



A readily-prepared and efficient solid-supported scavenger for molybdenum alkoxides and a structurally characterized model complex

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ABSTRACT

A very effective solid support for the removal of molybdenum-based metathesis catalysts can be prepared by placing a salicylimine on a polystyrene support. The resin is produced by treating Merrifield's resin with H_2NBU^n , 4-chloromethylsalicylaldehyde, and *p*-toluidine in succession. The final resin had an identifiable C=N stretch in the IR and a resonance assigned to the HC=N hydrogen was found by MAS ^1H NMR of the swelled resin. Solutions of $\text{Mo}[\text{C}(\text{H})\text{CMe}_2\text{Ph}](\text{NAr})(\text{OBU}^n)_2$ (Mo_{F6}) and $\text{Mo}[\text{C}(\text{H})\text{CMe}_2\text{Ph}](\text{NAr})(\text{OAd})_2$ (Mo_{Ad}), where Ar = 2,6-diisopropylphenyl and Ad = 1-adamantyl, were treated with the scavenger, which reduced the remaining molybdenum concentration as examined by ICP-MS to 30–50 ppb. Catalyst was also scavenged from ring-closing metathesis of diethyl diallylmalonate by Mo_{F6} ; the decrease in molybdenum concentration on addition of scavenger followed first order kinetics with initial and final concentrations of 54000 and 15 ppb, respectively. We also prepared a model system where a soluble salicylimine (H-DIB) was reacted with $\text{Mo}[\text{C}(\text{H})\text{CMe}_2\text{Ph}](\text{NAr})(\text{OAd})_2$ to produce $\text{Mo}[\text{C}(\text{H})\text{CMe}_2\text{Ph}](\text{NAr})(\text{DIB})_2$, which was structurally characterized.

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1. Introduction

The scavenging of metal catalysts from solution can be an important step in producing useful products [1]. In many cases, if the catalyst can be removed using a selective scavenger, time-consuming chromatography can be avoided [2]. In addition, clean removal of catalysts without quenching of the entire reaction mixture, which usually means addition of aqueous solutions, avoids aqueous waste streams and can leave the product ready for further reactions. Also, removal of a catalyst from the soluble polymers generated is sometimes essential for the stability and properties of the material [3].

We desired a readily-prepared scavenger for molybdenum olefin metathesis catalysts [4] that could be added to reaction mixtures and then filtered away to remove the metal complex. Another parameter was that the resin used needed to simply replace ancillary ligands, e.g. chloride or alkoxide, and not lead to complete decomposition of the catalyst and contamination of the reaction mixtures by all of the ligands on the metal. This unselective removal of all the ligands on the metal might be expected from supports like alumina and silica bearing terminal hydroxyls, and we chose to use a relatively inert polystyrene support. Lastly, the ideal quenching agent would be prepared in only a few steps using inexpensive reagents and would be reusable after some method of removing the metal from the resin.

2. Results and discussion

For this study, a simple bidentate salicylimine seemed well suited as these ligands are commonly employed across the transition series, and salicylimine derivatives have been incorporated onto solid supports for various applications [5].

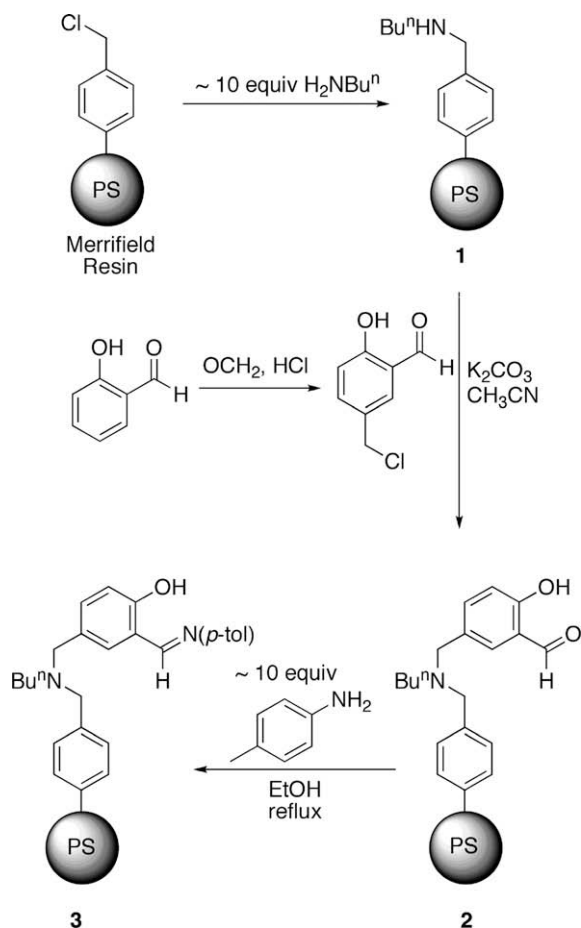
The design settled upon started with Merrifield Resin due to its relative affordability and ready availability from numerous commercial sources. In this work, a sample of 3.5–4.5 mmol of Cl/g of polystyrene (PS) resin was purchased from Aldrich with a 200–400 mesh size. In all of the steps, an internal standard, dodecane, was added, and the disappearance of the reagent from solution was monitored by GC–FID. The reactions were run until the reagent concentration in solution leveled. For all three steps, the loading of reagent as measured by loss of starting material was ~ 3.5 mmol/g of resin.

