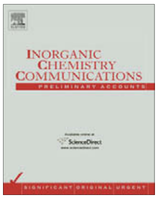
Inorganic Chemistry Communications 13 (2010) 342–345

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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



Synthesis of an osmafuran from photochemical hydrolysis of $OsCl_2(CH{=}C(PPh_3)C(O)\text{-}\eta^2\text{-}CH{=}CH_2)(PPh_3)_2$

Xu-Min He *, Qixuan Liu, Lei Gong, Yumei Lin, Ting Bin Wen *,[1]

Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China

ARTICLE INFO

Article history:
Received 6 July 2009
Accepted 17 December 2009
Available online 23 December 2009

Keywords:
Metallacycle
α,β-unsaturated ketone
Osmafuran
Ultraviolet radiation
Photochemical

ABSTRACT

The η^2-alkene coordinated α,β-unsaturated ketone complex $Os(CH{=}C(PPh_3)C(O)\text{-}\eta^2\text{-}CH{=}CH_2)Cl_2(PPh_3)_2$ (**3**) is very stable even at elevated temperature due to the strong steric hindrance effect of PPh_3 ligands. However, compound **3** in a chloroform solution can be almost quantitatively converted into the corresponding osmafuran $[OsCl(CO)(PPh_3)_2(CHC(PPh_3)C(CH_3)O)]Cl$ (**6**) *via* hydrolysis of the η^2-coordinated olefin under photochemical conditions. Osmafuran **6** has been characterized by single crystal X-ray diffraction analysis, NMR spectroscopy and elemental analysis data. The UV-induced reaction provides a new highly efficient method for preparation of osmafurans by hydrolysis of η^2-α,β-unsaturated ketone complexes.

© 2009 Elsevier B.V. All rights reserved.

Aromatic metallacycles continue to be the subject of extensive investigation [1]. The five-membered metalla-heteroaromatic representatives of this class of compounds include metallafurans [2], metallathiophenes [3] and metallapyrroles [4], among which metallafurans are the most common. Various synthetic routes developed to prepare metallafurans have been summarized by Wright [5].

We have recently reported that the η^2-olefin coordinated α,β-unsaturated ketone osmacycles $Os(CH{=}C(PPh_3)C(O)\text{-}\eta^2\text{-}CH{=}CH_2)Cl_2(PMe_3)_2$ (**1**) and $[Os(CH{=}C(PPh_3)C(O)\text{-}\eta^2\text{-}CH{=}CH_2)Cl(PMe_3)_3]Cl$ (**2**), when dissolved in commercially available chloroform, slowly transform into the osmafurans $[Os(CHC(PPh_3)C(CH_3)O)Cl(CO)(PMe_3)_2]Cl$ (**4**) and $[Os(CHC(PPh_3)C(CH_3)O)(CO)(PMe_3)_3]Cl_2$ (**5**), respectively, in good yields, *via* hydrolysis of the η^2-coordinated olefin (Scheme 1) [6]. The PPh_3 substituted analogue $Os(CH{=}C(PPh_3)C(O)\text{-}\eta^2\text{-}CH{=}CH_2)Cl_2(PPh_3)_2$ (**3**), however, exhibits excellent stability. Thus a solution of **3** in commercially available chloroform can be even heated under refluxed for several days without noticeable decomposition [6,7]. As our curiosity on the appreciable stability of **3**, we have investigated the behavior of **3** under photochemical condition. Somewhat surprisingly, irradiation of a solution of **3** in commercially available chloroform at 254 nm (in a darkroom) for 4 days led to the formation of osmafuran $[Os(CHC(PPh_3)C(CH_3)O)Cl(CO)(PPh_3)_2]Cl$ (**6**) almost quantitatively,

