

This article was downloaded by:

On: 23 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

Synthesis and characterization of a large bite angle iridium nixantphos complex

Thashree Marimuthu^a; Muhammad D. Bala^a; Holger B. Friedrich^a

^a School of Chemistry, University of KwaZulu-Natal, Durban, South Africa

To cite this Article Marimuthu, Thashree , Bala, Muhammad D. and Friedrich, Holger B.(2009) 'Synthesis and characterization of a large bite angle iridium nixantphos complex', *Journal of Coordination Chemistry*, 62: 9, 1407 – 1414

To link to this Article: DOI: 10.1080/00958970802626511

URL: <http://dx.doi.org/10.1080/00958970802626511>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Synthesis and characterization of a large bite angle iridium nixantphos complex

THASHREE MARIMUTHU, MUHAMMAD D. BALA*
and HOLGER B. FRIEDRICH*

School of Chemistry, University of KwaZulu-Natal, Durban, South Africa

(Received 15 April 2008; in final form 27 August 2008)

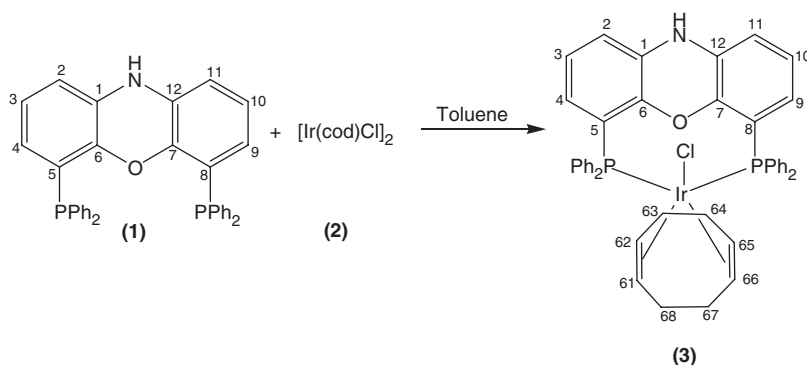
The complex (nixantphos)Ir(cod)Cl·CH₂Cl₂(0.5C₇H₈) **3** has been synthesized and structurally characterized by NMR, IR, and single crystal X-ray diffraction. The coordination around Ir is trigonal bipyramidal with both P groups of the nixantphos bound in a *bis*-equatorial mode. The *bis*-chelating cod (C₈H₁₂) occupies the remaining equatorial position and an axial position. This mode of bonding resulted in a large bite angle (P1—Ir—P2) of 106.49° (3) for **3**. The IR and NMR data support the elucidated structure. Thermal analyses of **3** indicate that it is thermally stable up to decomposition greater than 400°C.

Keywords: Nixantphos; Iridium complex; Bite angle; Catalyst

1. Introduction

The ability to control selectivities of coordination compounds in catalysis has been an area of intense research. In particular, ligands with large bite angles have been developed for preparation of catalysts that control the ratio of linear to branched products in the hydroformylation of olefins [1]. van Leeuwen and co-workers [1–3] studied a series of rigid diphenylphosphine-based ligands with bite angles that ranged between 102 and 131° and demonstrated that rhodium compounds containing these ligands show high selectivity in hydroformylation of 1-octene to 1-octanal. Brown and Kent [4] have proposed that the highest selectivity to linear aldehyde products was obtained when a chelated phosphine ligand is coordinated in the equatorial plane of a trigonal bipyramidal rhodium complex. In this article, we report the synthesis of an iridium complex, **3** (scheme 1 and figure 2, see section 3.5), with a nixantphos (xanthene diphenylphosphine) ligand backbone. Complex **3** was prepared as part of our ongoing study of scorpionate-type metal complexes [5] for use in hydroformylation reactions. The reported data on the full structural elucidation of **3** will serve as a reference point for the synthesis of related N-functionalized scorpionate-metal

*Corresponding authors. Email: bala@ukzn.ac.za; friedric@ukzn.ac.za

Scheme 1. Synthesis of **3** from nixantphos **1**.

complexes based on the nixantphos backbone. The route to the synthesis of **3** is presented in scheme 1.

