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# Synthesis of Pentacarbonyl(2,3-dialkoxycyclopropenylidene)chromium(0), -molybdenum(0), and -tungsten(0) Complexes by Reaction of Metal Hexacarbonyls with Lithium Ethoxyacetylide

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**Abstract:** The reaction between the anion of ethoxyacetylene and chromium, molybdenum, or tungsten hexacarbonyl followed by alkylation with Meerwein's reagent produced the unusual pentacarbonyl(2,3-dialkoxycyclopropenylidene) complexes in excellent yields. An X-ray crystal structure determination of the diethoxy chromium complex is reported. These unusual carbene complexes did not undergo the typical reactions of carbene complexes (e.g., thermal additions to alkynes, photochemical additions to imines) but rather suffered nucleophilic attack at an alkoxy-bearing position.

As part of a continuing program directed toward the synthesis of biologically active β-lactams by the photolytic reaction of imines with chromium carbene complexes,[2] synthetic approaches to chromium carbene complexes of the type $(CO)_5Cr{=}C(R)(H)$ were required. Chromium carbene complexes lacking the stabilizing effects of a heteroatom directly on the carbene carbon (e.g., $(CO)_5Cr{=}C(OMe)(R)$) generally lack sufficient stability to be of use synthetically.[3] However, a recent report of the synthesis and remarkable stability of a chromium carbene complex having *vinylogous* heteroatom stabilization[4] $[(CO)_5Cr{=}C\text{-}(CH{=}C(OR)(Ar)(R'))]$ prompted an investigation into the synthesis of simpler analogues of this type of complex.

## Results and Discussion

Chromium hexacarbonyl was treated with 1-ethoxy-2-lithioethyne, under typical Fischer carbene-forming conditions,[5] and the resulting acylate compound was alkylated with triethyloxonium tetrafluoroborate to produce an excellent yield of white, stable cyclopropenylidene complex **1** (eq 1). This was not the expected linear product from the reaction, although it is an isomer with the same molecular formula, as evidenced by the mass spectrum having a parent ion *m/e* 318 ($C_{12}H_{10}CrO_7$), and fragments corresponding to sequential loss of the five CO groups, as is typical for chromium carbene complexes. However, the infrared spectrum lacked a band assignable to an unsymmetric alkyne, and the $^1H$ NMR spectrum consisted of a single O-ethyl group (t, $\delta$ 1.56; q, $\delta$ 4.71). The $^{13}C$ NMR spectrum confirmed the assigned structure for **1**, having a singlet at $\delta$ 191.74 for the carbene carbon and a triplet ($^3J = 3$ Hz) at $\delta$ 170.73 for the equivalent ethoxy-bearing carbons. To confirm the structure assignment for **1**, its crystal structure was determined and is displayed in Figure 1, with bond lengths and angles in Table I. The observed bond lengths in the cyclopropenylidene fragment are remarkably similar to those observed in the corresponding pentacarbonyl(2,3-diphenylcyclopropenylidene)chromium(0) complex synthesized over 20 years ago by the reaction of 1,1-dichloro-2,3-diphenylcyclopropene with $Na_2Cr(CO)_5$.[6,7] Several other cyclopropenylidene complexes are known,[8] but they all were formed from starting materials already having the cyclopropene ring present.

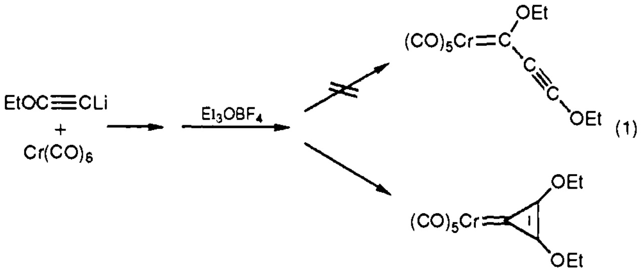

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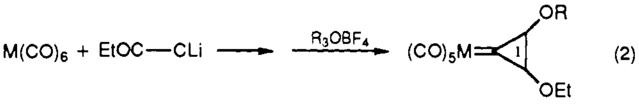
Table I. Bond Lengths (Å)[a] and Bond Angles (deg)[a] for Complex **1**

| | | | |
|---|---|---|---|
| | (A) Bond Lengths | | |
| Cr–C1 | 2.010 (7) | Cr–C5 | 1.891 (8) |
| Cr–C6 | 1.893 (4) | Cr–C7 | 1.892 (4) |
| Cr–C6′ | 1.893 (4) | Cr–C7′ | 1.892 (4) |
| O1–C2 | 1.300 (5) | O1–C3 | 1.472 (5) |
| O2–C5 | 1.129 (10) | O3–C6 | 1.139 (4) |
| O4–C7 | 1.139 (4) | C1–C2 | 1.410 (8) |
| C1–C2′ | 1.410 (8) | C2–C2′ | 1.337 (7) |
| C3–C4 | 1.483 (7) | | |
| | (B) Bond Angles | | |
| C1–Cr–C5 | 180.0 | C1–Cr–C6 | 89.9 (2) |
| C5–Cr–C6 | 90.1 (2) | C1–Cr–C7 | 90.7 (2) |
| C5–Cr–C7 | 89.3 (2) | C6–Cr–C7 | 91.3 (2) |
| C1–Cr–C6′ | 89.9 (2) | C5–Cr–C6′ | 90.1 (2) |
| C6–Cr–C6′ | 180.0 (6) | C7–Cr–C6′ | 88.7 (2) |
| C1–Cr–C7′ | 90.7 (2) | C5–Cr–C7′ | 89.3 (2) |
| C6–Cr–C7′ | 88.7 (2) | C7–Cr–C7′ | 178.6 (4) |
| C6′–Cr–C7′ | 91.3 (2) | C2–O1–C3 | 114.3 (3) |
| Cr–C1–C2 | 151.7 (2) | Cr–C1–C2′ | 151.7 (2) |
| C2–C1–C2′ | 56.6 (4) | O1–C2′–C2 | 149.1 (4) |
| O1–C2–C2′ | 149.2 (2) | C1–C2–C2′ | 61.7 (2) |
| O1–C3–C4 | 106.5 (4) | Cr–C5–O2 | 180.0 |
| Cr–C6–O3 | 178.4 (4) | Cr–C7–O4 | 178.2 (4) |

