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Preparation of Acylpentacarbonylchromate Salts and Alkoxycarbene Pentacarbonyl Complexes of Chromium Employing the Pentacarbonylchromate Dianion ($[Cr(CO)_5]^{2-}$)

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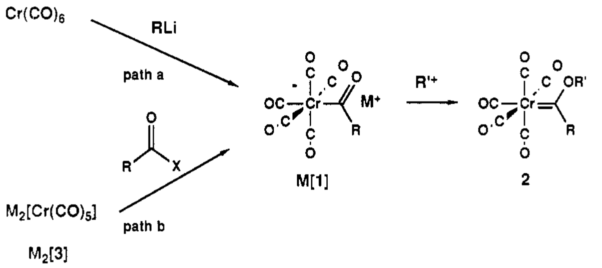
The in situ generated lithium and sodium salts of $[Cr(CO)_5]^{2-}$ (**3**) react rapidly and cleanly with a variety of aryl and alkyl acid chlorides at −78 °C in THF to provide solutions of the corresponding acylpentacarbonylchromate salts $M'[RC(O)Cr(CO)_5]$ ($M'[1]$, $M' = Li, Na$). Subsequent O-methylation of **1** produces Fischer-type alkoxycarbene complexes in yields competitive with established methodologies. This two-step procedure has enabled the preparation of arylmethoxycarbene complexes such as $(CO)_5Cr{=}C(OMe)\{2,5\text{-}(OAc)_2C_6H_3\}$ (**2g**) which are otherwise inaccessible by the standard Fischer synthesis. Alkoxycarbene complexes of molybdenum and tungsten may be prepared analogously from $[Mo(CO)_5]^{2-}$ and $[W(CO)_5]^{2-}$.

Introduction

Recent studies have demonstrated the remarkable versatility of low-valent heteroatom-substituted carbene complexes of chromium as reagents in organic synthesis.[1] The applicability of these reagents depends on the development of reliable, flexible, high-yield methods for their preparation. Since Fischer and Maasböl's initial report in 1964,[2] the predominant method for the preparation of alkoxycarbene complexes of chromium has involved the nucleophilic addition of aryl- or alkyllithium reagents to chromium hexacarbonyl to yield acylpentacarbonylchromate salts Li[1] (Scheme I, path a). Subsequent O-alkylation of 1 generates alkoxycarbene complex 2, which in favorable circumstances can be isolated in 50–90% yields relative to RLi.[3] The success of this approach requires that RLi be stable under the reaction conditions employed, thus restricting the range of functional groups which may be present in R. This limitation has prompted us to examine alternative strategies for the preparation of complexes 2.

In principle, the acylate complex 1 is also accessible through the nucleophilic attack of the pentacarbonylchromate dianion $[Cr(CO)_5]^{2-}$ (**3**) on an acyl-transfer agent (Scheme I, path b). The formation of related acylate salts of iron (e.g., iron analogues of 1 in Scheme I) from the reaction of $Na_2[Fe(CO)_4]$ with acid halides has previously been reported by Watanabe[4] and Collman.[5] Subsequent O-alkylation would be expected to provide alkoxycarbene complex 2 in strict analogy to the previously described sequence. The overall transformation 3 → 2 may be envisioned to possess several advantages relative to the standard Fischer synthesis, including the following: (a) circumvention of the need for lithium reagents which may be unstable or otherwise difficult to obtain; (b) tolerance toward functional groups or substituents otherwise incompatible with RLi; (c) removal of potential ambiguity concerning carbene carbon–R connectivity in 2; (d) accelerated reaction rates under mild conditions.

Scheme I



The preparation of chromium carbene complexes involving the coupling of 3 with carbon-based electrophiles has previously been examined in special cases. In 1968, Öfele reported the synthesis of the first non-heteroatom-substituted carbene complex of chromium, albeit in low yield (19.5%), from the reaction of $Na_2[3]$ with 3,3-dichloro-1,2 diphenylcyclopropene.[6] Low-valent carbene complexes of chromium have since been obtained from the reactions of $Na_2[3]$ with an alkoxycyclopropenium salt,[7] chloroformaminium halides,[8] 2-chlorothiazolium and 2-chloropyridinium salts,[9] (dichloromethylene)dimethylammonium chloride,[10] carbodiimides and ketenimines,[11] and iminium salts.[12] Given the range of unsaturated carbon electrophiles which react with 3, it was surprising to discover that no mention of the simple acylation of this dianion had appeared in the literature prior to a preliminary report from these laboratories in 1983.[13,14] This paper presents the results of our initial survey of the reactions of 3 with a variety of acyl chlorides and the con-

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[1] Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

[2] (a) Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580. (b) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445.

[3] Fischer, H. In *Transition Metal Carbene Complexes*; Verlag Chemie GmbH: Weinheim, 1983; pp 1–68 and references therein.

[4] Watanabe, Y.; Mitsudo, T.; Tanaka, M.; Yamamoto, K.; Okajima, T.; Takegami, Y. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2569.

[5] Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.

[6] Öfele, K. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 950.

[7] Rees, C. W.; von Angerer, E. *J. Chem. Soc., Chem. Commun.* **1972**, 420.

[8] (a) Cetinkaya, B.; Lappert, M. F.; Turner, K. J. *J. Chem. Soc., Chem. Commun.* **1972**, 851. (b) Fong, C. W.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1100. (c) Hartshorn, A. J.; Lappert, M. F.; Turner, K. *J. Chem. Soc., Dalton Trans.* **1978**, 348.

[9] Fraser, P. J.; Roper, W. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 760.

[10] Hartshorn, A. J.; Lappert, M. F.; Turner, K. *J. Chem. Soc., Chem. Commun.* **1975**, 929.

[11] (a) Fehlhammer, W. P.; Mayr, A.; Ritter, M. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 641. (b) Fehlhammer, W. P.; Christian, G.; Mayr, A. *J. Organomet. Chem.* **1980**, *199*, 87. (c) Fehlhammer, W. P.; Hirschmann, P.; Mayr, A. *J. Organomet. Chem.* **1982**, *224*, 153.

[12] Beatty, R. P.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 238.

[13] Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 4099.

[14] Ellis and coworkers have previously reported the *alkylation* of pentacarbonylmetalate salts of the group 6 metals. Ellis, J. E.; Hagen, G. P. *Inorg. Chem.* **1977**, *16*, 1357.

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version of the resultant acylate salts to alkoxycarbene complexes.

