新型的含硫族元素碳硼烷配体的三(3,5-二甲基-1-吡唑)硼氢钼配合物的合成和分子结构

李 玮 金国新*
(复旦大学化学系,上海市分子催化和功能材料重点实验室,上海 200433)

摘要: 三齿单核三(3,5-二甲基-1-吡唑)硼氢钼配合物 $Tp^*Mo(O)Cl_2$ (**1**)(Tp^*=三(3,5-二甲基-1-吡唑)硼氢 $HB(C_3H(Me_2)N_2)_3$)与含硫族元素碳硼烷的锂盐$[(THF)_3LiE_2C_2B_{10}H_{10}(THF)]_2$ [E=S(**2a**),Se(**2b**),Te(**2c**)]反应得到了单核配合物 $Tp^*Mo(O)E_2C_2B_{10}H_{10}$ [E=S(**3a**),Se(**3b**),Te(**3c**)], 产率较好。配合物 **3a~3c** 通过红外光谱和元素分析表征,解析了 **3b** 的 X-射线单晶结构。在空气中,配合物 **3a** 可以生成一新颖的含氧桥的双核钼的配合物$[HMe_2Pz][Tp^*Mo(O)(\mu_2\text{-}O)_2Mo(O)S_2C_2B_{10}H_{10}]$ **4a**。解析了 **4a** 的 X-射线单晶结构。Mo-Mo 间键长为 0.254 83(12) nm,为单键相互作用。

关键词: 三(3,5-二甲基-1-吡唑)硼氢; 钼配合物; 碳硼烷; 硫族元素;晶体结构
中图分类号: O611.4; O613.41; O613.8+1 **文献标识码**: A **文章编号**: 1001-4861(2005)06-0846-06

Synthesis and Molecular Structures of Novel Hydrotris (3,5-dimethyl-1-pyrazolyl)borate Molybdenum Complexes Containing 1,2-Dicarba-closo-dodecaborane-1,2-dichalcogenolato Ligands

LI Wei JIN Guo-Xin*
(*Laboratory of Molecular Catalysis and Innovative Material, Department of Chemistry, Fudan University, Shanghai* 200433)

Abstract: Reactions of tridentate mononuclear hydrotris (3,5-dimethyl-1-pyrazolyl) borate molybdenum(V) complex $Tp^*Mo(O)Cl_2$ (**1**) (Tp^*=hydrido-tris 3,5-dimethyl-1-pyrazolyl-borate, $HB(C_3H(Me_2)N_2)_3$) with dilithium dichalcogenolate carboranes $[(THF)_3LiE_2C_2B_{10}H_{10}(THF)]_2$ [E=S(**2a**), Se(**2b**), Te(**2c**)] afforded mononuclear complexes $Tp^*Mo(O)E_2C_2B_{10}H_{10}$ [E=S(**3a**), Se(**3b**), Te(**3c**)] in moderate yields. Complexes **3a~3c** have been characterized by IR and elemental analysis. The molecular structure of **3b** was determined by X-ray crystallographic analysis. In the air **3a** can convert into a novel binuclear oxo molybdenum complex $[HMe_2Pz][Tp^*Mo(O)(\mu_2\text{-}O)_2Mo(O)S_2C_2B_{10}H_{10}]$ **4a**. The molecular geometry of **4a** has been determined by a single crystal X-ray structure analysis. According to the short Mo-Mo distance (0.254 83(12) nm), direct metal-metal interaction exists. CCDC: 263618, **3b**; 263619, **4a**.

Key words: hydrotris(3,5-dimethyl-1-pyrazolyl)borate; molybdenum complex; carborane; chalcogenolato; crystal structures

0 Introduction

Tris(pyrazolyl)borate (TpR, R′=hydrotris(3-R-5-R′-pyrazolyl)-borate) ligands have proved very versatile reagents for the preparation of a huge range metal sandwich and half-sandwich complexes, in part due to the large number of substitutable positions available on the pyrazole rings[1], they are widely used in the design of functional molecules, catalysis of chiral induced asymmetric synthesis, liquid crystal materials, molecular′ electronic devices′ and biomimetic chemistry[2,3]. Half-sandwich mononuclear complexes with

