DOI: 10.1002/chem.200600854

Preparation and Structure of Mono- and Binuclear Half-Sandwich Iridium, Ruthenium, and Rhodium Carbene Complexes Containing 1,2-Dichalcogenolao 1,2-Dicarba-*closo*-Dodecaboranes

Xin Wang, Shuang Liu, Lin-Hong Weng, and Guo-Xin Jin*[a]

Dedicated to Herr Professor Gerhard Erker on the occasion of his 60th birthday

Abstract: The synthesis of half-sandwich transition metal complexes containing both 1,2-dichalcogenolato-1,2-dicarba-*closo*-docecaborane ($Cab^{E,E}$) [$Cab^{E,E} = E_2C_2(B_{10}H_{10})$; E = S, Se] and N-heterocyclic carbene (NHC) ligands is described. Addition of mono-NHC ligand to the 16e half-sandwich dichalcogenolato carborane complexes [Cp*Rh($Cab^{E,E}$)], [Cp*Ir($Cab^{S,S}$)], [(*p*-cymene)Ru($Cab^{S,S}$)] (Cp* = pentamethylcyclopentadienyl) gives corresponding mononuclear 18e dithiolate complexes of the type [LM($Cab^{E,E}$)(NHC)]: [Cp*M($Cab^{S,S}$)(1-ethenyl-3-methylimidazolin-2-ylidene)] (M = Ir (**2**), Rh (**3**)), [Cp*Rh($Cab^{E,E}$)(3-methyl-1-picolyimidazolin-2-ylidene)] [E = S (**6**), Se (**7**)], [(*p*-cymene)Ru($Cab^{S,S}$)(NHC)] [NHC = 1-ethenyl-3-methylimidazolin-2-ylidene (**4**), 3-methyl-1-picolyimidazolin-2-ylidene (**8**)], whereas bis-NHC give centrosymmetric binuclear complexes [{Cp*M($Cab^{S,S}$)}$_2$(1,1′-dimethyl-3,3′-methylene(imidazolin-2-ylidene))] [M = Rh (**10**), Ir (**11**)]. The complexes were characterized by IR, NMR spectroscopy and elemental analysis. In addition, X-ray structure analyses were performed on complexes **2**–**4**, **6**, **8**, **10** and **11**.

Keywords: carbenes · carborane · transition metals

Introduction

Since the first isolation of a free carbene by Arduengo,[1] N-heterocyclic carbenes (NHCs) have attracted increasing attention as ancillary ligands in organometallic chemistry and homogenous catalysis.[2–9] Recently, many efforts have been made in the design of compounds with different topologies, including mono-, bis-, and triscarbenes with a wide variety of coordination modes, such as bischelate, pincer and tripodal, but most of them are monometallic compounds. Therefore, the design of bimetallic and trimetallic NHCs has been of increasing importance.[10]

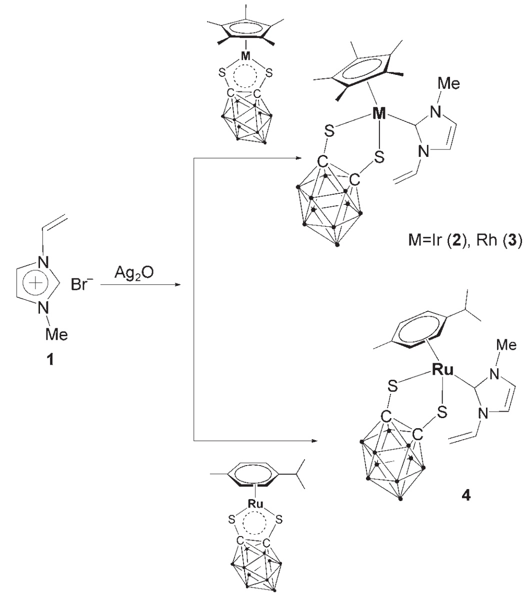
In recent years, derivatives of 1,2-dicarba-*closo*-dodecaborane have raised considerable interest in both their fundamental properties and wide-ranging potential applications.[11] Our group and Herberhold et al. have reported on the synthesis of the 16-electron metal complexes and suggested that this kind of species might be used as the acceptor, owing to the deficiency at the metal centre, which has allowed the construction of multi-carborane molecular architectures that take advantage of special attributes, such as an addition reaction at a metal atom in a dichalcogenolato metal heterocycle.[12] However, to the best of our knowledge, there is no report on using NHC ligands as donors for such addition reactions. Recently, we have reported the facile synthesis of pyridine-functionalized carbene or carborane transition-metal complexes and investigated their application in olefin polymerization.[13] In order to understand the chemistry of transition-metal complexes containing both NHC and carborane ligands, herein we report an easy way to synthesis mononuclear and dinuclear transition metal N-heterocyclic carbene complexes from 16-electron "pseudo-aromatic" complexes [LM{$E_2C_2(B_{10}H_{10})$}] (L = Cp*, *p*-cymene; M = Rh, Ir, Ru).

---

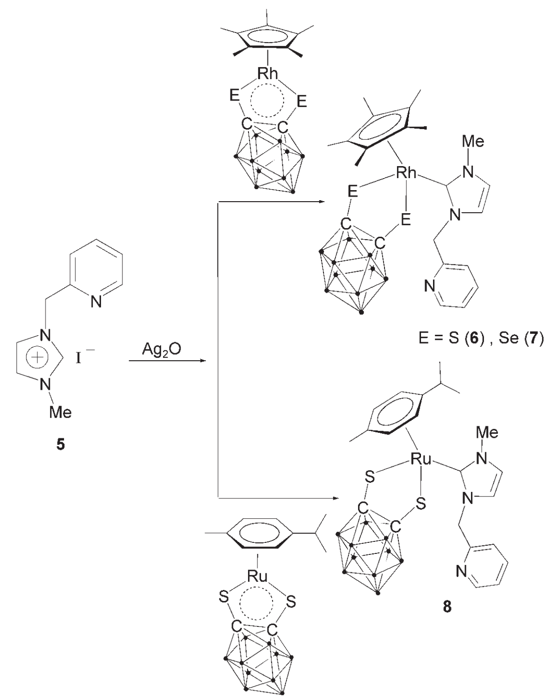
[a] Dr. X. Wang, S. Liu, Prof. Dr. L.-H. Weng, Prof. Dr. G.-X. Jin
Shanghai Key Laboratory of Molecular Catalysis
and Innovative Material
Department of Chemistry, Fudan University
Shanghai 200433 (PR China)
Fax: (+86) 21-6564-3776
E-mail: gxjin@fudan.edu.cn

Results and Discussion

Synthesis of half-sandwich mono-, dimetallic transition-metal N-heterocyclic carbene complexes: Metal complexes with NHC ligands were typically prepared from imidazolium salts via the three common routes: the free carbene reaction,[14] the metal acetate protocol,[15] and the silver carbene transfer.[16] Following our previous procedure of related compounds, we employed the synthesis of transition-metal complexes by transmetalation from the corresponding silver carbene derivatives which are used in situ. The reaction of the green 16-electron complexes with two-electron donor mono-carbene gave various red 18-electron mononuclear complexes in good yields, while the addition of bicarbenes gave the binuclear complexes also in good yields, as shown in Schemes 1–3.



