Tricyclic pentacarbonyl carbene complexes of chromium: a novel synthetic pathway *via* diazo precursors and benzannulation[1]

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9-Diazo-9*H*-fluorene 2, 9-diazo-9*H*-xanthene 3 and 5-diazo-5*H*-dibenzo[*a,d*]cycloheptene 4 react with pentacarbonyl(η^2-*cis*-cyclooctene)chromium(0) 1 to give the novel tricyclic Fischer-type carbene complexes 5–7, which undergo benzannulation upon reaction with hex-1-yne.

Fischer-type carbene complexes have been established as valuable synthons in organic synthesis based on either ligand or metal centred C–C bond formation.[2] Their most interesting application is the chromium mediated carbene annulation,[3] which involves a stepwise formal [3+2+1] cycloaddition of an α,β-unsaturated carbene ligand, an alkyne and a carbonyl ligand on a $Cr(CO)_3$-template affording chromium coordinated hydroxyarenes (Scheme 1).

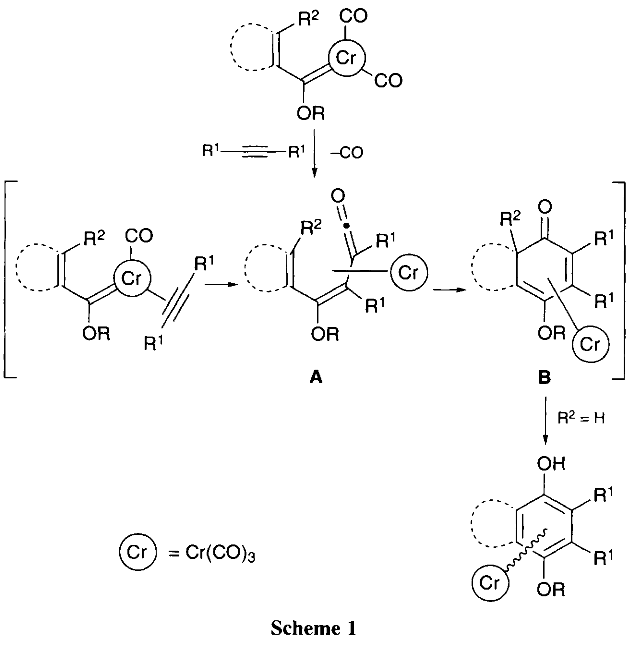
Recently, we observed that the cyclopropanation of electron-rich alkenes by ethyl diazoacetate is catalysed by pentacarbonyl(η^2-*cis*-cyclooctene)chromium(0)[4] **1**, suggesting the formation of a chromium carbene intermediate.[5] Subsequently, we focused our interest on bridged diaryldiazo methanes such as 9-diazo-9*H*-fluorene **2**, which we expected to allow the isolation of stable chromium diarylcarbene analogues. A similar approach has been exploited in the synthesis of $C_5H_5(CO)(L)M{=}CPh_2$ (M = Mn, L = CO; M = Cr, L = NO).[6] Furthermore, we wanted to explore the synthetic potential of fused carbene ligands in the benzannulation reaction.

A suspension of **1** in hexane–CH_2Cl_2 5 : 1 (*v*/*v*) reacts with 9-diazo-9*H*-fluorene **2**, 9-diazo-9*H*-xanthene **3** and 5-diazo-5*H*-dibenzo[*a,d*]cycloheptene **4** to give the carbene complexes **5–7**† in moderate to good yields along with the corresponding ketazines as the major by-products (Scheme 2). The reaction can be monitored according to the rate of N_2 evolution and to a colour change to violet, blue or red, respectively.