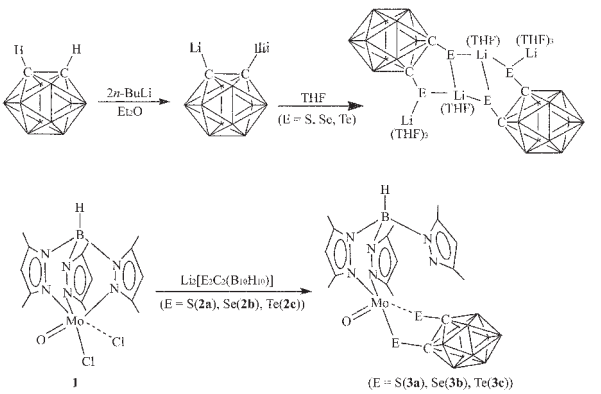
收稿日期:2005-03-05。收修改稿日期:2005-04-30。
国家自然科学杰出青年基金项目(No.29925101,20274008)和教育部博士点基金项目资助。
*通讯联系人。E-mail:gxjin@fudan.edu.cn; Tel: +86-21-65643776; Fax: +86-21-65641740
第一作者:李 玮,男,38 岁,博士研究生;研究方向:金属有机化学。

mono-hydrotris (pyrazolyl)borate ligand and small molecules or anions can be considered as the complexes of metalloenzymes such as carbonic anhydrase (CA)[4] and nitrite reductases[5], and as the precursors for the syntheses of various multinuclear model complexes[6]. Molybdenum is an essential trace element which is found in enzymes such as xanthine oxidase, sulfite oxidase, and nitrate reductase[7]. The chemical reactions catalyzed by these enzymes all involve a change in the number of oxygen atoms in the substrate, and there is strong evidence that these enzymes posses a common molybdenum cofactor[8]. EXAFS studies support a mononuclear molybdenum center with at least two RS^- ligands bound to the molybdenum atom[9]. Due to the unique molecular structures of 1,2-dicarba-*closo*-dodecaborane(12) and organothiolato complexes, during the past decade considerable attention has been devoted to transition metal complexes and organolanthanide complexes with dichalcogenolate o-carboranyl ligands. Recently, a large number of complexes with the chelating 1,2-dicarba-*closo*-dodecaborane (1,2)-dicalcogenolato ligands have been reported by our group and other groups[10]. However, to our knowledge, up to now complexes containing both tris (pyrazolyl)borate ($Tp^{R,R'}$=hydrotris (3-R-5-R′-pyrazolyl) -borate) ligands ($[HB(pz)_3]^-$ (Tp^-) and $[HB(Me_2pz)_3]^-$ (Tp^{*-}) as tridentate σ-bonding counterparts of the π-bonding $C_5H_5^-$ and $C_5Me_5^-$) and dichalcogenolate o-carboranyl ligands are scarcely investigated. This prompted us to investigate the syntheses of these complexes, we now report the syntheses and X-ray structural characterization of molybdenum complexes containing both hydrotris (3,5-dimethyl-1-pyrazolyl) borate and dichalcogenolate *o*-carboranyl ligands.

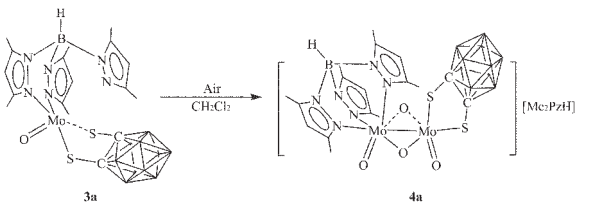
1　Results and discussion

The synthetic approach to the complexes (**3a**), (**3b**), (**3c**) is outlined in Scheme 1.

