ELSEVIER

Journal of Organometallic Chemistry 631 (2001) 139–142

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Mixed-metal cluster chemistry. Part 18. Synthesis and crystal structure of $W_3Ir_3(\mu_4\text{-}\eta^2\text{-}CO)(\mu\text{-}CO)(CO)_{10}(\eta\text{-}C_5H_4Me)_3$

Eleni G.A. Notaras, Nigel T. Lucas, Mark G. Humphrey *

Department of Chemistry, Australian National University, Canberra, ACT 0200, Australia

Received 3 April 2001; accepted 21 May 2001

Abstract

Heating a mixture of $W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_4Me)_2$ and 1,2-(*E*)-bis{4′-(oct-1″-ynyl)phenyl}ethene in refluxing CH_2Cl_2 affords a complex mixture from which $W_3Ir_3(\mu_4\text{-}\eta^2\text{-}CO)(\mu\text{-}CO)(CO)_{10}(\eta\text{-}C_5H_4Me)_3$ can be separated in low yield. The crystallographically characterized title cluster is the first hexametallic Group 6–Group 9 mixed-metal cluster, possesses an unusual edge-bridged trigonal bipyramidal core geometry, and has a $\mu_4\text{-}\eta^2$-CO ligand which has the longest carbonyl CO bond thus far. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Tungsten; Iridium; Carbonyl; Cyclopentadienyl; Cluster

1. Introduction

The chemistry of metal cluster complexes with alkynes is of long standing interest [1,2]. The tetrahedral Group 6–Group 9 mixed-metal clusters $M_2Ir_2(CO)_{10}(\eta\text{-}C_5H_5)_2$ (M = Mo, W) react with internal and terminal alkynes to afford complexes of composition $M_2Ir_2(\mu_4\text{-}\eta^2\text{-alkyne})(\mu\text{-}CO)_4(CO)_4(\eta\text{-}C_5H_5)_2$, in which the alkyne inserts into the M–M bond to give a *closo* octahedral $M_2Ir_2C_2$ core [3–5]. We were interested in the effect on reactivity of cyclopentadienyl ligand replacement. We have recently prepared the methylcyclopentadienyl-containing cluster $W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_4Me)_2$ [6], and report herein its reaction with the internal alkyne 1,2-(*E*)-bis{4′-(oct-1″-ynyl)phenyl}ethene which affords $W_3Ir_3(\mu_4\text{-}\eta^2\text{-}CO)(\mu\text{-}CO)(CO)_{10}(\eta\text{-}C_5H_4Me)_3$ in low yield, a product type not observed in the cyclopentadienyl system. The product is the first hexametallic Group 6–Group 9 cluster, possesses a highly unusual edge-bridged trigonal bipyramidal core, and its $\mu_4\text{-}\eta^2$-CO ligand has the longest carbonyl CO distance thus far observed.

2. Experimental

The reaction was performed under an atmosphere of Ar (high-purity, CIG) using standard Schlenk techniques [7]. The reaction solvent CH_2Cl_2 was analytical reagent (AR) grade, and was dried over CaH_2 and distilled under Ar. Petroleum spirit refers to a petroleum fraction of boiling range 60–80 °C. $W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_4Me)_2$ was prepared by literature methods [6]. 1,2-(*E*)-Bis{4′-(oct-1″-ynyl)phenyl}ethene was prepared by adapting literature procedures [8] to couple 1-octyne to 1,2-(*E*)-bis(4-bromo-1-phenyl)ethene [9]. Thin-layer chromatography (TLC) was on 20 × 20 cm glass plates coated with Merck GF_{254} silica gel (0.5 mm). Analytical TLC, used for monitoring the extent of reaction, was carried out on aluminium sheets coated with 0.25 mm silica gel. The infrared spectrum was recorded on a Perkin–Elmer System 2000 FTIR with CaF_2 solution cells; spectral frequencies are recorded in cm^{-1}. The secondary ion mass spectrum (SIMS) was recorded using a VG ZAB 2SEQ instrument (30 kV Cs^+ ions, current 1 mA, accelerating potential 8 kV, 3-nitrobenzyl alcohol matrix) at the Research School of Chemistry, Australian National University, and was calculated with *m*/*z* based on ^{183}W and ^{192}Ir assignments; it is reported in the form: *m*/*z* (assignment,

---

* Correspondence author. Tel.: +61-2-6125-2927; fax: +61-2-6125-0760.

