

Reaction of Pentacarbonyl(alkoxyalkylcarbene)chromium Complexes with *N,N*-Dimethylformamide Dialkyl Acetals: Synthesis of Pentacarbonyl-(alkoxyaminocarbene) and -(dialkoxycarbene)chromium Complexes

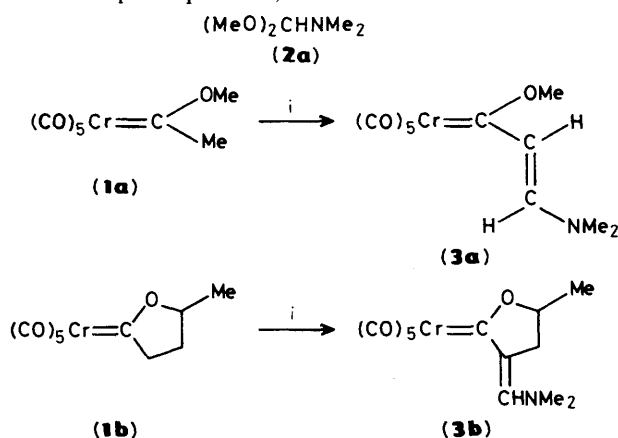
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On treatment of the carbene complexes (**1a–f**) with *N,N*-dimethylformamide dialkyl acetals (DMF-DAA) (**2a–d**) as electrophiles, the nature of the products, (**3**) or (**4**), depends on the structure of the starting carbene complexes.

Over the last few years pentacarbonyl(alkyl- and aryl-alkoxy-carbene)chromium complexes have attracted much interest as useful reagents for organic synthesis.¹ As examples, they have been employed as precursors of β -lactams, substituted naphthols and naphthoquinones, and vitamin K derivatives.² Thus



Scheme 1. Reagents and conditions: i, (**2a**), DMF, 20°C.

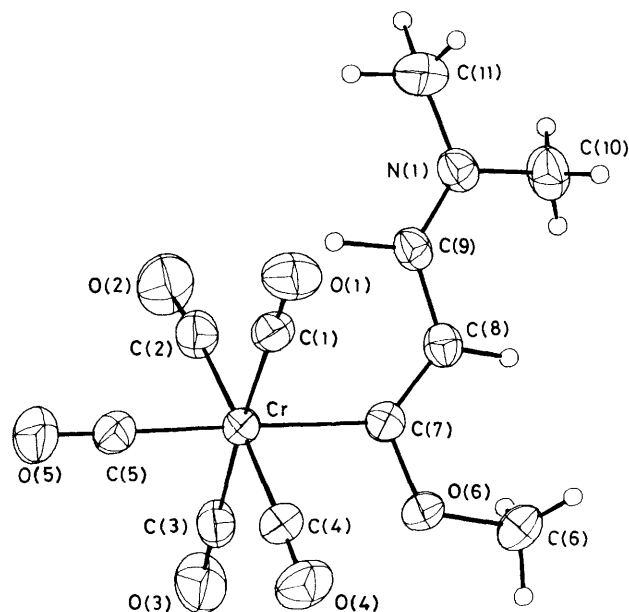


Figure 1. An ORTEP drawing of complex (**3a**) (37% probability ellipsoids). Bond distances (Å): Cr–C(7), 2.130(5); Cr–C(1), 1.886(5); Cr–C(2), 1.892(6); Cr–C(3), 1.895(5); Cr–C(4), 1.879(5); Cr–C(5), 1.864(5); O(6)–C(7), 1.349(5); C(7)–C(8), 1.385(7); C(8)–C(9), 1.386(6); N(1)–C(9), 1.315(6). Bond angles (°): Cr–C(7)–O(6), 111.1(3); Cr–C(7)–C(8), 132.0(3); O(6)–C(7)–C(8), 116.9(4); C(7)–C(8)–C(9), 121.4(4); C(8)–C(9)–N(1), 127.4(5); C(6)–O(6)–C(7), 121.6(4).

general syntheses of pentacarbonylcarbenechromium complexes are of interest, as are syntheses of new carbene derivatives. Moreover, the high acidity of protons attached to the α -carbon atom of carbenes of type (**1a**) has been exploited for the introduction of functionality into the carbene side chain *via* reaction with electrophiles.³ We now report results obtained for reactions of the carbene complexes (**1a–f**) with *N,N*-dimethylformamide dialkyl acetals (DMF-DAA) (**2a–d**) as electrophiles.

The reaction of (**1a**)⁴ and (**1b**)⁵ with (**2a**) affords, as expected, the new propenylidene (**3a**) and methylenefuran-ylidene (**3b**) chromium complexes, respectively (Scheme 1).[†] It is noteworthy that these reactions occur under milder conditions and more quickly than those reported for esters or lactones.⁷

[†] Only one example of a pentacarbonyl(alkoxyaminoethylenecarbene)chromium complex has been reported, synthesized⁶ from pentacarbonyl(ethoxyphenylacetylenylcarbene)chromium and dimethylamine at –20°C.