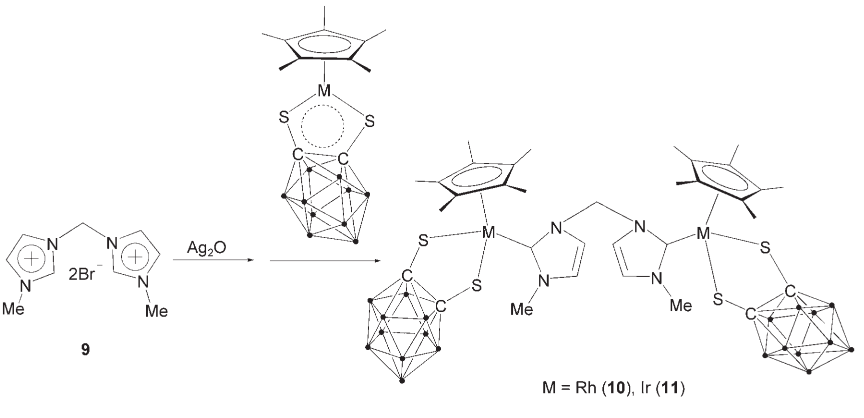
Scheme 1. Synthesis of complex **2**–**4**.



Scheme 2. Synthesis of complex **6**–**8**.

The ^{1}H NMR spectra of complexes **2**–**4**, **6**–**8** and **10**–**11** do not show any signal at δ 10–11 ppm, where the imidazolium C$_2$-H signals of precursors were found (δ 9.8 (**1**), 10.3 (**5**), 10.3 ppm (**9**)); the chemical shifts of other hydrogens are similar to those of corresponding precursors. In the ^{13}C NMR spectra the signals for the carbene carbon of complexes **2**, **3**, **6**–**8** appear at δ 156.4 (**2**), 173.7 (**3**), 171.8 (**6**), 171.6 (**7**), 176.4 ppm (**8**), respectively, which is characteristic for a metal–carbene signal.[5] Compounds **10** and **11** were fully characterized by NMR spectroscopy and elemental analysis. The ^{1}H NMR spectra of **10** and **11** show the typical pattern of the coordinated Cp* fragment. The methylene bridge appears as a singlet at δ 5.4–5.3. The equivalency of the imidazolyl rings confirms the two-fold symmetry of the ligand. Compounds **10** and **11** could hardly be re-dissolved in organic solvents after they precipitated, so that we couldn't obtain solutions concentrated enough for ^{13}C NMR spectrum.

All described mononuclear carbene complexes are soluble in CH$_2$Cl$_2$ and THF, but insoluble in diethyl ether and hydrocarbon solvents. All dinuclear carbene complexes are slightly soluble in DMSO, CH$_2$Cl$_2$ and THF, insoluble in diethyl ether and hydrocarbon. The complexes are moderately stable in dry air.



Scheme 3. Synthesis of complexes **10**–**11**.

Table 1. Summary of crystallographic data for **2**, **3** and **4**.

	2	**3**	**4**
formula	$C_{18}H_{33}B_{10}IrN_2S_2$	$C_{18}H_{33}B_{10}N_2RhS_2$	$C_{18}H_{32}B_{10}N_2RuS_2$
F_w	641.88	552.59	549.75
T [K]	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073
crystal system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$
a [Å]	10.578(4)	10.538(3)	19.228(5)
b [Å]	11.188(4)	11.152(4)	10.726(3)
c [Å]	12.877(5)	12.795(4)	25.172(6)
α [°]	88.674(4)	88.535(5)	90
β [°]	82.500(5)	82.513(4)	97.229(4)
γ [°]	62.167(4)	62.108(4)	90
V [Å^3]	1334.8(8)	1316.7(7)	5150(2)
Z	2	2	8
ρ_{calcd} [Mg m^{-3}]	1.597	1.394	1.418
μ [mm^{-1}]	5.169	0.818	0.782
$F(000)$	628	564	2240
crystal size [mm^3]	0.20×0.15×0.10	0.10×0.10×0.08	0.10×0.05×0.05
θ range for data collection [°]	1.60–25.01	1.61–25.01	1.42–26.01
limiting indices	$-12\leq h\leq 6$ $-13\leq k\leq 11$ $-15\leq l\leq 14$	$-12\leq h\leq 12$ $-8\leq k\leq 13$ $-12\leq l\leq 15$	$-23\leq h\leq 10$ $-13\leq k\leq 13$ $-31\leq l\leq 29$
reflections collected	5575	5578	23160
independent reflections	4616	4596	10076
R(int)	0.0233	0.0279	0.0642
completeness to θ [°]	25.01 (97.7%)	25.01 (98.8%)	26.01 (99.5%)
max. and min. transmission	0.6260 and 0.4246	0.9374 and 0.9226	0.9619 and 0.9259
data/restraints/parameters	4616/0/315	4596/0/314	10076/0/623
GoF on F^2	1.166	0.935	0.792
final R indices [$I>2\sigma(I)$]			
$R1$	0.0415	0.0442	0.0438
$wR2$	0.1079	0.0988	0.0667
largest diff. peak and hole [e Å^{-3}]	2.180 and −1.112	1.252 and −0.843	0.687 and −0.429

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR_2 = [\Sigma(|F_o|^2-|F_c|^2)^2/\Sigma(F_o^2)]^{1/2}$.

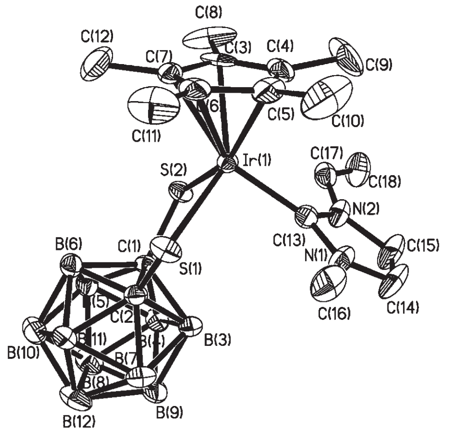


Figure 1. Crystal structure of complex **2** showing 30 % probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)−C(13) 2.030(9), Ir(1)−S(1) 2.380(2), Ir(1)−S(2) 2.381(2), C(1)−C(2) 1.666(11), C(17)−C(18) 1.291(14); C(13)-Ir(1)-S(1) 95.6(3), C(13)-Ir(1)-S(2) 91.9(2), S(1)-Ir(1)-S(2) 88.62(8).

