First Intramolecular Alkyne–CO Insertion Reactions in Aminocarbene Complexes of Chromium: Formation of Condensed Heterocycles following Extensive Hydrogen Migrations

M. Audouin, S. Blandinières, A. Parlier, and H. Rudler*

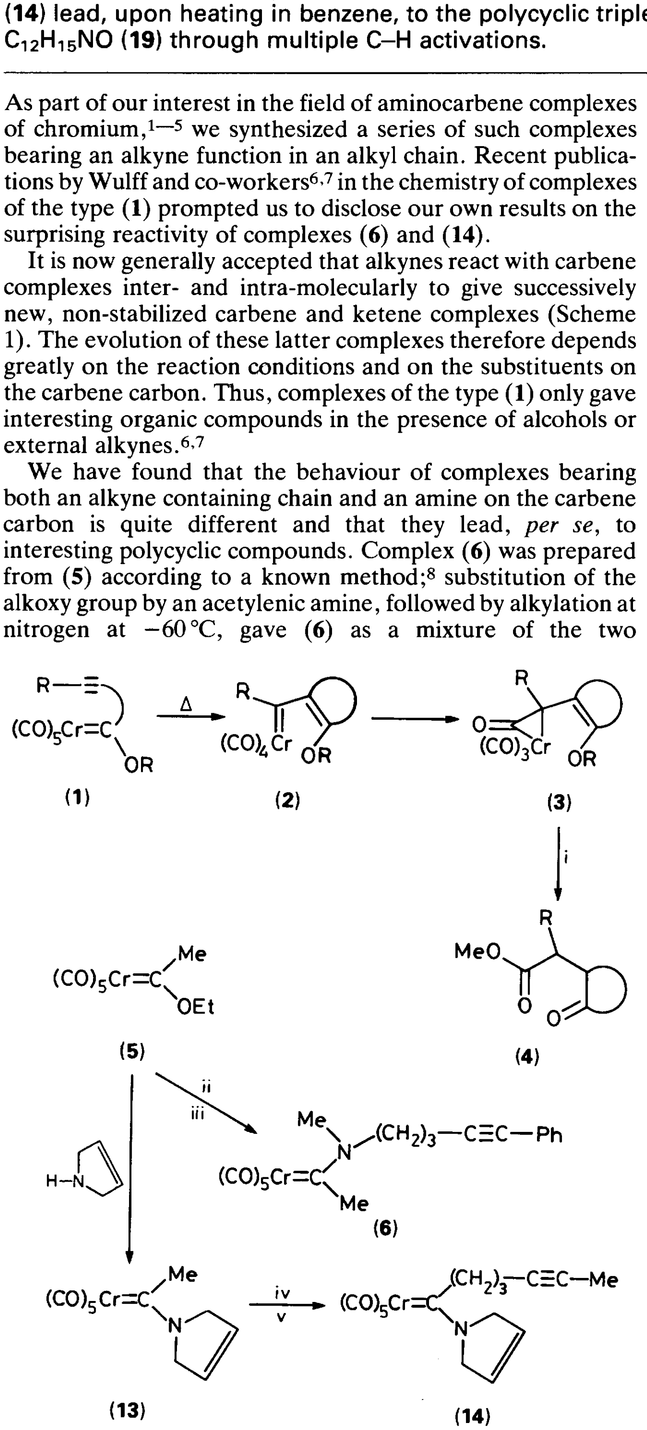
Laboratoire de Chimie Organique, UA 408, Université Pierre et Marie Curie T 44, 4 Place Jussieu, 75252 Paris Cedex 05, France

The aminocarbene complexes $(CO)_5Cr{=}C(Me)[N(Me)(CH_2)_3C{\equiv}CPh]$ (**6**) and $(CO)_5Cr{=}C(N\overline{CH_2CH{=}C}H_2)[(CH_2)_3C{\equiv}CMe]$ (**14**) lead, upon heating in benzene, to the polycyclic triple bond and CO inserted products $C_{15}H_{15}NO$ (**12**) and $C_{12}H_{15}NO$ (**19**) through multiple C–H activations.

As part of our interest in the field of aminocarbene complexes of chromium,[1—5] we synthesized a series of such complexes bearing an alkyne function in an alkyl chain. Recent publications by Wulff and co-workers[6,7] in the chemistry of complexes of the type (**1**) prompted us to disclose our own results on the surprising reactivity of complexes (**6**) and (**14**).