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Molybdenum and tungsten hexacarbonyls also produced dialkoxycyclopropenylidene complexes when treated with ethoxyacetylidene anion (eq 2). A very low yield of the corresponding



**1**: M = Cr, R = Et (84%)
**2**: M = Cr, R = Me (58%)
**3**: M = Mo, R = Et (86%)
**4**: M = W, R = Et (93%)

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(1) F. W. Roepke carried out the X-ray crystal structure determination.

(2) Hegedus, L. S.; D'Andrea, S. *J. Org. Chem.* **1988**, *53*, 3113 and references cited therein.

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(8) (a) Öfele, K. J. *J. Organomet. Chem.* **1970**, *22*, C9. (b) Gompper, R.; Bartmann, E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 456. (c) Weiss, R.; Priesner, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 457. (d) Kirchgäsener, U.; Schubert, U. *Organometallics* **1988**, *7*, 784.

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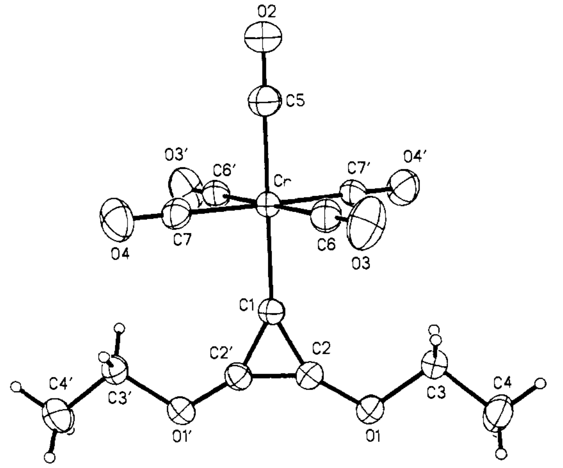
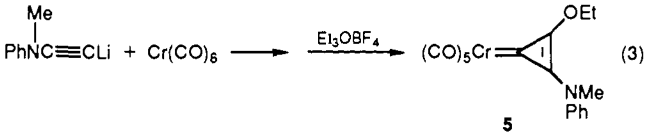


**Figure 1.**

aminoalkoxycyclopropenylidene chromium complex was obtained when the lithium salt of an ynamine was used (eq 3).



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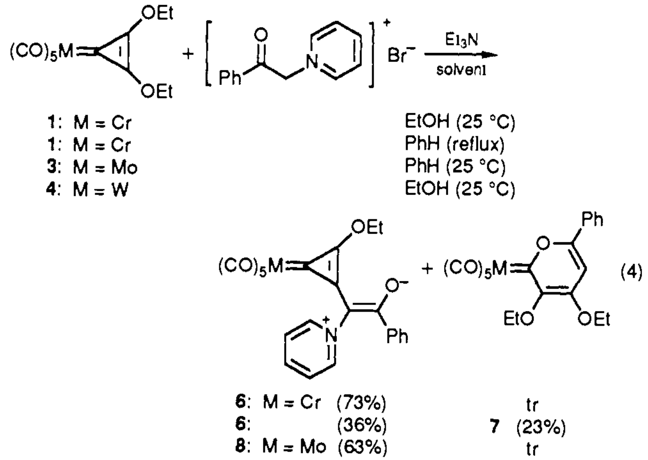
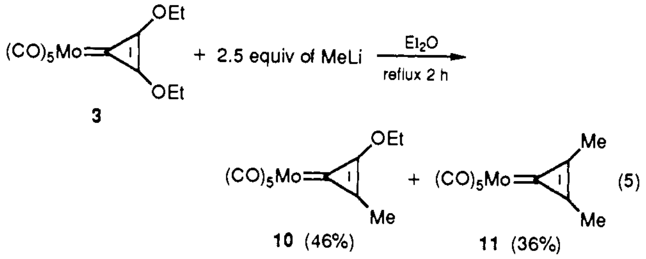
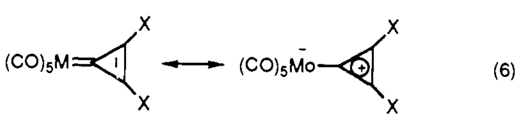
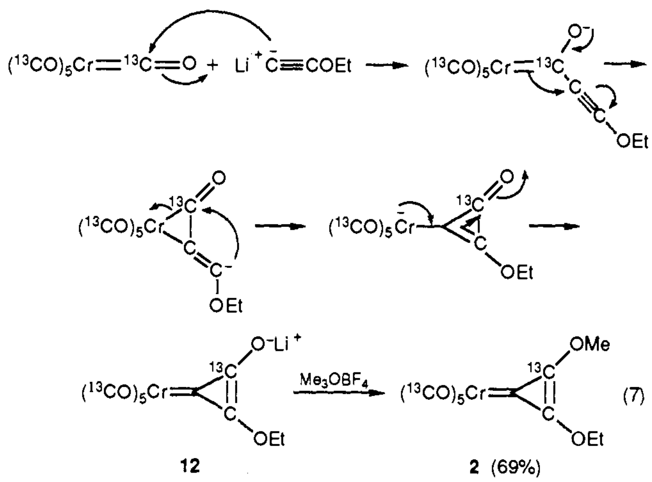
Since dialkoxycyclopropenylidene complexes were generally available by the above procedure, their reaction chemistry was briefly examined. Complexes **1**–**4** proved remarkably unreactive toward substrates typically reactive toward the metal–carbon double bond. Thus, in photolytic[9] as well as thermal[10] reactions with imines, alcohols, and alkynes, no productive reaction was observed. Rather, the complexes **1**–**4** persisted for days under the reaction conditions, slowly decomposing to intractable material without incorporation of substrate. Thus, these are not typical "Fischer carbene" complexes. Pentacarbonyl(2,3-diphenylcyclopropenylidene)molybdenum(0) undergoes reaction with pyridinium ylides to produce stable pyran-2-ylidene complexes.[11] Diethoxy complexes **1**, **3**, and **4** behave somewhat differently with the same ylide (eq 4). In only one case was the pyran-2-ylidene complex obtained, and that, as a minor product. The preferred products, **6**, **8**, and **9**, were those resulting from displacement of an ethoxy group by the ylide complexes. This difference is probably due to the poor leaving ability of a phenyl group relative to an ethoxy group. Indeed, addition/elimination at an alkoxy-bearing carbon seems to be a favored reaction pathway for complexes **1**–**4**. For example, treatment of **1** with lithium *N*-methylanilide gave **5** in 87% yield. Similarly, treatment of **3** with 2.5 equiv of methyllithium produced a mixture of the monomethyl- (**10**) and dimethyl cyclopropenylidene (**11**) complexes (eq 5). Although complexes **10** and **11** are moderately stable in solution, they blacken immediately upon removal of solvent. It is nevertheless remarkable that **11**, with no heteroatom or $\pi$-stabilization excepting the cyclopropene double bond, is sufficiently stable to permit separation by chromatography and characterization by spectroscopic methods. This stability is likely due to the cyclopropenium cation nature of the carbene ligand (eq 6).







