

# Synthesis and Crystal Structure of *N*-Heterocyclic Carbene Complexes of Bis( $\eta^5$ -cyclopentadienyl)molybdenum

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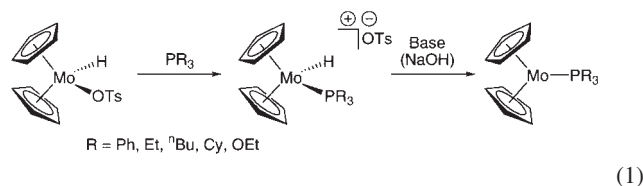
The one-pot reaction of  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{H})(\text{OTs})]$  (**1**) with 1,3-diisopropylimidazolium chloride ( $i\text{Pr}\cdot\text{HCl}$ , **2a**) in the presence of two equivalents of  $\text{KO}^t\text{Bu}$  in THF gave a bis( $\eta^5$ -cyclopentadienyl)molybdenum derivative bearing the 1,3-diisopropylimidazol-2-ylidene ligand,  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(i\text{Pr})]$  (**3a**). 1,3-Dimethyl- and 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene coordinated molybdenocene complexes (**3b**, **3c**) were prepared in a similar fashion (Method A). The treatment of  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{H})\text{Li}]_4$  (**6-Mo**) with the corresponding imidazolium salt in THF under photo-conditions also gave carbene complexes **3a–3c** (Method B). X-ray crystal structure analyses of **3a** and **3b** revealed that the *N*-heterocyclic carbene ligand is bonded to a bent molybdenocene skeleton. The Mo–C(carbene) bond distances are 2.219(7) Å for **3a** and 2.212(6) Å for **3b**. The five-membered carbene ligand in both complexes is located on the bisecting plane between two cyclopentadienyl rings.

Since the first preparation of bis( $\eta^5$ -cyclopentadienyl)molybdenum and -tungsten derivatives by Green, Wilkinson, and co-workers in 1961,<sup>1</sup> much effort has been made on the synthesis and reaction of their derivatives.<sup>2</sup> Studies on metallacyclobutane derivatives of  $\text{MCp}_2$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ), which were prepared by treating  $[\text{MCp}_2(\eta^3\text{-allyl})]^+$  with nucleophiles, such as  $\text{NaH}$ , have shown important aspects regarding the olefin metathesis process.<sup>3</sup> The photo-decomposition of the thus-formed metallacyclobutane complexes of tungsten evolved ethylene, suggesting a concomitant formation of the methyldiene derivative of  $\text{WCp}_2$ , although such a carbene species has been neither isolated nor detected spectroscopically due to its high reactivity.<sup>3</sup> Although there have been numerous studies on the carbene complexes of various transition metals to date, the isolation of  $\text{MCp}_2$  ( $\text{M} = \text{Mo}$  and  $\text{W}$ ) compounds bearing a carbene ligand is rather sparse.<sup>4</sup> In this paper we will report on the synthesis and crystal structure of bis(cyclopentadienyl)molybdenum derivatives bearing an *N*-heterocyclic carbene compound.

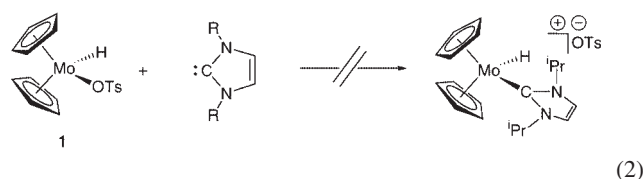
## Results and Discussion

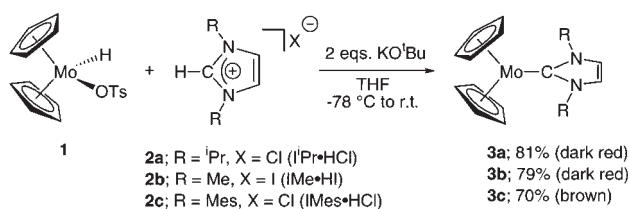
**Synthesis of  $[\text{MoCp}_2(\text{carbene})]$  Complexes from Hydrido(tosylato) Complex (Method A).** In the course of our systematic research on the preparation, structure, and reactivity of bis( $\eta^5$ -cyclopentadienyl)molybdenum and -tungsten compounds,<sup>5</sup> we successfully isolated a highly reactive hydrido(tosylato) complex,  $[\text{MoCp}_2(\text{H})(\text{OTs})]$  (**1**), and demonstrated that compound **1** is a useful starting material for preparing divalent  $\text{MoCp}_2$  derivatives.<sup>6</sup> In the reaction of complex **1** with two electron donor compounds (**L**), such as phosphines and/or phosphites, the OTs ligand in **1** is easily displaced by **L** to give cationic complexes formulated as  $[\text{MoCp}_2(\text{H})$

$(\text{L})]^+[\text{OTs}]^-$ , where **L** represents  $\text{PPh}_3$ ,  $\text{PEt}_3$ ,  $\text{P}^n\text{Bu}_3$ ,  $\text{PCy}_3$ , and  $\text{P}(\text{OEt})_3$ . The treatment of the cationic complexes with one equivalent of  $\text{NaOH}$  as a base afforded neutral divalent molybdenocene complexes having a trivalent phosphorus ligand (Eq. 1).



Recently, stable crystalline carbene compounds, i.e., an imidazol-2-ylidene and an imidazolin-2-ylidene (*N*-heterocyclic carbene), have been widely used as alternatives to phosphines in organometallic chemistry.<sup>7</sup> Therefore, we attempted to prepare a cationic hydrido(*N*-heterocyclic carbene) complex,  $[\text{MoCp}_2(\text{H})(\text{N-heterocyclic carbene})]^+[\text{OTs}]^-$ , by the reaction of complex **1** with an imidazol-2-ylidene generated in situ by the reaction of an imidazolium salt with a base. However, every trial was unsuccessful, presumably due to the highly reactive nature of *N*-heterocyclic carbenes toward air and moisture, even under an inert atmosphere (Eq. 2). We next examined a one-pot reaction for preparing  $[\text{MoCp}_2(\text{N-heterocyclic carbene})]$  complexes under a vacuum condition.

