7(2) & P(1)-Se(1)-Cr(1) & 55.66(5) \\ C(12)-Cr(1)-P(1) & 110.7(2) & C(6)-P(1)-Se(1) & 114.2(2) \\ C(13)-Cr(1)-Se(1) & 124.4(2) & C(6)-P(1)-P(1)\#1 & 104.5(2) \\ C(12)-Cr(1)-Se(1) & 82.3(2) & Se(1)-P(1)-P(1)\#1 & 108.70(11) \\ \hline \end{array}$	Cr(1) - P(1)	2.2700(18)	P(1)-P(1)#1	2.212(3)
$\begin{array}{cccc} Cr(1)-Cr(1)\#1 & 6.1018(19) & O(2)-C(13) & 1.148(8) \\ \hline Bond \ angles \\ C(13)-Cr(1)-P(1) & 86.7(2) & P(1)-Se(1)-Cr(1) & 55.66(5) \\ C(12)-Cr(1)-P(1) & 110.7(2) & C(6)-P(1)-Se(1) & 114.2(2) \\ C(13)-Cr(1)-Se(1) & 124.4(2) & C(6)-P(1)-P(1)\#1 & 104.5(2) \\ C(12)-Cr(1)-Se(1) & 82.3(2) & Se(1)-P(1)-P(1)\#1 & 108.70(11) \\ \end{array}$	Cr(1)-Se(1)	2.6309(12)	O(1)-C(12)	1.140(8)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Cr(1)-Cr(1)#1	6.1018(19)	O(2)-C(13)	1.148(8)
$\begin{array}{cccc} C(13)-Cr(1)-P(1) & 86.7(2) & P(1)-Se(1)-Cr(1) & 55.66(5) \\ C(12)-Cr(1)-P(1) & 110.7(2) & C(6)-P(1)-Se(1) & 114.2(2) \\ C(13)-Cr(1)-Se(1) & 124.4(2) & C(6)-P(1)-P(1)\#1 & 104.5(2) \\ C(12)-Cr(1)-Se(1) & 82.3(2) & Se(1)-P(1)-P(1)\#1 & 108.70(11) \\ \end{array}$	Bond angles			
$\begin{array}{cccc} C(12)-Cr(1)-P(1) & 110.7(2) & C(6)-P(1)-Se(1) & 114.2(2) \\ C(13)-Cr(1)-Se(1) & 124.4(2) & C(6)-P(1)-P(1)\#1 & 104.5(2) \\ C(12)-Cr(1)-Se(1) & 82.3(2) & Se(1)-P(1)-P(1)\#1 & 108.70(11) \\ \end{array}$	C(13) - Cr(1) - P(1)	86.7(2)	P(1)-Se(1)-Cr(1)	55.66(5)
$\begin{array}{ccc} C(13)-Cr(1)-Se(1) & 124.4(2) & C(6)-P(1)-P(1)\#1 & 104.5(2) \\ C(12)-Cr(1)-Se(1) & 82.3(2) & Se(1)-P(1)-P(1)\#1 & 108.70(11) \\ \end{array}$	C(12)-Cr(1)-P(1)	110.7(2)	C(6)-P(1)-Se(1)	114.2(2)
C(12)-Cr(1)-Se(1) 82.3(2) Se(1)-P(1)-P(1)#1 108.70(11)	C(13)-Cr(1)-Se(1)	124.4(2)	C(6)-P(1)-P(1)#1	104.5(2)
	C(12)-Cr(1)-Se(1)	82.3(2)	Se(1)-P(1)-P(1)#1	108.70(11)
P(1)-Cr(1)-Se(1) 51.20(5) C(6)-P(1)-Cr(1) 124.6(2)	P(1)-Cr(1)-Se(1)	51.20(5)	C(6)-P(1)-Cr(1)	124.6(2)
C(13)-Cr(1)-Cr(1)#1 73.60(19) $Se(1)-P(1)-Cr(1)$ 73.14(6)	C(13)-Cr(1)-Cr(1)#1	73.60(19)	Se(1)-P(1)-Cr(1)	73.14(6)
C(12)-Cr(1)-Cr(1)#1 97.4(2) $P(1)#1-P(1)-Cr(1)$ 125.74(11)	C(12)-Cr(1)-Cr(1)#1	97.4(2)	P(1)#1-P(1)-Cr(1)	125.74(11)
P(1)-Cr(1)-Cr(1)#1 17.11(4) O(1)-C(12)-Cr(1) 178.4(7)	P(1)-Cr(1)-Cr(1)#1	17.11(4)	O(1)-C(12)-Cr(1)	178.4(7)
Se(1)-Cr(1)-Cr(1)#1 56.34(2) O(2)-C(13)-Cr(1) 177.2(6)	Se(1)-Cr(1)-Cr(1)#1	56.34(2)	O(2)-C(13)-Cr(1)	177.2(6)

