$Me_3CCH{=}CHHgBr$, 108344-92-9; $Me_2C{=}CHHgBr$, 23010-28-8; (*E*)-ClCH=CHHgCl, 1190-78-9; (*Z*)-ClCH=CHHgCl, 2350-34-7; *t*-BuHgCl, 38442-51-2; C-C_6H_{11}HgCl, 24371-94-6; *i*-PrHgCl, 30615-19-1; $PhCH_2HgCl$, 2117-39-7; *t*-$BuCH_2HgCl$, 10284-47-6; (*E*)-2-MeO-$CC_6H_{10}HgO_2CCF_3$, 111823-10-0; $PhCH(OMe)CH_2HgO_2CCF_3$, 111823-11-1; $(PhCOCH_2)_2Hg$, 37160-45-5; (*E*)-PhCH=CHBu-*t*, 3846-66-0; (*Z*)-PhCH=CHBu-*t*, 3740-05-4; (*E*)-PhCH=CH-c-C_6H_{11}, 18869-27-7; (*Z*)-PhCH=CH-c-C_6H_{11}, 40132-69-2; (*E*)-PhCH=CHPr-*i*, 15325-61-8; (*Z*)-PhCH=CHPr-*i*, 15325-56-1; (*E*)-PhCH=$CHCH_2Ph$, 3412-44-0; (*Z*)-PhCH=$CHCH_2Ph$, 1138-83-6; (*E*)-PhCH=$CHCH_2$Bu-*t*, 40132-64-7; (*Z*)-PhCH=$CHCH_2$Bu-*t*, 40132-63-6; $Ph_2C{=}CHBu$-*t*, 23586-64-3; $Ph_2C{=}CHPr$-*i*, 35467-39-1; $Ph_2C{=}CH$-c-C_6H_{11}, 91083-83-9; $Ph_2C{=}CH$-c-C_6H_{10}-2-OMe, 111823-12-2; $Ph_2C{=}CHCH_2CH(OMe)Ph$, 111823-13-3; $Ph_2C{=}CHCH_2COPh$, 57694-83-4; $Ph_2C{=}CHCH_2Ph$, 737-79-1; $Ph_2C{=}CHCH_2$Bu-*t*, 66292-25-9; (*E*)-$Me_3CCH{=}CH$-c-C_6H_{11}, 109660-16-4; (*Z*)-$Me_3CCH{=}CH$-c-C_6H_{11}, 111823-14-4; $Me_2C{=}CH$-c-C_6H_{11}, 89656-98-4; (*E*)-ClCH=CHBu-*t*, 18314-62-0; (*Z*)-ClCH=CHBu-*t*, 18314-61-9; (*E*)-ClCH=CH-c-C_6H_{11}, 67404-71-1; (*Z*)-ClCH=CH-c-C_6H_{11}, 67404-70-0; (*E*)-PhCH=$CHSnBu_3$, 66680-88-4; $Ph_2C{=}CHSnBu_3$, 91083-76-0; $Me_2C{=}CHSnBu_3$, 66680-86-2; (*E*)-$MeO_2CCH{=}CHSnBu_3$, 82101-74-4; (*Z*)-$MeO_2CCH{=}CHSnBu_3$, 82101-75-5; $CH_2{=}CHSnBu_3$, 7486-35-3; (*E*)-$PhSO_2CH{=}CHSnBu_3$, 88486-41-3; Δ^5-C_6H_{11}HgCl, 63668-13-3; *n*-BuHgCl, 543-63-5; Δ^3-C_4H_7HgCl, 14660-38-9; c-$C_5H_9CH_2$HgCl, 33631-66-2; (*E*)-PhCH=$CHCH_2$-c-C_5H_9, 91083-79-3; (*Z*)-PhCH=$CHCH_2$-c-C_5H_9, 91083-80-6; (*E*)-PhCH=CHBu-*n*, 6111-82-6; (*Z*)-PhCH=CHBu-*n*, 15325-54-9; (*E*)-PhCH=CH-Δ^3-C_4H_7, 56644-04-3; (*Z*)-PhCH=CH-Δ^3-C_4H_7, 63779-64-6; (*E*)-$MeO_2CCH{=}CH$-c-C_6H_{11}, 26429-99-2; (*Z*)-$MeO_2CCH{=}CH$-c-C_6H_{11}, 26429-98-1; (*E*)-$MeO_2CCH{=}CHBu$-*t*, 20664-51-1; $CH_2{=}CH$-c-C_5H_9, 3742-34-5; $CH_2{=}CH$-c-C_6H_{11}, 695-12-5; $CH_2{=}CHBu$-*t*, 558-37-2; $Me_3CCH_2CH_2SnBu_3$, 111823-15-5; (*E*)-$PhSO_2CH{=}CHBu$-*t*, 68969-27-7; (*E*)-PhCH=CHHgBu-*t*, 111823-16-6; (*E*)-PhCH=CHHg-c-C_6H_{11}, 111823-17-7; (*E*)-PhCH=CHHgBu-*n*, 111823-18-8; (*E*)-PhCH=$CHHgCH_2Ph$, 111823-19-9; PhCH=CHMgBr, 30094-01-0; *t*-BuMgCl, 677-22-5; *t*-BuLi, 594-19-4; $Ph_2C{=}CHMgBr$, 22072-53-3; *i*-PrMgBr, 920-39-8; $(c\text{-}C_6H_{11})_3B$, 1088-01-3; *i*-Pr_3Al, 2397-67-3; $(PhC{\equiv}C)_2Hg$, 6077-10-7; $PhC{\equiv}CSnBu_3$, 3757-88-8; $PhC{\equiv}CLi$, 4440-01-1; $PhC{\equiv}CHgBu$-*t*, 108230-30-4; $(EtO)_2P(O)HgCl$, 111823-20-2; $PhC{\equiv}CBu$-*n*, 1129-65-3; $PhC{\equiv}C$-c-C_6H_{11}, 33414-83-4; $PhC{\equiv}CBu$-*t*, 4250-82-2; $PhC{\equiv}CP(O)$, 3450-67-7; $PhC{\equiv}CCH_2Ph$, 4980-70-5; $CH_2{=}CHCH_2SnBu_3$, 24850-33-7; (*E*)-PhCH=CHI, 42599-24-6; $PhC{\equiv}CI$, 932-88-7; $Ph_2C{=}CHI$, 19997-66-1; $Me_2C{=}CHMgBr$, 38614-36-7; (*Z*)-PhCH=CHHgBu-*t*, 111848-29-4; (Z)-PhCH=$CHHgC_6H_{11}$-c, 111868-87-2; (*Z*)-PhCH=CHHgBu-*n*, 111823-21-3; (*Z*)-PhCH=$CHHgCH_2Ph$, 111823-22-4; $PhC{\equiv}CH$, 536-74-3; $CH_2{=}CHCH_2MgCl$, 2622-05-1; Bu_3SnCl, 1461-22-9; $AlCl_3$, 7446-70-0; c-C_5H_9HgCl, 27008-70-4; bibenzyl, 103-29-7; mercuric bromide, 7789-47-1; mercuric chloride, 7487-94-7.

