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Synthesis and Deprotonation/Alkylation Reactions of the Chiral Carbene Complex $\mathrm{Tp'(CO)(NO)Mo{=}C(OMe)(Me)}$

T. Brent Gunnoe, P. S. White, and J. L. Templeton*

Department of Chemistry, The University of North Carolina,
Chapel Hill, North Carolina 27599-3290

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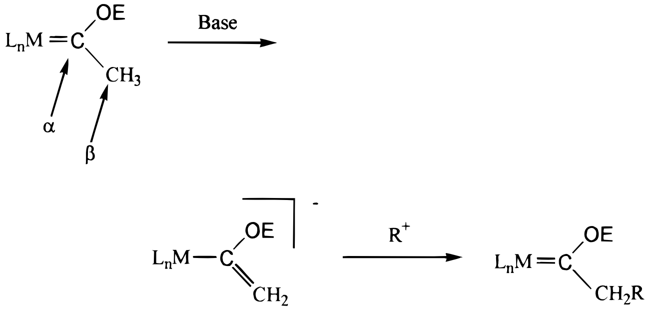
The Fischer carbene complex $\mathrm{Tp'(CO)(NO)Mo{=}C(OMe)(Me)}$ (**1**) has been synthesized, and functionalization of the carbene methyl substituent has been achieved via deprotonation/alkylation reaction sequences. The chiral metal center produced moderate diastereoselectivity. Isomeric, geometric, and thermodynamic features are discussed for the complexes $\mathrm{Tp'(CO)(NO)M{=}C(OMe)(R)}$ (M = W, R = Me; M = Mo, R = Me, Et, Ph, $-CH_2CH_2CH{=}CH_2$, $-C(H)(Me)CH_2CH{=}CH_2$), and evidence of a substantial metal carbene rotational barrier is presented. Important structural features for $\mathrm{Tp'(CO)(NO)Mo{=}C(OMe)(Ph)}$ (**7**), which was characterized by single-crystal X-ray crystallography, include a short molybdenum−carbon bond distance to the carbene (2.085(4) Å) and a carbene carbon−oxygen bond distance of 1.356(5) Å.

Introduction

Transition-metal carbene complexes are valuable in a wide range of organic syntheses.[1,2] The classical methodology for preparation of Fischer carbene complexes, i.e., nucleophilic attack on a carbon monoxide ligand followed by reaction at oxygen with an electrophilic alkylating reagent, dictates the range of easily accessible substituted carbenes.

Scheme 1. Deprotonation and Electrophilic Alkylation of Fischer Carbenes



The acidity of Fischer carbene methyl groups was established prior to 1970.[3] Fischer carbenes in basic methanol exhibited rapid H/D exchange at the β-methyl site (see Scheme 1 for labeling description). Subsequently, the complex $\mathrm{(CO)_5Cr{=}C(OMe)(Me)}$ was reported to have a pK_a near 8 in THF.[4a] Recent work has indicated a pK_a near 12 in acetonitrile/water for the pentacarbonylchromium methyl carbene.[4h−i] Casey utilized the acidity of the β-methyl group of Fischer carbene ligands for the functionalization of carbene ligands via deprotonation and alkylation reaction sequences (Scheme 1).[4a−g] Although reaction of chromium "carbenylates" has been reported with a variety of electrophiles, low yields and polyalkylations are problematic in these syntheses.[4f]

Pentacarbonyl carbene anions can be useful nucleophiles, but studies indicated that they react only with highly electrophilic compounds (i.e., alkyl triflates, activated epoxides,[5a] activated ketones and aldehydes[5b]). The reactivity of pentacarbonyl "carbene enolates" can be increased by replacing a CO ligand with a phosphine[6a] or by replacing the methoxide moiety with an amino

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⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1996.

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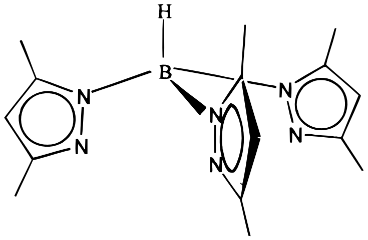
Chart 1. Hydridotris(3,5-dimethylpyrazolyl)borate



unit.[6b] Stereoselective α-alkylation of a tungsten metallacyclic zirconoxycarbene complex has been accomplished via deprotonation of the carbene and treatment with electrophilic alkylation reagents.[6c] Tungsten dimers have been prepared by reaction of a carbene anion with a vinyl carbene.[6d] Diastereoselective α-alkylation of an iminocarbene has been reported.[6e]

Recently, elaboration of β-methyl units in $(CO)_5M{=}C(Me)(OCH_2R)$ ($R = H$, Me, Ph; $M = Cr$, W) complexes has been achieved under aqueous biphasic conditions.[7] Reaction of the carbene complexes with alkyl, allyl, and benzyl halides in CH_2Cl_2 and an excess of 50% NaOH with $(t\text{-}Bu)_4NBr$ generates dialkylated products. In addition, Aumann *et al.* have reported the synthesis of a variety of carbene complexes upon treatment of pentacarbonyl ethoxycarbene complexes with base followed by addition of amides or tropylium ion.[8a−e] Also relevant to the chemistry reported herein is the functionalization of aminocarbenes possessing a chiral moiety.[8f−h]

The goal of work reported here was elaboration of a Fischer carbene complex with control of stereoselectivity at the β-position. Thus, we sought the synthesis of a chiral-at-metal Fischer carbene complex that would undergo deprotonation and alkylation in order to probe the stereoselectivity of these reactions.

Utilizing Tp′-tungsten metal fragments, we have previously reported elaborations of (1) the β-site of acyl ligands,[9] (2) the propargylic site of coordinated alkynes,[10] and (3) the β-site of carbyne ligands.[11] We now report an extension of this series to include diastereoselective elaboration of the β-methyl unit of a Fischer carbene. The Fischer carbenes Tp′(CO)(NO)M=C(OMe)(Me) (M = W, Mo; Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) have been prepared. The complexes possess the Tp′ ligand (Chart 1), which is well-known as a strong σ-donor. The presence of the ancillary Tp′ was expected to increase the reactivity of the deprotonated anion relative to carbonyl and cyclopentadienyl relatives, and the chiral metal center allows exploration of stereoselectivity at the β-carbon site.

Experimental Section

General Considerations. All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Methylene chloride was distilled over P_2O_5; THF and hexanes were distilled from sodium metal and benzophenone. All other solvents were purged with nitrogen prior to use. The complexes $Tp'Mo(CO)_2(NO)$ and $Tp'W(CO)_2(NO)$ were prepared according to a procedure published for the molybdenum complex.[12] All other reagents were used as obtained from commercial sources. IR spectra were recorded on a Mattson Polaris FT-IR spectrometer. One-dimensional NMR spectra were recorded on a Varian XL-400 spectrometer or a Bruker WM250 spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA, or by Galbraith Laboratories, Inc., Knoxville, TN.