Symmetry transformations used to generate equivalent atoms: #1 -x + 1, -y + 1, -z.

2.575(2) Å) [17]. However, both the C=O bonds (1.361(4) and 1.420(5) Å) for CpCr(CO)₂(SP(H)Ar) are longer than those in **4** (1.150(6) and 1.147(6) Å). The hydrogen atom bonded to phosphorus was confirmed by ³¹P proton coupled NMR (d, *J* = 387.6 Hz).

Table 5		
D 11	.1 (%)	

Bond	lengths	(A)	and	angles	(°,) for 6 .	•

Bond lengths			
Cr(1)-O(1)#1	1.954(2)	Se(1)-Se(1)#1	5.3724(7)
Cr(1)-Se(1)	2.4957(6)	Se(2)-P(1)	2.1842(8)
Cr(1)-Se(2)	2.5089(6)	Se(2)-Se(2)#1	5.3978(7)
Cr(1)-Cr(1)#1	5.0598(10)	P(1)-O(1)	1.514(2)
Se(1)-P(1)	2.1785(8)	P(1)-C(6)	1.804(3)
Se(1)-Se(2)	3.4112(4)	O(1)-Cr(1)#1	1.954(2)
Se(1)-Se(2)#1	4.1669(5)		
Bond angles			
O(1)#1-Cr(1)-C(1)	146.64(18)	P(1)-Se(1)-Se(1)#1	48.13(2)
O(1)#1-Cr(1)-C(5)	110.24(18)	Cr(1)-Se(1)-Se(1)#1	58.308(12)
O(1)#1-Cr(1)-C(2)	139.9(2)	Se(2)-Se(1)-Se(1)#1	50.859(8)
O(1)#1-Cr(1)-C(3)	103.8(2)	Se(2)#1-Se(1)-Se(1)#1	39.416(6)
O(1)#1-Cr(1)-C(4)	90.22(15)	P(1)-Se(2)-Cr(1)	81.66(3)
O(1)#1-Cr(1)-Se(1)	97.00(7)	P(1)-Se(2)-Se(1)	38.50(2)
O(1)#1-Cr(1)-Se(2)	97.53(7)	Cr(1)-Se(2)-Se(1)	46.868(14)
O(1)#1-Cr(1)-Cr(1)#1	45.70(6)	P(1)-Se(2)-Se(2)#1	47.90(2)
Se(1)-Cr(1)-Se(2)	85.941(19)	Cr(1)-Se(2)-Se(2)#1	57.992(13)
Se(1)-Cr(1)-Cr(1)#1	64.617(14)	Se(1)-Se(2)-Se(2)#1	50.530(8)
Se(2)-Cr(1)-Cr(1)#1	64.771(14)	O(1)-P(1)-C(6)	104.41(14)
P(1)-Se(1)-Cr(1)	82.08(2)	O(1)-P(1)-Se(1)	114.98(10)
P(1)-Se(1)-Se(2)	38.62(2)	C(6)-P(1)-Se(1)	110.03(10)
P(1)-Se(1)-Se(2)#1	77.23(2)	O(1)-P(1)-Se(2)	114.43(10)
Cr(1)-Se(1)-Se(2)	47.191(14)	C(6)-P(1)-Se(2)	110.22(11)
Cr(1)-Se(1)-Se(2)#1	83.049(14)	Se(1)-P(1)-Se(2)	102.87(3)
Se(2)-Se(1)-Se(2)#1	90.275(10)	P(1)-O(1)-Cr(1)#1	158.80(14)

Symmetry transformations used to generate equivalent atoms: #1 - x, -y, -z.

