Preparation of Fischer Carbene Complexes by Alkylation of Acylmetalates with Alkyl Iodides

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Neutral Fischer carbene complexes bearing alkoxy groups as the donor substituents on the carbene carbon atom have been synthesized by direct alkylation of the lithium acylmetalates (formed by classical addition of organolithium compounds to metal hexacarbonyl) by alkyl iodides. It was shown that the reaction proceeds under normal phase-transfer conditions (CH_2Cl_2/H_2O) or, preferably, in aqueous medium alone. However, in both cases the presence of a catalytic amount of a tetraalkylammonium salt (n-Bu_4NBr) was required. Attractive features of this methodology are (i) the economy of using alkyl iodides in place of the usual alkylating agents (like $Me_3O^+BF_4^-$, magic methyl, or methyl triflate), (ii) the procedural ease of "one-pot" preparation of the carbene complexes, and (iii) the greater variety of alkyl moieties that can be incorporated as part of the alkoxy substituent using the more readily available alkyl iodides containing nontrivial alkyl groups. The procedure is preparatively useful for accessing chromium-containing carbenes, but yields of the analogous molybdenum- and tungsten-containing species are only ≤10%. Mechanistic considerations suggest that products are formed by competing pathways involving direct S_N2 displacement vs electron-transfer-initiated $S_{RN}1$ processes.

Fischer carbene complexes [$L_m(CO)_nM{=}C(R)X$] were first described nearly 25 years ago,[1] and their chemistry has been extensively studied since. The most commonly used general method of preparing these complexes (where X = alkoxy, OR') is still the original method described by Aumann and Fischer[2] which involves alkylation of aqueous solutions of the lithium acylmetalate with Meerwein's salt (or methyl fluorosulfate or methyl triflate).[3] This procedure gives good yields but has some limitations. Most importantly, it is constrained to the preparation of simple methoxy- or ethoxy-bearing complexes, and the alkylating agents are expensive and/or toxic. Several modifications have been reported to incorporate more complex OR' groups. The simple complexes can be modified by direct alcoholysis with higher alcohols.[4] Tetraalkylammonium salts of acylchromates have been O-acylated with, e.g., acetyl chloride, acetyl bromide, or pivaloyl chloride, and the resulting "mixed anhydride" has been trapped by attack of more complex alcohols at the electrophilic carbene center.[5]

We recently needed to prepare a variety of group VI metal carbene complexes containing more sophisticated alkoxy substituents and wondered whether it might be possible to use a strategy whereby the intermediate acylmetalates were reacted directly with alkyl *halides*.[6] In particular, we thought that the use of phase-transfer conditions might sufficiently activate the acylmetalate to allow alkylation by a large variety of readily accessible alkyl halides. Variations of this strategy have been sufficiently successful that we report here observations and procedures which represent an alternative protocol for the synthesis of alkoxy-substituted Fischer carbene complexes.

Our first experiment involved dissolving the lithium acylchromate **1a** [see Table I, prepared following the usual procedure of methyllithium addition to $Cr(CO)_6$ in Et_2O][2] in water and performing the methylation under typical phase-transfer conditions. Namely, methyl iodide (4.0 equiv), methylene chloride (in equal volume with the H_2O), and tetrabutylammonium bromide (5 mol %, as the phase-transfer catalyst) were sequentially added at ambient temperature. After ~12 h simple extraction with hexanes gave the neutral carbene complex pentacarbonyl(1-methoxyethylidene)chromium (**2a**) in 36% yield. For descriptive convenience we will refer to the carbene complexes discussed in this paper with a shorthand notation that leads, e.g., to **2a** being called the "methoxy methyl chromium carbene". Several control experiments were instructive. When either Bu_4NBr or water was omitted, no neutral carbene was obtained. However, the reaction proceeded equally well with respect to yield and product purity and was noticeably faster when the organic solvent was omitted. Therefore, both the ammonium ion and an aqueous medium are essential for the alkylation step. We also noticed temperature effects. Thus, reaction time could be reduced to 1 h by heating the reaction mixture to 60–70 °C without lowering the yield. Under the optimum conditions of treating an aqueous solution of **1a** with 2 equiv of methyl iodide (the number of equivalents can be reduced to 1.1 when less volatile or more precious alkylating agents are used), the crude yield of the methoxy methyl chromium carbene **2a** was 79% on a 30-mmol scale. The material so-produced was a yellow solid whose ^1H NMR

