Supplementary Information:

Synthesis and Structure of an Imido-Tethered Schrock Carbene of Molybdenum

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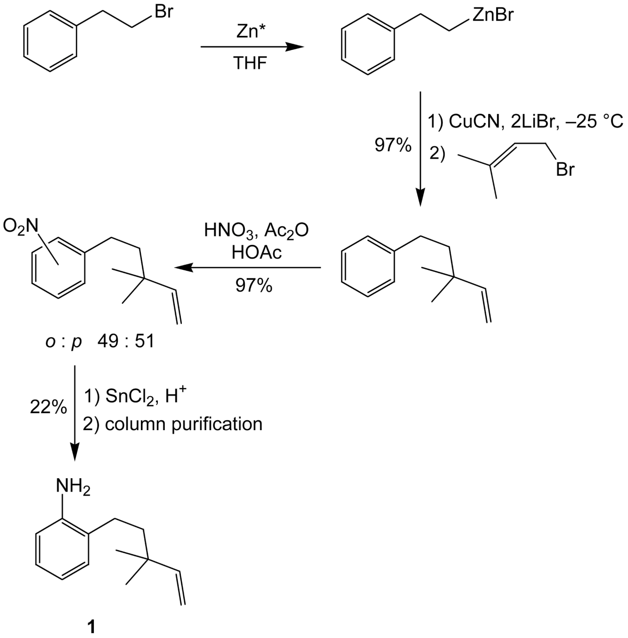
A. Details for the synthesis of 2-(3,3-dimethypent-4-enyl)aniline (**1**).

B. Details for the synthesis of the imido-tethered carbene **4**.

A. Details for the synthesis of 2-(3,3-dimethypent-4-enyl)aniline (**1**).

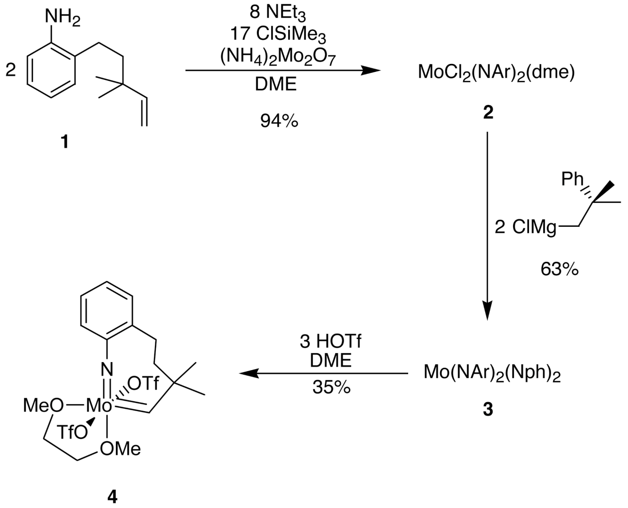


Preparation of 2-(3,3-dimethylpent-4-enyl)nitrobenzene: In a flask, was loaded fuming HNO_3 (18.7 mL, 90%, d = 1.5), HOAc (18 mL), Ac_2O (14 mL), which was allowed to cool back to room temperature before proceeding. This solution was added dropwise to 3,3-dimethyl-5-phenyl-1-pentene (45.8 g, 0.263 mol), which was prepared using the procedure of Reike and coworkers referenced as 12 in the manuscript, in Ac_2O (120 mL). The reaction was kept between 0 and –5 °C during the addition. After the addition, the mixture was stirred at 0 °C for 12 h. The reaction mixture was poured into crushed ice (300 g). The product was extracted with ethyl ether (3 □ 200 mL), and the combined organic layers were washed with portions of saturated $NaHCO_3$ (~300 mL total) until no gas formed on addition of the basic aqueous solution. The organic solution was filtered, and the separated solids were washed with ether (50 mL). The combined aqueous layers were extracted with ether (3 □ 200 mL). The combined ether solutions were dried with $MgSO_4$. The volatiles were removed in vacuo providing the product as a yellow oil in 97% yield (55.95 g) as a mixture of isomers. GC/FID analysis displayed an ortho:para ratio of 49 : 51. The compound was used without further purification.