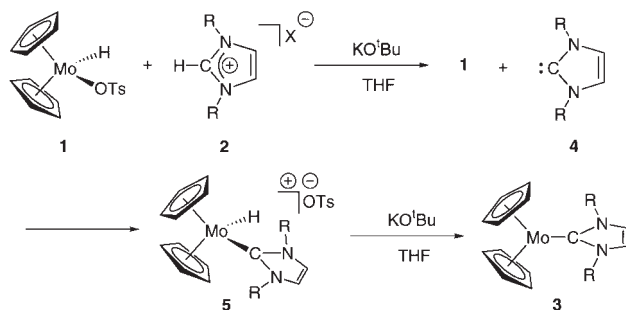


Scheme 1. Synthesis of [MoCp<sub>2</sub>(imidazol-2-ylidene)] complexes (Method A).

A hydrido(tosylato) complex **1** was treated with one equivalent of 1,3-diisopropylimidazolium chloride (I<sup>i</sup>Pr•HCl,<sup>8</sup> **2a**) in the presence of two equimolar amounts of KO<sup>t</sup>Bu as a base at -78 °C in THF under a vacuum; the reaction mixture was allowed to warm to room temperature. A clean reaction took place and, after a work-up, a 1,3-diisopropylimidazol-2-ylidene coordinated molybdenocene compound [MoCp<sub>2</sub>(I<sup>i</sup>Pr)] (**3a**) was isolated as a dark-red solid in good yield (81%) and characterized by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopies. In a similar fashion, **3b** and **3c**, a methyl and 2,4,6-trimethylphenyl (mesityl) analogues, respectively, of **3a**, were successfully prepared and characterized (Method A, Scheme 1). Complexes **3a** and **3b** were characterized by a single-crystal X-ray diffraction study (vide infra).

In the <sup>1</sup>H NMR spectra, products **3a–3c** showed no signal assignable to the CH-acidic proton in imidazolium salts **2**, whose resonance usually is known to appear at a low magnetic field ( $\delta = 8\text{--}10$ ).<sup>7,9</sup> Complex **3a** showed the characteristic septet signal assignable to the methine protons of the <sup>i</sup>Pr groups, which was observed at 6.86 ppm with the coupling constant <sup>3</sup>J<sub>HH</sub> = 6.6 Hz. This resonance is lower than that for the parent imidazolium salt **2a** ( $\delta = 4.70$ )<sup>9</sup> by 2.16 ppm and, moreover, about 2 ppm lower than that for the free I<sup>i</sup>Pr ( $\delta = \text{ca. } 4.90$ ).<sup>10</sup> Presumably, this may be due to a magnetic anisotropy of the Cp ligands and/or to an influence of the central transition metal. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, complex **3a** showed five signals and a resonance due to the carbene carbon bonded to molybdenum was observed at 193.6 ppm (in THF-*d*<sub>8</sub>). In cases of complexes **3b** and **3c**, the carbene carbons were observed at 197.3 and 201.8 ppm (in benzene-*d*<sub>6</sub>), respectively. These resonances for the coordinating carbene carbon are slightly higher than that for the free imidazol-2-ylidenes ( $\delta = 210\text{--}220$ ); a tendency normally seen in a series of these sorts of carbene complexes.<sup>7</sup>

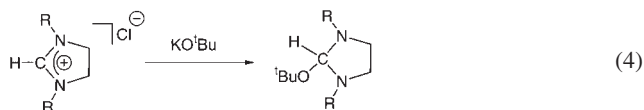
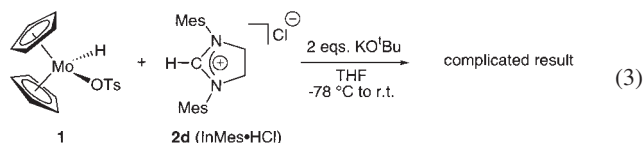
We propose the reaction pathway of the formation of imidazol-2-ylidene complexes (**3a–3c**; Method A), as shown in Scheme 2. In this reaction, an imidazol-2-ylidene (**4**) is first



Scheme 2. Reaction pathway for Method A.

formed by the deprotonation of an imidazolium salt (**2**) with KO<sup>t</sup>Bu as a base. The free carbene (**4**) generated in the system coordinates to the molybdenum center to produce a cationic hydrido(carbene) complex (**5**).<sup>11</sup> This intermediary cationic complex **5** may be easily neutralized by a second KO<sup>t</sup>Bu to afford the final product **3**.<sup>12</sup>

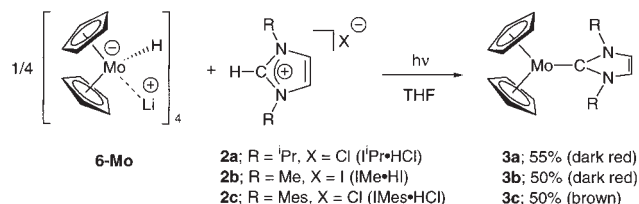
We next examined the preparation of a molybdenocene complex having an imidazolin-2-ylidene (CC-saturated *N*-heterocyclic carbene) instead of an imidazol-2-ylidene. A hydrido(tosylato) complex **1** was treated with one equivalent of 1,3-dimesitylimidazolinium chloride (InMes•HCl,<sup>13</sup> **2d**) in the presence of two equimolar amounts of KO<sup>t</sup>Bu as a base in THF under vacuum. However, although the desired reaction did not occur, unidentified products were formed (Eq. 3). It has been reported that, in the reaction of an imidazolinium salt with KO<sup>t</sup>Bu as a base, an alcoholate adduct of the imidazolinium salt forms (Eq. 4).<sup>14,15</sup> In this case, the <sup>t</sup>BuO adduct of InMes•HCl may be predominantly formed, which thus prevents the formation of the carbene complex.

