Rearrangement of Fischer Carbene Complexes to Ketones: Stereochemistry and Mechanism†

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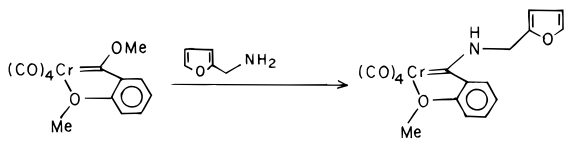
Fischer carbene complexes of general structure $(CO)_5M{=}C(Ar)(OCHRAr')$, where M = Cr or W and R = H or Me, rearrange to ketones, $ArC(O)CHRAr'Cr(CO)_3$ or ArC(O)CHRAr′ (for M = W), on heating. For M = W and Ar′ = 2-furyl, the rearrangement is the most facile. A probable mechanism is proposed. Rearrangement also occurs with $(CO)_5W{=}C(4\text{-}MeC_6H_4)(OCH_2CH{=}CMe_2)$ and $(CO)_5W{=}C(Ph)(OCH_2CH{=}CHPh)$; the ketones do not result from a [3,3]-sigmatropic shift alone. Excellent diastereoselectivity is observed with $(CO)_5Cr{=}C(Ph)\{OCH(Me)(C_6H_4\text{-}2\text{-}OMe)\}$; that the product obtained is a result of kinetic control is established by an equilibration experiment. The structure of this product was determined by X-ray crystallography.

Introduction

The chemistry of Fischer carbene complexes[1] relevant to organic synthesis is dominated by reactions of chromium complexes.[2] In comparison, use of tungsten complexes has been rather limited.[1d,3] The reason ascribed to this evident lack of popularity of the latter is the relatively high W−C bond strength,[4,5g] which does not permit ready decarbonylation. As a result, tungsten carbene complexes remain generally robust compounds which are easy to prepare, store, and handle but less useful in reactions like benzannulation.[5]

Scheme 1



However, intramolecular chelation has been shown to profoundly influence the kinetic barrier of decarbonylation[6] and thereby induce tungsten carbene complexes to take part in multistep annulation sequences.[1d]

Dötz reported[6b] an early example of competitive intramolecular chelation using a ((2-furylmethyl)amino)carbene complex of chromium. While the authors concluded that furan cannot displace an *o*-methoxy group for preferential chelation to the metal (Scheme 1), we surmised that, in the absence of competition, weak coordination by furan (either through oxygen or

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

(1) For reviews, see: (a) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 5. (b) Grotjahn, D. B.; Dötz, K. H. *Synlett* **1991**, 381. (c) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (d) Rudler, H.; Audouin, M.; Chelain, E.; Denise, B.; Goumont, R.; Massoud, A.; Parlier, A.; Pacreau, A.; Rudler, M.; Yefsah, R.; Alvarez, C.; Delgado-Reyes, F. *Chem. Soc. Rev.* **1991**, *20*, 503. (e) Hegedus, L. S. *Pure Appl. Chem.* **1990**, *62*, 691. (f) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L, S., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1. (g) Dötz, K. H. In *Organometallics in Organic Synthesis: Aspects of a Modern Interdisplinary Field*; tom Dieck, H., de Meijere, A., Eds.; Springer: Berlin, 1988. (h) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9. (i) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. (j) Semmelhack, M. F.; Bozell, J. J.; Keller, L.; Sato, T.; Spiess, E. J.; Wulff, W.; Zask, A. *Tetrahedron* **1985**, *41*, 5803. (k) Casey, C. P. *React. Intermed.* **1985**, *3*. (l) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (m) Dötz, K. H. *Pure Appl. Chem.* **1983**, *55*, 1689.

(2) (a) Tumer, S. U.; Herndon, J. W.; McMullen, L. A. *J. Am. Chem. Soc.* **1992**, *114*, 8394. (b) Harvey, D. F.; Lund, K. P.; Neil, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 8424. (c) Hegedus, L. S.; Bates, R. W.; Söderberg, B. C. *J. Am. Chem. Soc.* **1991**, *113*, 923. (d) Brandvold, T. A.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 5459. (e) Hegedus, L. S.; Schwindt, M. A.; De Lombaert, S.; Imwinkelried, R. *J. Am. Chem. Soc.* **1990**, *112*, 2264. (f) Söderberg, B. C.; Hegedus, L. S.; Sierra, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 4364. (g) Söderberg, B. C.; Hegedus, L. S. *Organometallics* **1990**, *9*, 3113. (h) Hoye, T. R.; Rehberg, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 2841. (i) Alvarez, C.; Parlier, A.; Rudler, H.; Yefsah, R.; Daran, J. C.; Knobler, C. *Organometallics* **1989**, *8*, 2253. (j) Herndon, J. W.; McMullen, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 6854. (k) Hoye, T. R.; Rehberg, G. M. *Organometallics* **1989**, *8*, 2070. (l) McCallum, J. S.; Kunng, F. A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346. (m) Dötz, K. H.; Kuhn, W.; Müller, G.; Huber, B.; Alt, H. G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 812. (n) Hegedus, L. S.; Schultze, L. M.; Toro, J.; Yijun, C. *Tetrahedron* **1985**, *41*, 5838. (o) Wulff, W. D.; Kaesler, R. W. *Organometallics* **1985**, *4*, 1461.

(3) (a) Wulff, W. D.; Bax, B. M.; Brandvold, T. A.; Chan, K. S.; Gilbert, A. M.; Hsung, R. P.; Mitchell, J.; Clardy, J. *Organometallics* **1994**, *13*, 102. (b) Herndon, J. W.; Chatterjee, G.; Patel, P. P.; Matasi, J. J.; Tumer, S. U.; Harp, J. J.; Reid, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 7808. (c) Fischer, H.; Hofmann, J.; Mauz, E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 998. (d) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737. (e) Casey, C. P.; Shusterman, A. J. *Organometallics* **1985**, *4*, 736. (f) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 3754. (g) Macomber, D. W. *Organometallics* **1984**, *3*, 1589. (h) Toledano, C. A.; Rudler, H.; Daran, J. C.; Geannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 574.

(4) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71.

(5) (a) Dragisich, V.; Murray, C. K.; Warner, B. P.; Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 1251. (b) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. (c) Dötz, K. H.; Popall, M. *Tetrahedron* **1985**, *41*, 5797. (d) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7565. (e) Wulff, W. D.; Tang, P. C. *J. Am. Chem. Soc.* **1984**, *106*, 1132. (f) Dötz, K. H.; Kuhn, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 732. (g) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064.

(6) (a) Dötz, K. H.; Rau, A.; Harms, K. *Chem. Ber.* **1992**, *125*, 2137. (b) Dötz, K. H.; Popall, M.; Muller, G. *J. Organomet. Chem.* **1987**, *334*, 57. For a study of insertion of CO in relation to intramolecular chelation, see: (c) Bos, M. E.; Wulff, W. D.; Miller, R. A.; Chamberlin, S.; Brandvold, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 9393.

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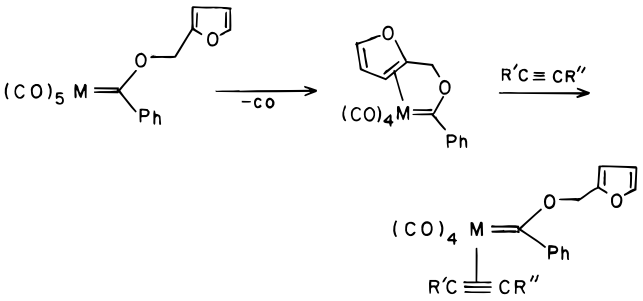
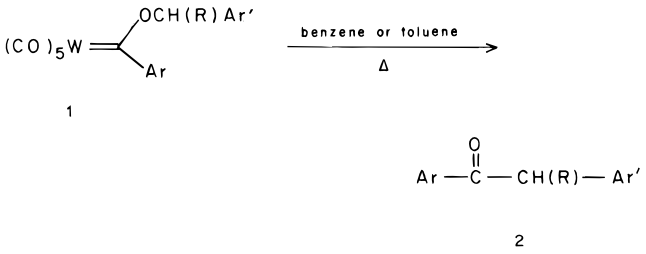
Scheme 2



Scheme 3



the relatively localized double bond of the ring) leading to a chelate was still a possibility (Scheme 2) and decarbonylation from a tungsten carbene complex should be facile in such a case.

To verify this facility of decarbonylation of tungsten carbene complexes, [phenyl((2-furylmethyl)oxy)carbene]-tungsten complex **1a** was prepared and heated in benzene under reflux. Instead of formation of the desired, intramolecularly chelated intermediate where furan stabilizes a 16e complex by coordination, a facile rearrangement of the organic ligand to a ketone was observed.

