Synthesis, X-Ray Structure and Rearrangement of Nitrogen Ylides obtained upon Alkyne and CO Insertion Reactions into Aminocarbene Complexes of Chromium

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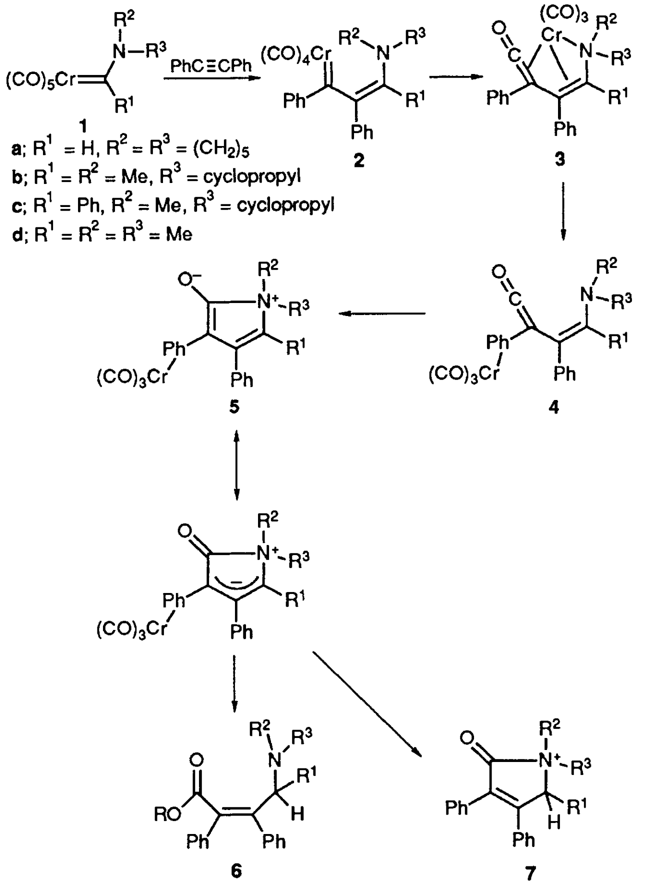
The aminocarbene complexes $(CO)_5Cr{=}C(R^1)N(R^2R^3)$ **1** [R^1 = H, Me, Ph, R^2 = Me, R^2R^3 = $(CH_2)_5$, R^3 = Me, cyclopropyl] react with diphenylacetylene to give nitrogen ylides **5** which were fully characterized by an X-ray analysis carried out on **5a** [$(CO)_3CrR^2R^3\overset{+}{N}(C_{16}H_{10}OR^1)^-$($R^1$ = H, R^2 = R^3 = $(CH_2)_5$] and which lead, upon nitrogen to carbon migrations of alkyl groups R^2 and R^3, to the expected lactams (*e.g.* **8** and **9**) $C_{16}H_{10}ONR^1R^2R^3$.

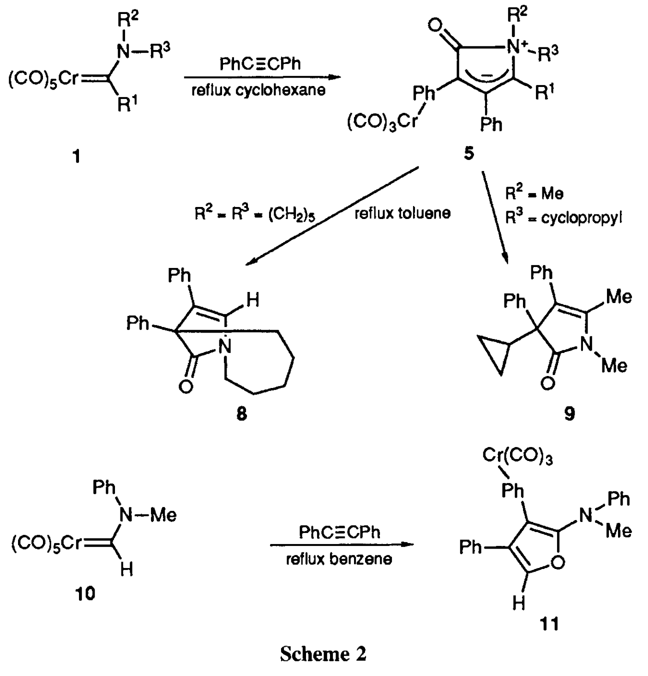
Ketene complexes have long been considered as elusive intermediates during the interaction of Fischer carbene complexes and alkynes, a reaction which leads for example to synthetic useful benzannulation products.[1–3] In a few instances such compounds have been isolated as side products in these insertion reactions. However, their transformation into rearranged products could not be achieved, a result assigned to unfavourable geometry.[4]

