Journal of Organometallic Chemistry 695 (2010) 2007–2013

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Synthesis and characterization of half-sandwich Rh, Ir complexes containing mono-thiolate-*ortho*-carborane ligand

Xian-Kuan Huo, Ge Su, Guo-Xin Jin*

Shanghai Key Laboratory of Molecular Catalysis and Innovative Material, Department of Chemistry, Fudan University, 200433 Shanghai, PR China

ARTICLE INFO

Article history:
Received 13 March 2010
Received in revised form
29 April 2010
Accepted 30 April 2010
Available online 6 May 2010

Keywords:
Carborane
Half-sandwich complexes
Iridium
Rhodium
Molecular structures

ABSTRACT

Two binuclear complexes $[Cp^*M(Cl)Carb^S]_2$ ($Cp^* = \eta^5$-C_5Me_5, M = Rh (**1a**), $Carb^S = SC_2(H)B_{10}H_{10}$, Ir (**1b**)) were synthesized by the reaction of $LiCarb^S$ with the dimeric metal complexes $[Cp^*MCl(\mu\text{-}Cl)]_2$ (M = Rh, Ir). Four mononuclear complexes $Cp^*M(Cl)(L)Carb^S$ (**L** = Bu^nPPh_2, M = Rh (**2a**), Ir (**2b**); **L** = PPh_3, M = Rh (**4a**), Ir (**4b**)) were synthesized by reactions of **1a** or **1b** with **L** (**L** = Bu^nPPh_2 (**2**); PPh_3 (**4**)) in moderate yields, respectively. Complexes **3a**, **3b**, **5a**, **5b** were obtained by treatment of **2a**, **2b**, **4a**, **4b** with $AgPF_6$ in high yields, respectively. All of these compounds were fully characterized by IR, NMR, and elemental analysis, and the crystal structures of **1a**, **1b**, **2a**, **2b**, **4a, 4b** were also confirmed by X-ray crystallography. Their structures showed **3a**, **3b** and **5a, 5b** could be expected as good candidates for heterolytic dihydrogen activation. Preliminary experiments on the dihydrogen activation driven by these half-sandwich Rh, Ir complexes were done under mild conditions.

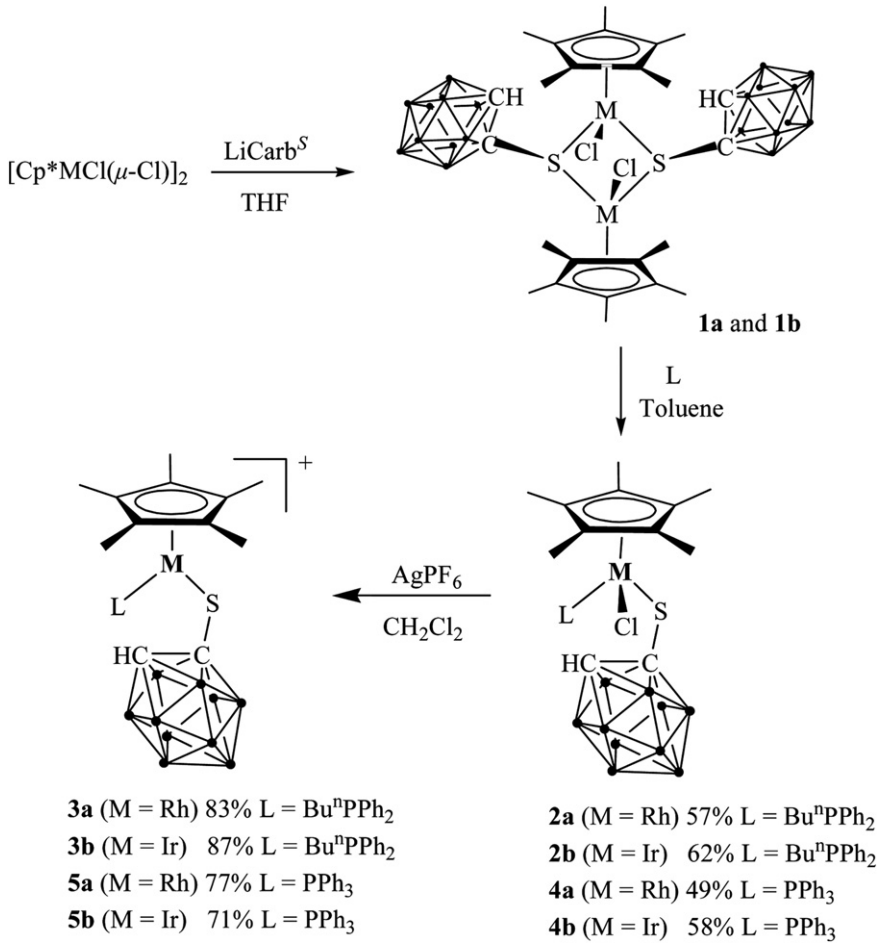
1. Introduction

During the past few years, tremendous attention and emphases have been devoted to the activation of dihydrogen by metal complexes [1–8], especially to the heterolytic dihydrogen activation by sulfide- or oxo-bridged transition metal complexes [9,10], which is not only regarded as the key reactions in the function of hydrogenases and catalytic desulfurization of fossil fuel, but also has some additional advantages [1–13]. All of these features spurred the study of transition metal thiolate chemistry, resulting in a considerate body of important and interesting work [11–13]. However, half-sandwich Rh, Ir complexes containing thiolate-ligands used for activation of dihydrogen occurring at metal sulfur site remain scarce to explore [9,10,14]. Hence, rational design and synthesis of such complexes as models for research on dihydrogen activation is required. At the same time, the very important factors influenced to the formation of such metal complexes, such as reversibility, excellent solubility in common organic solvents, unique rigidity and gross steric bulk [9–13] were also exhibited as the great advantages by our recent systematic *ortho*-carborane studies and related literature [15–18]. Additional, the chemistry of 1, 2-dicarba-*closo*-dodecaborane is a fascinating research area, not only for its chemical and thermal stability with a rigid three-dimensional electron deficient aromatic structure but also for its many promising applications such as boron neutron capture therapy (BNCT) of cancer, catalysts for olefin polymerization, molecular sensing and nonlinear optic (NLO) [19–29]. Meanwhile, C_{cage}–H is usually functionalized with different atoms such as S, S′, S, P, N, P, Si, Si′, P, P′, forming chelating metal complexes [15–18,30–36]. However, in view of the diversity of coordination modes and variety of coordination environment, the mono-substituted ligand is better than the bifunctional ligands in the formation of the model complexes for the dihydrogen activation [37–41]. In addition, half-sandwich Rh, Ir complexes bearing the mono-substituted *ortho*-carborane are scantly reported. Thus, it is of great interest to choose the monothiolate *o*-carboranyl half-sandwich Rh, Ir complexes as models to study the dihydrogen activation.