There are three independent reports in the literature where rearrangement of Fischer carbene complexes to ketones or related products is described. Fischer and Schubert reported[7a] the singular example of thermal rearrangement of a (pentafluorophenyl)ethoxycarbene complex of iron(0) to C_6F_5COEt in the presence of triphenylphosphine, while the normal products of thermolysis of group VI metal carbene complexes were known to be enol ethers or dimers of the carbene ligand. The rearrangement of a (triphenylsilyl)ethoxycarbene complex of chromium to the acylsilane derivative, as described later by Schubert,[7b] is a related instance where the C−Si bond was thought to be a crucial factor in such a transformation. Casey[3d] observed the rearrangement of a [*p*-toly(allyloxy)carbene]tungsten complex to *p*-tolyl allyl ketone.

In this paper, we present a detailed account of the rearrangement observed for aryl((arylalkyl)oxy)carbene complexes of chromium and tungsten to ketones.[7c] We have established that the rearrangement is fairly general, provided certain structural criteria of the carbene complexes are met. A probable mechanism has also been suggested to account for various experimental observations.

Results and Discussion

Preparation of the Complexes. The carbene complexes were prepared by the usual method *via* tetraethylammonium acylates, acetyl chloride, and alcohols.[8] They were completely characterized by infrared and ^1H and ^{13}C NMR spectroscopy. Most of the tungsten complexes were stable, red, crystalline solids for which satisfactory elemental analyses were obtained. However, the cinnamyloxy complex **11b** of tungsten was a liquid, as were a number of chromium carbene complexes, many of which did not provide satisfactory microanalytical data,[9] although their NMR spectra showed absence of impurities.

Thermolysis of Tungsten Complexes. The (2-furylmethyl)oxy complexes **1a**−**d** were heated in benzene under reflux for 2−10 h (Scheme 3). Progress of the reaction was monitored by TLC, and the reaction was terminated when the starting material completely disappeared. The products were isolated after evaporation of the solvent under reduced pressure followed by column chromatography of the residue (Table 1). The presence of a ketone was evident from the IR spectrum. The ^1H NMR spectra of these compounds could be readily related to their structures. The methylene signal appeared as a singlet at 4.20 ppm, shielded compared to the methylene protons of 2-furylmethyl benzoate (prepared independently), which resonates at 5.24 ppm. The molecular ion peak in the mass spectra further corroborated the structures for representative members of the series.

The (benzyloxy)carbene complexes **1e**−**g** did not rearrange readily in refluxing benzene. Rearrangement proceeded cleanly when the carbene complexes were heated in toluene under reflux for 1.5−3.0 h. Identification of the products was straightforward. Even ((α-methylbenzyl)oxy)carbene complex **1h** yielded the expected ketone in 2 h.

Thermolysis of Chromium Complexes. When chromium complexes **3a**−**h** were heated in benzene at 82−85 °C (bath temperature) for 1.5−5 h, rearrangement occurred to afford the set of (arene)chromium complexes **4a**−**h**, the aromatic ring of the oxygen substituent being complexed with the $Cr(CO)_3$ group (Scheme 4). Generally, these are yellow, crystalline solids, easily obtained in the pure state by flash chromatography. A certain degree of decomplexation (<10%) was also observed during the reaction. The yields, however, are based on isolated (arene)chromium complexes (Table 2).

The structures of these complexes were established from their spectroscopic and analytical data. The aromatic protons of the complexed ring appeared typically between 5.00 and 6.00 ppm, and the methylene protons appeared at 4.00−4.70 ppm.

Diastereoselectivity in Rearrangement of Chromium Complexes. Formation of (arene)chromium complexes as products of rearrangement prompted an examination of the diastereoselectivity of the process. A methyl substituent at the benzylic position and an unsymmetrically placed substituent on the adjacent

(7) (a) Fischer, E. O.; Schubert, U. *J. Organomet. Chem.* **1979**, *170*, C13. (b) Schubert, U.; Hörnig, H. *J. Organomet. Chem.* **1984**, *273*, C11. (c) A preliminary account of this work has been published: Nandi, M.; Sathe, K. M.; Sarkar, A. *J. Chem. Soc., Chem. Commun.* **1992**, 793. Part of this work is included in the Ph.D. theses of K.M.S. and M.N. submitted to the University of Poona.

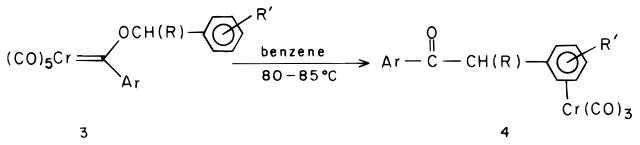
(8) (a) Connor, J. A.; Jones, E. M. *J. Chem. Soc. A* **1971**, 3368. (b) Connor, J. A.; Jones, E. M. *J. Chem. Soc. D* **1971**, 570.

(9) Complexes prone to low-energy decomposition often fail to provide accurate analytical data; for example, see: Söderberg, B. C.; Hegedus, L. S. *Organometallics* **1990**, *9*, 3113.

Table 1. Rearrangement of Tungsten Carbene Complexes 1a−h

entry no.	carbene complex	ketone	Ar	R	Ar′	solvent	time (h)	yield (%)
1	**1a**	**2a**	Ph	H	2-furyl	benzene	2	90
2	**1b**	**2b**	4-MeC_6H_4	H	2-furyl	benzene	3.5	65
3	**1c**	**2c**	4-OMeC_6H_4	H	2-furyl	benzene	10	50
4	**1d**	**2d**	2-OMeC_6H_4	H	2-furyl	benzene	10	63
5	**1e**	**2e**	Ph	H	Ph	toluene	2	56
6	**1f**	**2f**	Ph	H	4-OMeC_6H_4	toluene	2	56
7	**1g**	**2g**	2-OMeC_6H_4	H	4-OMeC_6H_4	toluene	3	57
8	**1h**	**2h**	Ph	CH_3	Ph	toluene	1.5	43

Scheme 4



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Scheme 5

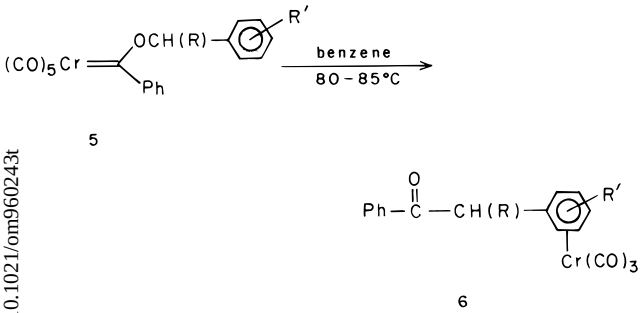

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Table 2. Rearrangement of Chromium Carbene Complexes 3a−h

entry no.	carbene complex	(arene)Cr	Ar	R	R′	time (h)	yield (%)
1	**3a**	**4a**	Ph	H	H	5	68
2	**3b**	**4b**	Ph	H	2-Me	3	47
3	**3c**	**4c**	Ph	H	3-Me	3	46
4	**3d**	**4d**	Ph	Me	H	3.5	43
5	**3e**	**4e**	Ph	H	4-OMe	1.5	77
6	**3f**	**4f**	Ph	H	2-OMe	3	50
7	**3g**	**4g**	4-OMeC_6H_4	H	H	4	27
8	**3h**	**4h**	4-ClC_6H_4	H	H	4	44

Table 3. Diastereoselectivity of Chromium Carbene Complexes 5a−d

entry no.	carbene complex	(arene)Cr	R	R′	time (h)	ratio	yield (%)
1	**5a**	**6a**	Me	2-Me	3.5	7:3	33
2	**5b**	**6b**	Me	2-OMe	3	single	48
3	**5c**	**6c**	Me	3-Me	3	1:1	45
4	**5d**	**6d**	Me	3-OMe	3.5	1:1	44

aromatic ring would generate two stereogenic elements in the product and therefore two pairs of diastereomers are possible. Thermolysis was carried out at 82−85 °C for all the substrates (Scheme 5, Table 3).

When the carbene complex **5b** was subjected to thermal rearrangement in benzene, the product complex was **6b**, isolated as a yellow solid. Care was taken to collect the colored band completely so as to minimize chance enrichment of one isomer. The 200 MHz ^{1}H NMR spectrum of **6b** showed peaks due to a single isomer (Figure 1a). In addition, there was no indication of the presence of a second isomer **6b′** evident from the ^{13}C NMR spectrum. In order to obtain the other isomer, base-induced equilibration using KF/18-crown-6 (catalytic) in nitromethane was carried out at room temperature for 4 days (the isomer ratio remained unchanged after this, as seen from the ^{1}H NMR spectra). After workup and purification by column chromatography, an 85% yield of a mixture of diastereoisomers was obtained. The diastereomeric mixture of **6b** and **6b′** could not be separated into pure isomers by chromatography, and the isomerism was further confirmed from their nearly identical ^{13}C spectra. The most deshielded proton of the complexed ring produced two sets of clearly resolved doublets of unequal intensity due to two isomers (Figure 1b), which could be used to determine the relative isomer ratio. When the mixture was spiked with the starting isomer obtained previously, the smaller peak gained in intensity (Figure 1c). This observation indicated that the isomer obtained from the rearrangement was the kinetic product. It also corroborated that the thermodynamically preferred isomer was practically absent in the original rearrangement product.

