

Synthesis and structure of an imido-tethered Schrock carbene of molybdenum†

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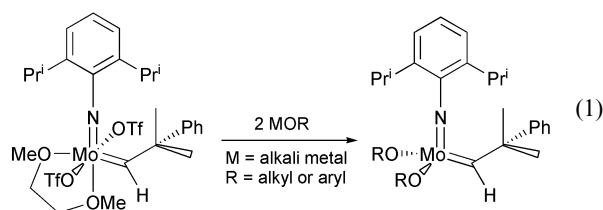
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An 8-membered molybdenum azametallacycle, where a Mo=C bond and a Mo=N bond are linked, incorporating two triflate co-ligands has been synthesized and structurally characterized.

Metal–carbon double bonds where the metal is in a moderate to high oxidation state, Schrock carbenes or alkylidenes, seem to have an ever-increasing importance in small molecule and polymer chemistry due to their activity in double-bond metathesis.^{1,2} Since the original discovery of high oxidation state carbenes by Schrock in 1973,³ a plethora of carbene complexes in moderate to high oxidation states have been prepared across much of the periodic table.⁴ Some of the most active double-bond metathesis catalysts are the molybdenum(vi) imido carbene complexes, which are prepared by addition of alkoxides to bis(triflate) precursors (Equation 1). The triflate ligands may be replaced by a variety of different alkoxides,⁵ including chiral ancillaries⁶ for use in enantioselective ring-closing metathesis and solid-supported alkoxides.⁷



Fürstner and co-workers provided the initial reports on tethering the reactive ruthenium carbene functional group to an *N*-heterocyclic carbene ancillary ligand (Fig. 1).⁸ These carbenes were investigated for ring-closing metathesis as catalysts capable of regenerating the original species on depletion of substrate. More recently, Grubbs and coworkers have examined tethered ruthenium carbenes for selective cyclo-polymerization of olefins by ring-opening metathesis polymerization.⁹ The tether retains a high local concentration of both termini of the growing polymer near the metal, enabling a final macrocyclic ring-closing metathesis event.

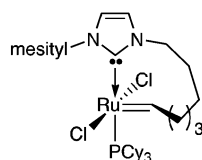


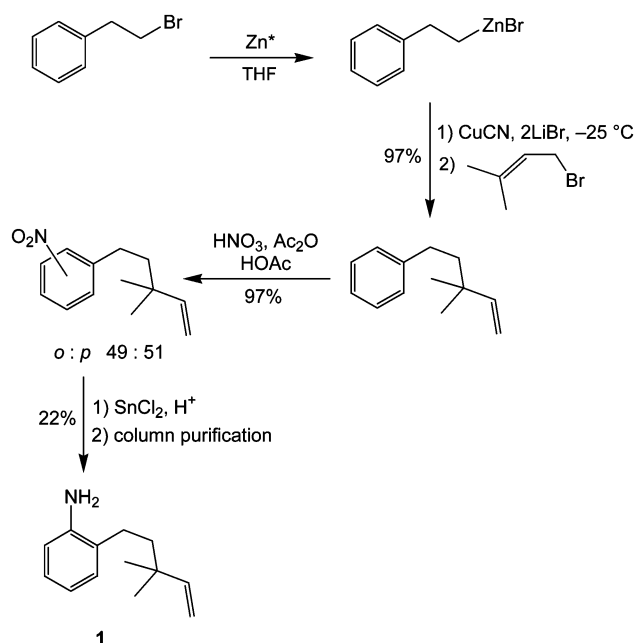
Fig. 1 Ruthenium catalyst with carbene tethered to ancillary ligand.

In a similar vein, we have been investigating the chemistry of tethered molybdenum carbenes, where the active carbene centre is attached through an aliphatic chain to an ancillary ligand on molybdenum. Like its ruthenium counterparts, it is hoped that

tethered catalysts would provide greater catalyst reusability by trapping less stable methyldiene intermediates once substrates are consumed. In addition, cyclo-oligomerization and -polymerization products with numerous possible applications may be accessible utilizing these new molybdenum complexes.

To generate a stable tethered carbene and provide a bis(triflate) precursor useful for a variety of purposes, it was desirable to use the imido substituent as the ancillary ligand of attachment. However, relatively few complexes are known where two molybdenum metal–ligand multiple bonds are tethered to form a metallacycle. A few Group-6 mutually tethered di-carbenes have been reported, usually prepared through oligomerization of alkynes by reduced complexes.¹⁰ Tethered Group-6 bis(imido), *ansa*-di(organoimido), complexes have been prepared as analogs of *ansa*-metallocenes of the Group-4 elements and studied for Zeigler–Natta polymerization activity.¹¹ The typical ring sizes used in the generation of tethered organoimidos are 7–8 membered metallacycles. Consequently, we sought a ring size in this regime.

