ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Cyclopentadienyl Molybdenum(II) N,C-Chelating Benzothiazole-Carbene Complexes: Synthesis, Structure, and Application in Cyclooctene Epoxidation Catalysis

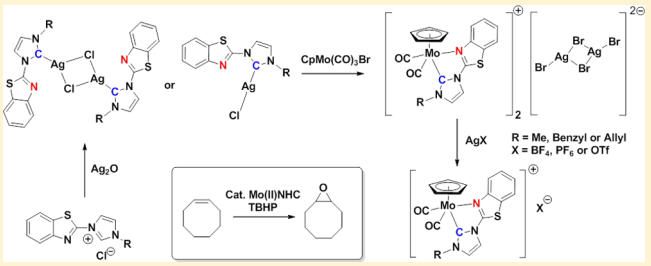
Zhe Wang,[†] Sin Wee Benny Ng,[†] Lu Jiang,[†] Wen Jin Leong,[†] Jin Zhao,*[,†,‡] and T. S. Andy Hor*[,†,‡]

[†]Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

[‡]Institute of Materials Research and Engineering, Agency for Science, Technology and Research, 3 Research Link, Singapore 117602, Singapore

Supporting Information

ABSTRACT: A series of new benzothiazolyl-imidazolium salts **1**−**3** (1-(benzothiazol-2-yl)-3-methylimidazolium chloride (**1**); 1-(benzothiazol-2-yl)-3-benzylimidazolium chloride (**2**); 1-(benzothiazol-2-yl)-3-allylimidazolium chloride (**3**)) have been prepared from nucleophilic substitution of 2-chlorobenzothiazole by imidazoles. They serve as the precursors of hybrid N-heterocyclic carbene (NHC) ligands **L1**−**L3** (**L1** = 1-(benzothiazolin-2-yl)-3-methylimidazol-2-ylidene; **L2** = 1-(benzothiazolin-2-yl)-3-benzylimidazol-2-ylidene; **L3** = 1-(benzothiazolin-2-yl)-3-allylimidazol-2-ylidene). Reactions of **1**−**3** with Ag_2O result in Ag(I) NHC complexes **4**−**6** $[Ag(L)(\mu\text{-}Cl)]_2$ (L = **L1**, **4**; L = **L2**, **5**) and Ag(**L3**)Cl (**6**), in which **L1**−**L3** act as monodentate carbene ligand with a benzothiazolyl pendant. Subsequent transmetalation of **4**−**6** with $CpMo(CO)_3Br$ (Cp = cyclopentadienyl) and anion exchange reaction with AgX (X = BF_4, PF_6, or OTf) give complexes $[CpMo(CO)_2(L)]_2[Ag_2Br_4]$ (L = **L1**, **7a**; L = **L2**, **8a**; L = **L3**, **9a**) and $[CpMo(CO)_2(L)][X]$ (L = **L1**, X = BF_4, **7b**; L = **L2**, X = BF_4, **8b**; X = PF_6, **8c**; X = OTf, **8d**; L = **L3**, X = BF_4, **9b**), whose structures are reported herein. The ligands **L1**−**L3** show their versatility by switching to be N,C-chelating in these Mo(II) complexes. The chelation of the hybrid NHC ligand results in shorter Mo−$C_{carbene}$ bonds (2.14−2.16 Å) comparing with known Mo(II) NHC complexes in the literature. These complexes are active toward cyclooctene epoxidation with *tert*-butyl hydroperoxide (TBHP) affording up to 90% yield of epoxide (for **8b**) in 3 h at 55 °C.



INTRODUCTION

N-Heterocyclic carbenes (NHCs) have attracted intense research interest as stable ligand supporting active catalysis.[1] Recently, many efforts have been dedicated to the design of hybrid NHC ligands containing other donor function in order to add coordinative flexibility with metal center. In many instances, these result in excellent catalytic outcomes.[2,3] As part of our continual interest in hybrid NHC ligands,[4] we herein report a series of new benzothiazolyl-imidazolium salts and their use as NHC precursor in the synthesis of Ag(I)-NHC complexes and cyclopentadienyl (Cp) molybdenum(II) NHC complexes. We have recently demonstrated catalytic activities of CpMo(II) complex with simple monodentate NHC ligand toward cyclooctene epoxidation using *tert*-butyl hydroperoxide (TBHP) as oxidant at 55 °C and found that with 1 mol % of catalyst loading the ionic complexes $[CpMo(CO)_2(IMes)]^+$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) and $[CpMo(CO)_2(IBz)]^+$ (IBz = 1,3-dibenzylimidazol-2-ylidene) gave epoxide yield of ca. 85% after 4 h reaction time.[5,6] Oxidation of these complexes leads to the high-valent dioxo-Mo(VI)-NHC ionic complexes, which are mechanistically related with the Mo(II) precursor in the epoxidation catalysis.[5,6] This has prompted us to investigate whether similar type of complexes but supported by hybrid-NHC ligands possesses higher catalytic performance and whether the counterion of these ionic NHC complexes has influence on the catalytic activities.

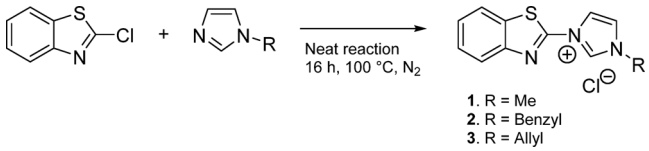
RESULTS AND DISCUSSION

Synthesis and Characterization of the NHC Precursors and the Ag(I)NHC Complexes. Nucleophilic substitution of 2-chlorobenzothiazole with substituted imidazoles under neat conditions (solvent free) gives new functionalized imidazolium salts **1**−**3** (1-(benzothiazol-2-yl)-3-methylimidazolium chloride, **1**; 1-(benzothiazol-2-yl)-3-benzylimidazolium chloride, **2**; 1-(benzothiazol-2-yl)-3-allylimidazolium chloride, **3**) (Scheme 1) in 60−73% yields. The ^1H and ^{13}C NMR spectra of **1**, **2**, and **3** in DMSO-d_6 show downfield resonances of the NC*H*N protons at δ 10.54, 10.84, and 10.48 ppm and of the NCHN carbon at δ 137.54, 137.12, and 137.12 ppm, respectively.

Received: November 21, 2013

   dx.doi.org/10.1021/om401128z | *Organometallics* XXXX, XXX, XXX−XXX

Scheme 1. Synthesis of the Benzothiazolyl-Imidazolium Salts 1−3



The salts **1**−**3** were refluxed with Ag_2O in 1,2-dichloroethane giving Ag(I)-NHC complexes **4**−**6** in 67−75% yields. Their molecular structures are revealed by single-crystal X-ray diffraction analysis (see below). Complex **4** and **5** are dinuclear with general formula of $[Ag(L)(\mu\text{-}Cl)]_2$, (L = **L1** = 1-(benzothiazolin-2-yl)-3-methylimidazol-2-ylidene, **4**; L = **L2** = 1-(benzothiazolin-2-yl)-3-benzylimidazol-2-ylidene, **5**). Complex **6** is a mononuclear complex as Ag(L)Cl, (L = **L3** = 1-(benzothiazolin-2-yl)-3-allylimidazol-2-ylidene). The signals at δ 180.75 ppm (**4**), 180.84 ppm (**5**), and 180.67 ppm (**6**) in their ^{13}C NMR spectra (in DMSO-d_6) are indicative of the Ag−$C_{carbene}$ bond formation.

As shown in the molecular structures of **4**−**6** (Figures 1−3), in all three complexes the hybrid NHCs **L1**−**L3** act only as monodentate ligand with the benzothiazolyl nitrogen and sulfur atoms uncoordinated. In **4** and **5**, the $[Ag_2Cl_2]$ core is planar with the chlorides asymmetrically bound to the silver center with different Ag(1)−Cl(1) (2.4089(7) Å in **4**, 2.7849(7) Å in **5**) and Ag(1)−Cl(1A) (2.7865(7) Å in **4**, 2.4005(7) Å in **5**) bond distances. The Ag···Ag distances of **4** (3.789 Å) and **5** (3.650 Å) indicate the absence of interactions. Close proximity between Ag and S atoms in **4** (3.133 Å) and **5** (2.982 Å) could suggest weak secondary interactions.[7] This is supported by the inward orientation of the sulfur facing the metal. The Ag−$C_{carbene}$ bond lengths (2.098(2) Å in **4** and 2.094(3) Å in **5**) are within the range expected for silver carbene complexes.[8]

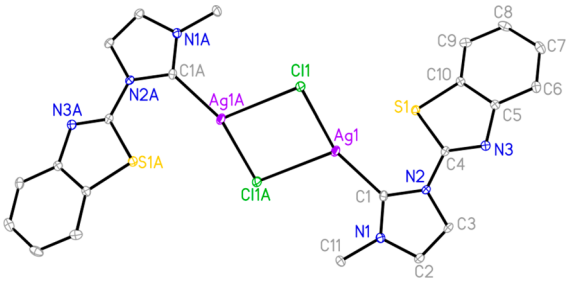


Figure 1. ORTEP diagram of **4** (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): Ag(1)−C(1) 2.098(2); Ag(1)−Cl(1) 2.4089(7); Ag(1)−Cl(1A) 2.7865(7); C(1)−Ag(1)−Cl(1) 156.41(7); C(1)−Ag(1)−Cl(1A) 114.51(7); Cl(1)−Ag(1) −Cl(1A) 86.63(2).