To ascertain the relative stereochemistry of different groups in the complex **6b**, a single-crystal X-ray structure determination was undertaken. The structure of the complex is depicted in Figure 2, and the crystallographic data are listed in Table 4.

As anticipated, the diastereoselectivity was governed by steric factors in the transition state, and it diminished to zero for *meta* substitution in the aromatic ring of the alkoxy moiety (see entries 3 and 4, Table 3). Even the *o*-methyl group provided inferior diastereoselectivity (entry 1, Table 3). It was also found that the diastereoselectivity was sensitive to reaction temperature. For instance, for the complex **6b**, the diastereomeric excess was reduced from >98% to 50% when the bath temperature was raised from 82 to 95 °C. That such reduction of diastereoselectivity could arise partly from intermolecular acid−base equilibria between two diastereomers was implied by the accidental observation described below.

When the complex **6a** (diastereomeric ratio 3:7) was mixed with an equimolar amount of the complex **4b** and heated in benzene at 82 °C for 3 h, the diastereomeric ratio of **6a** dramatically changed to 97:3 (the minor isomer became major and vice versa), as shown in Figure 3. The diastereomeric ratio remained unchanged when the complex **6a** was heated for the same period in the absence of **4b**. Similarly, the complexes **6d** (diastereomeric ratio 1:1) and **4b** created a diastereomeric enrichment of 4:1 in the complex **6d** (Figure 4). It appears that a properly "matched" pair could produce substantial diastereoselectivity in acid−base equilibria, though no obvious structural correlation between the partners could be drawn.

Mechanism of the Rearrangement. At first glance, it may appear that the product is derived from rearrangement of the free organic carbene ligand.[10] How-

(10) (a) Foster, A. M.; Agosta, W. C. *J. Am. Chem. Soc.* **1972**, *94*, 5777. (b) Agosta, W. C.; Foster, A. M. *J. Chem. Soc. D* **1971**, 433.
(11) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895.

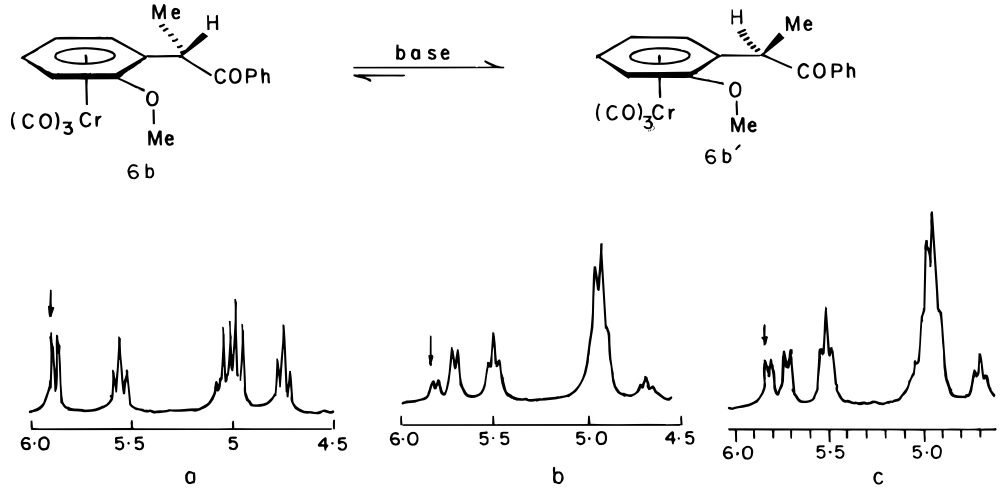


Figure 1. ^{1}H NMR spectra: (a) pure isomer **6b**; (b) mixture after equilibration (**6b** and **6b′**); (c) mixture after spiking the equilibrated mixture with pure isomer **6b**.

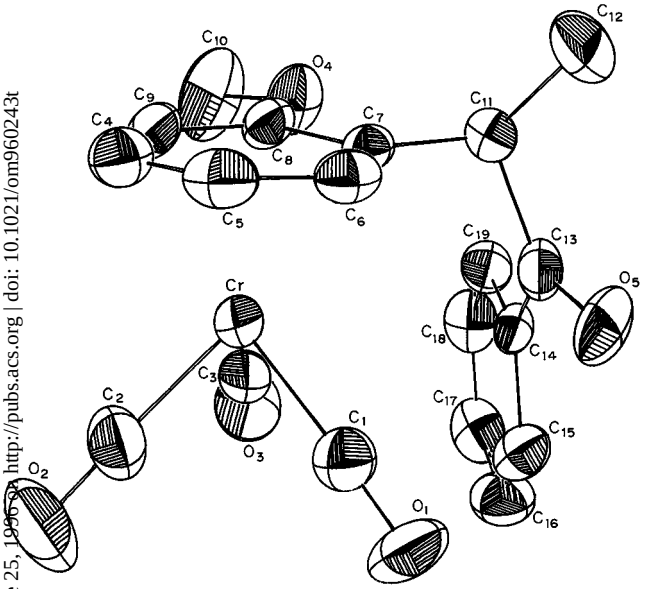


Figure 2. ORTEP diagram of complex **6b**. Important bond distances (Å): Cr−C(4), 2.210(6); Cr−C(5), 2.220(5); Cr−C(6), 2.205(5); Cr−C(7), 2.276(5); Cr−C(8), 2.302(5); Cr−C(9), 2.235(5); O(5)−C(13), 1.221(7); C(11)−C(12), 1.538(8).

Table 4. X-ray Crystallographic Data and Structure Refinement of Complex 6b

formula	$C_{19}H_{16}O_5Cr$
fw	376.32
cryst syst	orthorhombic
space group	*Pcab*
a (Å)	9.112(2)
b (Å)	18.217(2)
c (Å)	20.433(1)
V (Å^3)	3391.7(4)
Z	8
D_{calcd} (g cm^{-3})	1.474
μ (mm^{-1})	0.34
F(000)	776
radiation	Mo Kα (λ = 0.7107 Å)
cryst size (mm)	0.3 × 0.3 × 0.5
temp (K)	298
scan type	$\omega/2\theta$
scan width (deg)	0.80 + 0.35 tan θ
2θ range (deg)	3−47
no. of rflns collected	2510
no. of rflns obsd ($I \geq 2.5\sigma(I)$)	1569
no. of params varied	226
GOF	0.66
R	0.042
R_w	0.046

ever, the total lack of precedents concerning generation of free carbene from such complexes[11] calls for a mechanism where metal plays a vital role.

All experiments suggested that the initial CO loss could be the rate-determining step. The chromium carbene complexes **3a**−**h** rearrange in refluxing benzene, while the analogous tungsten complexes **1e**−**h** require heating in refluxing toluene, a trend consistent with the relative strengths of Cr−CO and W−CO bonds.[4,5g] For instance, a *p*-methoxy group on the aromatic ring attached to the carbene carbon would impede the rearrangement (compare entries 1 and 3 in Table 1). The 2-thienylcarbene complex **10** (Chart 1) failed to undergo the rearrangement, consistent with its electron-rich character (^{13}C NMR signal of a shielded carbene carbon at 317.07 ppm), and it was recovered (87%) after heating in benzene for 6 h. Once a CO ligand is dissociated by photolysis, the rearrangement proceeds even at room temperature. For instance, from the complex **1a**, the rearranged product **2a** was obtained in 57% isolated yield after irradiation at 300 nm for 10 h at room temperature. This experiment lends further credence to the suggestion that CO dissociation is the rate-determining step, and the rearrangement proceeds spontaneously thereafter.

If the aromatic ring attached to the carbene carbon contains an *o*-methoxy group as in the tungsten complex **1g** (Scheme 6), the 16e intermediate initially formed after the CO loss can be trapped as the 18e intramolecular chelate **7** under relatively mild conditions. The structure of this complex was deduced from its typical spectral features. The deshielded signal of the metal-coordinated methoxy group (3.80 ppm in starting material, 4.64 ppm after chelation) was diagnostic. When this intermediate was heated in refluxing toluene, the rearranged product **2g** was obtained.