E-mail address: mark.humphrey@anu.edu.au (M.G. Humphrey).

PII: S0022-328X(01)01048-8

relative intensity). The elemental microanalysis was carried out by the Microanalysis Service Unit in the Research School of Chemistry, Australian National University.

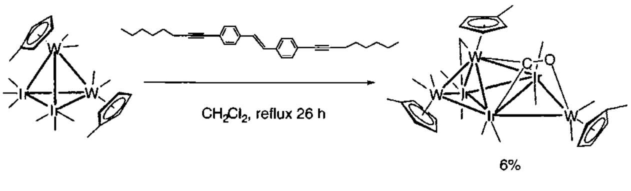
2.1. Synthesis of $W_3Ir_3(CO)_{12}(\eta\text{-}C_5H_4Me)_3$ (**1**)

$W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_4Me)_2$ (85.5 mg, 0.072 mmol) was added to 1,2-(*E*)-bis{4-(oct-1′-ynyl)-1-phenyl)ethene (12.8 mg, 0.033 mmol) in CH_2Cl_2 (40 ml) and heated at reflux for 26 h. Purification by preparative TLC with CH_2Cl_2–petroleum spirit (9/1) as eluent gave a number of bands. The contents of the second band ($R_f = 0.59$) were crystallized from CH_2Cl_2–MeOH at −3 °C to afford a dark brown crystalline solid identified as $W_3Ir_3(CO)_{12}(\eta\text{-}C_5H_4Me)_3$ (**1**) (6.4 mg, 0.0038 mmol, 6%). Anal. Found: C, 21.27; H, 1.39. Calc. for $C_{30}H_{21}Ir_3O_{12}W_3$: C, 21.17; H, 1.24%. IR (CH_2Cl_2): ν(CO) 2056s, 2037vs, 1992vs, 1927m, 1870m, 1812, 1755m, 1606w, 1424m cm^{-1}. MS (SI): 1701 ($[M]^+$, 65), 1645 ($[M-2CO]^+$, 25), 1589 ($[M-4CO]^+$, 28), 1533 ($[M-6CO]^+$, 35), 1477 ($[M-8CO]^+$, 33), 1365 ($[M-12CO]^+$, 59).

Table 1
Crystallographic data and structure refinement parameters for $W_3Ir_3(\mu_4\text{-}\eta^2\text{-}CO)(\mu\text{-}CO)(CO)_{10}(\eta\text{-}C_5H_4Me)_3$ (**1**)

Empirical formula	$C_{30.5}H_{22}ClIr_3O_{12.5}W_3$
Formula weight	1752.16
Crystal size (mm)	0.30 × 0.12 × 0.10
T (K)	200
Wavelength (Å)	0.71069
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	
a (Å)	11.2292(1)
b (Å)	18.0377(2)
c (Å)	18.6440(2)
α (°)	103.3944(8)
β (°)	102.6834(7)
γ (°)	98.6908(8)
V (Å^3)	3501.86(7)
Z	4
Theta range for data collection (°)	2.92–30.10
Index ranges	$-15 \leq h \leq 15$, $-25 \leq k \leq 24$, $-26 \leq l \leq 25$
μ (mm^{-1})	21.35
Max/min transmission	0.220 and 0.052
Reflections collected	96 500
Independent reflections	20517 ($R_{int} = 0.135$)
Data/restraints/parameters	13427/0/902
Goodness-of-fit	1.11
Final *R* indices [$I > 3\sigma(I)$] [a]	$R = 0.0460$, $R_w = 0.0551$
R indices (all data) [a]	$R = 0.0719$, $R_w = 0.0658$
Largest difference peak and hole (e Å^{-3})	3.03 and −5.20

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, $w = [\sigma^2(F_o) + 0.0001|F_o|^2]^{-1}$.