The initial step was the addition of excess *n*-butylamine (Scheme 1). In principle, almost any primary amine could be used, but this basic amine is small with a substantial enough boiling point to make it easy to use. After treatment with amine, poly(styrene)-tethered secondary amine **1** should result.

Secondary amines are known to react [6] cleanly with 5-(chloromethyl)salicylaldehyde, which is readily-prepared on large scales from salicylaldehyde, paraformaldehyde, and HCl [7]. The PS-tethered secondary amine was treated with 5-(chloromethyl)salicylaldehyde in the presence of K_2CO_3 in acetonitrile to provide salicylaldehyde attached to poly(styrene) **2**. Finally, treatment of the PS-tethered salicylaldehyde **2** with *p*-toluidine in EtOH

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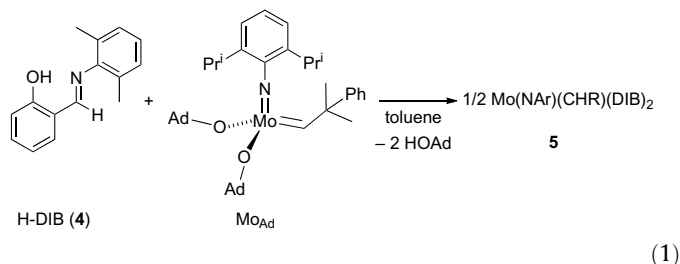
Scheme 1. Synthesis of the polystyrene (PS) scavenger **3**.

resulted in the bright yellow salicylimine scavenger **3**. Here also, a large variety of aniline derivatives are likely as applicable as *p*-toluidine.

Characterization of resins during reaction sequences was done using several techniques. The starting resin was reacted with H_2NBU . The amine loss was observed by GC–FID vs. dodecane internal standard, which is likely a rough gauge at best due to likely absorption of amine and standard by the resin. In all cases the loss of reagent from solution was higher than that expected for the amount of resin present using this technique. The beads were washed to remove as much of the physisorbed reagent as possible. The beads after reaction to form **1** and basic workup had a negative halide test indicating that all the chloromethyl groups of the starting Merrifield Resin had been consumed. In the next step, resin **2** showed a strong $\text{O}=\text{C}$ stretch in the IR. After production of **3**, the resonance in the IR ascribed to the carbonyl stretch had disappeared. A new resonance at 1640 cm^{-1} assigned to the $\text{C}=\text{N}$ stretch was found. Swelling the polymer with C_6D_6 and using MAS ^1H NMR led to an easily observed imine hydrogen resonance at 8.6 ppm, where expected for the surface bound imine as judged from the spectrum of molecular 2-(*p*-tolylimino)phenol.

Before reactions with material **3**, we tested replacement of alkoxides with a salicylimine derivative H-DIB (**4**) (Eq. (1)) in homogeneous solution on a derivative of Schrock's catalyst, $\text{Mo}(\text{NAr})(\text{OAd})_2(\text{CHR})$ (Mo_{Ad}) where $\text{Ar} = 2,6$ -diisopropylphenyl, $\text{R} = \text{dimethylphenylmethyl}$, and $\text{Ad} = 1$ -adamantyl. A salicylimine was prepared from salicylaldehyde and 2,6-dimethylaniline by refluxing in ethanol. The protio ligand 2-hydroxy-1-(2,6-dimethylphenyl)iminobenzaldehyde (H-DIB, **4**) crystallized readily as lemon yellow plates. Reaction of Mo_{Ad} with 1 equiv of **4** resulted in

formation of $\frac{1}{2}$ equiv of $\text{Mo}(\text{CHR})(\text{NAr})(\text{DIB})_2$ (**5**) and $\frac{1}{2}$ equiv of starting Mo_{Ad} . The reaction was complete in minutes at room temperature and appeared quantitative by NMR spectroscopy.