At this point, the issue of possible intramolecular coordination by furan may be addressed. We observed that tungsten ((2-furylmethyl)oxy) complexes **1a**−**d** rearranged readily in refluxing benzene while the corresponding benzyloxy complexes **1e**−**h** had to be heated in refluxing toluene for the rearrangement to occur. We also noted that the complex **1d** did not provide a stable chelated compound like the complex **1g**

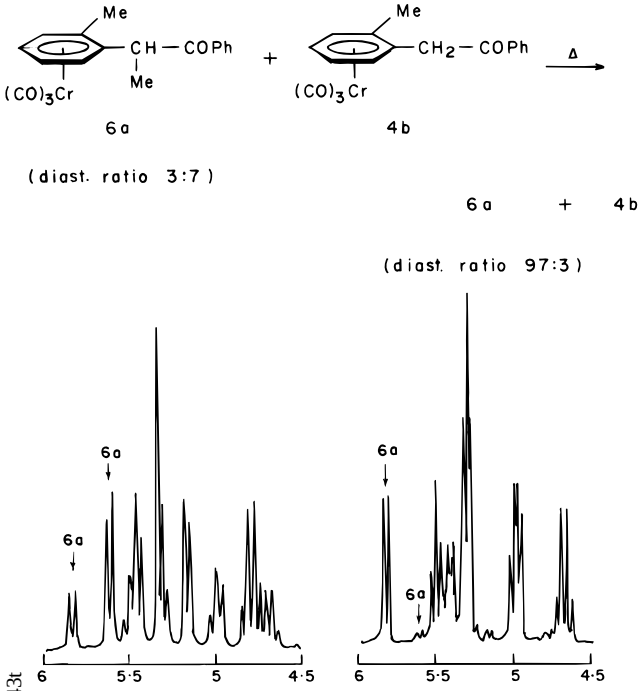


Figure 3.

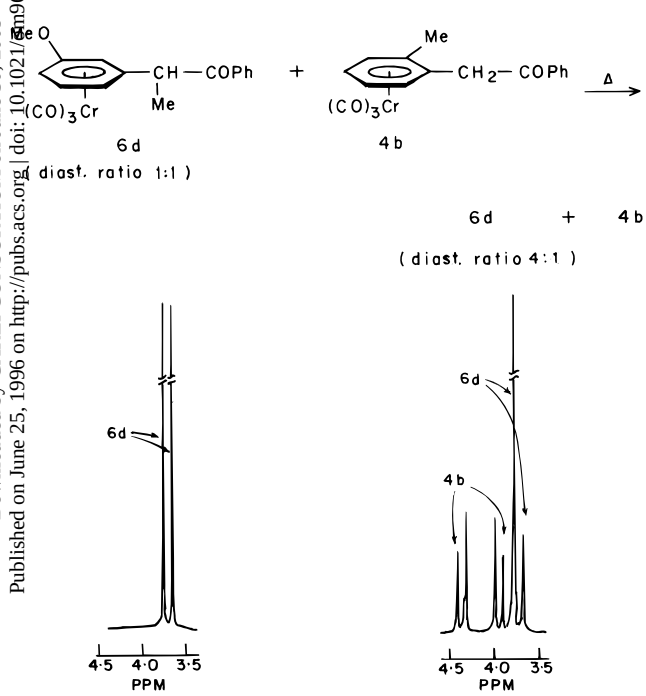


Figure 4.

on warming in benzene (a spot probably due to such a complex could be seen on TLC, but it eluded all attempts at isolation), and the rearrangement proceeded concurrently at a comparable rate. These facts do suggest possible coordination by furan being responsible for lowering the activation energy associated with initial decarbonylation. Unlike benzene, furan can coordinate either through oxygen or its relatively localized double bond. While it may make coordination more efficient, the chelated complex remained thermally unstable.[12] This augments our initial assessment of furan as a ligand, but the initial objective to use it to advantage in annulation reactions remained unattained. It is not clear how the benzenoid aromatic ring favors initial decarbonylation, which it surely does, a fact strongly suggested by the observation that the (phenylethoxycarbene)tungsten complex **8** (Chart 1) remained unchanged under prolonged reflux (>24 h) in toluene. This last experiment also suggests that the mechanism of rearrangement in the case of the iron carbene complex

(12) No intermediate was observed when the carbene complex **1a** was heated in C_6D_6 in the NMR probe at 50 °C. Only the peaks due to the starting material gradually disappeared and those of the product gained in intensity.

Chart 1

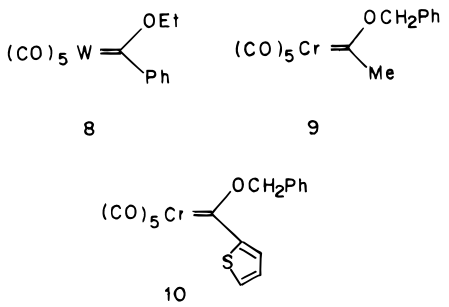
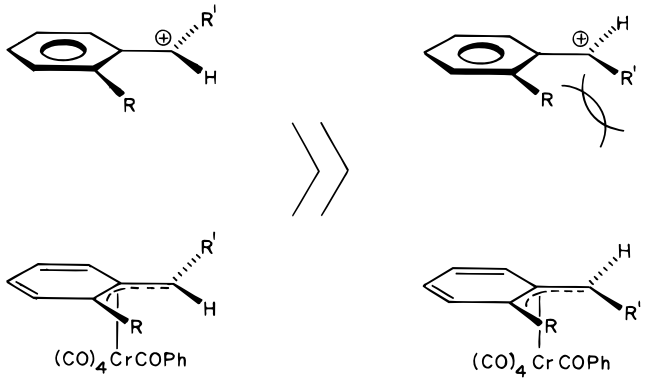
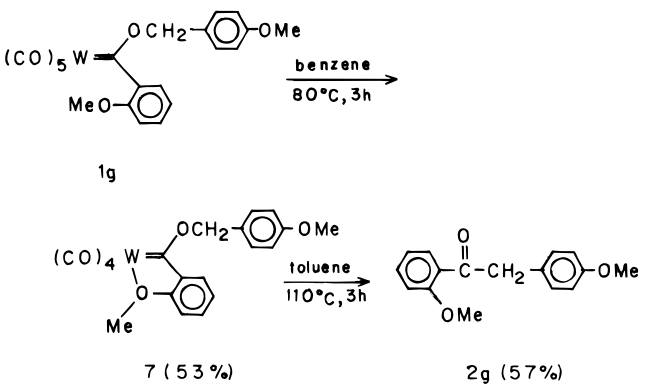


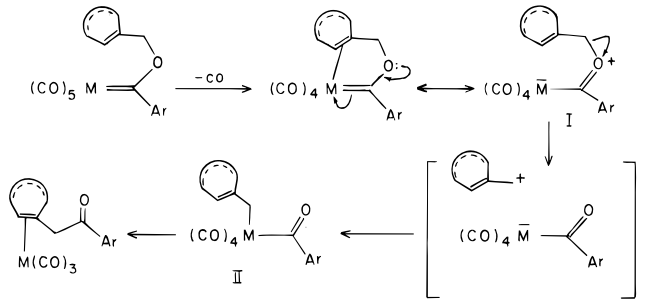
Chart 2



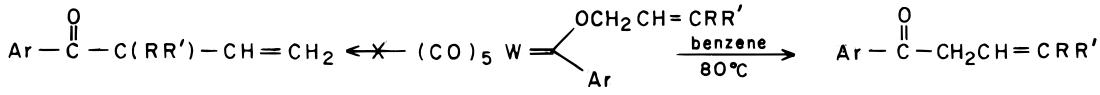
Scheme 6



Scheme 7



Scheme 8



11 12

	Ar	R	R′	time (h)	yield (%)
a:	4-MeC$_6$H$_4$	Me	Me	1·5	91
b:	Ph	H	Ph	1	34

reported by Fischer[7a] might be different from the present one.

After the loss of a CO ligand, a 16e complex would be generated, for which a canonical form **I** showing electronic polarization may be written (Scheme 7). Bond reorganization leads to the benzylacylmetal intermediate **II** which, on reductive elimination, affords the ketone.

The rearrangement proceeds with (aryl(alkylox))carbene complexes, and a benzylic carbocation seems relevant as an intermediate. A (*p*-methoxybenzyl)oxy group facilitates rearrangement, presumably by stabilizing the developing benzylic carbocation (see entries 4 and 5 in Table 2).

In this context it should also be mentioned that the methylcarbene complex of chromium **9** (Chart 1) does not undergo such a rearrangement. This is in keeping with known reactivity differences between alkyl- and arylcarbene complexes.[2f,g]

It may appear from the rearrangement step (**I** to **II**, Scheme 7) that a tight ion pair may be involved, and the configuration of a chiral center would be retained. However, an experiment with the optically pure substrate (−)-**3d** led to complete racemization, in contrast with expectation.

The results with chromium carbene complexes **5a**−**d** revealed that the extent of diastereoselectivity depended on the location of the substituent on the aromatic ring of the benzyloxy group (Table 3).