2. Experimental

2.1. Materials and methods

Chemicals were of reagent grade and reactions were carried out in distilled and dried solvents using standard Schlenk tube techniques under dry nitrogen. Iridium trichloride hydrate ($\text{IrCl}_3 \cdot x\text{H}_2\text{O}$) was obtained from Johnson Matthey and used as received. The ligand 4,6-*bis*(diphenylphosphino)phenoxazine (nixantphos) **1** was prepared by literature methods [6, 7]. The dimeric chloro-bridged precursor di- μ -*bis*(1,5-cyclooctadiene)diiridium(I) [$\text{Ir}(\text{cod})\text{Cl}$]₂ **2** was prepared [8] by reduction of IrCl_3 in the presence of excess 1,5-cyclooctadiene (cod) (Fluka $\geq 98\%$) in aqueous ethanol [Merck absolute American Chemical Society (ACS) grade]. Fourier transform infrared (FTIR) spectra were recorded in the 4000–400 cm^{-1} region on a Perkin Elmer attenuated total reflectance (ATR) infrared spectrophotometer. ¹H-, ³¹P- and ¹³C-NMR measurements were collected at 298 K with a Bruker 400 MHz spectrometer using 5 mm tubes and deuterated dimethylsulfoxide (DMSO) as solvent. Coupling constants (*J*) are given in Hertz. The melting point was determined using a Gallenkamp melting point apparatus and is uncorrected. High resolution mass spectroscopy was obtained with the Waters LCT Premier TOF (Time of Flight) mass spectrometer using direct infusion. Differential scanning calorimetry (DSC) measurements (Al_2O_3 reference standard) were performed on a Shimadzu DSC-60 at a heating rate of 10 °C min⁻¹. Elemental analyses were performed on a LECO CHNS-932 elemental analyzer.

2.2. Synthesis

A dry Schlenk tube was charged with [$\text{Ir}(\text{cod})\text{Cl}$]₂ (30 mg, 0.05 mM) in 5 cm³ of degassed toluene. Nixantphos (50 mg, 0.09 mM) was added to the stirring solution and the

resulting mixture was warmed to 50°C. The solution was stirred for 2 h over which time a yellow solid precipitated. The precipitate was filtered via a cannula and washed with dry methanol (MeOH) and hexane to afford **3** in 70% yield. Melting point was 469 K, and DSC 478 K. Mass calculated for $C_{44}H_{39}ClIrNOP_2$ was: C, 59.55; H, 4.43; N, 1.58. Mass found was: C, 59.02; H, 4.14; N, 1.46.

2.3. Structure analysis and refinement

Single-crystal structure determination by X-ray diffraction was performed on a Bruker APEXII CCD area-detector diffractometer with graphite monochromated Mo- $K\alpha$ radiation (50 kV, 30 mA) using the APEX 2 data collection software [9]. The collection method involved ω -scans of width 0.5° and 512 × 512 bit data frames. Data reduction was carried out using the SAINT+ software [10] and face indexed absorption corrections were made using XPREP. The crystal structure was solved by direct methods using SHELXTL. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full-matrix least-squares calculations based on F^2 using SHELXTL. Hydrogen atoms were first located in the difference map, then positioned geometrically and allowed to ride on their respective parent atoms with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The H atom attached to nitrogen was freely refined. The structure of **3** contains a toluene molecule disordered over an inversion center. While attempts were made to resolve this disorder by placing a toluene molecule in this position, it was not possible to determine the position of the toluene methyl group. Consequently, the disorder was modelled as a benzene molecule disordered over a center of symmetry. The contribution of the full toluene molecule has, however, been added to the unit cell contents F000 and density values. Diagram and publication material were generated

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{48.50}H_{45}Cl_3IrNOP_2$
Formula weight	1018.34
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	11.1353(2)
b	12.8360(2)
c	15.5385(2)
α	78.4230(10)
β	84.4520(10)
γ	67.8430(10)
V (Å ³)	2014.56(6)
Z	2
D_{Calcd} (mg m ⁻³)	1.679
Absorption coefficient (mm ⁻¹)	3.633
$F(000)$	1018
Reflections collected	32605
Independent reflections	9721 [R_{int}] = 0.0439]
Goodness-of-fit on F^2	1.073
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0288$, $wR_2 = 0.0757$
R indices (all data)	$R_1 = 0.0340$, $wR_2 = 0.0775$

Table 2. Bond lengths (Å) and angles (°) for **1**.