(1) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445.
(2) (a) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1968**, *101*, 954. (b) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M. In *Organic Syntheses*; Vedejs, E., Ed.; Wiley: New York, 1987; Vol. 65, pp 140–145.
(3) (a) Casey, C. P.; Cyr, C. R.; Boggs, R. A. *Synth. Inorg. Met-Org. Chem.* **1973**, *3*, 249. (b) Harvey, D. F.; Brown, M. F. *Tetrahedron Lett.* **1990**, *31*, 2529.
(4) (a) Kreiter, C. G.; Kiener, V. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 390. (b) Casey, C. P.; Shusterman, A. J. *J. Mol. Catal.* **1980**, *8*, 1.
(5) (a) Connor, J. A.; Jones, E. M. *J. Chem. Soc., Chem. Commun.* **1971**, 570. (b) Connor, J. A.; Jones, E. M. *J. Chem. Soc. A* **1971**, 3368. (c) Semmelhack, M. F.; Bozell, J. J.; Keller, L.; Sato, T.; Spiess, E. J.; Wulff, W.; Zask, A. *Tetrahedron* **1985**, *41*, 5803. (d) Söderberg, B. C.; Hegedus, L. S. *Organometallics* **1990**, *9*, 3113. (e) Söderberg, B. C.; Hegedus, L. S.; Sierra, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 4364. (f) Also cf.: Semmelhack, M. F.; Lee, G. R. *Organometallics* **1987**, *6*, 1839.

(6) (a) The only previous uses of alkyl halides for acylmetalate alkylations of which we are aware are reactions of a lithium acylmetalate with methyl iodide in very low yield[1] and of a stoichiometric tetramethylammonium acylmetalate with prenyl bromide (CH_2Cl_2, 12 equiv, 73%)[6b] or benzyl bromide (CH_2Cl_2, 87%).[6c] (b) Wulff, W. D.; McCallum, J. S.; Kunng, F. *J. Am. Chem. Soc.* **1988**, *110*, 7419. (c) Unpublished results of D. Thompson and L. Hegedus.

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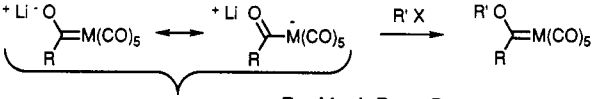
Table I. Alkylation[a] of Lithium Acylmetalates 1 with Alkyl Iodides[b] To Give Carbene Complexes 2



1 **a** R = Me, **b** R = *n*-Bu, **c** R = Ph, **d** R = Me_2C=CH **2**

entry	R	M	R′	acylmetalate anion	carbene product	yield, %[c,d]
1	Me	Cr	Me	**1a**	**2a**	79[e]–90 (51–77[e])
2	*n*-Bu	Cr	Me	**1b**	**2b**	66
3	Ph	Cr	Me	**1c**	**2c**	52
4	Me_2C=CH	Cr	Me	**1d**	**2d**	53
5	Me	Cr	*n*-Pr	**1a**	**2e**	58–67 (53)
6	Me	Cr	*n*-Bu	**1a**	**2f**	67–76 (50)
7	Me	Cr	*i*-Pr	**1a**	**2g**	64 (62)
8	Me	Cr	*s*-Bu	**1a**	**2h**	80–89 (56)
9	Me	Cr	*t*-Bu	**1a**	**2i**	7 (2)
10	Me	Cr	5-hexenyl	**1a**	**2j**	58–80 (19)[f]
11	Me	Cr	c-$C_3H_5CH_2$	**1a**	**2k**[g]	62
12	Me	Cr	CH_2=$CHCH_2$	**1a**	**2l**	56–75 (23–27[h])[f]
13	Me	Cr	$PhCH_2$[b]	**1a**	**2m**	56 (50)
14	Me	Cr	MeC≡CCH_2	**1a**	**2n**	41–74 (10)[f]
15	*n*-Bu	W	Et	**1e**	**2o**	40–50 (10)
16	*n*-Bu	Mo	Me	**1f**	**2p**	<10[3b]