Synthesis of (Aminocarbene)chromium(0) Complexes by the Reaction of $Na_2Cr(CO)_5$ with Amides in the Presence of Trimethylsilyl Chloride

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Addition of trimethylsilyl chloride to a mixture of $Na_2Cr(CO)_5$ and a variety of tertiary amides produced (aminocarbene)pentacarbonylchromium(0) complexes in fair to excellent yield. The procedure developed is a rapid, convenient, one-pot process and permits the synthesis of carbene complexes not readily available by other synthetic routes. These carbene complexes have potential application in the synthesis of β-lactams and α-amino acids.

Introduction

Heteroatom-stabilized ("Fischer") chromium carbene complexes[1] are being extensively developed as reagents for use in organic synthesis.[2] Most extensively studied are the thermal reactions of methoxyaryl- and methoxyvinylcarbenes with alkynes to produce hydroquinone,[3] heteroaromatic,[4] or cyclic ketone[5] derivatives, while similar thermal reactions with amino arylcarbenes produce indenones or aminoindenes.[6] Thermal reactions of methoxycarbene complexes with isonitriles produces cyclic bis imines.[7] In contrast, photolytic reaction of methoxy[8] and aminocarbene[9] complexes with imines produce β-lactams and with nucleophiles produce α-amino acid derivatives.[10]

Methoxycarbene complexes are normally synthesized by the original Fischer procedure, involving the reaction of

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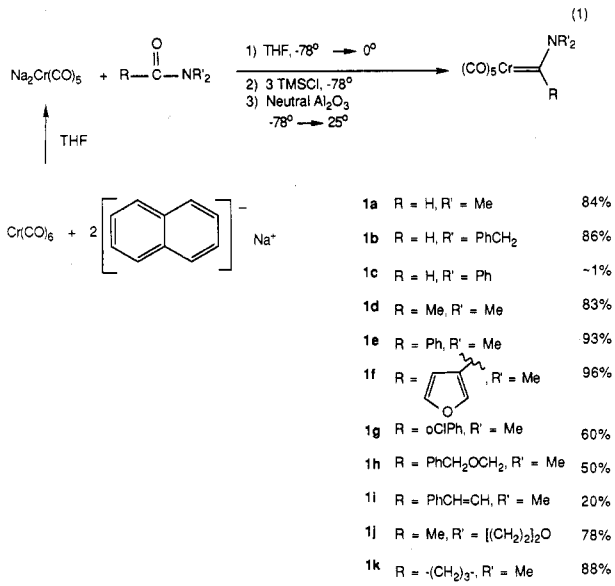
an organolithium reagent with chromium hexacarbonyl, followed by alkylation of the resulting "ate" complex with trimethyloxonium tetrafluoroborate.[11] This restricts the R group in $(CO)_5Cr{=}C(R)(OMe)$ carbenes to those available from organolithium reagents, although further elaboration of alkylcarbene complexes by aldol condensation chemistry[12] and of vinylcarbene complexes by cycloaddition chemistry[13] widens the range of carbene complexes available by this route.

Aminocarbene complexes are normally prepared by exchange processes involving displacement of alkoxy groups from alkoxycarbene complexes by amines, although this route is limited to the use of sterically unhindered amines.[14] Aminocarbene complexes having hydrogen on the carbene carbon—e.g. $(CO)_5Cr{=}C(H)(NR_2)$ are *not* available by this general route but can be made by the reaction of $Na_2Cr(CO)_5$ with (chloromethylene)dialkylammonium chlorides (Vilsmeier's reagents).[9,15] However, this route is limited by the relative instability of this class of compounds, the necessity of removing the corrosive reagents ($POCl_3$, $SOCl_2$, $(COCl)_2$, or phosgene) used to form these salts prior to reaction with $Na_2Cr(CO)_5$, and the modest yields of the carbene-forming process.