Scheme 1. Synthesis of $W_3Ir_3(\mu_4\text{-}\eta^2\text{-}CO)(\mu\text{-}CO)(CO)_{10}(\eta\text{-}C_5H_4Me)_3$ (**1**).

2.2. X-ray crystallographic study of **1**

Crystals suitable for the X-ray structural analysis were grown by liquid diffusion of MeOH into a CH_2Cl_2 of **1** at 276 K. A single dark brown needle was mounted on a fine glass capillary, and data were collected at 200 K on a Nonius KappaCCD diffractometer using graphite-monochromated Mo–K$_\alpha$ radiation. The unit cell parameters were obtained by least-squares refinement [10] of 85 307 reflections with $2.9 \leq \theta \leq 30.0°$. The data were corrected for absorption using numerical methods [11], implemented from within MAXUS [12]; equivalent reflections were merged. The structure was solved by direct methods [13] and expanded using Fourier techniques [14]. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in idealized positions which were frequently recalculated except those of the water molecule which could not be located. The final cycle of full-matrix least-squares refinement on *F* was based on 13 427 observed reflections ($I > 3\sigma(I)$) and 902 variable parameters, and converged to $R = 0.046$ and $R_w = 0.055$. Selected crystal data and structure refinement parameters are collected in Table 1.

3. Results and discussion

The reaction of $W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_4Me)_2$ with 1,2-(*E*)-bis{4′-(oct-1″-ynyl)phenyl}ethene in refluxing CH_2Cl_2 afforded a complex mixture from which the title complex $W_3Ir_3(\mu_4\text{-}\eta^2\text{-}CO)(\mu\text{-}CO)(CO)_{10}(\eta\text{-}C_5H_4Me)_3$ (**1**) was isolated in low yield (6%) following chromatography (Scheme 1). Cluster **1** was characterized by solution IR spectroscopy, SI mass spectrometry, satisfactory microanalysis and a single crystal X-ray structural determination. The IR contains nine ν(CO) bands, five in the terminal carbonyl region (2056–1870 cm^{-1}), three in the μ- and μ_3-bridging carbonyl region (1812–1606 cm^{-1}), and one stretching mode at 1424 cm^{-1}, the last mentioned consistent with a μ_4-η^2-CO ligand within the cluster. This μ_4-η^2-CO stretching frequency is similar to those reported for other μ_4-η^2-CO ligands, previously found within the range 1340–1457 cm^{-1} [15–17]. The mass spectrum contains a molecular ion envelope and sequential loss of 12 carbonyl ligands.

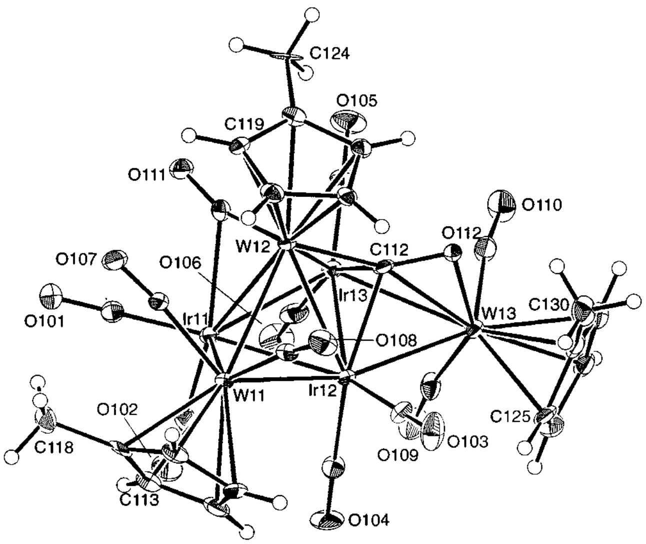


Fig. 1. ORTEP plot of $W_3Ir_3(\mu_4\text{-}\eta^2\text{-}CO)(\mu\text{-}CO)(CO)_{10}(\eta\text{-}C_5H_4Me)_3$ (**1**) showing the molecular structure and atomic labelling scheme. Displacement ellipsoids are shown at the 30% probability level for the non-hydrogen atoms.