In the case of aminocarbene complexes such intermediates have also been suspected (Scheme 1) and solvolysis products of them isolated and characterized.[5–10] Finally, in the case of an intramolecular alkyne insertion reaction, such a complex could be isolated.[11] However, again this intermediate did not react further, *per se*, to give rearranged products.

The purpose of the present communication is to describe the synthesis and the X-ray structure of ylides arising from the



Scheme 1



Scheme 2

intramolecular interaction of a tertiary nitrogen with a ketene intermediate and, for the first time, their rearrangement, upon heating, into the expected products resulting from nitrogen to carbon migrations of alkyl groups.

Thus, when a series of aminocarbene complexes **1**, bearing alkyl groups on nitrogen of low migratory aptitude, were reacted with diphenylacetylene in boiling cyclohexane, a yellow precipitate appeared after a few hours. These new very polar compounds were extremely moisture sensitive, giving rapidly, even on TLC plates the already characterized amino acids **6** (R = H).[9] Even so, addition of methanol rapidly converted them to the corresponding amino esters **6** (R = Me).

These transformations seemed to be indicative of the presence of ketene functions such as in **4**. However, a careful examination of the spectroscopic data indicated that this was probably not the case.† Indeed, the IR spectrum showed absorptions due to terminal CO groups, but no absorption due to a ketene function which was expected at slightly over 2000 cm^{-1}. Nevertheless, an absorption was present at 1700 cm^{-1} for all compounds. Furthermore, the ^{13}C NMR spectrum indicated, besides signals for an arene tricarbonyl chromium group, a signal around δ 170 being highfield with respect to the usual signals for ketenes and ketene complexes.[12,13] Moreover, no highfield signal for the second ketene-carbon atom was observed; instead, a signal for all compounds appeared around δ 110. All these data indicated that the nitrogen atom must already interact with the carbonyl function of the ketene in the same way as amines interact with the carbonyl group in mesocyclic aminoketones.[14,15]

After much effort and difficulties due to the hygroscopic character of these complexes, golden-yellow crystals of complex **5a** suitable for an X-ray analysis could be grown from hexane–methylene chloride. The X-ray structure determination revealed for the first time the structural parameters of an ylide intermediate. The molecular geometry, including essential bond lengths and angles, is shown in the Fig. 1;‡ mean estimated standard deviations are 0.005 Å and 0.3°.

The salient features for complex **5a** are the following: (*i*) as expected, no stabilization of the ketene function by the metal is observed, the $Cr(CO)_3$ group being linked to a phenyl group, (*ii*) the nitrogen atom is in a tetrahedral environment