Elemental chalcogen E (E=S, Se, Te) could easily insert into Li-C bonds of dilithium o-carborane in Et_2O solution, which afforded dimers of dilithium dichalcogenolate carboranes, $[(THF)_3LiE_2C_2B_{10}H_{10}(THF)]_2$ [E =S (**2a**), Se (**2b**), Te (**2c**)] in THF solution[10]. Tridentate mononuclear hydrotris (3,5-dimethyl-1-pyrazolyl)borate molybdenum(V) complex $Tp^*Mo(O)Cl_2$ (**1**) reacted with one equivalent of $[(THF)_3LiE_2C_2B_{10}H_{10}(THF)]_2$ [E=S(**2a**), Se(**2b**), Te(**2c**)] with the replacement of both chloride ligands to give **3a**, **3b**, **3c** in moderate yields, after chromatographic purification over silica gel, which all are characterized by IR and elemental analysis. ^1H NMR spectra of complexes **3a**, **3b** and **3c** show paramagnetic properties and indicate that the oxidation state of these complexes in molybdenum center is Mo(V). The IR spectra exhibit the expected bands for the B-H bond (*ca.* 2 600 cm^{-1} (carborane), *ca.* 2 500 cm^{-1} (Tp^*)) and the terminal Mo=O bond (*ca.* 960 cm^{-1}). The infrared spectrum of complex **1** of the (3,5-dimethylpyrazolyl) borate ligand, where it functions in a tridentate fashion, show a single sharp band at ~1 542 cm^{-1} in the region for an aromatic C-N stretch in the coordinated pyrazole ring, while the infrared spectra of complexes **3a~3c** show two infrared bands in this region, one at 1 570 cm^{-1} of the uncoordinated arm and one at 1 542 cm^{-1} for the coordinated rings, suggesting the ligand is bidentate. X-ray structure analysis of complex **3b** confirmed that it was really bidentate complex with one dangling 3,5-dimethylpyrazolyl ring (Fig.1). Such structures have been reported for other metals[11,12]. The strong preference of Mo unit to adopt a square-pyramidal geometry may be responsible for the bidentate binding of the ligand to the molybdenum. The facial geometry imposed by simultaneous coordination of all three rings is incompatible with a square-pyramidal,



Scheme 1　Synthesis of complexes **3a~3c**



Scheme 2　Synthesis of complexes **4a**

and the ligand adopts a bidentate mode in relatively uncoordinating solvent such as THF.

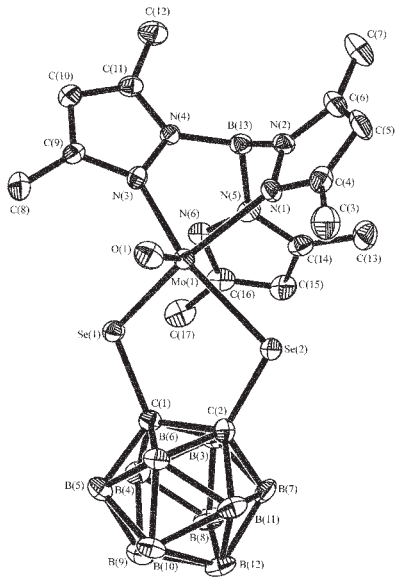


Fig.1 Molecular structure of **3b**

Selected lengths (nm) and angles (°):

Mo(1)-O(1) 0.166 8(4), Mo(1)-Se(1) 0.247 19(11), Mo(1)-Se(2) 0.246 04(11), Mo(1)-N(1) 0.217 6(4), Mo(1)-N(3) 0.218 1(5), C(1)-C(2) 0.163 3(7); O(1)-Mo(1)-N(1) 104.13(18), O(1)-Mo(1)-N(3) 104.3(2), N(1)-Mo(1)-N(3) 83.94 (18), Se(2)-Mo(1)-Se(1) 88.03(2), O(1)-Mo(1)-Se(1) 107.97(14), C(1)-Se(1)-Mo(1) 106.59(15).

In the air, complex **3a** can convert into the novel binuclear oxo molybdenum complex $[Me_2PzH][Tp^*Mo(O)(\mu_2\text{-}O)_2Mo(O)S_2C_2B_{10}H_{10}]$ **4a**, which contains two oxo-bridge. There is hydrogen bond interaction between one terminal oxygen and one Me_3pzH molecule (Fig.3). Single crystal X-ray diffraction analysis shows that Mo-Mo exists interactions, whose bond length is 0.254 83(12) nm, which is within a single bond length (Fig.2). Several potential pathways for decompositions of tris (pyrazolyl)borate compounds have been advanced. These include hydrolysis of the B-N bond by traces of water in the solvent used[13], or the abstraction of the oxophilic boron by oxygenated solvents [14]. Attempts to the synthesis of corresponding selenium and tellurium complexes **4b** and **4c** were not successful.