Herein we report a series of monothiolate *ortho*-carboranyl half-sandwich complexes employing an easy but feasible way (Scheme 1). Two of them are starting binuclear complexes $[Cp^*M(Cl)Carb^S]_2$ (M = Rh (**1a**), Ir (**1b**)); another eight are mononuclear complexes $Cp^*M(Cl)(Bu^nPPh_2)Carb^S$ (M = Rh (**2a**), Ir (**2b**)) and $[Cp^*M(Bu^nPPh_2)Carb^S](PF_6)$ (M = Rh (**3a**), Ir (**3b**)); $Cp^*M(Cl)(PPh_3)Carb^S$ (M = Rh (**4a**), Ir (**4b**)) and $[Cp^*M(PPh_3)Carb^S](PF_6)$ (M = Rh (**5a**), Ir (**5b**)). The structures of **1a**, **1b**, **2a**, **2b** and **4a**, **4b** were confirmed by X-ray crystallography, showing **2a**, **2b, 4a, 4b** could have a vacant coordination site when they was treated by $AgPF_6$. Preliminary experiments on the dihydrogen activation driven by these half-sandwich Rh, Ir complexes were done under mild conditions.

* Corresponding author. Tel.: +86 21 65643776; fax: +86 21 65641740.
E-mail address: gxjin@fudan.edu.cn (G.-X. Jin).

0022-328X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2010.04.038



Scheme 1. Synthesis of **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, **5a** and **5b**.

2. Results and discussion

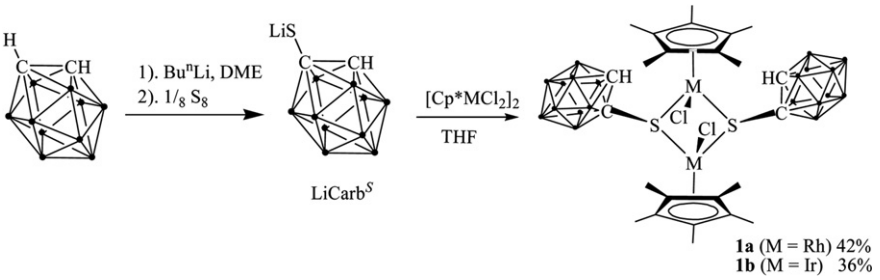
2.1. Synthesis of ligand LiCarb^S

The mono-substituted *o*-carborane derivatives have been synthesized in aromatic solvent, but the conversion was too low for further development of this kind of compounds, since the synthesis of mono-substituted *ortho*-caborane species is synthetically more difficult [42,43]. The preparation of them was improved by C. Vinãs and co-authors utilizing DME as solvent and the mono-substituted *o*-carborane derivatives such as 1-SH-1, 2-$C_2B_{10}H_{11}$ and 1-PPh_2-1,2-$C_2B_{10}H_{11}$ can be obtained in high yields [44]. In this contribution the ligand LiCarb^S was synthesized according to the literature except the last part of acidification of the reaction products, which was used directly for further reactions.

2.2. Synthesis and characterization of starting binuclear complexes [Cp*M(Cl)Carb^S]$_2$ (M = Rh (**1a**), Ir (**1b**))

The starting binuclear complexes were synthesized from the reactions LiCarb^S with 0.5 equiv of the dimeric metal complexes [Cp*MCl_2]$_2$ (M = Rh, Ir) in THF in moderate yields, as shown in Scheme 2. The complexes were obtained from recrystallization in form of air- and moist-stable, red, transparent blocks when the low temperature was employed. The formation of a new complex [Cp*M(Cl)Carb^S]$_2$ (M = Rh (**1a**), Ir(**1b**)) was initially indicated by the NMR, IR and elemental analysis, and **1a** was further confirmed by the X-ray crystallography. For **1a**, the IR spectra show a strong band for B–H vibration at approximately 2589, 2563 cm^{-1}, ^1H NMR signals showed two sharp signals at δ 1.63, 3.56 ppm, which can be ascribed to the two Cp* groups and the C_{cage}–H respectively. ^{11}B NMR spectra exhibit resonances at δ −2.5, −4.4, −7.1, −9.0, −11.3 ppm. Complex **1a** was found to be highly soluble in most chlorinated solvents and THF, insoluble in hexane, and partially soluble in ether and toluene. An iridium analog **1b** with the structure formula [Cp*Ir(Cl)Carb^S]$_2$ was prepared by the similar synthetically method. And a detailed analysis of the spectroscopic data (IR, ^1H NMR and ^{11}B NMR) shows the structure is similar to **1a**, which was also confirmed by X-ray crystallography.

The crystallographic data for complex **1a** and **1b** are summarized in Table 1; ORTEP drawings of complexes **1a** and **1b** and selected bonds and angles are shown in Figs. 1 and 2, respectively. The solid state molecular structure reveals there is an almost planar four-membered ring formed by two μ-M (Rh, Ir) atoms and two μ-S atoms with the distance 3.734, 3.742 Å between M(1) and M(2) and the dihedral angle between the planes [M(1), S(1), S(1A)] and [M(2), S(1),S(1A)] at the S···S vector of which is 13.09°, 12.56°, respectively. The geometry at the Rh(III) or Ir(III) center bears a three-legged piano-stool shape with M atom coordinated by the η^5-Cp*, two Carb^S ligands, and one chloride atom, which can be consequently described as pseudo-octahedron assuming η^5-Cp* group functions as a three-coordination ligand. An interesting feature of this solid state structure is two Cp* rings are in *cisoid* arrangements on one side of the M_2S_2 plane while the two Carb^S ligands and two chloride atoms in *cisoid* arrangements are on the other side. The distances Rh(1)–S(1) (2.4212(15) Å, Rh(2)–S(1)



Scheme 2. Synthesis of **1a**, **1b.**

2.4200(15) Å are a litter longer than that of Rh(1)–Cl(1) 2.388(2) Å, Rh(2)–Cl(2) 2.375(2) Å, which are in agreement with previous values for them in analogous complexes [45,46], The separation of the Ir(1)–Cl(1), Ir(1)–S(1), Ir(2)–Cl(2, Ir(2)–S(1) are in agreement with these of analogous complexes [47,48].