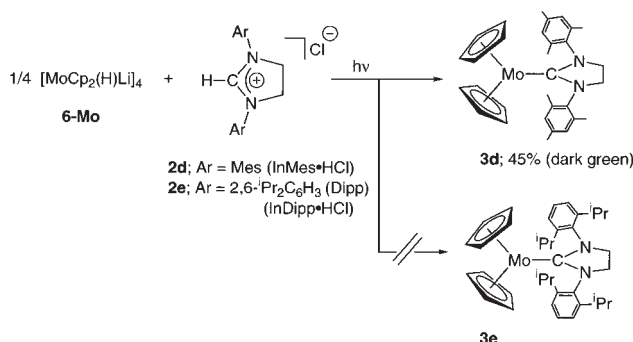


**Synthesis of [MoCp<sub>2</sub>(carbene)] Complexes from Lithiated Complex (Method B).** In 1968, Öfele reported the first preparation of a transition-metal complex having an imidazol-2-ylidene as a ligand using a deprotonation method of the CH-acidic proton on the imidazolium salt by an anionic metal precursor.<sup>16</sup> We employed a similar strategy in our approach to prepare [MoCp<sub>2</sub>(carbene)]. We thus examined the reaction of a lithiated molybdenocene compound, [MoCp<sub>2</sub>(H)Li]<sub>4</sub> (**6-Mo**),<sup>17</sup> instead of a hydrido(tosylato) compound **1**, with an imidazolium salt.

A tetrameric lithiated bis( $\eta^5$ -cyclopentadienyl)molybdenum compound, **6-Mo**, was treated with four equivalents of I<sup>i</sup>Pr•HCl (**2a**) in THF under irradiation with high-pressure mercury lamp. After a work-up, complex **3a** was isolated in moderate yield (55%). In a similar fashion, complexes **3b** and **3c** were successfully prepared (Method B, Scheme 3).

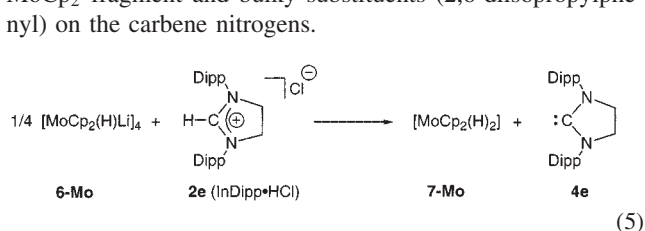
This method would be applied to the preparation of molybdenocene derivatives of an imidazolin-2-ylidene, CC-saturated *N*-heterocyclic carbene. In the reaction of InMes•HCl (**2d**)

Scheme 3. Synthesis of [MoCp<sub>2</sub>(imidazol-2-ylidene)] complexes (Method B).

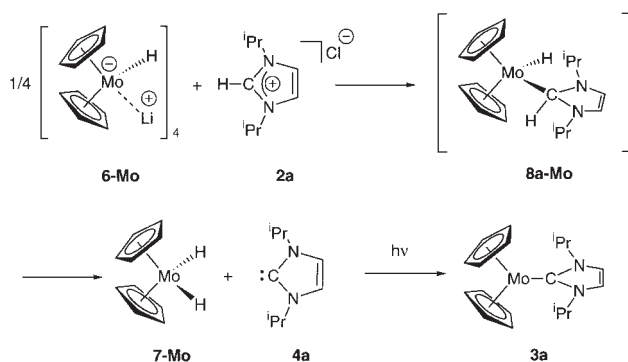


Scheme 4.

with **6-Mo**, InMes coordinated molybdenocene compound **3d**, which was unable to be prepared by method A, was successfully isolated as a dark-green solid in 45% yield (Scheme 4). Complex **3d** showed similar  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectral data to those of complex **3c**. The carbene carbon in **3d** was observed at 234.5 ppm (in benzene- $d_6$ ), which is a slightly higher magnetic field than that for the free carbene (243.8 ppm in benzene- $d_6$ ).<sup>18</sup> In the case of 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (InDipp·HCl, **2e**), in contrast, the desired carbene complex was not formed (Scheme 4). In the reaction, the formation of free InDipp (**4e**) and  $[\text{MoCp}_2(\text{H})_2]$  (**7-Mo**) was seen before irradiation in the  $^1\text{H}$  NMR spectrum of the reaction mixture (Eq. 5). After irradiation of this solution, however the carbene complex was not formed, presumably due to a steric problem between the  $\text{MoCp}_2$  fragment and bulky substituents (2,6-diisopropylphenyl) on the carbene nitrogens.



In order to obtain some insight into the pathway of the formation of **3** (Method B), we monitored the reaction of **6-Mo** with 1,3-diisopropylimidazolium chloride **2a** by  $^1\text{H}$  NMR spectroscopy, and now propose a plausible reaction path, as shown in Scheme 5. Before irradiation, the detectable products of this reaction were  $[\text{MoCp}_2(\text{H})_2]$  (**7-Mo**) and a free imidazol-2-ylidene **4a**, as mentioned above. These compounds

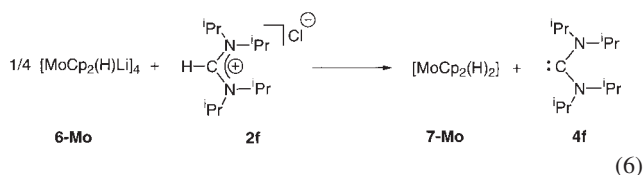


Scheme 5. Reaction pathway for Method B.

may be formed either via hydrido(alkyl) complex **8a** or by direct abstraction of the CH-acidic proton in **2a** by the anionic molybdenum compound **6-Mo** as a base, although the detection of **8a** has so far been unsuccessful. After the formation of a dihydrido compound **7-Mo** and a free carbene **4a**, irradiation of the resulting mixture led to the formation of a deep-red carbene complex **3a**.

In order to obtain further information regarding the reaction mechanism, we examined the reaction of a tungsten analogue of **6-Mo**,  $[\text{WCp}_2(\text{H})\text{Li}]_4$  (**6-W**), with **2a**. Even in this reaction, the compound corresponding to **8a** was not observed, but the formation of a tungsten analogue of **7-Mo**,  $[\text{WCp}_2(\text{H})_2]$  (**7-W**), and **4a** was observed.

