

Synthesis and structural studies of Rh^I, Pd^I, Ni^{II} complexes and one-pot synthesis of binuclear Ru^{II} complex [(η^6 -*p*-cymene)Ru(μ_2 -Cl)₃Ru{PhN(P(OC₆H₄OMe-*o*)₂)₂}Cl]

Chelladurai Ganesamoorthy ^a, Joel T. Mague ^b, Maravanji S. Balakrishna ^{a,*}

^a Phosphorus Laboratory, Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400 076, India

^b Department of Chemistry, Tulane University, New Orleans, LA 70118, USA

Received 12 February 2007; received in revised form 4 April 2007; accepted 4 April 2007

Available online 21 April 2007

Abstract

The Rh^I, Ru^{II}, Pd^I and Ni^{II} complexes of the aminobis(phosphonite), PhN(P(OC₆H₄OMe-*o*)₂)₂ (**1**) are reported. The reactions of **1** with [Rh(COD)Cl]₂ in 1:1 and 2:1 molar ratio afford the mono- and diolefin substituted chloro bridged chelate complexes, [(COD)Rh₂(μ_2 -Cl)₂{PhN(P(OC₆H₄OMe-*o*)₂)₂}]₂ (**2**) and [Rh(μ_2 -Cl){PhN(P(OC₆H₄OMe-*o*)₂)₂}]₂ (**3**), respectively. Similarly, the cationic mono- and bis-chelate complexes, [Rh(COD){PhN(P(OC₆H₄OMe-*o*)₂)₂}]OTf (**4**) and [Rh{PhN(P(OC₆H₄OMe-*o*)₂)₂}]OTf (**5**) are obtained by treating **1** with [Rh(COD)Cl]₂ in the presence of AgOTf in appropriate ratios. The dinuclear Rh^I carbonyl complex, [RhCl(CO){ μ -PhN(P(OC₆H₄OMe-*o*)₂)₂}]₂ (**6**) is prepared by treating **1** with 0.5 equiv. of [Rh(CO)₂Cl]₂. Reaction of **1** with *cis*-[NiBr₂(DME)] (DME = 1,2-dimethoxyethane) affords [PhN(P(OC₆H₄OMe-*o*)₂)₂]₂NiBr₂ (**7**) whereas with [Ru-(η^6 -*p*-cymene)Cl₂]₂ in refluxing THF medium produces an interesting and rare bimetallic Ru^{II} complex, [(η^6 -*p*-cymene)Ru(μ_2 -Cl)₃Ru{PhN(P(OC₆H₄OMe-*o*)₂)₂}Cl] (**8**). Redox condensation of the Pd⁰ and Pd^{II} derivatives with **1** affords the dinuclear Pd^I complex, [PdBr{ μ -PhN(P(OC₆H₄OMe-*o*)₂)₂}]₂ (**9**). The formation and structure of complexes **2–9** are assigned through various spectroscopic and micro analysis data. The molecular structures of **5** and **7–9** are confirmed by single crystal X-ray diffraction studies.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Aminobis(phosphonite); Transition metal chemistry; Crystal structures; Chelate and bridged bidentate complexes

1. Introduction

The transition metal chemistry of “short-bite” aminobis(phosphines) of the type X₂PN(R)PX₂ and their bis(chalcogenide) derivatives has attracted considerable attention in recent years because of the versatile coordination behavior of the former as it is similar to dppe [1] and the potential application of latter as single source precursors of various metal-, non-metal- and metalloid-telluride thin films and nanoparticles [2]. However, the ligands with P–N–P framework are found to be thermally more stable com-

pared to dppe and sterically less rigid in comparison with P–O–P systems [3]. Further, the binding properties of these ligands can be readily altered by changing the substituents on both the phosphorus and the nitrogen centers. As a result, the ligands with P–N–P framework have been successfully employed in various catalytical reactions such as Pauson-Khand reactions [4], copolymerization of CO and ethylene [5], ethylene tri- [6] and tetramerization reactions [7] and allylic substitution reactions [8]. In view of this, recently we have synthesized and reported transition metal chemistry and catalytic applications of several aminophosphines and aminobis(phosphines). As a part of our interest in designing new ligands and studying their coordination behavior [9] and catalytic applications [10], we report herein the synthesis and structural characterization of Rh^I, Ru^{II},

* Corresponding author. Tel.: +91 22 2576 7181; fax: +91 22 2576 7152/2572 3480.

E-mail address: krishna@chem.iitb.ac.in (M.S. Balakrishna).

Pd^I and Ni^{II} metal complexes of aminobis(phosphonite), PhN(P(OC₆H₄OMe-*o*)₂)₂ (**1**).

2. Results and discussion

2.1. Rh^I derivatives

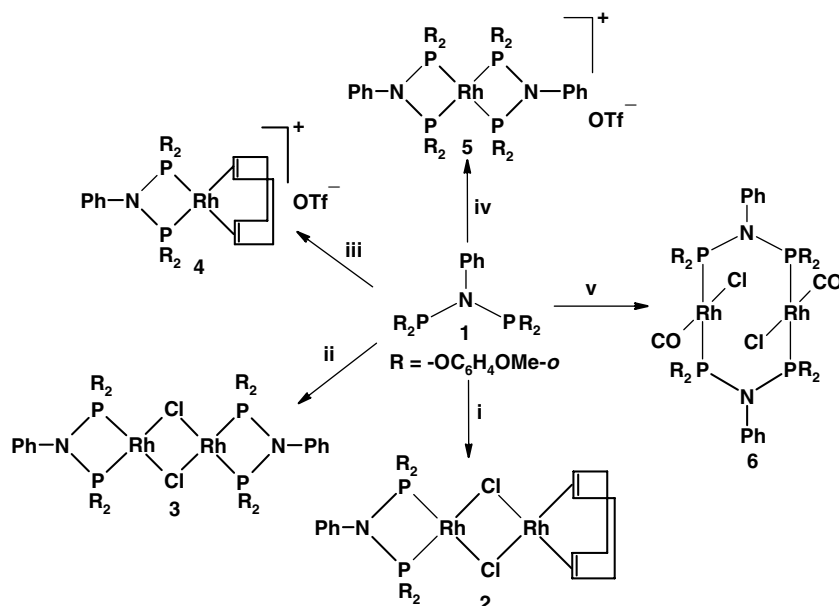
The reactions of PhN(P(OC₆H₄OMe-*o*)₂)₂ (**1**) with [Rh(COD)Cl]₂ in 1:1 and 2:1 molar ratio in CH₂Cl₂ lead to the successive replacement of the diene ligands and the formation of chloro bridged bimetallic chelate complexes, [Rh₂(μ₂-Cl)₂(COD){PhN(P(OC₆H₄OMe-*o*)₂)₂}] (**2**) and [Rh(μ₂-Cl){PhN(P(OC₆H₄OMe-*o*)₂)₂}]₂ (**3**), respectively. Similarly, the reactions of **1** with [Rh(COD)Cl]₂ in the presence of 2 equiv. of AgOTf in 2:1 and 4:1 molar ratio afford the cationic chelate complexes, [Rh(COD){PhN(P(OC₆H₄OMe-*o*)₂)₂}]⁺OTf⁻ (**4**) and [Rh{PhN{P(OC₆H₄OMe-*o*)₂}₂}]⁺OTf⁻ (**5**), respectively, as shown in Scheme 1 [11].