It is now generally accepted that alkynes react with carbene complexes inter- and intra-molecularly to give successively new, non-stabilized carbene and ketene complexes (Scheme 1). The evolution of these latter complexes therefore depends greatly on the reaction conditions and on the substituents on the carbene carbon. Thus, complexes of the type (**1**) only gave interesting organic compounds in the presence of alcohols or external alkynes.[6,7]

We have found that the behaviour of complexes bearing both an alkyne containing chain and an amine on the carbene carbon is quite different and that they lead, *per se*, to interesting polycyclic compounds. Complex (**6**) was prepared from (**5**) according to a known method;[8] substitution of the alkoxy group by an acetylenic amine, followed by alkylation at nitrogen at −60 °C, gave (**6**) as a mixture of the two *E,Z*-isomers. Complex (**14**) was obtained from the already described complex (**13**)[4] by selective monoalkylation at the methyl group.[9]



Scheme 1. *Reagents and conditions*: i, MeOH; ii, $H_2N(CH_2)_3C{\equiv}CPh$; iii, lithium di-isopropylamide, MeI; iv, BuLi; v, $MeC{\equiv}C(CH_2)_2OTf$ (Tf = SO_2CF_3).

When complex (**6**) was heated in refluxing benzene, a fast reaction took place. According to TLC, (**6**) disappeared within 30 s to give a more polar unstable pink complex, which after about 1 h, led finally to the formation of a single organic product. Filtration over silica gel gave (**12**) as white crystals (21%, m.p. 92 °C). EI MS gave a molecular ion, m/z = 225, which corresponds to a molecular formula $C_{15}H_{15}NO$. Both the IR (C=O, 1680 cm^{-1}) and the ^{13}C NMR spectra confirmed the presence of a conjugated ketone. The ^{13}C NMR spectrum revealed all 15 carbons, of which five were sp^2 carbons. Since these sp^2 carbons account for seven of the nine unsaturations present in the molecule, it was assumed that (**12**) contains, besides the aromatic ring, two other rings. Structure (**12**) could finally be confirmed by ^{13}C and ^1H NMR spectroscopy.† Partial structures $[-N(Me)CH_2CH_2C(H){=}C]$ and $[{=}C(H)C(O)C(H)(Ph)C]$, established by means of chemical shifts and proton–proton couplings, were connected on the basis of ^2J and $^3J_{C-H}$ correlations; the downshifted vinylic carbon [δ 167.1 (C-3)] was correlated with the *N*-methyl protons [δ 2.94 (H-16)], the vinylic protons [δ 5.12 (H-2) and 5.72 (H-7)], and the downshifted methylene protons [δ 3.27 (H-5)].

As far as complex (**14**) is concerned, treatment under the same conditions as for (**6**) led to a single organic product (41%, white crystals, m.p. 31 °C). EI MS gave a molecular ion, m/z = 189, which corresponds to a formula $C_{12}H_{15}NO$ (CO, 1640 cm^{-1}). The ^{13}C NMR spectrum revealed the presence of all the carbons of which five were sp^2, thus corresponding to three unsaturations. This means that (**19**) contains three rings. Its structure was also established by ^{13}C and ^1H NMR spectroscopy.† A heteronuclear chemical shift correlation spectrum furnished the attribution for all the protonated carbons whereas the others were connected *via* their long range couplings: C-1 with H-2, H-5; C-10 with H-7,7′ and H-9,9′.

A mechanism which can account for the formation of the two compounds can be disclosed starting from the two ketene complexes (**8**) and (**16**); due to the presence of nitrogen, the