[a] Unless otherwise noted all reactions performed on a 1-mmol scale by procedure B (see Experimental Section). [b] Only in the case of $PhCH_2Br$ was a halide other than iodide found to be effective. [c] Yields are reported for material isolated after direct extraction of the crude reaction mixtures. The major impurity was $Cr(CO)_6$ [^{13}C NMR analysis]. [d] Yields reported in parentheses are for material purified by chromatography on SiO_2; such purification always gave a slightly faster eluting bond of $Cr(CO)_6$. [e] Results from a 30-mmol scale experiment. [f] See text and refs 5d and 5e. [g] Accompanied by 5–10% (3-butenyloxy)methylcarbene. [h] By procedure A (see Experimental Section).

spectrum showed it to be uncontaminated within detectable limits. Purification by MPLC on SiO_2 (hexanes elution) returned, after a small forerun of $Cr(CO)_6$, pure **2a** in 77% overall yield.

It was of interest to know what structural variations within the acylmetalates **1** would be compatible with this strategy. Results from most of the reactions we have examined are summarized in Table I. Acylchromates **1a–1d**—containing higher alkyl, phenyl, and vinyl substituents—all gave respectable yields of carbene complexes **2a–2d** upon methylation with methyl iodide (entries 1–4). Notice, however, that analogous tungsten and molybdenum complexes **2o** and **2p** (entries 15 and 16) were generated in 10% yield or less. Attempts to use the sometimes more readily available Grignard reagents in place of alkyllithiums in the initial generation of acylmetalates were only marginally successful. For example, under the standard conditions described above (the solid bromomagnesium analog of **1a** was only slightly soluble in water) methylation gave a much less pure sample of **2a** in ~20% crude yield. An attempt to ion exchange Na^+ for Mg^{2+} by passing a dilute aqueous solution of $(CO)_5Cr$=C(Me)OMgBr through an ion-exchange resin was not productive.

We have also used a wide variety of alkyl halides to incorporate less conventional substituents into the alkoxy moiety of the carbene complex. With the exception of benzyl *bromide*,[6a,c] all of our successful preparations involved the use of alkyl *iodides* as the alkylating agents. Methyl and primary, secondary, and even tertiary alkyl iodides all gave carbene complexes upon reaction with **1a** (entries 1 and 5–11). Allyl-, benzyl-, and propargyloxy substituted carbenes **21**, **2m**, and **2n** were also produced (entries 12–14), but some in only marginal yield. In addition, chromatographic purification on silica gel of these carbenes, which all contain unsaturation in the alkoxy moiety, resulted in substantially reduced recoveries of pure carbene complex (entries 10, 12, and 14). This outcome is entirely consistent with the inherent thermal instability described by Söderberg and Hegedus[5d] for alkenyloxy-bearing carbenes due to the accessibility of facile intramolecular cyclopropanation pathways.

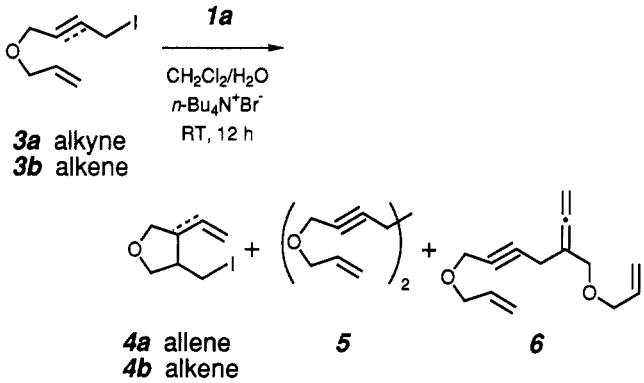
Attempts to use other alkylating agents included reactions of **1a** with ethyl bromide, 4-bromo-1-butene, dimethyl sulfate, allyl bromide, methyl bromoacetate, and neopentyl iodide. In the first case ~10% of carbene was obtained, although that could be improved to 22% when 1 equiv of NaI was included in the aqueous reaction mixture. With the homoallylic bromide less than 1% of a yellow solid was isolated, although its ^1H NMR spectrum suggested it to be a pure sample of the 3-butenyloxy methyl chromium carbene. Use of dimethyl sulfate produced ~25% mass yield of material containing **2a**; however, the product purity was substantially lower than when MeI was used. No carbene complex was detected with the last three of these substrates.