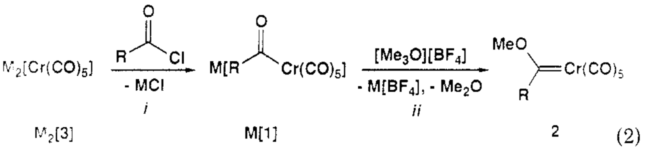
Results and Discussion

The utilization of the alkali-metal salts of **3** as reagents for the preparation of acylmetalates required a reproducible, high-yield route for the preparation of the dianion. In our hands, best results were obtained employing the reduction of $Cr(CO)_5NMe_3$ with an alkali-metal naphthalenide in THF as described by Cooper and coworkers (eq 1).[15] With appropriate precautions to rigorously exclude oxygen and water, this method provided homogeneous solutions of the desired dianion contaminated by only traces of $[Cr_2(CO)_{10}]^{2-}$ and/or $[HCr(CO)_5]^-$ as determined by solution IR spectroscopy.

$$\mathrm{Cr(CO)_5NMe_3} \xrightarrow[\mathrm{THF},\ -78^\circ]{2\,\mathrm{M'_2[C_{10}H_8]}} \underset{\mathrm{M'_2[3]}}{\mathrm{M'_2[Cr(CO)_5]}} + 2\,\mathrm{C_{10}H_8} + \mathrm{NMe_3} \qquad (1)$$

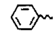
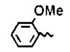
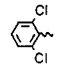
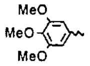
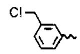
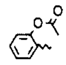
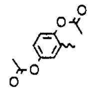
$$\mathrm{M' = Li,\ Na}$$

The reaction of $M'_2[3]$ (M' = Li, Na) with either benzoyl or *o*-anisoyl chloride in THF was chosen as a prototype for the more general transformation of eq 2, step i. In a typical experiment, the addition of 0.95–1.00 equiv of benzoyl chloride (based upon the quantity of $Cr(CO)_5NMe_3$ used to prepare **3**) in THF to a stirred solution of either $Li_2[3]$ or $Na_2[3]$ in THF at −78 °C (ca. 1 mmol of chromate salt) led to an immediate color transition from green-yellow to orange-red. Solution IR spectra of the homogeneous reaction mixture obtained as early as 2 min following acid chloride addition invariably showed the complete disappearance of ν_{CO} absorptions assigned to the $[Cr(CO)_5]^{2-}$ salt and contained new carbonyl stretching bands at 2035 (w) and 1900 (vs, br) cm^{-1}. A very weak absorption at 1975 cm^{-1} assigned to $Cr(CO)_6$ was detected in a few cases. The major ν_{CO} absorptions are similar to those reported for the acylate salt $[NMe_4][(CO)_5WC(O)Ph]$ in THF (2041 (w), 1952 (vw), 1905 (s), 1885 (m) cm^{-1})[16] and may be reasonably assigned to the analogous chromium salt $M'[(CO)_5CrC(O)Ph]$. Similar results were obtained employing *o*-anisoyl chloride in place of benzoyl chloride. The rapid generation of the desired acylate at −78 °C is in marked contrast to the slower addition of aryl lithiums to $Cr(CO)_6$, which most frequently requires at least 20 min at 25 °C.[17]

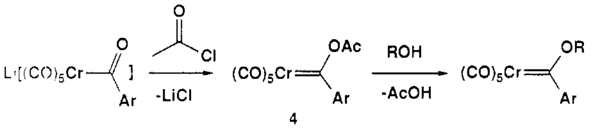


The freshly prepared acylate salts $M'[1]$ were not isolated but rather converted directly to the desired alkoxycarbene complexes **2** by methylation. Best results were obtained by replacing the THF solvent with chilled (4 °C) water and adding 1.0–1.1 equiv of solid $[Me_3O][BF_4]$ (eq 2, step ii). Chromatographic separation of the hexane-soluble product permitted the isolation of $(CO)_5Cr{=}C(OMe)Ph$ (**2a**)[18] in 30–60% yield after recrystallization based on acid halide. The product derived from *o*-anisoyl chloride, $(CO)_5Cr{=}C(OMe)(o\text{-}MeOC_6H_4)$ (**2b**),[19] was similarly isolated in 45–70% yield. The lithium salt of **3** was found to provide consistently higher yields of alkoxycarbene complex (e.g. 60–70% for **2b**) than the corresponding sodium salt (e.g. 45–50% for **2b**). Without further modification, the yields of **2a** and **2b** prepared from $Li_2[3]$ are competitive with those reported for the standard Fischer synthesis conducted on a comparable scale.

Table I. Alkoxycarbene Complexes $(CO)_5Cr{=}C(OMe)R$ Obtained from the Reaction of $Li_2[Cr(CO)_5]$ with RC(O)Cl Followed by Methylation Using $[Me_3O][BF_4]$

entry	R	complex	isolated yield, %
1		**2a**	54.5
2		**2b**	65.5
3		**2c**	43.8
4		**2d**	58.0
5		**2e**	47.4
6		**2f**	65.4
7		**2g**	61.7
8	H_3C	**2h**	34.9
9	$(CH_3)_3C$	**2i**	37.2
10	$C_6H_5C\equiv C$	**2j**	17.7
11	$H_3CC\equiv C$	**2k**	14.1
12		**2l**	44.7

The acylate salts Li[1] prepared by the reaction of $Li_2[3]$ with aroyl chlorides could also be converted to a variety of other alkoxycarbene complexes by means of initial acetylation with acetyl chloride followed by alcoholysis of the resultant acetoxycarbene complex **4** (eq 3).[20] In the case of the acylate salt derived from *o*-anisoyl chloride, acetylation was most easily accomplished by replacing the THF solvent with CH_2Cl_2 at −30 °C and then adding 1 equiv of acetyl chloride. Substitution of alkoxide for acetate proceeded smoothly in dichloromethane between −10 and 23 °C employing methanol, 2-methoxyethanol, or 2-propanol. After chromatographic separation and recrystallization, the corresponding alkoxycarbene complexes could be isolated in 45–60% yields based on acid chloride.



The synthetic sequence outlined for the preparation of complexes **2a** and **2b** was successfully applied to the synthesis of the hitherto unreported methoxycarbene complexes **2c–g** as indicated in Table I. Complexes **2e–g** are almost certainly inaccessible via the standard Fischer carbene synthesis as a result of the incompatibility of the aryl substituents with the required lithium reagent. For

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[15] (a) Maher, J. M.; Beatty, R. P.; Lee, G. R.; Cooper, N. J. *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Elsevier: New York, 1986; Vol. 3, pp 35–39. (b) Maher, J. M.; Beatty, R. P.; Cooper, N. J. *Organometallics* **1985**, *4*, 1354 and references therein.

[16] Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1978**, *100*, 7565.

[17] (a) See ref 2. (b) Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J.; Muller, J.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237.

[18] (a) See ref 2b. (b) Fischer, E. O.; Heckl, B.; Dötz, K. H.; Muller, J.; Werner, H. *J. Organomet. Chem.* **1969**, *16*, P29.

[19] (a) See ref 17b. (b) Dotz, K. H.; Sturm, W.; Popall, M.; Riede, J. *J. Organomet. Chem.* **1984**, *277*, 267.

[20] (a) Conner, J. A.; Jones, E. M. *J. Chem. Soc. A* **1971**, 3368. (b) Semmelhack, M. F.; Bozell, J. J. *Tetrahedron Lett.* **1982**, *23*, 2931. (c) Semmelhack, M. F.; Bozell, J. J.; Keller, L.; Sato, T.; Spiess, E. J.; Wulff, W.; Zask, A. *Tetrahedron* **1985**, *41*, 5803.

example, the synthesis of complex **2e** (entry 5, Table I) would require the preparation of an unstable aryllithium bearing a reactive chloromethyl group. It is interesting to note that the attack of **3** occurs preferentially at the carbonyl carbon of the acid halide in the presence of ester and benzylic halide functionalities. While the Fischer methodology has been employed to prepare chloro- and methoxyphenylcarbene complexes of chromium, the substitution patterns observed in complexes **2c**,**d** would be difficult to achieve.