Complex **5** was prepared for characterization by reaction of two equivalents of **4** with Mo_{Ad} . Separation of the complex from generated HOAd by crystallization afforded pure **5** as a red solid. The compound has been examined by X-ray diffraction, and an ORTEP diagram from the model is shown in Fig. 1.

As might be expected, the two metal–ligand multiple bonds are *cis* to avoid electronic competition between these strong *trans*-influencing ligands. Opposite these two strong donors are the relatively weakly donating imine groups. The $\text{Mo}(1)\text{--N}(2)$ distance *trans* to the imido is longer at $2.432(4)\text{ \AA}$ than the $\text{Mo}(1)\text{--N}(3)$ distance of $2.389(4)\text{ \AA}$ *trans* to the alkylidene. The $\text{Mo}(1)\text{--N}(1)$ imido and $\text{Mo}(1)\text{--C}(1)$ alkylidene distances are fairly typical at $1.731(4)$ and $1.931(4)\text{ \AA}$. The aryloxy oxygens are mutually *trans* in the solid-state structure and have distances from molybdenum of $2.006(3)$ and $2.032(3)\text{ \AA}$.

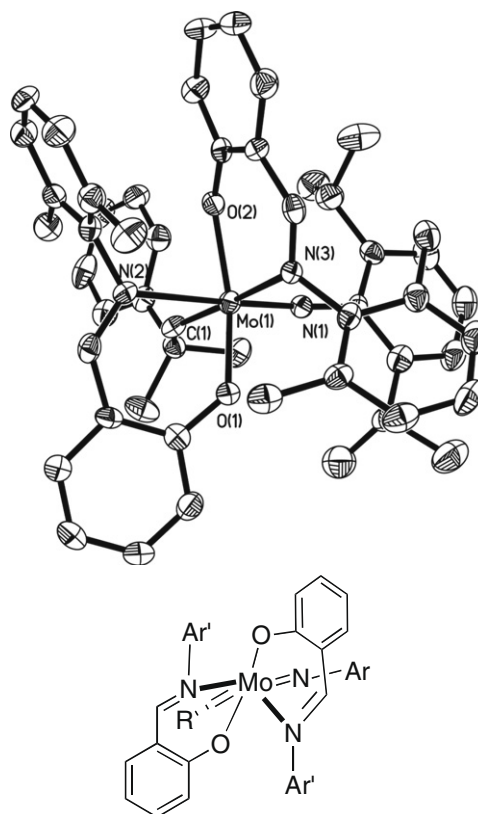


Fig. 1. ORTEP diagram of the model of **5** from the X-ray diffraction experiment and a line diagram showing a similar geometry where $\text{Ar} = 2,6$ -diisopropylphenyl, $\text{Ar}' = 2,6$ -dimethylphenyl, and $\text{R} = \text{CMe}_2\text{Ph}$. Selected bond distances (\AA) and angles ($^\circ$): $\text{Mo}(1)\text{--O}(1)$, $2.006(3)$; $\text{Mo}(1)\text{--O}(2)$, $2.032(3)$; $\text{Mo}(1)\text{--C}(1)$, $1.932(4)$; $\text{Mo}(1)\text{--N}(1)$, $1.731(4)$; $\text{Mo}(1)\text{--N}(3)$, $2.389(4)$; $\text{Mo}(1)\text{--N}(2)$, $2.432(4)$; $\text{N}(1)\text{--Mo}(1)\text{--C}(1)$ $97.69(18)$; $\text{N}(1)\text{--Mo}(1)\text{--O}(1)$ $101.14(14)$; $\text{C}(1)\text{--Mo}(1)\text{--O}(1)$, $94.68(15)$; $\text{N}(1)\text{--Mo}(1)\text{--O}(2)$, $100.15(14)$; $\text{C}(1)\text{--Mo}(1)\text{--O}(2)$, $98.04(15)$.