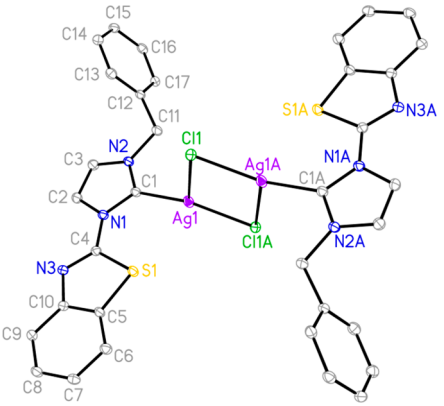


Figure 2. ORTEP diagram of **5** (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): Ag(1)−C(1) 2.094(3); Ag(1)−Cl(1A) 2.4005(7); Ag(1)−Cl(1) 2.7849(7); C(1)−Ag(1)−Cl(1A) 158.50(7); C(1)−Ag(1)−Cl(1) 110.59(7); Cl(1A)−Ag(1)−Cl(1) 90.84(2).

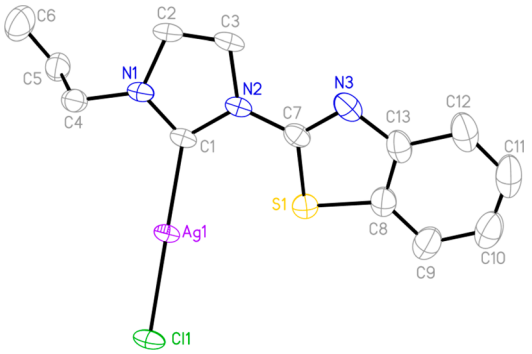
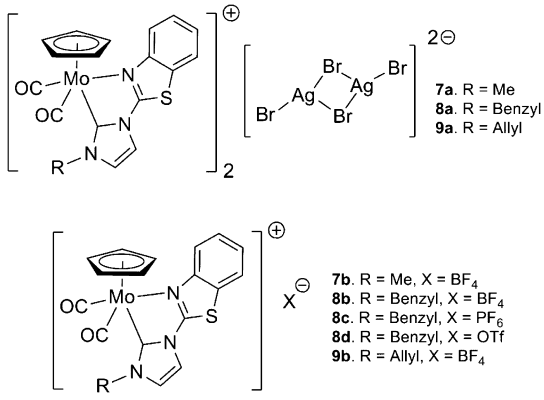


Figure 3. ORTEP diagram of **6** (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): Ag(1)−C(1) 2.084(3); Ag(1)−Cl(1) 2.3526(8); C(1)−Ag(1)−Cl(1) 176.50(8).

Complex **6** is the mononuclear version of **4** and **5**. The $C_{carbene}$−Ag−Cl is more linear (176.50(8)°) than that of the Ag(I) benzoxazole-carbene complex (168.5(1)°).[9] The Ag−$C_{carbene}$ bond length of 2.084(3) Å in **6** is comparable to those reported mononuclear Ag(I) NHC complexes.[8] A secondary interaction between Ag and S atoms is also observed in **6** with Ag(1)···S(1) of 3.135 Å.

Synthesis and Characterization of Cp Mo(II) Carbonyl NHC Complexes. Transmetalation of $CpMo(CO)_3Br$ with silver complexes **4**−**6** in toluene under reflux gave $[CpMo(CO)_2(L)]_2[Ag_2Br_4]$ (L = **L1**, **7a**; L = **L2**, **8a**; L = **L3**, **9a**) (Scheme 2) in 72−83% yields with the structures elucidated by single-crystal X-ray diffraction (see below). These complexes were further treated with AgX (X = BF_4, PF_6 or OTf) in acetonitrile at room temperature, affording $[CpMo(CO)_2(L)][X]$ (L = **L1**, X = BF_4, **7b**; L = **L2**, X = BF_4, **8b**; X = PF_6, **8c**; X = OTf, **8d**; L = **L3**, X = BF_4, **9b**) in high yields (Scheme 2). All the compounds have been characterized by ESI-MS, IR, NMR spectroscopy (^1H, ^{13}C) and elemental analysis, with **7a**, **7b**, **8a**,

Scheme 2



dx.doi.org/10.1021/om401128z | Organometallics XXXX, XXX, XXX−XXX

Table 1. CO Stretching Bands in IR Spectroscopy, Mo−$C_{carbene}$ Bond Lengths, and Turnover Frequencies (TOFs) for the Cyclooctene Epoxidation Catalysis of Known Mo(II) NHC Complexes

entry	complex[a]	IR: ν (CO) (cm^{-1})	Mo−$C_{carbene}$ (Å)	TOF[b] (h^{-1})	ref
1	$[CpMo(CO)_2(IMe)Br]$	1955, 1832	2.224(3)	1	5
2	$[CpMo(CO)_2(I^nPr)Br]$	1946, 1841	2.241(3)	2	5
3	$[CpMo(CO)_2(IBz)Br]$	1952, 1874	–	1	5
4	$[CpMo(CO)_2(IBz)Cl]$	1953, 1872	2.221(3)	5	5
5	$[CpMo(CO)_2(IMe^nPr)Br]$	1959, 1858	2.224(2)	1	5
6	$[CpMo(CO)_2(IMes)Br]$	1956, 1860	2.244(3)	4	5
7	$[CpMo(CO)_2(IMes)(CH_3CN)][BF_4]$	1953, 1870	2.249(3)	21	5
8	$[CpMo(CO)_2(IBz)(CH_3CN)][BF_4]$	1972, 1879	2.228(2)	21	6
9	$[CpMo(CO)_2(IMes)H]$	1930, 1858	2.187(8)	–	10
10	$[CpMo(CO)_2(Triazolylidene)Cl]$	1943, 1848	2.221(4)	9.5	11
11	$[CpMo(CO)_2(Tetrazolylidene)Cl]$	1940, 1844	2.173(2)	–	12
12	$[Mo(\eta^5\text{-}C_5Me_4\text{-}CH_2\text{-}CHPh\text{-}NHC^{Me})(CO)_2I]$	1933, 1834	2.207(3)	–	13
13	$[Mo(\eta^5\text{-}C_5Me_4\text{-}CH_2\text{-}CMePh\text{-}NHC^{Me})(CO)_2I]$	1935, 1832	–	–	13
14	$[Mo(\eta^5\text{-}C_5H_4\text{-}CMe_2\text{-}CHPh\text{-}NHC^{Me})(CO)_2I]$	1945, 1851	–	–	13
15	$[Mo(\eta^5\text{-}C_5(CH_2Ph)_4\text{-}CHPh\text{-}CHPh\text{-}NHC^{Me})(CO)_2I]$	1941, 1860	–	5.2[c]	13
16	$[Mo(\eta^3\text{-allyl})Cl(CO)_2(\text{bis-}NHC^{Bz})]$	1919, 1815	–	18[d]/20[e]	14
17	$[Mo(\eta^3\text{-allyl})(\eta^2\text{-}(NPh_2)_2CH)(CO)_2(IMes)]$	1906, 1811	2.285(9)	–	15
18	$[Mo(\eta^3\text{-allyl})(\eta^2\text{-}(NPh_2)_2CH)(CO)_2(I^iPr)]$	1913, 1829	2.276(4)	–	15
19	$[Mo(\eta^3\text{-}C_4H_7)(bipy)(CO)_2(IHMe)][OTf]$	1950, 1866	–	–	16
20	$[Mo(\eta^3\text{-}C_4H_7)(bipy)(CO)_2(IHMes)][OTf]$	–	2.240(3)	–	16
21	$[Mo(\eta^3\text{-}C_4H_7)(bipy)(CO)_2(IMeMes)][OTf]$	1946, 1865	–	–	16
22	$[Mo(\eta^3\text{-}C_4H_7)(bipy)(CO)_2(IMeEt)][OTf]$	1947, 1866	–	–	16
23	$[Mo(\eta^3\text{-}C_4H_7)(bipy)(CO)_2(IMeMes)][BAr_4]$	–	2.252(4)	–	16
24	$[Mo(\eta^3\text{-indenyl-}NHC^{Me})(\eta^3\text{-}C_4H_7)(CO)]$	1794, 1773	2.189(3)	–	17
25	$[(Cp)_2Mo(I^iPr)]$	–	2.219(7)	–	18
26	$[(Cp)_2Mo(IMe)]$	–	2.212(6)	–	18
27	$[Mo(CO)_2(IEt)_2(OSO_2CF_3)_2]$	–	2.152(5), 2.157(5)	–	19
28	$[CpMoO_2(IBz)]_2[Mo_6O_{19}]$[f]	–	2.173(4)	–	6
29	$[CpMoO_2(IBz)][BF_4]$[f]	–	–	21	6

[a]IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; IBz = 1,3-dibenzylimidazol-2-ylidene; IMe = 1,3-dimethylimidazol-2-ylidene; I^nPr = 1,3-dipropylimidazol-2-ylidene; IMe^nPr = 1-methyl-3-propylimidazol-2-ylidene; bis-NHC^{Bz} = 1,1′-dibenzyl-3,3′-methylenediimidazoline-2,2′-diylidene; I^iPr = 1,3-diisopropylimidazol-2-ylidene; IEt = 1,3-diethylimidazol-2-ylidene; IHMe = 1-*H*-3-methylimidazol-2-ylidene; IHMes = 1-*H*-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene; IMeMes = 1-methyl-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene; IMeEt = 1-methyl-3-ethylimidazol-2-ylidene. [b]TOFs are calculated on the basis of 4 h yield of cyclooctene oxide for all cases except entry 15. Catalytic reaction conditions: molar ratio of catalyst:*cis*-cyclooctene:TBHP = 1:100:200; 55 °C. [c]Catalytic reaction conditions: molar ratio of catalyst:*cis*-cyclooctene:TBHP = 1:100:300; 55 °C. TOF is calculated on the basis of 5 h yield of cyclooctene oxide. [d]Catalytic reaction conditions: molar ratio of catalyst:*cis*-cyclooctene:H_2O_2 = 1:100:300; 70 °C. [e]Catalytic reaction conditions: molar ratio of catalyst:*cis*-cyclooctene:TBHP = 1:100:300; 70 °C. [f]For the purpose of comparison, CpMo(VI)-NHC complexes are also included.