Typical procedure: To a solution of (**1**) (7.6 mmol) in anhydrous DMF (15 ml), the acetal (**2**) (7.6 mmol) was added. The reaction was allowed to proceed at 20°C, under argon, for the time indicated in Table 1. The mixture was then diluted with water (400 ml) and extracted with diethyl ether (2 \times 200 ml), and the ethereal layer dried (Na₂SO₄) and evaporated under reduced pressure. The products (**3a**) and (**3b**) were recovered by washing the solid residue with *n*-hexane and crystallized as indicated in Table 1. The products (**4a,b,e**) were purified directly from the crude residue with the solvents indicated in Table 1. Compounds (**4c,d**) were purified by flash chromatography on silica gel, with light petroleum–diethyl ether (95 : 5) as eluant for (**4c**) and pentane as eluant for (**4d**).

All new compounds gave satisfactory elemental analyses. **Spectral data** for the new compounds: (**3a**) i.r. (Nujol): ν_{\max} 2040, 1965, 1950–1870, 1615 cm⁻¹; ¹H n.m.r. (CDCl₃, 90 MHz): δ 3.1 (3H, s, NMe), 3.3 (3H, s, NMe), 4.1 (3H, s, OMe), 6.1 (1H, d, *J* 12 Hz, CH=CH–N), 7.8 (1H, d, *J* 12 Hz, CH=CH–N); ¹³C n.m.r. (CDCl₃, 300 MHz): δ 38 and 46.5 (NMe₂), 58.5 (OMe), 109.5 (CH=CH–N), 169.5 (CH=CH–N), 219.5 (*cis*-CO), 224 (*trans*-CO), 288.5 (carbene-C); *m/z* 305 (*M*⁺).

(**3b**) i.r. (Nujol): ν_{\max} 2050, 1975, 1930–1880, 1620 cm⁻¹; ¹H n.m.r. (CDCl₃, 90 MHz): δ 1.4 (3H, d, *J* 6 Hz, Me), 2.45 (1H, dd, *J*_{a,b} 13.5 Hz, H_a), 3.05 (1H, dd, *J*_{b,c} 9 *J*_{a,b} 13.5 Hz, H_b), 3.3 (6H, s, NMe₂), 4.85–5.15 (1H, m, H_c), 7.9 (1H, s, =CH–N); ¹³C n.m.r. (CDCl₃, 300 MHz): δ 22.1 (Me), 33.6 (–CH₂–), 38 and 47 (NMe₂), 86.9 (CH–Me), 125.2 (–C=CH), 162.2 (=CH–N), 219.2 (*cis*-CO), 223.8 (*trans*-CO), 283.8 (carbene-C); *m/z* 331 (*M*⁺).

(**4a**) i.r. (Nujol): ν_{\max} 2070, 1985, 1950, 1935 cm⁻¹; ¹H n.m.r. (CDCl₃, 90 MHz): δ 4.15 (s, OMe); *m/z* 266 (*M*⁺).

(**4b**) i.r. (Nujol): ν 2065, 1990–1890 cm⁻¹; ¹H n.m.r. (CDCl₃, 90 MHz): δ 1.45 (3H, t, OCH₂CH₃), 4.15 (3H, s, OCH₃), 4.6 (2H, q, OCH₂CH₃).

(**4c**) i.r. (Nujol): ν_{\max} 2070, 1985, 1950, 1935 cm⁻¹; ¹H n.m.r. (CDCl₃, 90 MHz): δ 4.2 (3H, s, OCH₃), 5.5 (2H, s, OCH₂), 7.35 (5H, s, Ph); *m/z* 342 (*M*⁺).

(**4d**) i.r. (*n*-hexane): ν_{\max} 2060, 1980, 1950, 1930 cm⁻¹; ¹H n.m.r. (CDCl₃, 90 MHz): δ 1.3–2.0 (10H, m, C[CH₂]₄CH₂), 4.05 (3H, s, OCH₃), 5.25 (1H, s, O-CH[CH₂]₄CH₂); *m/z* 334 (*M*⁺).

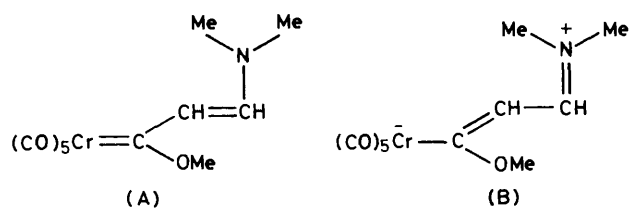


Table 1. Products from reactions of chromium carbene complexes (1a–f) with DMF-DAA (2a–d).