To gain insight into the mechanism of formation of complexes **1**–**4** from eq 2, the reaction was repeated using $^{13}$C-labeled chromium hexacarbonyl[12] diluted 3-fold by unlabeled material. Examination of the product **2** by $^{13}$C NMR spectroscopy showed the label to be exclusively at the carbon bearing the methoxy group. The fully coupled $^{13}$C NMR spectrum of **2** confirmed the position of the $^{13}$C-labeled carbon, enriched to approximately 23%, as a quartet [$^3J$(COCH) = 4.9 Hz] at $\delta$ 171.12 for the methoxy-bearing carbon of the cyclopropenylidene ring. The methoxy group is formed by methylation with trimethyloxonium tetrafluoroborate. The data indicate that a metal–carbon bond of chromium hexacarbonyl has been broken during the formation of compound **2**. A possible mechanism for formation of **2**, incorporating the spectral information, is shown (eq 7).



Studies of both the organic and organometallic chemistry of this unusual and now readily accessible class of complexes continue.

## Experimental Section

**General Procedures.** Melting points were taken on a Mel-Temp apparatus and are uncorrected. A Bruker/IBM-200 NMR spectrometer

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(10) For reviews see: (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (b) Sayatkovskii, A. I.; Babitskii, B. D. *Russ. Chem. Rev.* **1985**, *53*, 672. (c) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9.

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was used for the 200-MHz $^1$H NMR spectra. The 270-MHz $^1$H NMR and the 67-MHz $^{13}$C NMR spectra were obtained on a Bruker/IBM 270 NMR spectrometer. The 300-MHz $^1$H NMR and the 75-MHz $^{13}$C NMR spectra were obtained on a Bruker/IBM 300 NMR spectrometer. The 60-MHz $^1$H NMR spectra were obtained on a Varian T-60 spectrometer. NMR spectra were recorded in $\mathrm{CDCl_3}$, and chemical shifts are given in ppm relative to $\mathrm{Me_4Si}$ (=0 ppm; $^1$H), $\mathrm{CDCl_3}$(=7.24 ppm; $^1$H), or $\mathrm{CDCl_3}$(=77 ppm; $^{13}$C). IR spectra were recorded on a Beckman 4240 spectrophotometer, Perkin-Elmer 936 spectrophotometer, Nicolet MX-1 FTIR spectrometer, and Perkin-Elmer 1600 FTIR spectrometer.

Chemical ionization (CI) and electron impact (EI) mass spectra were obtained on a VG Micromass, Ltd., Model 16F spectrometer. All reactions were carried out under an argon atmosphere, and all solvents and reagents were thoroughly degassed by four cycles of evacuation and purging with argon.

For purification of crude reaction mixtures column chromatographic techniques were applied in most cases. Alfa silica gel, large pores (58 μm) and Baker silica gel (230–400 mesh) were used as stationary phases.

Elemental analyses were performed by MHW Laboratories, Phoenix, AZ.

**Materials.** Hexane (technical grade) was distilled at atmospheric pressure. Tetrahydrofuran (analytical reagent) and diethyl ether (analytical reagent) were predried over $\mathrm{CaH_2}$ and distilled from benzophenone ketyl under nitrogen atmosphere just prior to use. Methylene chloride (technical grade) was predried over $\mathrm{CaH_2}$ and distilled from $\mathrm{CaH_2}$. Ethyl ethynyl ether 50 wt % in hexane (Farchan and Aldrich) and carbon monoxide $^{13}$C, 99% (Cambridge Isotope Laboratories), chromium, molybdenum, and tungsten hexacarbonyl (Pressure Chemical Co.), and trimethyloxonium tetrafluoroborate (Lancaster Synthesis) were obtained from commercial suppliers and used without purification.