The ³¹P NMR spectra of complexes **2–5** show doublets centered at 92.0, 89.7, 87.1 and 98.8 ppm with ¹J_{RhP} couplings of 283, 282, 233 and 197 Hz, respectively, which indicate the chemically and magnetically equivalent nature of the phosphorus centers. The ¹H NMR spectra of complexes **2–5** show single resonances around the region of 3.4–3.8 ppm corresponding to the *ortho*-methoxy groups present in the phenyl rings. The resonance due to olefinic protons of COD in complexes **2** and **4** appear as broad singlets at 3.91 and 5.39 ppm. The methylenic protons present in complexes **2** and **4** exhibit two doublets at 2.29, 1.60 and 2.20, 1.61 ppm, respectively. The structure of the complex **5** was confirmed by the single crystal X-ray diffraction study.

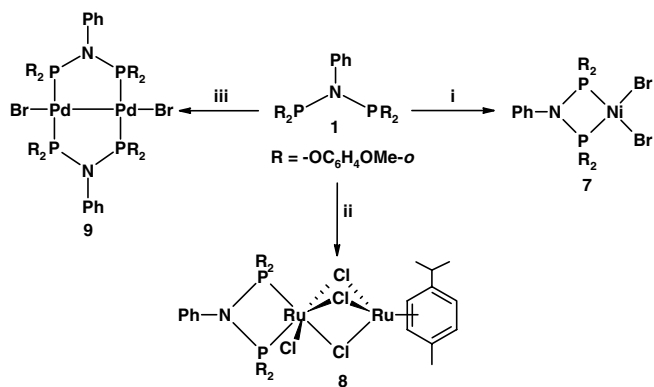
The reaction between **1** and [Rh(CO)₂Cl]₂ in CH₂Cl₂ at room temperature affords dinuclear complex [RhCl(CO){μ-PhN(P(OC₆H₄OMe-*o*)₂)₂}]₂ (**6**) as a yellow-orange color crystalline solid in good yield. In contrast, the same reaction when carried out in refluxing CH₃CN results in the formation of chloro-bridged dimeric complex **3** in quantitative yield. The phosphorus-31 NMR spectrum of complex **6** consists of an XAA'X' multiplet centered at 117.1 ppm with ¹J_{RhP} + ³J_{RhP} = 261 Hz and ²J_{PP} = 130 Hz. Such type of spin multiplicity was observed in analogous complexes containing bridging bis(phosphines) ligands [9c,9d,9h,12]. The IR spectrum of **6** shows two νCO absorptions at 2085 and 2021 cm⁻¹ which is consistent with the cis-related CO/phosphine structures proposed for similar complexes [13]. The microanalysis and ¹H NMR spectral data are consistent with the proposed structure of **6**.

2.2. Ni^{II}, Ru^{II} and Pd^I Derivatives

The diamagnetic nickel(II) chelate complex, [{PhN(P(OC₆H₄OMe-*o*)₂)₂}NiBr₂] (**7**) was prepared in high yield by reacting **1** with *cis*-[NiBr₂(DME)] (DME = 1,2-dimethoxyethane) in THF at room temperature (Scheme 2). An equimolar reaction between **1** and [Ru(η⁶-*p*-cymene)Cl]₂ in THF at 60 °C resulted in the formation of a rare trichloro-bridged bimetallic complex, [(η⁶-*p*-cymene)Ru(μ₂-Cl)₃Ru{PhN(P(OC₆H₄OMe-*o*)₂)₂}Cl] (**8**) in which one of the ruthenium(II) centers retains the cymene group irrespective of the stoichiometry of the ligand and the reaction conditions. This represents the first one-pot synthesis of a ruthenium(II) binuclear complex containing a bisphosphine ligand. The other known complexes of this type [(η⁶-*p*-cymene)Ru(μ₂-Cl)₃Ru{L₂}Cl] (L₂ = (PPh₃)₂,



Scheme 1. (i) [Rh(COD)Cl]₂, CH₂Cl₂. (ii) 1/2 [Rh(COD)Cl]₂, CH₂Cl₂ or 1/2 [Rh(CO)₂Cl]₂, CH₃CN, Δ with (iii) 1/2 [Rh(COD)Cl]₂, AgOTf, CH₂Cl₂/acetone. (iv) 1/4 [Rh(COD)Cl]₂, 1/2 AgOTf, CH₂Cl₂/acetone with (v) 1/2 [Rh(CO)₂Cl]₂, CH₂Cl₂.

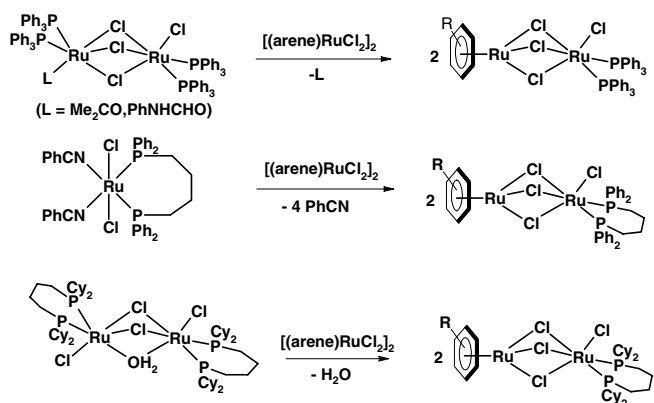


Scheme 2. (i) $\text{NiBr}_2(\text{DME})$, THF. (ii) $[\text{RuCl}_2(p\text{-Cym})]_2$, THF, 60°C with (iii) $1/4 \text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$, $1/2 \text{PdBr}_2(\text{CH}_3\text{CN})_2$, CH_2Cl_2 .

$\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$, $\text{Cy}_2\text{P}(\text{CH}_2)_4\text{PCy}_2$) were prepared by mixing symmetrically substituted binuclear complexes $[\text{L}_2\text{-ClRu}(\mu\text{-Cl})_2(\mu\text{-X})\text{RuClL}_2]$ with $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{Cl}_2]_2$ through con-proportionation reactions as shown in Scheme 3. The ^{31}P NMR spectra of complexes **7** and **8** show single resonances at 68.1 and 100.1 ppm, respectively and the ^1H NMR spectra show singlets at 3.59 and 3.66 ppm corresponding to the *ortho*-methoxy protons. The aromatic protons of *p*-cymene in complex **8** appear as two doublets at 5.34 and 5.18 ppm with J_{HH} coupling of 5.2 Hz. The methyl groups of isopropyl moiety appear as a doublet centered at 1.24 ppm with a J_{HH} coupling of 6.8 Hz, whereas the $-\text{CH}$ proton appears as a septet at 2.84 ppm. The binuclear Pd^{I} complex $[\text{Pd}^{\text{I}}\text{Br}\{\mu\text{-PhN}(\text{P}(\text{O}-\text{C}_6\text{H}_4\text{OMe-}o)_2)_2\}]_2$ (**9**) was prepared by a redox condensation process using a 1:2:4 mixture of $\text{Pd}_2^0(\text{dba})_3 \cdot \text{CHCl}_3$, $\text{Pd}^{\text{II}}\text{Br}_2(\text{CH}_3\text{CN})_2$ and **1** in refluxing CH_2Cl_2 . The ^{31}P NMR spectrum of **9** shows a single peak at 111.3 ppm and the ^1H NMR data are consistent with the proposed structure. The structures of complexes **7–9** were confirmed by single crystal X-ray diffraction studies.