The molecular structure[15] of **3b** is mononuclear complex, shown with the atomic labeling in Fig.1. Mo is five-coordinate with square-pyramidal coordination, having one terminal oxo ligand in the apical position

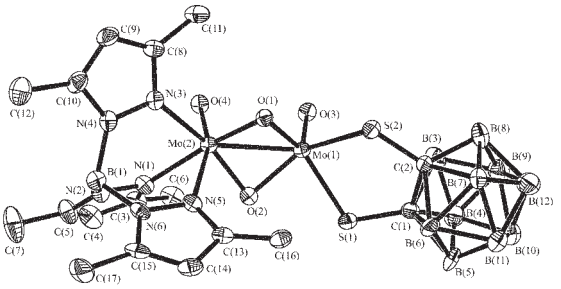


Fig.2 Anionic structure of complex **4a**

Selected lengths (nm) and angles (°):

Mo(1)-O(3) 0.168 5(4), Mo(1)-O(1) 0.194 6(4), Mo(1)-O(2) 0.194 8(4), Mo(1)-S(1) 0.239 9(2), Mo(2)-O(4) 0.169 4(4), Mo(2)-O(1) 0.191 6(4), Mo(1)-Mo(2) 0.2548 3(12), Mo(2)-N(1) 0.218 2(5); S(1)-Mo(1)-S(2) 127.26(6), O(3)-Mo(1)-O(1) 111.04(19), O(1)-Mo(1)-O(2) 91.15(17), O(3)-Mo(1)-Mo(2) 102.15(15), O(1)-Mo(1)-Mo(2) 48.21(13), Mo(1)-O(1)-Mo(2) 82.56(16), S(1)-Mo(1)-Mo(2) 127.26(6), O(4)-Mo(2)-O(1) 105.83(19), O(1)-Mo(2)-O(2) 92.77(17), O(1)-Mo(2)-N(1) 164.68(18), O(1)-Mo(2)-N(3) 88.81(19).

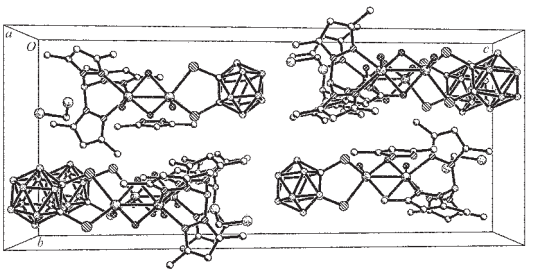


Fig.3 Stacking diagram of **4**

(Mo1-O1=0.166 8(4) nm), two bridging selenium atoms of diselenolato-carborane (Mo1-Se1=0.247 19(11) nm; Mo1-Se2=0.246 04(11) nm), two nitrogen atoms of pyrazole (Mo1-N1=0.217 6(4) nm; Mo1-N3=0.218 1(5) nm). The angles of O1-Mo1-N1 and the O1-Mo1-N3 are 104.3(2) and 104.13(18)° respectively. The N1-Mo-N3 angle is 83.94(18)°. The Se1-Mo-Se2 angle is 88.03(2)°. The large Se-Mo-O angles (O(1)-Mo(1)-Se(1) =107.97(14)° and O(1)-Mo(1)-Se(2)=108.89(15)°) can be explained by nonbonded repulsion between the filled pπ orbitals on selenium and the π-electron density in Mo=O bond[16].

The molecular structure[15] of **4a** is binuclear complex, shown with the atomic labeling in Fig.2. The molecule contains two distinct molybdenum atoms. Mo1 is five-coordinate with square-pyramidal coordination, having one terminal oxo ligand in the apical