Product	M.p./°C (solvent)	% Yield	Reaction time/h
(3a)	107–108 (CH ₂ Cl ₂ /n-hexane)	77.5	0.5
(3b)	113–114 (Et ₂ O/n-hexane, –78 °C)	46	3
(4a)	36–37 (n-hexane, –78 °C)	50	2
(4b)	Oil	50	2
(4c)	37–38 (n-hexane, –78 °C)	30	1
(4d)	58–59 (pentane, –78 °C)	15	5
(4e)	Oil	73	0.5

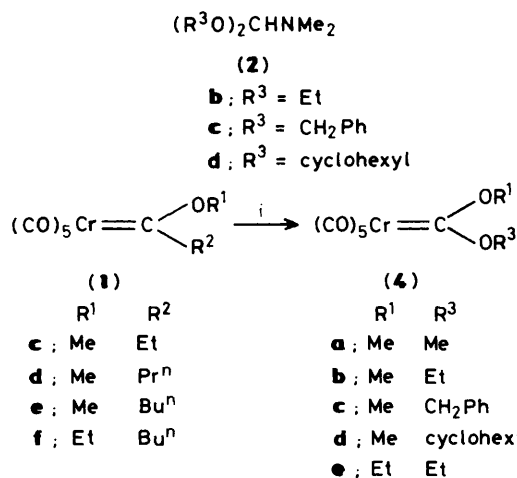
Compounds (3a) and (3b) do not react with 1,3-dipoles as nitrile imines and nitrile oxides, indicating that they do not behave like enamines. This fact, together with the high-field ¹³C resonance for the carbene carbon atom of (3a) (δ 288.5) and (3b) (δ 283.8)[‡] indicates extensive delocalization of the lone pair of the nitrogen atom, which reduces the electron deficiency of the carbene carbon atom and shifts the tautomerism from the enamino structure (A) towards the iminium structure (B). These observations are confirmed by single-crystal X-ray analysis of (3a).[§]

Figure 1 shows the structure of the complex with the most significant bond distances and angles. The main structural features concern the metal–carbene fragment. (i) The carbene ligand is nearly planar (excluding the methyl substituents) with the metal atom deviating 0.034(1) Å from the mean plane. (ii) The C–C [1.385(7), 1.386(6) Å], C–O [1.349(5) Å], and C–N distances [1.315(6) Å] are in agreement with π -delocalization over the substituted carbene ligand with a significant localization of the double bond between carbon and nitrogen and a lengthening of the C–O distance towards that appropriate for a single bond. (iii) The Cr–C(carbene) distance is in the upper part of the range of values generally observed and it is close to those found in carbene complexes containing amino groups.¹⁰ These values suggest that the best valence-bond description of the structure is (B) rather than (A).

In a development of this work, the reactivity of the carbenes (1c–e) was observed unexpectedly to differ from that of (1a) and (1b). The reaction of the complexes (1c–e) with (2a) resulted, surprisingly, in the formation of the pentacar-

[‡] The chemical shift for the carbene carbon atom of (1a) is δ 360.23.⁸

[§] *Crystal data:* C₁₁H₁₁CrNO₆, *M* = 305.2, monoclinic, space group *P*2₁/*n*, *a* = 9.818(1), *b* = 10.068(1), *c* = 14.639(1) Å, β = 97.92(1)°, *U* = 1433.2(2) Å³, *Z* = 4, *D*_c = 1.414 g cm^{–3}, Cu-K α radiation (λ = 1.5418 Å), μ (Cu-K α) = 68.76 cm^{–1}; crystal dimensions 0.11 × 0.32 × 0.40 mm. The structure was solved by the heavy atom method (Patterson and Fourier synthesis) and refined by full-matrix least-squares. For 1784 unique observed structure amplitudes [*I* > 2 σ (*I*)] collected at room temperature on a Siemens AED diffractometer in the range 6 < 2 θ < 140° and corrected for absorption using ABSORB⁹ the *R* value is 0.057 (*R*_w 0.062). All the hydrogen atoms were located in a difference Fourier map and introduced as fixed contributors in the final stage of refinement. All calculations were carried out using SHELX 76. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 2. Reagents and conditions: i, (2a–d), DMF, 20 °C.

bonyl(dimethoxycarbene)chromium complex (4a) (Scheme 2). This kind of reactivity proved to be quite general; in fact, the carbene complex (1e) afforded the pentacarbonyl(dialkoxycarbene)chromium complexes (4b–d)[†] by reaction with DMF-DAA (2b–d) (Scheme 2 and Table 1). In addition the carbene complex (1f) gave the pentacarbonyl(diethoxycarbene)chromium (4e) by reaction with (2b).

Compounds (4) are a new class of pentacarbonyl carbene complex, although (4e) had already been obtained in very low yield (0.07%) by the reaction of Cr(CO)₆ with EtOK, followed by alkylation.¹¹

The formation of compounds (4) arises from carbon–carbon bond fission of the carbenes (1c–f) with the formation of a new carbon–oxygen bond involving the R³O group present in the starting DMF–DAA (2).

A rationalization of the unexpected different behaviour of the carbene complexes (1a–b) and (1c–f) needs further work, which also has the aim of employing the compounds synthesized as new substrates in pentacarbonylcarbenechromium chemistry and organic synthesis; this work is in progress.

We thank the C.N.R. of Rome for financial support.

Received, 5th April 1988; Com. 8/01309H

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