The X-ray crystal structure of the complex **6b**, which was shown to be the kinetic product, reveals that the 4-methoxy substituent on the aromatic ring and the methyl group on the benzylic carbon are oriented away from each other. This could be a reflection of relative stabilities of two possible conformations of the intermediate benzylic cation or an η^3-benzyl complex (Chart 2). Such a difference in stability is not significant for *meta*-substituted aromatic rings, which would explain the lack of diastereoselectivity for these substrates (**5c** and **5d**).[13]

Both intramolecular chelation to assist decarbonylation and stabilization of adjacent carbocationic centers are possible by an allylic group. Casey[3d] reported that a [(*p*-tolyl(allyloxy))carbene]tungsten complex thermally rearranged to *p*-tolyl allyl ketone. This reaction (which is thematically related to the present rearrangement) could have proceeded via a [3,3]-sigmatropic shift involving the allyl group and the metal−carbon double bond,[14] followed by reductive elimination. Rearrangement of (prenyloxy)- and (cinnamyloxy)carbene complexes (**11a** and **11b**, respectively) was carried out to obtain direct evidence for the [3,3]-sigmatropic shift prior to reductive elimination (Scheme 8). The result was not consistent with a [3,3]-shift unless an (η^3-allyl)metal intermediate is postulated.

The absence of regioisomeric products in these reactions, however, raises questions regarding the intermediacy of an (η^3-allyl)metal intermediate. In that case one can only contend that the reductive-elimination step is preceded by an $\eta^3-\eta^1$ slippage favoring a sterically less encumbered metal−carbon bond.

Conclusion

A thermal rearrangement of aryl((arylmethyl)oxy)carbene complexes of chromium and tungsten to ketones has been described in detail. Analogous rearrangement has been found to be general with aryl(allyloxy)carbene complexes as well, where the product structures rule out a straightforward [3,3]-sigmatropic shift during the rearrangement. With appropriate chromium carbene complexes, a high degree of diastereoselectivity could be achieved, where the major diastereomer was characterized by crystal structure determination and was shown to be the kinetic product. A mechanism has been proposed to account for the experimental observations. The results suggest that a relatively electron-deficient carbene carbon promotes the rearrangement, as does a benzyloxy or allyloxy group which can stabilize a developing carbocation. In short, electron tuning on the carbene ligand substituents can profoundly influence the reactivity of the complex.

Experimental Section

All reactions were performed under an inert atmosphere of argon. Solvents were dried using standard procedures and distilled under an inert atmosphere prior to use. Infrared spectra were obtained on a Perkin-Elmer 599B spectrometer as chloroform solutions. The ^{1}H NMR spectra were recorded on Varian FT-80A, Bruker WH-90, or Bruker AC-200 spectrometers, whereas ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer at 50.3 MHz using $CDCl_3$ as the solvent and reported as parts per million downfield of tetramethylsilane. Elemental analyses of solid compounds were carried out on a Carlo-Erba 1100 automatic analyzer by Dr. S. Y. Kulkarni and his group at NCL. The liquid samples did not give satisfactory elemental analyses. Melting points on the Celsius scale were determined in open capillary tubes on a Thermonik Campbell melting point apparatus and are uncorrected. All carbene complexes undergo rearrangement

(13) If the steric interaction between the benzylic and the *ortho* substituent alone determines the relative stereochemistry of the kinetic product, the role of the metal in deciding stereoselection cannot be crucial. Though this could suggest the intermediacy of an alternative structure other than **II** (Scheme 7) to produce the rearranged product, such a structure is not immediately apparent.

(14) Christoffers, J.; Dötz, K. H. *Organometallics* **1994**, *13*, 4189. See also ref 2j.

in the range of their melting points (70−110 °C) and could not be recorded.

The carbene complexes were prepared essentially by following a reported procedure.[8] All reagents were purchased from Aldrich and used as received.

General Procedure for the Preparation of Carbene Complexes. To a solution of tetraethylammonium pentacarbonyl[1-oxyalkylidene]metalate(0) (*n* mmol) in dichloromethane (5*n* mL) was added dropwise freshly distilled acetyl chloride (1.2*n* mmol) at −40 °C. After the mixture was stirred for 1 h, the alcohol (1.2*n* mmol) was added dropwise at −40 °C and the reaction mixture was stirred at −20 °C for 2 h and then at 0 °C for 2−3 h. The solvent was evaporated under reduced pressure. The residue was extracted in petroleum ether, and the combined extracts were concentrated under reduced pressure. The residue was flash-chromatographed using 10% dichloromethane/90% petroleum ether as the eluant.

Complex 1a: red solid; IR 2040 (m), 1990 (sh), 1940 (s) cm^{-1}. ^1H NMR: δ 5.88 (s, 2H); 6.32−6.45 (m, 1H); 6.55−6.66 (m, 1H); 7.20−7.65 (m, 6H). ^{13}C NMR: δ 77.29; 111.18; 112.39; 126.51; 128.35; 131.90; 144.59; 148.04; 155.72; 197.44; 202.62; 320.48. Anal. Calcd for $C_{17}H_{10}O_7W$: C, 40.00; H, 1.96. Found: C, 40.85; H, 2.23.

Complex 1b: red solid; IR 2040 (m), 1985 (sh), 1940 (s) cm^{-1}. ^1H NMR: δ 2.33 (s, 3H); 5.91 (s, 2H); 6.35−6.48 (m, 2H); 6.74−6.82 (m, 1H); 7.15 (d, J = 8 Hz, 2H); 7.55 (d, J = 8 Hz, 2H). ^{13}C NMR: δ 21.76; 77.35; 111.12; 112.32; 128.29; 129.03; 143.82; 144.50; 148.04; 152.46; 197.62; 203.49; 317.26. Anal. Calcd for $C_{18}H_{12}O_7W$: C, 41.22; H, 2.29. Found: C, 41.12; H, 2.01.

Complex 1c: red solid; IR 2040 (m), 1980 (sh), 1935 (s) cm^{-1}. ^1H NMR: δ 3.82 (s, 3H); 5.88 (s, 2H); 6.33−6.50 (m, 1H); 6.53−6.61 (m, 1H); 6.82 (d, J = 9 Hz, 2H); 7.41−7.53 (m, 1H); 7.80 (d, J = 9 Hz, 2H). ^{13}C NMR: δ 55.74; 77.23; 111.06; 112.11; 113.57; 124.68; 132.58; 144.41; 148.19; 164.32; 197.80; 203.08; 312.93. Anal. Calcd for $C_{18}H_{12}O_8W$: C, 40.00; H, 2.22. Found: C, 39.18; H, 2.77.

Complex 1d: red solid; IR 2040 (m), 2000 (sh), 1950 (s) cm^{-1}. ^1H NMR: δ 3.87 (s, 3H); 5.50 (b, 2H); 6.41−6.47 (m, 1H); 6.52−6.60 (m, 1H); 6.78−7.05 (m, 3H); 7.22−7.38 (m, 1H); 7.50−7.55 (m, 1H). ^{13}C NMR: δ 55.63; 74.71; 111.08; 111.37; 112.19; 120.45; 122.39; 130.19; 144.27; 148.00; 150.20; 197.34; 205.78; 325.21. Anal. Calcd for $C_{18}H_{12}O_8W$: C, 40.00; H, 2.22. Found: C, 40.10; H, 2.43.

Complex 1e: red solid; IR 2035 (m), 1980 (sh), 1930 (s) cm^{-1}. ^1H NMR: δ 5.97 (s, 2H); 7.15−7.72 (m, 10H). ^{13}C NMR: δ 86.09; 126.94; 128.45; 128.84; 129.32; 129.54; 132.13; 134.51; 155.47; 197.64; 203.85; 320.18. Anal. Calcd for $C_{19}H_{12}O_6W$: C, 43.85; H, 2.31. Found: C, 44.12; H, 2.60.

Complex 1f: red solid; IR 2030 (m), 1970 (sh), 1930 (s) cm^{-1}. ^1H NMR: δ 3.82 (s, 3H); 5.88 (s, 2H); 6.95 (d, J = 9 Hz, 2H); 7.22−7.68 (m, 7H). ^{13}C NMR: 55.54; 86.20; 114.71; 126.45; 126.69; 128.30; 130.58; 131.89; 150.48; 160.79; 197.65; 203.81; 319.77. Anal. Calcd for $C_{20}H_{14}O_7W$: C, 43.64; H, 2.54. Found: C, 44.17; H, 2.98.

Complex 1g: red solid; IR 2030 (m), 1990 (sh), 1940 (s) cm^{-1}. ^1H NMR: δ 3.80 (s, 3H); 3.82 (s, 3H); 5.50 (b, 2H); 6.78−7.10 (m, 5H); 7.16−7.41 (m, 3H). ^{13}C NMR: δ 55.51; 83.48; 111.28; 114.38; 120.39; 122.15; 126.56; 130.00; 130.20; 150.11; 160.43; 197.49; 205.88; 325.17. Anal. Calcd for $C_{21}H_{16}O_8W$: C, 43.45; H, 2.76. Found: C, 43.37; H, 3.21.

Complex 1h: red solid; IR 2082 (m), 1985 (sh), 1915 (s) cm^{-1}. ^1H NMR: δ 1.90 (d, J = 7 Hz, 3H); 6.65 (q, J = 7 Hz, 1H); 7.30 (s, 10H). ^{13}C NMR: δ 23.81; 92.74; 125.97; 126.47; 128.32; 129.04; 131.52; 139.56; 155.97; 197.40; 203.90; 318.30. Anal. Calcd for $C_{20}H_{14}O_6W$: C, 44.94; H, 2.62. Found: C, 44.75; H, 2.86.