Tp′(CO)(NO)Mo=C(OMe)(Me) (1). To a cold (−78 °C) THF solution of $Tp'Mo(CO)_2(NO)$ (0.701 g, 1.46 mmol) was added 1.05 mL (1.46 mmol) of 1.4 M MeLi in diethyl ether. The solution slowly changed from orange to deep red. The solvent was removed under vacuum, and the red solid was dried in *vacuo* for approximately 1 h followed by dissolution in CH_2Cl_2. The red solution was cooled to −78 °C, and 0.16 mL (1.46 mmol) of MeOTf was added. After several hours, the solution had returned to orange, and the solvent was evaporated under reduced pressure. The resulting orange solid was chromatographed on alumina with 10:1 (v/v) hexanes/CH_2Cl_2. The air-stable product was isolated (0.653 g) in 88% yield. ^1H NMR indicated two isomers in a 6:1 ratio. The data listed below are for the major isomer only. IR (KBr): ν_{CO} 1940 cm^{-1}, ν_{NO} 1610 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 5.80, 5.77, 5.76 (3H, Tp′ CH); 4.68 (3H, OCH_3); 2.47 (3H, =C(OMe)(CH_3)); 2.41, 2.40, 2.34, 2.11, 2.10, 1.99 (18H, Tp′ CH_3). ^{13}C NMR ($CDCl_3$, δ): 342.9 (Mo=C(OMe)(Me)); 228.9 (CO); 152.4, 150.7, 150.5, 144.9, 144.2, 144.1 (Tp′ CCH$_3$); 106.7, 106.2, 106.1 (d, $^1J_{CH} = 170$ Hz, Tp′ CH); 65.6 (q, $^1J_{CH} = 145$ Hz, Mo=C(OCH$_3$)(Me)); 37.1 (q, $^1J_{CH} = 125$ Hz, Mo=C(OMe)(CH$_3$)); 15.1, 13.9, 12.9, 12.7, 12.4 (1:2:1:1:1, Tp′ CCH$_3$). Anal. Calcd for Tp′(CO)(NO)Mo=C(OMe)(Me), $C_{19}H_{28}N_7O_3BMo$: C, 44.81; H, 5.54; N, 19.25. Found: C, 44.62; H, 5.57; N, 19.10.

Tp′(CO)(NO)Mo=C(OMe)(CH_2CH_3) (2). Method A. *n*-BuLi (2.5 M in hexanes, 0.90 mL, 2.27 mmol) was added to a cold (−78 °C) THF solution of complex **1** (1.048 g, 2.06 mmol). The solution immediately turned from orange to green. MeI (0.64 mL, 10.3 mmol) was syringed into the reaction flask, and the solution was warmed to room temperature. After approximately 1 h, the solution color returned to orange. Volatiles were removed under reduced pressure, and the orange product was purified by chromatography on alumina with 5:1 hexanes/CH_2Cl_2. Solvent evaporation from an orange band yielded an orange air-stable solid in 86% yield (0.932 g, 1.78 mmol). ^1H NMR indicated two isomers in a 2:1 ratio. The data listed below are for the major isomer only. IR (KBr): ν_{CO} 1934 cm^{-1}, ν_{NO} 1614 cm^{-1}. ^1H NMR ($CDCl_3$, δ): 5.78, 5.76, 5.73 (3 H, Tp′ CH); 4.69 (3H, OCH_3); 2.50, 2.30 (2H, each a m, $^3J_{HH} = 7$ Hz; Mo=C(OMe)(CH_2CH$_3$)); 0.66 (3H, t, $^3J_{HH} = 7$ Hz, Mo=C(OMe)(CH$_2$CH_3)); 2.46, 2.40, 2.39, 2.31, 2.12, 2.11 (18H, Tp′ CH_3). ^{13}C NMR ($CDCl_3$, δ): 345.6 (Mo=C(OMe)(Et)); 229.4 (CO); 151.1, 150.9, 150.5, 144.9, 144.3, 144.0 (Tp′ CCH$_3$); 106.7, 106.2, 106.0 (Tp′ CH); 65.9 (q, $^1J_{CH} = 145$ Hz, Mo=C(OCH$_3$)(CH$_2$CH$_3$)); 43.0 (t of q, $^1J_{CH} = 125$ Hz, $^2J_{CH} = 5$ Hz, Mo=C(OMe)(CH$_2$CH$_3$)); 9.8 (q of t, $^1J_{CH} = 126$ Hz, $^2J_{CH} = 5$ Hz, Mo=C(OMe)(CH$_2$$CH_3$)); 15.4, 14.3, 13.9, 13.0, 12.8, 12.5 (Tp′CCH$_3$). Anal. Calcd for Tp′(CO)(NO)Mo=C(OMe)(Et), $C_{20}H_{30}N_7BMoO_3$: C, 45.91; H, 5.78; N, 18.74. Found: C, 46.00; H, 5.77; N, 18.80.

Method B. In a representative synthesis 1.38 g (2.7 mmol) of **1** was dissolved in cold (−78 °C) diethyl ether and 1.08 mL of *n*-BuLi (2.5 M in hexanes, 2.7 mmol) was added. The

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solution was warmed to room temperature and slowly turned from orange to green. After 1 h, 0.30 mL of MeOTf (2.7 mmol) was added. The green solution slowly returned to orange. The solvent was removed under vacuum, and the orange solid was precipitated by slow diffusion of MeOH into cold (0 °C) CH$_2$Cl$_2$. An orange product was obtained in 82% yield (1.16 g).

Tp′(CO)(NO)Mo=C(OMe)(CHMe$_2$) (3). Against a nitrogen flush, an excess of KH was added to a cold (−78 °C) THF solution of **1** (0.195 g, 0.383 mmol) and MeI (0.24 mL, 3.83 mmol). The solution was stirred overnight, and the solvent was removed under reduced pressure. The orange solid was washed with cold (0 °C) pentane (3 × 20 mL) and further purified utilizing alumina chromatography with a 5:1 mixture of hexanes/CH$_2$Cl$_2$ as eluent. An orange band was isolated, and removal of the solvent allowed the isolation of an orange product in 53% yield. ^{1}H NMR indicated two isomers in a 5:1 ratio. The data listed below are for the major isomer only. IR (KBr): ν_{CO} 1929 cm^{-1}, ν_{NO} 1616 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ): 5.80, 5.78, 5.73 (3 H, Tp′ C*H*); 3.45 (3H, OC*H*$_3$); 4.21 (1H, septet, $^3J_{HH}$ = 6.8 Hz, Mo=C(OMe)(C*H*(Me)$_2$); 1.12, 1.11 (6H, each a d, $^3J_{HH}$ = 6.8 Hz, Mo=C(OMe)(CH(C*H*$_3$)$_2$); 2.57, 2.40, 2.36, 2.31, 2.23, 2.15 (18H, Tp′ C*H*$_3$). ^{13}C NMR (CDCl$_3$, δ): 340.3 (Mo=*C*(OMe)(C(H)Me$_2$)); 230.9 (*C*O); 152.5, 151.5, 151.1, 145.0, 144.8, 144.0 (Tp′ *C*CH$_3$); 106.5, 106.2, 106.0 (Tp′ *C*H); 62.9 (q, $^1J_{CH}$ = 145 Hz, Mo=C(O*C*H$_3$)(C(H)Me$_2$); 51.5 (m, $^1J_{CH}$ = 140 Hz, $^2J_{CH}$ = 3 Hz, Mo=C(OMe)(*C*(H)Me$_2$); 20.0, 18.6 (m, $^2J_{CH}$ = 3 Hz, $^1J_{CH}$ = 125 Hz, Mo=C(OMe)(C(H)(*C*H$_3$)$_2$); 14.9, 14.3, 14.1, 12.8, 12.7, 12.2 (Tp′ C*C*H$_3$). Anal. Calcd for Tp′(CO)(NO)Mo=C(OMe)(C(H)Me$_2$), C$_{21}$H$_{32}$N$_7$BMoO$_3$: C, 46.95; H, 6.00; N, 18.25. Found: C, 47.02; H, 6.00; N, 18.31.