It is known that the structure of η^2-coordinated alkenes can vary between the limiting resonance forms of an olefin complex and a metallacyclopropane. The contribution of the resonance structure **3′** to the structure of **3** has also been established previously by X-ray diffraction [6]. The resonance form **3′** is structurally related to bicyclo [3.1.0] hexenones **7**, thus complex **3** can be regarded as an osmabicyclo[3.1.0]hexenone (Scheme 2). Bicyclo[3.1.0]hexenone compounds have attracted much attention due to their interesting photochemical behavior. For instance, upon exposure to the sunlight or when irradiated with UV (350 nm), compounds **7** quantitatively rearrange into corresponding *ortho*-phenols (**8**) *via* a diradical intermediate (Scheme 3) [8]. It would be, thus, of interest to investigate the photochemical reactivity of the η^2-olefin coordinated α,β-unsaturated ketone osmacycles, especially for $Os(CH{=}C(PPh_3)C(O)\text{-}\eta^2\text{-}CH{=}CH_2)Cl_2(PPh_3)_2$ (**3**) that shows an extraordinary thermal stability.

A preliminary study shows that photochemical hydrolysis was observed for the osmabicyclo[3.1.0]hexenone **3** (the α,β-unsaturated ketone complex) leading to the formation of an osmafuran, which is different from the photochemical rearrangements of organic bicyclo[3.1.0]hexenones. When a solution of **3** in commercially available chloroform-*d* sealed in an NMR tube under N_2 atmosphere was exposed to ultraviolet radiation ($\lambda = 254$ nm) and the reaction was periodically monitored by ^{31}P and ^1H NMR, osmafuran $[Os(CHC(PPh_3)C(CH_3)O)Cl(CO)(PPh_3)_2]Cl$ (**6**) could be detected after 24 h. The reaction was completed after 4 days. Formation of $CHDCl_2$ could be also detected, which can be reflected by the 1:1:1 triplet ($J(HD) \approx 0.9$ Hz) observed at 5.30 ppm in the ^1H NMR spectrum (in about an integration ratio of 1:1 compared to the ^1H signal of **6**). Complex **6** could be isolated as a yellow solid

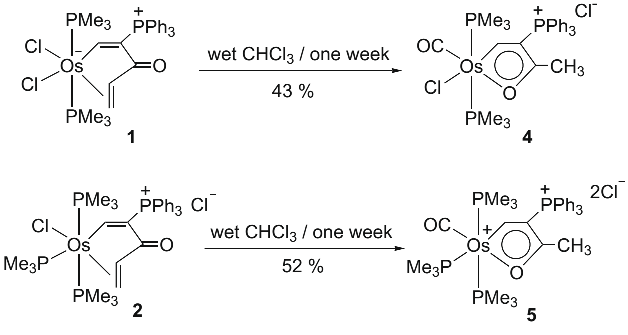
---

* Corresponding authors. Tel.: +86 592 218 4520; fax: +86 592 218 6628 (X.M. He).

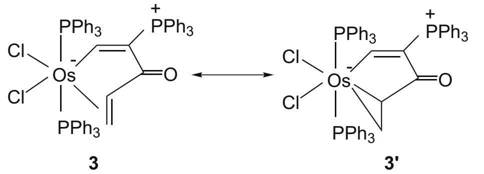
E-mail addresses: hejin@xmu.edu.cn (X.-M. He), chwtb@xmu.edu.cn (T.B. Wen).

[1] Tel.: +86 592 218 6085; fax: +86 592 218 6295 (T.B. Wen).

1387-7003/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2009.12.016

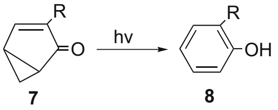


Scheme 1. Formation of complexes **4** and **5** from **1** and **2**.

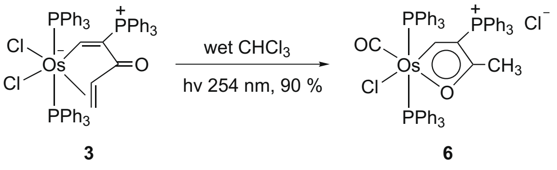


Scheme 2. Resonance forms of η^2-coordinated alkenes and metallacyclopropane.

in 90% yield in a preparative experiment using commercially available chloroform as the solvent (which has been bubbled with dinitrogen steam prior to use) (Scheme 4) [9].



Scheme 3. Formation of *ortho*-phenols **8** from bicyclo[3.1.0] hexenone **7**.



Scheme 4. Formation of complex **6** from **3** under photochemical condition.