C(1)–N(1)	1.412(5)	C(65)–Ir(1)–P(1)	148.85(10)
C(5)–P(1)	1.835(3)	C(62)–Ir(1)–P(1)	107.35(9)
C(6)–O(1)	1.390(4)	C(61)–Ir(1)–P(1)	81.34(10)
C(7)–O(1)	1.393(4)	C(66)–Ir(1)–Cl(1)	84.31(10)
C(12)–N(1)	1.415(5)	C(65)–Ir(1)–Cl(1)	88.23(10)
C(61)–Ir(1)	2.172(3)	C(62)–Ir(1)–Cl(1)	162.51(10)
C(62)–Ir(1)	2.150(3)	C(61)–Ir(1)–Cl(1)	155.79(9)
C(65)–Ir(1)	2.129(3)	P(1)–Ir(1)–Cl(1)	89.16(3)
C(66)–Ir(1)	2.119(3)	P(1)–Ir(1)–P(2)	106.49(3)
Cl(1)–Ir(1)	2.4227(8)	Cl(1)–Ir(1)–P(2)	86.37(3)
Ir(1)–P(1)	2.3802(9)	C(1)–N(1)–C(12)	116.9(3)
Ir(1)–P(2)	2.4761(8)	C(6)–O(1)–C(7)	113.8(3)
N(1)–H(1)	0.9200	C(5)–P(1)–Ir(1)	119.56(12)
C(66)–Ir(1)–P(1)	109.16(10)	C(8)–P(2)–Ir(1)	117.48(11)

using SHELXTL [11], PLATON [12], and ORTEP-3 [13]. Further details of the X-ray structural analysis are given in table 1, while selected bond lengths and angles for **3** are listed in table 2.

3. Results and discussion

3.1. Synthesis

The $[\text{Ir}(\text{cod})\text{Cl}]_2$ was synthesized from IrCl_3 [8, 14]. Substitution of the *bis*-chelated cod by bidentate nixantphos **1** yields (nixantphos)Ir(cod)Cl in high yield. Single crystals of **3** suitable for X-ray analysis were grown by slow diffusion of MeOH into a dichloromethane solution of the complex.

3.2. NMR data

The structure of **3** can be described as symmetrical about a mirror plane that bisects the molecule through the $\text{N}\cdots\text{O}\cdots\text{Ir}\cdots\text{Cl}$ vector. This renders the positions at carbons 2 and 11, 3 and 10, and 4 and 9 on the nixantphos ligand chemically equivalent as shown in table 3. Also, carbon positions on the cod ligand in chemically equivalent positions are summarized in table 3. The proton and carbon peaks of the coordinated nixantphos ligand exhibit slight downfield shifts in comparison to the chemical shifts previously reported for free **1** [15].

A 2-D correlation spectroscopy (COSY)-NMR experiment was recorded in CDCl_3 to investigate the correlations between the protons in **3** and the result is presented in figure 1. Data from the COSY-NMR experiment lead to the following observations on inter-proton coupling and the strength of the coupling constants in the coordinated nixantphos ligand of **3**: (i) $\text{H}^{2,11}$ coupled with $\text{H}^{3,10}$ corresponding to a doublet at 6.1 ppm (d, $J(\text{H}^{2,11}, \text{H}^{3,10}) = 6.5$ Hz); (ii) $\text{H}^{3,10}$ coupled with both $\text{H}^{2,11}$ and $\text{H}^{3,10}$ corresponding to a triplet at 6.8 ppm (t, $J(\text{H}^{3,10}, \text{H}^{2,11}, \text{and } \text{H}^{4,9}) = 7.5$ Hz); (iii) $\text{H}^{4,9}$ coupled with $\text{H}^{3,10}$ corresponding to a broad doublet at 6.7 ppm (bd, $J(\text{H}^{4,9}, \text{H}^{3,10}) = 7.7$ Hz).

Table 3. NMR spectroscopic data for **3**.

^a Carbon number	¹ H (δ = ppm)	¹³ C (δ = ppm)
2, 11	6.1 t [J (H, H) = 6.52]	115
3, 10	6.8 t [J (H, H) = 7.74]	123
4, 9	6.7 d [J (H, H) = 7.48]	124
Phenyl groups on P1 & P2	7.2–7.5(20)	128–129
63, 64, 67, 68	1.3 (m) 1.5 (m) 8H	49
61, 62, 65, 66	3.3 (bs) 4H	62

Note: ^aCarbon numbers relative to the numbering scheme for **3** in scheme 1.