Attempts to prepare methoxycarbene complexes from terephthaloyl chloride or 4-cyanobenzoyl chloride did not lead to thermally stable products, although the initial reaction with Li_2[**3**] appeared to produce the anticipated acylate salts as determined by IR spectroscopy. In contrast, essentially no acylate formation was observed for the corresponding reactions using 3-nitrobenzoyl chloride, 2-iodobenzoyl chloride, or *o*-phthaloyl chloride, despite the quantitative consumption of $Li_2[Cr(CO)_5]$. While insufficient data are currently available to address this apparent anomaly, it seems probable that electron-transfer processes may be involved in the latter three cases.

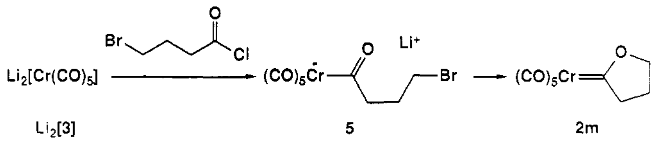
Initial studies of the reactions of alkyl acid halides (0.95–1.00 equiv based on chromium) with Li_2[**3**] in THF at −78 °C indicated that acylation was once again the dominant process for the examples cited in Table I. Alkylation of the chromium acylates (detected by solution IR spectroscopy) with 1 equiv of $[Me_3O][BF_4]$ in H_2O provided the corresponding volatile methoxycarbene complexes for R = Me (**2h**)[21] and R = *t*-Bu (**2e**) in 30–40% isolated yields. In these cases the actual product yield was probably somewhat higher, as considerable material was generally lost through sublimation during purification. Although complex **2h** has been extensively studied, complex **2i** apparently has not been previously reported.

Drastically reduced yields (10–18%) were obtained for substituted vinylcarbene complexes derived from *trans*-cinnamoyl (**2j**) and *trans*-crotonoyl (**2k**) chlorides. Casey has previously described the preparation of **2j** via the condensation of $Li[(CO)_5CrC(OMe){=}CH_2]$ with benzaldehyde,[22] while we have been unable to locate **2k** in the literature. In each of these cases, some product is probably lost as a result of alkene polymerization and/or carbene hydrolysis under the reaction conditions employed. The corresponding reaction sequence employing acryloyl chloride provides only traces of $(CO)_5Cr{=}C(OMe)(CH{=}CH_2)$.[23]

The preparation of the cyclobutyl derivative (entry 12, Table I) emphasizes a technical problem often encountered in procedures involving naphthalene ions: naphthalene is produced in stoichiometric amounts and is not always easy to remove. This new carbene complex (**2l**) could not be separated from naphthalene by simple chromatography; the yield (45%) is based on the weight of a purified sample of **2l** and naphthalene, and assuming the naphthalene is recovered quantitatively, the yield is a lower limit. In general the naphthalene does not interfere in further applications.

An interesting variation on the general theme of chromium alkoxycarbene synthesis employing acid halides involved the reaction of 4-bromobutyryl chloride with Li_2[**3**]. The addition of 1.0 mol equiv of the pentacarbonylchromate dianion in THF at −78 °C to a stirred THF solution of the acid halide led to immediate consumption of starting material and the rapid formation of (2-oxacyclopentylidene)pentacarbonylchromium (**2m**), which was isolated in ca. 38% yield. The product presumably results from rapid intramolecular alkylation of a transient acylate intermediate (**5**, Scheme II). An isoelectronic neutral acyl complex of manganese has been prepared from the reaction of $[Mn(CO)_5]^-$ with 4-chlorobutyryl chloride by Stone and co-workers.[24] Complex **2m** had been previously reported by Casey as a product of the reaction of $Li[(CO)_5CrC(OMe){=}CH_2]$ with ethylene oxide.[25] In contrast to the observed reactivity of 4-bromobutyryl chloride with Li_2[**3**], 3-bromopropionyl chloride did not give a cyclic carbene product under identical conditions; methylation of the initially formed acylate complex with $[Me_3O][BF_4]$ in H_2O provided traces of a thermally unstable methoxycarbene complex. In this case, the strain associated with the formation of the 2-oxacyclobutylidene ligand presumably inhibits ring closure.

Scheme II



The reaction of methyl oxalyl chloride (0.95 equiv) with Li_2[**3**] in THF at −78 °C led to the quantitative consumption of starting material and the apparent formation of a chromium acylate salt (as determined by solution IR spectroscopy). Subsequent methylation with $[Me_3O][BF_4]$ in H_2O led to the formation of a thermally unstable product which could not be isolated. No acylate formation was detected in the reaction of succinyl chloride (0.95 equiv) with $Li_2[Cr(CO)_5]$ in THF at −78 °C; $Cr(CO)_6$, $[ClCr(CO)_5]^-$, and (η^6-naphthalene)$Cr(CO)_3$ appeared as the major products. The course of this transformation remains under investigation.

Preliminary experiments have established that acylmetalate salts may also be obtained from the reactions of pentacarbonylmetalate dianions of molybdenum and tungsten with acyl halides and that these species may be alkylated to produce alkoxycarbenes. Employing conditions identical with those described for the preparation of the corresponding chromium complexes $(CO)_5Mo{=}C(OMe)\{3,4,5\text{-}(MeO)_3C_6H_2\}$ (**6**) and $(CO)_5W{=}C(OMe)MeOC_6H_4$ (**7**) could be isolated in 15.9 and 5.3% yields, respectively (relative to aroyl chloride). Further studies are underway to establish the scope of molybdenum and tungsten carbene synthesis using this procedure and to optimize product yields.

In summary, the reaction of $M'_2[Cr(CO)_5]$ with aryl and alkyl acid chlorides followed by alkylation of the initially formed acylmetalate salts provides a useful synthetic entry to a variety of chromium alkoxycarbene complexes. The flexibility of this approach allows the preparation of several alkoxycarbene complexes which would be difficult, if not impossible, to obtain employing alternative strategies. The methodology described is in many respects complementary to the standard Fischer synthesis and extends the range of chromium carbene complexes that may be employed in organic synthesis. For the preparation of simple alkoxycarbene complexes such as **2a**, however, the Fischer synthesis remains somewhat superior in terms of product yield and ease of scale-up. In those cases where either synthetic

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[21] (a) See ref 2b. (b) Aumann, R.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 879.

[22] (a) Casey, C. P.; Boggs, R. A.; Anderson, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 8947. (b) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1974**, *77*, 345.

[23] Wilson, J. W.; Fischer, E. O. *J. Organomet. Chem.* **1973**, *57*, C63.

[24] Game, C. H.; Green, M.; Moss, J. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 351.

[25] Casey, C. P.; Anderson, R. L. *J. Organomet. Chem.* **1974**, *73*, C28.

method may be employed, the choice of pathway will depend upon the ease of preparing and handling RLi vs. $M'_2[Cr(CO)_5]$. We are currently examining the reactions of $[M(CO)_5]^{2-}$ with milder acylating reagents (e.g. acid anhydrides and esters), as well as exploring the synthetic utility of novel carbene complexes such as **2g**.