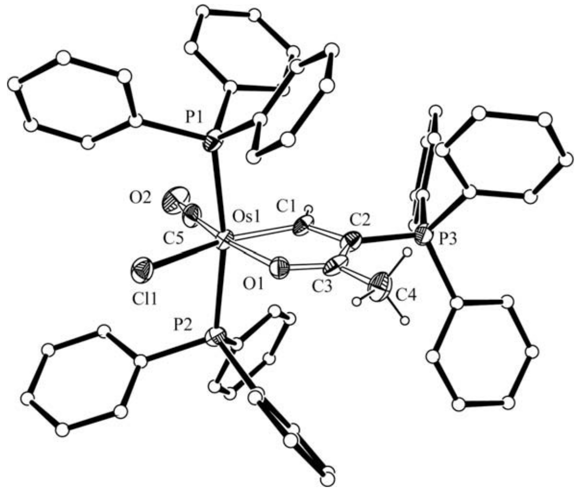
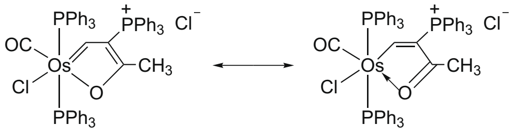


Fig. 1. Molecular structure for [OsCl(CO)(PPh$_3$)$_2$(CHC(PPh$_3$)C(CH$_3$)O)]Cl (**6**). The counteranion and some of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–C1 1.966(9), Os1–C5 1.845(7), Os1–O1 2.127(4), C1–C2 1.412(10), C2–C3 1.444(10), C3–C4 1.511(10), C3–O1 1.262(9), C5–O2 1.143(8), C2–P3 1.770(8); C1–Os1–O1 77.7(3), C2–C1–Os1 116.5(6), C3–O1–Os1 116.0(4), C1–C2–C3 114.0(7), C2–C3–C4 126.4(7), C2–C3–O1 115.8(6).



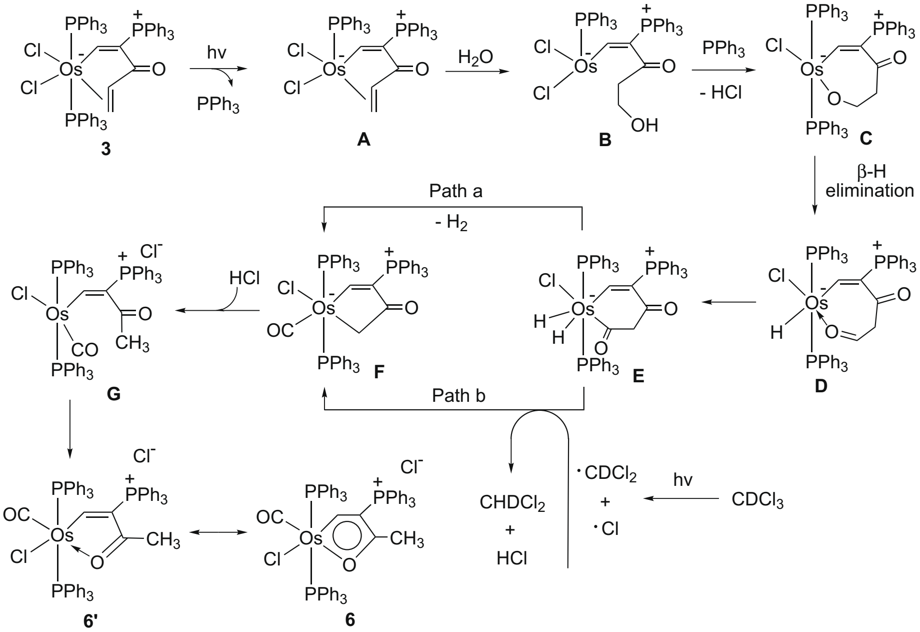
Scheme 5. Resonance forms contribute to the bonding pattern in **6**.