The successful strategy for the synthesis of the tethered carbene involved attachment to the *ortho*-position of an arylimido and generating an 8-membered azametallacycle. The synthesis of the aniline derivative is outlined in Scheme 1. The synthesis begins with commercially available 2-bromoethylbenzene, which is converted to the alkyl zinc by reaction with Reike zinc. Copper-mediated addition to 3,3-dimethylallyl bromide¹² occurs with the desired *S_N2'* to *S_N2* addition in a ratio of ~9 : 1 in 97% combined yield of isomers.¹³ The undesired isomer was not removed at this point, and the mixture was nitrated under standard conditions¹⁴ in high yield. The nitration occurs to generate a mixture of *ortho* and *para* isomers in a near equimolar ratio. Again, the mixture was carried forward

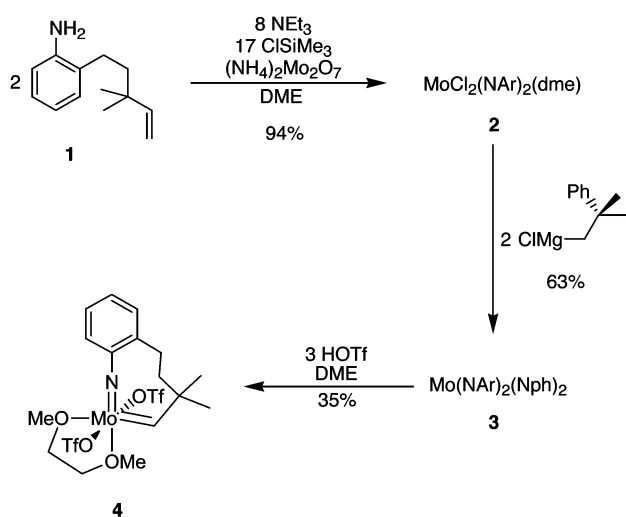


Scheme 1 Synthesis of 2-(3,3-dimethylpent-4-enyl)aniline (1).

† Electronic supplementary information (ESI) available: Synthetic details for the generation of 2-(3,3-dimethylpent-4-enyl)aniline (1) and the tethered molybdenum carbene 4. Tables for the X-ray diffraction study on 4. See <http://www.rsc.org/suppdata/dt/b3/b311320p/>

without separation of isomers. Reduction of the nitro group¹⁵ provided a mixture of aniline derivatives that were readily separable by column chromatography. The final step gave 22% yield of the desired *ortho*-substituted aniline **1** based on the crude mixture of nitro isomers.

The synthetic protocol for molybdenum carbene synthesis is a modification of the literature procedure (Scheme 2).⁵ Reaction of **1** (H_2NAr) with NEt_3 , ClSiMe_3 , and $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ in DME provided 94% yield of $\text{Mo}(\text{NAr})_2(\text{Cl})_2(\text{DME})$ (**2**). Alkylation of **2** with 2 equiv. of neophylmagnesium chloride (NphMgCl) afforded 64% yield of $\text{Mo}(\text{Nph})_2(\text{NAr})_2$ (**3**). Addition of 3 equiv. of triflic acid in DME removes one imido ligand as the anilinium triflate and presumably generates an intermediate neophylidene bis(triflate), which was not observed. Instead, the molybdenum carbene undergoes rapid cyclization with the alkene pendant to the arylimido producing the desired tethered carbene in 35% isolated yield. Examination of the bis(triflate) by multinuclear NMR in d_8 -THF suggested 3 isomers were present in fluid solution, a complication also observed in untethered systems.⁴



Scheme 2 Synthesis of imido tethered carbene.

Bis(triflate) **4** exhibits low solubility in many common solvents. However, crystals sufficient for a preliminary X-ray diffraction study were obtained.† The isomer observed is line drawn in Scheme 2, and a structural representation from the diffraction study is shown in Fig. 2. When the structure of

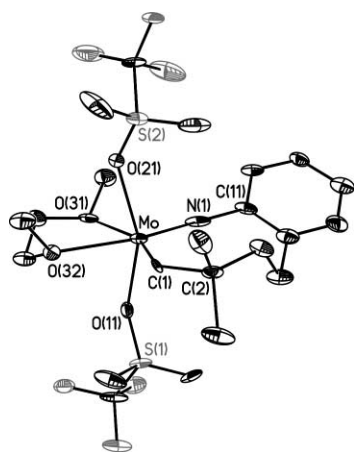


Fig. 2 Structure of **4** as found by X-ray diffraction. Selected bond distances (Å) and angles (°): Mo(1)–C(1) 1.827(19), Mo(1)–N(1) 1.723(16), Mo(1)–C(1)–C(2) 139.7(12), Mo(1)–N(1)–C(1) 173.3(14), N(1)–Mo–C(1) 101.4(7).

4 is compared to that reported for $\text{Mo}(\text{OTf})_2(\text{N-2,6-diPr}^i\text{-C}_6\text{H}_3)(\text{neopentylidene})(\text{DME})$,¹⁶ no ring strain is apparent in the metallacycle as judged by comparison of bond distances and angles.

As would be expected, the tethered carbene **4** is an active catalyst for the ROMP of norbornylene. The materials generated in those polymerizations are currently under scrutiny. Various substitution reactions on the triflate groups are being investigated as a means of synthesizing more functional metathesis catalysts.

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Notes and references

† The crystals isolated were relatively weak diffractors, but a satisfactory structure was obtained. Crystal data for **4**: $\text{C}_{18}\text{H}_{25}\text{F}_6\text{MoNO}_8\text{S}_2$, $M = 657.45$, monoclinic, $a = 12.669(3)$, $b = 15.745(5)$, $c = 12.809(4)$ Å, $\beta = 92.648(6)^\circ$, $U = 2552.3(12)$ Å³, $P2(1)/c$, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.764$, $T = 176(2)$ K, 11563 reflections, 3698 unique ($R_{\text{int}} = 0.2814$). The final $wR(F^2) = 0.2494$ and $R(F) = 0.1088$ for reflections $I > 2\sigma$. CCDC reference numbers 217504. See <http://www.rsc.org/suppdata/dt/b3/b311320p/> for crystallographic data in CIF or other electronic format.

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