

Unusual Rearrangement of Fischer Carbene Complexes to Ketones

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A thermal rearrangement of aryl arylmethoxy carbene complexes of chromium and tungsten to aryl arylmethyl ketones is described for the first time.

Fischer carbene complexes of group VI transition metals display a wide range of reactivity and have provided a number of synthetically useful reactions.¹ Recently, it has been observed that variation of the substituents on the carbene ligand can lead to new reaction pathways.² In this preliminary report we describe a novel rearrangement of tungsten and

chromium carbene complexes, which occurs as a result of modification of the oxygen substituent.

The carbene ligands of Fischer carbene complexes of group VI transition metals usually dimerise on thermolysis. However, when aryl arylmethoxy carbene complexes of tungsten and chromium were heated in refluxing benzene-

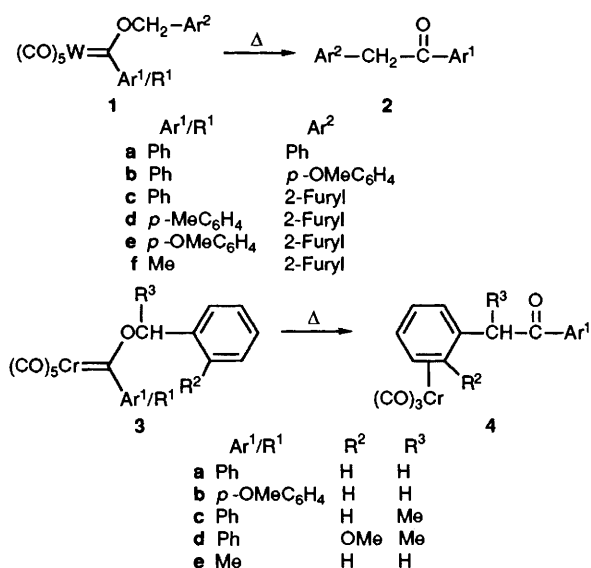
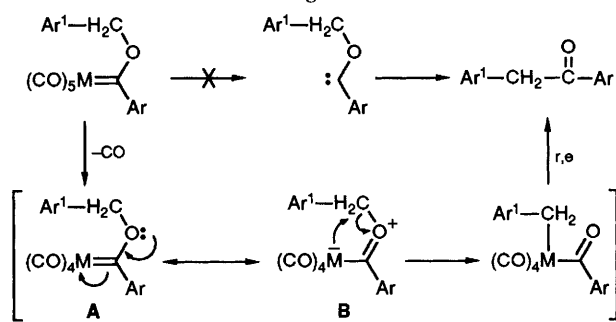


Fig. 1



Scheme 1

toluene, the carbene ligand underwent a rearrangement to furnish aryl arylmethoxy ketones in moderate to good yields. To the best of our knowledge such a rearrangement of group VI Fischer carbene complexes has no precedent. The results are summarized in Fig. 1 and Table 1.

Compared with the benzyloxy carbene complexes of tungsten **1a,b** (toluene, reflux or benzene, prolonged reflux), the 2-furylmethoxy carbene complexes **1c,d** were found to undergo rearrangement with greater facility (benzene, reflux, 2–3.5 h). Photolysis of the complex **1c** (300 nm) resulted in the formation of the rearranged product even at room temperature in reasonable yield, indicating that CO dissociation might be the rate-determining step in the overall transformation.

Although at first glance it might appear that the ketone is a rearrangement product of the free carbene derived from the alkylidene complex;³ formation of free carbenes from such complexes has not been observed so far. Thus, an alternative mechanistic pathway for this reaction has been proposed, as depicted in Scheme 1.

The initial loss of a CO ligand leads to a coordinatively unsaturated intermediate **A**. The possible electronic polarization of **A** can be represented by the zwitterionic intermediate **B**, which furnishes the product ketone *via* an acylmetal intermediate. For aryl arylmethoxy complexes, the stability of a developing benzylic carbocationic centre facilitates the rearrangement. The reaction failed with the methyl carbene complexes **1f** and **3e** revealing the inherent reactivity difference between alkyl and aryl Fischer carbene complexes of group VI transition metals.⁴

From the chromium carbene complexes **3a–d**, the major products were isolated as the arene–Cr(CO)₃ complexes with complete regioselectivity; the metal was always attached to the more electron rich aromatic ring as could be clearly seen from the ¹H NMR spectra. The formation of arene–Cr(CO)₃ complexes also provided the opportunity to probe the stereoselectivity of the reaction. The chromium carbene

Table 1 Rearrangement of Fischer carbene complexes^a

Carbene	Product	Time/h	Yield (%) ^b
1a^f	2a	2	56
1b	2b	16	56
1c	2c	2	90
1c^c	2c	10	55
1d	2d	3.5	65
1e	2e	10	36
1e^f	2e	1.5	50
1f	—	3 ^e	—
3a	4a	3.5	68(80) ^d
3b	4b	4	28
3c	4c	5	47(63) ^d
3d	4d	3.5	50(d.e. >95%) ^g
3e	—	3.5 ^e	—

^a The compounds were refluxed in benzene unless otherwise noted until complete consumption of starting material was observed.

^b Isolated yield after chromatography. ^c Photolysis at room temperature. ^d Figures in parentheses indicate the isolated yield of the product after oxidative decomplexation. ^e Decomposition of the carbene complex complete (TLC–IR). ^f In toluene. ^g d.e. = diastereoisomeric excess.

complex **3d** provided a single diastereoisomer of the product **4d**.[†] Such pronounced regioselectivity and high stereoselectivity of the rearrangement reaction would strongly imply an intimate involvement of the metal centre in the overall process.⁵

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[†] No trace of the other diastereoisomer could be detected by HPLC or in the ¹H or ¹³C NMR spectra recorded on a 200 MHz machine. A base catalysed epimerization of the chiral benzylic centre (KF/18-crown-6 in nitromethane) was carried out to obtain the other diastereoisomer for comparison (NMR and HPLC). It has been confirmed that the other diastereoisomer does not decompose under the reaction conditions.