8b, and **9b** supplemented by single-crystal X-ray diffraction analysis.

The ^1H and ^{13}C NMR spectra of all Mo(II) NHC complexes were measured in DMSO-d_6. The singlet signal of the Cp ring in ^1H NMR spectra appears at δ 5.85−5.98 ppm. In ^{13}C NMR, the Cp signals are shown at ca. δ 94.7 ppm, and the carbene signals at δ 198.9−199.9 ppm. The two carbonyls resonate at ca. δ 247.9−247.5/247.2−246.7 ppm in ^{13}C NMR. The characteristic ^{13}C NMR signal of triflate anion ($^-$OTf) in **8d** is found at δ 120.65 ppm (q, J_{C-F} = 322 Hz). The $[CpMo(CO)_2(L)]^+$ cation at m/z = 433.8 (for **7a** and **7b**), 509.8 (for **8a**, **8b**, **8c**, and **8d**) and 459.8 (for **9a** and **9b**) is verified by ESI-MS spectral analysis (+ve mode). The IR spectra of these complexes exhibit ν_{sym}(CO) between 1963 and 1988 cm^{-1}, and the ν_{asym}(CO) between 1864 and 1897 cm^{-1}. Comparing to the CO stretching bands reported in other CpMo(II) carbonyl NHC complexes (see Table 1, entries 1−15),[5,6,10−13] the higher carbonyl frequencies in **7**−**9** clearly indicate a more electron-deficient Mo center in the $[CpMo(CO)_2(L)]^+$ cation.

Molecular Structures of 7a, 7b, 8a, 8b, and 9b Determined by Single-Crystal X-ray Diffraction. The single crystals of **7a**, **7b**, **8a**, **8b**, and **9b** were obtained from slow diffusion method using the solvent pair of acetonitrile and diethyl ether. X-ray diffraction structural analysis reveals a common 4-legged piano stool structure of the $[CpMo(CO)_2NHC]^+$ cation in these compounds (Figures 4−8). The hybrid ligand coordinates to the Mo(II) center in a bidentate C,N chelating mode forming a five-member ring. The N−Mo−$C_{carbene}$ chelate angle is between 72.0(3) and 72.66(9)°, whereas Mo−N (benthiazolyl) bond lengths range between 2.195(5) and 2.217(2) Å. Complexes **7a** and **8a** consist of two $[CpMo(CO)_2NHC]^+$ cations and one $[Ag_2Br_4]^{2-}$ anion, whereas complexes **7b**, **8b**, and **9b** contain only one $[CpMo(CO)_2NHC]^+$ cation and one BF_4^- anion. Comparing with the Mo−$C_{carbene}$ bond lengths observed in those reported Mo(II) NHC complexes (see Table 1), **7a**, **7b**, **8a**, **8b**, and **9b** have much shorter Mo−$C_{carbene}$ bonds (2.143(2)−2.166(3) Å) because of the chelation effect of the hybrid NHC ligand. Complex **9b** has the shortest Mo−$C_{carbene}$ bond length (2.143(2) Å) among the crystallographically

dx.doi.org/10.1021/om401128z | *Organometallics* XXXX, XXX, XXX−XXX

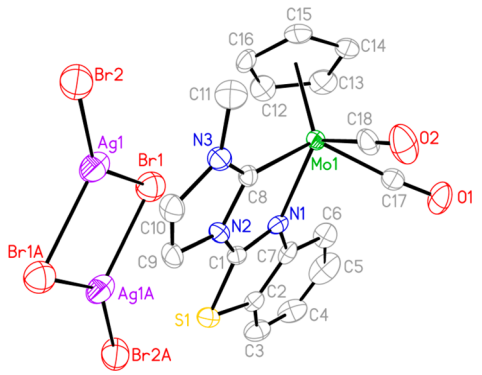


Figure 4. ORTEP diagram of one $[CpMo(CO)_2NHC]^+$ and $[Ag_2Br_4]^{2-}$ of **7a** (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): Mo(1)−C(18) 1.95(1); Mo(1)−C(17) 1.98(1); Mo(1)−C(8) 2.161(9); Mo(1)−N(1) 2.206(8); C(18)−Mo(1)−C(17) 75.0(5); C(8)−Mo(1)−N(1) 72.0(3).

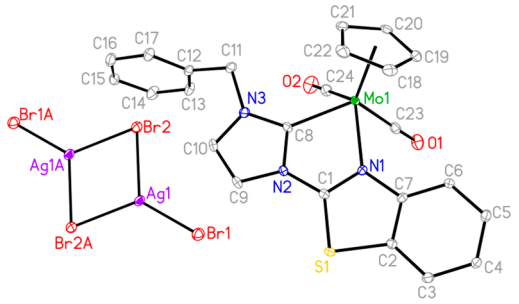


Figure 5. ORTEP diagram of one $[CpMo(CO)_2NHC]^+$ and $[Ag_2Br_4]^{2-}$ of **8a** (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): Mo(1)−C(24) 1.966(6); Mo(1)−C(23) 1.991(6); Mo(1)−C(8) 2.143(5); Mo(1)−N(1) 2.195(5); C(24)−Mo(1)−C(23) 75.8(3); C(8)−Mo(1)−N(1) 72.3(2).

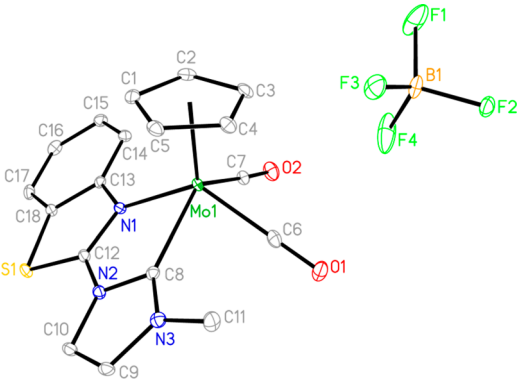


Figure 6. ORTEP diagram of **7b** (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): Mo(1)−C(6) 1.967(3); Mo(1)−C(7) 1.979(3); Mo(1)−C(8) 2.166(3); Mo(1)−N(1) 2.217(2); C(6)−Mo(1)−C(7) 76.7(1); C(8)−Mo(1)−N(1) 72.66(9).

established Mo NHC complexes in the literature (See Table 1).[5,6,10−19] Only $[Mo(CO)_2(IEt)_2(OSO_2CF_3)_2]$ (IEt = 1,3-diethylimidazol-2-ylidene) (2.152(5) and 2.157(5) Å) (see Table 1, entry 27)[19] has comparable lengths.

Application of Mo(II) NHC Complexes in Epoxidation Catalysis. The present ionic Mo complexes provide a

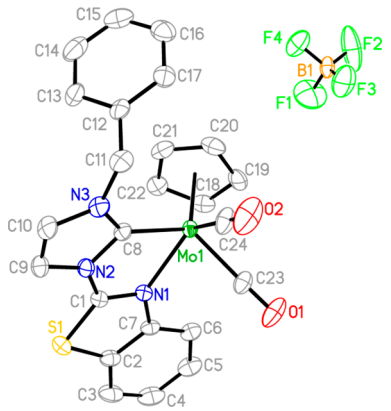


Figure 7. ORTEP diagram of **8b** (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): Mo(1)−C(23) 1.988(4); Mo(1)−C(24) 1.944(3); Mo(1)−C(8) 2.162(3); Mo(1)−N(1) 2.206(2); C(18)−Mo(1)−C(19) 75.2(2); C(8)−Mo(1)−N(1) 72.6(1).

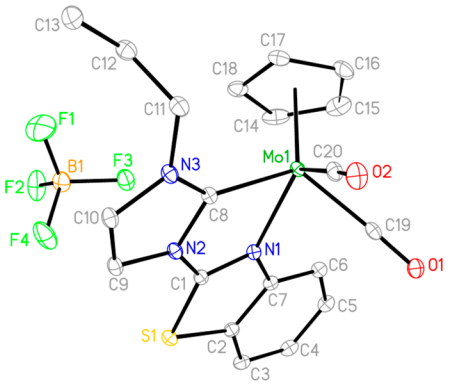


Figure 8. ORTEP diagram of **9b** (30% probability ellipsoids). Hydrogen atoms are omitted. Selective bond lengths (Å) and angles (deg): Mo(1)−C(20) 1.975(2); Mo(1)−C(19) 1.994(2); Mo(1)−C(8) 2.143(2); Mo(1)−N(1) 2.196(1); C(20)−Mo(1)−C(19) 75.45(7); C(8)−Mo(1)−N(1) 72.58(6).