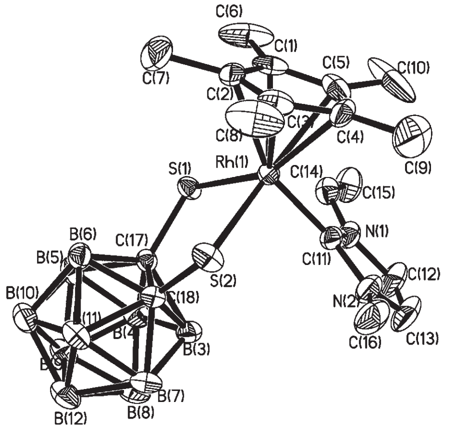


Figure 2. Crystal structure of complex **3** showing 30 % probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh(1)−C(11) 2.035(5), Rh(1)−S(2) 2.3646(14), Rh(1)−S(1) 2.3685(13), S(1)−C(17) 1.775(4), S(2)−C(18) 1.764(4), C(14)−C(15) 1.299(7), C(17)−C(18) 1.653(6), C(11)-Rh(1)-S(1) 92.62(12), C(11)-Rh(1)-S(1) 92.62(12), S(2)-Rh(1)-S(1) 88.43(5).

Crystals suitable for X-ray crystallography of **2**–**4** were obtained by slow diffusion of hexane into dichloromethane solution of the corresponding compounds. The crystallographic data and processing parameters are given in Table 1. The ORTEP diagrams of **2**–**4** (Figures 1–3) show that the three complexes have similar structures. The molecular structures confirm the six-coordinate geometry about the metal atom, assuming that the Cp or the benzene ring serves as three-coordinated ligand. The M–S distance (2.380(2) (**2**), 2.3646(14) (**3**), 2.3880(13) Å (**4**)) at the formally 18-electron metal centre is significantly longer than that of corresponding 16-electron complexes, which is due to π-orbital donation of the lone pairs from the sulfur atoms to the electron-deficient metal centre.[17] The bond angels C_{Cent}-M(1)-C(carbene) (C_{Cent} is the central point of the Cp* or *p*-cymene ring) are 126.0 (**2**), 126.6 (**3**), 125.3° (**4**), respectively, thus minimizing the repulsion between the Cp*/*p*-cymene and the imidazole ring. The metal atom environment is transferred from a two-legged piano-stool geometry in 16-electron complex to a three-legged version in 18-electron complex. And the 16-electron pseudoaromatic metalladichalcogenolene heterocyclic system is destroyed and bent with a dihedral angle of 166.1 for compound **2**, 163.2 for compound **3** and 166.2° for compound **4**, respectively, along the S···S vector, which is due to the coordination of the carbene atom to the metal centre. The M–C distances for imidazol-2-ylidene ligand are 2.030(9) (**2**), 2.035(5) (**3**), and 2.033 Å (**4**), typical for M−C σ bonds. This indicates that the back-donation is negligible for this compound, situation that has become typical for this kind of NHC–metal complexes.

Crystals suitable for X-ray crystallography of **6** and **8** were also obtained by slow diffusion of hexane into dichloromethane solution of the corresponding compounds.

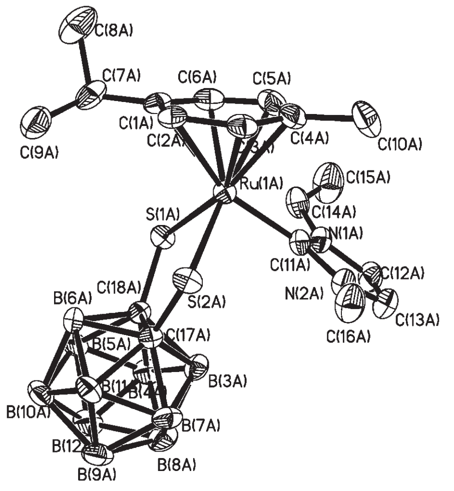


Figure 3. Crystal structure of complex **4** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru(1A)−C(11A) 2.033(5), C(17A)−C(18A) 1.663(5), Ru(1A)−S(2A) 2.3880(13), Ru(1A)−S(1A) 2.4086(13), S(1A)−C(17A) 1.784(4), S(2A)−C(18A) 1.782(4), C(14A)−C(15A) 1.270(6); C(11A)-Ru(1A)-S(2A) 92.69(14), C(11A)-Ru(1A)-S(1A) 89.87(13), S(2A)-Ru(1A)-S(1A) 87.28(4).

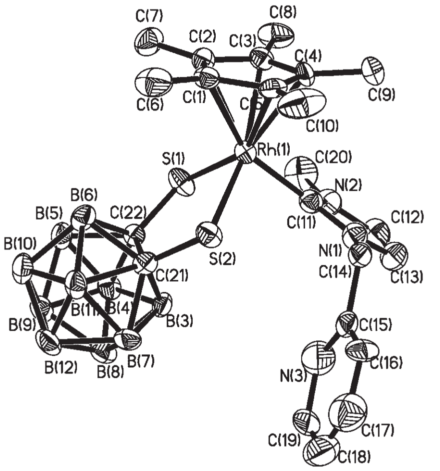


Figure 4. Crystal structure of complex **6** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh(1)−C(11) 2.009(5), Rh(1)−S(2) 2.3608(14), Rh(1)−S(1) 2.3669(15), S(1)−C(21) 1.753(5), S(2)−C(22) 1.769(5), C(21)−C(22) 1.680(6); C(11)-Rh(1)-S(2) 93.15(17), C(11)-Rh(1)-S(1) 91.49(18), S(2)-Rh(1)-S(1) 90.13(5).

Table 2. Summary of crystallographic data for **6**, **8**, **10** and **11**.

	6	**8**	**10**	**11**
formula	$C_{22}H_{36}B_{10}N_3RhS_2$	$C_{22}H_{35}B_{10}N_3RuS_2$	$C_{33}H_{62}B_{20}N_4Rh_2S_4$	$C_{33}H_{62}B_{20}Ir_2N_4S_4$
F_w	617.67	614.82	1065.13	1243.71
T [K]	293(2)	293(2)	293(2)	298(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2(1)/n$	P2(1)/n	$P2(1)/c$	$P2(1)/c$
a [Å]	12.100(2)	13.370(4)	14.513(4)	14.516(4)
b [Å]	17.040(3)	11.101(3)	16.803(5)	16.753(5)
c [Å]	15.139(3)	19.760(6)	26.686(7)	27.001(7)
α [°]	90	90	90	90
β [°]	108.49(3)	92.877(4)	93.216(5)	94.147(4)
γ [°]	90	90	90	90
V [Å^3]	2960.3(10)	2929.2(14)	6498(3)	6549(3)
Z	4	4	4	4
ρ_{calcd} [Mg m^{-3}]	1.386	1.394	1.089	1.261
μ [mm^{-1}]	0.737	0.697	0.661	4.212
F(000)	1264	1256	2168	2424
crystal size [mm^3]	0.02×0.02×0.02	0.10×0.10×0.05	0.05×0.05×0.02	0.15×0.15×0.05
θ range for data collection [°]	1.85–25.01	1.80–26.01	1.41–25.01	1.43–25.01
limiting	$-13 \leq h \leq 14$	$-14 \leq h \leq 16$	$-11 \leq h \leq 17$	$-17 \leq h \leq 17$
indices	$-20 \leq k \leq 20$	$-13 \leq k \leq 13$	$-19 \leq k \leq 19$	$-19 \leq k \leq 18$
	$-18 \leq l \leq 11$	$-23 \leq l \leq 24$	$-31 \leq l \leq 31$	$-29 \leq l \leq 32$
reflections collected	12275	13138	26986	27145
independent reflections	5215	5740	11451	11501
R(int)	0.0817	0.0344	0.0754	0.0445
completeness to θ [°]	25.01 (99.9%)	26.01 (99.5%)	25.01 (99.9%)	25.01 (99.5%)
max. and min. transmission	0.9854 and 0.9854	0.9660 and 0.9336	0.9869 and 0.9677	0.8170 and 0.5707
data/restraints/parameters	5215/0/359	5740/0/358	11451/0/600	11501/0/600
GoF on F^2	0.631	0.904	0.599	0.841
final R indices [$I > 2\sigma(I)$]				
$R1$	0.0445	0.0344	0.0430	0.0310
$wR2$	0.0527	0.0651	0.0743	0.0641
largest diff. peak and hole [e Å^{-3}]	0.767 and −0.496	0.521 and −0.300	0.717 and −0.401	0.847 and −0.516