position, two bridging sulfur atoms of dithio-carborane, two equatorial oxo bridges to Mo2. The two bridging oxygen atoms and the two sulfur atoms forms the basal plane (coplanar to within 0.004 5 nm), the Mo1 atom being displaced by 0.068 03 nm from this plane and the apical oxygen atom by 0.236 594 nm. The bond angles about the Mo1 atom deviate from square-pyramidal geometry. The angles of O3-Mo1-O1 and O3-Mo1-O2 are 111.04(19)°, 110.49(19)°, respectively. The angles of O3-Mo1-S1 and O3-Mo1-S2 are 106.09 (15)°, 106.19 (16)°, respectively. The dihedral angle between the plane Mo1, S1, S2 and the plane containing S1, C1, C2, S2 is 158.13°. The five-membered metallacycle Mo(1)S(1)C(1)C(2)S(2) has a distorted envelop conformation. The Mo2 atom has distorted-octahedral coordination geometry, with Tp* ligand occupying one trigonal face. A terminal oxo ligand (Mo2-O4=0.169 4(4) nm) and two bridging oxo ligands (Mo2-O1=0.191 6(4) nm; Mo2-O2=0.192 5(4) nm) occupy the opposite face. The Mo2-N distances show the usual trans influence with Mo2-N5 trans to O4 being longer than the other Mo2-N bond distances (Mo2-N1=0.218 2(5) nm; Mo2-N3=0.219 5(5) nm; Mo2-N5=0.234 6(5) nm). Other bond distances and angles in the Tp* ligand and the coordination spheres are normal[17]. The dihedral angle between the Mo1-O1-Mo2 plane and the Mo1-O2-Mo2 plane is 145.82°. Similar to that $[Tp^*MoS(\mu\text{-}S)_2MoO(\mu\text{-}OH)]_2$ with syn stereochemistry (148°)[18]. The two terminal oxo groups are syn with respect to each other and the Mo1-O1-Mo2-O2 four-membered ring is puckered. The Mo1=O3 bond is shorter than the Mo2=O4 bond because of the pyrazolylborate ligand nitrogen atom in the position trans to Mo2=O4. In general, Mo=E (E=O, S) bonds are shorter in square pyramidal than in octahedral complexes[19]. The five-coordinate Mo1 atom is bonded to O3 in the apical position at a distance of 0.168 5(4) nm. O3 and one Me_3pzH molecule has hydrogen bond interaction (N7-H7=0.089 7(10) nm, O3-H7=0.188 7(15) nm, N7-O3=0.278 1(8) nm, N7-H7-O3=174(6)°) (Fig.3). The oxygen atoms bridging to Mo2 at distances of 0.194 6(4) and 0.194 8(4) nm while the oxygens bridging to Mo1 at distances of 0.191 6(4) and 0.192 5(4) nm. The distance between Mo1 and Mo2 is 0.254 83(12) nm, indicating the presence of a single bond[20]. In the di-μ-oxo- bis [di (benzenethiolato)oxomolybdate(V)] dianion, which is based on the same central atomic configuration, mean bond lengths are Mo-S 0.244 7 nm, Mo-O (bridging) 0.193 7 nm and Mo-O (terminal) 0.167 7 nm, Mo-Mo 0.261 nm[20]. Similarly, in the dimeric anion $[\{Mo(=O)(\mu\text{-}O)(S_2C_2B_{10}H_{10})_2\}]^{2-}$, which is based on the same central atomic configuration, mean bond lengths are Mo-S 0.242 3 nm, Mo-O (bridging) 0.193 8 nm and Mo-O (terminal) 0.167 3 nm, Mo-Mo 0.256 5(1) nm[21].

2 Experimental

2.1 General procedures

All manipulations were performed under a dry, oxygen-free, nitrogen or argon atmosphere using standard Schlenk techniques. THF, toluene, ether, and hexane were freshly distilled over sodium benzophenone. Dicholomethane was dried and distilled over CaH_2. The starting materials potassium hydrotris (3,5-dimethyl-1-pyrazolyl) borate (KTp^*)[22], $Tp^*Mo(O)Cl_2$ (**1**)[23] and $[(THF)_3LiE_2C_2B_{10}H_{10}Li(THF)]_2$ (E=S(**2a**), Se(**2b**), Te(**2c**))[10b] were prepared according to the literature methods, while other chemicals were obtained commercially and used without further purification. IR spectra were measured on a Nicolet Avatar-360 spectrophotometer (as the KBr pellet). NMR spectra were recorded on a Brucker DMX-500 spectrometer. Mass spectra were carried out on a Finnigan MAT 8500 (70) instrument. Elemental analyses were carried out on a German Elementar Vario EI analyzer.

2.2 Preparations of complexes $\{HB(Me_2Pz)(Me_2Pz)_2\}Mo(O)E_2C_2B_{10}H_{10}$ [E=S(3a), Se(3b), Te(3c)]

A solution of 2 mmol (0.29 g) o-carborane, 1,2-$C_2B_{10}H_{10}$, in 40 mL of diethylether was lithiated by addition of 2.75 mL of a 1.6 mol·L^{-1} solution of butyllithium (4.4 mmol) in hexane. The corresponding amount (4.4 mmol) of the elemental chalcogen (E=S, Se, Te) was added and the solution stirred for 1-6 h (depending on the chalcogen E=S (1 h), Se (3 h), Te (6 h) at ambient temperature to give the corresponding 1,2-carborane-1,2-dichalcogenolates, and afforded dimers of dilithium dichalcogenolate carboranes, $[(THF)_3LiE_2C_2B_{10}H_{10}(THF)]_2$ [E=S(**2a**), Se(**2b**), Te(**2c**)] in THF solution.