Our continuing studies on the use of chromium carbene complexes for the synthesis of β-lactams and α-amino acids required a general, convenient, high-yield synthetic approach to a wide range of differently substituted aminocarbene complexes. Herein we report the development of such a system.

Results and Discussion

A general synthetic approach to aminocarbene complexes of chromium is shown in eq 1. Tertiary amides

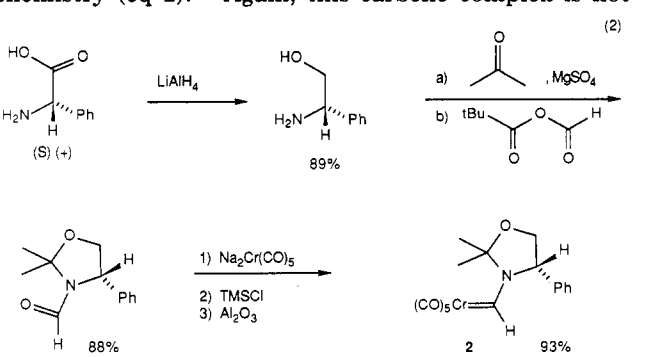


were treated with 1.3–2 equiv of $Na_2Cr(CO)_5$ at −78 °C in THF for $^1/_2$ h, warmed to 0 °C for $^1/_2$ h, cooled back to −78 °C, and 3 equiv of trimethylsilyl chloride was added. After $^1/_2$ h at −78 °C, neutral alumina was added, and the mixture was brought to room temperature. Removal of solvent under reduced pressure followed by purification by column chromatography produced aminocarbene complexes **1a–k** in good to excellent yield.

The procedure is very convenient to carry out. Stock solutions of $Na_2Cr(CO)_5$ can be generated by the reaction of chromium hexacarbonyl with sodium naphthalenide and stored for over 2 months in the freezer under an inert atmosphere (see Experimental Section) without significant loss of titer. Sequential addition of reagents, without isolation of intermediates, over the course of ~2 h in a one-pot process results in good yields of aminocarbene complexes on a 1–40 mmol scale. Rapid silica gel column chromatography to separate the carbene complex from naphthalene (introduced with the $Na_2Cr(CO)_5$) yields pure compounds. Compared with reagents used to generate Vilsmeier's salts, $(R_2N^+{=}C(R)Cl)$, such as $POCl_3$, $(COCl)_2$, or phosgene, trimethylsilyl chloride is easy to handle, relatively nontoxic and noncorrosive, and well-tolerated by $Na_2Cr(CO)_5$, so that preforming of an activated amide adduct and removal of excess trimethylsilyl chloride are not necessary.

A wide range of amides is readily convertible to aminocarbene complexes by this procedure. Dimethyl- and dibenzylformamides form the corresponding carbenes **1a** and **1b** in excellent yield. In contrast, diphenylformamide undergoes reaction with $Na_2Cr(CO)_5$ but does *not* produce the desired carbene complex **1c**. Instead, large amounts of diphenylamine are isolated after completion of the reaction. *N,N*-Dimethylacetamide, -benzamide, and -3-furoic acid amide are converted to the corresponding carbenes **1d**, **1e**, and **1f** in excellent yield. Although these carbenes are available by the standard Fischer synthesis (formation of the alkoxycarbene complex using organolithium reagents, followed by exchange with dimethylamine), the approach in eq 1 is considerably more convenient. *N,N*-Dimethyl-*o*-chlorobenzamide also forms the corresponding aminocarbene complex **1g**, a complex not accessible by the organolithium/exchange route, in good yield, as does *N,N*-dimethyl(benzyloxy)acetamide (**1h**). In contrast, conjugated amides such as *N,N*-dimethylacrylamide gives no carbene or, in the case of *N,N*-dimethylcinnamide, only a low yield of carbene **1i**. In these cases, the amide is partially recovered. Finally, the morpholine amide of acetic acid and *N*-methylpyrrolidinone are converted to the corresponding carbenes **1j–k** in good to excellent yield. Again, **1k** is not available by the organolithium/exchange route.

In relation to synthetic studies involving biologically active β-lactams[8,9] and α-amino acids,[10] aminocarbene complexes having optically active amino groups were needed. The procedure in eq 1 is very efficient for this purpose, producing chiral, nonracemic aminocarbene complex **2** in excellent yield and with no loss of stereochemistry (eq 2). Again, this carbene complex is not



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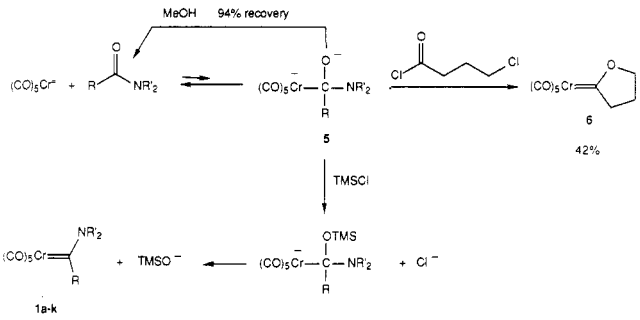
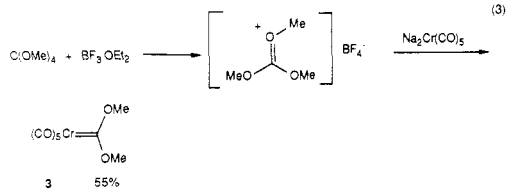
Scheme I

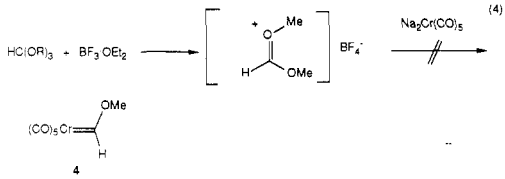


accessible by the organolithium/exchange route, since the chiral, cyclic aminal precursor to the formamide is in equilibrium with its open-chain imino alcohol (see Experimental Section).