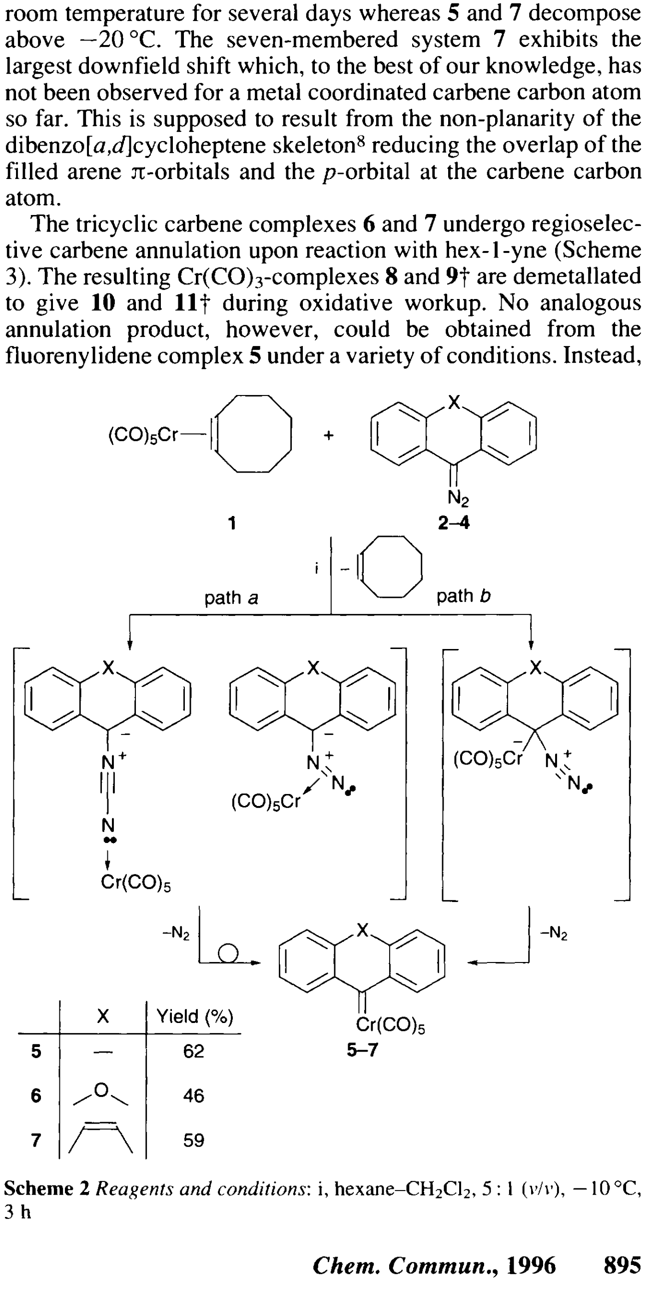
The metal carbene formation can be rationalized in terms of an end-on or side-on coordination[7] of the diazo compound to the $Cr(CO)_5$-fragment (path *a*) followed by metal migration to the diazo carbon or by a direct attack of the $Cr(CO)_5$ electrophile at the diazo carbon atom (path *b*) and subsequent N_2-elimination.

The ^{13}C NMR data (**5**: δ 361.6, **6**: δ 316.4, **7**: δ 404.2) reflect the thermal stability of the carbene complexes: Owing to vinylogous resonance stabilization **6** is stable under inert gas at room temperature for several days whereas **5** and **7** decompose above −20 °C. The seven-membered system **7** exhibits the largest downfield shift which, to the best of our knowledge, has not been observed for a metal coordinated carbene carbon atom so far. This is supposed to result from the non-planarity of the dibenzo[*a,d*]cycloheptene skeleton[8] reducing the overlap of the filled arene π-orbitals and the *p*-orbital at the carbene carbon atom.

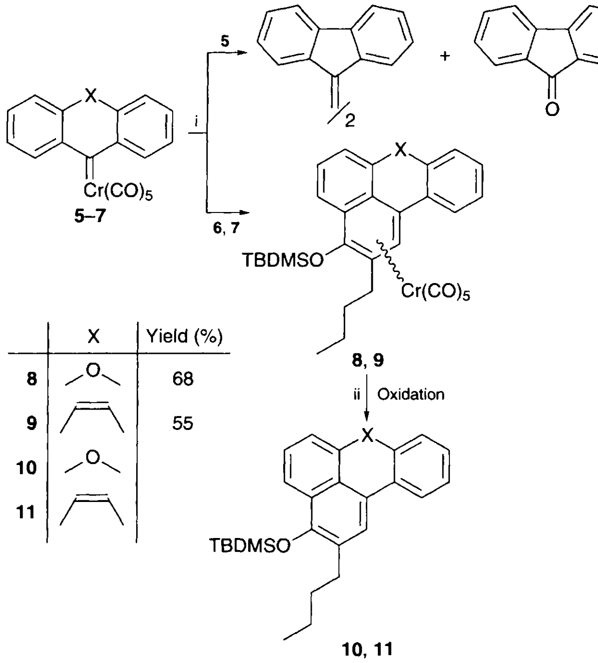
The tricyclic carbene complexes **6** and **7** undergo regioselective carbene annulation upon reaction with hex-1-yne (Scheme 3). The resulting $Cr(CO)_3$-complexes **8** and **9**† are demetallated to give **10** and **11**† during oxidative workup. No analogous annulation product, however, could be obtained from the fluorenylidene complex **5** under a variety of conditions. Instead,



Scheme 1



Scheme 2 *Reagents and conditions*: i, hexane–CH_2Cl_2, 5 : 1 (*v*/*v*), −10 °C, 3 h



Scheme 3 *Reagents and conditions*: i, hex-1-yne, Bu^{t}OMe, 20 °C (**5**,**7**) or 45 °C (**6**), 90 min; then TBDMSCl–NEt$_3$, CH_2Cl_2, 20 °C, 90 min; ii, air, CH_2Cl_2, 20 °C, 48 h. TBDMSCl = *tert*-butyldimethylsilyl chloride.

the carbene dimerization and oxidation products have been isolated.

On the basis of the generally accepted mechanism for the carbene annulation[2] one might speculate that the formation of the cyclohexadienone complex **B** by electrocyclic ring closure of the vinylketene complex intermediate **A** is hampered by the distance between the *ortho*-aryl and the ketene carbonyl carbon atoms which is enlarged as a consequence of the smaller bond angles in the central five-membered ring (Scheme 1).