The following chemicals were prepared according to literature procedures: $^{13}$C-labeled chromium hexacarbonyl,[12] lithium (*N*-methylanilino)acetylide,[13] *N*-methyl-2,2,2-trichlorovinylamine,[14] triammoniochromium tricarbonyl,[15] and triethyloxonium tetrafluoroborate.[16]

**Synthesis of Pentacarbonyl(2,3-diethoxycyclopropenylidene)chromium(0) (1).** Ethyl ethynyl ether (0.52 g, 7.3 mmol, 50% wt in hexane) was added to 20 mL of argon-saturated tetrahydrofuran in a 100-mL Airless-ware flask capped with a septum, and the resulting solution was cooled to −78 °C. Butyllithium (3.4 mL of 1.54 M solution in hexane, 5.2 mmol) was added dropwise by syringe, and the resulting brown-orange solution was stirred at −78 °C for 1 h.

A suspension of chromium hexacarbonyl (1.11 g, 5.00 mmol) in tetrahydrofuran (25 mL) in a 100-mL Airless-ware flask was evacuated and purged with argon (3×) and cooled to −78 °C, and the lithium ethynyl ether solution prepared above was transferred via a cannula under a slight argon pressure into the suspension over the course of 10 min. After stirring 0.5 h at −78 °C, the suspension was warmed to 0 °C. After 2 h at 0 °C, it was warmed to ambient temperature, and after an additional 0.5 h, the solvent was removed under vacuum giving a brown solid.

This was redissolved in methylene chloride (60 mL) and cooled to 0 °C under argon. Triethyloxonium tetrafluoroborate (1.6 g, 8.5 mmol) as a solid was added over 5 min with an argon flow, and the mixture was stirred 2.5 h at 0 °C. Solvent was removed under vacuum at 0 °C. The brown residue was dissolved in ether (25 mL) and filtered through a pad of Celite and neutral alumina. Removal of solvent gave a white solid (1.35 g, 4.2 mmol, 84%): mp 62–64 °C; $^1$H NMR (60 MHz, $\mathrm{CDCl_3}$) δ 4.71 (q, *J* = 7 Hz, 2, $\mathrm{OC\mathit{H}_2CH_3}$), 1.56 (t, *J* = 7 Hz, 3, $\mathrm{OCH_2C\mathit{H}_3}$); $^{13}$C NMR (67 MHz, $\mathrm{CDCl_3}$) δ 222.29 (*trans*-CO), 217.79 (*cis*-CO), 191.74 ($\mathrm{Cr{=}C}$), 170.73 ($\mathrm{C{=}C}$), 72.23 ($\mathrm{OCH_2}$), 14.83 ($\mathrm{CH_3}$); MS (EI) *m/e* 318 ($\mathrm{M^+}$), 290 (M − CO), 262 (M − 2 CO), 234 (M − 3 CO), 206 (M − 4 CO), 178 (M − 5 CO); IR (film) ν 2055, 1960, 1915, 1873 (CO) cm$^{-1}$. Anal. Calcd for $\mathrm{C_{12}H_{10}CrO_7}$: C, 45.28; H, 3.15. Found: C, 45.39; H, 3.39.

**Synthesis of Pentacarbonyl(2-ethoxy-3-methoxycyclopropenylidene)chromium(0) (2).** Complex **2** was synthesized as above using 1.14 g (4.99 mmol) of chromium hexacarbonyl, 0.47 g (6.66 mmol) of ethyl ethynyl ether, and trimethyloxonium tetrafluoroborate (0.96 g, 6.47 mmol) to give a cream solid (0.68 g, 2.23 mmol, 58%): mp 51.5–52.5 °C; $^1$H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 4.74 (q, *J* = 7 Hz, 2, $\mathrm{OC\mathit{H}_2CH_3}$), 4.40 (s, 3, $\mathrm{OC\mathit{H}_3}$), 1.58 (t, *J* = 7 Hz, 3, $\mathrm{OCH_2C\mathit{H}_3}$); $^{13}$C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 222.27 (*trans*-CO), 217.76 (*cis*-CO), 191.65 ($\mathrm{Cr{=}C}$), 171.10 ($\mathrm{{=}\mathit{C}OCH_3}$), 170.25 ($\mathrm{{=}\mathit{C}OCH_2CH_3}$), 72.30 ($\mathrm{O\mathit{C}H_2CH_3}$), 62.02 ($\mathrm{O\mathit{C}H_3}$), 15.13 ($\mathrm{OCH_2\mathit{C}H_3}$); MS (EI) *m/e* 304 ($\mathrm{M^+}$), 276 (M − CO), 248 (M − 2 CO), 220 (M − 3 CO), 192 (M − 4 CO),164 (M − 5 CO); IR (film) ν 2045, 1972, 1960, 1925, 1867 (CO) cm$^{-1}$. Anal. Calcd for $\mathrm{C_{11}H_8CrO_7}$: C, 43.42; H, 2.63. Found: C, 43.53; H, 2.79.