prototype for studying the effects of hybrid NHC ligand and counterions on the catalytic activities of CpMo(II) carbonyl NHC systems toward olefin epoxidation catalysis. In this context, the catalytic activities of all Mo complexes have been examined as catalyst for cyclooctene epoxidation with *tert*-butyl hydroperoxide (TBHP) as oxidant at 55 °C in the absence of any cosolvent (see Experimental Section). The time-dependent epoxide yields catalyzed by **7a**, **7b**, **8a**, **8b**, **8c**, **8d**, **9a**, and **9b** are given in Figure 9. No induction period has been observed in the course of the catalysis. The complexes with BF_4^- as counteranion, **7b**, **8b**, and **9b**, are most active, giving epoxide yield of ca. 90% after 4 h of reaction time (TOF of 22.5 h^{-1}, calculated at 4 h), are comparable to the most active Mo(II)/(VI) NHC complexes under similar reaction conditions viz. $[CpMo(CO)_2(IMes)(CH_3CN)][BF_4]$[5] and $[CpMo(CO)_2(IBz)(CH_3CN)][BF_4]$[6] (TOF of ca. 21 h^{-1}, calculated at 4 h; Table 1 entries 7−8) . Complex **8b** could reach as high as 90% yield of epoxide after 3 h. Complexes **7a**, **8a**, and **9a** with $[Ag_2Br_4]^{2-}$ anion are significantly inferior with epoxide yield of 10% after 4 h. Although complexes **8b**, **8c**, and **8d** share the same cation $[CpMo(CO)_2(L2)]^+$, complexes **8c** and **8d** (with PF_6^- and ^-OTf anions, respectively) are less active with ca. 70% epoxide yield after 4 h (TOF of ca. 17.5 h^{-1}). Reaction

dx.doi.org/10.1021/om401128z | *Organometallics* XXXX, XXX, XXX−XXX

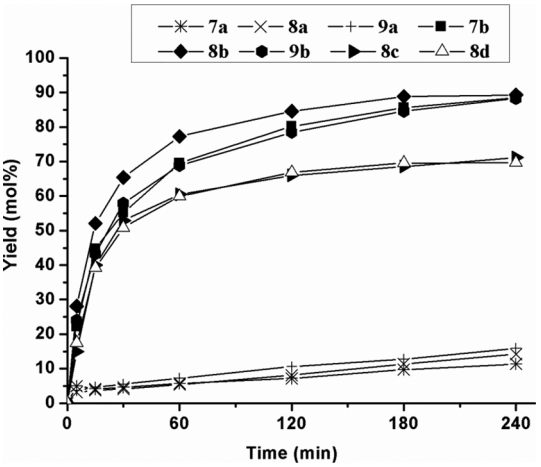


Figure 9. Time-dependent yields of cyclooctene epoxide using compounds **7a**, **7b**, **8a**, **8b**, **8c**, **8d**, **9a**, and **9b** as catalysts and using TBHP as oxidant at 55 °C (catalyst:substrate:oxidant =1:100:200).

temperature has significant influence on the catalytic performance. For **8b**, only 37% (4 h) epoxide yields are obtained at room temperature. The low catalytic activity at rt is also observed in other Mo complexes/TBHP catalytic systems.[20,21] [Mo(η^3-allyl)Cl(CO)$_2$(bis-NHC^{Bz})] was reported to be as active catalyst for the epoxidation of *cis*-cyclooctene with either TBHP or H_2O_2 as oxidant (TOF of 18 h^{-1} with H_2O_2, TOF of 20 h^{-1} with TBHP, Table 1, entry 16)[14] with molar ratio of catalyst: *cis*-cyclooctene: TBHP or H_2O_2 = 1:100:300 at 70 °C. However, H_2O_2 is not a suitable oxidant for the Mo(II) NHC complexes studied in this work. This is illustrated by **9b** giving only 4% epoxide yield in 4 h when H_2O_2 was employed as oxidant at 55 °C.

Reactivity of 9b under Oxidative Condition. Complex **9b** was treated with 5-fold excess of TBHP (~5.5 M in decane over molecular sieves 4 Å) at rt in CD_3CN under stirring. The orange solution was changed to greenish yellow after 5 min reaction. The time-dependent ^{1}H NMR spectra (see Figure 10) show that the Cp fingerprint peak of **9b** at δ 5.68 ppm can still be observed after 5 min reaction, as well as emergence of a new peak at δ 6.58 ppm. After 15 min, the new peak remains while the Cp peak of **9b** disappears. Similar observation has been

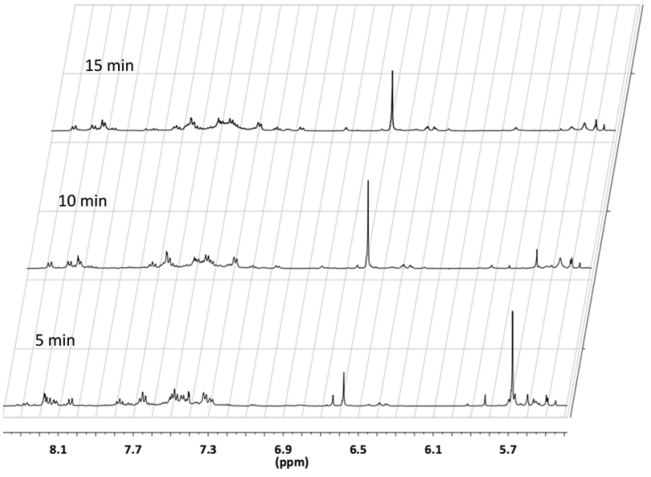


Figure 10. Time-dependent ^{1}H NMR spectra of the reaction mixture of **9b** and TBHP at rt in CD_3CN.

noted in the time dependent ^{1}H NMR spectral study of the oxidation of [CpMo(CO)$_2$(IMes)(CH$_3$CN)][BF$_4$] and [CpMo(CO)$_2$(IBz)(CH$_3$CN)][BF$_4$] with TBHP to the oxidation products [CpMoO$_2$(NHC)][BF$_4$] under similar conditions, in which there are downfield shifts of Cp peaks from δ 4.94 to 6.26 ppm and δ 5.59 to 6.50 ppm, respectively.[5,6] The emerged new peak at δ 6.58 ppm could hence be assigned to the Cp signal of [CpMoO$_2$(**L2**)]$^+$. The formation of Mo(VI)NHC species from the oxidation of **9b** is also supported by ESI-MS analysis (see Figure 11). The sets of peaks at 480−490 *m*/*z* and 676−686 *m*/*z* in the positive mode spectrum correspond to [CpMoO$_2$(**L2**)]$^+$ and ([CpMoO$_3$(**L2**)] + 2TBHP)$^+$, respectively, in which the Mo(VI) center coordinates to oxo and/or peroxo ligands. The fragments related to the NHC ligand **L2** are also observed at 292 *m*/*z* and 336 *m*/*z*, which correspond to [**L2**H]$^+$ and [**L2** + COOH]$^+$, respectively. The [**L2** + COOH]$^+$ could be attributed to the reaction between free carbene (**L2**) and CO_2.[5,22] Additionally, the weak peaks observed in the ^{1}H NMR spectrum at δ 6.53−6.27 ppm and δ 9.45 ppm could be assigned to the decomposed products of the Cp ligand and the formation of imidazolium salt, thus revealing the partial decomposition of **9b** during the oxidation process. Although the molecular structure of [CpMoO$_2$(**L2**)]$^+$ species is still unclear, this spectroscopic study indicates the in situ generation of Mo(VI) NHC species upon the treatment of TBHP during epoxidation catalysis.

CONCLUSION

We have demonstrated the transmetalation methodology of cationic Mo(II) NHC carbene complexes by taking advantage of the coordinative switch of hybrid carbene-thiazolyl C−N ligands from Ag(I) to Mo(II). Concomitant generation of a cationic coordination sphere with a stable chelate that comes with a shorter Mo−C$_{carbene}$ bond has created a new model for catalytic olefin epoxidation. It is encouraging to observe an epoxide yield as high as ~90% under facile conditions (3 h at 55 °C). The anions in these complexes also show significant influences on catalytic activities in epoxidation. These findings have prompted us to extend the study to other related stable cationic carbene catalysts with different counterions, especially additional chiral features on the hybrid ligand skeleton for asymmetric epoxidation catalysis.

EXPERIMENTAL SECTION

All commercial chemicals were used as purchased. All preparations and manipulations were performed using standard Schlenk techniques under a nitrogen atmosphere. Solvents were dried by standard procedures and distilled under nitrogen and used immediately. TBHP (*tert*-butyl hydroperoxide, 5.0−6.0 M in decane), 1-methylimidazole (99%), 2-chlorobenzothiazole (99%), 1-benzylimidazole (98%) and 1-allylimidazole (99%) were purchased from commercial sources and used as received. CpMo(CO)$_3$Br was prepared on the basis of a literature method.[23] Elemental analyses for C, H, N, and S were performed on a CHNS elemental analyzer and vario MICRO Cube. ^{1}H and ^{13}C NMR were measured at rt with 300 MHz and 500 MHz FT NMR spectrometers. Electrospray ionization mass spectrometric (ESI-MS) analysis was performed on a LCQ quadrapole ion trap mass spectrometer and amaZon X ion trap mass spectrometer. Infrared spectra were obtained on the FT-IR spectrometer using samples in KBr disc. Catalytic reactions were monitored by GC methods on a GC with a DB-5 column.

Synthesis of 1-(Benzothiazol-2-yl)-3-methylimidazolium Chloride (1). 1-Methylimidazole (1.232 g, 15 mmol) was added to 2-chlorobenzothiazole (2.544 g, 15 mmol) in a 25 mL Schlenk flask,

dx.doi.org/10.1021/om401128z | *Organometallics* XXXX, XXX, XXX−XXX

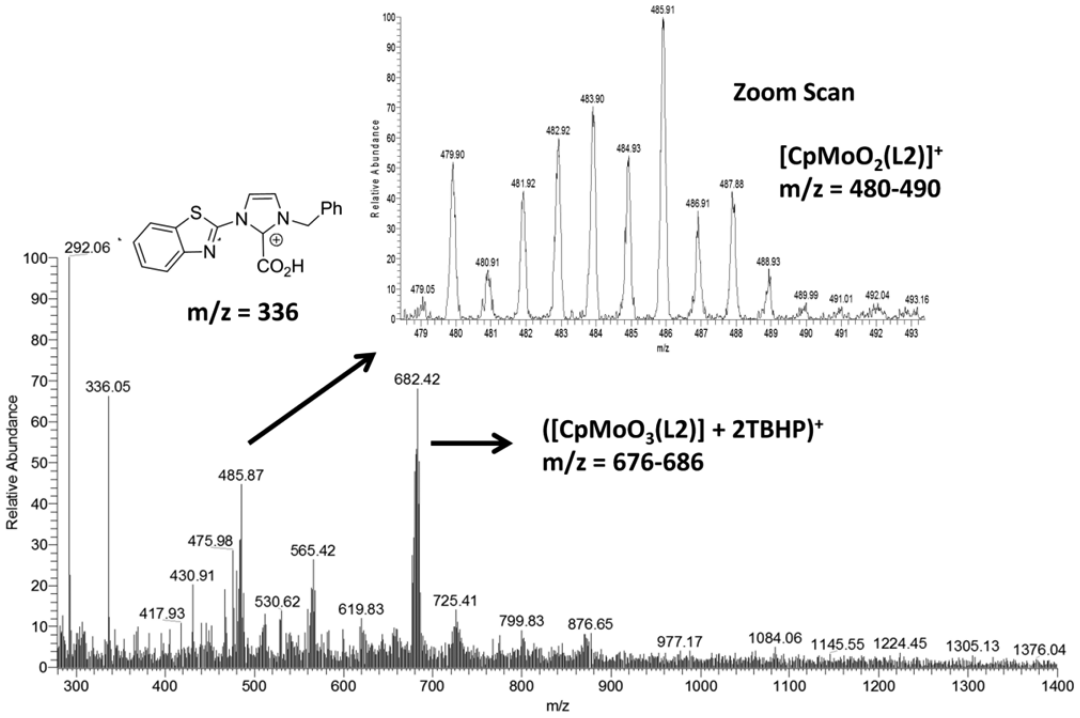
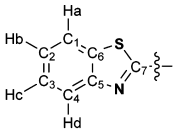


