Supporting Information

Nucleophilic Addition of Carborane Anion to Ir, Rh-Coordinated Cp* Ring: C-C Bond Formation Accompany with Reduction of Metal Center

Zi-Jian Yao,[a] Yue-Jian Lin,[a] Bin Xu,[a] and Guo-Xin Jin*[a,b]

[a] Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200433, P. R. China

[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, Shanghai 200032, P. R. China.

Tel: (+86)-21-65643776, Fax: (+86)-21-65641740; E-mail: gxjin@fudan.edu.cn

Experimental Details

General Data. 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, or calcium hydride (dichloromethane) and methanol was distilled over Mg/I_2. The starting materials A-C[1], $[Cp^*MCl_2]_2$[2] (M = Ir, Rh) were synthesized according to the literature. Other chemical reagents were obtained from commercial sources and used without further purification. ^1H NMR (400 MHz) and ^{31}P NMR (162 MHz) spectra were obtained on a VAVCE DMX-400 spectrometer. ^{11}B NMR (160 MHz) was obtained on a Bruker DMX-500 spectrometer. Elemental analysis was performed on an Elementar vario EL III analyzer. IR (KBr) spectra were recorded on the Nicolet FT-IR spectrophotometer.

Synthesis of 1. *n*-BuLi (1.6 M in hexane, 0.13 mL, 0.2 mmol) was added to a solution of *o*-$C_2B_{10}H_{12}$ (29 mg, 0.2 mmol) in THF at -78 °C, the mixture was slowly warmed to 0 °C and stirred for 2h. Then the mixture was transferred by means of a cannula to a solution of A (144 mg, 0.2 mmol) in THF at 0 °C. After the above mixture was stirred for 5h at room temperature, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel. Elution with petroleum ether/CH_2Cl_2 (3:1) gave **1** as an orange solid (54.8 mg, 33%). Crystals suitable for X-ray crystallography were grown from a CH_2Cl_2 / hexane solution at room temperature. ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.25-8.20 (m, 2H, Ph), 8.04-7.98 (m, 4H, Ph), 7.69-7.60 (m, 4H, Ph), 4.66 (s, 1H, HC_{cage}), 2.00 (s, 6H, CH_3 in Cp), 1.81 (s, 6H, CH_3 in Cp), 1.53 ppm (s, 3H, CH_3–C–C_{cage}); ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C): 1.68 (2B), -3.47 (4B), -4.27 (2B) -6.01 (2B), -9.34 (5B), -11.62 (2B), -13.73 (3B); ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4, 25 °C): δ = 59.7 ppm (s, PPh_2); IR (KBr, disk): υ = 2565 (B-H), 625 cm^{-1} (P=S); elemental analysis calcd (%) for $C_{26}H_{46}B_{20}IrPS$: C 37.62, H 5.59; found: C 37.47, H 5.56.

Synthesis of 2. In a procedure analogous to the preparation of **1**, the mixture was transferred by means of a cannula to a solution of B (126 mg, 0.2 mmol) in THF at 0 °C. Yield: 53.3 mg, 36%. Crystals suitable for X-ray crystallography were grown from a CH_2Cl_2 / hexane solution at room temperature. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.01 (brs, 2H, Ph), 7.65 (brs, 4H, Ph), 7.56-7.52 (m, 4H, Ph), 4.70 (s, 1H, HC_{cage}), 2.02 (s, 6H, CH_3 in Cp*), 1.88 (s, 6H, CH_3 in Cp*), 1.54 ppm (s, 3H, CH_3-C-C_{cage}); ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C): 1.62 (2B), -3.50 (4B), -4.24 (2B) -5.98 (2B), -9.30 (5B), -11.65 (2B), -13.77 (3B); ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4, 25°C): δ = 59.9 ppm (s, PPh_2); IR (KBr, disk): υ = 2567 (B-H), 626 cm^{-1} (P=S); elemental analysis calcd (%) for $C_{26}H_{46}B_{20}IrPS$: C 42.15, H 6.26; found: C 42.36, H 6.46.