Experimental Section

General Information. All manipulations were conducted under an argon atmosphere employing a dual manifold vacuum/inert gas Schlenk line and standard Schlenk techniques unless otherwise indicated. Glassware was soaked in KOH-saturated 2-propanol for ca. 12 h, rinsed thoroughly with distilled water, and oven-dried at 150 °C. Glass reaction vessels were cooled under vacuum (ca. 0.01 torr) immediately before use.

The term "concentrated" refers to removal of solvent at full line vacuum (ca. 0.01 torr); rotary evaporators employing water aspiration were strictly avoided. Reported melting points were uncorrected. Elemental analyses were performed by Galbraith Laboratories Inc., Knowville, TN, or by Scandinavian Microanalytical Labs, Herlev, Denmark.

Solvents. Ethereal solvents (THF and diethyl ether) were predried over CaH_2 and distilled under argon from sodium benzophenone ketyl. *n*-Pentane was stirred over concentrated H_2SO_4 for 24 h, neutralized over anhydrous K_2CO_3 for 12 h, and distilled under argon from CaH_2. *n*-Hexane was distilled from powdered CaH_2, while dichloromethane was distilled from anhydrous P_2O_5. All solvents were degassed via a minimum of three evacuation/inert gas purge cycles immediately before use. Acetone-d_6 and benzene-d_6 were purchased from Merck, Sharpe, and Dohme and saturated with dry argon before use.

Reagents. The following reagents were purchased from the specified supplier and used as received: chromium hexacarbonyl (Pressure Chemical Co.), NMe_3 (Aldrich), $ONMe_3{\cdot}2H_2O$ (Aldrich), naphthalene (Fisher), $[NMe_4]Br$ (Aldrich), $[Me_3O][BF_4]$ (Alfa), methanol (anhydrous, Mallinckrodt), 2-propanol (Baker), 2-methoxyethanol (Fisher), methyl chloroformate (Eastman), and 2,5-dihydroxybenzoic acid (Aldrich). Lithium wire (alloyed with 1% Na, Alfa) and sodium metal (Fisher) were freshly cut under argon before use.

Benzoyl chloride (MCB), *o*-anisoyl chloride (Aldrich), and 3-bromopropionyl chloride (Aldrich) were bulb-to-bulb distilled before use. Acetyl chloride (Aldrich) was distilled first from PCl_5 and then from quinoline. Methyl fluorosulfonate (Columbia Organic Chemicals) was distilled from dimethyl sulfate. 2,5-Diacetoxybenzoyl chloride was prepared in two steps from 2,5-dihydroxybenzoic acid by modification of established literature procedures.[26]

The following acid halides were purchased from Aldrich Chemical Co. and used without further purification; *m*-nitrobenzoyl chloride, terephthaloyl chloride, pivaloyl chloride, 4-cyanobenzoyl chloride, acetylsalicyloyl chloride, 2,6-dichlorobenzoyl chloride, acryloyl chloride, 4-bromobutyryl chloride, 3-(chloromethyl)benzoyl chloride, cinnamoyl chloride, methyl oxalyl chloride, 3,4,5-trimethoxybenzoyl chloride, *o*-phthaloyl chloride, succinyl chloride, 2-iodobenzoyl chloride, 2-bromoethyl chloroformate, crotonoyl chloride, cyclobutanecarbonyl chloride, and oxalyl chloride.

The pentacarbonylchromate salts $Li_2[Cr(CO)_5]$ and $Na_2[Cr(CO)_5]$ were prepared by the reduction of $Cr(CO)_5NMe_3$ in THF employing the corresponding alkali-metal naphthalenides as described by Cooper and co-workers. The precursor amine complex was prepared from $Cr(CO)_6$ and trimethylamine *N*-oxide in the presence of excess NMe_3 according to the literature procedure.[15]

Physical Measurements. Infrared spectra were recorded by using either a Perkin-Elmer Model 299 or a Pye-Unicam Model 3-200 continuous-wave spectrophotometer. Solution samples were analyzed in gas-tight demountable sodium chloride disk solution cells (0.1-mm path length) sealed with 5-mm rubber serum caps. Absorbances are reported in wavenumbers (cm^{-1}) calibrated relative to the sharp 1601.4 cm^{-1} band of a thin polystyrene film. Absorption intensities are indicated as very strong (vs), strong (s), medium (m), weak (w), or very weak (vw).

Mass spectra of solid and liquid samples were obtained employing an AEI MS-902 electron-impact ionization spectrometer. Reported m/e values refer to the most intense peak within a given molecular fragment ion envelope.

Proton NMR spectra were recorded employing a IBM NR-80 (80 MHz), JEOL FX-90Q (90 MHz), or Bruker WM-250 (250 MHz) NMR spectrometer operating in Fourier transform mode. Proton chemical shifts were indirectly referenced to external tetramethylsilane employing the resonances due to trace monoprotio solvent as internal standard (acetone-d_5, 2.04 ppm; benzene-d_5, 7.15 ppm). Carbon-13 NMR spectra were recorded by using either a JEOL FX-90Q (22.5 MHz) or a Bruker WM-250 (62.9 MHz) NMR spectrometer operating in Fourier transform mode. Chemical shifts were indirectly referenced to tetramethylsilane employing the carbonyl carbon resonance of acetone-d_6 (206.0 ppm) or the carbon resonance of benzene-d_6 (128.0 ppm) as internal standard.

Chromatography. Analytical thin-layer chromatography (TLC) was conducted employing Macherey-Nagel SIL G/UV$_{254}$ plastic-backed silica gel plates with a 0.25-mm thickness. Developed plates were visualized under UV light or by oxidation with 10% phosphomolybdic acid/ethanol. Flash column chromatography was performed by using E. Merck Silica gel 60 (0.040–0.063 mm).

Preparation of $(CO)_5Cr{=}C(OMe)Ph$ (2a) from $M_2[Cr(CO)_5]$ (M = Li, Na). 1. From $Na_2[Cr(CO)_5]$. To a stirred, freshly prepared 0.041 M solution of $Na_2[Cr(CO)_5]$ in THF (22.3 mL, 0.91 mmol) at −78 °C was added a clear, colorless solution of benzoyl chloride (103 μL, 0.89 mmol) in 5.0 mL of THF via cannula. After 5 min, solvent was stripped in vacuo from the resultant orange-red solution to give a dark orange-red gum. This residue was suspended in 20 mL of chilled (4 °C) H_2O, and 0.131 g of solid $[Me_3O][BF_4]$ (0.89 mmol) was added in a single portion. The reaction mixture was permitted to warm to 25 °C over 10 min and then was extracted with three 15-mL portions of *n*-hexane. The combined extracts were dried over anhydrous Na_2SO_4 (1.5 g) and then concentrated to ca. 3 mL. Flash chromatography (8 g of silica gel, *n*-hexane eluant) afforded an orange-red fraction which deposited bright orange-red needle crystals upon gradual removal of solvent under reduced pressure: yield 0.089 g (32.1% based on acid halide); ^1H NMR (acetone-d_6, 80 MHz) δ 7.8–7.1 (m, 5 H), 4.73 (s, 3 H); IR (*n*-hexane) 2065 (w), 1989 (vw), 1964 (ms), 1955 (s) cm^{-1}.

