Aminocarbene Annulation by Alkynes: A Regio- and Diastereo-selective Route to Indanone Complexes[1]

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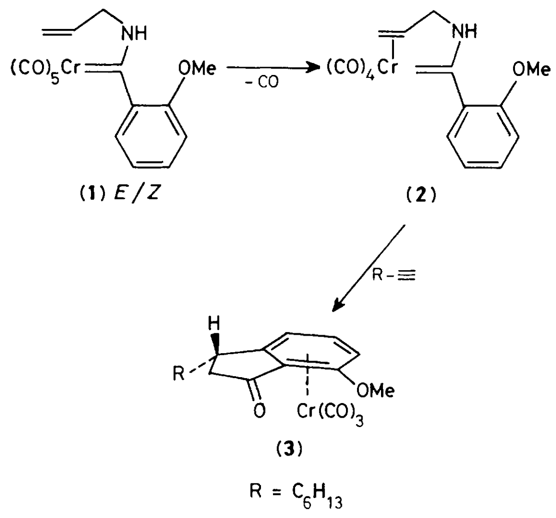
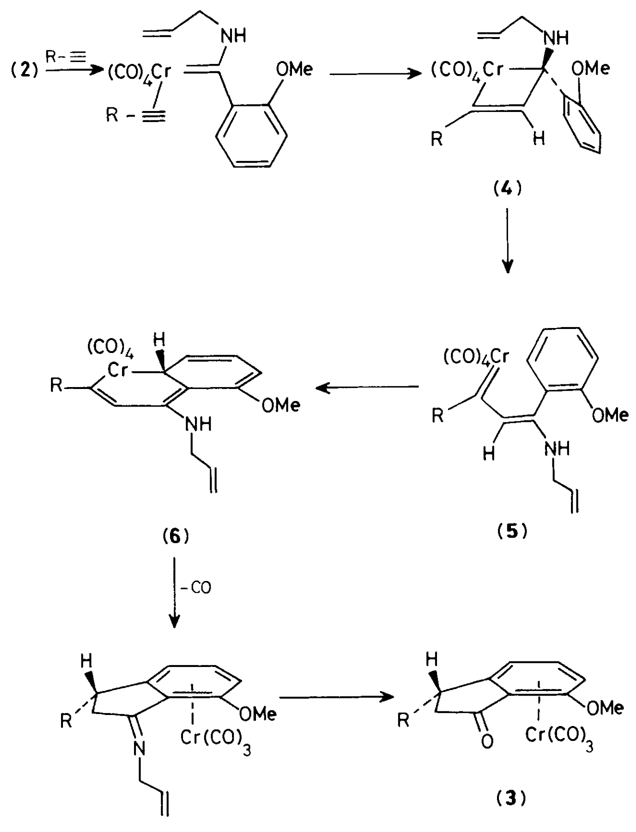
Upon reaction with oct-1-yne, pentacarbonyl[allylamino(2-methoxyphenyl)methylene]chromium undergoes a regio- and diastereo-selective carbene annulation leading finally to a *syn*-tricarbonyl(3-hexyl-7-methoxy-indanone)chromium complex, the crystal structure of which has been established by *X*-ray analysis.

Carbonyl carbene complexes have become powerful reagents for organic synthesis since they provide both CO and carbene synthons as well as a low-valent metal centre which may act as a template in transition metal-induced cycloaddition reactions.[2] By this strategy highly substituted arenes,[3a] indenes,[3b] furans,[3c] cyclobutenones,[3d] cyclopropanes,[3e] and β-lactams[3f] are accessible in one-pot reactions. Most attention has been paid to the formation of hydroquinones *via* carbene annulation of alkoxycarbene ligands by alkynes and carbon monoxide,[4] and this type of reaction has also been evaluated in natural product synthesis.[5] The formation of five-membered rings such as in indenes has been studied in less detail, although it seems compatible with various substitution patterns both in the carbene ligand and in the alkyne.[6]



Scheme 1. Conditions for the one-pot reaction from (1) to (3): Di-n-butyl ether/tetrahydrofuran (THF) (10/1), 90 °C, 1 h; SiO_2; 45% isolated yield of (3).



Scheme 2. Suggested mechanistic scheme for the formation of (3).

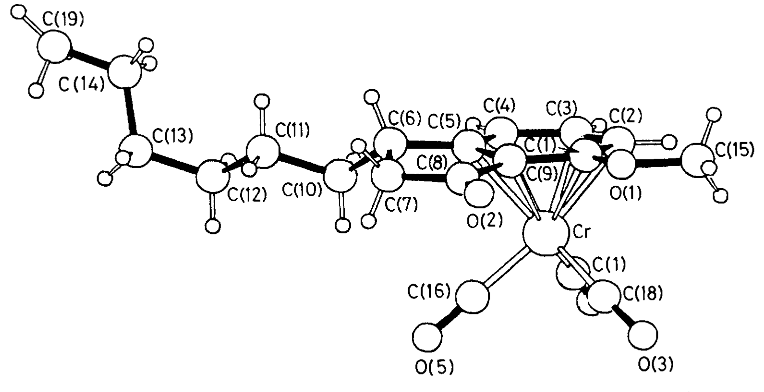


Figure 1. Molecular structure of (3) (SCHAKAL, all atoms with arbitrary radii). Important distances (Å) and angles (°): C(1)–C(2) 1.413(6), C(2)–C(3) 1.391(6), C(3)–C(4) 1.413(6), C(4)–C(5) 1.384(6), C(5)–C(9) 1.415(5), C(5)–C(6) 1.504(5), C(6)–C(7) 1.533(6), C(7)–C(8) 1.510(6), C(8)–C(9) 1.482(6); C(5)–C(6)–C(7) 103.3(3), C(6)–C(7)–C(8) 108.1(3), C(7)–C(8)–C(9) 106.0(4), C(5)–C(9)–C(8) 109.8(3). Torsion angles (°): C(4)–C(5)–C(9)–C(1) 6.2(7), C(4)–C(5)–C(9)–C(8) −175.1(4), C(6)–C(5)–C(9)–C(1) 170.9(4), C(6)–C(5)–C(9)–C(8) 7.9(5), C(4)–C(5)–C(6)–C(10) 41.6(6), C(10)–C(6)–C(7)–C(8) 141.8(4).