[a] $R_1 = \Sigma||F_o|-|F_c||)/\Sigma|F_o|$. $wR_2 = [\Sigma(|F_o|^2-|F_c|^2)^2/\Sigma(F_o^2)]^{1/2}$.

The ORTEP diagram of **6** and **8** are presented in Figures 4 and 5, respectively, and show that the two complexes have similar structures. Crystallographic data and processing parameters are given in Table 2. The metal atom environment is transferred from a two-legged piano-stool geometry in 16-electron complex to a three-legged version in 18-electron complex. The metal centre is in a distorted octahedral environment with Cp as three-coordinated ligand, chelating *ortho*-carborane dithiolate, monodentate NHC and dangling pyridine groups. The coordination of the ligand by the carbene end, instead of the nitrogen end, may be due to its better ability to release electron density from the low valence metal by back-donation.[18] It has been suggested that the preferential C-binding versus N-binding in imidazolyl ligands depends on the metal fragment involved.[12] In this sense, C-bound imidazoles are predicted to be thermodynamically more stable than the con-

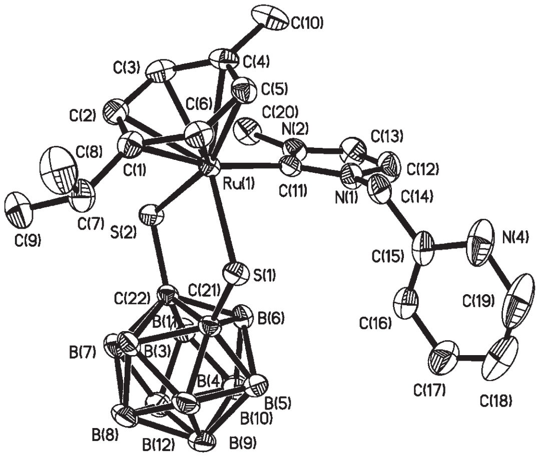


Figure 5. Crystal structure of complex **8** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru(1)−C(11) 2.066(3), Ru(1)−S(1) 2.3900(10), Ru(1)−S(2) 2.3907(9), S(1)−C(21) 1.784(3), S(2)−C(22) 1.777(3), C(21)−C(22) 1.645(4); C(11)-Ru(1)-S(1) 90.18(9), C(11)-Ru(1)-S(2) 92.68(8), S(1)-Ru(1)-S(2) 87.68(3).

ventional N-bound forms for several second- and third-row transition metals. In any case, the synthesis of these complexes argues against the idea that the pyridine unit acts as the initial binding site for the ligand, bringing the imidazolium rings into the vicinity of the metal in those cases where the bidentate coordination is obtained. The 16-electron pseudoaromatic metalladichalcogenolene heterocyclic system is also destroyed and bent with a dihedral angle of 169.3° for compound **6** and 169.7° for compound **8**, respectively, along the S···S vector, which results from the coordination of the carbene to the metal centre. The M–C distance is 2.009(5) for compound **6** and 2.066(3) Å for compound **8**, typical σ bonds, which indicates very little back-donation.[19]

Crystals suitable for X-ray crystallography of **10** and **11** were also obtained by slow diffusion of hexane into dichloromethane solution of the corresponding compounds. The ORTEP diagram of **10** and **11** are presented in Figures 6 and 7. Crystallographic data and processing parameters are given in Table 2. The dimetallic structure consists of two metal atoms bridged by the methylene-imidazolyl ligand, with the two imidazole rings at a dihedral angle of 75.3 (**10**), 74.8° (**11**). Three-coordinated Cp* and chelating *ortho*-carborane dithiolate complete the coordination sphere of each distorted octahedral metal atom. The M–M distance discards any possible bonding interaction ($d_{\text{Ir–Ir}} = 6.870$, $d_{\text{Rh–Rh}} = 6.880$ Å). The M–C distances for the carbene ligand are 2.026, 2.030 Å (**10**) and 2.032, 2.025 Å (**11**) again typical for Rh–C σ bonds with very little back-donation. Due to the coordination of the carbene to the metal centre, the pseudoaromatic metalladithiolate heterocyclic system is destroyed and bent with a dihedral angle of 173 (**10**) and 105.2° (**11**) along the S···S vector.

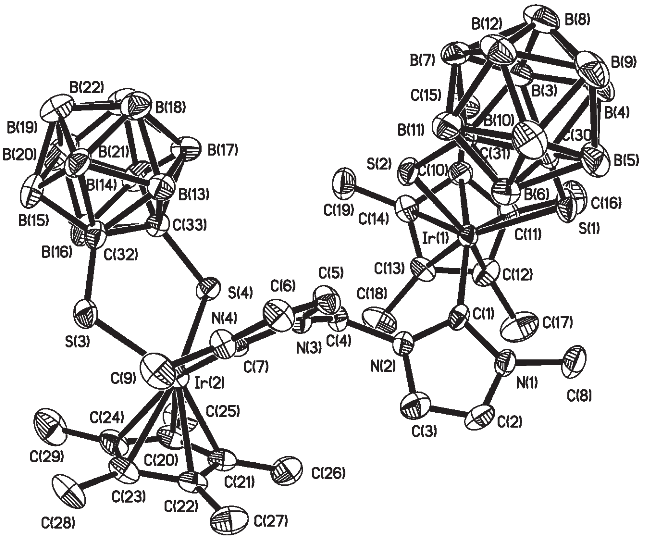


Figure 7. Crystal structure of complex **11** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)−C(1) 2.032(6), Ir(1)−S(1) 2.3706(17), Ir(1)−S(2) 2.3731(16), C(30)−C(31) 1.661(7), Ir(2)−C(7) 2.025(6), Ir(2)−S(4) 2.3721(15), Ir(2)−S(3) 2.3746(17), C(32)−C(33) 1.651(7); C(1)-Ir(1)-S(1) 92.25(16), C(1)-Ir(1)-S(2) 92.92(16), S(1)-Ir(1)-S(2) 89.31(6), C(7)-Ir(2)-S(3) 91.53(16), C(7)-Ir(2)-S(4) 91.59(15), S(4)-Ir(2)-S(3) 89.23(5).