Tp′(CO)(NO)Mo=C(OMe)(CH$_2$CH$_2$CH=CH$_2$) (4). A THF solution of **1** (0.900 g, 1.77 mmol) was cooled to −78 °C, and 0.85 mL (2.5 M in hexanes, 2.12 mmol) of *n*-BuLi was added. Upon addition of *n*-BuLi, the orange solution of **1** immediately turned green. Allyl bromide (3.06 mL, 35.4 mmol) was syringed into the reaction flask, and the solution was warmed to room temperature. After 1 h, the solution had returned to orange and the solvent was removed under vacuum. The orange solid was purified by chromatography on alumina with hexanes/CH$_2$Cl$_2$ (10:1) as eluent. Solvent evaporation from an orange band allowed the isolation of a bright orange, air-stable solid (0.468 g, 48% yield). ^{1}H NMR indicated two isomers in a 1.5:1 ratio. The data listed below are for the major isomer only. IR (KBr): ν_{CO} 1943 cm^{-1}, ν_{NO} 1612 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ): 5.78, 5.76, 5.74 (3 H, Tp′ C*H*); 5.91 (1H, tdd, $^3J_{HH}$ = 17 Hz, $^3J_{HH}$ = 10 Hz, $^3J_{HH}$ = 7 Hz, Mo=C(OMe)(CH$_2$CH$_2$C*H*=CH$_2$); 5.09 (1H, d of d, $^2J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 17 Hz, Mo=C(OMe)(CH$_2$CH$_2$CH=C(*H*)H); 4.97 (1H, d of d, $^2J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 10 Hz, Mo=C(OMe)(CH$_2$CH$_2$CH=C(H)*H*); 4.68 (3H, OC*H*$_3$); 3.47 (1H, m, Mo=C(OMe)(C(*H*)HCH$_2$CH=CH$_2$); 3.29 (1H, m, Mo=C(OMe)(C(*H*)HCH$_2$CH=CH$_2$); 2.62 (2H, m, Mo=C(OMe)(CH$_2$C*H*$_2$CH=CH$_2$); 2.45, 2.40, 2.39, 2.31, 2.11 (3:3:3:3:6, 18H, Tp′ C*H*$_3$). ^{13}C NMR (CDCl$_3$, δ): 343.3 (Mo=*C*(OMe)(CH$_2$CH$_2$CH=CH$_2$)); 228.8 (*C*O); 152.2, 150.7, 150.5, 145.0, 144.3, 144.0 (Tp′ *C*CH$_3$); 138.6 (d, $^1J_{CH}$ = 150 Hz, Mo=C(OMe)(CH$_2$CH$_2$*C*H=CH$_2$); 114.1 (t, $^1J_{CH}$ = 150 Hz, Mo=C(OMe)(CH$_2$CH$_2$CH=*C*H$_2$); 106.4, 106.3, 106.2 (Tp′ *C*H); 65.9 (q, $^1J_{CH}$ = 145 Hz, Mo=C(O*C*H$_3$)(CH$_2$CH$_2$CH=CH$_2$)); 49.2 (t, $^1J_{CH}$ = 126 Hz, Mo=C(OMe)(*C*H$_2$CH$_2$CH=CH$_2$)); 29.6 (t, $^1J_{CH}$ = 130 Hz, Mo=C(OMe)(CH$_2$*C*H$_2$CH=CH$_2$)); 15.4, 14.7, 14.2, 13.9, 12.8, 12.4 (Tp′ C*C*H$_3$). Anal. Calcd for Tp′(CO)(NO)Mo=C(OMe)(CH$_2$CH$_2$CH=CH$_2$), C$_{22}$H$_{32}$N$_7$BMoO$_3$: C, 48.11; H, 5.87; N, 17.85. Found: C, 48.09; H, 5.85; N, 17.92.

Tp′(CO)(NO)Mo=C(OMe)(C(H)(Me)CH$_2$CH=CH$_2$) (5a). *n*-BuLi (2.5 M in hexanes, 0.21 mL, 0.524 mmol) was syringed into a cold (−78 °C) THF solution of **2** (0.233 g, 0.445 mmol). The solution immediately turned from orange to green. Allyl bromide (0.77 mL, 8.9 mmol) was added to the reaction flask, and the solution was warmed to 0 °C. After about 1 h the solution had turned orange and the solvent was removed under reduced pressure. The resulting orange solid was chromatographed on an alumina column using hexanes/CH$_2$Cl$_2$ (5:1) as eluent. An orange band yielded an air-stable product in 80% yield (0.200 g). IR (KBr): ν_{CO} 1930 cm^{-1}, ν_{NO} 1615 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ): Two diastereomers were observed (major isomer 80%) in addition to two rotamers (major rotamer >90%). Chemical shifts for the minor rotamer are not listed; where not coincidental, peaks of the minor diastereomer are given in parentheses. ^{1}H NMR (CDCl$_3$, δ): 5.79, 5.76, 5.71 (3 H, Tp′ C*H*); 5.89 (1H, m, Mo=C(OMe)(C(H)(Me)CH$_2$C*H*=CH$_2$); 5.04 (2H, m, Mo=C(OMe)(C(H)(Me)CH$_2$CH=C*H*$_2$); 3.45 (3H, OC*H*$_3$) (minor: 3.46); 4.04 (1H, m, Mo=C(OMe)(C(*H*)(Me)CH$_2$CH=CH$_2$); 1.96 (2H, m, Mo=C(OMe)(C(H)(Me)C*H*$_2$CH=CH$_2$); 2.54, 2.38, 2.34, 2.29, 2.23, 2.13 (18H, Tp′ C*H*$_3$) (minor: 2.54, 2.38, 2.34, 2.29, 2.21, 2.14); 1.08 (3H, d, $^3J_{HH}$ = 7 Hz, Mo=C(OMe)(C(H)(C*H*$_3$)CH$_2$CH=CH$_2$)) (minor: 1.07; 3H, d, $^3J_{HH}$ = 7 Hz). ^{13}C NMR (CDCl$_3$, δ): 338.2 (Mo=*C*(OMe)(C(H)(Me)CH$_2$CH=CH$_2$)); 230.5 (*C*O); 152.5, 151.1, 145.0, 144.8, 144.0, (2:1:1:1:1, Tp′ *C*CH$_3$); 137.4 (d, $^1J_{CH}$ = 150 Hz, Mo=C(OMe)(C(H)(Me)CH$_2$*C*H=CH$_2$); 116.0 (t, $^1J_{CH}$ = 150 Hz, Mo=C(OMe)(C(H)(Me)CH$_2$CH=*C*H$_2$); 106.5, 106.2, 106.0 (Tp′ *C*H); 65.9 (q, $^1J_{CH}$ = 145 Hz, Mo=C(O*C*H$_3$)(C(H)(Me)CH$_2$CH=CH$_2$)); 56.3 (d, $^1J_{CH}$ = 136 Hz, Mo=C(OMe)(*C*(H)(Me)CH$_2$CH=CH$_2$)); 38.2 (t, $^1J_{CH}$ = 125 Hz, Mo=C(OMe)(C(H)(Me)*C*H$_2$CH=CH$_2$)); 15.3, 14.5, 14.2, 13.9, 12.8, 12.4 (Tp′ C*C*H$_3$). Anal. Calcd for Tp′(CO)(NO)Mo=C(OMe)(C(H)(Me)CH$_2$CH=CH$_2$), C$_{23}$H$_{34}$N$_7$BMoO$_3$: C, 49.04; H, 6.08; N, 17.41. Found: C, 48.97; H, 6.05; N, 17.46.