The acyclic carbene, bis(diisopropylamino)carbene, was prepared and isolated by Alder and co-workers in 1996,<sup>19</sup> and its first transition-metal complexes were recently reported by Herrmann et al.<sup>15</sup> The reaction of the acyclic diaminocarbene precursor **2f** with a lithiated tetramer **6-Mo** resulted in the formation of a free diaminocarbene **4f** and  $[\text{MoCp}_2(\text{H})_2]$  (**7-Mo**), as is observed by  $^1\text{H}$  NMR spectroscopy; also the molybdenocene derivative of the diaminocarbene was not formed by this reaction (Eq. 6). It has been reported that the N–C–N angle in the free diaminocarbene **4f** is much larger than that in any cyclic diaminocarbene derivative (imidazolin-2-ylidene) and that the N–C–N angle is almost intact in their transition-metal complexes in the solid state.<sup>15,19</sup> The steric hindrance may be the main reason for preventing its coordination to the  $\text{MoCp}_2$  fragment, although the electronic feature of the diaminocarbene<sup>15</sup> might not be ruled out.



**Crystal Structures of Molybdenocene-Carbene Complexes 3a and 3b.** The molecular structures of **3a** and **3b** were determined by X-ray crystallography. ORTEP drawings of **3a** and **3b** are displayed in Figs. 1 and 2, respectively. The crystal data and the selected bond distances and angles are summarized in Tables 1–3.

A single-crystal X-ray diffraction study confirmed that **3a** and **3b** possess a bent molybdenocene skeleton bearing a 1,3-imidazol-2-ylidene as a carbene ligand. The Mo–C(carbene) bond distances are 2.219(7) Å for **3a** and 2.212(6) Å for **3b**, which are in good agreement with the Mo–C(*N*-heterocyclic carbene) bond distances reported so far; the reported Mo–C(carbene) bond distances are in the range from 2.152(5) to 2.35(1) Å.<sup>20</sup> The bond distances of C1–N1 (**3a**; 1.366(6) Å, **3b**; 1.359(5) Å) and angles of N1–C1–N1\* (**3a**; 103.9(6)°, **3b**; 103.5(5)°) are similar to those of free imidazol-2-ylidenes reported by Arduengo et al.<sup>7</sup> The carbene carbons of the ligand have a trigonal-planar geometry; the sum of the angles at the carbon is 360.1° for **3a** and 360.0° for **3b**. The nitrogen atoms on both carbene ligands also have a trigonal-planar structure; the sum of angles is 359.9° for **3a** and 360.0° for **3b**.

It is worth discussing the orientation of the carbene ligand in the complexes. The carbene ligand in both complexes (**3a** and

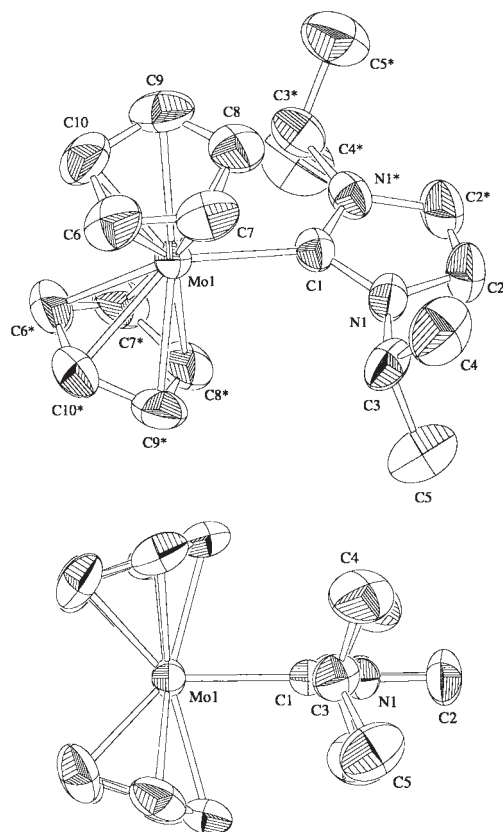


Fig. 1. Molecular structure of **3a** (normal view (upper) and side view (under)) with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

**3b**) is located on the bisecting plane between two Cp rings (Figs. 1, 2). Since the HOMO of the MoCp<sub>2</sub> fragment also lies on the same plane,<sup>21</sup> the empty p orbital of the carbene carbon lies perpendicular to the bent MoCp<sub>2</sub>'s HOMO. Although the HOMO (metal fragment) orbital has a strong electron-donating character, there must be no interaction between it and the LUMO (carbene carbon) in these complexes. It is known that the divalent carbon compound exhibits both  $\sigma$ -donor and  $\pi$ -acceptor properties upon binding to a transition metal. In fact, this HOMO–LUMO overlap is seen in a bent tungstenocene–carbene complex, [W(Cp<sub>2</sub>)=C(H)OZr(H)( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>].<sup>4</sup> However, there have been several studies recently which reveal that imidazol-2-ylidene acts only as a  $\sigma$ -donor to a metal, and that its  $\pi$ -acceptability is negligible.<sup>7</sup> In the solid state, the orientation of the carbene ligand in **3a** and **3b** mentioned above may come from a steric hindrance between two Cp rings and substituents on both nitrogen atoms, resulting in a loss of its  $\pi$ -acceptor ability. The same geometrical arrangement has been seen in a related divalent silicon compound coordinated to the Cp<sub>2</sub>Mo fragment, [MoCp<sub>2</sub>{SiN(*i*Bu)CHCHN*i*Bu}].<sup>22</sup>

### Conclusion

We examined the preparation of the molybdenocene derivatives of an *N*-heterocyclic carbene as a ligand. A preparative method utilizing a hydrido(tosylato) complex **1** as a starting material proved to be simple, easy, and effective for the pre-