The structure of **6** has been established by X-ray diffraction [10]. Complex **6** co-crystallizes with one and a half molecules of CH$_2$Cl$_2$ solvent and half of one solvent water molecule in the chiral space group $P2_1$. As shown in Fig. 1, the coordination geometry around the osmium atom can be best described as a distorted octahedron with the two phosphorus atoms of the PPh$_3$ ligands occupying the axial positions. The structure confirms the presence of a planar five-membered metallacycle containing osmium, oxygen, and three carbon atoms, i.e., a 2-osmafuran. The coplanarity is reflected by the small deviations (0.0169 Å) from the best fitted RMS plane through the five atoms Os1, C1, C2, C3, and O1. Furthermore, within the metallaheterocycle, the C1–C2 and C2–C3 bond lengths are 1.412(10) and 1.444(10) Å, respectively, which are between those expected for single and double carbon–carbon bonds. The Os1–C1 bond length of 1.966(9) Å is considerably shorter than the typical value (1.995(2)–2.105(5) Å) expected for an Os–C single bond [11]. The C3–O1 (1.262(9) Å) and Os1–O1 (2.127(4) Å) bond distances agree well with those found in the osmafuran OsCl(CO)(P*i*Pr$_3$)$_2$(CHCHC(Ph)O) (1.283(4) Å and 2.126(3) Å, respectively) reported by Esteruelas [12]. The two resonance forms shown in Scheme 5 should be taken into account to describe the bonding pattern of the heterocycle [12].

In a solution, the NMR spectroscopy data for **6** are consistent with the solid-state structure. The *trans*-disposed phosphine ligands are equivalent and exhibit a singlet at 13.7 ppm in the ^{31}P{^{1}H} NMR spectrum. The ^{31}P signal for the phosphonium substituent C*P*Ph$_3$ is observed as a singlet at 16.0 ppm. The ^{1}H NMR spectrum shows a characteristic OsC*H* proton signal at δ = 12.8 ppm as a doublet (^3J(PH) = 15.9 Hz). The signal for methyl protons appears as a singlet at δ = 1.4 ppm. In ^{13}C{^{1}H} NMR spectrum, there are three carbon signals of the metallacycle at δ = 245.8 (Os*C*H), 203.0 (OsO*C*(CH$_3$)) and 113.5 (*C*PPh$_3$) ppm, respectively. Those for the CO ligand on the metal atom and the methyl substituent are observed at δ = 182.3 (*C*O) and 25.5 (*C*H$_3$) ppm.

The CO ligand in **6** is presumably derived from the hydrolysis of the coordinated terminal alkene. It is worth to note that complex **3** exhibits excellent stability under thermal conditions, a solution of which in commercially available chloroform could remain almost unchanged even after it has been heated under reflux for several days. In view of the fact that the related PMe$_3$ substituted complexes **1** and **2** can slowly transform into osmafurans **4** and **5** in a chloroform solution at room temperature (Scheme 1), the extraordinary stabilization of **3** compared to that of **1** and **2** could mostly ascribe to the steric hindrance of PPh$_3$ ligands which protect the coordinated alkene effectively from the attack of water. Because of the strong steric protecting effect of ligands in complex **3**, the UV irradiation probably causes the dissociation of one PPh$_3$ ligand first, which could not be replaced thermochemically.

A plausible mechanism for the reaction is proposed in Scheme 6. Initially, one of the PPh$_3$ ligand is dissociated by ultraviolet radiation to give intermediate **A**, which results in the addition of water to the coordinated terminal double bond to give intermediate **B**. Recombination of the dissociated PPh$_3$ and subsequent



Scheme 6. Proposed mechanism for the formation of complex **6**.

dehydrochlorination generates **C**, which then undergoes β-H elimination to produce the metal hydride **D**. Oxidative addition of the aldehyde C–H to osmium centre gives the dihydride-acyl intermediate **E**. It is possible for **E** to lose H_2 together with deinsertion of the carbonyl from the acyl to give **F** (Path a), as was the case in the previously reported mechanism proposed for the formation of osmafurans **4** and **5** from the hydrolysis of **1** and **2** [6]. Unfortunately, we cannot provide evidence for the evolution of dihydrogen either from the ^{1}H NMR spectrum of the reaction solution or the GC chromatograms of the gaseous atmosphere for the monitored NMR tube reaction in $CDCl_3$. However, formation of $CHDCl_2$ has been detected in the monitored reaction in about an integration ratio of 1:1 to the ^{1}H signal of **6** (see above), and the acidic nature of the reaction solution which may indicate formation of HCl has also been confirmed by testing the pH value. In this context, it should be noted that chloroform is well known to form free radicals easily, especially with UV light. Thus, it is more likely that the $CDCl_2$ and Cl radicals generated from $CDCl_3$ under UV radiation abstract the two hydrogen radicals from **E** to produce $CHDCl_2$, HCl and intermediate **F** (Path b), as suggested by one of the refrees. Protolysis of the alky by HCl affords **G** and subsequent coordination of the lone pair of oxygen atom in carbonyl group to osmium centre produces the osmafuran **6**.