Table 2
Selected bond lengths (Å) for $W_3Ir_3(\mu_4\text{-}\eta^2\text{-}CO)(\mu\text{-}CO)(CO)_{10}(\eta\text{-}C_5H_4Me)_3$ (**1**)

Bond	Molecule 1 (Å)	Molecule 2 (Å)
Ir1–Ir2	2.7584(6)	2.7454(6)
Ir1–Ir3	2.7452(7)	2.7523(7)
Ir2–Ir3	2.7123(6)	2.7113(7)
Ir1–W1	2.7342(6)	2.7478(7)
Ir1–W2	2.8172(6)	2.8368(7)
Ir2–W1	2.8417(6)	2.8508(7)
Ir2–W2	2.8454(6)	2.8467(7)
Ir2–W3	2.8475(7)	2.8499(7)
Ir3–W2	2.8981(6)	2.8891(7)
Ir3–W3	2.8723(7)	2.8555(7)
W1–W2	2.9161(6)	2.9057(9)
Ir–C(terminal)	1.83(1)–1.91(1)	1.81(1)–1.90(1)
W–C(terminal)	1.96(1)–2.00(1)	1.96(2)–2.00(1)
Ir/W–C11(bridging)	2.33(1)/1.99(1)	2.30(1)/1.99(1)
Ir2/Ir3–C12(μ_4-η^2)	2.15(1)/2.16(1)	2.17(1)/2.17(1)
W2/W3–C12(μ_4-η^2)	1.99(1)/2.48(1)	2.00(1)/2.48(1)
W3–O12(μ_4-η^2)	2.137(7)	2.141(8)
C–O(terminal)	1.13(2)–1.17(2)	1.11(2)–1.19(2)
C–O(bridging)	1.21(1)	1.17(2)
C–O(μ_4-η^2)	1.30(1)	1.29(1)

The spectral data were insufficient to establish the molecular structure, so an X-ray diffraction study was undertaken. Fig. 1 contains an ORTEP plot of **1** showing the molecular structure and the atomic labelling scheme for one of two independent molecules in the asymmetric unit; Table 1 lists crystal data and important structure refinement details and Table 2 contains selected bond lengths for both independent molecules.

The structural study reveals that **1** has an unusual edge-bridged trigonal bipyramidal core geometry; with 86 cluster valence electrons (c.v.e.) [3×6 (W) + 3×9 (Ir) + 3×5 (Cp′) + 11×2 (CO) + 1×4 (μ_4-η^2-CO)], it is electron precise. The great majority of metal clusters with 86 c.v.e. possess octahedral core geometries; the edge-bridged trigonal bipyramidal core geometry has been observed only once previously for 86 c.v.e. clusters, namely $WRu_5(\mu\text{-}H)_4(\mu_4\text{-}C)(\mu_3\text{-}CCH_2Ph)(CO)_{12}(\eta\text{-}C_5Me_5)$ [18] [several 84 c.v.e. clusters possessing this geometry, in which a copper atom occupies the edge-bridging site, have been characterized, namely $Cu_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}P(CH_2Ph)_2(\eta^2\text{-}CH_2Ph)\}(CO)_{12}$ [19], $Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}\{P(CH_2Ph)_3\}_2$ [19,20], and $Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PR_3)_2$ (where R = cyclo-C_6H_{11} or $CHMe_2$) [21])]. The edge-bridged Ru-containing unit and adjacent WRu_2 face in $WRu_5(\mu\text{-}H)_4(\mu_4\text{-}C)(\mu\text{-}CCH_2Ph)(CO)_{12}$ define a butterfly sub-unit which is supported by a μ_4-C in the butterfly 'cleft'. Similarly in **1**, the edge-bridged W-containing unit and adjacent WIr_2 face define a butterfly, supported in this case by a μ_4-η^2-CO within the cleft. Although coordinated alkene does not appear in the product cluster, its presence in the reaction mixture may be critical; heating $W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_5)_2$ in the presence of one equivalent of triphenylamine affords $W_3Ir_4(\mu\text{-}H)(CO)_{12}(\eta\text{-}C_5H_5)_3$, whereas thermolyzing this cluster in the absence of amine is reported to afford $WIr_3(CO)_{11}(\eta\text{-}C_5H_5)$ [22].

