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Preliminary Communication

Trapping of a carbanionic intermediate in the reaction of alkynylalkoxy carbene metal (Cr) complexes and ethyl diethoxyacrylate

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Abstract

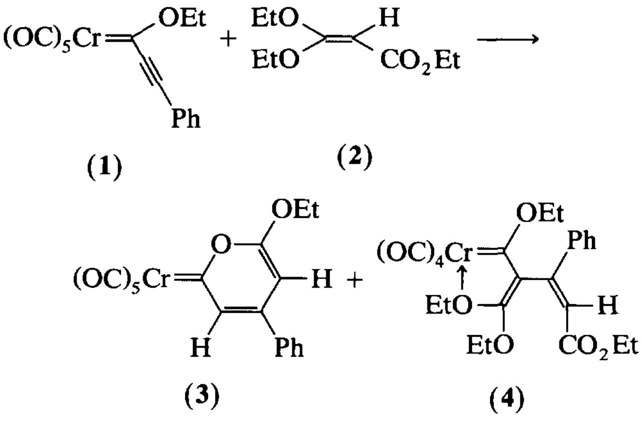
A new bis(carbene) metal complex was isolated and fully characterized in the reaction of alkynylalkoxy carbene metal complexes and ethyl diethoxyacrylate. This complex represents the trapping of a carbanionic intermediate in the above mentioned reaction.

We recently reported that the reaction of alkynylalkoxy carbene metal (Cr or W) complexes **1** with ethyl diethoxyacrylate **2** afforded complexes of type **3** (Cr, 13%; W, 40%) and **4** (Cr, 30%; W, traces) [1].

Subsequently, two new pyranylidene complexes were isolated, **5** (13%) and **6** (8%).

We soon realized that the product distribution depended very much on two factors: the purity of **2**, and the excess of **2** in the reaction mixture. Therefore the reaction was carried out under limiting conditions. Thus, using freshly distilled **2** in slight excess (1/2) the yield of **5** (22%) was improved within a reasonable reaction time (3 h). By the use of a very limited amount of **2** (1/0.5), the reaction proceeded very slowly and it stopped after 24 h. In this case, yield of complex **6** was substantially increased (21%) [2].

The structures of **5** and **6** were elucidated by single crystal X-ray diffractometry.



Scheme 1.

Originally, we supposed that **4** was an intermediate in pyranylidene complex formation. However, when pure **4** was treated with freshly distilled **2**, it gave only limited amounts of **3** and the reaction then stopped. Furthermore, the rate for formation of **3** in the general reaction **1** + **2** (Scheme 1) was, under similar reaction conditions, faster than when **4** was treated with **2**. Moreover, no **5** and **6** were produced from **4**.

In our effort to explain mechanistically all the products, we envisaged a common anionic pyranylidene complex intermediate **10** for the formation of **3**, **5** and **6**, through the sequence of reactions in Scheme 2.

The evidence for the formation of **10** is the reported stability of trialkoxy carbenium ions [3], and the fact that **3** did not react with **1** to give **6**. On the other hand, formation of **6** may be due to trapping of **10** by its precursor **1**. A similar trapping occurred when the reaction was carried out in the presence of added MeI. In this case, **11** (8%) was also identified in the reaction mixture.

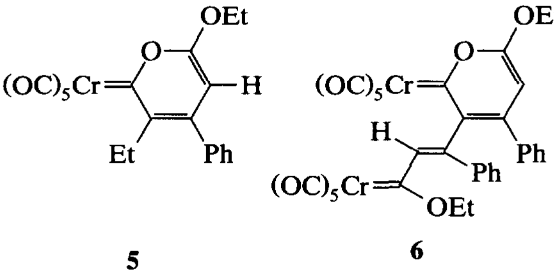


Fig. 1.