2. From $Li_2[Cr(CO)_5]$. To a stirred, freshly prepared 0.044 M solution of $Li_2[Cr(CO)_5]$ in THF (23.6 mL, 1.05 mmol) at −78 °C was added a solution of benzoyl chloride (114 μL, 0.98 mmol) in 5.0 mL of THF via cannula. A solution IR spectrum of the resultant orange-brown solution obtained after 4 min revealed the quantitative consumption of $Li_2[Cr(CO)_5]$ and contained ν_{CO} absorptions at 2038 (w), 1973 (w), and 1905 (vs, br) cm^{-1}. Solvent was removed in vacuo at or below ambient temperature, and the gummy red-brown residue was suspended in 15 mL of chilled (4 °C) H_2O. Trimethyloxonium tetrafluoroborate (0.150 g, 1.01 mmole was added in a single protion, and the resultant orange-red mixture was permitted to warm to 25 °C. After 5 min, the mixture was extracted with three 15-mL portions of *n*-hexane. The combined orange-red extracts were dried over anhydrous Na_2SO_4 (2 g, 10 min), the dessicant pad was rinsed with 5 mL of hexane, and the combined hexane solutions were concentrated to 20 mL. Flash chromatography (7 g of silica gel, *n*-hexane eluant) provided an orange-red fraction (R_f 0.13 by analytical TLC, *n*-hexane eluant) from which solvent was removed under reduced pressure. The resultant viscous red oil solidified to a microcrystalline orange-red powder after 1 h at −20 °C; yield 0.166 g (54.5% based on acid halide).

Preparation of $(CO)_5Cr{=}C(OMe)(o\text{-}MeOC_6H_4)$ (2b) from $M_2[Cr(CO)_5]$ (M = Li, Na). 1. From $Na_2[Cr(CO)_5]$. To a stirred 0.049 M solution of $Na_2[Cr(CO)_5]$ in THF (24.6 mL, 1.20 mmol) at −78 °C was added via cannula a solution of *o*-anisoyl chloride (164 μL, 1.16 mmol) in 5.0 mL of THF, producing a deep orange-red solution. An IR spectrum of the reaction mixture obtained after 4 min showed the complete consumption of

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[26] (a) Kloetzel, M. C.; Dayton, R. P.; Abadir, B. Y. *J. Org. Chem.* **1955**, *20*, 38. (b) McCorkindale, N. J.; Roy, T. P.; Hutchinson, S. A. *Tetrahedron* **1972**, *28*, 1107. (c) Dhoubhadel, S. P.; Joshi, S. M. *J. Indian Chem. Soc.* **1975**, *52*, 440.

$Na_2[Cr(CO)_5]$ and contained ν_{CO} absorptions at 2038 cm^{-1} (mw) and 1900 (vs, distorted) cm^{-1}. The solvent was removed in vacuo, and the gummy red-brown residue was suspended in 20 mL of 4 °C water. Trimethyloxonium tetrafluoroborate (0.170 g, 1.15 mol) was added as a single portion, and the resultant mixture was warmed to room temperature. The suspension was extracted with two 20-mL portions of *n*-hexane; the combined extracts were dried over anhydrous Na_2SO_4 (1 g) and then concentrated to ca. 10 mL. Flash chromatography (8 g of silica gel, *n*-hexane eluant) afforded an orange-red fraction (R_f 0.06 by analytical TLC, *n*-hexane eluant) from which a microcrystalline orange solid was obtained by concentration of the hexane solution: yield 0.192 g (48.2% based on acid halide): ^{1}H NMR (acetone-d_6, 80 MHz) δ 7.5–6.7 (m, 4 H), 4.23 (s, 3 H), 3.88 (s, 3 H); IR (*n*-hexane) 2065 (mw), 1989 (w), 1955 (s, distorted) cm^{-1}.

2. From $Li_2[Cr(CO)_5]$ (Method a). A solution of *o*-anisoyl chloride (150 µL, 1.07 mmol) in 5.0 mL of THF was added via cannula to a stirred, freshly prepared 0.046 M solution of $Li_2[Cr(CO)_5]$ in THF (24.4 mL, 1.12 mmol) at −78 °C. After 6 min, an IR spectrum of the orange-red solution showed the quantitative consumption of starting material and contained ν_{CO} absorptions at 2040 (mw), 1975 (vw), 1914 (s), and 1900 (s) cm^{-1}. Solvent was stripped from the mixture in vacuo at or below 0 °C, and the gummy orange-red residue was suspended in 15 mL of 4 °C water. Trimethyloxonium tetrafluoroborate (0.157 g, 1.06 mmol) was added to the stirred suspension, and the resultant orange mixture was permitted to warm to room temperature over 10 min. The suspension was extracted with three 15-mL portions of *n*-hexane, the combined extracts were dried over anhydrous sodium sulfate, and the red solution was concentrated to 15 mL. Flash chromatography (5 g of silica gel, *n*-hexane eluant) provided an orange-red fraction, which deposited a microcrystalline orange solid upon removal of solvent in vacuo; yield 0.239 g (65.5% based on acid chloride).

Method b. A solution of *o*-anisoyl chloride (146 µL, 1.04 mmol) in 5.0 mL of THF was transferred via cannula to a stirred, freshly prepared 0.045 M solution of $Li_2[Cr(CO)_5]$ in THF (24.4 mL, 1.09 mmol) at −78 °C. A solution IR spectrum recorded after 4 min revealed the quantitative consumption of $Li_2[Cr(CO)_5]$ and contained ν_{CO} absorptions at 2040 (w), 1980 (w), 1910 (vs), and 1890 (s) cm^{-1}. Solvent was stripped in vacuo at or below 0 °C, and the resultant orange-red residue was redissolved in 15 mL of cold (−40 °C) CH_2Cl_2. The orange-red solution was warmed to −30 °C, and a cold (−30 °C) solution of acetyl chloride (75 µL, 1.05 mmol) in 5.0 mL of CH_2Cl_2 was added via cannula. A very intense red-purple color developed as the reaction mixture was permitted to warm to −10 °C. After the reaction mixture was recooled to −40 °C, a solution IR spectrum showed the complete consumption of the acylate salt and contained ν_{CO} absorptions at 2070 (ms), 1965 (vs), 1950 (s), and 1790 (mw) cm^{-1}. To the stirred solution was added 0.50 mL of anhydrous methanol (12.3 mmol), and the reaction mixture was gradually warmed to 25 °C. After 20 min, an IR spectrum of the clear red solution revealed the complete disappearance of the acetoxycarbene complex and exhibited ν_{CO} absorptions at 2061 (w) and 1940 (vs) cm^{-1}. Solvent was removed in vacuo, and the orange-red residue was extracted with 20 mL of *n*-hexane. Flash chromatography (5 g of silica gel, *n*-hexane eluant) provided an orange-red fraction which deposited a microcrystalline orange solid upon concentration of the eluate; yield 0.208 g (58.4% based on acid halide).