2.3. The crystal and molecular structures of **5** and **7–9**

Perspective views of the molecular structures of compounds **5** and **7–9** with atom numbering schemes are shown



Scheme 3.

in Figs. 1–4, respectively. The selected bond lengths and bond angles of compounds **5** and **7–9** are given in Tables 1 and 2, while crystal data and the details of the structure determinations are given in Table 3. The X-ray crystal structural determination of complex **5** shows that it exists as a cationic bis-chelate complex. The rhodium occupies the center of the distorted square planar geometry and the corners are occupied by four phosphorus centers of the diphosphazane ligands. Due to the formation of strained four-membered chelate ring the P-N-P angle of the free ligand shrinks from $116.07(12)^\circ$ to 99° ($\text{P1-N1-P2} = 99.1(3)^\circ$ and $\text{P3-N2-P4} = 98.7(3)^\circ$). The bite angles created by the chelating ligands

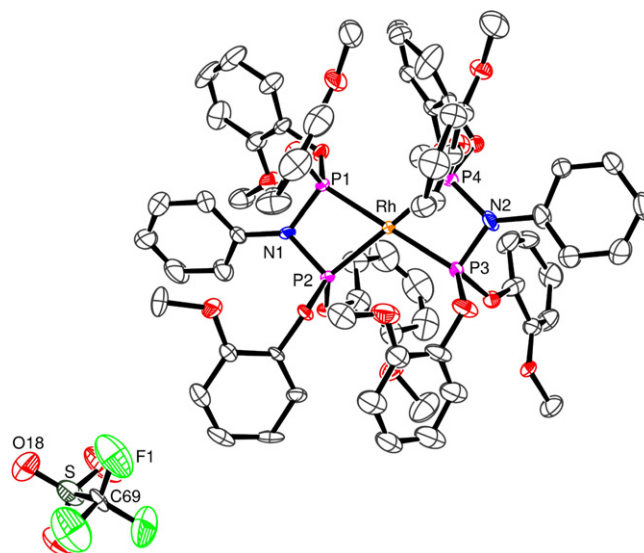


Fig. 1. Molecular structure of **5**. All hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

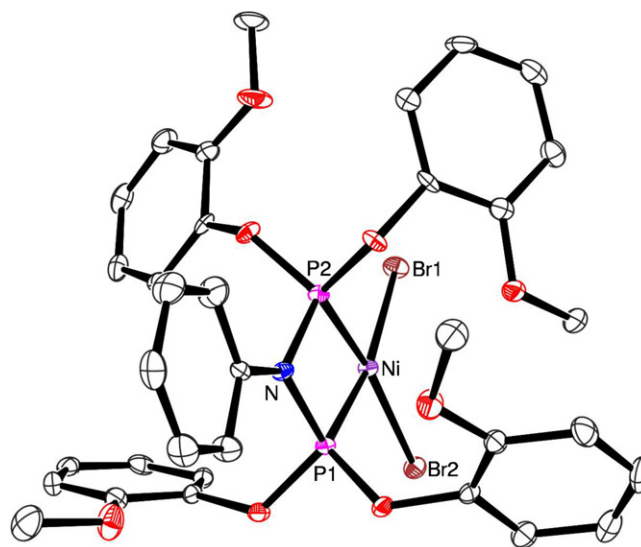


Fig. 2. Molecular structure of **7**. All hydrogen atoms and lattice solvent have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

P1–Rh–P2 and P3–Rh–P4 with Rh center are 69.98(6)° and 69.52(7)°, respectively, which are $\sim 4.5^\circ$ larger than that observed in molybdenum tetra carbonyl derivative (P1–Mo–P2 = 65.02(4)°) [14]. The P1–Rh–P3 and P2–Rh–P4 bond angles (179.22(6)° and 173.01(7)°) are slightly deviated from the linear geometry. The Rh–P distances ranges from 2.241(2) Å (for Rh–P4) to 2.249(2) Å (for Rh–P1).

Crystals of **7** suitable for X-ray diffraction analysis were grown by keeping the saturated THF solution of **7** at room temperature for several days. The diamagnetism of the compound had indicated the distorted square planar coordination geometry about the nickel center and is surrounded by two *cis*-bromides and phosphorus atoms. The four-mem-

bered NP₂Ni chelate ring is nearly planar. The Ni–P bonds are almost equidistant (Ni–P1 = 2.101(1) Å and Ni–P2 = 2.088(1) Å) and are slightly shorter than those in the related *cis*-[NiBr₂{allyl-N(PPh₂)₂}] (2.112(1) Å and 2.122(2) Å), *cis*-[NiCl₂{*p*-C₆H₄OMe-N(PPh₂)₂}] (2.115(2) Å and 2.123(2) Å) [15], [1,3-{*cis*-NiBr₂(PPh₂)₂N}C₆H₄] (2.116(4) Å) [5a], *cis*-[NiBr₂{Ph₂PN(Ph)P(N^tBu)₂SiMe₂}] (2.127(1) Å and 2.115(1) Å) [16] and *cis*-[NiBr₂{Ar₂PN(Me)PAr₂}], (Ar = ^tBuC₆H₄-*o*) (2.161(1) Å) [5b] complexes. Due to the formation of strained four-membered NP₂Ni ring, the P–N–P angle of free ligand is reduced from 116.07(12)° to 95.73(13)°. The P1–Ni–P2 and Br1–Ni–Br2 angles are 73.24(4)° and 100.70(2)°, respectively.

Complex **8** is a bimetallic Ru^{II} complex with Ru2 center having η^6 -coordinated cymene ligand and Ru1 center is surrounded by chlorides and a chelating diphosphazane ligand.

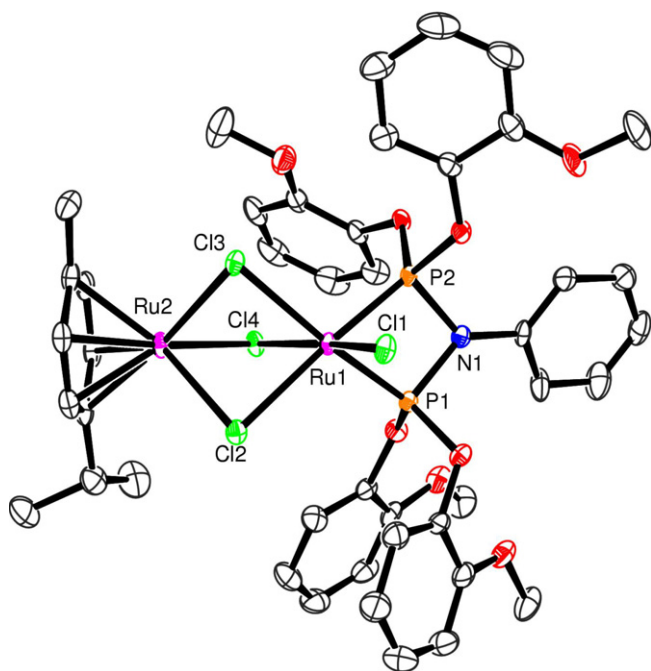


Fig. 3. Molecular structure of **8**. All hydrogen atoms and lattice solvent have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