Tp′(CO)(NO)Mo=C(OMe)(C(Me)(H)CH$_2$CH=CH$_2$) (5b). To a cold (−78 °C) THF solution of **4** (0.454 g, 0.826 mmol) was added 0.36 mL of *n*-BuLi (2.5 M in hexanes, 0.909 mmol). The solution immediately turned from orange to green. Methyl iodide (1.0 mL, 1.65 mmol) was added to the reaction flask, and the solution was warmed to room temperature. After 1 h, the solution had turned orange, and the solvent was removed under reduced pressure. The resulting orange solid was chromatographed on an alumina column using hexanes/CH$_2$Cl$_2$ (5:1) as eluent. An orange band yielded an air-stable product in 67% yield (0.311 g). NMR spectroscopic data were identical with the spectrum of **5a** but indicated that the opposite diastereomer was the major stereoisomer for **5b** (major diastereomer >90%).

Tp′(CO)(NO)W=C(OMe)(Me) (6). Tp′W(CO)$_2$(NO) (2.595 g, 0.458 mmol) was dissolved in approximately 250 mL of THF. To the cooled solution (−78 °C) was added 3.30 mL of MeLi (0.458 mmol). After the MeLi addition, the solution was warmed to room temperature. Over a period of 1 h, the solution turned from orange to red. A red oil was produced by solvent evaporation under reduced pressure. The red oil was dissolved in CH$_2$Cl$_2$, and 0.52 mL of MeOTf (0.458 mmol) was added. Overnight, the solution changed to an orange color, the solvent was evaporated, and chromatography on alumina with 5:1 hexanes/CH$_2$Cl$_2$ then yielded an orange band. Solvent removal left an orange solid, which was isolated in 33% yield. ^{1}H NMR indicated two isomers in a 6:1 ratio. The data listed below are for the major isomer only. IR (KBr): ν_{CO} 1919 cm^{-1}, ν_{NO} 1596 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ): 5.83, 5.80, 5.79 (3H, Tp′ C*H*); 4.56 (3H, OC*H*$_3$); 2.51 (3H, W=C(OMe)(C*H*$_3$)); 2.41, 2.39, 2.33, 2.17, 2.16, 1.88 (18H, Tp′ C*H*$_3$). ^{13}C NMR (CDCl$_3$, δ): 322.7 ($^1J_{WC}$ = 150 Hz, W=*C*(OMe)(Me)); 228.1 ($^1J_{WC}$ = 160 Hz, *C*O); 153.3, 151.6, 145.1, 144.2, (1:2:1:2, Tp′ *C*CH$_3$); 107.0, 106.6, 106.4 (Tp′ *C*H); 65.4 (q, $^1J_{CH}$ = 146 Hz, W=C(Me)(O*C*H$_3$)); 37.4 (q, $^1J_{CH}$ = 125 Hz, W=C(OMe)(*C*H$_3$)); 15.7, 14.3, 14.2, 12.9, 12.6, 12.4 (Tp′ C*C*H$_3$). Anal. Calcd for T′(CO)(NO)W=C(OMe)(Me), C$_{19}$H$_{28}$N$_7$BWO$_3$: C, 38.22; H, 4.73; N, 16.42. Found: C, 38.20; H, 5.11; N, 16.31.

Tp′(CO)(NO)Mo=C(OMe)(Ph) (7). Substituting PhLi for MeLi in the route for the preparation of the methyl carbene **1** yields the phenylcarbene **7**. A dark orange solid was isolated in 81% yield after chromatography on alumina (5:1 hexanes/CH$_2$Cl$_2$ used as eluent) and solvent evaporation. ^{1}H NMR indicated two isomers in a 6:1 ratio. The data listed below are for the major isomer only. IR (KBr): ν_{CO} 1948 cm^{-1}, ν_{NO} 1607 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ): 7.06 (1H, t, $^3J_{HH}$ = 7 Hz,

Table 1. Selected Spectroscopic Data for the Major Isomer of Complexes 1−7

complex	δ(carbene carbon), ppm	δ($-OCH_3$), ppm	IR ν_{NO}, cm^{-1}	IR ν_{CO}, cm^{-1}
Tp′(CO)(NO)Mo═C(OMe)(Me) (**1**)	342.9	4.68	1610	1940
Tp′(CO)(NO)Mo═C(OMe)(Et) (**2**)	345.6	4.69	1614	1934
Tp′(CO)(NO)Mo═C(OMe)(CHMe$_2$) (**3**)	340.3	3.45	1616	1929
Tp′(CO)(NO)Mo═C(OMe)(CH$_2$CH$_2$CH═CH$_2$) (**4**)	343.3	4.68	1612	1943
Tp′(CO)(NO)Mo═C(OMe)(C(H)(Me)CH$_2$CH═CH$_2$) (**5a**)	338.2	3.45	1615	1930
Tp′(CO)(NO)W═C(OMe)(Me) (**6**)	322.7	4.56	1596	1919
Tp′(CO)(NO)Mo═C(OMe)(Ph) (**7**)	325.0	4.87	1607	1948

Table 2. Crystallographic Data for Tp′(CO)(NO)Mo═C(OMe)(Ph) (7)

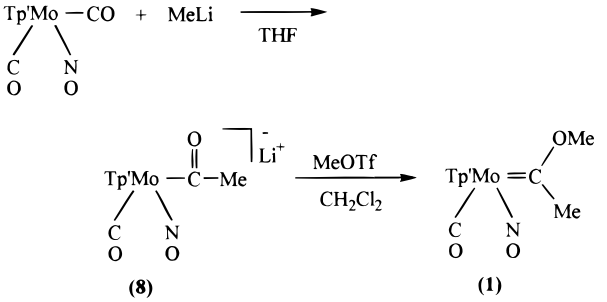
formula	$C_{25}H_{30}BMoO_3N_6$
mol wt	569.30
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	10.1703(8)
b, Å	11.3045(9)
c, Å	12.8048(10)
α, deg	92.9184(11)
β, deg	101.6056(12)
γ, deg	110.9178(11)
V, Å^3	1334.86(18)
Z	2
D_{calcd}, g cm^{-3}	1.416
F(000)	585.80
cryst dimens, mm	0.35 × 0.35 × 0.20
temp, °C	20
radiation (λ, Å)	Mo Kα (0.710 73)
2θ range, deg	$5.00 < \theta < 45.00$
μ, mm^{-1}	0.51
scan mode	ω
total no. of data	5241
total no. of unique data	3693
no. of obsd data ($I > 2.5\sigma(I)$)	3518
R_F	0.032
R_w	0.047
GOF	2.18

para phenyl), 6.86 (2H, t, $^3J_{HH} = 7$ Hz, meta phenyl), 6.58 (2H, d, $^3J_{HH} = 7$ Hz, ortho phenyl); 5.87, 5.79, 5.33 (3H, Tp′ C*H*); 4.87 (3H, OC*H*$_3$); 2.54, 2.52, 2.37, 2.36, 2.19, 1.43 (18H, Tp′ C*H*$_3$). ^{13}C NMR (CDCl$_3$, δ): 325.0 (Mo═*C*(OMe)(Ph)); 225.9 (*C*O); 152.1, 151.6, 151.4, 148.5, 144.8, 144.1 (Tp′ *C*CH$_3$); 144.4, 129.2, 126.6, 126.2 (1:2:2:1, Mo═C(OMe)(*C*$_6$H$_5$)); 106.8, 106.2, 106.1 (Tp′ *C*H); 65.7 (q, $^1J_{CH} = 145$ Hz, Mo═C(O*C*H$_3$)(Ph)); 14.5, 14.3, 13.9, 12.9, 12.7, 12.4 (Tp′ C*C*H$_3$). Anal. Calcd for Tp′(CO)(NO)Mo═C(OMe)(Ph), $C_{24}H_{30}N_7BMoO_3$: C, 50.46; H, 5.29; N, 17.16. Found: C, 50.22; H, 5.29; N, 17.04.