Trans-[CpCr(CO)₂(SePPh)]₂ (**5**) consists of a similar framework with its sulfur analogue, *trans*-[CpCr(CO)₂(SPPhOMe)]₂ [23]. The dimer is bridged by a P–P bond (2.212(3) Å) with both CpCr(CO)₂ moieties and bridged [–SePAr]₂ ligand in a *trans* orientation which is comparable to that of *trans*-[CpCr(CO)₂(SPPhOMe)]₂ (2.219(2) Å) [23]. The C(6)–P(1)–P(1)#1 angle (104.5(2)°) is more than 90° indicates that the phenyl ring was experiencing steric repulsion from the CpCr(CO)₂ moiety. The P–Se (2.1425(17) Å) and Cr–Se bond (2.6309(12) Å) distances of **5** are longer than the P–S (2.0003(15) Å) and Cr–S bonds (2.4962(15) Å) found in *trans*-[CpCr(CO)₂(SPPhOMe)]₂ which is possibly due to the larger atomic radii of Se as compared to S.

6 is isostructural with [CpCr(S₂P(O)PhOMe]₂ isolated from the reaction of **1** with Lawesson's reagent [23]. The molecule comprises of two CpCr and two [SeP(O)Ar] moieties attached to an eight-membered ring center. The almost equivalent Cr(1)–Se(1) and Cr(1)–Se(2) bond lengths (2.4957(6) and 2.5089(6) Å, respectively) are significantly longer than the Cr–S bond distance (2.3862(10) and 2.3951(10) Å) of the sulfur analogue. Such observation is likely due to the lower electronegativity of Se as compared to S, resulting in lower electron density at the metal centre hence reducing its π back bonding effect.

Acknowledgments

We would like to thank the University of Malaya (RG024/09AFR and FP052/2008C) for financial support is gratefully acknowledged. We also thank Ms. G.K. Tan (CMMAC, National University of Singapore) for crystallographic data collection.

Appendix A. Supplementary material

CCDC 735485, 735486 and 735487 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.11.034.

References

- R.C.S. Wong, M.L. Ooi/Inorganica Chimica Acta 366 (2011) 350-356
- C.A. McAullffe (Ed.), Transition Metal Complexes of Phosphorus, Antimony, Macmillian, London, 1973.
- [2] L. Vaska, Acc. Chem. Res. 1 (1968) 335.
- [3] L.Y. Goh, W. Chen, R.C.S. Wong, W.-H. Yip, T.C.W. Mak, Organometallics 10 (1991) 875 (and references therein).
- [4] I. Bernal, H. Brunner, W. Meier, H. Pfisterer, J. Wachter, M.L. Ziegler, Angew. Chem., Int. Ed. Engl. 23 (1984) 438.
- [5] M. Di Vaira, M. Peruzzini, P. Stoppioni, J. Chem. Soc., Chem. Commun. (1983) 903.
- [6] M. Di Vaira, M. Peruzzini, P. Stoppioni, Inorg. Chim. Acta 132 (1987) 37.
- [7] H. Brunner, H. Kauermann, B. Nuber, J. Wachter, M.L. Ziegler, Angew. Chem., Int. Ed. Engl. 25 (1986) 557.
- [8] L.Y. Goh, W. Chen, R.C.S. Wong, Angew. Chem., Int. Ed. Engl. 32 (1993) 1728.
 [9] L.Y. Goh, W. Chen, R.C.S. Wong, K. Karaghiosoff, Organometallics 14 (1995) 3886
- [10] M. Di Vaira, M. Peruzzini, P. Stoppioni, Inorg. Chem. 22 (1983) 2196.
- [11] M. Di Vaira, M. Peruzzini, P. Stoppioni, J. Organomet. Chem. 258 (1983) 373.
- [12] R. Jefferson, H.F. Klein, J.F. Nixon, J. Chem. Soc., Chem. Commun. (1969) 536.
- [13] A.W. Cordes, R.D. Joyner, R.D. Shores, E.D. Hill, Inorg. Chem. 13 (1974) 132.
- [14] H. Brunner, U. Klement, W. Meier, J. Wachter, J. Organomet. Chem. 335 (1987) 339.
- [15] L.Y. Goh, W. Chen, R.C.S. Wong, Phosphorus Sulphur Silicon 93–94 (1994) 209.
- [16] L.Y. Goh, W. Chen, R.C.S. Wong, Z.Y. Zhou, H.K. Fun, Mendeleev Commun. (1995) 60.
- [17] L.Y. Goh, W. Chen, R.C.S. Wong, Organometallics 18 (1999) 306.
- [18] M. Di Vaira, B.E. mann, M. Peruzzini, P. Stoppioni, Inorg. Chem. 27 (1988) 3725.
 [19] P. Stoppioni, M. Di Vaira, M. Peruzzini, S. Moneti, L. Sacconi, Phosphorus Sulfur
- Relat. Elem. 18 (1983) 295. [20] M. Di Vaira, I. de los Rios, F. Mani, M. Peruzzini, P. Stoppioni, Eur. J. Inorg. Chem. 2 (2004) 293.
- [21] I. de los Rios, F. Mani, M. Peruzzini, P. Stoppioni, J. Organomet. Chem. 689 (2004) 164.