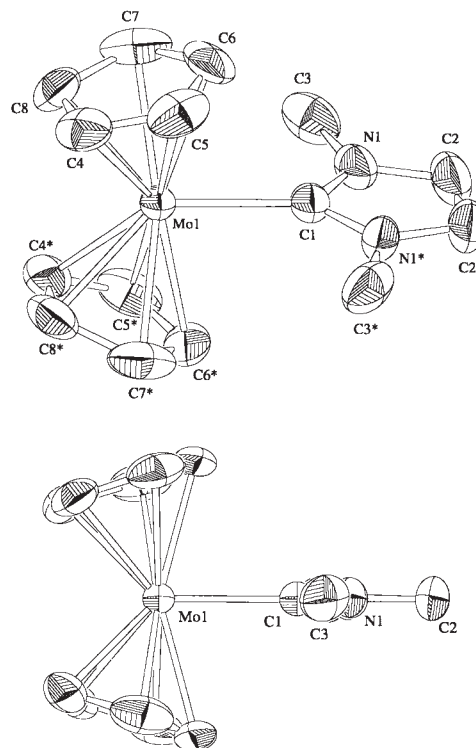


Fig. 2. Molecular structure of **3b** (normal view (upper) and side view (under)) with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

paration of molybdenocene–carbene complexes (Method A). A tetrameric lithiated molybdenocene compound **6-Mo** was also found to be a useful starting material for the preparation of molybdenocene–carbene complexes (Method B). In addition, the reaction of **6-Mo** with an imidazolinium salt afforded an imidazolin-2-ylidene coordinated molybdenocene complex, which could not be prepared by a treatment of complex **1** with an imidazolinium salt. Hydrido(tosylato) and tetrameric-lithiated complexes of MoCp<sub>2</sub> can be considered to be a cationic and anionic molybdenocene compounds, respectively (Chart 1). In this work, we demonstrated the effective preparation of molybdenocene–carbene complexes starting from both cationic and anionic compounds. Molybdenocene derivatives of imidazol-2-ylidene were characterized by an X-ray diffraction study. To our best knowledge, this is the first crystallographical study on a bent molybdenocene–carbene complex. A further investigation of the reactivity of these compounds is now in progress.

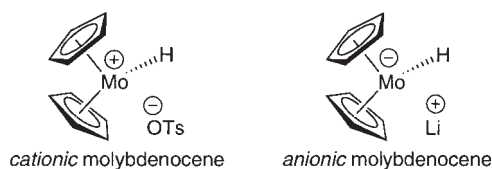


Chart 1.

Table 1. Summary of Crystal Data for **3a** and **3b**

|                                                      | <b>3a</b>                                        | <b>3b</b>                                        |
|------------------------------------------------------|--------------------------------------------------|--------------------------------------------------|
| Empirical formula                                    | C <sub>19</sub> H <sub>26</sub> MoN <sub>2</sub> | C <sub>15</sub> H <sub>18</sub> MoN <sub>2</sub> |
| Formula weight                                       | 378.37                                           | 322.26                                           |
| Crystal color, Habit                                 | red, prismatic                                   | red, prismatic                                   |
| Crystal size/mm                                      | 0.40 × 0.40 × 0.25                               | 0.20 × 0.10 × 0.10                               |
| Crystal system                                       | orthorhombic                                     | orthorhombic                                     |
| Space group                                          | <i>Fdd2</i> (#43)                                | <i>Fdd2</i> (#43)                                |
| Lattice parameters                                   |                                                  |                                                  |
| <i>a</i> /Å                                          | 23.777(3)                                        | 12.465(3)                                        |
| <i>b</i> /Å                                          | 8.690(3)                                         | 22.357(3)                                        |
| <i>c</i> /Å                                          | 17.370(3)                                        | 9.519(3)                                         |
| <i>V</i> /Å <sup>3</sup>                             | 3588(2)                                          | 2652(1)                                          |
| Z value                                              | 8                                                | 8                                                |
| <i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>         | 1.400                                            | 1.614                                            |
| <i>F</i> (000)                                       | 1568.00                                          | 1312.00                                          |
| $\mu$ (Mo K $\alpha$ ) cm <sup>-1</sup>              | 7.29                                             | 9.70                                             |
| Reflections measured                                 | 1456                                             | 1091                                             |
| Independent reflections                              | 1342                                             | 1022                                             |
| No. variables                                        | 152                                              | 118                                              |
| Reflection/parameter ratio                           | 8.83                                             | 8.66                                             |
| Residuals: <i>R</i> ; <i>R</i> <sub>w</sub>          | 0.052; 0.086                                     | 0.045; 0.061                                     |
| Residuals: <i>R</i> 1                                | 0.028                                            | 0.021                                            |
| No. of Reflections to calcd <i>R</i> 1               | 1015 ( <i>I</i> > 2.0 $\sigma$ ( <i>I</i> ))     | 884 ( <i>I</i> > 2.0 $\sigma$ ( <i>I</i> ))      |
| Goodness of fit indicator                            | 0.92                                             | 0.93                                             |
| Maximum peak in final<br>diff. map/e Å <sup>-3</sup> | 0.54                                             | 0.19                                             |
| Minimum peak in final<br>diff. map/e Å <sup>-3</sup> | -0.75                                            | -0.68                                            |

Table 2. Selected Bond Distances (Å) and Angles (deg) for **3a**

| Bond distances |          |           |          |
|----------------|----------|-----------|----------|
| Mo1–C1         | 2.219(7) | Mo1–C10   | 2.222(7) |
| Mo1–C6         | 2.222(7) | N1–C1     | 1.366(6) |
| Mo1–C7         | 2.292(6) | N1–C2     | 1.383(8) |
| Mo1–C8         | 2.300(7) | N1–C3     | 1.474(9) |
| Mo1–C9         | 2.289(6) | C2–C2*    | 1.34(2)  |
| Bond angles    |          |           |          |
| C1–N1–C2       | 110.9(6) | Mo1–C1–N1 | 128.1(3) |
| C1–N1–C3       | 125.8(5) | N1–C1–N1* | 103.9(6) |
| C2–N1–C3       | 123.2(6) | N1–C2–C2* | 107.1(4) |

Table 3. Selected Bond Distances (Å) and Angles (deg) for **3b**

| Bond distances |          |           |          |
|----------------|----------|-----------|----------|
| Mo1–C1         | 2.212(6) | Mo1–C8    | 2.228(4) |
| Mo1–C4         | 2.219(4) | N1–C1     | 1.359(5) |
| Mo1–C5         | 2.286(4) | N1–C2     | 1.370(6) |
| Mo1–C6         | 2.295(4) | N1–C3     | 1.463(8) |
| Mo1–C7         | 2.287(5) | C2–C2*    | 1.38(2)  |
| Bond angles    |          |           |          |
| C1–N1–C2       | 112.3(5) | Mo1–C1–N1 | 128.3(3) |
| C1–N1–C3       | 125.3(4) | N1–C1–N1* | 103.5(5) |
| C2–N1–C3       | 122.4(5) | N1–C2–C2* | 106.0(4) |