X-ray Structure Determination of Tp′(CO)(NO)Mo═C(OMe)(Ph) (7). Crystals of **7** were grown by slow diffusion of methanol into a methylene chloride solution of the phenylcarbene **7**. The intensity data were collected on a Siemens SMART diffractometer using the ω scan mode. The number of unique reflections was 3693, with 3518 reflections possessing $I > 2.5\sigma(I)$. Additional experimental details are given in Table 2.

Results and Discussion

Synthesis of Tp′(CO)(NO)Mo═C(OMe)(Me) (1). The classic Fischer carbene synthetic methodology yields Tp′(CO)(NO)Mo═C(OMe)(Me) (**1**) when Tp′Mo(CO)$_2$(NO) is the metal reagent (eq 1). Addition of MeLi to a THF solution of the dicarbonyl nitrosyl complex generates an anionic acyl complex, [Li][Tp′(CO)(NO)Mo(C(O)Me)] (**8**), which eluded isolation. Formation of the acyl **8** is reflected in the disappearance of CO stretching frequencies for Tp′Mo(CO)$_2$(NO) (2009 and 1917 cm^{-1}) and growth of new CO stretches at 1886 and 1871 cm^{-1}. The presence of two terminal metal−CO stretching frequencies is attributed to geometric isomers, but the identity of these isomers is not known for the putative acyl complex **8**.



(1)

MeOTf slowly reacts with the anionic acyl intermediate **8** at room temperature to yield the methylcarbene complex **1** (eq 1). Formation of the methylcarbene **1** in CH$_2$Cl$_2$ is evidenced by a CO stretching absorption at 1950 cm^{-1}. The 1:1:1 pattern observed in the ^{1}H NMR for the protons of the Tp′ ligand is consistent with the presence of a chiral metal center; i.e., each Tp′ ring is unique in the C_1 symmetry. NMR data are typical for Fischer carbene complexes with the carbene carbon resonance at 342.9 ppm in the ^{13}C NMR spectrum. At room temperature, two isomers are apparent for the methyl complex **1** in the ^{1}H NMR spectrum (6:1 ratio). Important spectroscopic data are summarized for the series of carbene complexes in Table 1.

Synthesis and Crystal Structure of Tp′(CO)(NO)Mo═C(OMe)(Ph) (7). Addition of PhLi to Tp′Mo(CO)$_2$(NO) in THF followed by reaction with MeOTf in CH$_2$Cl$_2$ results in formation of Tp′(CO)(NO)Mo═C(OMe)(Ph) (**7**). The phenylcarbene **7** is a dark orange solid that reveals spectroscopic features similar to those for the methylcarbene **1**. Most importantly, two isomers are apparent at room temperature in a 6:1 ratio in the ^{1}H NMR of **7**, and the chemical shift of the −OMe protons for the major isomer is downfield of the minor isomer, as was true for the methylcarbene **1**.

Slow diffusion of methanol into a CH$_2$Cl$_2$ solution of **7** at −30 °C yields reddish orange crystals. A satisfactory crystal (0.35 × 0.35 × 0.20 mm) was selected for a single-crystal X-ray diffraction study. Crystallographic data and collection parameters are given in Table 2. Selected bond distances and angles for **7** are presented in Table 3. Figures 1 and 2 show different views of **7**.

The molybdenum−carbene carbon bond distance of 2.085(4) Å lies on the short end of previously reported structures.[13] Conversely, the carbene carbon−oxygen bond distance is 1.356(5) Å, a slightly longer C−O bond distance than is typically observed for Fischer carbene complexes.[13] Figure 2 evinces that the plane of the :C(Ph)(OMe) fragment is canted toward the molybdenum−nitrosyl bond, revealing the preference of the carbene ligand to compete with CO rather than NO$^+$

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[13] Schubert, U. In *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983; p 73.

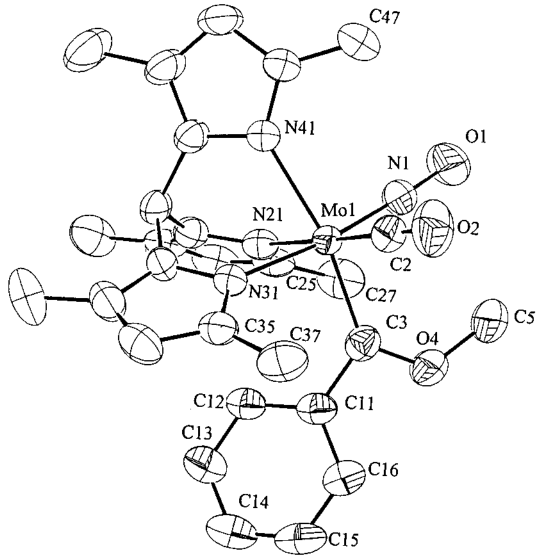


Figure 1. ORTEP diagram of Tp′(CO)(NO)Mo=C(OMe)(Ph) (**7**).

Table 3. Selected Bond Distances and Bond Angles for Tp′(CO)(NO)Mo=C(OMe)(Ph) (7)

Bond Distances (Å)

Mo(1)−N(1)	1.782(3)	O(4)−C(5)	1.437(6)
Mo(1)−C(2)	1.999(4)	C(11)−C(12)	1.404(6)
Mo(1)−C(3)	2.085(4)	C(12)−C(13)	1.391(6)
Mo(1)−N(21)	2.221(3)	C(13)−C(14)	1.367(6)
Mo(1)−N(31)	2.243(3)	C(14)−C(15)	1.370(8)
Mo(1)−N(41)	2.275(3)	C(15)−C(16)	1.389(7)
N(1)−O(1)	1.211(4)	C(11)−C(16)	1.392(6)
C(2)−O(2)	1.151(5)	C(3)−C(11)	1.488(6)
C(3)−O(4)	1.356(5)		

Bond Angles (deg)

N(1)−Mo(1)−C(2)	84.92(16)	N(21)−Mo(1)−N(31)	87.56(11)
N(1)−Mo(1)−C(3)	97.06(16)	N(21)−Mo(1)−N(41)	80.31(11)
N(1)−Mo(1)−N(21)	96.98(14)	N(31)−Mo(1)−N(41)	78.52(11)
N(1)−Mo(1)−N(31)	170.27(13)	Mo(1)−N(1)−O(1)	173.0(3)
N(1)−Mo(1)−N(41)	93.71(13)	Mo(1)−C(2)−O(2)	173.6(4)
C(2)−Mo(1)−C(3)	89.93(15)	Mo(1)−C(3)−O(4)	130.4(3)
C(2)−Mo(1)−N(21)	176.86(14)	Mo(1)−C(3)−C(11)	125.4(3)
C(2)−Mo(1)−N(31)	90.20(14)	O(4)−C(3)−C(11)	104.2(3)
C(2)−Mo(1)−N(41)	97.09(13)	C(3)−O(4)−C(5)	120.8(3)
C(3)−Mo(1)−N(21)	92.32(13)	C(3)−C(11)−C(12)	121.3(3)
C(3)−Mo(1)−N(31)	91.33(14)	C(3)−C(11)−C(16)	121.4(4)
C(3)−Mo(1)−N(41)	167.63(14)		

for dπ electrons. The carbene phenyl ring is sandwiched between two of the Tp′ pyrazolyl rings (Figure 1).