2.3. Synthesis and characterization of the mononuclear complexes $Cp^*M(Cl)(Bu^nPPh_2)Carb^S$ (M = Rh (**2a**), Ir (**2b**)) and $Cp^*M(Bu^nPPh_2)Carb^S(PF_6)$ (M = Rh (**3a**), Ir (**3b**))

A fresh kind of metal complexes with the chemical formula $Cp^*M(PMe_3)Cl$(S-Dmp) (M = Ir, Rh) were recently reported by K. Tatsumi and co-workers [9,10]. They have excellent capabilities of the activation of dihydrogen and can also help us understand the mechanism of [NiFe] hydrogenases. Based on these results, two new *o*-carboranyl compounds (**2a** and **2b**) coordinated by sulfur, phosphorous atoms were designed and synthesized, which may be also good precursors to reproduce the mechanism of [NiFe] hydrogenases through the activation of dihydrogen at metal sulfur site. **2a** and **2b** were obtained from the reactions of **1a** or **1b** with Bu^nPPh_2 in toluene in moderate yields, as shown in Scheme 1.

The complexes (**2a** and **2b**) were obtained from recrystallization in form of air- and moist-stable, red, transparent prisms when the low temperature was applied. For **2a**, the IR spectra show a strong band for B–H vibration at approximately 2583 cm^{-1}, the formation is also confirmed by the appearance of ^1H NMR signals at δ 1.36 ppm with $^4J(PH) = 1.6$ Hz, which can be ascribed to the Cp^* groups. The ^1H NMR signals of H–C_{cage}, –PPh_2 and Bu^nPPh_2 groups were also confirmed, respectively (in experiment section). ^{11}B NMR spectra exhibit resonances at δ −1.9, −4.4, −9.1,−11.3 ppm. These spectroscopic data and the combustion analyses for H and C indicate the formation of a new complex $Cp^*Rh(Cl)(Bu^nPPh_2)Carb^S$, which was further confirmed by the X-ray crystallography. An analog Ir complex **2b** was prepared by the same synthetically method. And a comprehensive analysis of the spectroscopic data (IR, ^1H NMR, and ^{11}B NMR) also shows the structure is analogous to **2a**, which was demonstrated by the X-ray crystallography.

The crystallographic data for complex **2a** and **2b** are summarized in Table 1; An ORTEP drawing of complex **2a**, **2b** and selected bonds and angles are shown in Figs. 3 and 4, respectively. The solid state molecular structure reveals the geometry at the Rh(III) center is a three-legged piano-stool shape with Rh atom coordintated by the η^5-Cp^*, one $Carb^S$ ligands, one phosphorus atom and one chloride atom, consequently it can be described as pseudo-octahedron in which η^5-Cp^* group occupies three *fac* coordination side. Within our expectation, the coordination environment and crystal structure of Ir(III) centre are analogous to that of Rh(III) centre. The Ir (III) center is also a three-legged piano-stool with Ir atom coordinated by the η^5-Cp^*, one $Carb^S$ ligand, one phosphorus atom and one chloride atom. The distances Rh(1)–S(1) 2.3848(9) Å, Rh(1)–P (1) 2.3157(10) Å are a litter shorter than that of Rh(1)–Cl(1) 2.4122 (9) Å, which are all within the range of known values for them in analogous complexes [10,31,49]. And the lengths Ir(1)–P(1) 2.2998 (13) Å, Ir(1)–S(1) 2.3821(12) Å and Ir(1)–Cl(1) 2.4088(12) Å, are all comparable to those reported for the Ir(III) complexes with P,S-ligands [48].

Table 1
Crystallographic Data and Structure Refinement Parameters for **1a**, **1b**, **2a**, **2b** and **4b.**

	1a	**1b**·0.5CH_2Cl_2	**2a**	**2b**·0.5CH_2Cl_2	**4b**
Empirical formula	$C_{24}H_{52}B_{20}Cl_2S_2Rh_2$	$C_{25}H_{54}B_{20}Cl_4S_2Ir_2$	$C_{28}H_{45}B_{10}ClPRhS$	$C_{28.5}H_{46}B_{10}Cl_2IrPS$	$C_{30}H_{41}B_{10}ClIrPS$
Formula weight	897.70	1161.20	691.13	822.88	800.41
Crystal syst.	Orthorhombic	Orthorhombic,	Monoclinic	Monoclinic	Monoclinic,
Space group	Pnma	Pnma	C2/c	C2/c	P2(1)/c
a (Å)	17.057(10)	16.987(6)	34.153(11)	33.921(12)	9.013(3)
b (Å)	8.286(11)	18.503(6)	10.620(3)	10.697(4)	18.281(6)
c (Å)	14.431(9)	14.119(5)	20.173(6)	20.256(7)	21.619(8)
α (°)	90	90	90	90	90
β (°)	90	90	104.187	103.899(5)	99.772(4)
γ (°)	90	90	90	90	90
volume (Å^3), *Z*	4501(5), 4	4438(3), 4	7094(4), 8	7135(4), 8	3510(2), 4
Dc(g cm^{-3})	1.325	1.738	1.294	1.532	1.514
μ (Mo Kα) (mm^{-1})	0.963	6.348	0.680	4.017	4.006
F(000)	1808	2232	2848	3272	1584
θ range (°)	1.80–27.90	1.81–27.01	2.01–27.01	2.00–27.01	1.47–27.01
Limited indices	−15,22; −22,23; −16,18	−21,18; −20,23; −15,17	−43,38; −12,13; −16,25	−41,43; −11,13; −25,20	−11,11; −22,14; −27,27
Reflections/unque [R(int)]	21414/5292 [0.1049]	20551/4937 [0.0415]	16487/7558 [0.0355]	16777/7641 [0.0352]	16494/7515 [0.0534]
Completeness to θ (°)	27.90 (95.6%)	27.01(98.9%)	27.01 (97.4%)	27.01 (97.9%)	27.01(97.9%)
Data/restraints/parameters	5294/0/257	4937/0/273	7558/0/399	7641/0/413	7515/0/416
Goodness-of-fit on F^2	0.914	0.930	0.985	0.974	0.972
R_1, wR_2 [I > 2σ(*I*)][a]	0.0491, 0.0978	0.0262, 0.0582	0.0350, 0.0803	0.0323, 0.0625	0.0390, 0.0864
R_1, wR_2 (all data)	0.0866, 0.1033	0.0423, 0.0623	0.0618, 0.0897	0.0512, 0.0659	0.0560, 0.0906

[a] $R_1 = \sum||F0|-|Fc||$ (based on reflections with $F_o^2 > 2\sigma F^2$) [2]. $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o{}^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma F^2$).