## Experimental

**General Procedures.** All manipulations involving air and moisture-sensitive organometallic compounds were carried out under an atmosphere of dry argon by using a standard Schlenk tube or high vacuum techniques. All solvents were distilled over appropriate drying agents prior to use. MoCl<sub>5</sub> and WCl<sub>6</sub> were purchased from Mitsuwa Pure Chemicals and Kanto Chemical Co., Inc., respectively, and used as received. <sup>n</sup>BuLi in a hexane solution was purchased from Kanto Chemical Co., Inc. and titrated prior to use. Other reagents employed in this research were used without further purification. [MoCp<sub>2</sub>(H)(OTs)] (**1**),<sup>6</sup> 1,3-diisopropylimidazolium chloride (iPr·HCl, **2a**),<sup>9</sup> 1,3-dimethylimidazolium iodide (IMe·HI, **2b**),<sup>23</sup> 1,3-bis(2,4,6-trimethylphenyl)-imidazolium chloride (IMes·HCl, **2c**),<sup>24</sup> 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (InMes·HCl, **2d**),<sup>18</sup> 1,3-bis(2,6-

diisopropylphenyl)imidazolium chloride (InDipp·HCl, **2e**),<sup>18</sup> and *N,N,N',N'*-tetraisopropylformamidinium chloride (**2f**),<sup>19</sup> [MoCp<sub>2</sub>(H)Li]<sub>4</sub> (**6-Mo**),<sup>17</sup> and [WCp<sub>2</sub>(H)Li]<sub>4</sub> (**6-W**)<sup>17</sup> were prepared according to literature methods.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL EX-270 spectrometer at ambient temperature. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were reported in ppm relative to Me<sub>4</sub>Si. All coupling constants were reported in Hz. A photo-reaction was performed with a Riko Kagaku Sangyo 100 W high-pressure Hg lamp placed in a water-cooled Pyrex jacket. Complexes **3a–3d** were so unstable toward air and moisture that correct elemental analysis data could not be obtained, though satisfactory spectroscopic data were obtained (vide infra).

**Preparation of [MoCp<sub>2</sub>(iPr)] (**3a**). Method A:** [MoCp<sub>2</sub>(H)(OTs)] (**1**) (710 mg, 1.78 mmol), iPr·HCl (**2a**) (351 mg, 1.86 mmol), and KO<sup>t</sup>Bu (413 mg, 3.38 mmol) were put into a

Schlenk tube, which was attached to a high-vacuum line. THF (ca. 15 mL) was added by a trap-to-trap-transfer technique at  $-78^{\circ}\text{C}$ , and the reaction mixture was allowed to warm to room temperature. The solution was then stirred over-night to give a dark-red solution. After removing the volatiles under reduced pressure, the residual solid was extracted with toluene. The filtrate was evaporated off under high vacuum, and spectroscopically pure **3a** was obtained (yield, 546 mg, 1.44 mmol, 81%).  $^1\text{H}$ NMR (in  $\text{THF}-d_8$ )  $\delta$  1.24 (d,  $^3J_{\text{HH}} = 6.6$  Hz, 12H,  $\text{NCCH}_3$ ), 3.65 (s, 10H,  $\text{C}_5\text{H}_5$ ), 6.86 (sept,  $^3J_{\text{HH}} = 6.6$  Hz, 2H,  $\text{NCHCH}_3$ ), 7.15 (s, 2H,  $\text{HCCH}$ ); (in benzene- $d_6$ )  $\delta$  0.89 (d,  $^3J_{\text{HH}} = 6.4$  Hz, 12H,  $\text{NCCH}_3$ ), 3.99 (s, 10H,  $\text{C}_5\text{H}_5$ ), 6.24 (s, 2H,  $\text{HCCH}$ ) 6.89 (sept,  $^3J_{\text{HH}} = 6.4$  Hz, 2H,  $\text{NCHCH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$ NMR (in  $\text{THF}-d_8$ )  $\delta$  23.5 ( $\text{NCCH}_3$ ), 55.2 ( $\text{NCCH}_3$ ), 70.2 ( $\text{C}_5\text{H}_5$ ), 118.4 ( $\text{NCC}$ ), 193.6 ( $\text{NCN}$ ); (in benzene- $d_6$ )  $\delta$  23.1 ( $\text{NCCH}_3$ ), 54.3 ( $\text{NCCH}_3$ ), 70.4 ( $\text{C}_5\text{H}_5$ ), 117.0 ( $\text{NCC}$ ), 193.7 ( $\text{NCN}$ ).

**Method B:**  $[\text{MoCp}_2(\text{H})\text{Li}]_4$  (**6-Mo**) (355 mg, 0.38 mmol) and **2a** (286 mg, 1.52 mmol) were put into a Schlenk tube, which was attached to a high-vacuum line. THF (ca. 15 mL) was added by a trap-to-trap-transfer technique at  $-78^{\circ}\text{C}$ , and the reaction mixture was allowed to warm to room temperature. The solution was then irradiated with a 100 W high-pressure Hg lamp at ambient temperature for 3 h to give a dark-red solution. After removing the volatiles in vacuo, the residual solid was extracted with benzene. The filtrate was evaporated off; the removal of a concomitantly formed  $[\text{MoCp}_2(\text{H})_2]$  (**7-Mo**) by sublimation ( $60^{\circ}\text{C}$ ,  $10^{-2}$  mmHg) afforded **3a** (yield, 316 mg, 0.84 mmol, 55%). Complex **3a** can be further purified by sublimation at  $120^{\circ}\text{C}$  in vacuo ( $10^{-2}$  mmHg).