To date, this synthesis of aminocarbene complexes is restricted to dialkylamide substrates. Esters, carbonates, and carbamates fail to convert to the corresponding alkoxy-, dialkoxy-, and alkoxyaminocarbene complexes when treated as in eq 1. Primary and secondary amides decompose the $Na_2Cr(CO)_5$, probably by protonation of this basic species. Dimethoxycarbene complex **3** can be made in modest yield by the related process shown in eq 3, from



tetramethoxymethane[16] (the corresponding diethoxycarbene complex has been made in 0.08% yield from potassium ethoxide and chromium hexacarbonyl[17]). The related methoxymethylene complex **4** could not be made in this manner, decomposition of the reagents upon reaction being observed instead (eq 4).



Although the mechanism of the carbene-forming process described in eq 1 has not been studied, the chemistry described in Scheme I is consistent with the following observations. There is no apparent reaction between trimethylsilyl chloride and amides under the mild conditions of the reaction, and addition of $Na_2Cr(CO)_5$ to a mixture of amide and trimethylsilyl chloride gives only a 40% yield of carbene. Addition of trimethylsilyl chloride to the chromium dianion at −78 °C followed by addition of the amide similarly resulted in low yields of carbene complex. High yields are obtained *only* when the chromium dianion and the amide are allowed to react, for 30 min at 0 °C and trimethylsilyl chloride is then added at −78 °C. This is most consistent with reversible formation of the tetrahedral intermediate **5**, followed by rapid O-silylation and loss of trimethylsilyloxide. The reversible formation of **5** is suggested by two observations. Treatment of dibenzylformamide with $Na_2Cr(CO)_5$ at −78 °C for $^1/_2$ h followed by warming to 0 °C for $^1/_2$ h, recooling to −78 °C, and addition of methanol rather than trimethylsilyl chloride leads to recovery of 94% of the amide. Similarly, addition of γ-chloropropionyl chloride instead of trimethylsilyl chloride leads to production of a 40% yield of alkoxycarbene complex **6**, indicating the presence of substantial amounts of $Na_2Cr(CO)_5$, notwithstanding its pretreatment with dibenzylformamide. If tetrahedral intermediate **5** is formed, it is quite stable and shows no propensity to eject R_2N^-. Stirring dibenzylformamide and $Na_2Cr(CO)_5$ at 25 °C for 24 h results in no production of dibenzylamine. Cooling this mixture to −78 °C followed by addition of trimethylsilyl chloride again produces (dibenzylamino)carbene complex **1b**. In contrast, when diphenylformamide is subjected to these conditions, diphenylamine is obtained in over 40% yield and only traces of carbene **1c** are formed. With the much less basic, more stabilized Ph_2N^- as a leaving group tetrahedral intermediate **5** apparently ejects Ph_2N^-. Whatever the mechanistic nuances of this process, it affords an efficient and convenient synthetic approach to a wide variety of (aminocarbene)chromium complexes.

Experimental Section

General Procedure. Melting points were taken on a Mel-Temp apparatus and are uncorrected. A Bruker IBM-200 NMR spectrometer was used for the 200-MHz ^1H NMR spectra. The 270-MHz ^1H NMR and the 67-MHz ^{13}C NMR spectra were obtained on a Bruker IBM-270 NMR spectrometer. NMR spectra were recorded in $CDCl_3$, and chemical shifts are given in parts per million relative to Me_4Si (0 ppm, ^1H) or $CDCl_3$ (77 ppm, ^{13}C). Optical rotations were obtained on a Perkin-Elmer 24 polarimeter at a wavelength of 589 nm (sodium D line) using a 1.0-dm cell with a total volume of 1 mL. Specific rotation $[\alpha]_D$, were measured at room temperature, and the concentration (*c*) is given in grams per 100 mL in the specific solvent. Baker silica gel (60–200 mesh) was used for column chromatography. Activated, neutral aluminum oxide was obtained from Alfa.

Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Materials. Tetrahydrofuran (Fisher, reagent grade) and diethyl ether (ASP, analytical reagent) were predried over CaH_2 and distilled from benzophenone ketyl under a nitrogen atmosphere just prior to use. Hexane (technical grade) was distilled at atmospheric pressure. Methylene chloride was distilled over CaH_2. Chromium hexacarbonyl (Pressure Chemicals), naphthalene (Baker), chrlorotrimethylsilane (Petrarch), tetramethyl orthocarbonate (Aldrich), boron trifluoride etherate (Alfa), and (*S*)-(+)-phenylglycine (Aldrich) were obtained from commercial suppliers and used without further purification.