Carbonyl ligands coordinated in a μ_4-η^2 manner have attracted considerable interest as this bonding mode involves significant C–O weakening and may therefore model putative intermediates in Fischer–Tropsch-mediated CO cleavage. The 24 previous examples of this bonding mode span butterfly clusters or clefts containing Group 8, mixed Group 6–Group 8 or mixed Group 8–Group 9 metals, with C–O distances in the range 1.19–1.286 Å [23–43]. The title cluster has the longest μ_4-η^2-CO bonds thus far, although estimated S.D. values in the present study render differences to the previously reported longest bonds not statistically significant. The polar metal–metal bonds in very mixed-metal clusters should enhance organic substrate activation [44]. In this light, it is perhaps significant that the title cluster contains the most disparate metals (oxophilic Group 6, carbophilic Group 9) for a μ_4-η^2-CO-ligated cluster thus far and the longest CO bonds. The weakening of the CO bond suggests that it may be possible to cleave it. However, the low yields of the title cluster have precluded reactions to effect C–O cleavage.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 160112 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccd.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Australian Research Council (ARC) for financial support in the form of a Large Grant and the funds to purchase the diffractometer, and Johnson–Matthey Technology Centre for the generous loan of iridium salts. M.G.H. holds an ARC Australian Senior Research Fellowship and N.T.L. was an Australian Postgraduate Awardee.

References

[1] P.R. Raithby, M.J. Rosales, Adv. Inorg. Chem. Radiochem. 29 (1985) 169.

[2] E. Sappa, A. Tiripicchio, P. Braunstein, Chem. Rev. 83 (1983) 203.

[3] J.R. Shapley, C.H. McAteer, M.R. Churchill, L.V. Biondi, Organometallics 3 (1984) 1595.

[4] N.T. Lucas, M.G. Humphrey, P.C. Healy, M.L. Williams, J. Organomet. Chem. 545–546 (1997) 519.

[5] S.M. Waterman, M.G. Humphrey, V.-A. Tolhurst, M.I. Bruce, P.J. Low, D.C.R. Hockless, Organometallics 17 (1998) 5789.

[6] N.T. Lucas, E.G.A. Notaras, M.G. Humphrey, Acta Crystallogr. E 57 (2001) m132.

[7] D.F. Shriver, M.A. Drezdzon, The Manipulation of Air-Sensitive Compounds, Wiley, New York, 1986.

[8] S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, Synthesis (1980) 627.

[9] M. Baumgarten, T. Yuksel, Phys. Chem. Chem. Phys. 1 (1999) 1699.

[10] Z. Otwinowski, W. Minor, Methods in Enzymology, Academic Press, New York, 1997, p. 307.

[11] P. Coppens, Crystallographic Computing, Munksgaard, Copenhagen, 1970, p. 255.

[12] S. Mackay, C.J. Gilmore, C. Edwards, N. Stewart, K. Shankland, MAXUS. Computer Program for the Solution and Refinement of Crystal Structures, Nonius MacScience, Japan, The University of Glasgow, The Netherlands, 1999.

[13] A. Altomare, M. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Cryst. 27 (1994) 425.

[14] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, The DIRDIF-94 Program System. Technical Report of the Crystallography Laboratory, University of Nijmegen, Nijmegen, The Netherlands, 1994.

[15] R.D. Adams, Z. Li, J.-C. Lii, W. Wu, J. Am. Chem. Soc. 114 (1992) 4918.

[16] C.E. Anson, P.J. Bailey, G. Conole, B.F.G. Johnson, J. Lewis, M. McPartlin, H.R. Powell, J. Chem. Soc. Chem. Commun. (1989) 442.

[17] P.J. Bailey, M.J. Duer, B.F.G. Johnson, J. Lewis, G. Conole, M. McPartlin, H.R. Powell, C.E. Anson, J. Organomet. Chem. 383 (1990) 441.

[18] W.-J. Chao, C.-J. Way, I.J. Mavunkal, S.-L. Wang, F.-L. Liao, L.J. Farrugia, Organometallics 16 (1997) 3523.