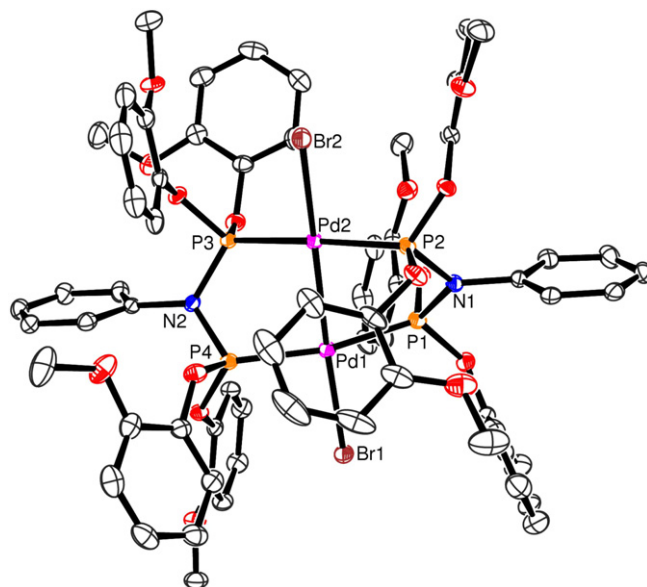


Fig. 4. Molecular structure of **9**. All hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

Table 1
Selected bond distances and bond angles for complexes **5** and **7**

Complex 5		Complex 7	
Bond distances (Å)	Bond angles (°)	Bond distances (Å)	Bond angles (°)
P1–N1	1.692(6)	P1–N	1.689(3)
P2–N1	1.696(5)	P2–N	1.681(3)
P3–N2	1.698(7)	P1–Ni	2.101(1)
P4–N2	1.680(7)	P2–Ni	2.088(1)
Rh–P1	2.249(2)	Br1–Ni	2.317(1)
Rh–P2	2.246(2)	Br2–Ni	2.327(1)
Rh–P3	2.253(2)	P1–O1	1.591(3)
Rh–P4	2.241(2)	P1–O3	1.577(3)
P1–O1	1.576(5)	P2–O5	1.577(3)
P1–O3	1.602(5)	P2–O7	1.588(3)
P2–O5	1.585(5)		
P2–O7	1.599(5)		
P1–N1–P2	99.1(3)	P1–N–P2	95.73(13)
P3–N2–P4	98.7(3)	P1–Ni–P2	73.24(4)
P1–Rh–P2	69.98(6)	Br1–Ni–Br2	100.70(2)
P3–Rh–P4	69.52(7)	Br1–Ni–P1	166.68(4)
P1–Rh–P4	109.81(7)	Br1–Ni–P2	93.70(3)
P2–Rh–P3	110.74(7)	Br2–Ni–P1	92.44(3)
P1–Rh–P3	179.22(6)	Br2–Ni–P2	165.50(4)
P2–Rh–P4	173.01(7)	Ni–P1–N	95.01(9)
Rh–P1–N1	95.47(19)	Ni–P2–N	95.70(9)
Rh–P2–N1	95.5(2)		
Rh–P3–N2	95.4(2)		
Rh–P4–N2	96.4(2)		

Table 2
Selected bond distances and bond angles for complexes **8** and **9**

Complex 8				Complex 9			
Bond distances (Å)		Bond angles (°)		Bond distances (Å)		Bond angles (°)	
P1–N1	1.689(3)	P1–N1–P2	94.89(16)	P1–N1	1.685(3)	P1–N1–P2	111.81(14)
P2–N1	1.699(3)	P1–Ru1–P2	69.97(4)	P2–N1	1.691(3)	P3–N2–P4	114.02(14)
Ru1–Ru2	3.260(1)	Cl1–Ru1–Cl2	91.61(3)	P3–N2	1.677(3)	Br1–Pd1–P1	96.42(3)
Ru1–Cl1	2.375(1)	Cl1–Ru1–Cl3	91.48(3)	P4–N2	1.682(3)	Br1–Pd1–P4	92.96(3)
Ru1–Cl2	2.532(1)	Cl1–Ru1–Cl4	168.53(3)	P1–Pd1	2.240(2)	Br2–Pd2–P2	89.11(3)
Ru1–Cl3	2.500(1)	Cl1–Ru1–P1	93.13(4)	P2–Pd2	2.256(3)	Br2–Pd2–P3	95.21(3)
Ru1–Cl4	2.398(1)	Cl1–Ru1–P2	89.39(4)	P4–Pd1	2.257(2)	Pd1–Pd2–Br2	173.78(1)
Ru1–P1	2.174(1)	Cl2–Ru1–Cl3	79.72(3)	P3–Pd2	2.249(3)	Pd2–Pd1–Br1	170.21(1)
Ru1–P2	2.178(1)	Cl2–Ru1–Cl4	78.51(3)	Pd1–Br1	2.480(1)	Pd1–Pd2–P2	88.36(2)
Ru2–Cl2	2.444(1)	Ru1–Cl2–Ru2	81.84(3)	Pd2–Br2	2.481(1)	Pd1–Pd2–P3	87.69(2)
Ru2–Cl3	2.440(1)	Ru1–Cl3–Ru2	82.56(3)	Pd1–Pd2	2.618(1)	Pd2–Pd1–P1	83.65(3)
Ru2–Cl4	2.412(1)	Ru1–Cl4–Ru2	85.36(2)			Pd2–Pd1–P4	88.62(2)
Ru2–C36	2.193(4)	Cl3–Ru1–Cl4	81.11(3)			P1–Pd1–P4	167.06(3)
Ru2–C37	2.182(4)	Cl2–Ru1–P1	106.00(3)			P2–Pd2–P3	174.39(3)
Ru2–C38	2.142(4)	Cl2–Ru1–P2	175.90(3)				
Ru2–C39	2.170(4)	Cl3–Ru1–P1	172.54(3)				
Ru2–C40	2.136(4)	Cl3–Ru1–P2	104.23(3)				
Ru2–C41	2.166(4)	Cl4–Ru1–P1	95.19(3)				
		Cl4–Ru1–P2	100.88(3)				

Table 3
Crystallographic information for compounds **5**, **7–9**

	5	7	8	9
Formula	C ₆₉ H ₆₅ F ₃ N ₂ O ₁₉ P ₄ RhS	C ₃₆ H ₃₃ Br ₂ NNiO ₈ P ₂	C _{48.75} H ₅₁ Cl ₄ N _{1.25} O _{8.75} P ₂ Ru ₂	C _{68.5} H ₆₈ Br ₂ N ₂ O _{16.5} P ₄ Pd ₂
Fw	1542.09	888.06	1200.29	1679.77
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	<i>Pna</i> 21 (No. 33)	<i>P</i> 21/ <i>c</i> (No. 14)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	13.929(2)	11.835(2)	34.040(2)	13.5040(10)
<i>b</i> (Å)	39.565(7)	11.467(2)	19.1510(10)	14.0960(10)
<i>c</i> (Å)	12.385(2)	27.074(4)	18.5610(10)	19.865(2)
α °	90	90	90	84.118(2)
β °	90	101.3060(10)	96.4370(10)	82.292(2)
γ °	90	90	90	63.3880(10)
<i>V</i> (Å ³)	6825.4(19)	3603.0(10)	12023.6(11)	3346.4(5)
<i>Z</i>	4	4	8	2
ρ_{calc} (g cm ⁻³)	1.501	1.637	1.326	1.667
μ (Mo K α) (mm ⁻¹)	0.458	2.898	0.779	1.898
<i>F</i> (000)	3172	1792	4866	1694
Crystal size (mm ³)	0.05 × 0.16 × 0.20	0.18 × 0.20 × 0.20	0.15 × 0.16 × 0.23	0.11 × 0.12 × 0.16
<i>T</i> (K)	293	100	100	100
2 θ Range °	1.5–28.3	2.1–26.4	2.1–28.3	2.1–28.3
Total no. reflections	58,948	17,216	105,063	59,811
No. of independent reflections (<i>R</i> _{int})	16,198 (0.058)	17,236 (0.000)	14,962 (0.060)	16,477 (0.052)
GOF (<i>F</i> ²)	1.21	1.01	1.11	1.01
<i>R</i> ₁ ^a	0.0803	0.0582	0.0508	0.0406
<i>wR</i> ₂ ^b	0.1655	0.1621	0.1437	0.0934

^a $R = \sum |F_o| - |F_c| / \sum |F_o|$.