We report here on a novel regio- and diastereo-selective one-pot access to indanone complexes based on the annulation of aminocarbene ligands. So far, the application of aminocarbene complexes in cycloaddition reactions has been hampered by the thermal stability of these compounds resulting either in low yields of carbene annulation products[7] or in uncontrolled loss of the transition metal.[8] A promising strategy to overcome these drawbacks involves the use of allylaminocarbene chelate complexes in which the required vacant site at the metal is reversibly blocked by η^2-alkene co-ordination.[9]

The allylaminocarbene chelate complex (**2**), accessible *via* either thermal or photochemical decarbonylation from its pentacarbonyl precursor (**1**), reacts with oct-1-yne on warming in di-n-butyl ether to give initially a five-membered carbene annulation product. Subsequent work-up by column chromatography on silica gel leads to the indanone complex (**3**)[†] (Scheme 1). The reaction is conveniently run as a one-pot tandem decarbonylation/annulation process starting from an *E*/*Z* mixture of the allylaminocarbene pentacarbonyl complex (**1**). The decarbonylation occurs with concomitant isomerization across the $C_{carbene}$–N bond. Only one diastereoisomer of (**3**) is observed which demonstrates the regio- and diastereo-selective incorporation of the alkyne.

The relative configuration of the indanone complex (**3**) was established by *X*-ray analysis[‡] (Figure 1). The chromium fragment co-ordinated to the arene ring and the hexyl substituent in the five-membered ring are both bonded to the same face of the bicyclic ring system. The carbonyl ligands are eclipsed with respect to the arene ring carbon atoms which have slightly alternating bond distances. The five-membered ring is puckered containing the alkyl substituent in a pseudo-equatorial position.

The stereoselective carbene annulation can be rationalized in terms of a regioselective addition of the alkyne ligand across the metal carbene bond which occurs under steric control (Scheme 2).[10] Ring-opening of the metallacyclobutene (**4**) is expected to give preferentially the *E*-isomer (**5**) which may undergo a cyclization to the chromacyclohexadiene (**6**). A sigmatropic suprafacial 1,5 hydrogen shift, accompanied by reductive elimination and migration of the metal fragment, may be made responsible for the diastereoselective formation of the annulation product.

Thus the carbene annulation provides a novel stereoselective access to indanone–$Cr(CO)_3$ complexes which are valuable intermediates for further stereoselective functionalization.[11] An extension of this work to enantioselective synthesis is under current study.

We thank Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for their financial support.

Received, 2nd November 1988; Com. 8/04361B

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[†] *Selected spectroscopic data* (**3**): i.r.: ν_{CO} (CH_2Cl_2) 1973vs, 1900vs, 1717s cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$) 5.81 (t, 5-H), 5.10 (d), and 5.01 (d) (4-H, 6-H), 3.86 (s, OMe), 3.29 (ddt, 3-H), 2.77 (dd, 2-C*H*H), 2.52 (dd, 2-CH*H*), 1.93 (m, 1′-CH*H*), 1.81 (m, 1′-C*H*H), 1.38 [m, $(CH_2)_4$], 0.90 (t, Me); ^{13}C n.m.r. δ ($CDCl_3$) 230.8 [$Cr(CO)_3$], 200.0 (C=O), 142.2, 129.4, 95.1, 86.6, 81.0, 72.4 (3a-7a-C), 56.2 (OMe), 42.9 (2-C), 37.0 (3-C), 32.2, 31.6, 29.2, 28.4, 22.5 [$(CH_2)_5$], 14.0 (Me).

[‡] *Crystal data* for (**3**): monoclinic, space group *C*2/*c*, $a = 22.736(5)$, $b = 6.809(1)$, $c = 25.373(10)$ Å, $\beta = 107.86(2)°$, $U = 3738.7$ Å^3, $D_c = 1.359$ g cm^{-3}. $Z = 8$, $\mu(\text{Mo-}K_\alpha) = 6.2$ cm^{-1}. 3667 Reflections were recorded on an Enraf-Nonius CAD4 diffractometer [ω-scans, $\Delta\omega = (0.8 + 0.35 \tan \theta)°$, $\theta_{max} = 25°$, Mo-K_α-radiation (0.71069 Å), graphite monochromator], 2804 unique reflections ($R_{int} = 0.043$). Solution by direct methods (SHELXS-86, G. M. Sheldrick, Göttingen, FRG, 1986), refinement with SHELX76 (G. M. Sheldrick, Cambridge, U.K., 1976) to $R = 0.0499$, $R_w = 0.0459$ for 2373 'observed' reflections with $F \geqslant 4\,\sigma(F)$, all non-hydrogen atoms anisotropic, H-atoms isotropic with a common temperature factor, 230 parameters. $\Delta\rho_{fin}$ (max./min.) = 0.49/−0.28 e/Å.^{3} Absorption correction with 'DIFABS' (N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 159). 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.