Complex 3a: red solid; IR 2060 (m), 1990 (sh), 1950 (s) cm^{-1}. ^1H NMR: δ 5.77 (s, 2H); 7.15−7.44 (m, 10H). ^{13}C NMR: δ 82.11; 122.40; 128.15; 128.87; 129.88; 134.43; 153.46; 216.10; 224.21; 350.40. Anal. Calcd for $C_{19}H_{12}O_6Cr$: C, 58.76; H, 3.09. Found: C, 58.71; H, 3.00.

Complex 3b: red oil; IR 2060 (m), 1980 (sh), 1950 (s) cm^{-1}. ^1H NMR: δ 2.45 (s, 3H); 5.85 (s, 2H); 7.20−7.50 (m, 9H). ^{13}C NMR: δ 18.86; 81.04; 122.29; 126.24; 128.12; 129.41; 129.82; 130.64; 132.42; 137.14; 153.48; 216.06; 224.12; 350.12.

Complex 3c: red oil; IR 2060 (m), 1980 (sh), 1950 (s) cm^{-1}. ^1H NMR: δ 2.35 (s, 3H); 4.75 (s, 2H); 7.00−7.50 (m, 9H). ^{13}C NMR: δ 21.49; 82.66; 122.95; 125.43; 128.39; 129.06; 130.04; 130.29; 134.47; 138.89; 153.62; 216.42; 224.52; 349.81.

Complex 3d: red oil; IR 2060 (m), 1990 (sh), 1940 (s) cm^{-1}. ^1H NMR: δ 1.80 (d, J = 7 Hz, 3H); 6.06 (q, J = 7 Hz, 1H); 7.24−7.40 (m, 10H). ^{13}C NMR: δ 23.73; 88.84; 121.04; 125.80; 128.03; 128.52; 128.76; 129.03; 140.16; 153.02; 215.96; 224.54; 349.32.

Complex 3e: red solid; IR 2050 (m), 1970 (sh), 1950 (s) cm^{-1}. ^1H NMR: δ 3.90 (s, 3H); 5.80 (s, 2H); 7.00 (d, J = 8 Hz, 2H); 7.25−7.50 (m, 7H). ^{13}C NMR: δ 55.39; 82.68; 114.45; 122.92; 126.47; 128.32; 130.25; 153.59; 160.48; 216.37; 224.46; 349.20. Anal. Calcd for $C_{20}H_{14}O_7Cr$: C, 57.42; H, 3.35. Found: C, 57.65; H, 3.52.

Complex 3f: red solid; IR 2050 (m), 1990 (sh), 1950 (s) cm^{-1}. ^1H NMR: δ 3.80 (s, 3H); 5.90 (s, 2H); 6.90−7.50 (m, 9H). ^{13}C NMR: δ 55.21; 78.86; 110.57; 120.47; 122.52; 127.98; 129.74; 130.32; 130.74; 153.59; 157.87; 216.10; 224.34; 348.98. Anal. Calcd for $C_{20}H_{14}O_7Cr$: C, 57.42; H, 3.35. Found: C, 57.91; H, 3.34.

Complex 3g: red oil; IR 2040 (m), 1990 (sh), 1940 (s) cm^{-1}. ^1H NMR: δ 3.85 (s, 3H); 6.00 (s, 2H); 6.80 (d, J = 8 Hz, 2H); 7.50 (s, 5H); 7.75 (d, J = 8 Hz, 2H). ^{13}C NMR: δ 55.27; 82.43; 113.12; 115.62; 128.27; 128.81; 128.94; 129.40; 132.06; 134.53; 145.78; 163.10; 216.77; 223.66; 339.28.

Complex 3h: red solid; IR 2018 (m), 1970 (sh), 1920 (s) cm^{-1}. ^1H NMR: δ 5.96 (s, 2H); 7.25−7.60 (m, 9H). ^{13}C NMR: δ 82.92; 125.31; 128.51; 128.70; 129.27; 129.51; 134.43; 137.04; 151.70; 216.28; 224.08; 347.06. Anal. Calcd for $C_{19}H_{12}O_6ClCr$: C, 53.96; H, 2.60, Cl, 8.40. Found: C, 53.70; H, 2.97; Cl, 8.48.

Complex 5a: red oil; IR 2050 (m), 1990 (sh), 1950 (s) cm^{-1}. ^1H NMR: δ 0.90−1.55 (m, 6H); 5.60 (bs, 1H); 6.10−7.50 (m, 9H). ^{13}C NMR: δ 18.46; 23.38; 85.71; 120.10; 125.86; 126.98; 128.27; 128.59; 130.55; 133.66; 139.78; 153.16; 216.15; 225.00; 351.57.

Complex 5b: red oil; IR 2040 (m), 1990 (sh), 1950 (s) cm^{-1}. ^1H NMR: δ 1.80 (bd, 3H); 3.75 (s, 3H); 6.50 (bs, 1H); 6.72−7.70 (m, 9H). ^{13}C NMR: δ 22.30; 55.31; 84.25; 110.60; 121.05; 126.79; 127.91; 129.01; 129.83; 153.61; 156.00; 216.36; 225.16; 350.62.

Complex 5c: red oil; IR 2030 (m), 1970 (sh), 1940 (s) cm^{-1}. ^1H NMR: δ 1.85 (d, J = 7 Hz, 3H); 2.40 (s, 3H); 6.05 (bs, 1H); 6.90−7.50 (m, 9H). ^{13}C NMR: δ 21.21; 23.63; 88.94; 120.88; 122.84; 126.49; 127.98; 128.62; 128.90; 129.24; 138.49; 140.16; 153.01; 216.04; 224.66; 349.60.

Complex 5d: red oil; IR 2030 (m), 1980 (sh), 1950 (s) cm^{-1}. ^1H NMR: δ 1.80 (d, J = 7 Hz, 3H); 3.80 (s, 3H); 6.05 (bs, 1H); 6.75−7.05 (bm, 5H); 7.25−7.45 (m, 4H). ^{13}C NMR: δ 23.68; 55.11; 88.60; 111.25; 114.16; 117.94; 120.90; 128.03; 128.97; 129.82; 141.72; 152.95; 159.90; 215.99; 224.57; 349.69.

Complex 7: dark yellow solid; IR 2022 (m), 1912 (s), 1895 (sh), 1840 (s) cm^{-1}. ^1H NMR: δ 3.90 (s, 3H); 4.64 (s, 3H); 5.95 (s, 2H); 6.95−7.25 (m, 4H); 7.46−7.65 (m, 3H); 7.70−7.83 (m, 1H). ^{13}C NMR: δ 55.50; 67.59; 85.05; 111.16; 114.31; 120.70; 123.28; 127.93; 130.40; 134.30; 136.85; 160.24; 165.70; 168.28; 202.06; 215.50; 220.63; 310.98. Anal. Calcd for $C_{20}H_{16}O_7W$: C, 43.48; H, 2.89. Found: C, 43.13; H, 2.87.

Complex 10: red solid; IR 2015 (m), 1965 (sh), 1920 (s) cm^{-1}. ^1H NMR: δ 6.16 (s, 2H); 7.21−7.28 (m, 1H); 7.45−7.55 (m, 5H); 7.72 (dd, J = 1 and 5 Hz, 1H); 8.30 (dd, J = 1 and 4 Hz, 1H). ^{13}C NMR: δ 81.83; 127.67; 128.30; 129.19; 129.70; 130.81; 134.95; 142.98; 155.87; 217.28; 223.34; 317.08. Anal. Calcd for $C_{17}H_{10}O_6SCr$: C, 51.77; H, 2.54; S, 8.12. Found: C, 52.27; H, 3.15; S, 8.03.

Complex 11a: red solid; IR 2032 (m), 1956 (sh), 1920 (s) cm^{-1}. ^1H NMR: δ 1.90 (s, 3H); 1.95 (s, 3H); 2.40 (s, 3H); 5.50 (d, J = 6 Hz, 2H); 5.67−5.82 (m, 1H); 7.28 (d, J = 8 Hz, 2H); 7.62 (d, J = 8 Hz, 2H). ^{13}C NMR: δ 18.72; 21.77; 26.09; 81.53; 117.68; 127.89; 129.03; 142.09; 143.35; 152.71; 197.88; 203.96; 317.47. Anal. Calcd for $C_{18}H_{16}O_6W$: C, 42.18; H, 3.12. Found: C, 42.13; H, 3.25.

Complex 11b: red oil; IR 2030 (m), 1985 (sh), 1945 (s) cm^{-1}. ^1H NMR: δ 5.65 (d, J = 4 Hz, 2H); 6.50−6.71 (m, 1H); 6.90−7.02 (m, 1H); 7.18−7.76 (m, 10H). ^{13}C NMR: δ 84.66; 121.65; 126.45; 127.11; 128.32; 128.97; 131.85; 136.76; 135.93; 155.61; 197.51; 203.78; 320.38.