In solution, **5** has several different isomers available with one major compound and 5 minor isomers judging from the alkylidene region of the ^1H and ^{13}C NMR spectra. In the solid state, the observed isomer has the donor imines *trans* to the mutually *cis* metal ligand multiple bonds. The alkylidene substituent is *syn* to the imido nitrogen. Presumably, the other available isomers involve various combinations of alkoxides *trans* to metal ligand multiple bonds in combination with alkylidene rotations.

The compound was also investigated by ^{95}Mo NMR spectroscopy, and a single peak was observed at 548 ppm ($\nu_{1/2} = 2050$ Hz), which was somewhat broad due to the quadrupolar nature of the nucleus and perhaps the number of isomers in solution. For comparison, the ^{95}Mo NMR spectrum of $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{-Ph})(\text{OAd})_2$ (Mo_{Ad}) was also measured; a single resonance at 284 ppm ($\nu_{1/2} = 1632$ Hz) was found.

The salicylimine–PS system was tested as a scavenger for imido alkylidenes of molybdenum. Here, we used $\text{Mo}[\text{C}(\text{H})\text{CMe}_2\text{Ph}](\text{NAr})(\text{O}^t\text{Bu}_{\text{F}_6})_2$ (Mo_{F_6}) and $\text{Mo}[\text{C}(\text{H})\text{CMe}_2\text{Ph}](\text{NAr})(\text{OAd})_2$ (Mo_{Ad}), where Ar = 2,6-diisopropylphenyl and Ad = 1-adamantyl. The hexafluoro-*tert*-butoxide derivative Mo_{F_6} is one of the most commonly used metathesis catalysts and is commercially available [4]. Nonfluorinated alkoxides are often used in ring-opening metathesis polymerizations [4]; the most commonly employed of these being *tert*-butoxide. However, the *tert*-butoxide complex is quite lipophilic, and we have preferred to use the more crystalline but otherwise similar 1-adamantoxide complex Mo_{Ad} [8].

Toluene solutions of Mo_{F_6} and Mo_{Ad} were stirred for 1 h with the salicylimine–PS beads at room temperature. The yellow solutions of the complex quickly became colorless after the beads were added, and the light yellow beads darkened somewhat. The concentration of molybdenum [9] was measured using ICP-MS calibrated using an internal standard (Table 1). The concentration of molybdenum that remained in solution and on the beads was measured [10]. As shown in Table 1, this readily-prepared scavenger removed the molybdenum complex from solution down to the 30–50 ppb range. By comparison, the concentration on the beads was 90–130 ppm depending on the concentration of catalyst solution treated.

The beads were recycled by refluxing the molybdenum-loaded material in methanol under air for 6 h. After vacuum drying, the recycled beads were treated with solutions similar to those used previously. The recycled beads provided very similar results to the first use material and also removed molybdenum from solution down to the 30–50 ppb range according to ICP-MS (Table 1).

We also tested the new scavenger's ability to remove molybdenum from a ring-closing metathesis (RCM) reaction. For this test reaction, diethyl diallylmalonate (DEDAM) was used with 3.3 mol% Mo_{F_6} (Fig. 2). The RCM reaction was allowed to run for 2 h; when, it was found to be complete by GC–FID. To the crude reaction mixture was added the scavenger. Aliquots were taken periodically from the DEDAM RCM reaction after the scavenger was added. The aliquots were tested by ICP-MS to track the decrease in molybdenum concentration over time. The detected concentration of the metal dropped in an apparent first order [11] process from 54,000 ppb to 15 ppb over the course of about 50 min using an excess of the scavenger (Fig. 2). The half-life under

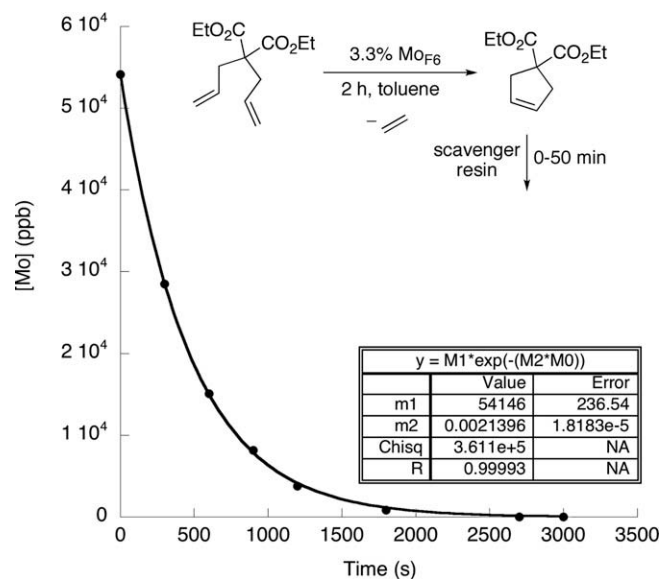


Fig. 2. Plot of molybdenum concentration vs. time after addition of scavenger to an RCM reaction.