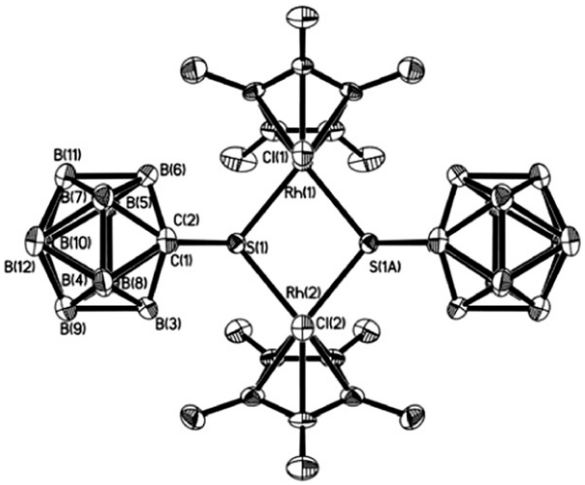


Fig. 1. ORTEP drawing of **1a** with thermal ellipsoids drawn at the 30% level, all hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Rh (1)–Cl(1) 2.388(2), Rh(1)–S(1) 2.4212(15), Rh(2)–Cl(2) 2.375(2), Rh(2)–S(1) 2.4200 (15); Cl(1)–Rh(1)–S(1) 95.77(4), S(1)–Rh(1)–S(1A) 78.13(7), Cl(2)–Rh(2)–S(1) 94.07 (4), S(1A) –Rh(2)–S(1) 78.17(7).

3a and **3b** can be easily obtained by treatment of **2a** and **2b** with 1.2 equiv $AgPF_6$ in CH_2Cl_2, and purified by recrystallization with CH_2Cl_2/hexane, whose structures were characterized by IR ^{1}H NMR and elemental analysis. Comparing with the **2a** and **2b**, the spectra of IR suffer a minor change and the ^{1}H NMR shift to a litter low field (the ^{1}H NMR of the Cp^* shift from 1.36 to 1.87 ppm for the trans-formation from **2a** to **3a**). Complex **3a** and **3b** were found to be readily soluble in CH_2Cl_2, $CHCl_3$ and acetonitrile, soluble in alcohols, and partially soluble in ether, toluene and THF, insoluble in hexane.

*2.4. Synthesis and characterization of $Cp^*M(Cl)(PPh_3)Carb^S$ (M = Rh (**4a**), Ir (**4b**)) and $Cp^*M(PPh_3)Carb^S(PF_6)$ (M = Rh (**5a**), Ir (**5b**))*

In order to systemically investigate the dihydrogen activation driven by the half-sandwich Rh, Ir complexes bearing the P, S coordinated atoms, another two *o*-carboranyl compounds (**4a** and **4b**) coordinated by sulfur, phosphorous atoms were synthesized. **4a** and **4b** were obtained directly from the reactions of **1a** or **1b** with PPh_3 in toluene in moderate yields, as shown in Scheme 1.

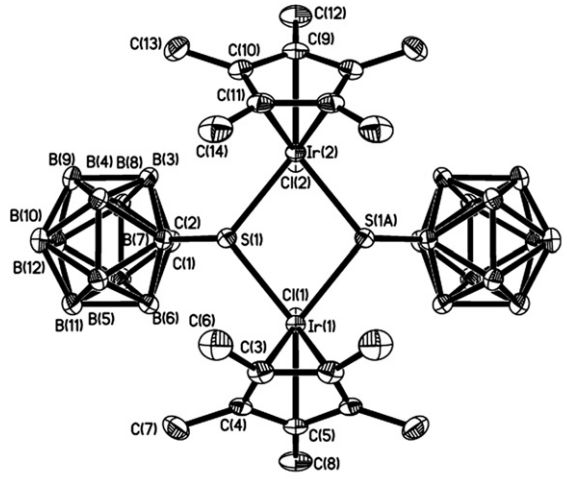


Fig. 2. ORTEP drawing of **1b** with thermal ellipsoids drawn at the 30% level, all hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Ir (1)–Cl(1) 2.3940(16), Ir(1)–S(1) 2.4016(12), Ir(2)–Cl(2) 2.3889(16), Ir(2)–S(1) 2.4047 (12); Cl(1)–Ir(1)–S(1) 94.27(4), S(1A)–Ir(1)–S(1) 77.01(6), S(1)–Ir(2)–S(1A) 76.90(5), Ir(1)–S(1)–Ir(2) 102.26(5).

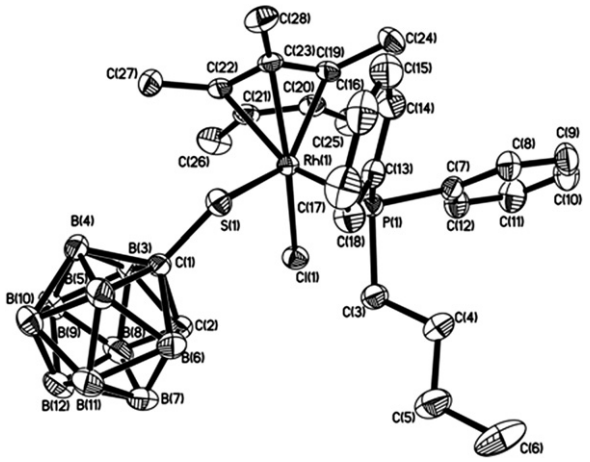


Fig. 3. ORTEP drawing of **2a** with thermal ellipsoids drawn at the 30% level, all hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Rh (1)–P(1) 2.3157(10), Rh(1)–S(1) 2.3848(9), Rh(1)–Cl(1) 2.4122(9), P(1)–Rh(1)–S(1) 81.94(3), P(1)–Rh(1)–Cl(1) 89.59(3), P(1)–Rh(1)–Cl(1) 89.59(3).

The complexes (**4a** and **4b**) were obtained from recrystallization in form of air- and moist-stable, red, transparent prisms at −18 °C. For **4a**, the IR spectra show a strong band for B–H vibration at approximately 2573, 2551, 2529 cm^{-1}, the formation is also confirmed by the appearance of ^{1}H NMR signals at δ 1.42 with the ^4J (PH) = 4.0 Hz, 4.36, 7.47–7.61 and 7.79–7.81 ppm, which can be ascribed to the Cp^* groups, C_{cage}–H, and phenyl (PPh_2,PPh_3), respectively. ^{11}B NMR spectra exhibit resonances at δ −3.6, −4.4, −8.9,−13.4 ppm.

These spectroscopic data and the combustion analyses for H and C indicate the formation of a new complex $Cp^*Rh(Cl)(PPh_3)Carb^S$. In order to unambiguously elucidate the detailed cluster structures, the **4b** was also studied by the single crystal X-ray diffraction.