[19] C.J. Brown, P.J. McCarthy, I.D. Salter, K.P. Armstrong, M. McPartlin, H.R. Powell, J. Organomet. Chem. 394 (1990) 711.

[20] P.J. McCarthy, I.D. Salter, K.P. Armstrong, M. McPartlin, H.R. Powell, J. Organomet. Chem. 377 (1989) C73.

[21] T. Adatia, P.J. McCarthy, M. McPartlin, M. Rizza, I.D. Salter, J. Chem. Soc. Chem. Commun. (1988) 1106.

[22] S.M. Waterman, M.G. Humphrey, D.C.R. Hockless, Organometallics 15 (1996) 1745.

[23] R.D. Adams, J.E. Babin, M. Tasi, Angew. Chem. Int. Ed. Engl. 26 (1987) 685.

[24] R.D. Adams, J.E. Babin, M. Tasi, Inorg. Chem. 27 (1988) 2618.

[25] R.D. Adams, M.S. Alexander, I. Arafa, W. Wu, Inorg. Chem. 30 (1991) 4717.

[26] D.B. Brown, P.J. Dyson, B.F.G. Johnson, C.M. Martin, D.G. Parker, S. Parsons, J. Chem. Soc. Dalton Trans. (1997) 1909.

[27] Y. Chi, F.-J. Wu, B.-J. Liu, C.-C. Wang, S.-L. Wang, J. Chem. Soc. Chem. Commun. (1989) 873.

[28] Y. Chi, S.-H. Chuang, L.-K. Liu, Y.-S. Wen, Organometallics 10 (1991) 2485.

[29] Y. Chi, C.-J. Su, L.J. Farrugia, S.-M. Peng, G.-H. Lee, Organometallics 13 (1994) 4167.

[30] Y. Chi, C.-J. Su, S.-M. Peng, G.-H. Lee, J. Am. Chem. Soc. 119 (1997) 11114.

[31] W. Clegg, N. Feeder, S. Nahar, P.R. Raithby, G.P. Shields, S.J. Teat, New J. Chem. 22 (1998) 1111.

[32] J.F. Corrigan, S. Doherty, N.J. Taylor, A.J. Carty, Organometallics 12 (1993) 993.

[33] J.E. Davies, S. Nahar, P.R. Raithby, G.P. Shields, J. Chem. Soc. Dalton Trans. (1997) 13.

[34] C.P. Gibson, L.F. Dahl, Organometallics 7 (1988) 535.

[35] C.P. Horwitz, E.M. Holt, C.P. Brock, D.F. Shriver, J. Am. Chem. Soc. 107 (1985) 8136.

[36] S.L. Ingham, B.F.G. Johnson, C.M. Martin, D. Parker, J. Chem. Soc. Chem. Commun. (1995) 159.

[37] E. Kolehmainen, K. Rissanen, K. Laihia, Z.A. Kerzina, M.I. Rybinskaya, M. Nieger, J. Organomet. Chem. 524 (1996) 219.

[38] C.M. Martin, P.J. Dyson, S.L. Ingham, B.F.G. Johnson, A.J. Blake, J. Chem. Soc. Dalton Trans. (1995) 2741.

[39] C.-J. Su, Y. Chi, S.-M. Peng, G.-H. Lee, Organometallics 14 (1995) 4286.

[40] P.-C. Su, Y. Chi, C.-J. Su, S.-M. Peng, G.-H. Lee, Organometallics 16 (1997) 1870.

[41] J. Wang, M. Sabat, C.P. Horwitz, D.F. Shriver, Inorg. Chem. 27 (1988) 552.

[42] J.-C. Wang, R.-C. Lin, Y. Chi, S.-M. Peng, G.-H. Lee, Organometallics 12 (1993) 4061.

[43] J.-C. Wang, Y. Chi, S.-M. Peng, G.-H. Lee, S.-G. Shyu, F.-H. Tu, J. Organomet. Chem. 481 (1994) 143.

[44] S.M. Waterman, N.T. Lucas, M.G. Humphrey, Adv. Organomet. Chem. 46 (2000) 47.