Figure 11. Positive mode ESI-MS spectrum of the reaction mixture of **9b** and TBHP (1:5) after 10 min of reaction time.



Labelling benzothiazolyl moiety for NMR signal assignments

and the mixture was stirred and heated to 100 °C under N_2 atmosphere for 16 h. The resultant slurry was washed with CH_3CN (3 × 15 mL) followed by Et_2O (20 mL). An off-white solid was collected and dried in vacuo. Yield: 2.341 g, 62%. ^{1}H NMR(500 MHz, DMSO-d_6): δ (ppm) = 10.54 (s, 1H, NC*H*N), 8.57 (s, 1H, =C*H*N(benzothiazole)), 8.31 (d, J = 8.0 Hz, 1H, Hd), 8.14 (s, 1H, =C*H*N(CH_3)), 8.05 (d, J = 8.0 Hz, 1H, Ha), 7.64 (dd, J = 8.0, 7.0 Hz, 1H, Hc), 7.58 (dd, J = 8.0, 7.5 Hz, 1H, Hb), 4.04 (s, 3H, N(C*H*$_3$)). ^{13}C NMR (125.77 MHz, DMSO-d_6): δ (ppm) = 154.65 (C_7), 148.99 (C_5), 137.54 (NCHN), 133.29 (C_6), 127.66, 126.70, 125.20 (=CHN(benzothiazole)), 123.32, 122.95, 120.28 (=CHN(CH_3)), 36.49 (NCH_3). Anal. Calcd for $C_{11}H_{10}N_3SCl$: C, 52.48; H, 4.00; N, 16.69; S, 12.74; Found: C, 52.20; H, 3.68; N, 16.52; S, 12.84. ESI-MS (in MeOH, m/z (%)): $[M - Cl]^+$ = 216.1 (100).

Synthesis of 1-(Benzothiazol-2-yl)-3-benzylimidazolium Chloride (2). Compound **2** was prepared and purified with a similar method as described for compound **1**. 1-Benzylimidazole (2.373 g, 15 mmol) and 2-chlorobenzothiazole (2.544 g, 15 mmol) were used as starting materials. Yield: 3.589 g, 73%. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 10.84 (s, 1H, NC*H*N), 8.61 (s, 1H, =C*H*N-(benzothiazole)), 8.32 (d, J = 8.0 Hz, 1H, Hd), 8.23 (s, 1H, =C*H*N(Bz)), 8.06 (d, J = 8 Hz, 1H, Ha), 7.66–7.57 (m, 4H), 7.46–7.39 (m, 3H), 5.66 (s, 2H, −C*H*$_2$Ph). ^{13}C NMR (125.77 MHz, DMSO-d_6): δ (ppm) = 154.76 (C_7), 148.96 (C_5), 137.12 (NCHN), 134.21, 133,37 (C_6), 128.87, 128.85, 128.70, 127.64, 126.69, 123.77, 123.30 (=CHN(benzothiazole)), 122.95, 121.14 (=CHN(Bz)), 52.44 (−CH_2Ph). Anal. Calcd for $C_{17}H_{14}ClN_3S$: C, 62.28; H, 4.30; N, 12.82; S, 9.78; Found: C, 62.47; H, 4.14; N, 12.90; S, 9.39. ESI-MS (in MeOH, m/z (%)): $[M - Cl]^+$ = 292.1 (100).

Synthesis of 1-(Benzothiazol-2-yl)-3-allylimidazolium Chloride (3). Compound **3** was prepared with a similar method as described for compound **1**. 1-Allylimidazole (1.622 g, 15 mmol) and 2-chlorobenzothiazole (2.544 g, 15 mmol) were used as starting materials. The resultant oily product was purified by column chromatography on silica gel using dichloromethane and methanol as eluents. Yield: 2.499 g, 60%. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 10.48 (s, 1H, NC*H*N), 8.62 (s, 1H, =C*H*N(benzothiazole)), 8.32 (d, J = 8 Hz, 1H, Hd), 8.12 (s, 1H, =C*H*N(Allyl)), 8.09 (d, J = 8.0 Hz, Ha), 7.66 (dd, J = 8.0, 7.5 Hz, 1H, Hc), 7.60 (t, J = 7.5 Hz, 1H, Hb), 6.18–6.10 (m, 1H, −CH_2C*H*=CH_2), 5.47–5.42 (m, 2H, —CH=C*H*$_2$), 5.04 (s, 2H, —C*H*$_2$CH=CH_2). ^{13}C NMR (125.77 MHz, DMSO-d_6): δ (ppm) = 154.66 (C_7), 148.94 (C_5), 137.12 (NCHN), 133.34 (C_6), 131.06 (—CH_2CH=CH_2), 127.63, 126.68, 123.86, 123.28, 122.94, 120.85 (—CH=CH_2), 51.47 (—CH_2CH=CH_2). Anal. Calcd for $C_{13}H_{12}ClN_3S$: C, 56.21; H, 4.35; N, 15.13; S, 11.54; Found: C, 56.11; H, 4.05; N, 15.11; S, 11.36. ESI-MS (in MeOH, m/z (%)): $[M - Cl]^+$ = 242.1 (100).

Synthesis of Silver Carbene Complexes 4, 5, and 6. Ag_2O (0.139 g, 0.6 mmol) was added to the respective imidazolium chloride salts (**1**, 0.252 g, 1.0 mmol; **2**, 0.328 g, 1.0 mmol; **3**, 0.278 g, 1.0 mmol) in 1,2-dichloroethane (30 mL). After refluxing for overnight with the exclusion of light, the reaction mixture was filtered through Celite. The filtrate was dried under a vacuum and washed with deionized water, hexane, and Et_2O. The characterization data for the silver-NHC complexes **4**, **5**, and **6** are as follows.

Complex ***4***. Light brown solid (Yield: 0.267 g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.16 (d, J = 1.8 Hz, 2H, =C*H*N(benzothiazole)), 7.95 (dd, J = 7.8, 0.9 Hz, 2H, Hd), 7.88 (dd, J = 7.8, 0.9 Hz, 2H, Ha), 7.54 (dt, J = 7.5, 1.2 Hz, 2H, Hc), 7.46 (dt, J = 7.5, 1.2 Hz, 2H, Hb), 7.19 (d, J = 1.8 Hz, 2H, =C*H*N(CH_3)), 4.01 (s, 6H, N(C*H*$_3$)). ^{13}C NMR (125.77 MHz, DMSO-d_6): δ (ppm) = 180.75 (NCN), 158.72, 149.20, 131.99, 127.26, 126.13, 125.09, 122.73, 122.43, 120.00, 39.26 (NCH_3). ESI-MS (in CH_3CN: m/z (%)): $[M - AgCl_2]^+$ = $[Ag(L1)_2]^+$ = 539.0 (100), $[L1 + H]^+$ = 216.1 (75). Anal. Calcd for $C_{22}H_{18}N_6S_2Ag_2Cl_2$: C, 36.84; H, 2.53; N, 11.72; S, 8.94. Found: C, 37.02; H, 2.84; N, 11.95; S, 8.69.

Complex ***5***. Brown solid (Yield: 0.282 g, 67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.16 (d, J = 2.1 Hz, 2H, =C*H*N(benzothiazole)), 7.94 (dd, J = 7.8, 0.9 Hz, 2H, Hd), 7.89 (dd, J = 7.8, 0.9 Hz, 2H, Ha), 7.56–7.32 (m, 14H), 7.13 (d, J = 2.1 Hz, 2H, =C*H*N(Bz)), 5.44 (s, 4H, −C*H*$_2$Ph). ^{13}C NMR (125.77 MHz, DMSO-d_6): δ (ppm) = 180.84 (NCN), 158.79, 149.21, 137.14, 136.19, 132.03, 128.91, 127.94, 127.54, 126.21, 124.23, 122.73, 122.49, 120.56,

dx.doi.org/10.1021/om401128z | *Organometallics* XXXX, XXX, XXX–XXX

54.28 ($PhCH_2N$). ESI-MS (in CH_3CN: m/z): $[M - AgCl_2]^+$ = $[Ag(L2)_2]^+$ = 691.0 (100), $[L2 + H]^+$ = 292.1 (15). Anal. Calcd for $C_{34}H_{26}N_6S_2Ag_2Cl_2$: C, 46.97; H, 3.01; N, 9.67; S, 7.38. Found: C, 46.95; H, 3.26; N, 9.56; S, 7.52.