**Synthesis of $^{13}$C-Enriched Pentacarbonyl(2-ethoxy-3-methoxycyclopropenylidene)chromium(0) ([$^{13}$C]-2).** Similar treatment of 0.22 g of chromium hexacarbonyl [0.05 g, 0.24 mmol of $\mathrm{(^{13}CO)_6Cr}$ and 0.17 g, 0.74 mmol, of $\mathrm{(CO)_6Cr}$] with 0.09 g (1.2 mmol) of ethyl ethynyl ether and 0.27 g (1.8 mmol) of trimethyloxonium tetrafluoroborate gave after filtration through neutral alumina and silica gel (Alfa), a cream white solid (0.21 g, 0.68 mmol, 69%; spectral data from an ca. 1:4 mixture of [$^{13}$C]-**2** and **2**): $^{13}$C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 222.25 (*trans*-$^{13}$CO), 217.77 (*cis*-$^{13}$CO), 191.71 ($\mathrm{Cr{=}C}$), 171.10 ($\mathrm{C{=}^{13}\mathit{C}OCH_3}$), 170.25 ($\mathrm{{=}\mathit{C}OCH_2CH_3}$), 72.29 ($\mathrm{O\mathit{C}H_2CH_3}$), 62.01 ($\mathrm{O\mathit{C}H_3}$), 14.98 ($\mathrm{OCH_2\mathit{C}H_3}$); $^{13}$C NMR (75 MHz, $\mathrm{CDCl_3}$, fully coupled) δ 222.30 (m, *trans*-$^{13}$CO), 217.74 (d, *cis*-$^{13}$CO), 191.54 (s, $\mathrm{Cr{=}C}$), 171.12 (q, $^3J$(COCH) = 4.9 Hz, $\mathrm{C{=}^{13}\mathit{C}OCH_3}$), 170.23 ($\mathrm{{=}\mathit{C}OCH_2CH_3}$), 72.36 (t, *J*(CH) = 151.5 Hz, $\mathrm{O\mathit{C}H_2CH_3}$), 62.03 (q, *J*(CH) = 149.4 Hz, $\mathrm{O\mathit{C}H_3}$), 14.96 (q, *J*(CH) = 127.4 Hz, $\mathrm{OCH_2\mathit{C}H_3}$); MS (EI) *m/e* 310 ($\mathrm{M^+}$).

**Synthesis of Pentacarbonyl(2,3-diethoxycyclopropenylidene)molybdenum(0) (3).** Similar treatment of 1.57 g (5.95 mmol) of molybdenum hexacarbonyl with 0.47 g (6.7 mmol) of ethyl ethynyl ether and then 1.4 g (7.6 mmol) of triethyloxonium tetrafluoroborate, filtration through neutral alumina and silica gel, and recrystallization from pentane gave a white solid (1.85 g, 5.1 mmol, 86%): mp 53–54 °C; $^1$H NMR (60 MHz, $\mathrm{CDCl_3}$) δ 4.75 (q, *J* = 7 Hz, 2, $\mathrm{OC\mathit{H}_2CH_3}$), 1.60 (t, *J* = 7 Hz, 3, $\mathrm{OCH_2C\mathit{H}_3}$); $^{13}$C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 211.93 (*trans*-CO), 206.31 (*cis*-CO), 183.12 ($\mathrm{Cr{=}C}$), 169.10 ($\mathrm{C{=}C}$), 71.54 ($\mathrm{O\mathit{C}H_2CH_3}$), 15.11 ($\mathrm{OCH_2\mathit{C}H_3}$); IR (film) ν 2066, 1905, 1870 (CO) cm$^{-1}$. MS (EI) *m/e* 364 ($\mathrm{M^+}$). Anal. Calcd for $\mathrm{C_{12}H_{10}MoO_7}$: C, 39.80; H, 2.78. Found: C, 39.80; H, 2.91.

**Synthesis of Pentacarbonyl(2,3-diethoxycyclopropenylidene)tungsten(0) (4).** Similar treatment of 2.23 g (5.9 mmol) of tungsten hexacarbonyl with 0.47 g (6.7 mmol) of ethyl ethynyl ether and then 2.7 g (14.2 mmol) of triethyloxonium tetrafluoroborate gave a cream solid (2.45 g, 5.4 mmol, 93%): mp 58.5–59.5 °C; $^1$H NMR (60 MHz, $\mathrm{CDCl_3}$) δ 4.74 (q, *J* = 7 Hz, 2, $\mathrm{OC\mathit{H}_2CH_3}$), 1.62 (t, *J* = 7 Hz, 3, $\mathrm{OCH_2C\mathit{H}_3}$); $^{13}$C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 201.90 (*trans*-CO), 197.37 (*cis*-CO), 197.38 (*cis*-CO), 170.21 ($\mathrm{W{=}C}$), 167.01 ($\mathrm{C{=}C}$), 71.70 ($\mathrm{O\mathit{C}H_2CH_3}$), 15.14 ($\mathrm{OCH_2\mathit{C}H_3}$); MS (EI) *m/e* 450 ($\mathrm{M^+}$); IR (film) ν 2063, 1897, 1868 (CO) cm$^{-1}$. Anal. Calcd for $\mathrm{C_{12}H_{10}O_7W}$: C, 32.03; H, 2.24. Found: C, 32.00; H, 2.48.