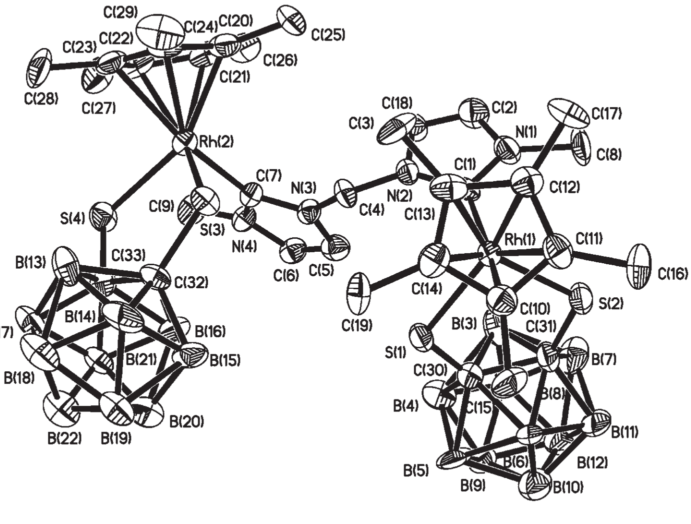


Figure 6. Crystal structure of complex **10** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles [°]: Rh(1)−C(1) 2.026(5), Rh(1)−S(2) 2.3657(16), Rh(1)−S(1) 2.3768(15), Rh(2)−C(7) 2.030(6), C(30)−C(31) 1.669(7); C(1)-Rh(1)-S(2) 93.55(17), C(1)-Rh(1)-S(1) 93.30(16), S(2)-Rh(1)-S(1) 89.12(6).

Conclusion

In summary, we have synthesized a series of mononuclear and binuclear half-sandwich iridium, rhodium and ruthenium complexes containing both carborane and NHCs mixed ligands system. A combination of X-ray crystallographic and spectroscopic studies confirms the nature of these half-sandwich complexes. For the first time, N-heterocyclic carbenes and carborane are joined together by an easy way from 16-

electron complexes to 18-electron complexes, giving novel structures.

Experimental Section

General procedures: All manipulations were performed using standard Schlenk techniques under an atmosphere of argon. Methanol was dried over Mg, CH_2Cl_2, and then distilled under nitrogen immediately prior to use. 2-Picolychloride hydrochloride was purchased from Witco and Acros, respectively. Other solvents were used as received as technical grade solvents. 3-Methyl-1-picolyimidazolium iodide,[5i] 1,1′-dimethyl-3,3′-methylenediimidazolium dibromide,[20] $[Cp^*MCl_2]_2$ (M = Rh, Ir),[21] [*p*-cymene-$RuCl_2]_2$,[22] $[Cp^*M\{E_2C_2(B_{10}H_{10})\}]$,[12a,b] (M = Rh, Ir; E = S, Se), [*p*-cymene-$Ru\{S_2C_2(B_{10}H_{10})\}]$[23] were prepared according to literatures. ^1H, ^{13}C and ^{11}B NMR spectra were recorded on a Bruker Avance-DMX 500 Spectrometer in $CDCl_3$. Elemental analysis was performed on an Elementar vario EL III Analyzer. IR (KBr) spectra were recorded on the Nicolet FT-IR spectrophotometer.

1-Ethenyl-3-methylimidazolium bromide (1): A stirred solution of THF (20 mL), 1-methylimidazole (4.1 g, 50 mmol) and CH_2BrCH_2Br (9.4 g, 50 mmol) was heated under reflux for 6 h to yield a white powder, which was collected, washed with THF, and dried in vacuo (8.55 g, 90 %). ^1H NMR (500 MHz, $CDCl_3$): δ = 9.3 (s, 1H, NCHN), 7.3 (m, 1H, HCCH), 7.2 (m, 1H, HCCH), 7.0 (d, 1H, $HCCH_2$), 5.2 (d, 1H, $HCCH_2$), 4.9 (d, 1H, $HCCH_2$), 3.9 (s, 3H, CH_3).

[Cp*Ir(1-ethenyl-3-methylimidazolin-2-ylidene)($S_2C_2(B_{10}H_{10})$)] (2): A mixture of **1** (95 mg, 0.5 mmol) and silver(I) oxide (290 mg, 1.3 mmol) was taken up in CH_2Cl_2 (20 mL) and was stirred for 24 h. The solution was filtered through Celite, and then $Cp^*Ir[S_2C_2(B_{10}H_{10})]$ (266 mg, 0.5 mmol) was added. The solution was stirred at room temperature overnight and then filtered; the resulting solid was washed with CH_2Cl_2, and then dried in vacuo. The product was recrystallized from CH_2Cl_2/hexane to give red crystals (258 mg, 84 %). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.3 (m, 1H, HCCH), 7.2 (m, 1H, HCCH), 7.0 (d, 1H, $HCCH_2$), 5.2 (d, 1H, $HCCH_2$), 4.9 (d, 1H, $HCCH_2$), 3.8 (s, 3H, CH_3), 1.63 (s, 15H, $C(CH_3)_5$); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.4 (Ir-C), 135.4 ($HCCH_2$), 124.0 (NCCN), 118.2 (NCCN), 101.8 ($HCCH_2$), 93.6 ($C_5(CH_3)_5$), 90.6 ($C_2B_{10}H_{10}$), 39.0 (NCH_3), 8.9 ($C_5(CH_3)_5$); ^{11}B NMR (160 MHz, $CDCl_3$): δ = −11.4, −8.4, −7.6, −4.1, −2.5 (2:4:2:1:1); elemental analysis calcd (%) for $C_{18}H_{33}B_{10}N_2IrS_2$: C 33.65; H 5.14, N 4.36; found: C 33.26, H 5.19, N 3.95.

[Cp*Rh(1-ethenyl-3-methylimidazolin-2-ylidene)($S_2C_2(B_{10}H_{10})$)] (3): A mixture of **1** (95 mg, 0.5 mmol) and silver(I) oxide (290 mg, 1.3 mmol) was taken up in CH_2Cl_2 (20 mL) and the reaction mixture was stirred for 24 h. The solution was filtered through Celite, and then $Cp^*Rh[S_2C_2(B_{10}H_{10})]$ (220 mg, 0.5 mmol) was added. The solution was stirred at room temperature overnight and filtered; the resulting solid was washed with CH_2Cl_2, and then dried in vacuo. The product was recrystallized from CH_2Cl_2/hexane to give red crystals (238 mg, 86 %). ^1H NMR: δ = 7.5 (m, 1H, HCCH), 7.4 (m, 1H, HCCH), 7.0 (d, 1H, $HCCH_2$), 5.3 (d, 1H, $HCCH_2$), 5.0 (d, 1H, HCCH2), 3.9 (s, 3H, CH_3), 1.61 (s, 15H, $C(CH_3)_5$); ^{13}C NMR: δ = 173.7 (Rh-C), 135.5 ($HCCH_2$), 124.7 (NCCN), 119.0 (NCCN), 102.2 ($HCCH_2$), 99.0 ($Cp^*(CH_3)_5$), 92.8 ($C_2B_{10}H_{10}$), 39.6 (NCH_3), 9.2 ($Cp^*(CH_3)_5$): ^{11}B NMR (160 MHz, $CDCl_3$): δ = −11.6, −10.7, −9.6, −8.6, −7.2, −4.8 (1:1:2:4:2); elemental analysis calcd (%) for $C_{18}H_{33}B_{10}N_2RhS_2$: C 39.08, H 5.97, N 5.07; found: C 38.64, H 5.91, N 4.86.