In summary, the η^2-alkene coordinated α,β-unsaturated ketone complex $Os(CH{=}C(PPh_3)C(O)\text{-}\eta^2\text{-}CH{=}CH_2)Cl_2(PPh_3)_2$ (**3**) which is very stable thermally can be almost quantitatively converted into the corresponding osmafuran $[OsCl(CO)(PPh_3)_2(CHC(PPh_3)C(CH_3)O)]Cl$ (**6**) by ultraviolet irradiation. The UV-induced reaction provides a new highly efficient method for preparation of osmafurans by hydrolysis of η^2-α,β-unsaturated ketone complexes.

Acknowledgements

This work was supported by the National Science Foundation of China (20772100), the program for New Century Excellent Talents in University of China (NCET-08-0471), the Program for New Century Excellent Talents in Fujian Province University, and the Young Talent Project of the Department of Science and Technology of Fujian Province (2007F3095).

Appendix A. Supplementary material

CCDC 675886 contains 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.inoche.2009.12.016.

References

[1] J.R. Bleeke, Chem. Rev. 11 (2001) 1205.

[2] J.R. Bleeke, P.R. New, J.M.B. Blanchard, T. Haile, A.M. Beatty, Organometallics 14 (1995) 5127. and Ref. [6] therein.

[3] (a) J.R. Bleeke, M.F. Ortwerth, M.Y. Chiang, Organometallics 12 (1993) 985;
(b) J.R. Bleeke, M.F. Ortwerth, A.M. Rohde, Organometallics 14 (1995) 2813;
(c) G.L. Lu, W.R. Roper, L.J. Wright, G.R. Clark, J. Organomet. Chem. 690 (2005) 972.

[4] F.M. Alías, P.J. Daff, M. Paneque, M.L. Poveda, E. Carmona, P.J. Pérez, V. Salazar, Y. Alvarado, R. Atencio, R. Sánchez-Delgado, Chem. Eur. J. 8 (2002) 5132.

[5] A. Bierstedt, G.R. Clark, W.R. Roper, L.J. Wright, J. Organomet. Chem. 691 (2006) 3846.

[6] L. Gong, Y. Lin, T.B. Wen, H. Xia, Organometallics 28 (2009) 1101.

[7] L. Gong, Y. Lin, G. He, H. Zhang, H. Wang, T.B. Wen, H. Xia, Organometallics 27 (2008) 309.

[8] (a) I. Marchueta, S. Olivella, L. Sola, A. Moyano, M.A. Pericas, A. Riera, Org. Lett. 3 (2001) 3197;
(b) I. Gomez, S. Olivella, M. Reguero, A. Riera, A. Sole, J. Am. Chem. Soc. 124 (2002) 15375.

[9] Preparation and characterization of complex **6**: A suspension of $Os(CH{=}C(PPh_3)C(O)\text{-}\eta^2\text{-}CH{=}CH_2)Cl_2(PPh_3)_2$ (**3**) (0.20 g, 0.18 mmol) in commercially available $CHCl_3$ (6 mL, which has been bubbled with dinitrogen for over 15 min prior to use) was sealed in a quartz tube under N_2 atmosphere and exposed to ultraviolet radiation (MX10-Y20WX1, 254 nm, 20 W, 220 V, 50 Hz) for 4 days to give a yellow solution. Then the volume of the mixture was reduced to approximately 1 mL under vacuum. Addition of diethyl ether (8 mL) to the solution gave a yellow precipitate, which was collected by filtration, washed with diethyl ether (5 × 2 mL), and dried under vacuum. Yield: 0.18 g, 90%. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 12.8 (d, $^3J(PH) = 15.9$ Hz, 1H, OsCH), 1.4 (s, 3H, CH_3), 6.6–7.9 ppm (m, 45H, PPh_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 16.0 (s, $CPPh_3$), 13.7 ppm (s, $OsPPh_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 245.8 (br, OsCH), 203.0 (d, $^2J(PC) = 10.6$ Hz, $OsOC(CH_3)$), 182.3 (t, $^2J(PC) = 24.2$ Hz, CO), 113.5 (d, $^1J(PC) = 85.3$ Hz, $C(PPh_3)$), 25.5 (s, CH_3), 117.0–134.4 ppm (m, PPh_3). Anal. Calcd for $C_{59}H_{49}O_2P_3Cl_2Os$: C, 61.94; H, 4.32; found: C, 61.55; H, 4.77.