General Procedure for the Rearrangement Reaction of Carbene Complexes. The carbene complex (*n* mmol) was heated under reflux in benzene or toluene (50*n* mL) until the reaction was completed (TLC). The reaction mixture was cooled and filtered through a thin pad of Celite or through a small column of neutral alumina. The filtrate was concentrated under reduced pressure, and the residue was flash-chromatographed using 5−20% ethyl acetate/95−80% petroleum ether as the eluant to isolate the product.

Photolysis of the Carbene Complex 1a. The carbene complex **1a** was photolyzed at 350 nm in benzene at room temperature for 10 h. The initial red color of the solution gradually disappeared. The compound **2a** was isolated (57%) as the only product after purification by column chromatography.

Ketone 2a: pale yellow liquid; IR 1680 (m) cm^{-1}. ^1H NMR: δ 4.26 (s, 2H); 6.11−6.32 (m, 2H); 7.13−7.65 (m, 4H); 7.84−8.05 (m, 2H). MS: 186 (M^+), 105, 81, 77.

Ketone 2b: pale yellow liquid; IR 1680 (m) cm^{-1}. ^1H NMR: δ 2.34 (s, 3H); 4.24 (s, 2H); 6.08−6.37 (m, 2H); 7.11−7.34 (m, 3H); 7.86 (d, J = 8 Hz, 2H). MS: 200 (M^+), 119, 91, 77.

Ketone 2c: pale yellow liquid; IR 1670 (m) cm^{-1}. ^1H NMR: δ 3.84 (s, 3H); 4.23 (s, 2H); 6.12−6.38 (m, 2H); 6.92 (d, J = 9 Hz, 2H); 7.21−7.40 (m, 1H); 7.97 (d, J = 9 Hz, 2H). MS: 216 (M^+), 135, 107, 92, 81, 77.

Ketone 2d: pale yellow liquid; IR 1684 (m) cm^{-1}. ^1H NMR: δ 3.95 (s, 3H); 4.40 (s, 2H); 6.16−6.21 (m, 1H); 6.32−6.39 (m, 1H); 6.92−7.08 (m, 3H); 7.43−7.54 (m, 1H); 7.71−7.82 (m, 1H). MS: 216 (M^+), 135, 107, 81, 77.

Ketone 2e: pale yellow liquid; IR 1680 (m) cm^{-1}. ^1H NMR: δ 4.26 (s, 2H); 6.91−7.72 (m, 8H); 7.97 (dd, J = 8 and 2 Hz, 2H). MS: 196 (M^+), 105, 91, 77.

Ketone 2f: white solid; mp 110 °C; IR 1690 (m) cm^{-1}. ^1H NMR: δ 3.71 (s, 3H); 4.04 (s, 2H); 6.78 (d, J = 8 Hz, 2H); 7.14 (d, J = 8 Hz, 2H); 7.23−7.50 (m, 3H); 7.78−8.02 (m, 2H). MS: 226 (M^+), 121, 105, 91, 77.

Ketone 2g: white solid; mp 89 °C; IR 1680 (m) cm^{-1}. ^1H NMR: δ 3.68 (s, 6H); 3.84 (s, 2H); 6.62−7.12 (m, 8H). MS: 256 (M^+), 135, 121, 107.

Ketone 2h: pale yellow liquid; IR 1680 (m) cm^{-1}. ^1H NMR: δ 1.55 (d, J = 7 Hz, 3H); 4.72 (q, J = 7 Hz, 1H); 7.20−7.55 (m, 8H); 8.00 (dd, J = 8 and 1 Hz, 2H). MS: 210 (M^+), 105, 90, 77.

Ketone 4a: yellow, crystalline solid; mp 164 °C; IR 1970 (s), 1890 (s), 1680 (m) cm^{-1}. ^1H NMR: δ 4.02 (s, 2H); 5.13−5.48 (m, 5H); 7.40−7.66 (m, 3H); 7.98 (dd, J = 8 and 2 Hz, 2H). ^{13}C NMR: δ 44.68; 92.26; 95.55; 108.05; 129.09; 129.59; 134.25; 137.36; 196.62; 234.58. Anal. Calcd for $C_{17}H_{12}O_4Cr$: C, 61.44; H, 3.61. Found: C, 61.52; H, 4.03.

Ketone 4b: yellow, crystalline solid; mp 188 °C; IR 1970 (s), 1890 (s), 1680 (m) cm^{-1}. ^1H NMR: δ 2.18 (s, 3H); 3.92 (d, J = 18 Hz, 1H); 4.34 (d, J = 18 Hz, 1H); 5.26−5.36 (m, 3H); 5.38−5.45 (m, 1H); 7.50−7.70 (m, 3H); 8.02−8.08 (m, 2H). ^{13}C NMR: δ 18.59; 42.38; 91.02; 92.92; 94.47; 95.97; 103.69; 108.82; 128.05; 128.76; 133.65; 136.07; 195.48; 233.10. Anal. Calcd for $C_{18}H_{14}O_4Cr$: C, 62.43; H, 4.05. Found: C, 62.07; H, 4.31.

Ketone 4c: yellow, crystalline solid; mp 128 °C; IR 1980 (s), 1900 (s), 1680 (m) cm^{-1}. ^1H NMR: δ 2.30 (s, 3H); 4.10 (s, 2H); 5.09−5.19 (m, 3H); 5.54 (m, 1H); 7.50−7.71 (m, 3H); 8.02−8.07 (m, 2H). ^{13}C NMR: δ 20.93; 44.51; 91.61; 91.68; 95.04; 106.27; 110.37; 128.50; 129.13; 134.13; 136.15; 196.14; 233.55. Anal. Calcd for $C_{18}H_{14}O_4Cr$: C, 62.43; H, 4.05. Found: C, 62.34; H, 4.08.

Ketone 4d: yellow oil; IR 1970 (s), 1900 (s), 1680 (m) cm^{-1}. ^1H NMR: δ 1.50 (d, J = 7 Hz, 3H); 4.46 (q, J = 7 Hz, 1H); 5.10−5.55 (m, 5H); 7.37−7.71 (m, 3H); 7.97 (dd, J = 8 and 2 Hz, 2H). ^{13}C NMR: δ 18.35; 44.49; 91.20; 91.35; 92.62; 93.03; 93.14; 94.83; 110.32; 119.69; 128.51; 128.80; 133.64; 135.48; 232.59.

Ketone 4e: yellow, crystalline solid; mp 166 °C; IR 1970 (s), 1890 (s), 1680 (m) cm^{-1}. ^1H NMR: δ 3.74 (s, 3H); 3.96 (s, 2H); 5.21 (d, J = 7 Hz, 2H); 5.54 (d, J = 7 Hz, 2H); 7.54−7.66 (m, 3H); 8.00−8.05 (m, 2H). ^{13}C NMR: δ 43.29; 55.99; 78.56; 96.75; 97.49; 128.55; 129.13; 134.09; 136.10; 142.73; 196.10; 233.32. Anal. Calcd for $C_{18}H_{14}O_5Cr$: C, 59.67; H, 3.87. Found: C, 59.26; H, 3.86.

Ketone 4f: yellow, crystalline solid; mp 156 °C; IR 1970 (s), 1890 (s), 1680 (m) cm^{-1}. ^1H NMR: δ 3.73 (s, 3H); 3.75 (d, J = 18 Hz, 1H); 4.63 (d, J = 18 Hz, 1H); 5.01 (m, 1H); 5.16 (d, J = 7 Hz, 1H); 5.56−5.62 (m, 2H); 7.50−7.71 (m, 3H); 8.05−8.15 (m, 2H). ^{13}C NMR: δ 39.34; 55.67; 74.57; 85.89; 93.69; 94.02; 97.53; 110.41; 128.02; 128.51; 133.36; 135.84; 141.46; 195.66; 233.06. Anal. Calcd for $C_{18}H_{14}O_5Cr$: C, 59.67; H, 3.87. Found: C, 59.85; H, 4.04.

Ketone 4g: yellow solid; mp 138 °C; IR 1970 (s), 1890 (s), 1680 (m) cm^{-1}. ^1H NMR: δ 3.86 (s, 3H); 3.95 (s, 2H); 5.13−5.51 (m, 5H); 6.95 (d, J = 8 Hz, 2H); 7.95 (d, J = 8 Hz, 2H). ^{13}C NMR: δ 43.98; 55.74; 91.34; 93.81; 94.41; 105.65; 114.28; 129.10; 130.85; 164.35; 194.37; 233.14. Anal. Calcd for $C_{18}H_{14}O_5Cr$: C, 59.67; H, 3.87. Found: C, 59.34; H, 4.08.