these conditions for molybdenum removal was about five and a half minutes.

3. Concluding remarks

The scavenger production employed here simply involves sequential addition of butylamine, 5-(chloromethyl)salicylaldehyde, and *p*-toluidine to Merrifield resin. Using this simple resin, aqueous work up can be avoided and little waste is generated while employing the reusable material.

From the model study it appeared that $\text{Mo}(\text{OR})_2(\text{NAr})(=\text{CHR})$ complexes treated with salicylimine ligands only reacted at the alkoxide ligands, and reaction with either the imido or alkylidene was not observed. In one further test for the site of reactivity for the resin, we added resin to a 1:1 toluene- d_7 solution of Mo_{OAd} and ferrocene as an internal standard. As expected from the model study, NMR of the resin-treated solution only shows 1 equivalent of HOAd, relative to the standard, being generated; no other products were visible. In other words, consistent with the model system, the site of reaction on the molybdenum catalyst appears to be the alkoxide ligands. Unlike the model system, only one alkoxide is replaced, presumably due to ligand localization on the polystyrene beads.

We have developed a very simple and reusable resin to remove the catalyst down to the part per billion range. Consequently in cases where ring-closing metathesis provides clean products, treating with the scavenger and filtering would provide solutions ready for the next step of the synthesis.

4. Experimental

4.1. General considerations

All manipulations of air sensitive materials were carried out in an MBraun glove box under an atmosphere of purified nitrogen. Etheral solvents, pentane, and toluene were purchased from Aldrich Chemical Co. and purified through alumina columns to remove water after sparging with N_2 to remove oxygen. NMR solvents (C_6D_6 and CDCl_3) were purchased from Cambridge Isotopes Laboratories, Inc. Deuterated benzene was distilled from purple sodium benzophenone ketyl. Deuterated chloroform was

Table 1
Scavenger **3** test results for molybdenum catalysts.

		$[\text{Mo}_{\text{Ad}}]$ (ppm)	$[\text{Mo}_{\text{F}_6}]$ (ppm)
First use	Solution	0.046	0.042
	Beads	113.16	130.12
Recycled	Solution	0.050	0.036
	Beads	92.82	101.80

distilled from CaH_2 under dry N_2 . NMR solvents were stored under sealed containers equipped with a Teflon stopcock in the dry box prior to use. Spectra were taken on Varian instruments located in the Max T. Rogers Instrumentation Facility at Michigan State University. Routine coupling constants are not reported. The ^{95}Mo NMR spectra are reported relative to external $0.147\text{ M } (\text{NH}_4)_2\text{Mo}_2\text{O}_7$ in D_2O as 0 ppm. KBr was dried at 130°C under dynamic vacuum for at least 3 d, then stored under inert atmosphere. Celite was dried at $>200^\circ\text{C}$ under dynamic vacuum for at least 16 h, then stored under inert atmosphere. $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{OBU}^{\text{t}}_{\text{F6}})_2$ and $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{OAd})_2$ were prepared as reported in the literature [8]. Merrifield peptide resin (200–400 mesh, 3.5–4.5 mmol Cl^-/g), 2-hydroxybenzaldehyde, and para-formaldehyde were purchased from Aldrich Chemical Co. and were used without further purification. *n*-Butylamine was purchased from Aldrich Chemical Co. and distilled from potassium hydroxide prior to use. 5-(Chloromethyl)-2-hydroxybenzaldehyde was prepared as reported in the literature [7]. The Schiff bases 2-[(2,6-dimethyl-phenylimino)-methyl]-phenol (H-DIB, **4**) and 2-(*p*-tolylimino)phenol were prepared as reported in the literature [12]. Molybdenum-containing samples were analyzed on a Micro-mass (now Thermo Electron Corporation) Platform quadrupole ICP-MS with Hexapole collision cell using a CECTAC ASX-500 auto-sampler at Michigan State University. Combustion analyses were performed by facilities in the Department of Chemistry at Michigan State University. Tune conditions were optimized using a $10\ \mu\text{g/L}$ (ppb) solution of Be, Co, In, Ce, Bi, and U. The final nebulizer gas flow rate was $0.75\ \text{L/min}$. Samples were scanned for 1.0 min using a dwell time of 0.1 s. The instrument response was corrected using ^{115}In as an internal standard for the Mo samples. Final sample concentrations were quantified using a set of multi-element external calibration standards ranging from 0 to 1000 ppb.