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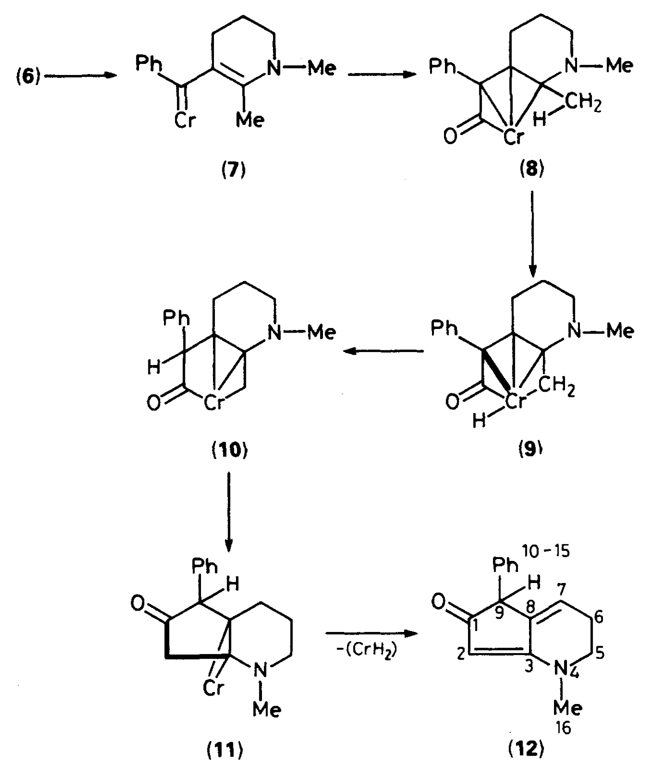
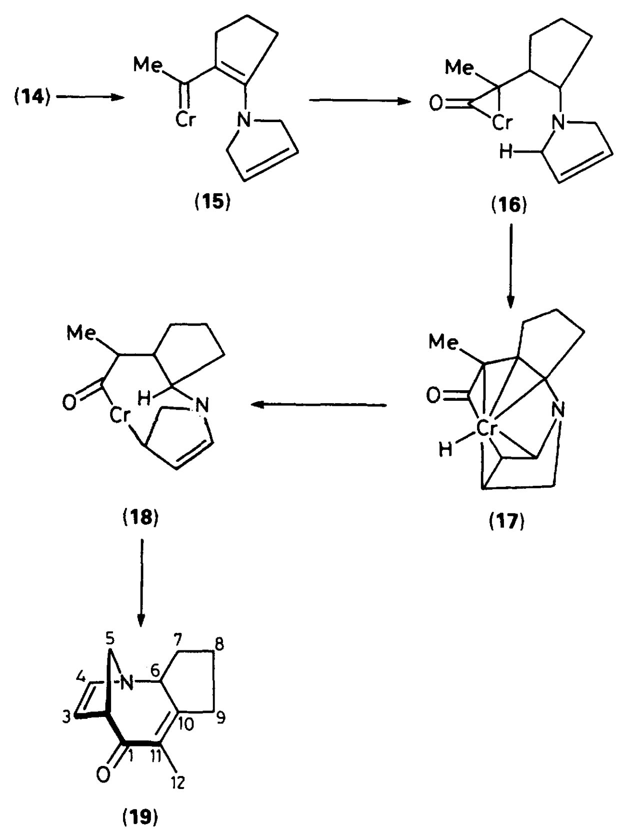
† All compounds were isolated as analytically pure samples. ^1H and ^{13}C NMR data: (**12**), ^1H NMR, (200 MHz, $CDCl_3$) δ 6.15 (1H, d, H-4), 5.51 (1H, t, H-3), 3.67 (1H, m, H-6), 3.29 (1H, m, H-2), 3.24 (1H, d, H-5), 3.06 (1H, dd, H-5′), 2.39 (2H, m, H-9,9′), 1.98 (1H, m, H-7′), 1.67 (4H, m, H-7, H-8,8′, H-12); ^{13}C NMR, (50 MHz, $CDCl_3$) δ 203.7 (C-1), 154.3 (C-10), 141.9 (C-4), 125.8 (C-11), 117.9 (C-3), 72.9 (C-6), 56.9 (C-2), 50.7 (C-5), 33.4 (C-7), 31.7 (C-9), 19.2 (C-8), 15.7 (C-12). (**19**), ^1H NMR, (200 MHz, $CDCl_3$) 7.19 (5H, m, Ph), 5.72 (1H, t, H-7), 5.12 (1H, s, H-2), 3.98 (1H, s, H-9), 3.27 (2H, m, H-5), 2.94 (3H, s, Me), 2.40 (2H, m, H-6); ^{13}C NMR (50 MHz, $CDCl_3$), δ 199.4 (C-1), 167.1 (C-3), 139.1 (C-10), 137.0 (C-8), 128.4 (C-11 and C-15), 128.3 (C-12 and C-14), 126.6 (C-13), 121.8 (C-7), 99.2 (C-2), 54.2 (C-9), 47.6 (C-5), 39.3 (C-16), 23.9 (C-6).



Scheme 2



metal centre is very nucleophilic and oxidative addition of the C–H bonds can take place giving complex (**9**) in one case and complex (**17**) in the other. Hydrogen migration, followed by carbon–carbon coupling, would finally lead to (**11**) and (**19**). Since (**11**) is the complex of a β-γ-unsaturated ketone, deco-ordination of the metal to give (**12**) can occur after a double β-elimination.

It is surprising to notice that in both cases, no carbon–nitrogen bond rupture, established previously,[3] is observed and that the course of the reaction is not modified by the presence of an external alkyne such as diphenylacetylene.

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