The following chemicals were prepared according to literature procedure: *N,N*-dibenzylformamide,[9] *N,N*-dimethyl-3-furylcarboxylic acid amide,[18] *N,N*-dimethylcinnamic acid amide,[19] 2-(benzyloxy)-*N,N*-dimethylacetamide,[20] prepared from 2-(benzyloxy)acetic acid chloride[21] with $HNMe_2$, *N,N*-dimethyl-3-chlorobenzamide,[22] prepared from the acid chloride (Aldrich) with $HNMe_2$, *N*-acetylmorpholine,[23] prepared from morpholine and acetyl chloride (Aldrich), and trimethylacetic formic anhydride.[24]

Preparation of Disodium Pentacarbonylchromium.[9] $Na_2Cr(CO)_5$ was prepared by addition of 88 mmol of sodium naphthalenide, in ~160 mL of THF, to 40 mmol of $Cr(CO)_6$ in

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~240 mL of THF. The $Na_2Cr(CO)_5$ solution was transferred into a 500-mL graduated cylinder to estimate its concentration (in most experiments 0.09–0.1 M solutions were used). This solution can be stored under argon at −20 °C for at least 2 months without any decomposition. For the carbene syntheses aliquots of this solutions were transferred via a double-ended needle to the reaction vessel.

General Procedure for the Preparation of the Aminochromium Carbenes. In a thoroughly dried, 500-mL, round-bottomed flask equipped with a magnetic stirring bar, a septum inlet, and an argon supply tube was placed 45 mmol of the THF solution of the disodium pentacarbonylchromium under argon. The solution was cooled to −78 °C, and the amide (22.5 mmol) in 50 mL of THF was added, over 2 min, through a double-ended needle. The solution was stirred at −78 °C for 0.5 h. The dry ice/acetone cooling bath was then removed and replaced by an ice/water bath, and stirring was continued for 0.5 h at 0 °C. The mixture was cooled to −78 °C and treated with 67.5 mmol (8.6 mL) of trimethylsilyl chloride (fast addition via a syringe). After the solution was stirred at −78 °C for 0.5 h, ~70 g of neutral Al_2O_3 was added. The cooling bath was removed, the mixture warmed to room temperature, and the solvent removed under a reduced pressure on a rotatory evaporator. The residue was dried under high vacuum, then crushed in a mortar, and again dried under vacuum for a short time to remove all the THF. The yellow brown powder was then transferred on the top of a column filled with 250 g of SiO_2. Elution with hexane gave all naphthalene. Further elution with CH_2Cl_2/hexane (1/2) gave the pure chromium carbene complex as a yellow solid.

Pentacarbonyl[(*N*,*N*-dimethylamino)methylene]chromium (1a).[9] The above procedure was used to produce 627 mg (84%) of carbene **1a** from 219 mg (3 mmol) of dimethylformamide, 6 mmol of $Na_2Cr(CO)_5$, and 1.15 mL (9 mmol) of TMSCl, as yellow crystals: mp 68–69 °C (lit.[9] 69–70 °C); ^{13}C NMR (67 MHz, $CDCl_3$) δ 46.45, 55.33, 217.58, 223.87, 265.19. Further spectroscopic data are identical with those in ref. 9. A reaction using 10 mmol of dimethylformamide gave 1.70 g (68%).

Pentacarbonyl[(*N*,*N*-dibenzylamino)methylene]chromium (1b).[9] The above procedure using 45 mmol of $Na_2Cr(CO)_5$, 5.06 g (22.5 mmol) of *N*,*N*-dibenzylformamide, and 8.6 mL (67.5 mmol) of TMSCl gave 7.7 g (86%) of yellow powder [elution of the carbene with hexane/CH_2Cl_2 (3/1)], identical in all respects with authentic material.[9]

Pentacarbonyl[(*N*,*N*-dimethylamino)methylcarbene]chromium (1d).[25] The reaction of 261 mg (3 mmol) of *N*,*N*-dimethylacetamide with 6 mmol of $Na_2Cr(CO)_5$ gave 652 mg (83%) of a yellow solid: mp 50–51 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 2.70 (s, 3 CH_3), 3.32 (s, 3 NCH_3), 3.89 (s, 3, NCH_3); IR ($CHCl_3$) ν 2050 (m), 1980 (w), 1935 (s) cm^{-1}.

Pentacarbonyl[(*N*,*N*-dimethylamino)phenylcarbene]chromium (1e).[26] The above procedure using 6 mmol of $Na_2Cr(CO)_5$ and 450 mg (3 mmol) of *N*,*N*-dimethylbenzamide gave 906 mg (93%) of carbene as yellow crystals: mp 86–87 °C (lit.[26] 88 °C); ^1H NMR (270 MHz, $CDCl_3$) δ 2.98 (s, 3 NCH_3), 3.93 (s, 3, NCH_3), 6.62–6.65 (m, 2, ArH), 7.06–7.12 (m, 1, ArH), 7.28–7.33 (m, 2, ArH); ^{13}C NMR (67 MHz, $CDCl_3$) δ 45.85, 51.30, 118.90, 125.88, 128.56, 152.98, 217.28, 223.87, 275.58; IR ($CHCl_3$) ν 2040 (m), 1965 (w), 1925 (s) cm^{-1}.

Pentacarbonyl[(*N*,*N*-dimethylamino)-3-furfurylcarbene]chromium (1f). The reaction of 417 mg (3 mmol) of *N*,*N*-dimethyl-3-furylcarboxamide and 6 mmol of $Na_2Cr(CO)_5$ gave 910 mg (96%) of a yellow powder: mp 74–75 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 3.23 (s, 3, NCH_3), 3.96 (s, 3, NCH_3), 6.14 (s, 1 ArH), 7.18 (s, 1, ArH), 7.43 (s, 1 ArH); ^{13}C NMR (67 MHz, $CDCl_3$) δ 45.90, 51.27, 106.33, 132.24, 137.77, 143.17, 217.20, 223.70, 267.33. IR ($CHCl_3$) ν 2035 (w), 1970 (w), 1930 (s) cm^{-1}. Anal. Calcd for $C_{12}H_9NO_6Cr$: C, 45.73; H, 2.88; N, 4.44. Found: C, 45.65; H, 3.05; N, 4.45.