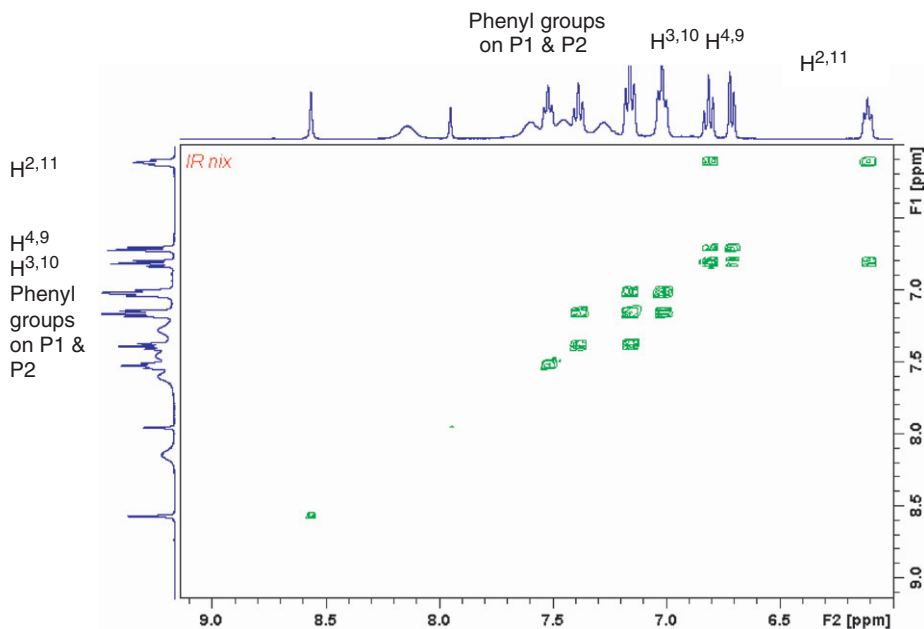
Figure 1. COSY NMR of **3** in d-DMSO.

Table 3 shows that protons of the phenyl groups on P1 and P2 are assigned chemical shifts (ppm) at 7.4 (8H aromatic CH) and 7.5 (12H aromatic CH). Correlations between these protons are also observed in figure 1.

The heteronuclear multiple quantum coherence (HMQC) data confirmed the assignment of the ¹³C signals for C^{2,11}, C^{3,10}, and C^{4,9} at 115, 121, and 124 ppm, respectively. The ¹³C peaks for the carbons of the phenyl groups attached to P1 and P2 are centered at 130 ppm. The amine proton is a broad singlet at 8.4 ppm.

On the ¹H-NMR spectrum, the olefinic proton of the coordinated cod is a broad signal at 3.2 ppm, implying that these protons are in chemically equivalent environments. The weak and broad resonances at δ = 1.5 (m) and 1.3 (m) ppm integrating for 8H were assigned to the methylenic protons of the cod (table 3). A single peak was observed in the ¹³C NMR spectrum at 49 ppm (CH₂), assigned to C63, C64, C67, and C68. The signal for the allylic double bond in the ¹³C NMR spectrum appeared at 62 ppm, shifted slightly downfield compared to free alkene bonds.

Analysis of the ^{31}P NMR data shows that the coordinated phosphines exhibit a slight downfield shift (0.8 ppm) compared to the free ligand [15], suggesting coordination. The peak was observed as a singlet at -19.4 ppm, indicating that the two phosphines reside in similar environment, i.e. both are equatorial as confirmed by the single crystal X-ray analysis (see below).

3.3. Mass spectroscopy (high resolution), elemental and DSC thermal analyses

The exact mass for **3** was calculated as 887. Mass spectroscopy spectrum identified: MS (FAB), $m/z(\%)$ [frag.]: 852(100)[Ir(cod)(nixantphos)]⁺. Similar fragmentation results were reported for [Ir(cod)(dppe)Cl] complexes [16], where dppe is 1, 2-*bis*(diphenylphosphino)ethane.

The DSC revealed no phase change up to the melting point observed as an endotherm at 198°C . The DSC results indicate that the complex has good thermal stability with the onset of decomposition at temperatures greater than 400°C .