In the ^{1}H NMR spectra, we have previously observed significant shielding of protons proximal to the aromatic Tp′ rings.[14] The −OMe group for **7** in the solid state is directed away from the Tp′ ligand, consistent with ^{1}H NMR data for the major isomer of **7** in CD_2Cl_2 (*vide supra*).

Isomer Identities. In order for the carbene moiety to compete with the CO ligand rather than with NO$^+$ for dπ electrons, a molecular geometry placing the plane of the neutral :C(OMe)(R) fragment parallel with the Mo−NO bond is optimal (Chart 2). The crystal structure of the phenylcarbene **7** revealed the :C(Ph)(OMe) plane to be tilted toward the molybdenum−nitrosyl bond (Figure 2). Four distinct rotational isomers, corresponding to *syn* or *anti* geometries with respect to the location of the β-alkyl group juxtaposed against the Tp′ ligand, as well as rotational isomers about the C−O bond of the carbene ligand, are possible for the metal carbene moiety (Chart 3).

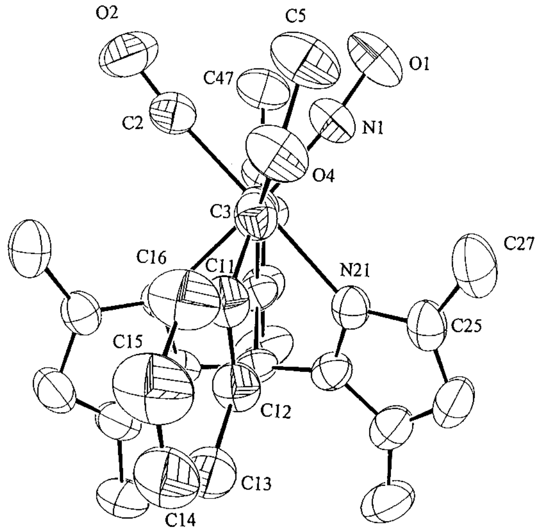


Figure 2. ORTEP diagram of Tp′(CO)(NO)Mo=C(OMe)(Ph) (**7**).

Chart 2. Orientation of the Carbene Ligand

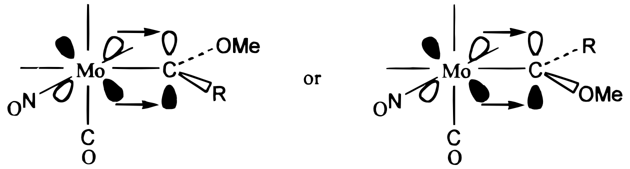
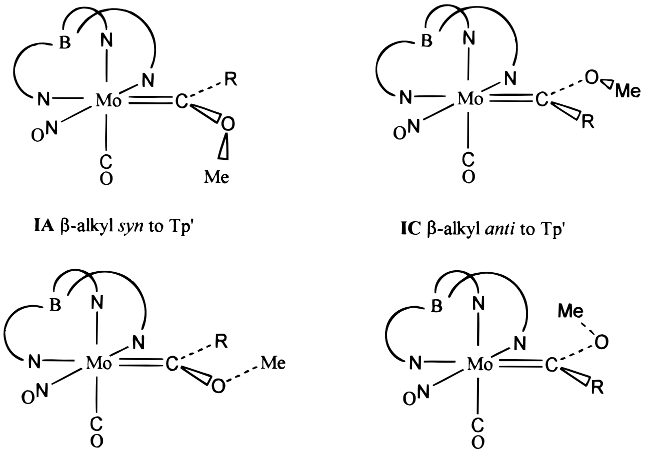


Chart 3. Possible Rotational Isomers for Tp′(CO)(NO)Mo=C(OMe)(R)



IA β-alkyl *syn* to Tp'

IC β-alkyl *anti* to Tp'

IB β-alkyl *syn* to Tp'

ID β-alkyl *anti* to Tp'

For a Fischer carbene with a potential heteroatom π-donor and an alkyl group as substituents, three resonance forms are dominant (Scheme 2).[15] For Fischer carbene complexes resonance form IIB contributes significantly, and hindered rotation about the C−O bond in Fischer carbenes is common. For example, C−O rotational barriers for chromium carbene complexes of

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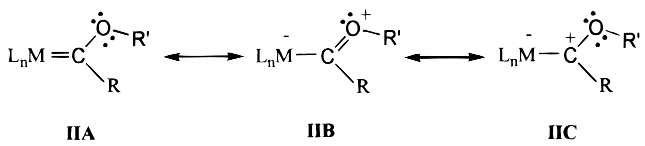
(14) See for example: Feng, S. G.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 2951.

(15) For a discussion on bonding in carbene complexes, see: Schubert, U. *Coord. Chem. Rev.* **1984**, *55*, 261.

(16) (a) Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J.; Müller, J.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237. (b) See also ref 1e, p 152.

(17) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1.

Scheme 2. Classical Resonance Forms for Fischer Carbenes



the type $(CO)_5Cr{=}C(OMe)(R)$ range from 11 to 14 kcal/mol, and larger barriers are common.[16]

Observation of a barrier to rotation about the metal–carbene carbon bond is rare.[17] Most Fischer carbene complexes possess multiple π-acid ligands in the metal coordination sphere, and the dominant resonance form may well be IIA, but unless the dπ orbitals are differentiated by divergent π-acceptor ligands in cis positions, no substantial electronic barrier to rotation results. Here, the presence of the strong σ-donor ligand Tp′ could increase the contribution of resonance form IIA. For reasons discussed below, we propose that the two isomers observed at room temperature for complexes **1**–**7** result from hindered rotation about the metal–carbene carbon bond, rather than restricted rotation about the C–O bond of the carbene moiety.

Variable-temperature NMR experiments were performed in order to identify the geometric isomers present for complexes **1**–**7** and to determine the interconversion barriers. Use of conventional line-broadening techniques revealed a barrier of approximately 18.5 kcal/mol for interconversion of the two isomers of Tp′(CO)(NO)Mo=C(OMe)(Me) (**1**). The dπ orbital discrimination created by CO and NO ligands supports the hypothesis that isomerization is due to restricted metal–carbon rotation. Furthermore, this barrier is higher than most rotational barriers for C–O bonds in Fischer carbene complexes, and given the donor properties of Tp′, a lower C–O bond rotation barrier would be expected for these complexes compared to $X(CO)_4M{=}C(OR)(R)$ systems.

More significantly, lowering the temperature of a solution of **1** in 60% CD_2Cl_2, 27% CCl_4, and 13% $CDCl_3$ (by volume) to −110 °C revealed the presence of a second fluxional process, thus elucidating the presence of four separate isomers (Figure 3). The barrier for this process was calculated to be 9.6 kcal/mol, and we assign this as a C–O bond rotation barrier. This is consistent with a decrease in the barrier for rotation about the C–O bond in the carbene ligand of these Tp′ derivatives relative to the $X(CO)_4M{=}C(OR)(R)$ class of compounds.