- [22] M. Di Vaira, I. de los Rios, F. Mani, M. Peruzzini, P. Stoppioni, Inorg. Chem. Commun. 5 (2002) 879.
- [23] Z. Weng, W.K. Leong, J.J. Vittal, L.Y. Goh, Organometallics 22 (2003) 1645.
- [24] H. Alper, F.W.B. Einstein, J.F. Petrignani, A.C. Willis, Organometallics 2 (1983)
- 1422. [25] R.C.S. Wong, M.L. Ooi, S.W. Ng, N.F. Thomas, Inorg. Chim. Acta 363 (2010) 2307.
- [26] A.C. Cano, R.A. Toscano, S. Bernes, O.G. Mellado, C. Alvarez-Toledano, H. Rudler, J. Organomet. Chem. 496 (1995) 153.
- [27] I.P. Parkin, M.J. Pilkington, A.M. Slawin, D.J. Williams, Polyhedron 7 (1990) 987.
- [28] W. Kuchen, B. Knop, Angew. Chem., Int. Ed. Engl. 3 (1964) 507.
- [29] W. Kuchen, B. Knop, Angew. Chem., Int. Ed. Engl. 4 (1965) 245.
- [30] M.J. Pilkington, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, Polyhedron 10 (1991) 2641.
- [31] R.P. Davies, M.G. Martinelli, Inorg. Chem. 41 (2002) 348.
- [32] R.P. Davies, M.G. Martinelli, A.E.H. Wheatley, A.J.P. White, D.J. Williams, Eur. J. Inorg. Chem. 43 (2004) 4802.
- [33] R. Birdwhistell, P. Hackett, A.R. Manning, J. Organomet. Chem. 157 (1978) 239.
- [34] L.Y. Goh, W. Chen, S. Ekk, J. Chem. Soc., Chem. Commun. (1985) 462.
- [35] L.Y. Goh, W. Chen, S. Ekk, Organometallics 7 (1988) 2020.
- [36] G.M. Sheldrick, SADABS, Bruker Nonius Area Detector Scaling and Absorption Correction – V2.05, University of Gottingen, Germany, 1999.
 [37] G.M. Sheldrick, SHELXS97 and SHELXL97, University of Göttingen, 1997.
- [38] N.A. Cooley, P.T.F. MacConnachie, M.C. Baird, Polyhedron 7 (1988) 1965 (and refs. therein).
- [39] P. Hackett, P.O. O'Neill, A.R. Manning, J. Chem. Soc., Dalton Trans. (1974) 1625.
- [40] R.D. Adams, D.E. Collins, F.A. Cotton, J. Am. Chem. Soc. 96 (1974) 749.
- [41] L.Y. Goh, Y.Y. Lim, M.S. Tay, T.C.W. Mak, Z.Y. Zhou, J. Chem. Soc., Chem. Commun. (1992) 1239.
- [42] M.J. Pilkington, A.M.Z. Slawin, D.J. Williams, P.T. Wood, J.D. Woollins, Heteroatom Chem. 1 (5) (1990) 351.
- [43] M. Alonso, M.A. Alvarez, M.E. Garcia, M.A. Ruiz, H. Hamidov, J.C. Jeffery, J. Am. Chem. Soc. 127 (2005) 15012.
- [44] L.Y. Goh, Z. Weng, W.K. Leong, J.J. Vittal, I. Haiduc, Organometallics 21 (2002) 5287.