Pentacarbonyl[(2-chlorophenyl)(*N*,*N*-dimethylamino)carbene]chromium (1g). The reaction of 6.4 mmol of $Na_2Cr(CO)_5$ and 591 mg (3.2 mmol) of *N*,*N*-dimethyl-2-chlorobenzamide gave 693 mg (60%) of a yellow solid: mp 93–94 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 3.09 (s, 3, NCH_3), 4.01 (s, 3, NCH_3), 6.84–6.88 (m, 1, ArH), 7.10–7.16 (m, 1, ArH), 7.29–7.37 (m, 2, ArH); ^{13}C NMR (67 MHz, $CDCl_3$) δ 45.59, 50.84, 121.73, 123.42, 127.17, 127.42, 129.91, 149.78, 216.87, 223.60, 272.00; IR ($CHCl_3$) ν 2040 (m), 1975 (m), 1935 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{10}ClNO_5Cr$: C, 46.75; H, 2.80; Cl, 9.86; N, 3.89. Found: C, 46.70; H, 3.05; Cl, 9.69; N, 3.91.

Pentacarbonyl[(*N*,*N*-dimethylamino)((benzyloxy)methyl)carbene]chromium (1h). The above procedure using 6 mmol of $Na_2Cr(CO)_5$ and 580 mg (3 mmol) of (*N*,*N*-dimethylamino)-2-benzyloxyacetamide gave 640 mg (58%) of a yellow solid, which was recrystallized from hexane to give 550 mg (50%) of yellow crystals: mp 123–125 °C dec; ^1H NMR (270 MHz, $CDCl_3$) δ 3.30 (s, 3, NCH_3), 3.86 (s, 3, NCH_3), 4.35 (s, 2, OCH_2), 4.61 (s, 2, OCH_2), 7.35 (s, 5, ArH); ^{13}C NMR (67 MHz, $CDCl_3$) δ 44.30, 52.89, 73.30, 80.41, 127.63, 127.71, 128.03, 136.70, 217.18, 223.27, 273.19; IR ($CHCl_3$) ν 2040 (m), 1975 (m), 1930 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{15}NO_6Cr$: C, 52.04; H, 4.09; N, 3.79. Found: C, 51.96; H, 4.18; N, 3.82.

Pentacarbonyl[(*N*,*N*-dimethylamino)(2-phenylvinyl)carbene]chromium (1i). The reaction of 3 mmol of $Na_2Cr(CO)_5$, 350 mg (2 mmol) of (*E*)-*N*,*N*-dimethylcinnamic acid amide, and 0.8 mL (6 mmol) of TMSCl gave 220 mg of orange oil, which contained a small amount of an impurity. A second chromatography through SiO_2 gave 150 mg (20%) of an orange oil: ^1H NMR (270 MHz, $CDCl_3$) δ 3.46 (s, 3, NCH_3), 3.91 (s, 3, NCH_3), 5.83 (d, *J* = 16.8 Hz, 1, HC=), 7.13 (d, *J* = 16.8 Hz, HC=), 7.20–7.43 (m, 5, ArH); ^{13}C NMR (67 MHz, $CDCl_3$) δ 45.66, 50.99, 121.08, 126.53, 127.90, 128.80, 136.20, 137.89, 217.49, 223.52, 270.93. Anal. Calcd for $C_{16}H_{13}NO_5Cr$: C, 54.71; H, 3.73; N, 3.99. Found: C, 54.56; H, 3.81; N, 4.05.

Pentacarbonyl(methylmorpholinocarbene)chromium (1j). The reaction of 6 mmol of $Na_2Cr(CO)_5$ and 388 mg (3 mmol) of *N*-acetylmorpholine gave 716 mg (78%) of yellow crystals: mp 99–102 °C dec; ^1H NMR (270 MHz, $CDCl_3$) δ 2.76 (s, 3, CH_3), 3.73–3.83 (m, 2, CH_2), 3.85–3.92 (m, 2, CH_2), 3.94–4.00 (m, 2, CH_2), 4.40–4.49 (m, 2, CH_2); ^{13}C NMR (67 MHz, $CDCl_3$) δ 38.80, 51.58, 61.68, 66.83, 67.90, 217.57, 223.38, 273.02; IR ($CHCl_3$) ν 2040 (w), 1970 (w), 1930 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{11}NO_6Cr$: C, 43.29; H, 3.63; N, 4.59. Found: C, 43.16; H, 3.69; N, 4.61.

(*N*-Methyl-2-azacyclopentylidene)chromium(0) Pentacarbonyl (1k). The reaction of 1.19 g (12 mmol) of *N*-methylpyrrolidinone, 24 mmol of $Na_2Cr(CO)_5$, and 4.55 mL (36 mmol) of TMSCl gave 2.9 g (88%) of pale yellow powder after recrystallization from hexane to remove a small amount of an orange byproduct: mp 66–67 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.92 (quint, *J* = 8 Hz, 2, CH_2), 3.35 (t, *J* = 8 Hz, 2, CH_2), 3.68 (s, 3, NCH_3), 3.79 (t, *J* = 8 Hz, 2, CH_2); ^{13}C NMR (67 MHz, $CDCl_3$) δ 20.99, 42.05, 56.43, 62.57, 218.17, 223.12, 266.38; IR ($CHCl_3$) ν 2050 (w), 1975 (w), 1930 (s), 1920 (s) cm^{-1}. Anal. Calcd for $C_{10}H_9NO_5Cr$: C, 43.65; H, 3.30; N, 5.09. Found: C, 43.71; H, 3.39; N, 5.10.