It is appropriate to comment on the possible mechanism(s) for these alkylation reactions. Although the fact that alkyl iodides are the only class of common alkylating agents that function with generality in this reaction make it tempting to suggest the possibility that all of these reactions proceed by an electron-transfer initiated $S_{RN}1$ mechanistic pathway, several of the results tend to counter this hypothesis. Namely, neopentyl iodide was unreactive; 6-iodo-1-hexene (as well as 2-(allyloxy)ethyl iodide) gave no evidence of carbene product containing a cyclopentylmethyl (or 3-tetrahydrofuranylmethyl) moiety (entry 10); and cyclopropylmethyl iodide reacted to give predominantly the intact (cyclopropylmethoxy)carbene **2k** (entry 11), although this process was always accompanied by the formation of small amounts of the ring opened (3-butenyloxy)carbene (note f, Table I).[7] These results

(7) (a) Although the presence of small amounts of (3-butenyloxy)methylcarbene product formed upon reaction of **1a** with cyclopropyl iodide is not necessarily proof for a cyclopropylmethyl radical intermediate (background atom-transfer rearrangement of c-$C_3H_5CH_2I$ to CH_2=$CHCH_2CH_2I$ could well be occurring),[7b] the fact that the (cyclopropylmethoxy)methylcarbene **2e** was the dominant product implies that most, if not all, of the alkylation events in that reaction occurred by direct S_N2 displacement. (b) E.g.: Alnajjar, M. S.; Smith, G. F.; Kuivila, H. G. *J. Org. Chem.* **1984**, *49*, 1271.

imply that there is significant S_N2 mechanistic character to the process.

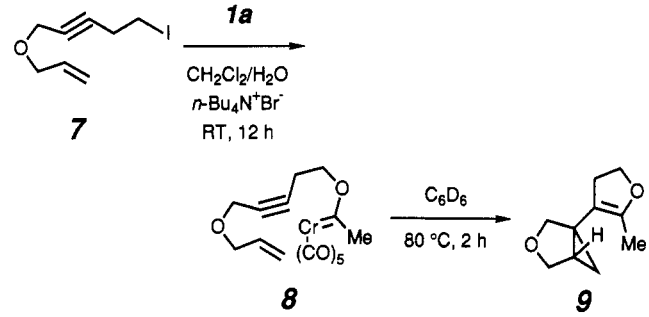
Several other observations suggest that the $S_{RN}1$ process is operative to some extent. The tertiary iodide, *t*-BuI, definitely reacted with **1a** to give the (*tert*-butoxymethyl)-carbene **2i**, albeit in low yield (entry 9); as noted above cyclopropylmethyl iodide consistently gave rise to 5–10% of $(CO)_5Cr{=}C(Me)O(CH_2)_2CH{=}CH_2$;[7] and, perhaps most convincingly, the propargylic and allylic iodides **3a** and **3b** gave predominantly the interesting cyclic products **4a**



and **4b** (along with small amounts of the coupled products **5** and **6** in the case of **3a**). The tetrahydrofuranylmethyl iodides **4** are formally atom-transfer radical cyclization products[8] which we envision arising from electron-transfer-initiated, radical ion fragmentation to the first propargylic/allylic radical in the atom-transfer chain cyclization.

Taken as a collection, the facts lead us to suggest that these alkylation reactions are proceeding by two different and competitive mechanisms. With methyl and primary (and, perhaps, secondary and benzylic) alkyl iodides direct S_N2-displacement is apparently favored whereas tertiary (and, perhaps, secondary and benzylic), allylic, and propargylic substrates are sufficiently readily reduced that electron-transfer-initiated alkylation can now compete with an S_N2 mechanism. The requirement for the n-Bu_4N^+ ion suggests that disruption of the presumably strong ion-pairing[9] in the lithium acylmetalates is necessary to generate a species with sufficiently high nucleophilicity and/or reduction potential to promote alkylation.