The chromium mediated benzannulation of metal carbenes such as **6** and **7** provides a straightforward synthetic access to novel oxygenated benzo[*k*,*l*]xanthenes **10** and benzo[4.5]-cyclohepta[1,2,3-de]naphthalenes **11**[9] with control over the regiochemistry at positions 1–3.

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Footnote

† *Selected spectroscopic data* for **7**: IR (hexane): ν_{CO}/cm^{-1} 2068m, 1978vs and 1953sh; ^1H NMR (500 MHz, $CDCl_3$, 253 K): δ 7.53 (t, 2 H), 7.47 (d, 2 H), 7.32 (t, 2 H), 7.31 (d, 2 H) and 6.92 (s, 2 H, H-10, H-11); ^{13}C NMR (100.6 MHz, $CDCl_3$, 253 K): δ 404.2 ($C_{carbene}$), 237.5 (CO_{trans}), 214.4 (CO_{cis}), 162.6 (2 C, C_{arene}), 131.5, 128.3, 127.9, 126.7, 122.6 (10 C, HC_{arene}) and 119.4 (2 C, C_{arene}); HR-MS: *m*/*z* 353.9964 (M^+ −CO, calc. 353.9944); MS: *m*/*z* 354 (M^+ −CO, 5%), 298 (M^+ −3 CO, 8%), 270 (M^+ −4 CO, 12%), 242 (M^+ −5 CO, 25%), 190 (M^+ −5 CO −Cr, 100%), 94 (34%) and 52 (Cr^+, 41%). For **9**: IR (hexane): ν_{CO}/cm^{-1} 1957s, 1894m and 1880m; ^1H NMR (500 MHz, $CDCl_3$, 253 K): δ 7.65 (d, 1 H), 7.39 (d, 1 H), 7.37–7.33 (m, 2 H), 7.3 (t, 1 H), 7.15 (d, 1 H), 7.05 (d, 1 H), 6.58 (d, 1 H, $^3J_{HH}$ 12.32 Hz, H-8), 6.46 (d, 1 H, $^3J_{HH}$ 12.31 Hz, H-7), 5.67 (s, 1 H, H-1), 2.82 (dt, 1 H), 2.52 (dt, 1 H), 1.7 (quintet, 2 H), 1.51 (m, 2 H), 1.01 (t, 3 H), 1.12 (s, 9 H) and 0.45 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$, 253 K): δ 233.68 [3 C, $Cr(CO)_3$], 133.75 (1 C, C-7), 132.66 (1 C, C-8), 137.29, 137.13, 135.83, 131.89, 131.16, 130.69, 129.76, 129.42, 127.74, 122.63 (9 C, C_{arene}), 130.24 (1 C, C-3), 106.61, 106.11, 105.06 103.08 (4 C, C_{arene}), 93.93 (1 C, C-1), 33.18, 29.97, 22.99, 14.23 (4 C, $CH_2CH_2CH_2CH_3$), 25.59 [3 C, $Si\mathit{C}(CH_3)_3$], 18.73 (1 C, $SiC(\mathit{C}H_3)_3$], −2.04 and −3.53 [2 C, $Si(CH_3)_2$]; HR-MS: *m*/*z* 550.1629 (calc. 550.1627); MS: *m*/*z* 550.2 (M^+, 8%), 494.1 (M^+ −2 CO, 4%), 466.3 (M^+ −3 CO, 100%), 414.3 (M^+ −3 CO −Cr, 40%), 357 (M^+ − 3 CO − Cr − C_4H_9, 14%), 300 (M^+ −3 CO −Cr −2 C_4H_9, 16%) and 126 (31%). For **11**: ^1H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, 1 H, 7.35 (s, 1 H, H-1), 7.32 (t, 1 H), 7.3–7.2 (m, 3 H), 7.1 (d, 2 H), 6.48 (d, 1 H, $^3J_{HH}$ 12.02 Hz, H-8), 6.44 (d, 1 H, $^3J_{HH}$ 11.82 Hz, H-7), 2.78 (t, 2 H), 1.63 (quintet, 2 H), 1.39 (sex, 2 H), 1.14 (s, 9 H), 0.95 (t, 3 H) and 0.21 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.3 (1 C, C-3), 140.69, 137.63, 136.24, 130.4, 125.5, 125.32, 121.78 (7 C, C_{arene}), 135.46, 134.91, 132.94, 131.76, 130.9, 130.29, 128.73, 127.28, 124.51, 122.39 (10 C, HC_{arene}), 32.4, 30.07, 22.63, 14.21 (4 C, $CH_2CH_2CH_2CH_3$), 18.67 [1 C, $Si\mathit{C}(CH_3)_3$], 25.77 [3 C, $SiC(\mathit{C}H_3)_3$] and −3.25 [2 C, $Si(\mathit{C}H_3)_2$]; HR-MS: *m*/*z* 414.2374 (calc. 414.2369); MS: *m*/*z* 414.3 (M^+, 100%), 357.2 (M^+ − C_4H_9, 19%), 300.2 (M^+ − C_4H_9 − C_4H_9, 22%), 285.1 (M^+ −C_4H_9 −C_4H_9 −CH_3, 7%) and 73 (34%).

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