^b $R_w = \{[\sum w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}$ where $P = (F_o^2 + 2F_c^2) / 3$.

The tetrahedral $\{(\eta^6\text{-cymene})\text{Ru}2\}$ fragment is connected through three chloro bridges to the octahedral $\{\text{Ru}1\text{Cl}(\text{PNP})\}$ moiety. The two phosphorus centers (P1 and P2) are in *cis* positions and *trans* to chlorides (Cl3 and Cl2) with remaining chlorides (Cl1 and Cl4) are coordinated *trans* to each other. As expected, the Ru–Cl bonds of the bridging chlorides are longer (Ru1–Cl4 = 2.398(1) Å–Ru1–Cl2 = 2.532(1) Å) than the terminal Ru–Cl bond

(Ru1–Cl1 = 2.375(1) Å). The Ru···Ru distance (Ru1–Ru2 = 3.260(1) Å) is well outside the range (2.28–2.95 Å) usually observed for a Ru–Ru bond and is some what shorter than that observed in analogous complexes $[(1,3,5\text{-C}_6\text{H}_3\text{Et}_3)\text{Ru}(\mu_2\text{-Cl})_3\text{Ru}(\text{dppb})\text{Cl}]$ (3.326(1) Å), $[(\eta^6\text{-C}_6\text{H}_6)\text{-Ru}(\mu_2\text{-Cl})_3\text{Ru}(\text{dppb})\text{Cl}]$ (3.314(1) Å) (dppb = 1,4-bis(diphenylphosphanyl)butane) and $[(1,3,5\text{-C}_6\text{H}_3\text{Pr}_3)\text{Ru}(\mu_2\text{-Cl})_3\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ (3.360(2) Å) [17]. As observed for the

above complexes, the plane defined by η^6 -cymene ligand is almost parallel to that defined by the bridging chloro ligands. The non-bonded P...P separations in complex **7** and **8** are 2.499(1) Å and 2.495(1) Å, respectively, which are shorter than that observed in complex **5** (P1...P2 = 2.578 Å and P3...P4 = 2.562 Å).

In complex **9**, both the Pd^I centers are having distorted square planar geometry and are surrounded by one Pd, two P and one Br ligands. The Pd–Pd bond length in **9** (2.6182(5) Å) is almost identical to the same in the analogous complex [Pd{ μ -PhN(P(OPh)₂)₂}Cl]₂ (2.619(1) Å) [18] and ~0.08 Å shorter than that in [Pd(μ -dppm)Br]₂ (2.699(5) Å) [19]. The Pd–P bond distances in **9** ranges from 2.239(1) Å to 2.257(1) Å, which are shorter than those observed for [Pd(μ -dppm)Br]₂ complex. The P–N bond lengths varies from 1.677(3) Å to 1.691(3) Å, which are statistically equivalent to the average distances found in [Pd(μ -dppa)Cl]₂ [20] and [Pd{ μ -PhN(P(OPh)₂)₂}Cl]₂ [18]. The four *cis* angles (Br–Pd–P) centered at the Pd1 and Pd2 centers with bromine atoms are 96.42(3)°, 92.96(3)°, 89.11(3)° and 95.21(3)°, respectively. There is a pronounced twist about the Pd–Pd bond with dihedral angles of P1–Pd1–Pd2–P2 and P4–Pd1–Pd2–P3 are –41.31(3)° and –34.90(3)°, respectively, which are typical for the M₂(μ -LL)₂²⁺ skeleton. For example, the dihedral angle between the square planes in [Pd(μ -dppm)Br]₂ is 39°. Because of the bridging nature of the ligand, the complex **9** shows much longer P...P separation when compare to the chelate complexes.

3. Conclusion

The ‘short bite’ bidentate ligand **1** readily reacts with various low valent transition metals to give either mono-nuclear chelates or binuclear complexes depending upon the reaction conditions and stoichiometry. With Rh^I derivatives, various neutral and cationic complexes were prepared. Reaction of **1** with Ni^{II} derivative yielded four-membered chelate complex and with Ru^{II} derivative half sandwich homo bimetallic complex **8** was formed. This is the first report on one-pot synthesis of a binuclear complex of the type **8** in excellent yield; the other two known complexes were prepared involving two step comproportionation reactions. The redox reaction between Pd⁰ and Pd^{II} in the presence of ligand **1** resulted in a Pd^I dimer. The work on catalytic aspects of these complexes is in progress.

4. Experimental

All experimental manipulations were performed under rigorously anaerobic conditions using Schlenk techniques. All the solvents were purified by conventional procedures and distilled prior to use [21]. The aminobis(phosphonite), PhN{P(OC₆H₄OMe-*o*)₂}₂ (**1**) was prepared as previously reported [14]. The metal precursors [Rh(COD)Cl]₂ [22], [Rh(CO)₂Cl]₂ [23], [Ru(η^6 -cymene)Cl₂]₂ [24], Pd²-

(dba)₃·CHCl₃ [25] and NiBr₂(DME) [26] were prepared according to the published procedures. AgOTf was purchased from Aldrich chemicals and used as such without further purification. The ¹H and ³¹P{¹H} NMR (δ in ppm) spectra were recorded using Varian VXR 300 or VXR 400 spectrometer operating at the appropriate frequencies using TMS and 85% H₃PO₄ as internal and external references, respectively. The spectra were recorded in CDCl₃ solutions with CDCl₃ as an internal lock; positive shifts lie downfield of the standard in all of the cases. Infrared spectra were recorded on a Nicolet Impact 400 FTIR instrument as KBr disks. The microanalyses were performed using Carlo Erba Model 1112 elemental analyzer. The melting points were observed in capillary tubes and are uncorrected.

4.1. Synthesis of [(COD)Rh(μ -Cl)₂Rh{PhN(P(OC₆H₄-OMe-*o*)₂)₂}]₂ (**2**)

A solution of **1** (0.026 g, 0.040 mmol) in CH₂Cl₂ (5 mL) was added dropwise to a solution of [RhCl(COD)]₂ (0.020 g, 0.040 mmol) also in CH₂Cl₂ (5 mL) with constant stirring. The reaction mixture was allowed to stir at room temperature for 4 h. The resulting solution was concentrated to 2 mL, layered with 1 mL of petroleum ether, and stored at –30 °C for 1 day to give analytically pure product of **2**. Yield: 79% (0.033 g), m.p.: 144–146 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.80–6.76 (m, 21H, ArH), 3.91 (br s, 4H, CH), 3.52 (s, 12H, OCH₃), 2.29 and 1.60 ppm (d, 8H, CH₂). ³¹P{¹H}NMR (162 MHz, CDCl₃): δ 92.0 ppm (d, ¹J_{Rh,P} = 283 Hz). Anal. Calcd for C₄₂H₄₅NO₈P₂Rh₂Cl₂(1030.47): C, 48.95; H, 4.40; N, 1.36. Found: C, 48.90; H, 4.42; N, 1.34%.