[(*p*-Cymene)Ru(1-ethenyl-3-methylimidazolin-2-ylidene)($S_2C_2(B_{10}H_{10})$)] (4): A mixture of **3** (95 mg, 0.5 mmol) and silver(I) oxide (290 mg, 1.3 mmol) was taken up in CH_2Cl_2 (20 mL) and was stirred for 24 h. The solution was filtered through Celite, and then [(*p*-cymene)Ru($S_2C_2B_{10}H_{10}$)] (654 mg, 1 mmol) was added. The solution was stirred at room temperature overnight and filtered. The resulting solid was washed with CH_2Cl_2, and then dried in vacuo. The product was recrystallized from CH_2Cl_2/hexane to give red crystals (178 mg, 65 %). ^1H NMR: δ = 7.6 (m, 1H, HCCH), 7.4 (m, 1H, HCCH), 7.0 (d, 1H, $HCCH_2$), 5.2 (m, 4H, C_6H_4), 5.1 (d, 1H, $HCCH_2$), 5.0 (d, 1H, $HCCH_2$), 3.9 (s, 3H, CH_3), 2.7 (m, 1H, CH), 2.0 (m, 3H, CH_3), 1.1 (m, 6H, $CH(CH_3)_2$); elemental analysis calcd (%) for $C_{18}H_{33}B_{10}N_2RuS_2$: C 39.29, H 5.82, N 5.09; found: C 39.12, H 5.77, N 5.02.

[Cp*Rh(3-methyl-1-picolyimidazolin-2-ylidene)($S_2C_2(B_{10}H_{10})$] (6): A solution of $[Cp^*Rh\{S_2C_2(B_{10}H_{10})\}]$ (88 mg, 0.2 mmol) in CH_2Cl_2 (20 mL) was added to a suspension of **5** (116 mg, 0.2 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature overnight and filtered. The resulting solid was washed with CH_2Cl_2, and then dried in vacuo. The product was recrystallized from CH_2Cl_2/hexane to give red crystals (100 mg, 81 %). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.56 (d, 1H, pyridyl), 7.77 (m, 1H, pyridyl), 7.6 (d, 1H, HCCH), 7.4 (m, 1H, HCCH), 7.0 (d, 1H, pyridyl), 6.9 (d, 1H, pyridyl), 5.7 (d, 1H, NCH_2), 5.0 (d, 1H, NCH_2), 3.9 (s, 3H, CH_3), 1.6 (s, 15H, $C(CH_3)_5$); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.8 (Rh-C), 156.4 (pyridyl, C2), 149.1 (pyridyl, C6), 137.2 (pyridyl, C4), 124.6 (pyridyl, C3), 123.9 (pyridyl, C5), 123.3 (NCCN), 122.8 (NCCN), 99.1 ($C_5(CH_3)_5$), 93.3 ($C_2B_{10}H_{10}$), 56.5 (NCH_2), 39.6 (NCH_3), 9.4 ($C_5(CH_3)_5$); ^{11}B NMR (160 MHz, $CDCl_3$): δ = −11.4, −8.8, −7.7, −4.5, −2.1 (2:4:2:1:1); elemental analysis calcd (%) for $C_{22}H_{36}B_{10}N_3RhS_2{\cdot}0.5\,CH_2Cl_2$: C 40.90, H 5.60, N 6.36; found: C 41.10, H 5.58, N 6.36.

[Cp*Rh(3-methyl-1-picolyimidazolin-2-ylidene)($Se_2C_2(B_{10}H_{10})$)] (7): A solution of $Cp^*Rh[Se_2C_2(B_{10}H_{10})]$ (107 mg, 0.2 mmol) in CH_2Cl_2 (20 mL) was added to a suspension of **5** (116 mg, 0.2 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature overnight and filtered. The resulting solid was washed with CH_2Cl_2, and then dried in vacuo. The product was recrystallized from CH_2Cl_2/hexane to give red crystals (101 mg, 71 %). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.6 (d, 1H, pyridyl), 7.8 (m, 1H, pyridyl), 7.5 (d, 2H, HCCH), 7.0 (m, 1H, pyridyl), 6.9 (d, 1H, pyridyl), 5.7 (d, 1H, NCH_2), 5.0 (d, 1H, NCH_2), 3.8 (s, 3H, CH_3), 1.6 (s, 15H, $C(CH_3)_5$); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.6 (Rh-C), 156.3 (pyridyl, C2), 149.2 (pyridyl, C6), 137.2 (pyridyl, C4), 124.4 (pyridyl, C3), 123.7 (pyridyl, C5), 123.3 (NCCN), 122.8 (NCCN), 98.6 ($C_5(CH_3)_5$), 69.0 ($C_2B_{10}H_{10}$), 56.9 (NCH_2), 40.2 (NCH_3), 9.7 ($C_5(CH_3)_5$); ^{11}B NMR (160 MHz, $CDCl_3$): δ = −11.9, −11.0, −8.6, −7.5, −3.1 (2:4:2:1:1); elemental analysis calcd (%) for $C_{22}H_{36}B_{10}N_3RhSe_2{\cdot}0.5\,C_6H_{14}$: C 39.75, H 5.70, N 5.57, found: C 40.15, H 5.30, N 5.33.

[(*p*-Cymene)Ru(3-methyl-1-picolyimidazolin-2-ylidene)($S_2C_2(B_{10}H_{10})$)] (8): A solution of [(*p*-cymene)$Ru\{S_2C_2(B_{10}H_{10})\}$] (88 mg, 0.2 mmol) in CH_2Cl_2 (10 mL) was added to a suspension of **5** (116 mg, 0.2 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature overnight and filtered. The resulting solid was washed with CH_2Cl_2, and then dried in vacuo. The product was recrystallized from CH_2Cl_2/hexane to give red crystals (78 mg, 64 %). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.6 (d, 1H, pyridyl), 7.8 (m, 1H, pyridyl), 7.5 (d, 2H, HCCH), 7.0 (d, 1H, pyridyl), 6.9 (d, 1H, pyridyl), 5.6 (4H, m, C_6H_4), 5.3 (d, 1H, NCH_2), 5.1 (d, 1H, NCH_2), 3.9 (s, 3H, CH_3), 2.7 (m, 1H, CH), 2.0 (m, 3H, CH_3), 1.1 (m, 6H, $CH(CH_3)_2$); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 176.4 (Ru-C), 156.5 (pyridyl, C2), 149.5 (pyridyl, C6), 137.3 (pyridyl, C4), 124.0 (pyridyl, C3), 123.6 (pyridyl, C5), 123.3 (NCCN), 122.4 (NCCN), 112.1, 104.1, 88.8, 88.7 (C_6H_4), 85.3 ($C_2B_{10}H_{10}$), 57.1 (NCH_2), 40.4 (NCH_3), 30.3 ($CH_3C_6H_4CH(CH_3)_2$), 23.6 ($CH_3C_6H_4CH(CH_3)_2$), 21.6 ($CH_3C_6H_4CH(CH_3)_2$), 18.2 ($CH_3C_6H_4CH(CH_3)_2$); elemental analysis calcd (%) for $C_{22}H_{35}B_{10}N_3RuS_2$: C 42.94, H 5.69, N 6.83; found: C 42.66, H 5.43, N 6.67.