Preparation of $(CO)_5Cr{=}C(OCH_2CH_2OMe)(o\text{-}MeOC_6H_4)$. A 0.045 M solution of $Li_2[Cr(CO)_5]$ in THF (24.5 mL, 1.11 mmol), *o*-anisoyl chloride (150 µL, 1.06 mmol), acetyl chloride (75 µL, 1.05 mmol), and 2-methoxyethanol (130 µL, 1.65 mmol) were combined according to the procedure employed to prepare **2b** (method b). In this case, the flash column was eluted with 4:1 *n*-hexane/Et_2O. The desired carbene was obtained as an orange-red solid, yield 0.191 g (46.8% based on acid halide). Recrystallization from *n*-pentane provided an orange-red microcrystalline solid: mp 40.5–42.5 °C; ^{1}H NMR (acetone-d_6, 80 MHz) δ 7.8–6.5 (m, 4 H), 4.48 (distorted triplet, 2 H), 3.87 (s, 3 H), 3.82 (distorted triplet, 2 H), 3.38 (s, 3 H); IR (*n*-hexane) 2062 (mw), 1987 (w), 1953 (vs) cm^{-1}; mass spectrum (EI), *m/e* (relative intensity) 386 (100), 358 (32), 330 (1), 302 (5), 274 (57), 246 (off scale).

Preparation of $(CO)_5Cr{=}C(O\text{-}i\text{-}Pr)(o\text{-}MeOC_6H_4)$. A 0.045 M solution of $Li_2[Cr(CO)_5]$ in THF (24.1 mL, 1.08 mmol), *o*-anisoyl chloride (147 µL, 1.05 mmol), acetyl chloride (75 µL, 1.05 mmol), and 2-propanol (0.5 mL, 6.5 mmol) were combined according to the procedure employed to prepare **2b** (method b). The desired carbene complex was obtained as an orange powder, yield 0.233 g (59.9% based on acid halide). Recrystallization from *n*-pentane provided a microcrystalline orange solid: mp 73.5–74.5 °C dec; ^{1}H NMR (acetone-d_6, 80 MHz) δ 7.5–6.7 (m, 4 H), 4.95 (septet, 1 H, J = 6.1 Hz), 3.88 (s, 3 H), 1.43 (d, 6 H, J = 6.1 Hz); ^{13}C NMR (benzene-d_6, 22.5 MHz) δ 350.8, 216.9, 149.3, 133.4, 129.5, 121.2, 120.8, 111.3, 84.9, 55.0, 22.2; IR (*n*-hexane) 2063 (m), 1986 (mw), 1950 (vs), 1073 (m), 910 (m), 652 (m) cm^{-1}; mass spectrum (EI), *m/e* (relative intensity) 370 (20), 342 (13), 314 (24), 286 (19), 258 (100), 230 (off scale). Anal. (crystals from n-pentane) Calcd for $C_{16}H_{14}CrO_7$: C, 51.90; H, 3.81. Found: C, 51.97; H, 3.86.

Preparation of $(CO)_5Cr{=}C(OR)(o\text{-}MeOC_6H_4)$ (R = $CH_2CH_2OCH(Me)C{\equiv}CCH_2CH{=}CH_2$). To a solution of $Li_2[Cr(CO)_5]$ in THF (0.029 M, 13.2 mL, 0.38 mmol) were added sequentially *o*-anisoyl chloride (53 µL, 0.38 mmol), acetyl chloride (27 µL, 0.38 mmol), and a solution of $HOCH_2CH_2OCH(Me)C{\equiv}CCH_2CH{=}CH_2$[27] in CH_2Cl_2 (0.1 M, 4.1 mL, 0.41 mmol) according to the procedure employed to prepare **2b** (method b). In this case, the flash column was eluted with 4:1 *n*-hexane/Et_2O. The desired carbene complex was obtained as an orange-red oil: Yield 0.068 g (39.7% based on acid halide); ^{1}H NMR (benzene-d_6, 250 MHz) δ 6.94–6.79 (m, 4 H), 5.69–5.49 (m, 1 H), 5.39–5.24 (m, 1 H), 5.00 (m, 1 H), 4.05 (q, 1 H, J = 6.5 Hz), 4.04–3.24 (featureless broadened multiplets, 4 H), 3.17 (s, 3 H), 2.68 (m, 2 H), 1.37 (d, 3 H, J = 6.5 Hz); IR (*n*-hexane) 2280 (w), 2062 (w), 1983 (w), 1952 (s) cm^{-1}. The complex was unstable toward rearrangement and was obtained in about 95% purity, by spectral analysis. It has been obtained before by conventional procedures.[28]

Preparation of $(CO)_5Cr{=}C(OMe)(2,6\text{-}Cl_2C_6H_3)$ (2c). A 0.045 M solution of $Li_2[Cr(CO)_5]$ in THF (23.7 mL, 1.07 mmol), 2,6-dichlorobenzoyl chloride (175 µL, 1.01 mol), and $[Me_3O][BF_4]$ (0.157 g, 1.06 mmol) were combined according to the procedure employed to prepare **2a**. The desired carbene complex was isolated as a microcrystalline red solid, yield 0.169 g (43.8% based on acid halide). Recrystallization from *n*-pentane provided orange-red flakes: mp 97.5–98.0 °C; ^{1}H NMR (benzene-d_6, 80 MHz) δ 6.8–6.1 (m, 3 H), 3.38 (s, 3 H); ^{1}H NMR (acetone-d_6, 90 MHz) δ 7.60–7.30 (m, 3 H), 4.35 (s, 3 H); ^{13}C NMR (acetone-d_6, 250 MHz, 273 K) δ 348.4, 225.0, 216.5, 145.6, 131.3, 129.5, 125.7, 67.6; IR (*n*-hexane) 2065 (w), 1968 (ms), 1953 (m) cm^{-1}; mass spectrum (EI), *m/e* (relative intensity) 380 (12), 352 (11), 324 (8), 296 (22), 268 (26), 240 (100). Anal. (crystals from *n*-pentane) Calcd for $C_{13}H_6Cl_2CrO_6$: C, 40.97; H, 1.59. Found: C, 41.07; H, 1.81.

Preparation of $(CO)_5Cr{=}C(OMe)(3,4,5\text{-}(MeO)_3C_6H_2)$ (2d). A 0.044 M solution of $Li_2[Cr(CO)_5]$ in THF (23.6 mL, 1.05 mmol), 3,4,5-trimethoxybenzoyl chloride (0.237 g, 1.03 mmol), and $[Me_3O][BF_4]$ (0.159 g, 1.08 mmol) were combined according to the procedure employed to prepared **2a**. In this case, the flash column was eluted with 4:1 *n*-hexane/CH_2Cl_2. The desired carbene complex was isolated as a deep red oil, yield 0.240 g (58.0% based on acid halide). Recrystallization from *n*-pentane provided deep red needles (0.190 g, 45.9% based on acid halide): mp 85.0–87.0 °C; ^{1}H NMR (acetone-d_6, 90 MHz) δ 6.86 (s, 2 H), 4.82 (s, 3 H), 3.88 (s, 6 H), 3.81 (s, 3 H); ^{13}C NMR (acetone-d_6, 62.9 MHz, 273 K) δ 346.5, 225.0, 217.3, 153.4, 148.9, 141.3, 103.1, 68.4, 60.6, 56.2; IR (*n*-hexane) 2060 (mw), 1985 (w), 1953 (sh), 1943 (ms) cm^{-1}; mass spectrum (EI), (relative intensity) 402 (2.3), 374 (15.0), 346 (12.2), 318 (10.4), 290 (40.6), 262 (100.0). Anal. (crystals from *n*-pentane) Calcd for $C_{16}H_{14}CrO_9$: C, 47.77; H, 3.51. Found: C, 48.21; H, 3.77.