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† All compounds were isolated as analytically pure samples. **5a**: ^{1}H NMR (200 MHz, C_6D_6) δ: 7.39–7.15 (5H, m), 5.74 (2H, d), 5.25 [1H, s, C(1)-H], 4.74 (2H, t), 4.12 (1H, t), 3.05 (2H, m, N-CH_2), 2.30 (2H, m, N-CH_2), 0.90 [6H, m, $(CH_2)_3$]; ^{13}C NMR (50MHz, CD_2Cl_2) δ: 235.5 (CO), 169.8 (CO), 147.6, 134.2, 129.0, 128.8, 128.3 [C(2), aromatics], 115.1 [C(3)], 111.6 [C(1)], 96.4, 89.1, 87.4 [Ar-$Cr(CO)_3$], 56.4 (N-CH_2), 22.1, 21.7 (CH_2). **5c**: ^{1}H NMR (200 MHz, CD_2Cl_2) δ: 7.45–7.25 (5H, m), 5.47 (1H, d), 5.36 (1H, m), 5.25 (2H, m), 4.84 (1H, m), 2.84 (3H, s, NCH_3), 2.80 (1H, m, N–CH), 1.82 (3H, s,), 1.53 (1H, m), 1.15 (1H, m), 0.76 (2H, m); ^{13}C NMR (50 MHz, CD_2Cl_2) δ: 235.8 (CO), 168.9 (CO), 142.0, 134.0, 129.3, 129.1, 128.6 [C-aromatic, C(2)], 122.0 [C(3)], 115.5 [C(1)], 96.3, 88.8, 88.7, 87.5 [Ar-$Cr(CO)_3$], 42.7 (N-CH), 42.0 (N-CH_3), 18.0 (CH_3), 9.65 [$(CH_2)_2$]. **9a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.29–7.07 (10H, m), 7.04 (1H, s, CH), 4.18 (1H, m, N-CH), 3.35 (1H, m, N-CH), 2.63 (2H, m, CH_2), 1.97–1.24 (6H, m); ^{13}C NMR (200 MHz, $CDCl_3$) δ: 187.50 (CO), 138.5–124.9 [C(2), aromatics], 60.8 [C(3)], 46.6 (N-CH_2), 41.75 (N-CH_2), 36.3, 25.6, 24.0(CH_2). **9c**: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.47–6.78 (10H, m), 3.11 (3H, s, N-CH_3), 2.13 (3H, s, CH_3), 1.35 (1H, m), 0.94 (1H, m), 0.61 (1H, m), 0.40 (1H, m), −0.02 (1H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 179.2 (CO), 140.7, 122.6 [aromatic, C(1), C(2)], 59.8 [C(3)], 26.6 (N-CH_3), 14.6 (CH_3), 11.5 (CH), 1.68 (CH_2–CH_2).

‡ *Crystal data*: $C_{24}H_{21}O_4NCr$, $M = 439.43$, monoclinic, space group $P2_1/c$, $a = 15.032(4)$, $b = 6.488(6)$, $c = 22.058(6)$ Å, $\beta = 106.49(2)°$, $D_c = 1.415$ g cm^{-3}, $Z = 4$, crystal size 0.18 × 0.20 × 0.80 mm, μ(Mo-Kα) = 5.69 cm^{-1}, 3630 data collected at room temperature on a Nonius CAD4 diffractometer. Empirical absorption correction using DIFABS (min, 0.86, max. 1.14) was applied. Anomalous dispersion terms and a correction of secondary extinction were applied. The structure was solved by standard Patterson-Fourier technique and refined by least-squares analysis using anisotopic thermal parameters for all non-hydrogen atoms. H atoms were located on difference Fourier maps. Reflections 2162, with $I > 3\sigma(I)$ were used to solve and refine the structure to $R = 0.0391$ and $R_w = 0.0400$, 336 least-squares parameters. The programs used were CRYSTALS and ORTEP-2. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