3.4. IR data

IR analysis confirmed the presence of C=C and CH (cod) stretching and bending vibrations at 3053, 3010, 2931, 2853, and 2829 cm^{-1} . The aromatic C–C stretch bands (for the phenyl ring carbons) appear at 1574 cm^{-1} . The bands for C–H bends appear at 1091 cm^{-1} for the in-plane bends and at 693 cm^{-1} for the out-of-plane bend. Medium to strong absorptions were present in the regions 1452(s), 1400(s), 1293(s), 1263(m), and $1210(\text{m})\text{ cm}^{-1}$ for the weak C–H stretch of the aromatic rings. The secondary amine (NH) stretching bands ($3329, 741\text{ cm}^{-1}$) and C–N absorptions (1350 cm^{-1}) are also diagnostic.

3.5. X-ray diffraction data

A simplified (for clarity) ORTEP representation of **3** is presented in figure 2. The coordination of ligands around Ir in **3** can be described as approximately trigonal bipyramidal, if the cod ligand, the *bis*-phosphino chelated nixantphos ligand, and the Cl atom are considered. The equatorial plane contains the two *cis* phosphines (P1 and P2) and the mid point of the C65=C66 cod double bond, while the two axial positions include the mid point of C61=C62 cod double bond and the chloro ligand. A similar *bis*-equatorial coordination of chelated P ligands has also been observed in [Rh(CO)H(PPh₃)-xantphos] [1]. The net result is that this mode of coordination is responsible for the large bite angle observed around Ir of 106.49° (**3**) in **3**, which is higher than the $100\text{--}103^\circ$ reported by Fox *et al.* [17] for IrX(CO)₂(xantphos) and IrH₂Cl(CO)(xantphos), where X=halide or COEt.

The bond length of the equatorial Ir-cod is $1.443(5)\text{ \AA}$ and that of the axial is $1.412(5)\text{ \AA}$, significantly longer than the $1.38(2)\text{ \AA}$ for [Ir(cod)(PPh₃)₂][PF₆] and [Ir(C₅H₄NOS)(cod)] containing non-chelating monodentate ligands reported by Chaloner *et al.* [18] and Theron *et al.* [19]. However, this result is similar to the $1.428(8)\text{ \AA}$ bond length reported by Hahn *et al.* [20] for cod C=C bonds formed in the equatorial plane of similar trigonal bipyramidal iridium complexes. Considering a mean plane of planarity involving the 14 ring atoms of the nixantphos ligand **1**, it can be concluded that **3** is slightly bent about an N1–O1 axis in order to accommodate added

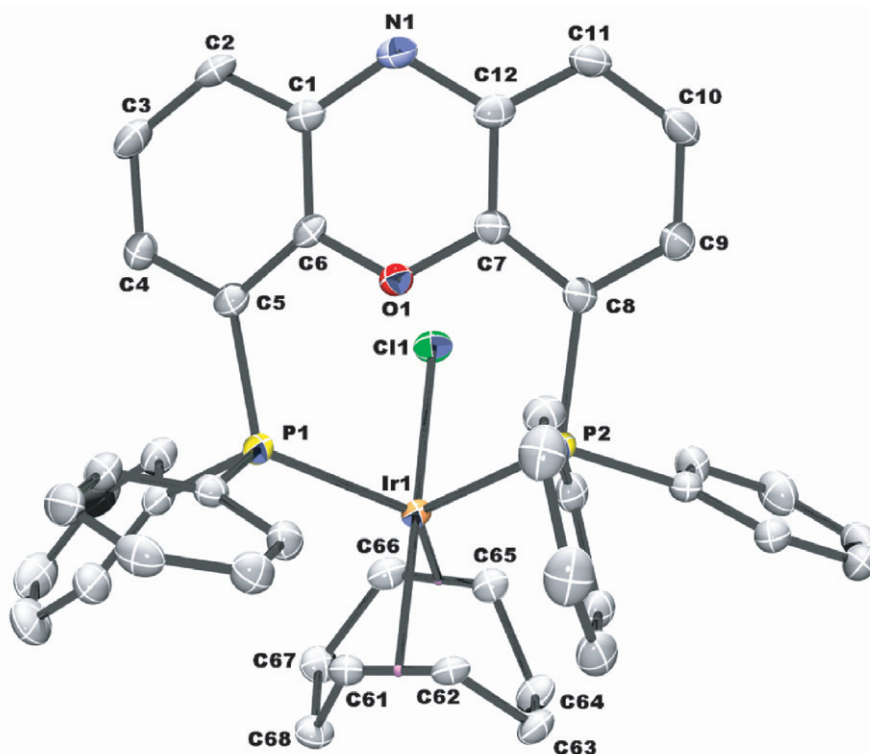


Figure 2. ORTEP drawing of **3** showing the atom numbering scheme. Thermal ellipsoids are shown at 50% probability with hydrogen atoms omitted for clarity.

strain due to Ir metal coordination. Uncoordinated **1** is essentially planar with a maximum deviation from planarity of only 0.094(2) Å for the O1 atom [15]. However in **3**, the heteroatoms N1 and O1 show large deviations from planarity (0.408(2) and 0.618(2) Å, respectively), resulting in a strained nixantphos ligand.