Synthesis of 3. In a procedure analogous to the preparation of **1**, the mixture was transferred by means of a cannula to a solution of C (133 mg, 0.2 mmol) in THF at 0 °C. Yield: 64.8 mg, 42%. Crystals suitable for X-ray crystallography were grown from a CH_2Cl_2 / hexane solution at room temperature. Crystals suitable for X-ray crystallography were grown from a CH_2Cl_2 / hexane solution at room temperature. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.61-8.58 (m, 2H, Ph), 8.08-8.04 (m, 4H, Ph), 7.58-7.52 (m, 4H, Ph), 4.59 (s, 1H, HC_{cage}), 2.00 (s, 6H, CH_3 in Cp), 1.86 (s, 6H, CH_3 in Cp), 1.52 ppm (s, 3H, CH_3-C-C_{cage}); ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4, 25°C): δ = 60.8 ppm (s, PPh_2); IR (KBr, disk): υ = 2567 (B-H), 632 cm^{-1} (P=S); elemental analysis calcd (%) for $C_{26}H_{46}B_{20}PRhS_2$: C 40.40, H 6.00; found: C 40.36, H 6.06.

Synthesis of 4. *n*-BuLi (1.6 M in hexane, 0.13 mL, 0.2 mmol) was added through a syringe to a stirred solution of *o*-$C_2B_{10}H_{12}$ (29 mg, 0.2 mmol) in Et_2O at -78 °C. The resulting mixture was stirred for 1 h at room temperature and then slowly added to suspension of sulfur (6.4 mg, 0.2 mmol) in THF. The solution was stirred for 2 h and transferred by means of a cannula to a solution of C (133 mg, 0.2 mmol) in THF. After stirring for 16 h, the solvent was removed under vacuum; Yield:

77.2 mg, 48%. Crystals suitable for X-ray crystallography were grown from a CH_2Cl_2 / hexane solution at room temperature. Crystals suitable for X-ray crystallography were grown from a CH_2Cl_2 / hexane solution at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.67-8.62 (m, 2H, Ph), 7.87-7.70 (m, 8H, Ph), 4.36 (s, 1H, HC_{cage}), 1.55 (s, 15H, Cp*); ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C): 1.88 (2B), -2.66(2B), -3.98 (2B), -5.44 (3B), -7.53 (4B), -10.11 (3B), -12.84 (4B); ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4, 25 °C): δ = 60.6 ppm (s, PPh_2); IR (KBr, disk): υ = 2565 (B-H), 628 cm^{-1} (P=S); elemental analysis calcd (%) for $C_{26}H_{46}B_{20}PRhS_3$: C 38.80, H 5.76; found: C 38.66, H 5.79.

X-Ray Crystallography. Diffraction data of **1-4** were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromated MoKa radiation (λ = 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),[3] SADABS[4] absorption corrections were applied to the data. All the non-hydrogen atoms except those disordered ones were refined anisotropically. In asymmetric unit of 3 and 4, the disordered dichloromethane molecules could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. A summary of the crystallographic data and selected experimental information are given in Table 1.

Computational details. All total energy density functional theory (DFT) calculations were carried out using the SIESTA package with numerical atomic orbital basis sets and Troullier-Martins norm-conserving pseudopotentials.[5, 6] The DFT functional utilized is the PBE functional,[7] a generalized gradient approximation DFT method. A double-ζ plus polarization (DZP) basis set was employed. The orbital-confining cutoff radii were determined from an energy shift of 0.01 eV. The energy cutoff for the real space grid used to represent the density was set as 150 Ry. The “External” function of the Gaussian 03 program [8] was used to call SIESTA to return energy and Cartesian forces on the atoms to the geometry optimizer of the Gaussian 03 program. The default geometry convergence criteria of the Gaussian 03 program was used where the forces and displacements of the relaxed coordinates were all less than 0.00045 Hartree/Bohr and 0.0018 Bohr, respectively. The molecule was placed in the center of a cubic supercell with a length of 50 Å for each edge. Only Γ-point was used to sample the Brillouin zone in our calculations due to the large lattice parameter of the supercell.

The DFT study showed that the salt metathesis product is obviously more stable than the isomer 4' with the C-C bond formation (Fig 1).