As an additional probe of isomer identities and interconversion barriers, the tungsten methylcarbene **6** was synthesized. Since steric differences between **1** and **6** should be negligible, if hindered rotation for the high-energy process is in fact due to metal-to-carbene π-donation, the presence of a more electron rich metal center should increase the barrier to rotation. Conversely, if the rotational barrier of 18.5 kcal/mol is due to restricted rotation about the C–O bond, the presence of a more electron rich metal center should decrease this barrier by increasing the contribution of resonance form IIA (Scheme 2). The experimental rotational barrier for the tungsten methylcarbene complex **6** was calculated to be >22 kcal/mol, as determined by line-broadening techniques, thus reinforcing our interpretation of fluxional processes relating the various isomers: the higher barrier reflects metal–carbon π-bonding, and the lower barrier is due to oxygen–carbon π-bonding.

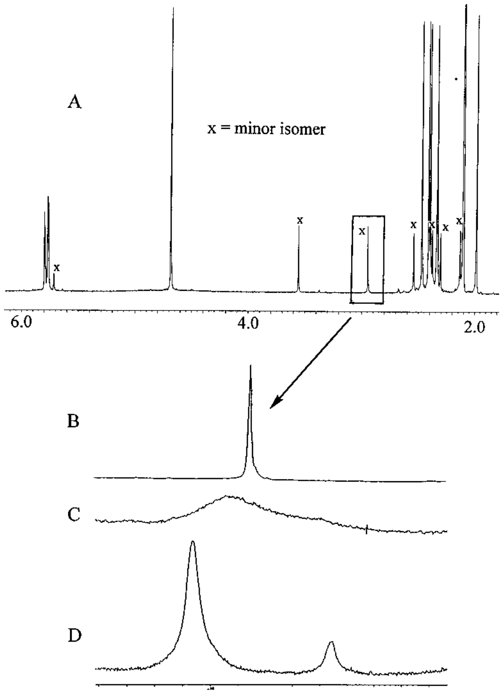


Figure 3. Variable-temperature ^{1}H NMR for Tp′(CO)(NO)Mo=C(OMe)(Me) (**1**) in 60% CD_2Cl_2, 27% CCl_4, and 13% $CDCl_3$ (by volume). The figure shows the β-methyl region (2.70–3.30 ppm) of the minor rotational isomer at room temperature. As the temperature is decreased, additional rotational isomers are observed: (A) room temperature, 1.70 to 6.30 ppm; (B) room temperature, 2.70–3.30 ppm; (C) −80 °C, 2.70–3.30 ppm; (D) −110 °C, 2.70–3.30 ppm.

The crystal structure of **7** divulged a shorter molybdenum–carbene carbon bond distance and a longer carbene carbon–oxygen bond distance than is typical for Fischer carbene complexes (*vide supra*). These data provide additional evidence for the importance of resonance form IIA in these complexes (Scheme 2).

The chemical shift of the methoxy group is a convenient diagnostic peak for the two isomers present at room temperature. The resonance for the –OMe protons of the major isomer is downfield of the minor isomer by approximately 1.2 ppm for the methyl complex **1**. Due to the downfield shift for the –OMe group, we expect that the –OMe unit is *anti* and the β-methyl group is *syn* to Tp′ for the major isomer of the methyl carbene **1** (Chart 4; IIIA). In addition, the resonance for the β-methyl group of the major isomer is upfield of the minor isomer in the ^{1}H NMR spectrum of **1**. As the steric bulk of the β-group is increased, it may become more sterically favored to position the –OMe group syn to Tp′, thus resulting in the β-moiety positioned *anti* to Tp′ (Chart 4; IIIB). It is evident from the ORTEP diagram for the phenylcarbene **7** that substitution of protons on the β-carbon with one or more alkyl groups ($-CH_3$ or $-CH_2CH{=}CH_2$) could cause significant steric repulsion with the voluminous Tp′ ligand (Figure 1). Subsequent synthesis of substituted carbenes revealed trends in isomer ratios that are consistent with this hypothesis (Table 4).

Synthesis of Tp′(CO)(NO)Mo=C(OMe)(Et) (2). Addition of *n*-BuLi to an orange THF solution of the

Chart 4. Proposed Orientation of Alkyl Group R for the Major Isomer of the Complexes (IIIA, 1, 2, 4, 7; IIIB, 3, 5a, 5b)

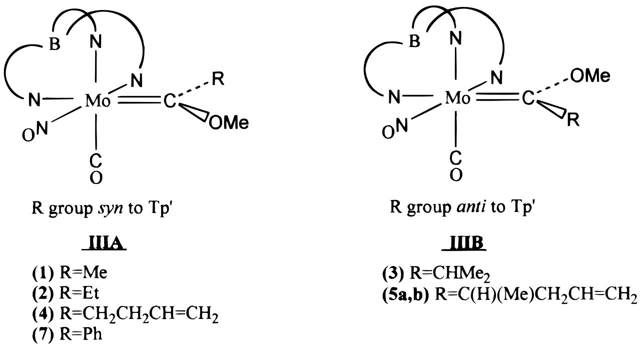
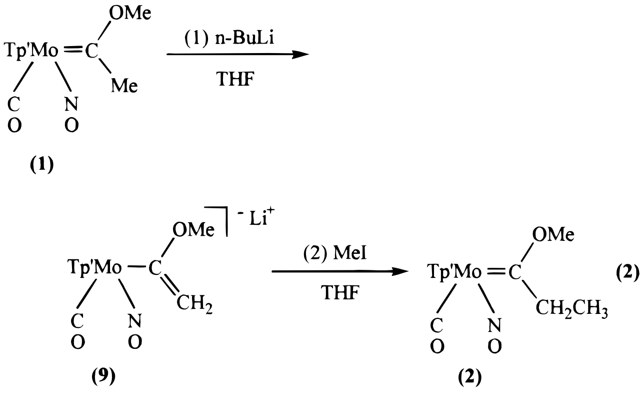


Table 4. Rotamer Ratios for Complexes 1−6

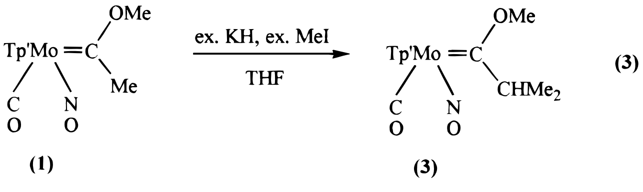
complex	rotamer ratio	$\delta(\mathrm{OC}H_3)$,[a] ppm
Tp′(CO)(NO)Mo=C(OMe)(Me) (**1**)	6:1	4.68
Tp′(CO)(NO)Mo=C(OMe)(Et) (**2**)	2:1	4.69
Tp′(CO)(NO)Mo=C(OMe)($CHMe_2$) (**3**)	1:5	3.45
Tp′(CO)(NO)Mo=C(OMe)-($CH_2CH_2CH{=}CH_2$) (**4**)	1.5:1	4.68
Tp′(CO)(NO)Mo=C(OMe)-(C(H)(Me)$CH_2CH{=}CH_2$) (**5a,b**)	1:10	3.45
Tp′(CO)(NO)W=C(OMe)(Me) (**6**)	6:1	4.56

[a] Chemical shift for major isomer.

methyl complex **1** results in the formation of a green solution of the anionic complex [Li][Tp′(CO)(NO)Mo=C-(OMe)(CH_2)] (**9**; eq 2). IR spectroscopy in THF reveals a CO stretch for **9** at 1866 cm^{-1}, a decrease of 79 cm^{-1} from **1**. The anion of **9** reacts with MeI to produce the ethylcarbene complex **2** in 86% yield (eq 2). ^{1}H NMR again indicates the presence of two isomers, this time in a 2:1 ratio.