In summary and regardless of the mechanistic details, we have developed a process that offers a number of advantages over, and in many cases complements, existing methodology for the preparation of alkoxy-bearing Fischer carbene complexes. There is an economic advantage as well as convenience over the use of the classic Meerwein methylating and ethylating agents. In addition a wide variety of more exotic alkoxy groups can be incorporated into the carbenes via this protocol. As a final example of the potential made available by this strategy, we note the facile construction of the polycyclic species **9** which relies in part on the alkylation of **1a** with iodide **7** to give the carbene precursor **8**.[8c,10,11]



Experimental Section

Unless otherwise noted, all NMR spectral data were recorded in $CDCl_3$ at 300 MHz for ^1H and 75 MHz for ^{13}C. Chemical shifts are reported relative to TMS (δ = 0.00) and $CDCl_3$ (δ = 77.0), respectively. All IR spectra were recorded as $CDCl_3$ solutions. Ether was distilled from benzophenone ketyl just prior to use. As a precaution, reaction and extraction solvents were typically purged with N_2. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

General Procedures for the Preparation of Pentacarbonyl(1-alkoxyalkylidene)chromium Complexes 2a–2n. Procedure A. A 10-mL round-bottomed flask charged with $Cr(CO)_6$ (n mmol) was flushed with argon or N_2 using a Firestone valve. Ether (3n mL) was added, and to the stirred suspension was introduced CH_3Li (1.4 M in ether, 1.1n mmol) at room temperature. The slurry became a homogeneous yellow solution which turned dark brown while stirring for 10 min at room temperature.[2b] Solvent was removed under reduced pressure. The flask was again flushed with argon or N_2 and charged with n-Bu_4NBr [0.05–0.10n mmol in H_2O (n mL)], CH_2Cl_2 (n mL), and the alkyl iodide (1.2–2.0n mmol, larger excesses were used for readily available iodides). The mixture was stirred ca. overnight at room temperature. The layers were separated, and the aqueous layer was extracted with hexanes. The combined extracts were dried over $MgSO_4$, filtered, and evaporated to give the carbene complex **2** as a yellow solid or orange oil.

Procedure B comprises procedure A with the following differences. The alkylation step was performed in aqueous n-Bu_4NBr only (i.e., without any methylene chloride) at 65–70 °C for ~2 h. The entire reaction sequence was carried out in a capped culture tube in order to retain volatile alkyl iodides at elevated temperature. An orange-red oil settled to the bottom of the tube as the reaction proceeded. Procedure B is generally preferred to A for its shorter reaction time, easier workup, and often improved yield.

Pentacarbonyl(1-methoxypentylidene)chromium (2b):[12] ^1H NMR (500 MHz) δ 4.77 (s, OCH_3), 3.30 (t, J = 7.2 Hz, $=CCH_2$), 1.46 (m, $CH_2CH_2CH_2CH_3$), 1.33 (m, $CH_2CH_2CH_2CH_3$), 0.91 (t, J = 7.2 Hz, CH_3); ^{13}C NMR (125 MHz) δ 363.7 (C=Cr), 223.2 (trans CO), 216.4 (cis CO's), 67.6 (OCH_3), 63.0 ($Cr{=}CCH_2$), 28.3 ($CH_2CH_2CH_3$), 22.4 ($CH_2CH_2CH_3$), 13.7 ($CH_2CH_2CH_3$); IR 2062, 1942 (s), 1258 cm^{-1}.

Pentacarbonyl(methoxy-1-phenylmethylidene)chromium (2c):[2] ^1H NMR δ 7.41–7.26 (m, ArH), 4.70 (s, OCH_3); ^{13}C NMR δ 351.2 (C=Cr), 224.2 (trans CO), 216.2 (cis CO's), 153.7, 130.4, 128.2, 123.0, 67.1 (CH_3); IR 2070, 1950 (s), 1260 cm^{-1}.

(8) (a) In fact the **3** to **4** transformation can be effected more cleanly using the Curran $Bu_3SnSnBu_3/h\nu$ protocol.[8b,c] (b) Curran, D. P. In *Free Radicals in Synthesis and Biology*; Minisci, F., Ed.; Mathematical and Physical Sciences; NATO ASI Series C; Kluwer Academic Publishers: Boston, 1989; Vol. 260, Chapter 3. (c) Chen, K. Ph.D. Thesis, University of Minnestoa, 1991.

(9) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 2515.

(10) Cf.: (a) Harvey, D. F.; Brown, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 7806. (b) Hoye, T. R.; Korkowski, P. F. *J. Am. Chem. Soc.* **1988**, *110*, 2676.