4.2. Preparation of secondary amine resin (**1**)

In a 500 mL round bottom flask was loaded Merrifield peptide resin (5.0 g, 200–400 mesh, 3.5–4.5 mmol Cl^-/g). To this was added 200 mL CH_2Cl_2 , *n*- BuNH_2 (13.31 g, 182 mmol), and dodecane (3.835 g, 22.5 mmol). This reaction mixture was then refluxed for 2 d. After 2 d, the reaction mixture was cooled to room temperature and another batch of *n*- BuNH_2 (2.5 mL) was added, and the reaction mixture was refluxed for 2 h to ensure complete conversion. Finally, the volatiles were removed, and the resulting resin was washed with 2% NaOH solution ($3 \times 100\ \text{mL}$). The resin was washed again with hexanes ($5 \times 50\ \text{mL}$), and dried under vacuum at 40°C for 24 h to afford a white solid (5.683 g). This mass suggests $\sim 3.7\ \text{mmol amine/g}$. The resin had a negative halide test using AgNO_3 . FT-IR (KBr): 3000 (str br, NH) cm^{-1} .

4.3. Preparation of tethered salicylaldehyde resin (**2**)

This synthesis was adapted from that reported by Wei et al. [6d]. In a 500 mL round bottom flask was taken **1** (5.5 g), K_2CO_3 (8.55 g, 62 mmol), and acetonitrile (250 mL). To this was added 2-hydroxy-5-(chloromethyl)benzaldehyde (8.445 g, 50 mmol) in acetonitrile (50 mL) over a period of 1 h. This mixture was refluxed for 36 h. After 36 h, the solvent was evaporated, and distilled water (250 mL) was added to the reaction mixture. Stirring was continued for 6 h, and the mixture was filtered. The resin was then washed with ethanol ($5 \times 100\ \text{mL}$) and dried under vacuum at 35°C for 48 h to afford an off-white solid. This solid was transferred in a 250 mL round bottom flask with CH_2Cl_2 (200 mL). The slurry was refluxed for 24 h. The reaction mixture was cooled to room temperature and filtered. The resin was washed with CH_2Cl_2 ($3 \times 100\ \text{mL}$) until the washings were colorless to afford an off-white solid. The resin was dried under vacuum at 50°C to a

constant weight. This process of swelling and drying of the resin was repeated twice to remove any trace contaminants from the resulting resin (7.510 g). Using $3.7\ \text{mmol amine/g}$ from previous step, the weight suggests 74% of the available amine sites reacted or $\sim 2.7\ \text{mmol salicylaldehyde groups/g}$ of resin. FT-IR (KBr): 3227 (br str, OH), 2878 (str Fermi d, CH stretch), 1859 (str, C=O) cm^{-1} .

4.4. Preparation of tethered salicylimine scavenger resin (**3**)

In a 500 mL round bottom flask was taken **2** (6.0 g) in EtOH (150 mL). To this was added *p*-toluidine (11.57 g, 108.0 mmol) and formic acid (0.100 mL). The reaction mixture was heated at 80°C for 48 h. After 48 h, the reaction mixture was cooled to room temperature and washed with ethanol ($5 \times 100\ \text{mL}$) to remove the excess *p*-toluidine. The final solid was washed with hexanes ($5 \times 50\ \text{mL}$) and dried under vacuum at 35°C for 24 h to afford a bright yellow solid. This solid was transferred in a 250 mL round bottom flask with CH_2Cl_2 (200 mL). The slurry was refluxed for 12 h. The reaction mixture was cooled to room temperature and filtered. The resin was washed with CH_2Cl_2 ($3 \times 100\ \text{mL}$) until the washings were colorless to afford a bright yellow solid. The resin was dried under vacuum at 65°C to a constant weight. This process of swelling and drying of the resin was repeated three times to remove any trace contaminants from the resulting resin each time drying to constant weight. The final weight was 7.121 g, which suggests $\sim 78\%$ yield for this step. However, loss of colored compound in the washings, which is likely unbound salicylimine, suggests that there was trapped aldehyde in the resin. In other words, it is likely that there is little salicylaldehyde on the resin after *p*-toluidine addition. Instead, the yield of substituted sites in the production of **2** is probably not as high as calculated from the mass. Consistent with this, the C=O stretch in the FT-IR is completely quenched during this step. FT-IR (KBr): 3200 (br str, OH), 1640 (w, C=N) cm^{-1} .