Preparation of $(CO)_5Cr{=}C(OMe)(3\text{-}(CH_2Cl)C_6H_4)$ (2e). A 0.042 M solution of $Li_2[Cr(CO)_5]$ in THF (23.0 mL, 0.97 mmol), 3-(chloromethyl)benzoyl chloride (130 µL, 0.92 mmol), and $[Me_3O][BF_4]$ (0.141 g, 0.95 mmol) were combined via a modification of the procedure employed to prepare **2a**, wherein the freshly prepared chromium(II−) reagent was added to the aroyl halide in 5 mL of THF at −78 °C. In this case, the flash column was eluted with 4:1 *n*-hexane/CH_2Cl_2. The desired carbene complex was obtained as a dark red oil, yield 0.157 g (47.4% based

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[27] Previously prepared by T. Sato, unpublished observations at Princeton.

[28] Unpublished results of J. Bozell, Princeton University.

on acid halide). Recrystallization from *n*-pentane afforded an orange-red microcrystalline solid at temperatures below −20 °C which melted at ca. 0 °C. It was less stable than the other carbene complexes reported here, and a satisfactory analysis could not be obtained: ^{1}H NMR (benzene-d_6, 250 MHz) δ 6.97–6.82 (m, 4 H), 3.95 (s, 2 H), 3.75 (s, 3 H); IR (*n*-hexane) 2058 (m), 1981 (mw), 1948 (vs) cm^{-1}; mass spectrum (EI), *m/e* (relative intensity) 360 (8), 332 (7), 304 (12), 276 (5), 248 (18), 220 (100).

Preparation of $(CO)_5Cr{=}C(OMe)(o\text{-}AcOC_6H_4)$ (2f). A 0.046 M solution of $Li_2[Cr(CO)_5]$ in THF (24.0 mL, 1.11 mmol), *O*-acetylsalicyloyl chloride (180 μL, 1.04 mmol), and $[Me_3O][BF_4]$ (0.160 g, 1.08 mmol) were combined according to the procedure employed to prepare **2a**. In this case, the flash column was eluted with 4:1 *n*-hexane/CH_2Cl_2. The desired carbene was isolated as an orange-red solid, yield 0.324 g (84.2% based on acid halide). Recrystallization from *n*-pentane afforded a microcrystalline orange-red solid: mp 50.0–51.5 °C; ^{1}H NMR (benzene-d_6, 90 MHz) δ 7.2–6.4 (m, 4 H), 3.45 (s, 3 H), 1.75 (s, 3 H); ^{1}H NMR (acetone-d_6, 90 MHz) δ 7.47–7.02 (m, 4 H), 4.37 (s, 3 H), 2.25 (s, 3 H); ^{13}C NMR (acetone-d_6, 62.9 MHz, 253 K) δ 352.0, 225.3, 216.2, 169.0, 144.3, 140.0, 129.9, 126.4, 123.8, 121.6, 67.2, 20.6; IR (*n*-hexane) 2071 (mw), 1990 (w), 1962 (sh), 1955 (vs) cm^{-1}; mass spectrum (EI), *m/e* (relative intensity) 370 (16), 314 (5), 286, (11), 258 (30), 230 (100). Anal. (crystals from *n*-pentane) Calcd for $C_{15}H_{10}CrO_8$: C, 48.66; H, 2.72. Found: C, 48.76; H, 2.82.

Preparation of $(CO)_5Cr{=}C(OMe)\{2,5\text{-}(AcO)_2C_6H_3\}$ (2g). A 0.069 M solution of $Li_2[Cr(CO)_5]$ in THF (76.0 mL, 5.25 mmol), 2,5-diacetoxybenzoyl chloride (1.317 g, 5.13 mmol), and $[Me_3O][BF_4]$ (0.788 g, 5.26 mmol) were combined according to the procedure employed to prepare **2a**. In this case, the flash column was eluted with 16:6:3 *n*-hexane/Et_2O/CH_2Cl_2. The desired carbene complex was isolated as a bright red microcrystalline solid, yield 1.487 g (67.7% based on acid halide). Recrystallization from 3:2 Et_2O/*n*-pentane afforded red prisms (yield 1.355 g, 61.7% based on acid halide): mp 105.0–106.0 °C; ^{1}H NMR (acetone-d_6, 90 MHz) δ 7.34 (d of d, 1 H, J_1 = 8.35 Hz, J_2 = 0.66 Hz), 7.16 (d of d, 1 H, J_1 = 7.91 Hz, J_2 = 2.42 Hz), 6.87 (d of d, 1 H, J_1 = 2.64 Hz, J_2 = 0.66 Hz), 4.43 (s, 3 H), 2.26 (s, 3 H), 2.25 (s, 3 H); ^{13}C NMR (acetone-d_6, 62.9 MHz, 273 K) 350.7, 225.5, 216.3, 169.2, 148.9, 146.0, 137.9, 125.2, 123.3, 115.7, 68.0, 20.8; IR (*n*-hexane) 2062 (w), 1991 (vw), 1961 (s), 1773 (w) cm^{-1}; mass spectrum (EI), *m/e* (relative intensity) 428 (11.7), 372 (8.2), 344 (12.4), 316 (43.1), 288 (100.0). Anal. (crystals from 3:2 Et_2O/n-pentane) Calcd for $C_{17}H_{12}CrO_{10}$: C, 47.68; H, 2.82. Found: C, 47.85; H, 3.18.

Preparation of $(CO)_5Cr{=}C(OMe)Me$ (2h). A 0.045 M solution of $Li_2[Cr(CO)_5]$ in THF (23.9 mL, 1.09 mmol), acetyl chloride (73 μL, 1.03 mmol), and $[Me_3O][BF_4]$ (0.156 g, 1.05 mmol) were combined according to the procedure employed to prepare **2a**. In this case, naphthalene was extracted away from the initially formed acylate salt by washing with *n*-hexane (3 × 10 mL). The desired carbene complex was isolated as a volatile crystalline yellow solid: yield 0.090 g (34.9% based on acid halide); ^{1}H NMR (benzene-d_6, 90 MHz) δ 3.8 (s, 3 H), 2.4 (s, 3 H); IR (*n*-hexane) 2065 (w), 1984 (vw), 1961 (m), 1947 (s) cm^{-1}.