4.2. Synthesis of [Rh(μ -Cl){PhN(P(OC₆H₄OMe-*o*)₂)₂}]₂ (**3**)

- A solution of [RhCl(COD)]₂ (0.035 g, 0.071 mmol) in CH₂Cl₂ (5 mL) was added dropwise to a solution of **1** (0.092 g, 0.142 mmol) also in CH₂Cl₂ (5 mL) with constant stirring. The reaction mixture was allowed to stir at room temperature for 4 h. The resulting solution was concentrated to 4 mL, layered with 2 mL of petroleum ether, and stored at –30 °C for 1 day to give orange precipitate of **3**. Yield: 89% (0.099 g).
- A mixture of [Rh(CO)₂Cl]₂ (0.027 g, 0.070 mmol) and **1** (0.091 g, 0.141 mmol) in acetonitrile (15 mL) was stirred under reflux condition for 4 h. The solvent was removed under reduced pressure, the residue was redissolved in 3 mL of CH₂Cl₂ and diluted with 1 mL of petroleum ether. Keeping this solution at –30 °C for 1 day afforded orange colored crystalline solid **3**. Yield: 80% (0.088 g), m.p.: 168–170 °C (dec). ¹H NMR (400 MHz, CDCl₃): δ 7.72–6.64 (m, 42 H, ArH), 3.46 ppm (s, 24H, OCH₃). ³¹P{¹H}NMR (121 MHz, CDCl₃): δ 89.7 ppm (d, ¹J_{Rh,P} = 282 Hz).

Anal. Calcd for $C_{68}H_{66}N_2O_{16}P_4Rh_2Cl_2$ (1567.87): C, 52.09; H, 4.24; N, 1.79. Found: C, 52.02; H, 4.22; N, 1.84%.

4.3. Synthesis of $[Rh(COD)\{PhN(P(OC_6H_4OMe-o)_2)_2\}]OTf$ (**4**)

AgOTf (0.021 g, 0.081 mmol) was added to the stirred solution of $[Rh(COD)Cl]_2$ (0.020 g, 0.041 mmol) in 5 mL of acetone. After 30 min, a solution of **1** (0.052 g, 0.081 mmol) in 6 mL of CH_2Cl_2 was added dropwise and stirred for 4 h. The suspension obtained was filtered to remove AgCl, and the yellowish-orange filtrate was concentrated to 5 mL. Cooling this solution to $-30^\circ C$, gave **1** as an analytically pure yellow crystalline solid. Yield: 66% (0.054 g), m.p.: $155-157^\circ C$ (dec). 1H NMR (400 MHz, $CDCl_3$): δ 7.67–6.90 (m, 21H, ArH), 5.39 (br s, 4H, CH), 3.81 (s, 12H, OMe), 2.20 and 1.61 ppm (d, 8H, CH_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 87.1 ppm (d, $^1J_{Rh,P} = 233$ Hz). Anal. Calcd for $C_{43}H_{45}F_3NO_{11}P_2SRh$ (1005.73): C, 51.35; H, 4.51; N, 1.39; S, 3.19. Found: C, 51.41; H, 4.49; N, 1.33; S, 3.14%.

4.4. Synthesis of $[Rh\{PhN(P(OC_6H_4OMe-o)_2)_2\}]OTf$ (**5**)

This was synthesized by a procedure similar to that of **4** using AgOTf (0.026 g, 0.101 mmol), $[Rh(COD)Cl]_2$ (0.025 g, 0.051 mmol) and **1** (0.131 g, 0.203 mmol). Crystals suitable for X-ray diffraction analysis were grown from 2:1 mixture of tetrahydrofuran/pet ether at $-30^\circ C$. Yield: 91% (0.142 g), m.p.: $190-192^\circ C$ (dec). 1H NMR (400 MHz, $CDCl_3$): δ 7.26–6.61 (m, 42 H, ArH), 3.45 ppm (s, 24H, OCH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 98.8 ppm (d, $^1J_{Rh,P} = 197$ Hz). Anal. Calcd for $C_{69}H_{66}F_3N_2O_{19}P_4SRh$ (1543.13): C, 53.70; H, 4.31; N, 1.82; S, 2.08. Found: C, 53.63; H, 4.34; N, 1.86; S, 2.05%.

4.5. Synthesis of $[Rh(CO)Cl\{PhN(P(OC_6H_4OMe-o)_2)_2\}]_2$ (**6**)

This was synthesized by a procedure similar to that of **2** using $[Rh(CO)_2Cl]_2$ (0.020 g, 0.051 mmol) and **1** (0.066 g, 0.103 mmol). Yield: 76% (0.063 g); m.p.: $118-120^\circ C$. 1H NMR (400 MHz, $CDCl_3$): δ 7.75–6.73 (m, 42H, ArH), 3.78 ppm (s, 24H, OCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 117.1 ppm (m, $|^1J_{Rh,P} + ^3J_{Rh,P}| = 262$ Hz, $^2J_{P,P} = 130$ Hz); FT-IR (KBr disc) cm^{-1} : $\nu(CO)$ 2085, 2021. Anal. Calcd for $C_{70}H_{66}N_2O_{18}P_4Rh_2Cl_2$ (1623.89): C, 51.77; H, 4.10; N, 1.72. Found: C, 51.70; H, 4.14; N, 1.78%.

4.6. Synthesis of $[NiBr_2\{PhN(P(OC_6H_4OMe-o)_2)_2\}]$ (**7**)

A solution of **1** (0.085 g, 0.132 mmol) in THF (6 mL) was added dropwise to a solution of $NiBr_2(DME)$ (0.041 g, 0.132 mmol) also in THF (5 mL) with constant

stirring. After 1 h, the resulting red solution was kept at room temperature for 2 days to give analytically pure red crystals of **7**. Yield: 92% (0.104 g), m.p.: $198-200^\circ C$ (dec). 1H NMR (400 MHz, $CDCl_3$): δ 7.66–6.64 (m, 21 H, ArH), 3.59 ppm (s, 12H, OCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 68.1 ppm (s). Anal. Calcd for $C_{34}H_{33}NO_8P_2NiBr_2$ (864.08): C, 47.26; H, 3.85; N, 1.62. Found: C, 47.20; H, 3.88; N, 1.63%.

4.7. Synthesis of $[(\eta^6\text{-cymene})Ru(\mu-Cl)_3-Ru(Cl)\{PhN(P(OC_6H_4OMe-o)_2)_2\}]$ (**8**)

A mixture of $[Ru(\eta^6\text{-cymene})Cl_2]_2$ (0.041 g, 0.067 mmol) and **1** (0.043 g, 0.067 mmol) in THF (15 mL) was stirred under reflux condition for 5 h. It was cooled to room temperature and concentrated to 5 mL under vacuum. Keeping this solution at $-30^\circ C$ for several days afforded red crystals of **8**. Yield: 80% (0.060 g), m.p.: $210-212^\circ C$ (dec). 1H NMR (400 MHz, $CDCl_3$): δ 8.26–6.70 (m, 21H, ArH), 5.34 (d, $J_{H,H} = 5.2$ Hz, 2H, cymene Ph), 5.18 (d, 2H, cymene Ph), 3.66 (s, 12H, OCH_3), 2.84 (sep, 1H, CH), 2.17 (s, 3H, CH_3), 1.24 ppm (d, $J_{H,H} = 6.8$ Hz, 6H, $C(CH_3)_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 100.1 ppm (s). Anal. Calcd for $C_{44}H_{47}NO_8P_2Ru_2Cl_4$ (1123.74): C, 47.03; H, 4.22; N, 1.25. Found: C, 47.01; H, 4.26; N, 1.21%.