The crystallographic data for complex **4b** are summarized in Table 1; An ORTEP drawing of complex **4b** and selected bonds and angles are shown in Fig. 5. The solid state molecular structure reveals the geometry at the Ir(III) center are analogous to these of

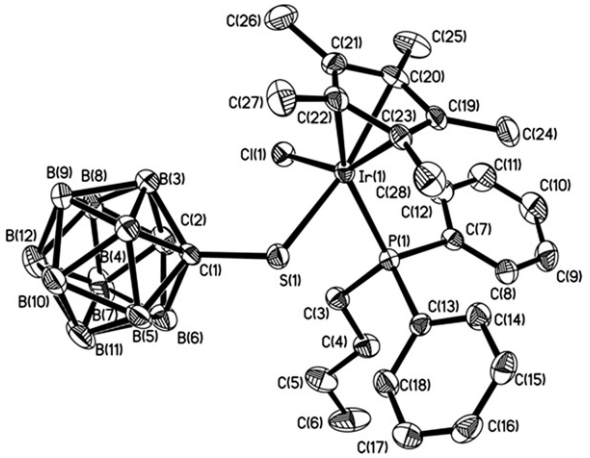


Fig. 4. ORTEP drawing of **2b** with thermal ellipsoids drawn at the 30% level, all hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Ir (1)–P(1) 2.2998(13), Ir(1)–S(1) 2.3821(12), Ir(1)–Cl(1) 2.4088(12), P(1)–Ir(1)–S(1) 82.30(4), P(1)–Ir(1)–Cl(1) 89.63(4), S(1)–Ir(1)–Cl(1) 100.65(5).

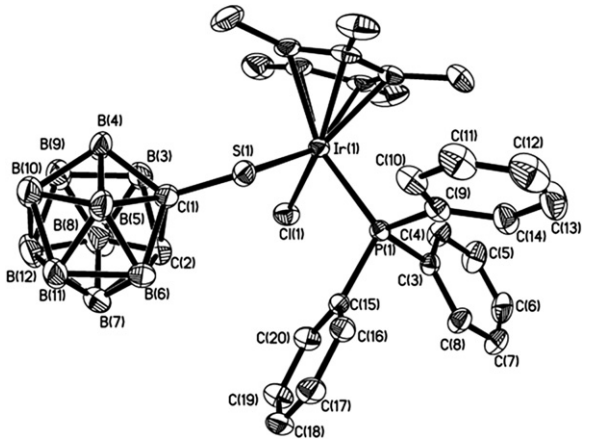


Fig. 5. ORTEP drawing of **4b** with thermal ellipsoids drawn at the 30% level, all hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Ir(1)–P(1) 2.3082(13), Ir(1)–S(1) 2.3734(15), Ir(1)–Cl(1) 2.4104(16); P(1)–Ir(1)–S(1) 86.00(5), P(1)–Ir(1)–Cl(1) 87.26(5), S(1)–Ir(1)–Cl(1) 101.13(5).

2b except that the Bu^nPPh_2 was substituted by the PPh_3. The coordination environment of metal centers are pseudo-octahedron, coordinated by the η^5-Cp*, one $Carb^S$ ligands, one phosphorus atom and one chloride atom. The distances Rh(1)–S(1) 2.3855(10) Å, Rh(1)–P(1) 2.3291(9) Å are all within the range of known values for them in analogous complexes [10,31]. And the lengths Ir(1)–P(1) 2.3082(13) Å, Ir(1)–S(1) 2.3734(15) Å and Ir(1)–Cl(1) 2.4104(16) Å, are all comparable to those reported for the Ir(III) complexes with P,S-ligands [49,50].

5a and **5b** were also obtained by treatment of **4a** and **4b** with 1.2 equiv $AgPF_6$ in CH_2Cl_2, and purified by recrystallization with CH_2Cl_2/hexane, which were supported by IR, ^1H NMR and elemental analysis. Comparing with the corresponding starting materials, the spectra of IR suffer a minor change but the ^1H NMR of the Cp* shift to low field a little. Complex **5a** and **5b** were found to be soluble in most chlorinated solvents and alcohols, as well as in acetonitrile, insoluble in hexane, and partially soluble in ether, toluene and THF.

2.5. The study of the model complexes for heterolytic dihydrogen activation at metal sulfur site

From the description of these complexes, only in the view of the structures of **3a**, **3b**, **5a** and **5b**, they are unsaturated and have a vacant coordination site at the metal center, which may offer a chance to bind H_2 to the metal center. However, when the H_2 gas (1 atm) was bubbled into the Schlenk of **3a**, **3b** or **5a**, **5b** in CH_2Cl_2 at room temperature or at 0 °C, ^1H NMR of the products don't exhibit any corresponding signals about heterolytic dihydrogen activation. Although the results are not exciting, the research on the heterolytic dihydrogen activation driven by these complexes using other anions such as $B(C_6F_5)_4$, BF_4 or at harsh conditions (at −80 °C or refluxed temperature in toluene) is still in progress.

3. Conclusions

Aimed to synthesize carboranyl complexes coordinated by hetero atoms and to systemically investigate their application on dihydrogen activation, a series of monothiolate *ortho*-carboranyl half-sandwich Rh, Ir complexes have been synthesized and fully characterized. Determined by X-ray analysis, their structures revealed that they are binuclear, mononuclear complexes coordinated by hetero atoms (Sulfur and Phosphorus atoms), respectively. The vacant coordination sites at the metal center in these complexes were also obtained easily. Although the preliminary experiments on the dihydrogen activation induced by these half-sandwich Rh, Ir complexes were not exciting, further experiments under harsh conditions or under the conditions of other anion will be expected in the near future.

4. Experimental

4.1. Materials and instrumentation

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, diethyl ether, THF, dimethoxyethane ($CH_3OCH_2CH_2OCH_3$, DME)) or calcium hydride (dichloromethane). The starting materials $[Cp^*MCl(\mu\text{-}Cl)]_2$ (M = Ir, Rh) [51] and 1-(lithiumthiolato)-1,2-dicarba-*closo*-dodecaborate ($LiCarb^S$) [44], and Bu^nPPh_2 [52] were synthesized according to the literature. Other chemical reagents were obtained from commercial sources and used without further purification. ^1H NMR (400 MHz), and ^{11}B NMR (160 MHz) spectra were obtained on a VAVCE DMX-400 spectrometer. Elemental analysis was performed on an Elementar vario EL III analyzer. IR (KBr) spectra were recorded on the Nicolet FT-IR spectrophotometer.