Complex ***6***. Light brown solid (Yield: 0.269 g, 70.0%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.18 (d, J = 1.8 Hz, 1H, =C*H*N(benzothiazole)), 7.95 (dd, J = 7.8, 0.9 Hz, 1H, Hd), 7.89 (dd, J = 7.8, 0.9 Hz, 1H, Ha), 7.54 (dt, J = 7.8, 1.5 Hz, 1H, Hc), 7.46 (dt, J = 7.8, 1.5 Hz, 1H, Hb), 7.20 (d, J = 1.8 Hz, 1H, =C*H*N(Allyl)), 6.08–5.95 (m, 1H, $-CH_2CH$=CH_2), 5.47–5.35 (m, 2H, $-CH$=CH_2), 4.89 (d, J = 6 Hz, 2H, $-CH_2CH$=CH_2). ^{13}C NMR (125.77 MHz, DMSO-d_6): δ (ppm) = 180.67 (NCN), 158.78, 149.19, 133.42, 131.99, 127.28, 126.18, 124.22, 122.72, 122.46, 120.19, 119.24, 54.10 ($-CH_2CH$=CH_2). ESI-MS (in CH_3CN: m/z (%)): $[M + L3 - Cl]^+$ = $[Ag(L3)_2]^+$ = 591.0 (100), $[L3 + H]^+$ = 242.1 (50). Anal. Calcd for $C_{13}H_{11}N_3SAgCl$: C, 40.59; H, 2.88; N, 10.92; S, 8.34. Found: C, 40.13; H, 3.34; N, 10.73; S, 8.74.

Synthesis of $[CpMo(CO)_2(NHC)]_2[Ag_2Br_4]$ Complexes 7a, 8a, and 9a. The respective silver-NHC complex (**4**, 0.179 g, 0.25 mmol; **5**, 0.217 g, 0.25 mmol; **6**, 0.192 g, 0.5 mmol) and the $CpMo(CO)_3Br$ precursor (0.357 g, 1.1 mmol) were added to dry toluene (30 mL). The mixture was refluxed for 1 h with the exclusion of light under N_2 protection. The precipitate was collected and was washed with toluene, hexane, and diethyl ether. The characterization data for complexes **7a**, **8a**, and **9a** are as follows.

Complex ***7a***. Yellowish brown solid (Yield: 0.252 g, 72%). ^{1}H NMR(500 MHz, DMSO-d_6): δ (ppm) = 8.78 (d, J = 2.0 Hz, 2H, =C*H*N(benzothiazole)), 8.36 (d, J = 8.0 Hz, 2H, Hd), 8.11 (d, J = 8.5 Hz, 2H, Ha), 7.97 (d, J = 2.5 Hz, 2H, =C*H*N(CH_3)), 7.75 (dd, J = 8.0, 7.5 Hz, 2H, Hc), 7.65 (dd, J = 8.0, 7.0 Hz, 2H, Hb), 5.98 (s, 10H, *Cp*), 4.05 (s, 6H, N(CH_3)). ^{13}C NMR (125.77 MHz, DMSO): δ (ppm) = 247.87 (Mo-CO), 247.16 (Mo-CO), 198.85 (NCN), 159.07, 148.76, 130.28, 128.58, 128.31, 126.57, 124.66, 121.07, 119.10, 94.65 (*Cp*), 37.88 (N(CH_3)). IR (KBr)/ cm^{-1}: ν_{sym}(CO) = 1963, ν_{asym}(CO) = 1889. ESI-MS (in CH_3CN: m/z (%)): $[M - CpMo(CO)_2(L1) - Ag_2Br_4]^+$ = $[CpMo(CO)_2(L1)]^+$ = 433.8 (100), $[L1 + H]^+$ = 216.2 (10). Anal. Calcd for $Mo_2C_{36}H_{28}N_6S_2O_4Ag_2Br_4$: C, 30.88; H, 2.02; N,6.00; S, 4.58. Found: C, 30.66; H, 2.11; N, 6.03; S, 4.62.

Complex ***8a***. Orange brown solid (Yield: 0.322 g, 83%). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 8.87 (d, J = 2.0 Hz, 2H, =C*H*N(benzothiazole)), 8.38 (d, J = 8.0 Hz, 2H, Hd), 8.11 (d, J = 8.0 Hz, 2H, Ha), 7.80 (d, J = 2.5 Hz, 2H, =C*H*N(Bz)), 7.76 (dd, J = 8.5, 7.0 Hz, 2H, Hc), 7.66 (dd, J = 8.5, 7.0 Hz, 2H, Hb), 7.47 (dd, J = 8.0, 7.0 Hz, 4H), 7.41 (t, J = 7.5 Hz, 2H), 7.34 (d, J = 7.0 Hz, 4H), 5.85 (s, 10H, *Cp*), 5.76–5.56 (m, 4H, $-CH_2Ph$). ^{13}C NMR (125.77 MHz, DMSO): δ (ppm) = 247.80 (Mo-CO), 247.03 (Mo-CO), 199.83 (NCN), 159.18, 148.73, 135.71, 130.26, 128.86, 128.32, 128.18, 127.39, 127.35, 126.61, 124.64, 121.03, 119.97, 94.69 (*Cp*), 53.75 ($PhCH_2N$). IR (KBr)/ cm^{-1}: ν_{sym}(CO) = 1973, ν_{asym}(CO) = 1897. ESI-MS (in CH_3CN: m/z (%)):$[M - CpMo(CO)_2(L2) - Ag_2Br_4]^+$= $[CpMo(CO)_2(L2)]^+$ = 509.8 (100), $[M - CpMo(CO)_2(L2) - Ag_2Br_4 - 2(CO)]^+$= $[CpMo(L)]^+$ = 454.1 (90), $[M - CpMo(CO)_2(L2) - Ag_2Br_4 - CO]^+$= $[CpMo(CO)(L2)]^+$ = 481.9 (60). Anal. Calcd for $Mo_2C_{48}H_{36}N_6S_2O_4Ag_2Br_4$: C, 37.14; H, 2.34; N, 5.41; S, 4.13. Found: C, 37.66; H, 2.39; N, 5.56; S, 4.18.

Complex ***9a***. Reddish brown solid (Yield: 0.272 g, 75%). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 8.86 (d, J = 2.0 Hz, 2H, =C*H*N(benzothiazole)), 8.37 (d, J = 8.0 Hz, 2H, Hd), 8.11 (d, J = 8.0 Hz, 2H, Ha), 7.94 (d, J = 2.0 Hz, 2H, =C*H*N(Allyl)), 7.75 (dd, J = 8.5, 7.5 Hz, 2H, Hc), 7.65 (dd, J = 8.0, 7.5 Hz, 2H, Hb), 6.23–6.15 (m, 2H), 5.94 (s, 10H, *Cp*), 5.43–5.31 (m, 4H), 5.08–4.98 (m, 4H). ^{13}C NMR (125.77 MHz, DMSO-d_6): δ (ppm) = 247.82 (Mo-CO), 247.09 (Mo-CO), 199.20 (NCN), 159.07, 148.71, 132.89, 130.24, 128.30, 127.04, 126.58, 124.62, 121.02, 119.80, 119.05, 94.68 (*Cp*), 52.65 ($-CH_2CH$=CH_2). IR (KBr)/ cm^{-1}: ν_{sym}(CO) = 1972, ν_{asym}(CO) = 1897. ESI-MS (in CH_3CN: m/z (%)):$[M - CpMo(CO)_2(L3) - Ag_2Br_4]^+$= $[CpMo(CO)_2(L3)]^+$ = 459.8 (100), $[L3 + H]^+$ = 242.2 (55). Anal. Calcd for $Mo_2C_{40}H_{32}N_6S_2O_4Ag_2Br_4$: C, 33.08; H, 2.22; N, 5.79; S, 4.42. Found: C, 33.29; H, 2.26; N, 5.97; S, 4.42.

Synthesis of 7b, 8b, 8c, 8d, and 9b Complexes. $AgBF_4$ (0.0389 g, 0.2 mmol), $AgPF_6$ (0.0506 g, 0.2 mmol) or $AgCF_3SO_3$ (0.0514 g, 0.2 mmol) was added to solution of complex **7a** (0.14 g, 0.1 mmol), **8a** (0.155 g, 0.1 mmol), or **9a** (0.145 g, 0.1 mmol) in dry CH_3CN (20 mL). After stirring overnight at rt, the mixture was filtered through Celite, and the orange filtrate was vacuum dried. The resulting solid was recrystallized from CH_3CN and Et_2O twice, yielding orange red crystals. The characterizations for complexes are as follows.

Complex ***7b***. Orange red solid (Yield: 0.088 g, 85%). ^{1}H NMR(500 MHz, DMSO-d_6): δ (ppm) = 8.78 (d, J = 2.0 Hz, 1H, =C*H*N(benzothiazole)), 8.36 (d, J = 8.0 Hz, 1H, Hd), 8.11 (d, J = 8.0 Hz, 1H, Ha), 7.97 (d, J = 2.5 Hz, 1H, =C*H*N(CH_3)), 7.75 (dd, J = 8.5, 7.0 Hz, 1H, Hc), 7.65 (dd, J = 8.0, 7.5 Hz, 1H, Hb), 5.98 (s, 5H, *Cp*), 4.05 (s, 3H, N(CH_3)). ^{13}C NMR (125.77 MHz, DMSO-d_6): δ (ppm) = 247.76 (Mo-CO), 247.05 (Mo-CO), 198.86 (NCN), 159.04, 148.75, 130.25, 128.55, 128.30, 126.57, 124.61, 121.06, 119.06, 94.63 (*Cp*), 37.85 (N(CH_3)). IR (KBr)/ cm^{-1}: ν_{sym}(CO) = 1988, ν_{asym}(CO) = 1884. ESI-MS (in CH_3CN: m/z (%)): $[M - BF_4]^+$ = $[CpMo(CO)_2(L1)]^+$ = 433.8 (100). Anal. Calcd for $MoC_{18}H_{14}N_3SO_2BF_4$: C, 41.64; H, 2.72; N, 8.09; S, 6.18. Found: C, 41.31; H, 2.70; N, 8.18; S, 6.24.