4.8. Synthesis of $[PdBr\{\mu-PhN(P(OC_6H_4OMe-o)_2)_2\}]_2$ (**9**)

A mixture of $Pd_2(dba)_3 \cdot CHCl_3$ (0.031 g, 0.030 mmol), $Pd(CH_3CN)_2Br_2$ (0.021 g, 0.060 mmol) and **1** (0.077 g, 0.120 mmol) in CH_2Cl_2 (20 mL) was stirred under reflux condition for 1 h. The resulting red-orange solution was cooled and filtered. The filtrate was concentrated to 5 mL and methanol (10 mL) was added to precipitate the product. Recrystallization from $CH_2Cl_2/MeOH$ mixture followed by vacuum drying afforded analytically pure product of **9**. Yield: 45% (0.045 g), m.p.: $160-162^\circ C$ (dec). 1H NMR (400 MHz, $CDCl_3$): δ 7.79–6.62 (m, 42H, ArH), 3.59 ppm (s, 24H, OCH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 111.3 ppm (s). Anal. Calcd for $C_{68}H_{66}N_2O_{16}P_4Pd_2Br_2$ (1663.80): C, 49.09; H, 4.00; N, 1.68. Found: C, 49.11; H, 4.05; N, 1.66%.

4.9. X-ray crystallography

Crystals of **5** and **7–9** were mounted in a Cryloop™ with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex™ attachment of the Bruker APEX CCD diffractometer. A full sphere of data was collected using 606 scans in ω (0.3° per scan) at $\phi = 0^\circ$, 120° and 240° or 400 scans in ω (0.5° per scan) at $\phi = 0^\circ$, 90° and 180° plus 800 scans in ϕ (0.45° per scan) at $\omega = 0$ and 210° using the SMART software package [27]. The raw data were reduced to F^2 values using the SAINT+ software [28] and global refinements of unit cell parameters using

6800–9550 reflections chosen from the full data sets were performed. Multiple measurements of equivalent reflections provided the basis for empirical absorption corrections as well as corrections for any crystal deterioration during the data collection (SADABS [29]). All the structures were solved by direct methods and refined by full-matrix least-squares procedures using the SHELXTL program package [30]. Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. Pertinent crystallographic data and other experimental details are summarized in Table 3.

Acknowledgements

We are grateful to the Department of Science and Technology (DST), New Delhi, for funding through Grant SR/S1/IC-05/2003. C.G. thanks CSIR for Junior Research Fellowship (JRF). We also thank SAIF, Mumbai, Department of Chemistry Instrumentation Facilities, Bombay, for spectral and analytical data and the Louisiana Board of Regents through grant LEQSF(2002-03)-ENH-TR-67 for purchase of the CCD diffractometer and the Tulane University for support of the X-ray laboratory.

Appendix A. Supplementary material

CCDC 631331, 631332, 631333 and 631334 contain the supplementary crystallographic data for **5**, **7**, **8** and **9**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.04.019.

References

- [1] (a) S.K. Mandal, T.S. Venkatakrisnan, A. Sarkar, S.S. Krishnamurthy, *J. Organomet. Chem.* 691 (2006) 2969; (b) M.S. Balakrishna, K. Ramaswamy, R.M. Abhyankar, *J. Organomet. Chem.* 560 (1998) 131; (c) T.S. Venkatakrisnan, S.S. Krishnamurthy, M. Nethaji, *J. Organomet. Chem.* 690 (2005) 4001; (d) A.S. Veige, T.G. Gray, D.G. Nocera, *Inorg. Chem.* 44 (2005) 17; (e) T.G. Gray, A.S. Veige, D.G. Nocera, *J. Am. Chem. Soc.* 126 (2004) 9760; (f) M.S. Balakrishna, R. Panda, D.C. Smith, A. Klamann, S.P. Nolan, *J. Organomet. Chem.* 599 (2000) 159; (g) A.F. Heyduk, D.G. Nocera, *J. Am. Chem. Soc.* 122 (2000) 9415; (h) T.Q. Ly, J.D. Woollins, *Coord. Chem. Rev.* 176 (1998) 451; (i) P. Bhattacharyya, J.D. Woollins, *Polyhedron* 14 (1995) 3367; (j) M.S. Balakrishna, S.V. Reddy, S.S. Krishnamurthy, J.F. Nixon, J.C.T.R.B. St. Laurent, *Coord. Chem. Rev.* 129 (1994) 1.
- [2] (a) S.S. Garje, D.J. Eisler, J.S. Ritch, M. Afzaal, P. O'Brien, T. Chivers, *J. Am. Chem. Soc.* 128 (2006) 3120; (b) M. Afzaal, D.J. Crouch, P. O'Brien, J. Raftery, P.J. Skabara, A.J.P. White, D.J. Williams, *J. Mater. Chem.* (2004) 233; (c) M. Afzaal, D. Crouch, M.A. Malik, M. Motevalli, P. O'Brien, J.-H. Park, J.D. Woollins, *Eur. J. Inorg. Chem.* 1 (2004) 171; (d) J. Waters, D. Crouch, J. Raftery, P. O'Brien, *Chem. Mater.* 16 (2004) 3289; (e) D.J. Crouch, P. O'Brien, M.A. Malik, P.J. Skabara, S.P. Wright, *Chem. Commun.* (2003) 1454; (f) J.-H. Park, M. Afzaal, M. Helliwell, M.A. Malik, P. O'Brien, J. Raftery, *Chem. Mater.* 15 (2003) 4205.
- [3] (a) C.M. Alvarez, B. Galan, M.E. Garcia, V. Riera, M.A. Ruiz, C. Bois, *Organometallics* 22 (2003) 3039; (b) J. Perez, D. Morales, V. Riera, A. Rodriguez, S. Garcia-Granda, *Dalton Trans.* (2003) 1641; (c) M.A. Alvarez, C. Alvarez, M.E. Garcia, V. Riera, M.A. Ruiz, C. Bois, *Organometallics* 16 (1997) 2581; (d) X. Liu, V. Riera, M.A. Ruiz, M. Lanfranchi, A. Tiripicchio, M. Tiripicchio-Camellini, *Organometallics* 13 (1994) 1940; (e) R.J. Haines, A. Pidcock, M. Safari, *J. Chem. Soc., Dalton Trans.* (1977) 830; (f) A.L. Du Preez, I.L. Marais, R.J. Haines, A. Pidcock, M. Safari, *J. Organomet. Chem.* 141 (1977) C10.
- [4] Y. Gimbert, F. Robert, A. Durif, M.-T. Averbuch, N. Kann, A.E. Greene, *J. Org. Chem.* 64 (1999) 3492.
- [5] (a) F. Majoumo-Mbe, P. Loennecke, E.V. Novikova, G.P. Belov, E. Hey-Hawkins, *Dalton Trans.* (2005) 3326; (b) N.A. Cooley, S.M. Green, D.F. Wass, K. Heslop, A.G. Orpen, P.G. Pringle, *Organometallics* 20 (2001) 4769.
- [6] (a) T. Agapie, M.W. Day, L.M. Henling, J.A. Labinger, J.E. Bercaw, *Organometallics* 25 (2006) 2733; (b) L.E. Bowen, D.F. Wass, *Organometallics* 25 (2006) 555; (c) S.J. Schofer, M.W. Day, L.M. Henling, J.A. Labinger, J.E. Bercaw, *Organometallics* 25 (2006) 2743; (d) K. Blann, A. Bollmann, J.T. Dixon, F.M. Hess, E. Killian, H. Maumela, D.H. Morgan, A. Neveling, S. Otto, M.J. Overett, *Chem. Commun.* (2005) 620; (e) T. Agapie, S.J. Schofer, J.A. Labinger, J.E. Bercaw, *J. Am. Chem. Soc.* 126 (2004) 1304; (f) A. Carter, S.A. Cohen, N.A. Cooley, A. Murphy, J. Scutt, D.F. Wass, *Chem. Commun.* (2002) 858.
- [7] (a) A. Jabri, P. Crewdson, S. Gambarotta, I. Korobkov, R. Duchateau, *Organometallics* 25 (2006) 715; (b) M.J. Overett, K. Blann, A. Bollmann, J.T. Dixon, F. Hess, E. Killian, H. Maumela, D.H. Morgan, A. Neveling, S. Otto, *Chem. Commun.* (2005) 622; (c) M.J. Overett, K. Blann, A. Bollmann, J.T. Dixon, D. Haasbroek, E. Killian, H. Maumela, D.S. McGuinness, D.H. Morgan, *J. Am. Chem. Soc.* 127 (2005) 10723; (d) A. Bollmann, K. Blann, J.T. Dixon, F.M. Hess, E. Killian, H. Maumela, D.S. McGuinness, D.H. Morgan, A. Neveling, S. Otto, M. Overett, A.M.Z. Slawin, P. Wasserscheid, S. Kuhlmann, *J. Am. Chem. Soc.* 126 (2004) 14712.
- [8] G. Calabrò, D. Drommi, G. Bruno, F. Faraone, *Dalton Trans.* (2004) 81.
- [9] (a) C. Ganesamoorthy, M.S. Balakrishna, P.P. George, J.T. Mague, *Inorg. Chem.* 46 (2007) 848; (b) P. Chandrasekaran, J.T. Mague, M.S. Balakrishna, *Inorg. Chem.* 45 (2006) 5893; (c) P. Chandrasekaran, J.T. Mague, M.S. Balakrishna, *Inorg. Chem.* 45 (2006) 6678; (d) P. Chandrasekaran, J.T. Mague, M.S. Balakrishna, *Organometallics* 24 (2005) 3780; (e) P. Chandrasekaran, J.T. Mague, M.S. Balakrishna, *Inorg. Chem.* 44 (2005) 7925; (f) M.S. Balakrishna, P.P. George, S.M. Mobin, *Polyhedron* 24 (2005) 475; (g) S. Priya, M.S. Balakrishna, J.T. Mague, S.M. Mobin, *Inorg. Chem.* 42 (2003) 1272; (h) M.S. Balakrishna, R. Panda, J.T. Mague, *J. Chem. Soc., Dalton Trans.* (2002) 4617;