4.5. Preparation of $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{DIB})_2$ (**5**)

In a glove box, a 20 mL vial was loaded with $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{OAd})_2$ (70 mg, 0.099 mmol) in toluene (5 mL). To this was added a solution of 2-[(2,6-dimethylphenylimino)methyl]phenol (H-DIB (**4**), 45 mg, 0.198 mmol, 2 equiv) in toluene (2 mL). The reaction mixture was stirred for 30 min. The solvent was removed, and the crude product was dissolved in hexanes. The liberated 1-adamantanol was removed by filtration through Celite. The solvent was removed in vacuo, and the desired product was crystallized from a minimum amount of ether/pentane (1:10) as orange-red microcrystals (56 mg, 0.066 mmol, 66%). The NMR spectroscopic data are consistent with a mixture of at least six isomers in CDCl_3 . As a result, the spectra are more complex than expected, and the assignments are difficult due to the multitude of overlapping peaks. Assignments are made where possible. ^1H NMR (500 MHz, CDCl_3): 14.09 (Major isomer alkylidene, $J_{\text{CH}} = 122\ \text{Hz}$), 13.86, 13.11, 13.00, 12.04, 7.89 (2H, $J_{\text{CH}} = 2.5\ \text{Hz}$, CH=N), 7.34–7.38 (m, 1H), 6.89–7.21 (m, 18H), 6.82–6.78 (m, 3 H), 6.59–6.69 (m, 5H), 6.44–6.48 (m, 2H), 3.97 (sept, $J_{\text{CH}} = 7\ \text{Hz}$, 1H), 3.56 (sept, $J_{\text{CH}} = 7\ \text{Hz}$, 1H), 2.85 (s, 3H), 2.41 (s, 3H), 1.76 (s, 3H), 1.27 (d, $J_{\text{CH}} = 7\ \text{Hz}$, 3H), 1.19 (s, 3H), 0.81 (d, $J_{\text{CH}} = 7\ \text{Hz}$, 3H), 0.79 (d, $J_{\text{CH}} = 7\ \text{Hz}$, 3H), 0.73 (d, $J_{\text{CH}} = 7\ \text{Hz}$, 3H), 0.4 (s, 3H). ^{13}C NMR (C_6D_6): 326.58, 326.48, 309.46, 298.47, 172.12, 170.71, 167.89, 165.04, 159.68, 154.89, 152.37, 151.59, 149.68, 148.45, 136.35, 135.82, 135.49, 132.18, 132.01, 131.26, 130.47, 129.79, 129.50, 128.75, 128.35, 128.12, 128.03, 127.86, 127.66, 127.33, 126.27, 125.90, 125.81, 125.32, 125.05, 124.96, 122.89, 122.76, 121.94, 121.81, 120.75, 119.60, 115.21, 113.54, 55.7, 30.45, 27.81, 27.71, 27.51, 26.89, 26.34, 23.73, 23.43, 22.28, 20.09, 19.68, 19.41,

18.69, 18.11. ^{95}Mo NMR (CDCl_3): 548 ppm. Elemental Anal. Calc. for $\text{C}_{52}\text{H}_{57}\text{N}_3\text{O}_2\text{Mo}$: C, 73.29; H, 6.76; N, 4.93. Found: C, 73.12; H, 6.64; N, 4.89%. M.p. = 138–140 °C.

4.6. Procedure for the scavenging experiments with **3**

The solution of metal complex was prepared by dissolving ~10 mg of $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{OR})_2$ [OR = OAd, OBu^t_{F6}] in toluene (see Table 1). To this solution was added 550 mg of **3**, and the resulting mixture was stirred vigorously for 1 h. After 1 h, the beads were filtered and dried under vacuum (Sample A). The volatiles from the resulting mother liquor were removed under vacuum (Sample B). Both Sample A and B were analyzed by ICP-MS for their molybdenum content.