(*S*)-Phenylglycinol.[27] A suspension of 9.9 g (260 mmol) of $LiAlH_4$ in 500 mL of THF was treated at 0 °C carefully with small portions of (*S*)-phenylglycine (20 g, 132 mmol). After the addition was completed, the mixture was stirred at room temperature for 1.5 h and then heated at reflux for 15 h. The resulting suspension was cooled to 0 °C and 10 mL of water (1 mL per 1 g of $LiAlH_4$), 10 mL of 15% NaOH (1 mL per 1 g of $LiAlH_4$), and 30 mL of water (3 mL per 1 g of $LiAlH_4$) were added successively. The orange mixture was heated at reflux for 15 min and then filtered through a sintered-glass funnel. The filter cake was rinsed twice with 50 mL of THF. Removal of the solvent on a rotatory evaporator gave 17.2 g of a yellow, viscous oil. The crude product was purified by short-path distillation to give 16.1 g (89%) of a slightly yellow oil, which solidifies on standing: mp 74–75 °C (lit.[27] mp 75–78 °C); $[\alpha]_D$ +31.7° (*c* 0.82, 1 N HCl) (lit.[27] $[\alpha]_D$ +33° (*c* 0.75, 1 N HCl); ^1H NMR (270 MHz, $CDCl_3$) δ 2.45 (br s, 3, OH and NH_2), 3.53 (dd, *J* = 8.3 and 10.8 Hz, 1), 3.71 (dd, *J* = 4.2 and 10.8 Hz, 1), 4.02 (dd, *J* = 4.2 and 8.3 Hz), 7.20–7.35 (m, 5, ArH).

(5*S*)-*N*-Formyl-2,2-dimethyl-5-phenyl-1,3-oxazolidine. A mixture of 10.73 g (78.2 mmol) of (*S*)-phenylglycinol and 57 mL (780 mmol) of acetone was stirred at room temperature for 0.5

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h and then diluted with 300 mL of CH_2Cl_2. After addition of 30 g of anhydrous $MgSO_4$, stirring was continued for 13.5 h. The mixture was filtered and the solvent removed on a rotatory evaporator and then in high vacuum for 1 h to give a pale yellow liquid; ^1H NMR (270 MHz, $CDCl_3$) δ 1.39 (s, 3, CH_3), 1.45 (s, 3, CH_3), 2.25 (br s, 1, NH), 3.62 (t, J = 7.5 Hz, 1, NCH), 4.20 (t, J = 7.5 Hz, 1, OCH), 4.45 (t, J = 7.5 Hz, 1, OCH), 7.15–7.45 (m, 5, ArH). The product contains about 5–10% of the open-chain imino alcohol form[28] (^1H NMR δ 1.78 (s, =CMe), 2.03 (s, =CMe)). The equilibrium between the cyclic aminal-form and the open-chain imino alcohol form *cannot* be changed by prolonged stirring of the reaction mixture but it is shifted to the open-chain form by keeping the crude, solvent-free product at room temperature for 1–2 days. The imino alcohol eventually crystallizes. To prevent the formation of open-chain form the above-mentioned oil was immediately dissolved in 300 mL of CH_2Cl_2 after removal of the solvent in vacuo. The flask was flushed with argon and the mixture cooled to 0 °C. Triethylamine (13.1 mL, 94 mmol) was added dropwise, followed by 12.25 g (94 mmol) of the mixed anhydride of pivalic and formic acid. Stirring was continued at 0° for 30 min and then at room temperature for 3.5 h. The mixture was extracted three times with 0.1 N NaOH, dried over anhydrous $MgSO_4$, and filtered. The solvent was evaporated on a rotary evaporator. Excess NEt_3 was removed in high vacuum to give 16.9 g of a yellow, viscous oil. The crude products contained some pivalic acid anhydride [^1H NMR ($CDCl_3$) δ 1.30 (s)], which could be removed by fractional short-path distillation [30 °C (0.07 mm)]. The *N*-formyloxazolidine distilled at 100–105 °C (0.07 mm) as a highly viscous, colorless oil: 14.10 g (88%); ^1H NMR analysis (270 MHz, $CDCl_3$) indicated the presence of two rotameric species in a ~1:1 ratio; $[\alpha]_D$ +133.2° (*c* 1, CH_2Cl_2); ^1H NMR (270 MHz, $CDCl_3$) δ 1.61 (s, 3, CH_3), 1.67 (s, 3, CH_3), 1.70 (s, 3, CH_3), 1.77 (s, 3, CH_3), 3.94 (dd, J = 5.8 and 9.1 Hz, 1, HCN), 4.04 (dd, J = 3.4 and 9.1 Hz, 1, HCN), 4.30–4.38 (m, 1 and 1, HCO), 4.89 (dd, J = 6.1 and 6.1 Hz, 1, HCO), 5.13 (dd, J = 3.3 and 6.7 Hz, 1, HCO), 7.18–7.50 (m, 5, ArH), 8.06 (s, 1, CHO), 8.32 (s, 1, CHO); IR ($CHCl_3$) ν 1670 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 69.99; H, 7.29; N, 6.83.