Preparation of 2-(3,3-dimethylpent-4-enyl)aniline: In a 2000 mL round-bottomed three-necked flask with a thermometer and a mechanical stirrer was loaded $SnCl_2{\cdot}2H_2O$ (270 g, 1.056 mol) and ethanol (500 mL). The mixture was heated to 55 ^{o}C, and the crude mixture of nitroarenes prepared in the previous step (55.95 g, 0.26 mol) was added very carefully so that the temperature was kept between 65-70 ^{o}C. After addition, the reaction mixture was stirred at 70 ^{o}C for 7 h. After cooling to room temperature, water (200 mL) was added. The pH of the solution was adjusted to 12 by addition of 40 % NaOH. Extraction with hexane:ethyl acetate (v:v = 1:1) was carried out until the extract was colorless (~5 □ 500 mL). The combined extracts were dried with $MgSO_4$. Removing volatiles in vacuo provided 44.8 g of crude product as a red oil. GC/FID analysis show that the ratio of *ortho* to *para* products was 40:60. Column separation (silica gel, 250 ~ 400 mesh, 6:1 hexane:ethyl acetate) gave 2-(3,3-dimethylpent-4-enyl)aniline (**1**) in 22 % yield (8.8 g). M = 189.30 g/mol. ^{1}H NMR (300 MHz, $CDCl_3$): □ = 7.02 (m, 2 H, -C_6H_4-), 6.62-

6.80 (m, 2 H, -C_6H_4-), 5.78-5.96 (m, 1 H, -C*H*=CH_2), 5.03 (dd, 1 H, *J* = 3 Hz, 5 Hz, CH=C*H*$_2$), 4.99 (dd, 1 H, *J* = 5 Hz, 3 Hz, -CH=C*H*$_2$), 3.56 (s, br, 2 H, -NH_2), 2.31-2.46 (m, 2 H, -C_6H_4C*H*$_2$$CH_2$-), 1.48-1.66 (m, 2 H, -$C_6H_4CH_2$C*H*$_2$-), 1.08 (s, 6 H, -$CH_3$). ^{13}C NMR ($CDCl_3$): δ = 147.8, 143.9, 129.2, 127.1, 126.8, 118.8, 115.4, 111.2, 41.7, 36.7, 26.6, 26.4. Elemental Analysis: Calc. For $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.71; H, 10.23; N, 7.56. MS (EI) *m/z* = 189 (M^+). The other isomer of 4-(3,3-dimethylpent-4-enyl)aniline was isolated in 40% yield (16.0 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.02 (dd, 2 H, *J* = 208 Hz, 8 Hz, -C_6H_4-), 6.69 (dd, 2 H, *J* = 6 Hz, 4 Hz, -C_6H_4-), 5.80-6.01 (m, 1 H, -C*H*=CH_2), 5.07 (m, 2 H, -CH=C*H*$_2$), 3.58 (s, br, 2 H, -NH_2), 2.42-2.58 (m, 2 H, -C_6H_4C*H*$_2$$CH_2$-), 1.56-1.70 (m, 2 H, -$C_6H_4CH_2$C*H*$_2$-), 1.13 (s, 6 H, -$CH_3$). ^{13}C NMR ($C_6D_6$): δ = 163.1, 148.4, 144.8, 132.9, 129.3, 115.3, 110.8, 45.6, 36.8, 30.7, 26.8. Elemental Analysis: Calc. For $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.43; H, 9.57; N, 7.45. MS (EI) *m/z* = 189 (M^+).