[{Cp*Rh($S_2C_2(B_{10}H_{10})$)}$_2${1,1′-dimethyl-3,3′-methylene(imidazolin-2-ylidene)}] (10): A mixture of **9** (169 mg, 0.5 mmol) and silver(I) oxide (290 mg, 1.3 mmol) was taken up in CH_2Cl_2 (20 mL) and was stirred for 24 h. The solution was filtered through Celite, and then $[Cp^*Rh\{S_2C_2(B_{10}H_{10})\}]$ (440 mg, 1 mmol) was added. The solution was stirred at room temperature overnight and filtered. The resulting solid was washed with CH_2Cl_2, and then dried in vacuo. The product was recrystallized from CH_2Cl_2/hexane to give red crystals (394 mg, 74 %). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.1 (s, 2H, HCCH), 6.7 (s, 2H, HCCH), 5.3 (d, 1H, NCH_2), 5.2 (d, 1H, NCH_2), 3.9 (s, 6H, CH_3), 1.55 (s, 30H, $C(CH_3)_5$); elemental analysis calcd (%) for $C_{33}H_{62}B_{20}N_4Rh_2S_4{\cdot}CH_2Cl_2$: C 37.18, H 5.82, N 5.26; found: C 37.51, H 6.02, N 5.28.

[{Cp*Ir($S_2C_2(B_{10}H_{10})$)}$_2${1,1′-dimethyl-3,3′-methylene(imidazolin-2-ylidene)}] (11): A mixture of **9** (169 mg, 0.5 mmol) and silver(I) oxide

(290 mg, 1.3 mmol) was taken up in CH_2Cl_2 (20 mL) and was stirred for 24 h. The solution was filtered through Celite, and then [Cp*Ir{S_2C_2-($B_{10}H_{10}$)}] (532 mg, 1 mmol) was added. The solution was stirred at room temperature overnight and filtered. The resulting solid was washed with CH_2Cl_2, and then dried in vacuo. The product was recrystallized from CH_2Cl_2/hexane to give red crystals (485 mg, 78%). ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.2$ (s, 2H, HCCH), 6.6 (s, 2H, HCCH), 5.4 (d, 1H, NCH_2), 5.3 (d, 1H, NCH_2), 3.8 (s, 6H, CH_3), 1.63 (s, 30H, $C(CH_3)_5$); elemental analysis calcd (%) for $C_{33}H_{62}B_{20}N_4Rh_2S_4$: C 31.86, H 4.99, N 4.50; found: C 32.17, H 4.58, N 4.20.

X-ray crystallography: Suitable crystals for X-ray analysis of **2**, **3**, **4**, **6**, **8**, **10**, **11** were obtained by slow diffusion of hexane into dichloromethane solutions of the corresponding compound, respectively. None showed signals of decomposition during X-ray data collection, which was carried out at room temperature. Details of the data collection and refinement are summarized in Tables 1 and 2. The structure were solved by direct methods using SHELX-97 and refined by full-matrix least-square calculations, using program system SHELXTL-97.

CCDC-611420 (**2**), -611421 (**3**), -611422 (**4**), -611423 (**6**), -611424 (**8**), -611418 (**10**), -611419 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif/

Acknowledgements

Financial support by the National Science Foundation of China for Distinguished Young Scholars (20421303, 20531020), by the National Basic Research Program of China (2005CB623800) and by Shanghai Science and Technology Committee (05JC14003, 05DZ22313) is gratefully acknowledged.

[1] a) A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363; b) A. J. Arduengo, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534.

[2] a) F. E. Hahn, *Angew. Chem.* **2006**, *118*, 1374–1378; *Angew. Chem. Int. Ed.* **2006**, *45*, 1348–1352; b) F. E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, *Chem. Eur. J.* **1999**, *5*, 1931–1935; c) F. E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, *Angew. Chem.* **2000**, *112*, 551–554; *Angew. Chem. Int. Ed.* **2000**, *39*, 541–544; d) F. E. Hahn, V. Langenhahn, N. Meier, T. Lügger, W. P. Fehlhammer, *Chem. Eur. J.* **2003**, *9*, 704–712; e) F. E. Hahn, C. García Plumed, M. Münder, T. Lügger, *Chem. Eur. J.* **2004**, *10*, 6285–6293; f) F. E. Hahn, V. Langenhahn, T. Pape, *Chem. Commun.* **2005**, 5390–5392.

[3] H. M. Lee, D. C. Smith, Z. J. He, E. D. Stevens, C. S. Yi, S. P. Nolan, *Organometallics* **2001**, *20*, 794–797.

[4] a) M. Poyatos, P. Uriz, J. A. Mata, C. Claver, E. Fernandez, E. Peris, *Organometallics* **2003**, *22*, 440–444; b) A. C. Chen, L. Ren, A. Decken, C. M. Crudden, *Organometallics* **2000**, *19*, 3459–3461.

[5] a) E. Peris, J. A. Loch, J. Mata, R. H. Crabtree, *Chem. Commun.* **2001**, 201–202; b) W. A. Herrmann, C. P. Reisinger, M. Spiegler, *J. Organomet. Chem.* **1998**, *557*, 93–96; c) J. A. Loch, M. Albrecht, E. Peris, J. Mata, J. W. Faller, R. H. Crabtree, *Organometallics* **2002**, *21*, 700–706; d) M. Poyatos, F. Marquez, E. Peris, C. Claver, E. Fernandez, *New J. Chem.* **2003**, *27*, 425–431; e) J. Schwarz, V. P. W. Bohm, M. G. Gardiner, M. Grosche, W. A. Herrmann, W. Hieringer, G. Raudaschl-Sieber, *Chem. Eur. J.* **2000**, *6*, 1773–1780; f) W. A. Herrmann, M. Elison, J. Fischer, C. Kocher, G. R. J. Artus, *Angew. Chem.* **1995**, *107*, 2602–2605; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2371–2374; g) W. A. Herrmann, C. Brossmer, K. Öfele, C. P. Reisinger, T. Priermeier, M. Beller, H. Fischer, *Angew. Chem.* **1995**, *107*, 1989–1992; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1844–1848; h) A. M. Magill, D. S. McGuinness, K. J. Cavell, G. J. P. Britovsek, V. C. Gibson, A. J. P. White, D. J. Williams, A. H. White, B. W. Skelton, *J. Organomet. Chem.* **2001**, *617*, 546–560; i) D. S. McGuinness, K. J. Cavell, *Organometallics* **2000**, *19*, 741–748; j) S. Grundemann, M. Albrecht, J. A. Loch, J. W. Faller, R. H. Crabtree, *Organometallics* **2001**, *20*, 5485–5488; k) V. P. W. Boehm, W. A. Herrmann, *Chem. Eur. J.* **2000**, *6*, 1017–1025; l) V. P. W. Boehm, C. W. K. Gstöttmayr, T. Weskamp, W. A. Herrmann, *J. Organomet. Chem.* **2000**, *595*, 186–190; m) W. A. Herrmann, J. Schwarz, M. G. Gardiner, *Organometallics* **1999**, *18*, 4082–4089; n) A. A. D. Tulloch, A. A. Danopoulos, R. P. Tooze, S. M. Cafferkey, S. Kleinhenz, *Chem. Commun.* **2000**, 1247–1248; o) H. Lebel, M. K. Janes, A. Charette, S. P. Nolan, *J. Am. Chem. Soc.* **2004**, *126*, 5046–5047.