4. Conclusions

The nixantphos-based iridium complex has been synthesized and fully characterized. Coordination around Ir has been confirmed by NMR and single-crystal X-ray diffraction to be trigonal bipyramidal with both P groups of the nixantphos bound equatorially. The axial positions are occupied by Cl and one C=C bond of the cod ligand. This mode of bonding results in a large (P1—Ir—P2) bite angle of 106.49° (3) for **3**.

Supplementary material

Crystallographic data for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC 684172. These data can be obtained

free of charge at <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; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

We wish to thank Dr Manuel Fernandez (University of the Witwatersrand) for crystal data collection, SASOL, THRIP and the University of KwaZulu-Natal for financial support. We gratefully acknowledge Johnson Matthey for a loan of iridium trichloride.

References

- [1] P.C.J. Kamer, P.W.N.M. van Leeuwen, J.N.H. Reek. *Acc. Chem. Res.*, **34**, 895 (2001).
- [2] M. Kranenburg, P.C.J. Kamer, P.W.N.M. van Leeuwen, D. Vogt, W. Keim. *J. Chem. Soc., Chem. Commun.*, 2177 (1995).
- [3] M. Kranenburg, Y.E.M. Vanderburgt, P.C.J. Kamer, P.W.N.M. van Leeuwen, K. Goubitz, J. Fraanje. *Organometallics*, **14**, 3081 (1995).
- [4] J.M. Brown, A.G. Kent. *J. Chem. Soc., Perkin Trans.*, **2**, 1597 (1987).
- [5] T. Marimuthu, M. Bala, H.B. Friedrich. *Acta Cryst.*, **E64**, o772 (2008).
- [6] H.M. Petrassi, T. Klabunde, J. Sacchettini, J.W. Kelly. *J. Amer. Chem. Soc.*, **122**, 2178 (2000).
- [7] L.A. van der Veen, P.H. Keeven, G.C. Schoemaker, J.N.H. Reek, P.C.J. Kamer, P. van Leeuwen, M. Lutz, A.L. Spek. *Organometallics*, **19**, 872 (2000).
- [8] G.W. Parshall. *Inorganic Syntheses*, McGraw-Hill, New York (1974).
- [9] Bruker APEX2, (Version 2.0-1), Bruker AXS Inc., Madison, Wisconsin, USA (2005).
- [10] Bruker SAINT-NT, (Version 6.0.) (includes XPREP and SADABS), Bruker AXS Inc., Madison, Wisconsin, USA (2005).
- [11] G.M. Sheldrick. *Acta Cryst.*, **A64**, 112 (2008).
- [12] A.L. Spek. *J. Appl. Cryst.*, **36**, 7 (2003).
- [13] L.J. Farrugia. *J. Appl. Cryst.*, **30**, 565 (1997).
- [14] M. Martin, E. Sola, O. Torres, P. Plou, L.A. Oro. *Organometallics*, **22**, 5406 (2003).
- [15] T. Marimuthu, M. Bala, H.B. Friedrich. *Acta Cryst.*, **E64**, o711 (2008).
- [16] T. Makino, Y. Yamamoto, K. Itoh. *Organometallics*, **23**, 1730 (2004).
- [17] D.J. Fox, S.B. Duckett, C. Flaschenriem, W.W. Brennessel, J. Schneider, A. Gunay, R. Eisenberg. *Inorg. Chem.*, **45**, 7197 (2006).
- [18] P.A. Chaloner, P.B. Hitchcock, M. Reisinger. *Acta Crystallogr.*, **48**, 735 (1992).
- [19] M. Theron, W. Purcell, S.S. Basson. *Acta Crystallogr.*, **53**, 336 (1996).
- [20] F.E. Hahn, B. Heidrich, T. Pape, A. Hepp, M. Martin, E. Sola, L.A. Oro. *Inorg. Chim. Acta*, **359**, 4840 (2006).