(11) A C_6D_6 solution of **8** was warmed at 80 °C for 2 h to give a solution containing the tricyclic cyclopropane **9**, as judged by ^1H NMR [300 MHz, δ 7.13 (C_6D_5H reference), 3.9–4.0 (m, 2H, $CH_2OC{=}$), 3.76 (two overlapped ms, 2H, $H_aH_bCOCH_cCH_dCH$), 3.60 (dd, J = 8.0 and 2.5 Hz, H_aH_b-$COCH_cCH_dCH$), 3.51 (br d, J = 8.3 Hz, $H_aH_bCOCH_cCH_dCH$), 2.0–2.3 (m, 2H, $CH_2C{=}$), 1.64 (t, J = 2.0 Hz, Me), 1.08 (m, 1H, $CHCC$), 0.77 (dd, J = 4.2 and 4.2 Hz, CCH_eH_fCHCC), and 0.52 (dd, J = 8.0 and 4.2 Hz, CCH_eH_fCHCC)] and GC–MS [70 eV, m/e, 166 (91, M^+), 151 (3, M^+ – Me), 136 (69, $M^+ - CH_2O$), 121 (47, M^+ – Me – CH_2O), and 43 (100)] analyses. Attempted isolation by chromatography on silica gel was unsuccessful but not surprisingly so given the expected lability of the tetrasubstituted enol ether (cf. ref 10b).

(12) Yamashita, A. Eur. Pat. Appl. EP 146,348, 1985.

Pentacarbonyl(1-methoxy-3-methyl-2-butenylidene)chromium (2d):[13] ^{1}H NMR δ 7.27 (s, CH=C), 4.72 (s, Cr=COCH$_3$), 1.89 (s, CH$_3$), 1.86 (s, CH$_3$); ^{13}C NMR δ 338.9 (C=Cr), 224.0 (trans CO), 216.8 (cis CO's), 141.5 (*C*H=C), 140.1 (*C*=CH), 66.2 (OCH$_3$), 30.5 (CH$_3$), 20.0 (CH$_3$); IR 2070, 1940 (s) cm^{-1}.

Pentacarbonyl(1-propoxyethylidene)chromium (2e): ^{1}H NMR δ 4.86 (bs, OCH$_2$), 2.93 (s, Cr=CCH$_3$), 2.00 (m, C*H*$_2$CH$_3$), 1.10 (t, J = 7.1 Hz, CH$_2$C*H*$_3$); ^{13}C NMR δ 357.2 (C=Cr), 223.5 (trans CO), 216.4 (cis CO's), 83.4 (b, OCH$_2$), 49.9 (b, Cr=C*C*H$_3$), 22.8 (*C*H$_2$CH$_3$), 10.3 (CH$_2$*C*H$_3$); IR 2080, 1950 (s), 1270 cm^{-1}. Anal. Calcd for $C_{10}H_{10}O_6Cr$: C, 43.18; H, 3.62. Found: C, 42.91; H, 3.89.

Pentacarbonyl(1-butoxyethylidene)chromium (2f): ^{1}H NMR δ 4.90 (bs, OCH$_2$), 2.93 (s, Cr=CCH$_3$), 1.97 (m, C*H*$_2$CH$_2$CH$_3$), 1.54 (m, CH$_2$C*H*$_2$CH$_3$), 1.01 (t, J = 7.3 Hz, CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR δ 357.3 (C=Cr), 223.3 (trans CO), 216.6 (cis CO's), 81.9 (b, OCH$_2$), 49.9 (b, Cr=C*C*H$_3$), 31.3 (*C*H$_2$CH$_2$CH$_3$), 19.2 (CH$_2$*C*H$_2$CH$_3$), 13.7 (CH$_2$CH$_2$*C*H$_3$); IR 2050, 1940 (s), 1260 cm^{-1}. Anal. Calcd for $C_{11}H_{12}O_6Cr$: C, 45.20; H, 4.14. Found: C, 45.06; H, 4.13.

Pentacarbonyl[1-(methylethoxy)ethylidene]chromium (2g): ^{1}H NMR δ 5.82 (bs, OCH), 2.90 (s, Cr=CCH$_3$), 1.55 [d, J = 6.3 Hz, CH(C*H*$_3$)$_2$]; ^{13}C NMR δ 351.7 (C=Cr), 223.3 (trans CO), 216.4 (cis CO's), 87.2 (b, OCH), 50.2 (b, Cr=C*C*H$_3$), 22.4 [CH(*C*H$_3$)$_2$]; IR 2080, 1950 (s), 1270 cm^{-1}. Anal. Calcd for $C_{10}H_{10}O_6Cr$: C, 43.18; H, 3.62. Found: C, 43.18; H, 3.84.