4.7. Recycling procedure for scavenger **3**

A 100 mL round bottom flask was loaded with 1.00 g of beads, a magnetic stir bar, and methanol (30 mL). The resulting slurry was refluxed in air for 6 h. The mixture was cooled to room temperature, and the beads were filtered through a frit. The beads were washed with 100 mL of methanol and dried at 45 °C for 24 h. These beads were tested using the scavenging procedure (vide supra). See Table 1.

4.8. Procedure for scavenging from crude ring-closing metathesis reaction

Ring-closing metathesis followed by scavenging was performed inside a well-purged drybox. To a solution of $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{OBu}^t_{\text{F6}})_2$ (Mo_{F6} , 12 mg, 0.0157 mmol) and toluene (5 mL) in a 20 mL vial was added diethyl diallylmalonate (30 equiv, 113 mg, 0.470 mmol) in toluene (1 mL). The solution was stirred at room temperature for 2 h, and 600 mg of the scavenger resin was added to the reaction mixture. The resulting slurry was stirred vigorously. Samples (200 μL) were withdrawn from the reaction mixture at regular intervals and filtered. The volatiles from the samples were removed in vacuo, and the samples were analyzed by ICP-MS for

Table 2
Crystallographic data and structure refinement parameters for $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{DIB})_2$ (**5**).

	5
Formula	$\text{C}_{52}\text{H}_{57}\text{MoN}_3\text{O}_2$
Formula weight	851.95
Crystal size (mm)	$0.11 \times 0.10 \times 0.09$
Crystal shape	Parallel piped
Temperature (K)	173(2)
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions	
<i>a</i> (Å)	18.8488(9)
<i>b</i> (Å)	11.2898(6)
<i>c</i> (Å)	20.9115(12)
α (°)	90
β (°)	103.169(4)
γ (°)	90
<i>V</i> (Å ³)	4332.9(4)
<i>Z</i>	4
<i>D</i> (g cm ⁻³)	1.306
μ (mm ⁻¹)	0.347
θ Range (°)	2.00–27.50
Reflections measured	33 319
Independent reflections (R_{int})	9524 (0.1387)
Number of parameters	533
$R(F)$ for $I > 2\sigma(I)$	0.0586
$wR(F^2)$ (all data)	0.0965
GOF (F^2)	0.950
Maximum, minimum $\Delta\rho$ (e Å ⁻³)	0.715, –0.817

their residual molybdenum contents. The concentration vs. time data are shown in Fig. 2.

4.9. X-ray crystallography

Crystals grown from concentrated solutions at –35 °C were moved quickly from a scintillation vial to a microscope slide containing Paratone N. Samples were selected and mounted on a glass fiber in wax and Paratone. The data collections were carried out at a sample temperature of 173 K on a Bruker AXS platform three-circle goniometer with a CCD detector. The data were processed and reduced using the program SAINTPLUS supplied by Bruker AXS. The structures were solved by direct methods (SHELXTL v5.1, Bruker AXS) in conjunction with standard difference Fourier techniques (Table 2).

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Appendix A. Supplementary material

CCDC 097070 contains the supplementary crystallographic data for **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. IR spectra of the resins, MAS ^1H NMR of **3** and full crystallographic tables from the X-ray diffraction experiment on **5** are also available. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.10.031](https://doi.org/10.1016/j.jorganchem.2008.10.031).

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- We attempted to measure the solid-state MAS ^{95}Mo NMR spectrum of the beads for comparison with our solution spectra of isolated Mo_{Ad} and **5**. Unfortunately, no signal was observed.

- [10] During calibration, the ICP-MS technique provided results within 1 ppb of standards.
- [11] The fit to the plot of [Mo] vs. time was done with the equation $[\text{Mo}] = [\text{Mo}]_0 e^{-k_{\text{obs}} t}$, which gave $[\text{Mo}]_0 = 54\,146$ ppm and $k = 0.00214 \text{ s}^{-1}$. While the exponential plot gave an $R = 0.99993$ as shown in Fig. 2, there were noticeable deviations from linearity in a $\ln[\text{Mo}]$ vs. time plot. The loss of molybdenum from solution in this heterogeneous reaction is likely sensitive to such factors as the stir rate.
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