4.2. Synthesis of complex **1a**

$[Cp^*RhCl(\mu\text{-}Cl)]_2$ (154.5 mg, 0.25 mmol) was added to the solution of $LiCarb^S$ (91 mg, 0.5 mmol) in THF (10 mL) at 0 °C. Then the solution was stirred for 24 h at room temperature. The solution gradually turned dark red suggesting a formation of $[Cp^*Rh(Cl)Carb^S]_2$ complex. The solvent was removed under reduced pressure, and the residue was extracted with toluene (20 mL × 2) and the solution was centrifuged to remove LiCl. After removal of the solvent under vacuum, the dark red solid was washed with hexane (5 mL × 2) and dried. Fine red crystals of **1a** (94.3 mg, 42%) were obtained through recrystallization from CH_2Cl_2–hexane at −18 °C. Anal. Calcd for $C_{24}H_{52}B_{20}Cl_2S_2Rh_2$: C, 32.1%; H, 5.84%. Found: C, 32.3%; H, 5.88%. IR (KBr, disk): υ (cm^{-1}), 2921 (C–H), 2589, 2563 (B–H). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 1.63 (s, 30H, Cp*), 3.56 (s, 2H, C_{cage}–H). ^{11}B NMR (160 MHz, $CDCl_3$, ppm): δ −2.5 (1B), −4.4 (2B), −7.1 (3B), −9.0 (1B), −11.3 (3B).

4.3. Synthesis of complex **1b**

The synthetic procedure is analogous to that of **1a**. $[Cp^*IrCl(\mu\text{-}Cl)]_2$ (197 mg, 0.25 mmol) was added to solution of $LiCarb^S$ (91 mg, 0.5 mmol) in THF (10 mL) at 0 °C. And solution was stirred for 24 h at room temperature with the color gradually turning red. The solvent was removed in vacuo, and the residue was extracted by toluene (20 mL × 2) and the solution was centrifuged to remove LiCl. After removal of the solvent under vacuum, the red or yellowish solid was washed with hexane (2 × 5 mL) and dried. Fine red crystals of **1b** (96.9 mg, 36%) were obtained through recrystallization from CH_2Cl_2–hexane at −18 °C. Anal. Calcd for $C_{24}H_{52}B_{20}Cl_2S_2Ir_2$: C, 26.78%; H, 4.87%. Found: C, 26.85%; H, 4.91%. IR (KBr, disk): υ (cm^{-1}), 2953 (C–H), 2593, 2568 (B–H). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 1.37 (s, 30H, Cp*), 3.48 (s, 2H, C_{cage}–H). ^{11}B NMR (160 MHz, $CDCl_3$, ppm): δ −1.7 (2B), −7.9 (2B), −8.8 (4B), −10.9 (2B).

4.4. Synthesis of complex **2a**

To a solution of **1a** (224.5 mg, 0.25 mmol) in toluene (15 mL) was added a solution of Bu^nPPh_2 (121.7 mg, 0.5 mmol) in toluene (5 mL) at 0 °C and the mixture was stirred at room temperature for 12 h to

give a dark red solution. The solvent was removed under vacuum and the residue was washed with hexane (5 mL) twice to afford **2a** as a red powder (197.1 mg, 57%). Crystals suitable for X-ray crystallography were grown from a CH_2Cl_2/hexane solution at room temperature. Anal. Calcd for $C_{28}H_{45}B_{10}ClPRhS$: C, 48.66%; H, 6.56%. Found: C, 48.74%; H, 6.61%. IR (KBr, disk): υ (cm^{-1}), 2937 (C–H), 2583 (B–H). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 0.85 (m, 3H, $-CH_3$), 1.25 (m, 4H, $-CH_2$), 1.36 (d, 15H, Cp^*, $^4J(PH) = 1.6$ Hz), 1.52 (m, 2H, $-CH_2$), 4.35 (s, 1H, C_{cage}–H), 7.47–7.61 (m, 6H, phenyl), 7.79–7.81 (m, 4H, phenyl). ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ −1.9 (1B), −4.4 (3B), −9.1 (2B),–11.3 (4B).

4.5. Synthesis of complex **2b**

A procedure analogous to the preparation of **2a** was used. To a solution of **1b** (269.1 mg, 0.25 mmol) in toluene (15 mL) was added the solution of Bu^nPPh_2 (121.7 mg, 0.5 mmol) in toluene (5 mL) at 0 °C and the mixture was stirred at room temperature for 12 h to give a dark red solution. The solvent was removed under vacuum and the residue was washed with hexane (5 mL) twice to afford **2b** as a red powder (241.9 mg, 62%). Crystals suitable for X-ray crystallography were grown from a CH_2Cl_2/hexane solution at room temperature. Anal. Calcd for $C_{28}H_{45}B_{10}ClIrPS$: C, 43.09%; H, 5.81%. Found: C, 43.77%; H, 6.64%. IR (KBr, disk): υ, 2933 (C–H), 2569 cm^{-1} (B–H). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 0.78 (m, 3H, $-CH_3$), 1.27 (m, 4H, $-CH_2$), 1.50 (m, 2H, $-CH_2$), 1.54 (d, 15H, Cp^*, $^4J(PH) = 2.2$ Hz), 4.33 (s, 1H, C_{cage}–H), 7.47–7.78 (m, 10H, phenyl). ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ −0.9 (1B), −3.0 (1B), −8.9 (6B), −12.1 (2B).

4.6. Synthesis of complex **3a**

Complex **2a** (69.1 mg, 0.1 mmol) and $AgPF_6$ (30.3 mg, 0.12 mmol) were charged into a schlenk tube. To this tube was added CH_2Cl_2 (10 mL) and the mixture was stirred at room temperature in dark for 4 h. The color of the solution was changed to purple or dark from the red. The solution was filtrated and the solvent was removed under reduced pressure. After washing with hexane (5 mL), the green solid was obtained (66.4 mg, 83%). Anal. Calcd for $C_{28}H_{45}B_{10}F_6P_2RhS$: C, 42.00%; H, 5.66%. Found: C, 42.07%; H, 5.72%. IR (KBr, disk): υ, 2956 (C–H), 2583 cm^{-1} (B–H). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 0.89 (m, 3H, $-CH_3$), 1.33 (m, 2H, $-CH_2$), 1.67 (m, 4H, $-CH_2$), 1.87 (d, 15H, Cp^*, $^4J(PH) = 4.0$ Hz), 4.31 (s, 1H, C_{cage}–H), 7.49–7.84 (m, 10H, phenyl). ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ −3.7 (1B), −6.5 (1B), −8.7 (3B), −11.4 (4B), −12.9 (1B).

4.7. Synthesis of complex **3b**

The synthetic procedure is analogous to that of **3a**. Complex **2b** (78.1 mg, 0.1 mmol) and $AgPF_6$ (30.3 mg, 0.12 mmol) were charged into a schlenk tube in CH_2Cl_2. The green solution was filtrated and the solvent was removed and the green solid was isolated (77.4 mg, 87%). Anal. Calcd for $C_{28}H_{45}B_{10}F_6P_2SIr$: C, 37.79%; H, 5.10%. Found: C, 37.85%; H, 5.16%. IR (KBr, disk): υ, 2955 (C–H), 2579 cm^{-1} (B–H). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 0.89 (m, 3H, $-CH_3$), 1.37 (m, 4H, $-CH_2$), 1.53 (m, 4H, $-CH_2$), 1.79 (d, 15H, Cp^*, $^4J(PH) = 2.8$ Hz), 4.36 (s, 1H, C_{cage}–H), 7.49–7.83 (m, 10H, phenyl).^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ −1.9 (1B), −4.4 (1B), −7.3 (2B), −8.4 (4B), −12.7 (2B).