Complex ***8b***. Orange red solid (Yield: 0.096 g, 81%). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 8.84 (d, J = 2.5 Hz, 1H, =C*H*N(benzothiazole)), 8.37 (d, J = 8.5 Hz, 1H, Hd), 8.11 (d, J = 8.0 Hz, 1H, Ha), 7.79 (d, J = 2.5 Hz, 1H, =C*H*N(Bz)), 7.76 (dd, J = 8.5, 7.0 Hz, 1H, Hc), 7.66 (dd, J = 8.0, 7.5 Hz, 1H, Hb), 7.47 (dd, J = 7.5, 7.0 Hz, 2H), 7.40 (dd, J = 7.5, 7.0 Hz, 1H), 7.34 (d, J = 7.0 Hz, 2H), 5.85 (s, 5H, *Cp*), 5.76–5.56 (m, 2H, $-CH_2Ph$). ^{13}C NMR (125.77 MHz, DMSO): δ (ppm) = 247.47 (Mo-CO), 246.74 (Mo-CO), 199.71 (NCN), 159.25, 148.75, 135.71, 130.28, 128.90, 128.36, 128.22, 127.40, 127.40 (overlap), 126.66, 124.63, 121.04, 119.97, 94.76 (*Cp*), 53.83 ($PhCH_2N$). IR (KBr)/ cm^{-1}: ν_{sym}(CO) = 1984, ν_{asym}(CO) = 1891. ESI-MS (in CH_3CN: m/z (%)): $[M - BF_4]^+$ = $[CpMo(CO)_2(L2)]^+$ = 509.8 (100). Anal. Calcd for $MoC_{24}H_{18}N_3SO_2BF_4$: C, 48.43 ; H, 3.05; N, 7.06 ; S, 5.39. Found: C, 48.01 ; H, 3.17 ; N, 7.07; S, 5.44.

Complex ***8c***. Orange red solid (Yield: 0.103 g, 79%). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 8.85 (d, J = 2.0 Hz, 1H, =C*H*N(benzothiazole)), 8.37 (d, J = 7.5 Hz, 1H, Hd), 8.11 (d, J = 8.0 Hz, 1H, Ha), 7.79 (d, J = 2.5 Hz, 1H, =C*H*N(Bz)), 7.76 (dd, J = 8.5, 7.0 Hz, 1H, Hc), 7.66 (dd, J = 8.0, 7.5 Hz, 1H, Hb), 7.47(dd, J = 7.5, 7.0 Hz, 2H), 7.41 (dd, J = 7.5, 7.0 Hz, 1H), 7.34 (d, J = 7.5 Hz, 2H), 5.86 (s, 5H, *Cp*), 5.77–5.56 (m, 2H, $-CH_2Ph$). ^{13}C NMR (125.77 MHz, DMSO): δ (ppm) = 247.60 (Mo-CO), 246.84 (Mo-CO), 199.78 (NCN), 159.21, 148.74, 135.70, 130.26, 128.87, 128.33, 128.19, 127.39, 127.38, 126.63, 124.62, 121.03, 119.95, 94.69 (*Cp*), 53.77 ($PhCH_2N$). (KBr)/ cm^{-1}: ν_{sym}(CO) = 1987, ν_{asym}(CO) = 1881. ESI-MS (in CH_3CN: m/z (%)): $[M - PF_6]^+$ = $[CpMo(CO)_2(L2)]^+$ = 509.8 (100). Anal. Calcd for $MoC_{24}H_{18}N_3SO_2PF_6$: C, 44.12; H, 2.78; N, 6.43 ; S, 4.91. Found: C, 44.02; H, 2.77 ; N, 6.56; S, 5.05.

Complex ***8d***. Orange red solid (Yield: 0.108 g, 82%). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 8.87 (d, J = 2.5 Hz, 1H, =C*H*N(benzothiazole)), 8.38 (d, J = 8.0 Hz, 1H, Hd), 8.12 (d, J = 8.5 Hz, 1H, Ha), 7.80 (d, J = 2.0 Hz, 1H, =C*H*N(Bz)), 7.78 (dd, J = 8.5, 7.0 Hz, 1H, Hc), 7.66 (dd, J = 8.0, 7.5 Hz, 1H, Hb), 7.47 (dd, J = 8.0, 7.0 Hz, 2H), 7.41 (dd, J = 7.5, 7.0 Hz, 1H), 7.35 (d, J = 7.5 Hz, 2H), 5.87 (s, 5H, *Cp*), 5.77–5.56 (m, 2H, $-CH_2Ph$). ^{13}C NMR (125.77 MHz, DMSO): δ (ppm) = 247.77 (Mo-CO), 246.99 (Mo-CO), 199.85 (NCN), 159.19, 148.74, 135.72, 130.27, 128.86, 128.32, 128.18, 127.39, 127.36, 126.61, 124.63, 121.04, 120.65 (q, J_{C-F} = 322 Hz, CF_3SO_3), 119.96, 94.69 (*Cp*), 53.75 ($PhCH_2N$). (KBr)/ cm^{-1}: ν_{sym}(CO) = 1988, ν_{asym}(CO) = 1864. ESI-MS (in CH_3CN: m/z (%)): $[M - CF_3SO_3]^+$ = $[CpMo(CO)_2(L2)]^+$ = 509.8 (100). Anal. Calcd for $MoC_{25}H_{18}N_3S_2O_5F_3$: C, 45.67; H, 2.76; N, 6.39 ; S, 9.75. Found: C, 45.62; H, 2.89; N, 6.49; S, 9.82.

Complex ***9b***. Orange red solid (Yield: 0.085 g, 78%). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 8.85 (d, J = 2.0 Hz, 1H, =C*H*N(benzothiazole)), 8.36 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 2.5 Hz, 1H, =C*H*N(Allyl)), 7.77–7.73 (m, 1H), 7.67–7.63 (m, 1H), 6.23–6.15 (m, 1H), 5.94 (s, 5H, *Cp*), 5.43–5.31

dx.doi.org/10.1021/om401128z | *Organometallics* XXXX, XXX, XXX–XXX

Table 2. X-ray Diffraction Data of complexes 4−6, 7a, 7b, 8a, 8b, and 9b

complex	4	5	6	7a	7b	8a	8b	9b
formula	$C_{22}H_{18}Ag_2Cl_2N_6S_2$	$C_{34}H_{26}Ag_2Cl_2N_6S_2$	$C_{13}H_{11}AgClN_3S$	$C_{18}H_{14}AgBr_2MoN_3O_2S$	$C_{20}H_{17}BF_4MoN_4O_2S$	$C_{24}H_{18}AgBr_2MoN_3O_2S$	$C_{48}H_{37}B_2F_8Mo_2N_6O_4S_2$	$C_{20}H_{16}BF_4MoN_3O_2S$
M_W	717.18	869.37	384.63	700.01	560.19	776.10	1191.46	545.17
T/K	100(2)	100(2)	223(2)	223(2)	100(2)	100(2)	100(2)	100(2)
cryst. syst.	triclinic	triclinic	triclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$
a/Å	6.9801(9)	9.3758(15)	7.1756(7)	9.5115(14)	12.6206(7)	9.2723(10)	13.725(2)	9.0828(12)
b/Å	7.1160(9)	9.5645(15)	9.6293(9)	11.3232(16)	8.8393(5)	11.9265(13)	14.292(2)	14.1502(18)
c/Å	12.9672(16)	10.1551(16)	11.2883(11)	19.407(3)	20.2483(11)	12.6157(14)	14.606(2)	16.363(2)
α/°	92.073(2)	107.138(3)	91.786(2)	90	90	90.535(2)	85.882(2)	90
β/°	105.116(2)	102.186(3)	105.081(2)	97.164(4)	107.9700(10)	107.422(2)	63.821(2)	101.860(3)
γ/°	107.034(2)	107.444(3)	109.104(2)	90	90	111.7790(10)	67.772(2)	90
V/Å^3	590.09(13)	784.1(2)	705.83(12)	2073.9(5)	2148.7(2)	1224.6(2)	2364.5(6)	2058.1(5)
Z	1	1	2	4	4	2	2	4
D_{calc}/g cm^{-3}	2.018	1.841	1.810	2.242	1.732	2.105	1.673	1.759
reflections collected	7596	10 251	9166	11 639	14 738	16 013	23 871	14 291
R_{int}	0.0288	0.0222	0.0294	0.0363	0.0368	0.0273	0.0343	0.0194
parameters	155	208	172	254	300	307	695	289
GOF	1.221	1.069	1.044	1.083	1.094	1.032	1.066	1.052
R_1 [$I > 2\sigma(I)$]	0.0253	0.0294	0.0352	0.0755	0.0374	0.0503	0.0502	0.0242
wR_2 (all data)	0.0652	0.0727	0.0863	0.2580	0.0989	0.1561	0.1438	0.0651

dx.doi.org/10.1021/om4011282 | Organometallics XXXX, XXX, XXX−XXX

(m, 2H), 5.08−4.98 (m, 2H). ^{13}C NMR (125.77 MHz, DMSO-d_6): δ (ppm) = 247.76 (Mo-CO), 247.05 (Mo-CO), 199.19 (NCN), 159.11, 148.73, 132.90, 130.26, 128.31, 127.05, 126.60, 124.62, 121.04, 119.80, 119.04, 94.70 (*Cp*), 52.65 (—CH_2CH═CH_2). IR (KBr)/ cm^{-1}: ν_{sym}(CO) = 1987, ν_{asym}(CO) = 1884. ESI-MS (in CH_3CN: m/z (%)): $[M - BF_4]^+ = [CpMo(CO)_2(L3)]^+$ = 459.8 (100). Anal. Calcd for $MoC_{20}H_{16}N_3SO_2BF_4$: C, 44.06; H, 2.96; N, 7.71; S, 5.88. Found: C, 44.04; H, 2.93; N, 7.78; S, 5.87.