A solution of 2 mmol (0.96 g) $Tp^*Mo(O)Cl_2$ (**1**) in 40 mL THF was added to the above Et2O/THF solutions slowly, respectively. The reaction mixture was

stirred 24 h at room temperature, then the solvents were evaporated under reduced pressure. The residue was redissolved in CH_2Cl_2 and the product purified by column chromatography on silical gel. Elution with CH_2Cl_2-hexane (4:1) gave a red zone of 5, 6, 7, respectively. Recrystallization from CH_2Cl_2-hexane got red crystals.

3a: red crystals, yield 0.67 g (55%). IR (KBr): ν(B-H) 2 578, 2 655 cm^{-1} (carborane), 2 536 cm^{-1} (Tp*); ν(C-N) 1 543, 1 575 cm^{-1}; ν(Mo=O): 963 cm^{-1}. Elemental analysis $C_{17}H_{33}B_{11}MoN_6OS_2$ (615.74), Anal. Calc. (%) C, 33.77; H, 5.33; N, 13.90; S, 10.61, found (%) C, 33.80; H, 5.57; N, 13.76; S, 10.33.

3b: red crystals, yield 0.84 g (60%). IR (KBr): ν(B-H) 2 574, 2 642 cm^{-1} (carborane), 2 566 cm^{-1} (Tp*); ν(C-N) 1 542, 1 570 cm^{-1}; ν(Mo=O): 965 cm^{-1}. Mp=192 ℃ (dec). Elemental analysis $C_{17}H_{33}B_{11}MoN_6OSe_2$ (709.66), Anal. Calc. (%) C, 29.23; H, 4.61; N, 12.04, found (%) C, 29.13; H, 4.78; N, 11.73.

3c: red crystals, yield 0.99 g (62%). IR (KBr): ν(B-H) 2 571, 2 640 cm^{-1} (carborane), 2 570 cm^{-1} (Tp*); ν(C-N) 1 542, 1 570 cm^{-1}; ν(Mo=O): 963 cm^{-1}. Elemental analysis $C_{17}H_{33}B_{11}MoN_6OTe_2$ (806.94), Anal. Calc. (%) C, 25.32; H, 4.00; N, 10.42, found (%) C, 25.40; H, 3.92; N, 10.44%.

4a: A solution of **3a** (0.12 g, 0.19 mmol) in CH_2Cl_2 was exposed in air for several days and **3a** as red needle crystals was formed and isolated (yield 0.024 g (29%)). IR (KBr): ν(B-H) 2 579, 2 668 cm^{-1} (carborane), 2 536 cm^{-1} (Tp*); ν(C-N) 1 543, 1 575 cm^{-1}; ν(Mo=O): 964 cm^{-1}. ^1H NMR ($CDCl_3$): δ=2.19 (s, 6H, CH_3), 2.36 (s, 6H, CH_3), 2.70 (s, 6H, CH_3), 6.11 (s, 2H, CH), 6.20 (s, 1H, CH). Elemental analysis $C_{22}H_{40}B_{11}Mo_2N_8O_4S_2$ (855.46), Anal. Calc. (%) C, 30.86; H, 4.68; N, 13.09; found (%): C, 30.80; H, 4.57; N, 13.14.

References:

[1] Trofimenko S. *Chem. Rev.*, **1993**,**93**:943~980

[2] Parkin G. *Adv. Inorg. Chem.*, **1995**,**42**:291~393

[3] Kitajima N., Talman W B. *Prog. Inorg. Chem.*, **1995**,**43**:419~531

[4] Han R Y, Parkin G. *J. Am. Chem. Soc.*, **1991**,**113**:9707~9708

[5] Ruggiero C E, Carries S M, Tolman W B. *Angew. Chem., Int. Ed. Engl.*, **1994**,**33**:895~897

[6] Cho S H, Whang D, Han K N, et al. *Inorg. Chem.*, **1992**,**31**:519~522

[7] Spence J T. *Coord. Chem. Rev.*, **1983**,**48**:59~82

[8] Johnson J L, Rajogopalan K V. *Proc. Natl. Acad. Sci. U. S. A.* 79, **1982**.6856~6863