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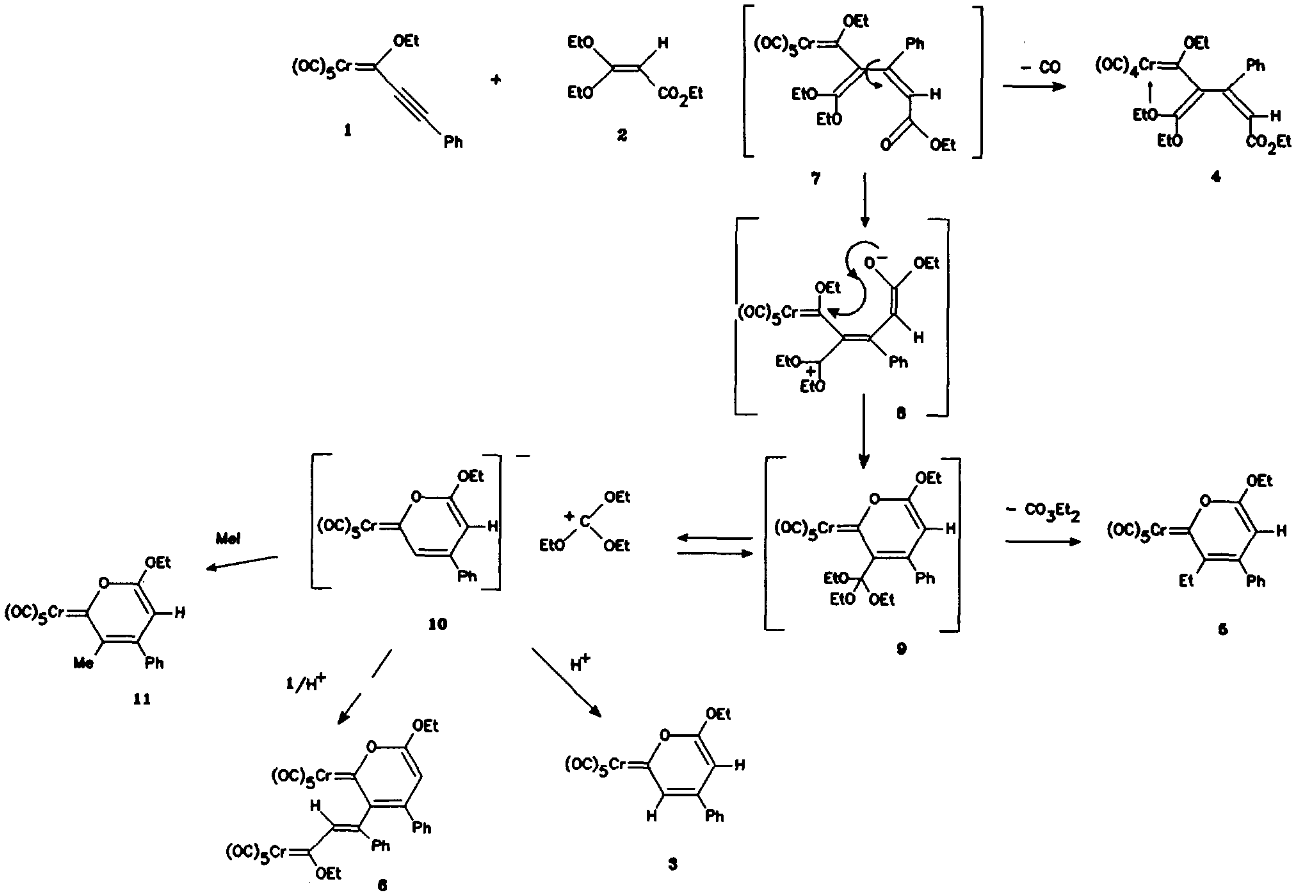

Scheme 2.

Given the sensitivity of **2** to organic and mineral acids any proton quenching of **10** is excluded.

Compound **6** was isolated as a mixture of *E* and *Z* isomers (9/2 ratio) [2]. The crystal whose structure was determined corresponded to the major isomer (*E*) and it represents a new type of non-symmetric bis(carbene) complex [4].

The structure consists of two chromium atoms in octahedral environments linked by an α-(6-ethoxy-4-phenyl-2-pyranyliden-3-yl)-β-(ethoxymethylidenyl)styrene unit (Fig. 3). The C(2)–O(1) distance is larger than usual (1.425(5), *cf.* C(12)–O(13), 1.322(5) Å). The C–C distances in the pyranylidene ring are in the range 1.41–1.36 Å and the Cr(2)–C(2) bond is 2.108(4) Å

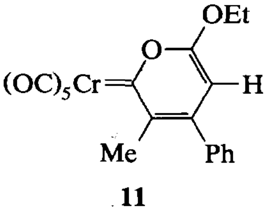

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Fig. 2.

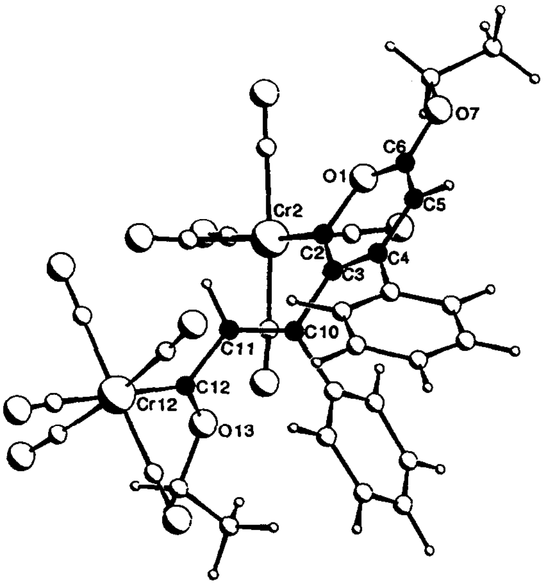

Fig. 3. Molecular structure of [$(OC)_5CrC(OEt)C(H) \cdot C(Ph)\overline{CC(Ph)}$-$C(H)C(OEt)OCCr(CO)_5$]. Selected bond lengths: Cr(2)-C(2), 2.108(4); C(2)-O(1), 1.425(5); C(2)-C(3), 1.405(6), C(3)-C(10), 1.507(5); C(10)-C(11), 1.340(6); C(11)-C(12), 1.489(6); Cr(12)-C(12), 2.030(4); C(12)-O(13), 1.322(5); C(3)-C(4), 1.409(6); C(4)-C(5), 1.380(6); C(5)-C(6), 1.360(7); C(6)-O(1), 1.305(6) Å.

long. These values point toward delocalization along the Cr(2)–C(2)–C(3)–C(4)–C(5)–C(6) chain.