**Preparation of  $[\text{MoCp}_2(\text{IME})]$  (**3b**). Method A:** Complex **3b** was prepared from  $[\text{MoCp}_2(\text{H})(\text{OTs})]$  (**1**) (245 mg, 0.62 mmol),  $\text{IME}\cdot\text{HI}$  (**2b**) (202 mg, 0.90 mmol), and  $\text{KO}^t\text{Bu}$  (158 mg, 1.41 mmol) in the same manner as that for **3a**. **3b** was isolated as a dark-red solid (yield, 157 mg, 0.49 mmol, 79%).  $^1\text{H}$ NMR (in benzene- $d_6$ )  $\delta$  3.55 (s, 6H,  $\text{NCH}_3$ ), 3.89 (s, 10H,  $\text{C}_5\text{H}_5$ ), 6.06 (s, 2H,  $\text{HCCH}$ );  $^{13}\text{C}\{^1\text{H}\}$ NMR (in benzene- $d_6$ )  $\delta$  39.8 ( $\text{NCH}_3$ ), 70.6 ( $\text{C}_5\text{H}_5$ ), 120.4 ( $\text{NCC}$ ), 197.3 ( $\text{NCN}$ ).

**Method B:** This complex was prepared from  $[\text{MoCp}_2(\text{H})\text{Li}]_4$  (**6-Mo**) (260 mg, 0.28 mmol) and **2b** (260 mg, 1.16 mmol) in the same manner as that for **3a**. **3b** was isolated as a dark-red solid (yield, 181 mg, 0.56 mmol, 50%).

**Preparation of  $[\text{MoCp}_2(\text{IMes})]$  (**3c**). Method A:** Complex **3c** was prepared from  $[\text{MoCp}_2(\text{H})(\text{OTs})]$  (**1**) (355 mg, 0.89 mmol),  $\text{IMes}\cdot\text{HCl}$  (**3c**) (303 mg, 0.89 mmol), and  $\text{KO}^t\text{Bu}$  (201 mg, 1.79 mmol) in the same manner as that for **3a**. **3c** was isolated as a brown solid (yield, 336 mg, 0.63 mmol, 71%).  $^1\text{H}$ NMR (in benzene- $d_6$ )  $\delta$  2.08 (s, 6H,  $p\text{-(CH}_3)_3\text{C}_6\text{H}_2$ ), 2.12 (s, 12H,  $o\text{-(CH}_3)_3\text{C}_6\text{H}_2$ ), 3.69 (s, 10H,  $\text{C}_5\text{H}_5$ ), 6.16 (s, 2H,  $\text{HCCH}$ ), 6.76 (s, 4H,  $m\text{-(CH}_3)_3\text{C}_6\text{H}_2$ );  $^{13}\text{C}\{^1\text{H}\}$ NMR (in benzene- $d_6$ )  $\delta$  19.2 ( $o\text{-(CH}_3)_3\text{C}_6\text{H}_2$ ), 20.9 ( $p\text{-(CH}_3)_3\text{C}_6\text{H}_2$ ), 71.0 ( $\text{C}_5\text{H}_5$ ), 123.2 ( $\text{NCC}$ ), 129.6 ( $m\text{-(CH}_3)_3\text{C}_6\text{H}_2$ ), 135.4 ( $o\text{-(CH}_3)_3\text{C}_6\text{H}_2$ ), 137.6 ( $p\text{-(CH}_3)_3\text{C}_6\text{H}_2$ ), 138.7 ( $ipso\text{-(CH}_3)_3\text{C}_6\text{H}_2$ ), 201.8 ( $\text{NCN}$ ).

**Method B:** This complex was prepared from  $[\text{MoCp}_2(\text{H})\text{Li}]_4$  (**6-Mo**) (238 mg, 0.25 mmol) and **3c** (341 mg, 1.00 mmol) in the same manner as that for **3a**. **3c** was isolated as a brown solid (yield, 265 mg, 0.50 mmol, 50%).

**Preparation of  $[\text{MoCp}_2(\text{InMes})]$  (**3d**). Method B:** This complex was prepared from  $[\text{MoCp}_2(\text{H})\text{Li}]_4$  (**6-Mo**) (208 mg, 0.22 mmol) and  $\text{InMes}\cdot\text{HCl}$  (**3d**) (304 mg, 0.89 mmol) in the same manner as that for **3a**. **3d** was isolated as a dark-green solid (yield, 213 mg, 0.40 mmol, 45%).  $^1\text{H}$ NMR (in benzene- $d_6$ )  $\delta$  2.14 (s, 6H,  $p\text{-(CH}_3)_3\text{C}_6\text{H}_2$ ), 2.26 (s, 12H,  $o\text{-(CH}_3)_3\text{C}_6\text{H}_2$ ), 3.04

(s, 4H,  $\text{H}_2\text{CCH}_2$ ), 3.77 (s, 10H,  $\text{C}_5\text{H}_5$ ), 6.79 (s, 4H,  $m\text{-(CH}_3)_3\text{C}_6\text{H}_2$ );  $^{13}\text{C}\{^1\text{H}\}$ NMR (in benzene- $d_6$ )  $\delta$  19.3 ( $o\text{-(CH}_3)_3\text{C}_6\text{H}_2$ ), 20.9 ( $p\text{-(CH}_3)_3\text{C}_6\text{H}_2$ ), 52.5 ( $\text{NCC}$ ), 73.0 ( $\text{C}_5\text{H}_5$ ), 130.1 ( $m\text{-(CH}_3)_3\text{C}_6\text{H}_2$ ), 135.8 ( $o\text{-(CH}_3)_3\text{C}_6\text{H}_2$ ), 136.3 ( $p\text{-(CH}_3)_3\text{C}_6\text{H}_2$ ), 140.5 ( $ipso\text{-(CH}_3)_3\text{C}_6\text{H}_2$ ), 234.5 ( $\text{NCN}$ ).