- (i) M.S. Balakrishna, R. Panda, J.T. Mague, *Inorg. Chem.* 40 (2001) 5620.
- [10] (a) B. Punji, J.T. Mague, M.S. Balakrishna, *Dalton Trans.* (2006) 1322;
(b) B. Punji, C. Ganesamoorthy, M.S. Balakrishna, *J. Mol. Catal. A: Chem.* 259 (2006) 78;
(c) B. Punji, J.T. Mague, M.S. Balakrishna, *J. Organomet. Chem.* 691 (2006) 4265;
(d) B. Punji, J.T. Mague, M.S. Balakrishna, *Inorg. Chem.* 45 (2006) 9454.
- [11] (a) M.S. Balakrishna, S.S. Krishnamurthy, *Inorg. Chim. Acta* 230 (1995) 245;
(b) J. Ellermann, G. Szucsanyi, *Z. Anorg. Allg. Chem.* 520 (1985) 113.
- [12] M. Cano, J.V. Heras, M.A. Lobo, E. Pinilla, M.A. Monge, *Polyhedron* 13 (1994) 1563.
- [13] M.S. Balakrishna, B.D. Santarsiero, R.G. Cavell, *Inorg. Chem.* 33 (1994) 3079.
- [14] M.S. Balakrishna, P.P. George, J.T. Mague, *J. Organomet. Chem.* 689 (2004) 3388.
- [15] (a) V.V. Sushev, A.N. Kornev, Y.A. Kurskii, O.V. Kuznetsova, G.K. Fukin, Y.H. Budnikova, G.A. Abakumov, *J. Organomet. Chem.* 690 (2005) 1814;
(b) Z. Sun, F. Zhu, Q. Wu, S. Lin, *Appl. Organomet. Chem.* 20 (2006) 175.
- [16] L.E. Anagho, J.F. Bickley, A. Steiner, L. Stahl, *Angew. Chem., Int. Ed.* 44 (2005) 3271.
- [17] (a) S. Gauthier, L. Quebatte, R. Scopelliti, K. Severin, *Chem. Eur. J.* 10 (2004) 2811;
(b) M.P. de Araujo, E.M.A. Valle, J. Ellena, E.E. Castellano, E.N. dos Santos, A.A. Batista, *Polyhedron* 23 (2004) 3163;
(c) A.C. da Silva, H. Piotrowski, P. Mayer, K. Polborn, K. Severin, *Eur. J. Inorg. Chem.* (2001) 685.
- [18] M.S. Balakrishna, S.S. Krishnamurthy, R. Murugavel, M. Nethaji, I.I. Mathews, *J. Chem. Soc., Dalton Trans.* (1993) 477.
- [19] R.G. Holloway, B.R. Penfold, R. Colton, M.J. McCormick, *J. Chem. Soc., Chem. Commun.* (1976) 485.
- [20] C.S. Browning, D.H. Farrar, D.C. Frankel, J.J. Vittal, *Inorg. Chem. Acta* 254 (1997) 329.
- [21] W.L.F. Armarego, D.D. Perrin, *Purification of Laboratory Chemicals*, 4th ed., Butterworth-Heinemann, Linacre House, Jordan Hill, Oxford, UK, 1996.
- [22] G. Giordano, R.H. Crabtree, *Inorg. Synth.* 28 (1990) 88.
- [23] J.A. McCleverty, G. Wilkinson, *Inorg. Synth.* 28 (1990) 84.
- [24] M.A. Bennett, T.N. Huang, T.W. Matheson, A.K. Smith, *Inorg. Synth.* 21 (1982) 74.
- [25] T. Ukai, H. Kawazura, Y. Ishii, J.J. Bonnet, J.A. Ibers, *J. Organomet. Chem.* 65 (1974) 253.
- [26] L.G.L. Ward, *Inorg. Synth.* 13 (1971) 54.
- [27] Bruker-AXS, SMART, Version 5.625, Madison, WI, 2000.
- [28] Bruker-AXS, SAINT+, Version 6.35A, Madison, WI, 2002.
- [29] G.M. Sheldrick, SADABS, Version 2.05, University of Göttingen, Germany, 2002.
- [30] (a) Bruker-AXS, SHELXTL, Version 6.10, Madison, WI, 2000;
(b) G.M. Sheldrick, SHELXS97 and SHELXL97, University of Göttingen, Germany, 1997.