Pentacarbonyl[1-(1-methylpropoxy)ethylidene]chromium (2h): ^{1}H NMR δ 5.55 (bs, OCH), 2.90 (s, Cr=CCH$_3$), 1.87 (m, C*H*$_2$CH$_3$), 1.49 (d, J = 5.8 Hz, CHC*H*$_3$), 1.00 (t, J = 7.4, Hz, CH$_2$C*H*$_3$); ^{13}C NMR δ 352.5 (C=Cr), 223.4 (trans CO), 216.6 (cis CO's), 91.7 (b, OCH), 50.4 (br, Cr=C*C*H$_3$), 29.5 (*C*H$_2$CH$_3$), 20.2 (CH*C*H$_3$), 9.3 (CH$_2$*C*H$_3$); IR 2070, 1940 (s), 1260 cm^{-1}. Anal. Calcd for $C_{11}H_{12}O_6Cr$: C, 45.20; H, 4.14. Found: C, 45.35; H, 4.34.

Pentacarbonyl[1-(dimethylethoxy)ethylidene]chromium (2i): ^{1}H NMR δ 3.20 (s, Cr=CCH$_3$), 1.67 [s, C(CH$_3$)$_3$]; ^{13}C NMR δ 353.3 (C=Cr), 224.3 (trans CO), 217.0 (cis CO's), 94.8 [*C*(CH$_3$)$_3$], 45.5 (Cr=C*C*H$_3$), 30.0 [C(*C*H$_3$)$_3$]; IR 2040, 1940 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{12}O_6Cr$: C, 45.20; H, 4.14. Found: C, 45.23; H, 3.99.

Pentacarbonyl[1-(5-hexenyloxy)ethylidene]chromium (2j): ^{1}H NMR δ 5.83 (ddt; J = 17.0, 10.3, and 6.6 Hz; CH$_2$C*H*=CH$_E$H$_Z$), 5.06 (bd, J = 17.0 Hz, CH$_2$CH=C*H*$_E$H$_Z$), 5.02 (bd, J = 10.3 Hz, CH$_2$CH=CH$_E$*H*$_Z$), 4.94 (bs, OCH$_2$), 2.95 (s, Cr=CCH$_3$), 2.17 (m, C*H*$_2$CH=CH$_E$H$_Z$), 2.01 (m, OCH$_2$C*H*$_2$CH$_2$), 1.64 (m, OCH$_2$CH$_2$C*H*$_2$); ^{13}C NMR δ 357.2 (Cr=C), 223.1 (trans CO), 216.3 (cis CO's), 137.7 (*C*H=CH$_2$), 115.1 (CH=*C*H$_2$), 82.2 (b, OCH$_2$), 49.9 (b, Cr=C*C*H$_3$), 33.0 (OCH$_2$CH$_2$CH$_2$*C*H$_2$), 28.6 (OCH$_2$CH$_2$CH$_2$*C*H$_2$), 24.9 (OCH$_2$CH$_2$*C*H$_2$CH$_2$), 13.9 (CH$_3$); IR 2064, 1942 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_6Cr$: C, 49.06; H, 4.43. Found: C, 49.35; H, 4.25.

Pentacarbonyl[1-(cyclopropylmethoxy)ethylidene]chromium (2k): ^{1}H NMR δ 4.74 (bs, OCH$_2$), 2.94 (s, Cr=CCH$_3$), 1.41 (m, CH), 0.76 (dd, J = 13.2 and 5.9 Hz, CH$_c$*H*$_t$), 0.47 (dd, J = 10.8 and 4.9 Hz, C*H*$_c$H$_t$); ^{13}C NMR δ 356.7 (C=Cr), 223.3 (trans CO), 216.4 (cis CO's), 86.6 (b, OCH$_2$), 49.8 (b, Cr=C*C*H$_3$), 10.2 (CH), 3.6 (CH$_2$); IR 2050, 1940 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{10}O_6Cr$: C, 45.53; H, 3.47. Found: C, 45.64; H, 3.52.