4.8. Synthesis of complex **4a**

To a solution of **1a** (224.5 mg, 0.25 mmol) in toluene (15 mL) was added a solution of PPh_3 (131.1 mg, 0.5 mmol) in toluene (5 mL) at 0 °C and the mixture was stirred at at 60 °C for 8 h to give a dark red solution. The solvent was removed under vacuum and the residue was washed with hexane (5 mL) twice to afford **2a** as a red powder (174.2 mg, 49%). Crystals suitable for X-ray crystallography were grown from a CH_2Cl_2/hexane solution at room temperature. Anal. Calcd for $C_{30}H_{41}B_{10}ClPSRh$: C, 50.67%; H, 5.81%. Found: C, 50.59%; H, 5.90%. IR (KBr, disk): υ (cm^{-1}), 2552, 2520. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 1.42 (d, 15H, Cp^*, $^4J(PH) = 4.0$ Hz), 4.36 (s, 1H, C_{cage}–H), 7.47–7.61 (m, 18H, phenyl), 7.79–7.81 (m, 12H, phenyl). ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ −3.6 (1B), −4.4 (3B), −8.9 (2B),–13.4 (4B).

4.9. Synthesis of complex **4b**

A procedure analogous to the preparation of **4a** was used. To a solution of **1b** (269.1 mg, 0.25 mmol) in toluene (15 mL) was added the solution of PPh_3 (131.1 mg, 0.5 mmol) in toluene (5 mL) at 0 °C and the mixture was stirred at 60 °C for 8 h to give a dark red solution. The solvent was removed under vacuum and the residue was washed with hexane (5 mL) twice to afford **4b** as a red powder (232.1 mg, 58%). Crystals suitable for X-ray crystallography were grown from a CH_2Cl_2/hexane solution at room temperature. Anal. Calcd for $C_{30}H_{41}B_{10}ClPSIr$: C, 45.01%; H, 5.16%. Found: C, 45.07%; H, 5.24%. IR (KBr, disk): υ, 2933 (C–H), 2559 cm^{-1} (B–H). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 1.47 (d, 15H, Cp^* $^4J(PH) = 3.6$ Hz), 4.30 (s, 1H, C_{cage}–H), 7.47–7.78 (m, 25H, phenyl). ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ −3.2 (1B), −4.4 (2B), −8.7 (4B),–12.2 (3B).

4.10. Synthesis of complex **5a**

Complex **4a** (89.7 mg, 0.1 mmol) and $AgPF_6$ (55.6 mg, 0.22 mmol) were charged into a schlenk tube. To this tube was added CH_2Cl_2 (10 mL) and the mixture was stirred at room temperature in dark for 4 h. The color of the solution was changed to purple or dark from the red. The solution was filtrated and the solvent was removed under reduced pressure. After washing with hexane (5 mL), the green solid was obtained (63.1 mg, 77%). Anal. Calcd for $C_{30}H_{41}B_{10}P_2RhSF_6$: C, 43.90%; H, 5.04%. Found: C, 43.82%; H, 5.10%. IR (KBr, disk): υ (cm^{-1}), 2943 (C–H), 2573, 2551, 2529 (B–H). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 1.63 (d, 15H, Cp^*, $^4J(PH) = 2.4$ Hz), 4.43 (s, 1H, C_{cage}–H), 7.39–7.83 (m, 25H, phenyl). ^{11}B NMR (160 MHz, $CDCl_3$, ppm): δ −2.9 (1B), −4.6 (1B), −7.9 (3B), −9.6 (3B), −13.4 (2B).

4.11. Synthesis of complex **5b**

The synthetic procedure is analogous to that of **5a**. Complex **4b** (80.0 mg, 0.1 mmol) and $AgPF_6$ (30.3 mg, 0.12 mmol) were charged into a schlenk tube in CH_2Cl_2 (15 mL). The green solution was filtrated and the solvent was removed and the green solid was isolated (64.6 mg, 71%). Anal. Calcd for $C_{30}H_{41}B_{10}P_2IrSF_6$: C, 39.60%; H, 4.54%. Found: C, 39.57%; H, 4.59%. IR (KBr, disk): υ (cm^{-1}), 2932 (C–H), 2572, 2554 (B–H). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 1.72 (d, 15H, Cp^*, $^4J(PH) = 4.6$ Hz), 4.54 (s, 1H, C_{cage}–H), 7.47–7.84 (m, 25H, phenyl). ^{11}B NMR (160 MHz, $CDCl_3$, ppm): δ −2.7 (1B), −5.5(1B), −9.6 (3B), −12.2 (1B), −13.4 (4B).

4.12. X-ray diffraction study

Diffraction data of **1a**, **1b**, **2a**, **2b** and **4b** were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). All the data were collected at room temperature and the structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL) [53], SADABS [54] absorption corrections were applied to the data. All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at

calculated positions except the hydrogen atoms of carborane (C_{cage}–H of **1a**, **1b, 2a, 2b** and **4b**) were found by difference Fourier Method. There are disordered solvent molecules in the crystal of **2a**, which can not be solved properly. Hence the SQUEEZE algorithm was used to omit them and the crystal data was refined to convergence. A summary of the crystallographic data and selected experimental information are given in Table 1.

Acknowledgments

This work was supported by the National Science Foundation of China (20721063, 20771028), Shanghai Science and Technology Committee (08DZ2270500, 08DJ1400103), Shanghai Leading Academic Discipline Project (B108) and the National Basic Research Program of China (2009CB825300).

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jorganchem.2010.04.038.

CCDC 769186–769190 contain the supplementary crystallographic data of **1a**, **1b***0.5CH_2Cl_2, **2a**, **2b***0.5CH_2Cl_2, and **4b** 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.