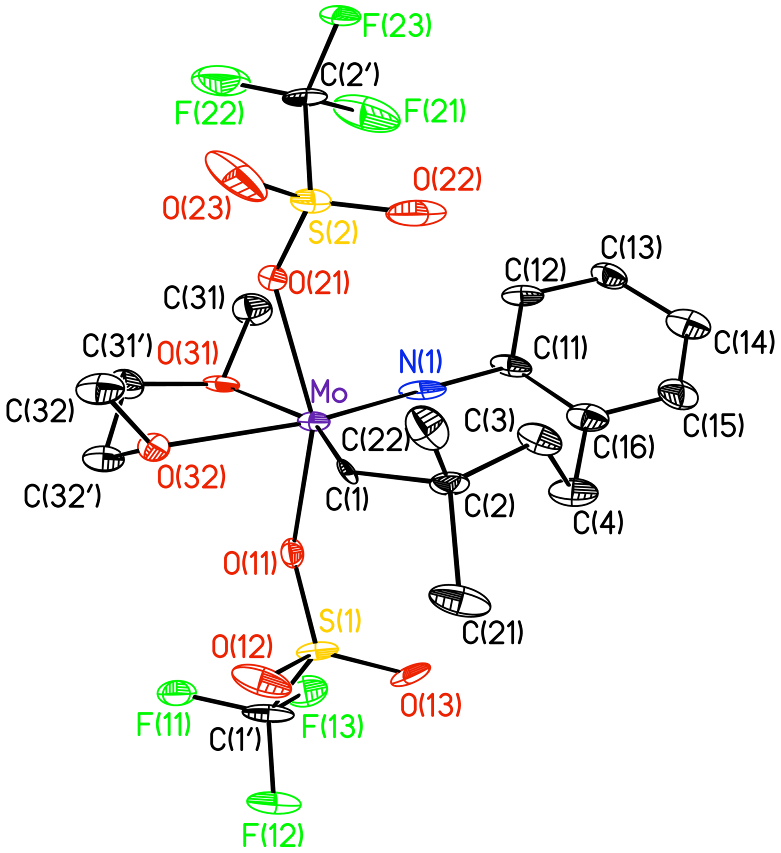
B. Details for the synthesis of the imido-tethered carbene **4**.



Synthesis of Mo(NAr)$_2$Cl$_2$(DME) (**2**). In a 250 mL Schlenk flask was loaded ammonium dimolybdate (0.529 g, 2.70 mmol), 100 mL 1,2-dimethoxyethane (DME), and a stir bar. To the suspension was added triethylamine (4.37 g, 43.2 mmol), chlorotrimethylsilane (10.0 g, 92.0 mmol), and **1** (1.02 g, 5.40 mmol). The suspension was stirred at 70 °C for 12 h. After cooling to room temperature, the solution was filtered. The volatiles of the filtrate were removed *in vacuo* to give 1.60 g of $Mo(NAr)_2Cl_2(DME)$ (**2**) as a red solid (2.53 mmol, 93.8%), which was used without further purification. ^{1}H NMR (299.9 MHz, C_6D_6): δ 7.73 (d, *J* = 7.62 Hz, 2 H), 6.94 (d, *J* = 7.03 Hz, 2 H), 6.88 (t, *J* = 7.62 Hz, 2 H), 6.75 (t, *J* = 7.03 Hz, 2 H), 5.97 (m, 2 H, =C*H*), 5.04 (m, 4 H, C*H$_2$*=), 3.46 (s, 4 H, O-C*H$_2$*), 3.19 (s, 6 H, O-C*H$_3$*), 2.85 (m, 4 H), 1.72 (m, 4 H, Mo-C*H$_2$*), 1.15 (s, 12 H, C*H$_3$*). ^{13}C NMR (75 MHz, C_6D_6): 156.14 (N–*C*(ipso)) 148.74, 135.84 *C(ipso)*-CH_2), 128.82, 127.23 (=*C*H), 126.53, 110.77 (*C*H_2=), 71.11 (O-*C*H_2), 63.02 (*C*Me_2), 44.30 (O-*C*H_3), 37.16 (Ar*C*H_2), 34.51 (*C*Me_2Ph), 27.80 (ArCH_2*C*H_2), 26.95 (C*Me$_2$*).