Pentacarbonyl[((5*S*)-1-aza-2,2-dimethyl-3-oxa-5-phenylcyclopentyl)methylene]chromium (2). The above-mentioned general procedure was used to produce 1.69 g (93%) of a bright yellow powder from 9.5 mmol of $Na_2Cr(CO)_5$, 975 mg (4.75 mmol) of (5*S*)-*N*-formyl-2,2-dimethyl-5-phenyl-1,3-oxazolidine (1:1 mixture of rotamers), and 1.80 mL (14.2 mmol) of TMSCl. Only one isomer (rotamer) of the carbene could be detected by ^1H NMR analysis: mp ≥120 °C dec; $[\alpha]_D$ +113.2° (*c* 1, CH_2Cl_2); ^1H NMR (270 MHz, $CDCl_3$) δ 1.50 (s, 3, CH_3), 1.68 (s, 3, CH_3), 4.16 (dd, J = 2.0 and 9.2 Hz, 1), 4.58 (dd, J = 6.3 and 9.2 Hz, 1), 5.58 (br d, J = 6.3 Hz, 1), 7.20–7.27 (m, 2, ArH), 7.30–7.43 (m, 3, ArH), 11.5 (s, 1, HCCr); ^{13}C NMR (67 MHz, $CDCl_3$) δ 26.08, 26.59, 67.72, 71.06, 101.36, 126.46, 128.32, 129.07, 138.95, 216.77, 223.82, 259.25; IR ($CHCl_3$) ν 2045 (w), 1980 (w), 1940 (s) cm^{-1}. Anal. Calcd for $C_{17}H_{15}NO_6Cr$: C, 53.55; H, 3.96; N, 3.67. Found: C, 53.61; H, 3.84; N, 3.72.

Pentacarbonyl(dimethoxycarbene)chromium (3). To an ice-cold solution of 1.33 mL (10 mmol) of tetramethyl orthocarbonate in 5 mL of diethyl ether was added dropwise 1.69 mL (13.3 mmol) of BF_3·OEt_2.[16] The resulting white suspension was stirred at room temperature for 15 min, and then the solvent was evaporated in vacuo. The white solid was then added to a cold (−78 °C) THF solution of $Na_2Cr(CO)_5$ (10 mmol, ~0.1 M) in five portions. The mixture was stirred at −78 °C for 2 h and then at room temperature for 3 h. After the addition of 5 g of SiO_2, the solvent was removed in vacuo on a rotatory evaporator and the residue put on a column filled with 150 g of SiO_2. Elution with hexane gave in a first fraction all the naphthalene and in a second, yellow fraction the dimethoxycarbene as a pale yellow oil (0.51 g, 19%), which solidified on standing; mp 33–34 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 4.18 (s); ^{13}C NMR (67 MHz, $CDCl_3$) δ 59.50, 216.34, 221.08, 269.11; IR ($CHCl_3$) ν 2060 (w), 1990 (w), 1940 (s) cm^{-1}. Anal. Calcd for $C_8H_6O_7Cr$: C, 36.11; H, 2.27. Found: C, 35.89; H, 2.26.

In a different experiment using naphthalene-free $Na_2Cr(CO)_5$[29] (~2.5 mmol), $C(OMe)_4$ (165 μL, 1.25 mmol), and BF_3·OEt_2 (210 μL, 1.66 mmol), carbene complex **3** (182 mg, 55%) was obtained.

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Registry No. **1a**, 38893-15-1; **1b**, 106502-05-0; **1c**, 112068-79-8; **1d**, 22852-52-4; **1e**, 30971-68-7; **1f**, 112044-01-6; **1g**, 112044-02-7; **1h**, 112068-80-1; **1i**, 112044-03-8; **1j**, 112044-04-9; **1k**, 112044-05-0; **2**, 112044-06-1; **3**, 112044-07-2; $Na_2Cr(CO)_5$, 51233-19-3; $Cr(CO)_6$, 13007-92-6; Me_2C=NCH(Ph)CH_2OH, 112043-99-9; (5*S*)-*N*-formyl-2,2-dimethyl-5-phenyl-1,3-oxazolidine, 112043-98-8; sodium naphthalenide, 3481-12-7; dimethylformamide, 68-12-2; *N*,*N*-dibenzylformamide, 5464-77-7; *N*,*N*-diphenylformamide, 607-00-1; *N*,*N*-dimethylacetamide, 127-19-5; *N*,*N*-dimethylbenzamide, 611-74-5; *N*,*N*-dimethyl-3-furylcarboxamide, 13156-75-7; *N*,*N*-dimethyl-3-chlorobenazmide, 24167-52-0; *N*,*N*-dimethyl-2-(phenylmethoxy), 41858-11-1; (*E*,-*N*,*N*-dimethylcinnamic acidamide, 17431-39-9; *N*-acetylmorpholine, 1696-20-4; *N*-methylpyrrolidinone, 872-50-4; (*S*)-phenylglycine, 2935-35-5; (*S*)-phenylglycinol, 20989-17-7; (5*R*)-*N*-formyl-2,2-dimethyl-5-phenyl-1,3-oxazolidine, 112044-00-5; tetramethyl orthocarbonate, 1445-45-0; (5*S*)-2,2-dimethyl-5-phenyl-1,3-oxazolidene, 112068-78-7.

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