**Synthesis of Pentacarbonyl[2-ethoxy-3-(*N*-methyl-*N*-phenylamino)cyclopropenylidene]chromium(0) (5). Procedure A**: Lithium (*N*-methylanilino)acetylide[13] (3.79 mmol, including LiCl and $\mathrm{C_4H_9Cl}$) in ether (15 mL) at −65 °C was transferred via cannula into a suspension of chromium hexacarbonyl (0.84 g, 3.8 mmol) in ether (16 mL) at −78 °C. After stirring at −78 °C for 0.5 h, 0 °C for 2 h, and ambient temperature for 1 h, solvent was removed and the residue dissolved in methylene chloride (25 mL) at 0 °C. A solution of triethyloxonium tetrafluoroborate (1.43 g, 7.5 mmol) in methylene chloride (20 mL) at ambient temperature was added via cannula, and the mixture was stirred for 3 h at 0 °C. Solvent was removed under vacuum, and the residue was taken up in ether, filtered through neutral alumina and silica gel, and recrystallized from pentane to give orange needles (36 mg, 0.09 mmol, 3%): mp 113–114 °C; $^1$H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 7.43 (m, 2, ArH), 7.19 (m, 3, ArH), 4.85 (q, *J* = 7.0 Hz, 2, $\mathrm{OC\mathit{H}_2CH_3}$), 3.82 (s, 3, $\mathrm{NC\mathit{H}_3}$), 1.60 (t, *J* = 7.0 Hz, 3, $\mathrm{OCH_2C\mathit{H}_3}$); $^{13}$C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 222.46 (*trans*-CO), 218.41 (*cis*-CO), 174.93 ($\mathrm{Cr{=}C}$), 167.03 ($\mathrm{{=}\mathit{C}OEt}$), 158.14 ($\mathrm{{=}\mathit{C}NPh(Me)}$), 141.96 ($\mathit{N}$-$\mathit{C}$(phenyl)), 129.74 (meta C), 124.64 (para C), 116.46 (ortho C), 71.19 ($\mathrm{O\mathit{C}H_2CH_3}$), 36.18 ($\mathit{N}$-$\mathrm{\mathit{C}H_3}$), 15.30 ($\mathrm{OCH_2\mathit{C}H_3}$); MS (EI) *m/e* 379 ($\mathrm{M^+}$); IR (film) ν 2054, 1966, 1904 (CO) cm$^{-1}$.

**Procedure B**: A solution of *N*-methylaniline (38.5 mg, 0.36 mmol) in tetrahydrofuran (15 mL) at 0 °C was treated dropwise with butyllithium (0.33 mmol, 1.23 M in hexane) and stirred 20 min at ambient temperature. Carbene **1** (0.11 g, 0.33 mmol) in tetrahydrofuran (15 mL) at 0 °C was treated with the lithium *N*-methylanilide solution. After stirring 36 h at ambient temperature, the solvent was removed under vacuum, and the residue was taken up in ether and filtered through a Celite and neutral alumina pad. The ether was removed, and the residue was recrystallized from pentane to yield carbene **5** (63.4 mg). Chromatography of the mother liquor on silica gel (Alfa) with methylene chloride/hexane (1:3) yielded additional **5** (45.2 mg). The total yield of pale cream crystals was 108.6 mg (87%); mp 111.5–113 °C. This material was identical in all respects to that obtained by procedure A. Anal. Calcd for $\mathrm{C_{17}H_{13}CrNO_6}$: C, 53.83; H, 3.46; N, 3.69. Found: C, 54.00; H, 3.52; N, 3.70.

**Synthesis of Chromium Ylide Complex (6).** Triethylamine (0.12 g, 1.2 mmol) was added dropwise to a suspension of *N*-(2-keto-2-phenylethyl)pyridinium bromide (0.31 g, 1.10 mmol) in absolute ethanol (30 mL). A solution of **1** (0.11 g, 0.36 mmol) in ethanol (1 mL) was added

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**Table II.** Crystallographic Experiment and Computations

| | |
|---|---|
| formula | $C_{12}H_{10}O_7Cr$ |
| formula wt, amu | 318 |
| cryst syst | orthorhombic F |
| space gp | *Fdd2* |
| $a$, Å | 18.105 (4) |
| $b$, Å | 11.965 (4) |
| $c$, Å | 13.186 (3) |
| $V$, Å$^3$ | 2856 |
| temp, °C | −120 |
| $Z$ | 8 |
| $F(000)$ | 1296 |
| $D_{\mathrm{calcd}}$, g cm$^{-3}$ | 1.48 |
| cryst dimens, mm | 0.20 × 0.20 × 0.48 |
| radiatn | Mo K$\alpha$ ($\lambda$ = 0.7107 Å) |
| monochromator | graphite |
| $\mu$, cm$^{-1}$ | 8.05 |
| scan type | $\theta/2\theta$ |
| $2\theta$ range, deg | 4.0–50.0 |
| scan speed, deg min$^{-1}$ | 4.0–30.0 |
| geometry | bisecting |
| index restrictions | $0 \le h \le 9, 0 \le k \le 10, 0 \le l \le 14$ |
| total no. of reflctns | 750 |
| no. of unique, obsd reflctns | 642 |
| obsd reflctns criterion | $\lvert F_o\rvert > 2.55\alpha(\lvert F_o\rvert)$ |
| no. of least-squares param | 95 |
| data/parameter | 6.76 |
| $R$[a] | 0.0035 |
| $R_w$[a] | 0.0037 |
| GOF[a] | 1.119 |
| $g$ | $1.16 \times 10^{-3}$ |
| slope, normal probability plot[b] | 1.079 |

[a] $R = (\sum\lvert(F_o - F_c)\rvert/\sum F_o)$; $R_w = \{(\sum w\lvert F_o - F_c\rvert^2)/(\sum w(F_o)^2)\}^{1/2}$; GOF $= \{(\sum w(\lvert F_o - F_c\rvert)^2)/(N_{\mathrm{data}} - N_{\mathrm{param}})\}^{1/2}$. [b] Abrahams, S. C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 261–268.