Preparation of $(CO)_5Cr{=}C(OMe)(t\text{-}Bu)$ (2i). A 0.044 M solution of $Li_2[Cr(CO)_5]$ in THF (23.9 mL, 1.04 mmol), pivaloyl chloride (125 μL, 1.01 mmol), and $[Me_3O][BF_4]$ (0.151 g, 1.02 mmole were combined according to the procedure employed to prepare **2a**. In this case, naphthalene was extracted away from the initially formed acylate salt by *n*-hexane (3 × 15 mL). The desired carbene complex was isolated as a volatile, amber yellow oil; yield 0.110 g (37.2% based on acid halide). Recrystallization from *n*-pentane afforded pale yellow plates at temperatures below −20 °C: ^{1}H NMR (benzene-d_6, 250 MHz) δ 3.99 (s, 3 H), 1.00 (s, 9 H); IR (*n*-hexane) 2062 (w), 1978 (w) 1943 (ms) cm^{-1}; mass spectrum (EI), *m/e* (relative intensity) 292 (47), 264 (41), 236 (42), 208 (24), 180 (100), 152 (off scale).

Preparation of $(CO)_5Cr{=}C(OMe)(CH{=}CHPh)$ (2j). A 0.044 M solution of $Li_2[Cr(CO)_5]$ in THF (24.5 mL, 1.07 mmol), cinnamoyl chloride (0.169 g, 1.02 mmol), and $[Me_3O][BF_4]$ (0.148 g, 1.00 mmol) were combined according to the procedure employed to prepare **2a**. The desired carbene complex was obtained as a waxy deep red-purple solid: yield 0.061 g (17.7% based on acid halide; ^{1}H NMR (acetone-d_6, 80 MHz) δ 8.09 (d, 1 H, *J* = 15.4 Hz), 7.83–7.40 (m, 5 H), 7.20 (d, 1 H, *J* = 15.4 Hz), 4.86 (s, 3 H); IR (*n*-hexane) 2060 (w), 1958 (sh), 1947 (s) cm^{-1}.

Preparation of $(CO)_5Cr{=}C(OMe)(CH{=}CHMe)$ (2k). A 0.047 M solution of $Li_2[Cr(CO)_5]$ in THF (24.9 mL, 1.18 mmol), crotonoyl chloride (110 μL, 1.15 mmol), and $[Me_3O][BF_4]$ (0.175 g, 1.18 mmol) were combined according to the procedure employed to prepare **2a**. The desired carbene was obtained as an impure red oil contaminated by naphthalene: yield 0.040 g (≤14.1% based on acid halide; ^{1}H NMR (acetone-d_6, 250 MHz) δ 7.43–7.35 (d of quartets, 1 H, J_1 = 1.51 Hz, J_2 = 14.95 Hz), 6.64–6.50 (d of quartets, 1 H, J_1 = 6.95 Hz, J_2 = 14.93 Hz), 4.76 (s, 3 H), 1.94–1.91 (d of d, 3 H, J_1 = 1.50 Hz, J_2 = 6.94 Hz); IR (*n*-hexane) 2060 (mw), 1983 (mw), 1943 (vs) cm^{-1}.

Preparation of $(CO)_5Cr{=}C(OMe)(c\text{-}C_4H_7)$ (2l). A 0.049 M solution of $Li_2[Cr(CO)_5]$ in THF (24.7 mL, 1.21 mmol), cyclobutane carbonyl chloride (122 μL, 1.18 mmol), and $[Me_3O][BF_4]$ (0.1798 g, 1.22 mmol) were combined according to the procedure employed to prepare **2a**. The desired carbene complex was isolated as a waxy yellow semisolid contaminated by naphthalene: yield (corrected for naphthalene) 0.152 g (44.7% based on acid halide); ^{1}H NMR (acetone-d_6, 250 MHz) δ 4.91 (s, 3 H), 4.53 (pseudopentet, 1 H, *J* = 8.32 Hz), 2.30–2.19 (m, 4 H), 1.96–1.78 (m, 1 H), 1.72–1.59 (m, 1 H); IR (*n*-hexane) 2060 (mw), 1982 (w), 1944 (vs, distorted) cm^{-1}.

Preparation of $(CO)_5Cr{=}C(OCH_2CH_2CH_2)$ (2m). A freshly prepared 0.044 M solution of $Li_2[Cr(CO)_5]$ in THF (23.5 mL, 1.04 mmol) at −78 °C was added via cannula to a stirred −78 °C solution of 4-bromobutyryl chloride (120 μL, 1.04 mmol) in 5.0 mL of THF. After 8 min, a solution IR spectrum of the resultant yellow-orange solution showed the complete consumption of $Li_2[Cr(CO)_5]$ and contained ν_{CO} absorptions at 2064 (w), 2040 (sh), 1973 (sh), 1940 (vs, br), 1905 (sh), and 1850 (sh) cm^{-1}. Solvent was removed in vacuo at or below 24 °C, and the gummy orange-red residue was extracted with three 15-mL portions of *n*-hexane. The combined orange-yellow extracts were concentrated to ca. 15 mL and then flash chromatographed (6 g of silica gel, 3:1 *n*-hexane/CH_2Cl_2 eluant) to provide a golden yellow fraction. Broad yellow needle crystals were obtained by gradual concentration of the eluate under reduced pressure: yield 0.105 g (38.3% based on acid halide); ^{1}H NMR (benzene-d_6, 80 MHz) δ 3.58 (t, 2 H, *J* = 7.56 Hz), 2.72 (t, 2 H, *J* = 7.73 Hz), 0.53 (pseudopentet, 2 H, *J* = 7.77 Hz); IR (*n*-hexane) 2062 (w), 1963 (sh), 1943 (s) cm^{-1}.

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Registry No. **2a**, 27436-93-7; **2b**, 27436-99-3; **2c**, 62343-07-1; **2d**, 109283-07-0; **2e**, 27436-98-2; **2f**, 109283-08-1; **2g**, 109283-09-2; **2h**, 20540-69-6; **2i**, 109283-10-5; **2j**, 54873-11-9; **2k**, 109362-35-8; **2l**, 109283-11-6; **2m**, 54040-15-2; $Na_2[Cr(CO)_5]$, 51233-19-3; $Li_2[Cr(CO)_5]$, 109283-12-7; $(CO)_5Cr{=}C(OCH_2CH_2OMe)(o\text{-}MeOC_6H_4)$, 109283-13-8; $(CO)_5Cr{=}C(O\text{-}i\text{-}Pr)(o\text{-}MeOC_6H_4)$, 109283-14-9; $(CO)_5Cr{=}C(OCH_2CH_2OCH(Me)C{\equiv}CCH_2CH{=}CH_2)(o\text{-}MeOC_6H_4)$, 109283-15-0; $HOCH_2CH_2OCH(Me)C{\equiv}CCH_2CH{=}CH_2$, 109306-35-6; benzoyl chloride, 98-88-4; *o*-anisoyl chloride, 21615-34-9; 2-methoxyethanol, 109-86-4; 2-propanol, 67-63-0; 2,6-dichlorobenzoyl chloride, 4659-45-4; 3,4,5-trimethoxybenzoyl chloride, 4521-61-3; 3-(chloromethyl)benzoyl chloride, 63024-77-1; *O*-acetylsalicyloyl chloride, 5538-51-2; 2,5-diacetoxybenzoyl chloride, 37785-02-7; pivaloyl chloride, 3282-30-2; cinnamoyl chloride, 102-92-1; crotonoyl chloride, 10487-71-5; cyclobutanecarbonyl chloride, 5006-22-4; 4-bromobutyryl chloride, 927-58-2.