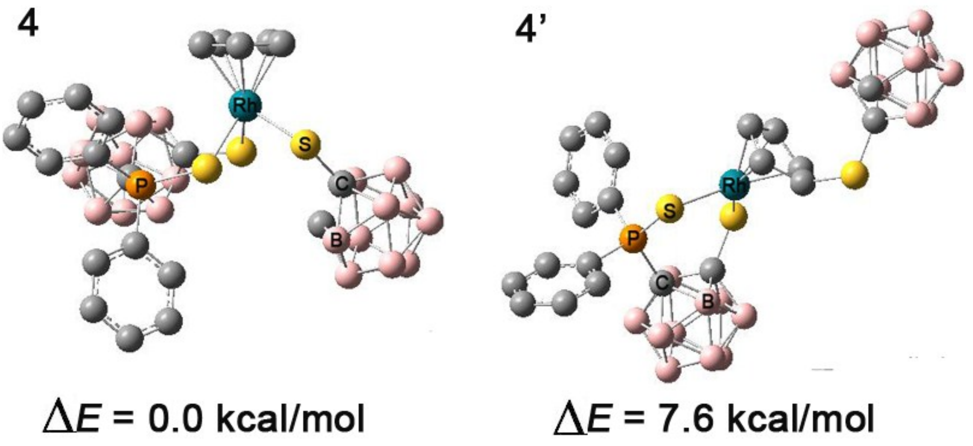

Fig. 1 DFT calculations of the two isomers.

1 Z. -J. Yao, G. -X. Jin, *Organometallics* **2011**, 30, 5365.

2 C. A. White, P. M. Yates, Maitlis, *Inorg. Synth.* **1992**, 29, 228.

3 Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*, Universität Gtötingen: Germany, 1997.

4 Sheldrick, G. M. *SADABS (2.01), Bruker/Siemens Area Detector Absorption Correction Program*; Bruker AXS: Madison, WI, 1998.

5 J. Junquera, O. Paz, D. Sanchez-Portal, E. Artacho, *Phys. Rev. B* **2001**, *64*, 235111.

6 N. Troullier, J. L. Martins, *Phys. Rev. B* **1991**, *43*, 1993.

7 J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.

8 Gaussian 03, Revision B.05, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Jr Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc.: Pittsburgh, PA, **2003**.

Table 1. Crystallographic Data and Structure Refinement Parameters for **1-4**

	1	**2**	**3**	**4**
Chemical Formula	$C_{26}H_{46}B_{20}IrPS$	$C_{26}H_{46}B_{20}RhPS$	$C_{27}H_{48}B_{20}Cl_2PRhS_2$	$C_{28}H_{50}B_{20}Cl_4PRhS_3$
FW	830.06	740.77	857.75	974.74
T/[K]	293(2)	293(2)	293(2)	293(2)
λ/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	*P*-1	*P*2(1)	*P*2(1)/n
a/Å	11.244(4)	11.212(5)	12.013(4)	14.916(9)
b/Å	11.832(4)	11.898(5)	29.317(9)	11.926(7)
c/Å	15.257(5)	15.278(6)	12.157(4)	27.143(15)
α/°	72.870(4)	72.745(5)	90	90
β/°	71.415(4)	71.626(5)	96.824(4)	101.332(9)
γ/°	86.425(4)	86.357(5)	90	90
V/$Å^3$	1837.5(11)	1846.2(13)	4251(2)	4734(5)
Z	2	2	4	4
ρ/Mg m^{-3}	1.500	1.333	1.340	1.368
μ/mm^{-1}	3.755	0.584	0.686	0.777
F(000)	820	756	1744	1976
θ range/°	1.80-25.01	1.47-25.01	1.389-26.010	1.451-25.008
Reflections collected	7588	7668	19307	19120
Completeness to θ	97.8 %	97.9 %	99.6 %	97.1 %
Data/restraints/param.	6333 / 1 / 471	6373 / 0 / 471	12762 / 3 / 920	8312 / 1 / 468
Goodness-of-fit on F^2	1.011	1.052	0.923	0.812
Final R indices [I>2σ(I)[a]]	R1 = 0.0349 wR2 = 0.0879	R1 = 0.0450, wR2 = 0.1386	R1 = 0.0419, wR2 = 0.0968,	R1 = 0.0641, wR2 = 0.1522
Largest diff.peak/ hole (e $Å^{-3}$)	2.141 / -1.489	0.622 / -0.452	0.673 / -0.267	2.160 / -0.394
Absolute structure parameter			0.00(5)	