**NMR Tube Reaction of 6-Mo with Salt 2.** A typical procedure for the tube reaction was as follows.  $[\text{MoCp}_2(\text{H})\text{Li}]_4$  (**6-Mo**) (ca. 20 mg, 0.021 mmol) and four equivalents of corresponding salt **2** were placed in an NMR tube, which was attached to a high-vacuum line.  $\text{THF}-d_8$  (ca. 0.4 mL) was introduced onto the mixture by a trap-to-trap-transfer technique at  $-78^{\circ}\text{C}$ , and then the NMR tube was flame-sealed. The reaction mixture was allowed to warm to room temperature. The resulting solution was subjected to a  $^1\text{H}$ NMR measurement, which indicated the formation of  $[\text{MoCp}_2(\text{H})_2]$  (**7-Mo**) and the free carbene (**4**).  $^1\text{H}$ NMR data for **7-Mo**:  $\delta$   $-9.24$  (s, 2H,  $\text{MoH}$ ), 4.54 (s, 10H,  $\text{C}_5\text{H}_5$ ). For **4a**:  $\delta$  1.34 (d,  $^3J_{\text{HH}} = 6.2$  Hz, 12H,  $\text{NCCH}_3$ ), 4.95 (sept,  $^3J_{\text{HH}} = 6.2$  Hz, 2H,  $\text{NCHCH}_3$ ), 6.99 (s, 2H,  $\text{HCCH}$ ). For **4e**:  $\delta$  1.19 (d,  $^3J_{\text{HH}} = 6.9$  Hz, 12H,  $\text{CHCH}_3$ ), 1.28 (d,  $^3J_{\text{HH}} = 6.9$  Hz, 12H,  $\text{CHCH}_3$ ), 3.22 (sept,  $^3J_{\text{HH}} = 6.9$  Hz, 4H,  $\text{CHCH}_3$ ), 3.78 (s, 4H,  $\text{H}_2\text{CCH}_2$ ), 7.15–7.27 (m, 6H,  $\text{Ph}$ ). For **4f**:  $\delta$  0.98 (d,  $^3J_{\text{HH}} = 6.4$  Hz, 24H,  $\text{CHCH}_3$ ), 3.30 (sept,  $^3J_{\text{HH}} = 6.4$  Hz, 4H,  $\text{CHCH}_3$ ).

**NMR Tube Reaction of 6-W with 2a.**  $[\text{Cp}_2\text{W}(\text{H})\text{Li}]_4$  (**6-W**) (28 mg, 0.022 mmol) and  $\text{I}^t\text{Pr}\cdot\text{HCl}$  **2a** (17 mg, 0.090 mmol) were placed in an NMR tube, which was attached to a high-vacuum line. After  $\text{THF}-d_8$  (ca. 0.4 mL) was introduced onto the mixture by a trap-to-trap-transfer technique at  $-78^{\circ}\text{C}$ , the NMR tube was flame-sealed. The reaction mixture was allowed to warm to room temperature. The resulting solution was subjected to a  $^1\text{H}$ NMR measurement, which indicated the formation of  $[\text{WCp}_2(\text{H})_2]$  (**7-W**) and  $\text{I}^t\text{Pr}$  (**4a**).  $^1\text{H}$ NMR data for **7-W**:  $\delta$   $-12.77$  (s, 2H,  $\text{WH}$ ,  $^1J_{\text{WH}} = 73.3$  Hz), 4.44 (s, 10H,  $\text{C}_5\text{H}_5$ ). For **4a**:  $\delta$  1.34 (d,  $^3J_{\text{HH}} = 6.4$  Hz, 12H,  $\text{NCCH}_3$ ), 4.85 (sept,  $^3J_{\text{HH}} = 6.4$  Hz, 2H,  $\text{NCHCH}_3$ ), 6.96 (s, 2H,  $\text{HCCH}$ ).

**X-ray Structure Analyses for 3a and 3b.** Single crystals of **3a** and **3b** were obtained from a toluene solution at  $-30^{\circ}\text{C}$  and sealed under Ar in a thin-walled glass capillary, respectively. X-ray crystallography was performed on a Rigaku AFC-7R diffractometer with graphite monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71069$  Å). The diffraction data for **3a** and **3b** were collected at 296(2) K using the  $\omega$ - $2\theta$  scan technique to a maximum  $2\theta$  value of  $60.0^{\circ}$ . Cell constants and an orientation matrix for data collection were determined from 25 reflections with  $2\theta$  angles in the ranges  $28.81$ – $29.77^{\circ}$  (for **3a**) and  $28.72$ – $29.93^{\circ}$  (for **3b**), respectively. The structure was solved by direct methods (SIR 92)<sup>25</sup> and expanded using Fourier techniques.<sup>26</sup> The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located from difference Fourier maps and refined isotropically. All calculations were performed using the teXsan<sup>27</sup> crystallographic software package of Molecular Structure Corporation.

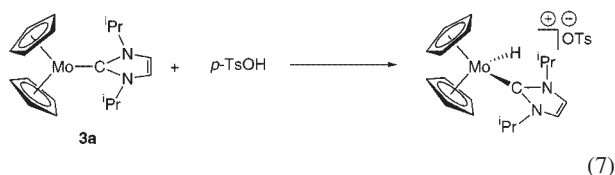
Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 188521 for **3a** and 188522 for **3b**.

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- 8 1,3-Disubstituted imidazol-2-ylidenes are abbreviated as IR, where "I" stands for a skeleton of the unsubstituted imidazol-2-ylidene and "R" stands for the substituents on nitrogens.
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- 10 See Experimental Section.
- 11 We now investigate the reactivity of molybdenocene derivatives of an *N*-heterocyclic carbene (**3**). We have obtained a preliminary result concerning the reaction of **3a** with *p*-TsOH. In the reaction, the cationic hydrido complex, [MoCp<sub>2</sub>(H)(*i*Pr)<sup>+</sup>[OTs]<sup>−</sup>, was formed (Eq. 7). Further details of the reaction of **3** with organic substrates will be reported elsewhere.



12 A referee suggested that, in method A, [MoCp<sub>2</sub>] may be initially formed in the reaction of compound **1** with KO<sup>t</sup>Bu and then it reacts with carbene **4** generated in situ to give final product **3** (Eqs. 8 and 9). Although such reaction pathway cannot be ruled out completely, the proposed mechanism shown in Scheme 2 seems to be more plausible taking into account our previous results on the reaction of **1** with phosphorus compounds (Eq. 1). We wish to thank a referee for insightful comments.



- 13 The abbreviation "In" stands for a five-membered imidazolin-2-ylidene skeleton.
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