References

[1] G.J. Kubas, Chem. Rev. 107 (2007) 4152.
[2] G.S. McGrady, G. Guilera, Chem. Soc. Rev. 32 (2003) 383.
[3] S.D. Brown, M.P. Mehn, J.C. Peters, J. Am. Chem. Soc. 127 (2005) 13146.
[4] C.A. Sandoval, T. Ohkuma, K. Muñiz, R. Noyori, J. Am. Chem. Soc. 125 (2003) 13490.
[5] R.C. Linck, R.J. Pafford, T.B. Rauchfuss, J. Am. Chem. Soc. 123 (2001) 8856.
[6] J.D. Gilbertson, N.K. Szymczak, J.L. Crossland, W.K. Miller, D.K. Lyon, B. M. Foxman, J. Davis, D.R. Tyler, Inorg. Chem. 46 (2007) 1205.
[7] R. Gelabert, M. Moreno, J.M. Lluch, A. Lledós, V. Pons, D.M. Heinekey, J. Am. Chem. Soc. 126 (2004) 8813.
[8] D. Sellmann, G.H. Rackelmann, F.W. Heinemann, Chem.-Eur. J. 3 (1997) 2071.
[9] T. Matsumoto, Y. Nakaya, K. Tatsumi, Angew. Chem. Int. Ed. 47 (2008) 1913.
[10] Y. Ohki, M. Sakamoto, K. Tatsumi, J. Am. Chem. Soc. 130 (2008) 11610.
[11] P.M. Vignais, B. Billoud, Chem. Rev. 107 (2007) 4206.
[12] A.L. De Lacey, V.M. Fernández, M. Rousset, R. Cammack, Chem. Rev. 107 (2007) 4304.
[13] P.E.M. Siegbahn, J.W. Tye, M.B. Hall, Chem. Rev. 107 (2007) 4414.
[14] W.T. Klooster, T.F. Koetzle, G. Jia, T.P. Fong, R.H. Morris, A. Albinati, J. Am. Chem. Soc. 116 (1994) 7677.
[15] G.-X. Jin, Coord. Chem. Rev. 248 (2004) 587.
[16] G.-X. Jin, J.-Q. Wang, C. Zhang, L.-H. Weng, M. Herberhold, Angew. Chem. Int. Ed. 44 (2005) 259.
[17] S. Liu, Y.-F. Han, G.-X. Jin, Chem. Soc. Rev. 36 (2007) 1543.
[18] S. Liu, G.-L. Wang, G.-X. Jin, Dalton. Trans. (2008) 425.
[19] M.F. Hawthorne, Z.-P. Zheng, Acc. Chem. Res. 30 (1997) 267.
[20] Z. Xie, Acc. Chem. Res. 36 (2003) 1.
[21] A.F. Armstronga, J.F. Valliant, Dalton Trans. (2007) 4240.
[22] R. Núñez, O. Tutusaus, F. Teixidor, C. Viñas, R. Sillanpää, R. Kivekäs, Organometallics 23 (2004) 2273.
[23] D.-H. Wu, C.-H. Wu, Y.-Z. Li, D.-D. Guo, X.-M. Wang, H. Yan, Dalton. Trans. (2009) 285.
[24] M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, Chem.-Eur. J. 6 (2000) 3026.
[25] J.-D. Lee, Y.J. Lee, K.-C. Son, M. Cheong, J. Ko, S.O. Kang, Organometallics 26 (2007) 3374.
[26] I.T. Chizhevsky, Coord. Chem. Rev. 251 (2007) 1590.
[27] M. Juhasz, S. Hoffmann, E. Stoyanov, K.-C. Kim, C.A. Reed, Angew. Chem. Int. Ed. 43 (2004) 5352.
[28] J. Plešek, Chem. Rev. 92 (1992) 269.
[29] M.F. Hawthorne, J.I. Zink, J.M. Skelton, M.J. Bayer, C. Liu, E. Livshits, R. Baer, D. Neuhauser, Science 303 (2004) 1849.
[30] L. Schwartz, L. Eriksson, R. Lomoth, F. Teixidor, C. Vinãs, S. Ott, Dalton. Trans. (2008) 2379.
[31] H.-S. Lee, J.-Y. Bae, D.-H. Kim, H.S. Kim, S.-J. Kim, S. Cho, J. Ko, S.O. Kang, Organometallics 21 (2002) 210.
[32] H.-S. Lee, J.-Y. Bae, Y.S. Kang, S.-J. Kim, J.-H. Chung, S.O. Kang, J. Organomet. Chem. 614–615 (2000) 83.
[33] F. Teixidor, C. Viñas, M.M. Abad, C. Whitaker, J. Rius, Organometallics 15 (1996) 3154.
[34] J.J. Adams, A.S. Del Negro, N. Arulsamy, B.P. Sullivan, Inorg. Chem. 47 (2008) 1871.
[35] D. Zhang, J. Dou, S. Gong, D. Li, D. Wang, Appl. Organometal. Chem. 20 (2006) 632.
[36] S.O. Kang, J. Lee, J. Ko, Coord. Chem. Rev. 231 (2002) 47.
[37] D.W. Stephan, T.T. Nadasdi, Coord. Chem. Rev. 147 (1996) 147.
[38] M.M. Artigas, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, M.D. Villacampa, Inorg. Chem. 36 (1997) 6454.
[39] K. Base, M.W. Grinstaff, Inorg. Chem. 37 (1998) 1432.
[40] J.A. Todd, L.M. Rendina, Inorg. Chem. 41 (2002) 3331.
[41] M.M. Artigas, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, M.D. Villacampa, J. Organomet. Chem. 561 (1998) 1.
[42] W.E. Hill, L.M. Silva-Trivino, Inorg. Chem. 18 (1979) 361.
[43] A. Laromaine, F. Teixidor, R. Kivekäs, R. Sillanpää, R. Benakki, B. Grüner, C. Viñas, Dalton. Trans. (2005) 1785.
[44] F. Teixidor, C. Viñas, R. Benakki, Inorg. Chem. 34 (1995) 3844.
[45] M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, Angew. Chem. Int. Ed. 38 (1999) 3689.
[46] X. Wang, G.-X. Jin, Chem. -Eur. J 11 (2005) 5758.
[47] J.-S. Zhang, Y.-J. Lin, G.-X. Jin, Dalton. Trans. (2009) 111.
[48] J.-Q. Wang, S. Cai, G.-X. Jin, L.-H. Weng, M. Herberhold, Chem. -Eur. J 11 (2005) 7342.
[49] N.A. Barnes, A.K. Brisdon, M. Nieuwenhuyzen, R.G. Pritchard, G.C. Saunders, J. Fluor. Chem. 128 (2007) 943.
[50] M. Gorol, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, Eur. J. Inorg. Chem. (2005) 4840.
[51] C. White, A. Yates, P.M. Maitlis, Inorg. Synth. 29 (1992) 228.
[52] W.D. Jones, V.L. Kuykendall, Inorg. Chem. 30 (1991) 2615.
[53] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures. Universität Gtötingen, Germany, 1997.
[54] G.M. Sheldrick, SADABS (2.01), Bruker/Siemens Area Detector Absorption Correction Program. Bruker AXS, Madison, WI, 1998.