Ketone 4h: yellow, crystalline solid; mp 148 °C; IR 1980 (s), 1900 (s), 1680 (m) cm^{-1}. ^1H NMR: δ 4.05 (s, 2H); 5.23−5.40 (m, 3H); 5.40−5.55 (m, 2H); 7.53 (d, J = 8 Hz, 2H); 7.98 (d, J = 8 Hz; 2H). ^{13}C NMR: δ 44.29; 91.48; 93.71; 94.32; 104.62; 129.43; 129.87; 134.37; 140.64; 194.78; 233.00. Anal. Calcd for $C_{17}H_{11}O_4ClCr$: C, 55.66; H, 3.00; Cl, 9.69. Found: C, 55.71; H, 3.22; Cl, 9.75.

Ketone 6a: yellow, crystalline solid; mp 154 °C; IR 1980 (s), 1900 (s), 1680 (m) cm^{-1}. ^1H NMR: δ 1.52 (d, J = 7 Hz) and 1.59 (d, J = 7 Hz), total 3H; 2.07 (s) and 2.39 (s), total 3H; 4.75 (q, J = 7 Hz) and 4.80 (q, J = 7 Hz), total 1H; 4.95−5.05 (m) and 5.15 (d, J = 7 Hz), total 1H; 5.25−5.37 (m, 1H); 5.40−5.55 (m, 1H); 5.61 (d, J = 7 Hz) and 5.83 (d, J = 7 Hz), total 1H; 7.45−7.75 (m, 3H); 8.00−8.15 (m, 2H). ^{13}C NMR: δ 17.37; 19.08; 21.16; 29.54; 39.30; 42.20; 87.52; 90.10; 90.81; 92.62; 93.34; 93.87; 95.43; 95.68; 105.96; 108.78; 109.11; 110.04; 128.23; 128.60; 128.76; 128.96; 133.47; 133.71; 135.26; 136.09; 198.48; 200.66; 232.39; 233.26. Anal. Calcd for $C_{19}H_{16}O_4Cr$: C, 63.33; H, 4.44. Found: C, 63.80; H, 4.13.

Ketone 6b: yellow, crystalline solid; mp 131 °C; IR 1980 (s), 1900 (s), 1680 (m) cm^{-1}. ^1H NMR: δ 1.45 (d, J = 6 Hz, 3H); 3.80 (s, 3H); 4.75 (dd, 1H); 4.95−5.10 (m, 2H); 5.50−5.60 (m, 1H); 5.85−5.90 (m, 1H); 7.45−7.65 (m, 3H); 8.10−8.20 (m, 2H). ^{13}C NMR: δ 20.87; 36.45; 56.15; 72.94; 84.18; 94.82; 96.33; 97.84; 128.84; 129.43; 133.62; 136.44; 141.58; 198.99; 232.67. Anal. Calcd for $C_{19}H_{16}O_5Cr$: C, 60.64; H, 4.25. Found: C, 61.00; H, 4.45.

Ketone 6c: yellow, crystalline solid; mp 142 °C; IR 1980 (s), 1900 (s), 1680 (m) cm^{-1}. ^1H NMR: δ 1.56 (d, J = 7 Hz) and 1.60 (d, J = 7 Hz), total 3H; 2.14 (s), total 3H; 4.52 (q, J = 7 Hz, 1H); 5.21−5.35 (m) and 5.44−5.50 (m), total 4H; 7.48−7.69 (m, 3H); 8.00−8.06 (m, 2H). ^{13}C NMR: δ 17.47; 17.54; 20.36; 20.63; 44.45; 44.59; 89.91; 91.77; 92.59; 92.96; 93.08; 93.28; 94.82; 108.58; 111.92; 128.45; 128.76; 133.58; 135.43; 200.08; 233.06. Anal. Calcd for $C_{19}H_{16}O_4Cr$: C, 63.33; H, 4.44. Found: C, 63.13; H, 4.47.

Ketone 6d: yellow, crystalline solid; mp 145 °C; IR 1980 (s), 1900 (s), 1680 (m) cm^{-1}. ^1H NMR: δ 1.55−1.70 (two doublets, J = 7 Hz), total 3H; 3.70 (s) and 3.80 (s), total 3H; 4.55−4.75 (two quartets, J = 7 Hz), total 1H; 4.84 (d, J = 8

Hz), 5.00−5.25 (m), and 5.35−5.40 (m), total 3H; 5.50−5.65 (two triplets, $J = 8$ Hz, 1H); 7.50−7.75 (m, 3H); 8.00−8.10 (m, 2H). ^{13}C NMR: δ 16.64; 16.94; 44.59; 45.02; 55.50; 77.97; 79.62; 85.27; 87.20; 93.93; 94.27; 113.02; 113.29; 128.51; 128.85; 133.69; 135.40; 142.65; 142.88; 200.30; 233.07. Anal. Calcd for $C_{19}H_{16}O_5Cr$: C, 60.64; H, 4.25. Found: C, 60.93; H, 4.35.

Ketone 12a: yellow oil; IR 1685 (m) cm^{-1}. ^{1}H NMR: δ 1.68 (s, 3H); 1.20 (s, 3H); 2.33 (s, 3H); 3.60 (d, $J = 6$ Hz, 2H); 5.30−5.42 (m, 1H); 7.18 (d, $J = 7.8$ Hz, 2H); 7.80 (d, $J = 7.8$ Hz, 2H). MS: 188 (M^+), 119, 91, 69.

Ketone 12b: white solid; mp 95 °C; IR 1687 (m) cm^{-1}. ^{1}H NMR: δ 3.95 (d, $J = 5.8$ Hz, 2H); 6.38−6.75 (m, 2H); 7.22−7.72 (m, 8H); 8.05 (dd, $J = 8$ Hz and 0.8 Hz, 2H). MS: 222 (M^+), 117, 105, 103, 77.

Base-Catalyzed Equilibration of Complex 6b. (Arene)-chromium complex **6b** (188 mg, 0.5 mmol), KF (145 mg, 2.5 mmol), and 18-crown-6 (27 mg, 0.1 mmol) were taken up in nitromethane (10 mL) and stirred for 4 days under an inert atmosphere. The reaction mixture was diluted with water, extracted with dichloromethane, and dried in vacuo. Flash chromatography yielded a diastereomeric mixture of compounds **6b** and **6b′** (160 mg, 85%).

^{1}H NMR: δ 1.49 and 1.54 (two doublets, $J = 6$ Hz, total 3H); 3.64 and 3.87 (two singlets, total 3H); 4.68−5.25 (m, 3H); 5.57 (t, $J = 5.8$ Hz, 1H); 5.77 and 5.88 (two doublets, $J = 6.8$ Hz, total 1H); 7.43−7.82 (m, 3H); 8.03 and 8.14 (two doublets, $J = 6.8$ Hz, total 2H).

Equilibration of a Diastereomeric Mixture. Equimolar quantities (ca. 1 mmol) of complexes **6a** or **6d** and **4b** were heated in benzene at 80 °C for 3 h. Benzene was evaporated, and the residue (92% mass recovery) was dissolved in $CDCl_3$; this solution was filtered through a plug of alumina and submitted for NMR. The diastereomeric ratio was directly determined from the integration of well-resolved signals.

Thermolysis of Optically Active Complex (−)-3d. The optically active carbene complex was prepared in the usual manner using (*S*)-(−)-α-methylbenzyl alcohol (Aldrich, $[\alpha]^{23} = -41.3°$ neat) in 54% yield. CD (methanol, 10^{-3} molar solution): 304, 374, 406 nm. Thermolysis in benzene at 82 °C yielded the (arene)chromium complex (47%) as a racemic mixture (CD-inactive).

X-ray Structure Solution of the Complex 6b. Yellow crystals were grown from toluene−hexane solution. A crystal of size 0.3 × 0.3 × 0.5 mm was used for diffraction data, collected on a PC-controlled Enraf-Nonius CAD-4 single-crystal X-ray diffractometer using Mo Kα ($\lambda = 0.7107$ Å) radiation. Unit cell parameters were refined using 25 machine-centered reflections in the range $28 \leq 2\theta \leq 40°$. Reflections were measured with an index range $h = 0-10$, $k = 0-20$, and $l = 0-22$ using the $\omega/2\theta$ scan mode and with an average speed of 1° min^{-1}. Three standard reflections measured every 1 h showed <4% variation in average intensity. Out of 2510 reflections collected within the θ range 0−23.5°, 1569 were observed with $I \geq 2.5\sigma(I)$. The structure was solved by direct methods using MULTAN-80. Least-squares refinements of scale factors and positional and anisotropic thermal parameters for non-hydrogen atoms converged to $R = 0.042$ and $R_w = 0.046$. Hydrogen atoms were geometrically fixed and confirmed by difference Fourier and were held fixed during refinement. Structure solution and refinement were carried out using the NRCVAX program.[15]

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Supporting Information Available: Tables of all bond distances, bond angles, anisotropic thermal parameters, and atom coordinates (5 pages). Ordering information is given on any current masthead page.

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