[9] Cramer S P. *Adv. Inorg. Bioinorg. Mech.*, **1983**,**2**:259~274

[10](a)Jin G X. *Coord. Chem. Rev.*, **2004**,**248**:587~602

(b)Yu X Y, Jin G X, Hu N H. *Organometallics*, **2002**,**21**:5540~5548

(c)Lu S X, Jin G X, Herberhold M. *Organometallics*, **2002**,**21**:2533~2535

(f)Herberhold M, Yan H, Milius W, et al. *Angew. Chem. Int. Ed. Engl.*, **1999**,**38**:3689~3691

(g)Herberhold M, Jin G X, Yan H, et al. *Eur. J. Inorg. Chem.*, **1999**:873~875

(h)Herberhold M, Jin G X, Yan H, et al. *J. Organomet. Chem.*, **1999**,**587**:252~257

(i)Kim D H, Ko J, Park K, et al. *Organometallics*, **1999**,**18**:2738~2740

(k)Jin G X, Wang J Q, Zhang C, et al. *Angew. Chem., Int. Ed. Engl.*, **2005**,**44**:259~262

(l)Li W, Weng L H, Jin G X. *Inorg. Chem. Commun.*, **2004**,**7**:1174~1177

[11]Cowley A H, Greerts R L, Nunn C M, et al. *J. Organomet. Chem.*, **1988**,**341**:C27~C30

[12]Ellen K H, Spartalian K, Nunn C M, et al. *Inorg. Chem.*, **1989**,**28**:4392~4399

[13]Cotton F A, Dori Z, Llusar R, et al. *Inorg. Chem.*, **1986**,**25**:3529~3532

[14]Hughes D L, Leigh G J, Walker D G. J. *Chem. Soc. Dalton. Trans.*, **1988**:1153~1157

[15]Crystal data. For **3b**: $C_{17}H_{33}B_{11}MoN_6OSe_2$, M_r=710.28, monoclinic, Space group, $P2_1$, a=0.982 6(4), b=1.599 8(6), c=1.061 2(4) nm, β=114.494(5)°, V=1.518 0(9) nm^3, Z=2, D_c=1.593 $Mg\cdot m^{-3}$, F(000)=720, 6 348 reflections measured ($2.11<\theta<25.01°$), 5 119 unique (R_{int}=0.035 6) and 5 119 observed reflections [$I>2\sigma(I)$], final R_1=0.036 1, wR_2=0.063 5. For **4a** $C_{23}H_{42}B_{11}Cl_2Mo_2N_8O_4S_2$, M_r=940.46, monoclinic, Space group, $P2_1/n$, a=1.044 2(4), b=1.295 9(5), c=3.072 8(11) nm, β=96.008(6)°, V=4.135(3) nm^3, Z=4, D_c=1.511 $Mg\cdot m^{-3}$), F(000)=1 892, 18 619 reflections measured ($1.33°<\theta<26.0°$), 8 112 unique (R_{int}=0.080 7) and 8 112 observed reflections [$I>2\sigma(I)$], final R_1=0.059 2, wR_2=0.059 2. Crystal structure measurements for **3b** and **4a** were performed on a Siemens SMART CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm) at room temperature. The structures are solved using direct methods and refined on F^2 by fullmatrix least-squares methods using the SHELX-97 program package. All atoms except for hydrogen were refined anisotropically. CCDC 263618 and CCDC 263619 for **3b** and **4a**, respectively, contain the supplementary

crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving. html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[16]Yamanouchi K, Enemark J H. *Inorg. Chem.*, **1979**,**18**:1626~1633

[17]Barnhart K M, Enemark J H. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun. C*40, **1984**:1362~1367

[18]Roberts S A, Charles G Y, Cleland W E. *J. H. Enemark, Inorg. Chem.*, **1988**,**27**:2647~2652

[19]Young C G, Roberts S A, Ortega R B, et al. *J. Am. Chem. Soc.*, **1987**,**109**:2938~2946

[20]Young H, Wong E H, Jasinski J P, et al. *Organometallics*, **1992**,**11**:1579~1586

[21]Mckinney J D, Chen H, Hamor T A, et al. *J. Chem. Soc. Dalton Trans.*, **1998**:2163~2168

[22]Trofimenko S. *J. Am. Chem. Soc.*, **1967**,**89**:6288~6294

[23]Cleland W E, Mabbs F E, Ortega R B, et al. I*norg. Chem.*, **1987**,**26**:1017~1025