Pentacarbonyl[1-(2-propenyloxy)ethylidene]chromium (21):[5e] ^{1}H NMR δ 6.14 (bm, CH$_2$C*H*=CH$_E$H$_Z$), 5.55–5.42 (bd, J = 15.9 Hz, CH$_2$CH=C*H*$_E$H$_Z$; bd, J = 9.1 Hz, CH$_2$CH=CH$_E$*H*$_Z$; bs, OCH$_2$), 2.97 (Cr=CCH$_3$); ^{13}C NMR δ 358.7 (C=Cr), 223.3 (trans CO), 216.3 (cis CO's), 130.7 (*C*H=CH$_2$), 120.4 (CH=*C*H$_2$), 81.1 (b, OCH$_2$), 48.0 (b, Cr=C*C*H$_3$); IR 2030, 1945 (s), 1265 cm^{-1}. Although this complex was stable for short periods at −30 °C under N$_2$, it slowly decomposed at room temperature and acceptable elemental analysis could not be obtained.[5e]

Pentacarbonyl[1-(phenylmethoxy)ethylidene]chromium (2m):[14] ^{1}H NMR δ 7.45 (m, ArH), 5.92 (bs, CH$_2$), 2.99 (s, CH$_3$); ^{13}C NMR δ 358.2 (C=Cr), 224.2 (trans CO), 216.3 (cis CO's), 133.9, 129.2, 128.9, 128.3, 82.9 (CH$_2$), 49.5 (CH$_3$); IR 2050, 1940 (s), 1250 cm^{-1}.

Pentacarbonyl[1-(2-butynyloxy)ethylidene]chromium (2n): ^{1}H NMR δ 5.47 (bs, OCH$_2$), 3.00 (s, Cr=CCH$_3$), 1.92 (s, C≡CCH$_3$); ^{13}C NMR δ 359.6 (C=Cr), 223.3 (trans CO), 216.3 (cis CO's), 86.7 (CH$_2$*C*≡C), 71.7 (C≡*C*CH$_3$), 68.4 (b, OCH$_2$), 49.3 (b, Cr=*C*CH$_3$), 3.7 (C≡C*C*H$_3$); IR 2060, 1950 (s) cm^{-1}. Anal. Calcd for $C_{11}H_8O_6Cr$: C, 45.85; H, 2.80. Found: C, 45.91; H, 3.11.

Pentacarbonyl(1-ethoxypentylidene)tungsten (2o):[15] ^{1}H NMR δ 4.87 (q, J = 7 Hz, OC*H*$_2$CH$_3$), 3.18 (t, J = 7.2 Hz, =CC*H*$_2$), 1.60 (t, J = 7 Hz, OCH$_2$C*H*$_3$), 1.52 (m, CH$_2$C*H*$_2$CH$_2$), 1.35 (sex, J = 7.2 Hz, CH$_2$C*H*$_2$CH$_3$), 0.90 (t, J = 7.2 Hz, CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR δ 334.50 (C=W), 203.33 (trans CO), 197.38 (cis CO's), 80.61 (OCH$_2$), 64.82 (W=*C*CH2), 28.52, 22.34, 14.75, 13.89; IR 2069, 1921, 1284, 1254, 1031 cm^{-1}.

Pentacarbonyl{1-[[5-(2-propenyloxy)-3-pentynyl]oxy]ethylidene}chromium (8): ^{1}H NMR δ 5.91 (ddt; J = 16.6, 10.3, and 5.9 Hz; CH$_2$C*H*=CH$_E$H$_Z$), 5.30 (bdd, J = 17.1 and 1.4 Hz, CH$_2$CH=C*H*$_E$H$_Z$), 5.22 (bd, J = 10.3 Hz, CH$_2$CH=CH$_E$*H*$_Z$), 4.98 (bs, OCH$_2$), 4.15 (t, J = 2.0 Hz, OCH$_2$C≡C), 4.04 (d, C*H*$_2$CH=CH$_E$H$_Z$), 2.98 (Cr=CCH$_3$), 2.94 (t, J = 2.0 Hz, C≡CC*H*$_2$CH$_2$); ^{13}C NMR δ 359.3 (Cr=C), 223.0 (trans CO), 216.2 (cis CO's), 133.9 (*C*H=CH$_2$), 117.8 (CH=*C*H$_2$), 81.1 (C≡*C*), 78.7 (*C*≡C), 70.6 (OCH$_2$), 65.8 (OCH$_2$CH=CH$_2$), 62.3 (OCH$_2$≡C), 57.5 (Cr=CCH$_3$), 19.3 (C≡CCH$_2$CH$_2$); IR 2064, 1943 (s), 1250 cm^{-1}.

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