via syringe (2 × $^1/_2$-mL rinses). After the solution was stirred for 2 days at ambient temperature, the solvent was removed under vacuum. The residue was dissolved in benzene and filtered through Celite and neutral alumina. Purification by column chromatography (silica gel, methanol/methylene chloride (1:25)) gave 0.12 g (73%) of a bright yellow solid: mp 147 °C dec; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.77 (d, $J$ = 5.7 Hz, 2 H), 8.23 (t, $J$ = 7.7 Hz, 1 H), 7.93 (t, $J$ = 7 Hz, 2 H), 7.54 (dd, $J$ = 6 Hz, $J$ = 1.8 Hz, 2 H), 7.42 (m, 3 H), 4.51 (q, $J$ = 7.1 Hz, $\mathrm{OC}H_2\mathrm{CH}_3$), 1.34 (t, $J$ = 7.1 Hz, $\mathrm{OCH_2C}H_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 222.7 (*trans*-CO), 218.68 (*cis*-CO), 182.23, 170.90 (=COEt), 169.56, 157.52, 146.70, 142.22, 139.25, 129.80, 128.02, 127.91, 127.02, 108.53, 69.91 ($\mathrm{O}C\mathrm{H_2CH_3}$), 14.93 ($\mathrm{OCH_2}C\mathrm{H_3}$); IR (film) $\nu$ 2052, 1912, 1898 (CO) cm$^{-1}$. Anal. Calcd for $C_{23}H_{15}CrNO_7$: C, 58.86; H, 3.22; N, 2.98. Found: C, 59.03; H, 3.49; N, 2.91.

**Synthesis of 7.** A suspension of *N*-(2-keto-2-phenylethyl)pyridinium bromide (0.47 g, 1.7 mmol) in benzene (30 mL) was treated with triethylamine (0.19 g, 1.9 mmol). To the resulting mixture was added via syringe, a solution of **1** (0.20 g, 0.64 mmol) in benzene (4 mL) and it was stirred at ambient temperature for 15 days. Purification by column chromatography (silica gel, methanol/methylene chloride (1:25)) gave a yellow solid **6** (54 mg, 36%) and a mixed fraction. A second silica gel column (Alfa; hexane/methylene chloride (1:1)) of the mixed fraction yielded pure **1** and a red solid **7** (32 mg, 23%): mp 72 °C (darken), 153–155 °C dec; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.00 (m, 2, ArH), 7.57 (m, 3, ArH), 7.00 (s, 1, =CH–), 4.35 (q, $J$ = 7.0 Hz, 2, $\mathrm{OC}H_2\mathrm{CH}_3$), 4.16 (q, $J$ = 7.0 Hz, 2, $\mathrm{OC}H_2\mathrm{CH}_3$), 1.58 (t, $J$ = 7.0 Hz, 3, $\mathrm{OCH_2C}H_3$), 1.52 (t, $J$ = 7.0 Hz, 3, $\mathrm{OCH_2C}H_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 264.41 (C=Cr), 224.59 (*trans*-CO), 218.51 (*cis*-CO), 173.03, 156.67, 132.23, 131.00, 129.54, 125.98, 98.37 (=*C*H–), 69.01 ($\mathrm{O}C\mathrm{H_2CH_3}$), 65.62 ($\mathrm{O}C\mathrm{H_2CH_3}$), 15.38 ($\mathrm{OCH_2}C\mathrm{H_3}$), 14.43 ($\mathrm{OCH_2}C\mathrm{H_3}$); MS (EI) *m/e* 436 ($M^+$), 408 (M − CO), 352 (M − 3 CO), 324 (M − 4 CO), 296 (M − 5 CO); IR (film) $\nu$ 2040, 1978, 1910, 1895, 1883 (CO) cm$^{-1}$.

**Synthesis of Molybdenum Ylide Complex (8).** A suspension of *N*-(2-keto-2-phenylethyl)pyridinium bromide (0.57 g, 2.4 mmol) in benzene (30 mL) was treated with triethylamine (0.51 g, 5.0 mmol) to give a bright yellow solution with a white solid. Carbene **3** (0.29 g, 0.80 mmol) in benzene (4 mL) was added via syringe. After it was stirred for 6 days at ambient temperature, the solution was filtered through Celite and chromatographed (silica gel, methanol/methylene chloride (1:25)) to give a bright yellow solid (0.30 g, 63%): mp 144 °C dec; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.75 (dd, $J$ = 5.4 Hz, $J$ = 1.3 Hz, 2 H), 8.23 (tt, $J$ = 7.8 Hz, $J$ = 1.3 Hz, 1 H), 7.89 (t, $J$ = 7.2 Hz, 2 H), 7.55 (dd, $J$ = 4.2 Hz, $J$ = 1.7 Hz, 2 H), 7.42 (m, 3 H), 4.49 (q, $J$ = 7.1 Hz, 2, $\mathrm{OC}H_2\mathrm{CH}_3$), 1.35 (t, $J$ = 7.1 Hz, 3, $\mathrm{OCH_2C}H_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 212.64 (*trans*-CO), 206.93 (*cis*-CO), 182.14, 169.53, 162.99, 156.28, 146.16, 142.00, 139.21, 129.75, 127.97, 127.85, 126.82, 108.58, 69.35 ($\mathrm{O}C\mathrm{H_2CH_3}$), 14.89 ($\mathrm{OCH_2}C\mathrm{H_3}$); IR (Nujol mull) $\nu$ 2059, 1996, 1904, 1875 (CO) cm$^{-1}$. Anal. Calcd for $C_{23}H_{15}MoNO_7$: C, 53.82; H, 2.95; N, 2.73. Found: C, 54.03; H, 3.06; N, 2.76.