The styrene unit does not seem to be conjugated with the carbene carbon atom (C(11)–C(12), 1.489(6)Å), but π-interaction also exists with the ethoxy group, as suggested by the shortening of the O(13)–C(12) distance (1.323(4) Å), also found in many alkoxycarbene complexes. In addition the Cr(12)–C(12) distance is 2.033(4) Å, consistent with the values reported for chromium carbene complexes [6]. The planar pyranylidene unit forms a dihedral angle (66.3°) with the styrene plane, thus indicating that there is no π-interaction between them. Confirming that there is no extended conjugation, the C(10)–C(3) bond is long, 1.507(5) Å, in the range of carbon–carbon single bonds.

In summary, we report here the trapping of the 2-pyranilidene metal carbanion intermediate by its dipolar precursor (alkynylalkoxy carbene metal complex), to give a new non-symmetric bis(carbene)complex, which has been isolated and characterized.

Acknowledgements

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2 *Typical procedure*. Metal carbene complex **1** (1 mmol) and diethoxyacrylate **2** were mixed at 20°C under argon. The mixture was then purified by flash chromatography on silica gel, (hexane–methylene chloride 10%).

Spectral data for new compounds. **6a**: IR ($CHCl_3$): ν_{max} cm^{-1} 2059, 1985, 1930, 1590. ^1H-NMR ($CDCl_3$, 300 MHz): δ 7.67 (s, 1H), 6.80–7.30 (m, 8H), 6.07 (s, 1H), 4.89 (q, 2H, J = 7.2 Hz), 4.86 (q, 2H, J = 7.2 Hz), 1.62 (t, 3H, J = 7.2 Hz), 0.86 (t, 3H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 75MHz): δ 337.3 (s), 261.7 (s), 223.4 (s), 222.8 (s), 217.6 (s), 216.2 (s), 172.5 (s), 158.0 (s), 146.9 (s), 147.0 (s), 139.4 (s), 137.5 (s), 137.0 (s), 129.9 (d), 128.9 (d), 128.1 (d), 127.3 (d), 127.2 (d), 127.1 (d), 100.5 (d), 76.9 (t), 67.7 (t), 14.5 (q), 13.5 (q). MS (EI): m/z 742 (M^+). Elemental analysis. Found: C, 55.06; H, 2.97. $C_{34}H_{22}O_{13}Cr_2$ calcd.: C, 54.99; H, 2.96%. **6b**: IR ($CHCL_3$): ν_{max} cm^{-1} 2050, 1975, 1930, 1585. ^1H-NMR ($CDCl_3$, 300 MHz): δ 8.20 (s, 1H), 6.85–7.50 (m, 10H), 6.20 (s, 1H), 4.90 (q, 2H, J = 7.2 Hz), 4.85 (q, 2H, J = 7.2 Hz), 1.62 (t, 3H, J = 7.2 Hz), 1.25 (t, 3H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 339.9 (s), 264.2 (s), 224.8 (s), 221.4 (s), 217.3 (s), 216.3 (s), 172.4 (s), 154.7 (s), 144.6 (s), 140.6 (s), 139.8 (d), 136.4 (s), 131.9 (s), 130.5 (d), 129.8 (d), 129.7 (d), 129.1 (d), 128.6 (d), 126.9 (d), 99.1 (d), 76.2 (t), 67.5 (t), 14.7 (q), 14.6 (q).

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5 *Crystal data*. $C_{34}H_{22}Cr_2O_{13}$; M = 742.2, monoclinic, a = 14.704(7), b = 14.532(2), c = 16.218(7) Å, β = 97.73(2)°, U = 3434(2) Å, Z = 4, D_c = 1.436 g cm^{-3}, Mo K_α radiation (graphite monochromator), λ = 0.71069 Å, μ = 6.49 cm^{-1}, space group $P2_1/n$, $F(000)$ = 1511.95, T = 294 K. A single crystal was mounted at the end of a glass fibre and centred in the Enraf-Nonius CAD4 diffractometer geometry. Cell parameters were determined by least-squares fitting of 25 high angle reflections. Lorentz and polarization effects were corrected but not for absorption. The chromium atoms were located by an automated Patterson search ROTSEARCH [6a] and a weighted Fourier synthesis showed the remaining non-H-atoms. Refinement was carried out using full-matrix least-squares methods SHELX-76 [6b] with anisotropic thermal parameters for non-H-atoms converging to R = 0.0889 and R_w = 0.0664. The final difference Fourier synthesis showed several hydrogen atoms which were not included in the refinement. Full lists of atomic coordinates, bond lengths and bond angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

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