Catalytic Reactions. Cyclooctene (0.4 g, 3.6 mmol), mesitylene (1 g, internal standard) and catalysts (1 mol %, molybdenum based) were added to the reaction vessel in air at 55 °C or rt. The reaction was initiated by the addition of TBHP (5.0−6.0 M in decane) (~7.2 mmol, 1.36 mL). The course of the reaction was monitored by quantitative GC analysis. The samples were taken in regular time intervals, diluted with CH_2Cl_2, and treated with a small amount of $MgSO_4$ and MnO_2 to remove water and to destroy the excess of TBHP. The resulting slurry was filtered, and the filtrate was injected into the GC column. The conversion of cyclooctene and formation of cyclooctene oxide were calculated from calibration curves (r^2 = 0.999).

X-ray Crystallography. Diffraction measurements were conducted at 100(2)−293(2) K on a CCD diffractometer by using Mo Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects with the SMART suite of programs and for absorption effects with SADABS.[24] Structure solutions and refinements were performed by using the programs SHELXS-97[25a] and SHELXL-97.[25b] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. Hydrogen atoms were placed geometrically and refined isotropically. Crystal data and experimental details for the crystals of **4**−**6**, **7a**, **7b**, **8a**, **8b**, and **9b** are shown in Table 2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystal data (CIF). CCDC reference numbers: 955019 (**4**), 955020 (**5**), 955021 (**6**), 900510 (**7a**), 900511 (**7b**), 955022 (**8a**), 987063 (**8b**) and 955024 (**9b**). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: chmzhaoj@nus.edu.sg.
*E-mail: andyhor@nus.edu.sg.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the Ministry of Education (R-143-000-361-112) and A* Star (R143-000-426-305) for funding support. Z. Wang and L. Jiang acknowledged MOE for graduate scholarship. We thank Dr. L. L. Koh, G. K. Tan and Y. M. Hong for X-ray diffractometry assistance.

■ REFERENCES

(1) (a) Heinemann, C.; Müller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023−2038. (b) Gründemann, S.; Albrecht, M.; Loch, J. A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2001**, *20*, 5485−5488. (c) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1596−1605. (d) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2000**, *46*, 181−222. (e) Muehlhofer, M.; Strassner, T.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1745−1747. (f) Ahrens, S.; Herdtweck, E.; Goutal, S.; Strassner, T. *Eur. J. Inorg. Chem.* **2006**, 1268−1274. (g) Muehlhofer, M.; Strassner, T.; Herdtweck, E.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *660*, 121−126. (h) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370−2375.

(2) (a) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612−3676. (b) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746−1787. (c) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B. *Chem. Rev.* **2009**, *109*, 3561−3598. (d) Poyatos, M.; Mata, J. A.; Peris, E. *Chem. Rev.* **2009**, *109*, 3677−3707. (e) Schuster, O.; Yang, L.; Raubenheimer, H. G.; Albrecht, M. *Chem. Rev.* **2009**, *109*, 3445−3478. (f) Monsaert, S.; Lozano Vila, A.; Drozdzak, R.; Van Der Voort, P.; Verpoort, F. *Chem. Soc. Rev.* **2009**, *38*, 3360−3372. (g) Federsel, C.; Jackstell, R.; Beller, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 6254−6257. (h) Selander, N.; Szabó, K. J. *Chem. Rev.* **2011**, *111*, 2048−2076.

(3) Zhang, W.-H.; Chien, S. W.; Hor, T. S. A. *Coord. Chem. Rev.* **2011**, *255*, 1991−2024.

(4) (a) Li, F.; Hu, J. J.; Koh, L. L.; Hor, T. S. A. *Dalton Trans.* **2010**, *39*, 5231−5241. (b) Li, F.; Bai, S.-Q.; Hor, T. S. A. *Organometallics* **2008**, *27*, 672−677.

(5) Li, S.; Kee, C. W.; Huang, K.-W.; Hor, T. S. A.; Zhao, J. *Organometallics* **2010**, *29*, 1924−1933.

(6) Li, S.; Wang, Z.; Hor, T. S. A.; Zhao, J. *Dalton Trans.* **2012**, *41*, 1454−1456.

(7) Silva, R. M.; Smith, M. D.; Gardinier, J. R. *Inorg. Chem.* **2006**, *45*, 2132−2142.

(8) (a) Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978−4008. (b) Lin, I. J. B.; Vasam, C. S. *Coord. Chem. Rev.* **2007**, *251*, 642−670.

(9) Poyatos, M.; Maisse-François, A.; Bellemin-Laponnaz, S.; Gade, L. H. *Organometallics* **2006**, *25*, 2634−2641.

(10) (a) Wu, F.; Dioumaev, V. K.; Szalda, D. J.; Hanson, J.; Bullock, R. M. *Organometallics* **2007**, *26*, 5079−5090. (b) Dioumaev, V. K.; Szalda, D. J.; Hanson, J.; Franz, J. A.; Bullock, R. M. *Chem. Commun.* **2003**, 1670−1671.

(11) Schaper, L.-A.; Graser, L.; Wei, X.; Zhong, R.; Öfele, K.; Pöthig, A.; Cokoja, M.; Bechlars, B.; Herrmann, W. A.; Kühn, F. E. *Inorg. Chem.* **2013**, *52*, 6142−6152.

(12) Schaper, L.-A.; Wei, X.; Altmann, P. J.; Öfele, K.; Pöthig, A.; Drees, M.; Mink, J.; Herdtweck, E.; Bechlars, B.; Herrmann, W. A.; Kühn, F. E. *Inorg. Chem.* **2013**, *52*, 7031−7044.

(13) Kandepi, V. V. K. M.; Pontes da Costa, A.; Peris, E.; Royo, B. *Organometallics* **2009**, *28*, 4544−4549.

(14) Kandepi, V. V. K. M.; Cardoso, J. M. S.; Royo, B. *Catal. Lett.* **2010**, *136*, 222−227.

(15) Ogata, K.; Yamaguchi, Y.; Kashiwabara, T.; Ito, T. *J. Organomet. Chem.* **2005**, *690*, 5701−5709.

(16) Brill, M.; Díaz, J.; Huertos, M. A.; López, R.; Pérez, J.; Riera, L. *Chem.—Eur. J.* **2011**, *17*, 8584−8595.

(17) Takaki, D.; Okayama, T.; Shuto, H.; Matsumoto, S.; Yamaguchi, Y.; Matsumoto, S. *Dalton Trans.* **2011**, *40*, 1445−1447.

(18) Yamaguchi, Y.; Oda, R.; Sado, K.; Kobayashi, K.; Minato, M.; Ito, T. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 991−997.

(19) Anderson, D. M.; Bristow, G. S.; Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Skelton, B. W. *J. Chem. Soc., Dalton Trans.* **1987**, 2843−2851.

(20) (a) Abrantes, M.; Santos, A. M.; Mink, J.; Kühn, F. E.; Romão, C. C. *Organometallics* **2003**, *22*, 2112−2118. (b) Martins, A. M.; Romão, C. C.; Abrantes, M.; Azevedo, M. C.; Cui, J.; Dias, A. R.; Duarte, M. T.; Lemos, M. A.; Lourenço, T.; Poli, R. *Organometallics* **2005**, *24*, 2582−2589. (c) Al-Ajlouni, A. M.; Veljanovski, D.; Capapé, A.; Zhao, J.; Herdtweck, E.; Calhorda, M. J.; Kühn, F. E. *Organometallics* **2009**, *28*, 639−645.

(21) (a) Zhao, J.; Santos, A. M.; Herdtweck, E.; Kühn, F. E. *J. Mol. Catal. A: Chem.* **2004**, *222*, 265−271. (b) Zhao, J.; Sakthivel, A.; Santos, A. M.; Kühn, F. E. *Inorg. Chim. Acta* **2005**, *358*, 4201−4207. (c) Zhao, J.; Herdtweck, E.; Kühn, F. E. *J. Organomet. Chem.* **2006**, *691*, 2199−2206. (d) Zhao, J.; Jain, K. R.; Herdtweck, E.; Kühn, F. E. *Dalton Trans.* **2007**, 5567−5571. (e) Abrantes, M.; Sakthivel, A.; Romão, C. C.; Kühn, F. E. *J. Organomet. Chem.* **2006**, *691*, 3137−3145. (f) Abrantes, M.; Paz, F. A. A.; Valente, A. A.; Pereira, C. C. L.; Gago,

S.; Rodrigues, A. E.; Klinowski, J.; Pillinger, M.; Gonçalves, I. S. *J. Organomet. Chem.* **2009**, *694*, 1826−1833.
(22) (a) Shirley, D. A.; Alley, P. W. *J. Am. Chem. Soc.* **1957**, *79*, 4922−4927. (b) Voutchkova, A. M.; Appelhans, L. N.; Chianese, A. R.; Crabtree, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 17624−17625. (c) Voutchkova, A. M.; Feliz, M.; Clot, E.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **2007**, *129*, 12834−12846. (d) Zhou, H.; Zhang, W.-Z.; Liu, C.-H.; Qu, J.-P.; Lu, X.-B. *J. Org. Chem.* **2008**, *73*, 8039−8044.
(23) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104−124.
(24) *SADABS: Area-Detection Absorption Correction*; Bruker AXS, Inc.: Madison, WI, 1995.
(25) (a) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on May 9, 2014, with an incorrect chemical notation in Table 1, entry 28. The corrected version was reposted on May 13, 2014.