Synthesis of Mo(NAr)$_2$Nph$_2$ (**3**). To a –90 °C solution of $Mo(NAr)_2Cl_2(DME)$ (**2**) (4.80 g, 7.60 mmol) in 300 mL THF was added 34 mL 0.5 M solution of neophyl magnesium chloride (17 mmol, 2.2 equiv.) The solution was allowed to reach room temperature, and then stirred for 18 h. Removal of the volatiles *in vacuo* left a red solid, which was dissolved in toluene and filtered to remove the magnesium chloride. The volatiles were removed from the toluene solution *in vacuo*, leaving a red solid which was recrystallized from ether at –35 °C to give 3.50 g of **3** (4.75 mmol, 62.5%). ^{1}H NMR (299.9 MHz, C_6D_6): □ 7.3 (m, 4 H), 7.1 (m, 6 H), 7.0 (m, 5 H), 6.8 (m, 3 H), 5.7 (m, 2 H, =C*H*), 4.9 (m, 4 H, =C*H$_2$*), 2.7 (m, 4 H), 1.90 (s, 4 H, Mo-C*H$_2$*), 1.6 (m, 4 H, -C*H$_2$*C*H$_2$*-), 1.46 (s, 12 H, CH$_2$C*Me$_2$*Ph), 1.00 (s, 12 H, imido-C*H$_3$*). ^{13}C NMR (75.4 MHz, C_6D_6): □ 155.46 (N–*C*(ipso)), 151.16, 148.35, 135.40, 128.90, 128.62, 126.51, 126.38, 126.23, 125.62, 111.07 (=*C*H$_2$), 78.63 (Mo-*C*H$_2$), 43.58 (Ar*C*H$_2$), 40.82 (*C*Me$_2$Ph), 36.93(*C*Me$_2$), 32.75 (C*Me$_2$*Ph), 27.38 (ArCH$_2$*C*H$_2$), 26.94 (C*Me$_2$*). Anal. Calc. for $C_{46}H_{60}N_2Mo$: C, 74.97; H, 8.21; N; 3.80. Found: C, 74.93; H, 8.44; N, 3.77.

Synthesis of tethered carbene (**4**). A –90 °C solution of 2.05 g triflic acid (13.7 mmol, 3.0 equiv.) in DME (10 mL) was added to a –90 °C solution of Mo(NAr)$_2$(Nph)$_2$ (**3**) (3.32 g, 4.35 mmol) in DME (300 mL). This solution was stirred for 22 h, and then volatiles were removed *in vacuo*. The anilinium triflate was removed by precipitation from a minimal amount of toluene. The remaining dark solid was recrystallized from ether/pentane, giving 1.01 g of a yellow **4** (1.52 mmol, 35.0%). In fluid solution, the compound apparently exists as 3 different isomers, which made definitive assignment of many of the peaks difficult. There is dependence on temperature to the NMR spectra, and the relative amounts of each isomer changes with temperature. Schrock and coworkers have reported similar observations, including the fact that the two minor isomers are more prevalent in polar solvents. However, the tethered carbene has low solubility in most solvents except THF. The spectra reported here were taken at room temperature. Assignments, where they could be definitively made, are given. ^{1}H NMR (299.9 MHz, THF-d$_8$): □ 14.30, 14.27, 13.65, 8.15 (d), 7.0-7.6 (m), 3.43 (s, 4 H, OC*H$_2$*), 3.40 (m), 3.27 (s, 6 H, OC*H$_3$*) 2.47 (m), 2.31 (s), 1.08 (m). ^{13}C NMR (75.4 MHz, THF-d$_8$): □ 333.83, 330.83, 326.96, 155.64, 154.83, 154.62, 149.77, 149.44, 148.55, 138.43, 130.801, 130.39, 129.67, 129.42, 129.21, 129.21, 129.11, 128.91, 128.29, 127.42, 126.90, 126.80, 126.29, 126.03, 122.39, 118.18, 72.75, 66.30, 59.92, 59.59, 59.52, 58.90, 45.98, 45.85, 45.00, 30.16, 29.74, 29.30, 28.51, 27.85, 21.48, 15.68. ^{19}F (282.2 MHz, THF-d$_8$): –78.45, –78.58, –79.56, –79.64. Anal. Calc. for $C_{18}H_{25}F_6MoNO_8S_2$: C, 32.98; H, 3.83; N; 2.13. Found: C, 33.43; H, 4.07; N, 2.12.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