**Synthesis of Tungsten Ylide Complex (9).** A suspension of *N*-(2-keto-2-phenylethyl)pyridinium bromide (0.37 g, 1.30 mmol) in absolute ethanol (30 mL) was treated with triethylamine (0.13 g, 1.30 mmol) at ambient temperature to give an immediate bright yellow suspension. Carbene **4** (0.13 g, 0.28 mmol) in absolute ethanol (10 mL) was added via cannula. After the solution was stirred for 24 h, the ethanol was removed under vacuum, and the residue was triturated with benzene and filtered through Celite. Purification by column chromatography (silica gel, methanol/methylene chloride (1:25)) yielded 0.14 g (81%) of a yellow solid; mp 160–163 °C dec; $^1$H NMR ($CDCl_3$) $\delta$ 8.80 (dd, $J$ = 5.4 Hz, $J$ = 1.2 Hz, 2 H), 8.30 (tt, $J$ = 7.9 Hz, $J$ = 1.3 Hz, 1 H), 7.96 (t, $J$ = 7.5 Hz, 2 H), 7.56 (m, 2 H), 7.43 (m, 3 H), 4.51 (q, $J$ = 7.1 Hz, 2, $\mathrm{OC}H_2\mathrm{CH}_3$), 1.36 (t, $J$ = 7.1 Hz, 3 H, $\mathrm{OCH_2C}H_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 202.81 (*trans*-CO), 198.21 (*cis*-CO), 182.61, 167.76, 154.38, 151.23, 146.48, 142.20, 139.10, 130.00, 128.10, 128.00, 127.01, 108.87, 69.59 ($\mathrm{O}C\mathrm{H_2CH_3}$), 15.06 ($\mathrm{OCH_2}C\mathrm{H_3}$); IR (film) $\nu$ 2050, 1902 (CO) cm$^{-1}$. Anal. Calcd for $C_{23}H_{15}NO_7W$: C, 45.95; H, 2.52; N, 2.33. Found: C, 45.69; H, 2.77; N, 2.25.

**Synthesis of Pentacarbonyl(2-ethoxy-3-methylcyclopropenylidene)-molybdenum(0) (10) and Pentacarbonyl(2,3-dimethylcyclopropenylidene)molybdenum(0) (11).** Carbene **3** (0.14 g, 0.37 mmol) was dissolved in ether (7 mL) under argon and cooled to 0 °C. Methyllithium (0.37 mmol) was added via syringe, and the mixture was stirred 15 min at 0 °C and warmed to ambient temperature. After the solution was stirred for 19 h, additional methyllithium (0.18 mmol) was added, and after 24 h of more stirring, methyllithium (0.37 mmol) was added to give a total of 2.5 equiv. After it was heated at reflux for 2 h, the solution was cooled and filtered through Celite. Purification by column chromatography (silica gel, ether/hexane (1:1)) gave complex **3** (34 mg), complex **10** (57 mg, 46%), and complex **11** (40 mg, 36%). Complex **10** was an unstable oily solid: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.85 (q, $J$ = 7.0 Hz, 2, $\mathrm{OC}H_2\mathrm{CH}_3$), 2.51 (s, 3, $\mathrm{C}H_3$), 1.60 (t, $J$ = 7.0 Hz, 3, $\mathrm{OCH_2C}H_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 212.98 (*trans*-CO), 209.56 (Mo=C), 206.33 (*cis*-CO), 186.71 (=$C\mathrm{CH_3}$), 172.87 (=*C*OEt), 72.41 ($\mathrm{O}C\mathrm{H_2CH_3}$), 15.27 ($\mathrm{OCH_2}C\mathrm{H_3}$), 12.08 (=$\mathrm{C}C\mathrm{H_3}$); IR (film) $\nu$ 2050, 1913, 1860 (CO) cm$^{-1}$. Complex **11** was an unstable white solid: $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 2.72 (s); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 231.25 (Mo=C), 214.16 (*trans*-CO), 206.43 (*cis*-CO), 193.13 (C=C), 13.49 (=$\mathrm{C}C\mathrm{H_3}$); MS (CI-$NH_3$) *m/e* 305 (M + 1); IR (film) $\nu$ 2049, 1911 (CO) cm$^{-1}$.

**Structure Determination for 1.** Crystal data and details of the X-ray diffraction experiment for **1** are presented in Table II. The unit cell dimensions were obtained from a least-squares fit to the setting angles for 25 reflections ($2\theta$(av) = 25.35°) on a Nicolet R3m diffractometer. Calculation of a reasonable density required 8 formula units per unit cell. The intensities of three reflections (400, 080, 004) were measured every 100 reflections. No significant change in the intensity of these reflections was noted during data collection. No correction was made for absorption, due to the small value of $\mu$. Lorentz and polarization corrections were applied to the data. The range of transmission factors was ±11% of the mean value. The space group was determined from the systematic absences.

Software used for the X-ray diffractometer operations and data collection was provided with the Nicolet R3m diffractometer. Crystallographic computations were carried out using the SHELXTL program library, written by G. M. Sheldrick and supplied by Nicolet XRD for the Data General Eclipse S/140 computer in the crystallography laboratory at Colorado State University.

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**Supplementary Material Available:** Tables of anisotropic thermal parameters for **1** (Table S-1), calculated hydrogen atom coordinates (Table S-2), and atomic coordinates and isotropic thermal parameters (Table S-4) and a view of the unit cell (Figure S-1) (4 pages); a listing of observed and calculated structure factors (Table S-3) (4 pages). Ordering information is given on any current masthead page.