[10] X-ray crystal structure determinations for complex $\mathbf{6}\cdot 1.5CH_2Cl_2\cdot 0.5H_2O$: Crystals suitable for X-ray diffraction analysis were grown from a CH_2Cl_2 solution layered with diethyl ether. Intensity data were collected on an Oxford

Diffraction Gemini S Ultra diffractomerter using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 173 K. The structure was solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares methods on F^2 by using the Bruker SHELXTL-97 program package. All non-hydrogen atoms were refined anisotropically. The hemi-solvating CH_2Cl_2 and H_2O molecules are disordered, which were refined with DFIX and DANG restrains for the C–Cl distances and Cl–C–Cl angle, and ISOR restrains for CL4S and O1W, respectively. The two hydrogen atoms for the hemi-solvating water molecule were located from the difference-Fourier maps and were constrained to ride on O1W in the refinement, the remaining hydrogen atoms were placed in the calculated positions and refined as riding atoms. Crystal data for **6**$\cdot 1.5CH_2Cl_2 \cdot 0.5H_2O$: $C_{60.5}H_{53}Cl_5OsO_{2.5}P_3$, $M_r = 1280.39$, Monoclinic, $P2_1$, $Z = 2$, $a = 9.67420(10)$ Å, $b = 16.7950(3)$ Å, $c = 17.7450(3)$ Å, $\alpha = 90°$, $\beta = 97.926(2)°$, $\gamma = 90°$, $V = 2855.63(8)$ Å^3; 12,939 reflections, 8043 independent reflections ($R_{\mathrm{int}} = 0.0280$); $R_1 = 0.0323$, $wR_2 = 0.0844$ for 667 parameters and 6909 reflections with $[I > 2\sigma(I)]$; Flack parameter of −0.011(7), 2918 Friedel pairs were used in the refinement.

[11] (a) $[Os(OTf)(NC_5H_4CH{=}CH)(NC_5H_4CH{=}CH_2)(PiPr_3)]OTf$ (1.995(2) Å) M.A. Esteruelas, F.J. Fernandez-Alvarez, M. Olivan, E. Onate, J. Am. Chem. Soc. 128 (2006) 4596;
(b) $CpOs(CH{=}CHCOMe)(PiPr)$ (1.989(4) Å)M.A. Esteruelas, Y.A. Hernandez, A.M. Lopez, M. Olivan, E. Onate, Organometallics 24 (2005) 5989;
(c) $Os(SnPh_2Cl)(NC_5H_4CH{=}CH)(H_2)(PiPr)_2$ (2.068(4) Å)B. Eguillor, M.A. Esteruelas, M. Olivan, E. Onate, Organometallics 24 (2005) 1428;
(d) $OsCl(CH{=}CH(p\text{-tolyl})(CO)(PPh_3)_3$ (2.105(7) Å)H. Xia, T.B. Wen, Q.Y. Hu, X. Wang, X. Chen, L.Y. Shek, I.D. Williams, K.S. Wong, G.K.L. Wong, G. Jia, Organometallics 24 (2005) 562.

[12] (a) M.A. Esteruelas, F.J. Lahoz, E. Oñate, L.A. Oro, B. Zeier, Organometallics 13 (1994) 1662;
(b) H. Werner, R. Weinand, H. Otto, J. Organomet. Chem. 307 (1986) 49.