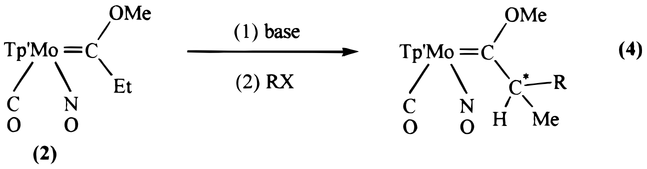
Synthesis of Tp′(CO)(NO)Mo=C(OMe)($CHMe_2$) (3). The isopropyl complex **3** can be synthesized from a THF solution of the ethylcarbene **2** upon addition of *n*-BuLi followed by MeI. As an alternate pathway, reaction of the methylcarbene **1** with an excess of KH and MeI yields **3** upon purification via alumina chromatography (eq 3). Isolation of the isopropyl complex **3** from the reaction of **1** with an excess of KH and MeI suggests that deprotonation of the isopropyl carbene complex **3** is difficult. Indeed, no reaction was observed when **3** was treated with *n*-BuLi.

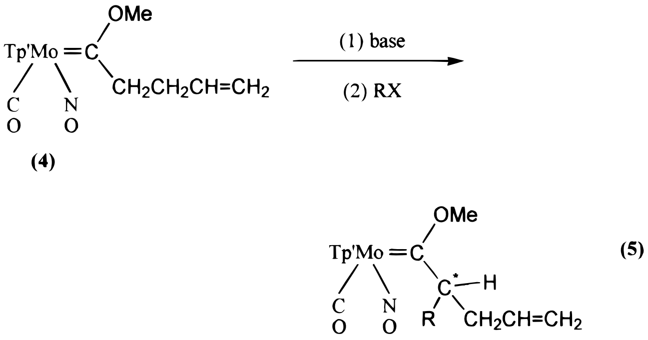


Two isomers are observed in the ^{1}H NMR of **3** in a 5:1 ratio. For complex **3**, the ^{1}H chemical shift of the carbene −OMe unit for the major isomer is upfield of the chemical shift for the minor isomer, in contrast to observations for **1** and **2**. Increasing the steric bulk of the carbene alkyl substituent increases the proportion of high-field −OMe isomer, presumably resulting from placing the isopropyl group *anti* to Tp′ (Chart 4; IIIB).

Synthesis of Tp′(CO)(NO)Mo=C(OMe)(CH_2CH_2-$CH{=}CH_2$) (4). Generation of the conjugate base of the methyl complex **1** by reaction with *n*-BuLi followed by addition of allyl bromide gives complex **4** in 48% yield. Two isomers are present in a 1.5:1 ratio by ^{1}H NMR spectroscopy. The near-thermodynamic equivalence of the two rotamers reflects approach to balanced steric effects of the lengthy alkyl chain and the methoxy group on the carbene moiety.

Diastereoselection in the Synthesis of Tp′(CO)-(NO)Mo=C(OMe)(C(H)(Me)$CH_2CH{=}CH_2$) (5a and 5b). Deprotonation and alkylation of **2** and **4** could yield a chirotopic carbon *β* to the metal in the carbene fragment (eqs 4 and 5). The presence of a chiral metal fragment allows the possibility of diastereoselective elaborations. Functionalization of the conjugate base of **2** with allyl bromide and of the conjugate base of **4** with MeI was performed to investigate the extent to which stereocontrol could be achieved with this system.

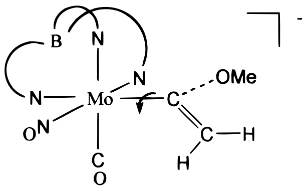




Reaction of the anion of **2** with allyl bromide at 0 °C yields the complex Tp′(CO)(NO)Mo=C(OMe)(C(H)(Me)-$CH_2CH{=}CH_2$) (**5a**) in 80% yield. Methyl groups on the Tp′ ligand, the −OMe unit, and the methyl group attached to the carbene *β*-carbon provide convenient probes for diastereomer identification. NMR studies were performed on the crude reaction product to monitor diastereomer selectivity directly and thus avoid serendipitous enrichment during workup. ^{1}H NMR of the crude product **5a** showed the presence of two diastereomers in a 4:1 ratio.

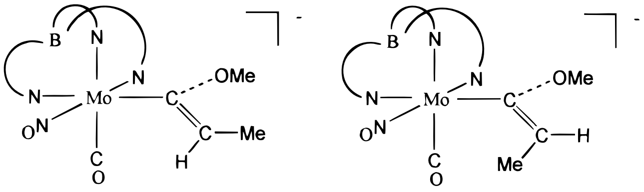
In order to understand the modest diastereoselectivity observed in the above reaction, ^{1}H NMR spectra were obtained for the anions of **1** and **2**, [Li][Tp′(CO)(NO)-MoC(=CH_2)(OMe)] (**9**), and [Li][Tp′(CO)(NO)MoC(=C-

Chart 5. Rapid Rotation about Mo−C for Deprotonated 1



(9)

Chart 6. *cis* and *trans* Isomers for the Anion of 10



Trans isomer *Cis* isomer

(H)Me)(OMe)] (**10**), respectively. The ^{1}H NMR of **9** indicated only a single isomer in solution with chemical shifts for the vinylic protons at 4.47 and 3.10 ppm. We attribute the observation of only a single isomer to the vinylic character of **9**, which would allow rapid rotation around the metal−carbon bond of the vinyl ether resonance form (Chart 5). Anion **10** offers the possibility of *E* and *Z* isomers for the methyl substituent on the vinyl group, and indeed the ^{1}H NMR of **10** showed two isomers in a 2:1 ratio. On the basis of the observation of only a single isomer for **9**, the two isomers of **10** have been assigned to *cis* and *trans* geometries relative to the molybdenum metal center and the methyl group (Chart 6).

Kinetic control of stereoselectivity is indicated by selective formation of the opposite diastereomer of the major product **5a** by reaction of **4** with base and MeI. Generation of the anion of **4** and subsequent reaction with MeI yield complex **5b** in 67% yield. Improved diastereoselectivity is achieved in the production of **5b** from **4** relative to formation of **5a** from **2**: the ^{1}H NMR spectrum revealed two stereoisomers in about a 10:1 ratio.

Conclusion

Synthesis of chiral-at-metal Tp′(CO)(NO)M=C(OMe)(R) (M = Mo, W) carbene complexes has provided an opportunity to explore the coupled issues of isomer geometries and diastereoselective deprotonation/alkylation sequences. The single-faced π carbene ligand encounters a barrier to M=C rotation near 20 kcal/mol (for M = Mo) due to the dπ differentiation accompanying *cis* CO and NO$^+$ ligands. Although rotation around the carbene C−O bond is restricted, the barrier is near 10 kcal/mol (M = Mo), less than comparable values in classic X(CO)$_4$M=C(OMe)(R) systems. The presence of *syn* and *anti* alkyl isomers in the carbene reagent leads to two isomers upon deprotonation, and modest diastereoselectivity results from alkylation of the prochiral anion intermediate.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE9208207) for generous support of this research.

Supporting Information Available: X-ray crystal structure information for **7**, including a labeled diagram of **7** and tables showing atomic positional parameters, complete bond lengths and angles, and anisotropic temperature factors (4 pages). Ordering information is given on any current masthead page.

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