[6] a) A. K. Chatterjee, D. P. Sanders, R. H. Grubbs, *Org. Lett.* **2002**, *4*, 1939–1942; b) M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Lett.* **1999**, *40*, 2247–2250; c) T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18–29; d) T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem.* **1998**, *110*, 2631–2633; *Angew. Chem. Int. Ed.* **1998**, *37*, 2490–2493.

[7] a) M. Poyatos, E. Mas-Marza, J. A. Mata, M. Sanau, E. Peris, *Eur. J. Inorg. Chem.* **2003**, 1215–1221; b) E. Mas-Marza, M. Poyatos, M. Sanau, E. Peris, *Inorg. Chem.* **2004**, *43*, 2213–2219.

[8] a) S. Burling, L. D. Field, H. L. Li, B. A. Messerle, P. Turner, *Eur. J. Inorg. Chem.* **2003**, 3179–3184; b) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342–1363; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309.

[9] M. Viciano, E. Mas-Marzae, M. Sanaue, E. Peris, *Organometallics* **2006**, *25*, 3063–3069.

[10] a) C. Kijcher, W. A. Herrmann, *J. Organomet. Chem.* **1997**, *532*, 261–265; b) M. Poyatos, M. Sanaue, E. Peris, *Inorg. Chem.* **2003**, *42*, 2572–2576; c) X. Hu, Y. Tang, P. Gantzel, K. Meyer, *Organometallics* **2003**, *22*, 612–614; d) N. Stylianides, A. A. Danopoulos, N. Tsoureas, *J. Organomet. Chem.* **2005**, *690*, 5948–5958.

[11] a) J. Plesek, *Chem. Rev.* **1992**, *92*, 269–278; b) V. I. Bregadze, *Chem. Rev.* **1992**, *92*, 209–223; c) M. F. Hawthorne, A. Maderna, *Chem. Rev.* **1999**, *99*, 3421–3434; d) Z. Xie, Acc. *Chem. Res.* **2003**, *36*, 1–9; e) G.-X. Jin, *Coord. Chem. Rev.* **2004**, *248*, 587.

[12] a) M. Herberhold, G.-X. Jin, H. Yan, W. Milius, B. Wrackmeyer, *J. Organomet. Chem.* **1999**, *587*, 252–257; b) M. Herberhold, G.-X. Jin, H. Yan, W. Milius, B. Wrackmeyer, *Eur. J. Inorg. Chem.* **1999**, 873–875; c) X.-F. Hou, X.-C. Wang, J.-Q. Wang, G.-X. Jin, *J. Organomet. Chem.* **2004**, *689*, 2228–2235; d) Q. A. Kong, G.-X. Jin, S.-Y. Cai, L.-H. Weng, *Chin. Sci. Bull.* **2003**, *48*, 1733; e) G.-X. Jin, J.-Q. Wang, Z. Zheng, L.-H. Weng, M. Herberhold, *Angew. Chem.* **2005**, *117*, 264–267; *Angew. Chem. Int. Ed.* **2005**, *44*, 259–262; f) J.-Q. Wang, X.-F. Hou, L.-H. Weng, G.-X. Jin, *Organometallics* **2005**, *24*, 826–830; g) J.-Q. Wang, L.-H. Weng, G.-X. Jin, *J. Organomet. Chem.* **2005**, *690*, 249–252.

[13] a) X. Wang, S. Liu, G.-X. Jin, *Organometallics* **2004**, *23*, 6002–6007; b) X. Wang, S. Liu, L.-H. Weng, G.-X. Jin, *Organometallics* **2006**, *25*, 3565–3569; c) X. Wang, G.-X. Jin, *Organometallics* **2004**, *23*, 6319–6322; d) X. Wang, G.-X. Jin, *Chem. Eur. J.* **2005**, *11*, 5758–5764.

[14] a) A. T. Termaten, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *Chem. Eur. J.* **2003**, *9*, 3577–3582; b) W. Baratta, E. Herdtweck, W. A. Herrmann, P. Rigo, J. Schwarz, *Organometallics* **2002**, *21*, 2101–2106.

[15] a) J. C. C. Chen, I. J. B. Lin, *Organometallics* **2000**, *19*, 5113–5121; b) K. Denk, P. Sirsch, W. A. Herrmann, *J. Organomet. Chem.* **2002**, *649* 219; c) C. A. Quezada, J. C. Garrison, M. J. Panzner, C. A. Tessier, W. J. Youngs, *Organometallics* **2004**, *23*, 4846–4848.

[16] a) Review: J. C. Garrison, W. J. Youngs, *Chem. Rev.* **2005**, *105*, 3978–4008; b) A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller, R. H. Crabtree, *Organometallics* **2003**, *22*, 1663–1667; c) X. Hu, I. Castro-Rodriguez, K. Meyer, *J. Am. Chem. Soc.* **2003**, *125*, 12237–12245; d) S. Roland, M. Audouin, P. Mangeney, *Organometallics* **2004**, *23*, 3075–3078; e) L. G. Bonnet, R. E. Douthwaite, R. Hodgson, *Organometallics* **2003**, *22*, 4384–4386; f) R. S. Simons, P. Custer, C. A. Tessier, W. J. Youngs, *Organometallics* **2003**, *22*, 1979–1982.

[17] a) D. P. Klein, G. M. Kloster, R. G. Bergman, *J. Am. Chem. Soc.* **1990**, *112*, 2022–2024; b) D. A. Dobbs, R. G. Bergman, *Inorg. Chem.* **1994**, *33*, 5329–5336.

[18] a) G. Sini, O. Eisenstein, R. H. Crabtree, *Inorg. Chem.* **2002**, *41*, 602–604; b) M. Poyatos, P. Uriz, J. A. Mata, C. Claver, E. Fernandez, E. Peris, *Organometallics* **2003**, *22*, 440–444.
[19] M. Poyatos, M. Sanau, E. Peris, *Inorg. Chem.* **2003**, *42*, 2572–2576.
[20] W. A. Herrmann, J. Schwarz, *Organometallics* **1999**, *18*, 4082–4089.
[21] C. White, A. Yates, P. M. Maitlis, *Inorg. Synth.* **1992**, *29*, 228–230.
[22] M. A. Bennett, A. K. Smith, *J. Chem. Soc. Dalton Trans.* **1974**, 233–241.
[23] M. Herberhold, H. Yan, W. Milius, *J. Organomet. Chem.* **2000**, *598* 142–149.

Received: June 19, 2006