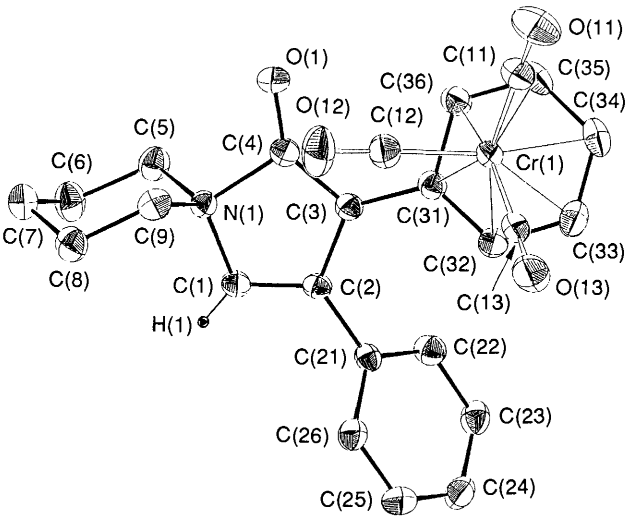

Fig. 1 ORTEP view of chromium tricarbonyl complex of ylide **5a**, important bond lengths (Å) and bond angles (°): C(1)–C(2) 1.327(5), C(2)–C(3) 1.458(5), C(3)–C(4) 1.368(5), C(4)–O(1) 1.225(5), C(4)–N(1) 1.590(5), C(1)–N(1) 1.449(5); N(1)–C(4)–O(1) 115.7(3), C(9)–N(1)–C(5) 110.6(3), C(4)–N(1)–C(1) 103.0(3), C(5)–N(1)–C(4) 109.1(3), C(9)–N(1)–C(4) 106.9(3), O(1)–C(4)–C(3) 138.6(4)

with a rather long N(1)–C(4) bond, (*iii*) N(1), C(1), H(1), C(2), C(3), C(4) and O(1) lie almost in the same plane forming a pyrrolinone ring-system.

A way to describe this structure is to consider it as the result of the interaction of the nucleophile N(1) with the ketene function;[16] as a result, the ketene function is no longer linear, the C(3)–C(4)–O(1) angle being equal to 138.6(4)°. The C(3)–C(4) distance (1.368 Å) is typical for a double bond, greater than in ketenes (1.27 Å), whereas the C(4)–O(1) bond (1.225 Å) is slightly longer than in free ketenes (1.18 Å).

Since C(1)–C(2), 1.327 Å, is also typical for a double bond, and since the geometry of the phenyl $Cr(CO)_3$ group has not been affected by the intramolecular interaction, the negative charge has delocalized towards oxygen, giving a nitrogen-oxygen centred zwitterionic intermediate **5a**. According to these structural features, it is clear that the weakest bond is N(1)–C(4); thus, solvolysis can lead very easily to the ring-opened amino acids and their derivatives **6**.

Finally protonation of **5** with trifluoroacetic acid leads to **7**, a result which clearly demonstrates that the negative charge can delocalize towards carbon atoms C(1) and C(3).

Though stable for hours in boiling cyclohexane, these complexes rearrange cleanly in boiling toluene to the expected lactams.[5–7] Thus complex **5a** [R^1 = H, R^2 = R^3 = $(CH_2)_5$] gives the bridgehead lactam **8** in up to 70% yield, whereas complex **5b** (R^1 = R^2 = Me, R^3 = cyclopropyl leads to the pyrrolinone **9** in 78% yield (Scheme 2).

It is therefore clear that ylides such as **5** rearranged like other carbonyl-stabilized ammonium ylides, which undergo the known Stevens rearrangement.[17,18] Moreover, as in the Stevens rearrangement of nitrogen-ylides, nitrogen to oxygen migrations can be observed;[19] this is for example the case for the transformation **10** → **11** which occurs directly, in boiling benzene, in 70% yield.[20]

As a conclusion, it appears now that the role of the metal in these insertion reactions is to bring together the carbene, the alkyne and CO, a reaction which leads to enaminoketene complexes then to non-metal-stabilized ylides. According to all the results gathered up to now in this field, the rearrangement of the ylides follows the general trends established for the Stevens rearrangement of other organic ylides.[18]

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