Hydrazinolysis of Fischer-type oxacarbenes made efficient: a new and easy entry to alkyl and aryl hydrazinocarbene complexes

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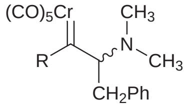
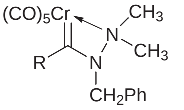
Hydrazinolysis of the pentacarbonyl[alkyl- or aryl-(methoxy)carbene] complexes of W^0 and Cr^0 with both 1,1- and 1,2-disubstituted hydrazines affords the corresponding new hydrazinocarbenes 15–18, 21 and 22, and the presence of LiCl in the reaction medium greatly increases their yields.

We have recently achieved the first synthesis of a number of new pentacarbonyl and chelate hydrazino(alkyl)carbene complexes **1–3**.[1]



1 R = Me
2 R = Et, but-3-enyl



3 R = Et, but-3-enyl, Pr^i

The synthesis of **1–3** is of general applicability only when applied to 1-substituted hydrazides.[2] The hydrazinolysis of oxacarbenes was a highly appealing procedure, even if Fischer[3] reported that, for the reaction between the 1,1-dimethylhydrazine and the pentacarbonyl[methoxy(methyl)carbene]chromium(0), it was unsuccessful. However, the hydrazinolysis of oxacarbenes has more recently been shown to be possible in a few specific cases.[4,5]

We here report on the reactions between the 1,1-disubstituted hydrazines **5** and **7–10** and the methoxy(methyl)carbene tungsten(0) complex **11**, as well as those between the 1,2-dimethylhydrazine **12** and the methoxy(methyl)- and methoxy(phenyl)-carbene chromium(0) complexes **4** and **13**. The results of this study eventually revealed a new and efficient entry to alkyl- and aryl-(hydrazino)carbenes.

We initially reacted under nitrogen the 1,1-dimethylhydrazine **5** (1.1 mmol) with the tungsten complex **11** (1 mmol) in dry THF solution at −78 °C for 30 min, but even the use of tungsten only afforded the $(CO)_5W{\leftarrow}N{\equiv}C{-}Me$ complex **14** (Table 1). However, when we reacted the hydrazines **7–10** with **11** under the same conditions, we isolated a reaction mixture containing the (*Z*)-hydrazinocarbenes **15–18**† and variable amounts of the acetonitrile complex **14**; the yields are shown in Table 1.

Although the yields of hydrazinocarbenes **15–18** were not very high, this first set of results showed us that it was possible to use the simple procedure described above to prepare stable and isolable alkyl hydrazinocarbene complexes of tungsten. We therefore decided to look carefully at the possible mechanism of the hydrazinolysis reaction. The aim was to identify the factors potentially capable of differentiating the pathway leading to the acetonitrile complex **14** from that affording the target hydrazinocarbenes **15–18**.

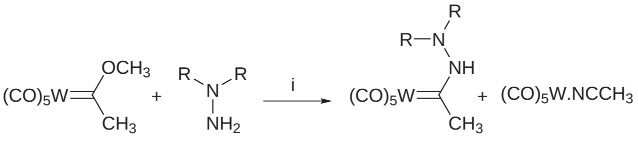
According to Aumann,[4] during the hydrazinolysis of alkoxy(alkynyl)carbenes, the hydrazinocarbenes **15–18** are formed through the elimination of MeOH from the tetrahedral intermediate of the reaction, whereas product **14** arises from the breaking of the N–N bond with amine elimination. This latter process is a consequence of the proton shift from the α- to the β-nitrogen.

All of the attempts to prevent this proton shift, *i.e.* (i) by increasing steric hindrance around the β-nitrogen, (ii) by running the reactions in the presence of an excess of Et_3N as an external competing base and, (iii) by reducing the β-nitrogen lone pair availability by means of acylation, failed, and there was no improvement in the yields of the complexes **15–18**. Looking for an alternative way to minimize the undesirable β-nitrogen protonation, we considered a Lewis acid as a possible coordinating species capable of engaging the β-nitrogen lone pair without transforming this nitrogen into a good leaving group: Li^+ (as LiCl) appeared to be a suitable reagent for achieving this goal.

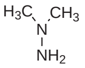
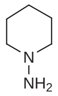
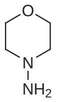
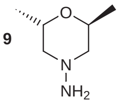
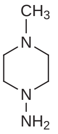
The results of the hydrazinolysis of complex **11** with the *N*-aminomorpholine **8** and *N*-amino-*trans*-2,6-dimethylmorpholine **9** in the presence of 2.2 equiv. of LiCl were surprisingly good, with the yields of complexes **16** and **17** being respectively double and eight times of those obtained in the absence of LiCl (Scheme 1).

The presence of LiCl also had a dramatic effect on the reaction times, which increased from 30 min to 5 h. We believe that this effect can be rationalized in terms of the formation of an aggregate in THF between LiCl and the hydrazines **8** and **9**,‡ in which the nucleophilic character of the hydrazines would be

Table 1 Reaction of **11** with various hydrazines[a]

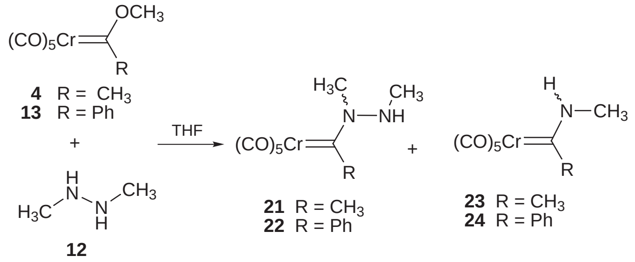


11 **5, 7–10** **15–18** **14**

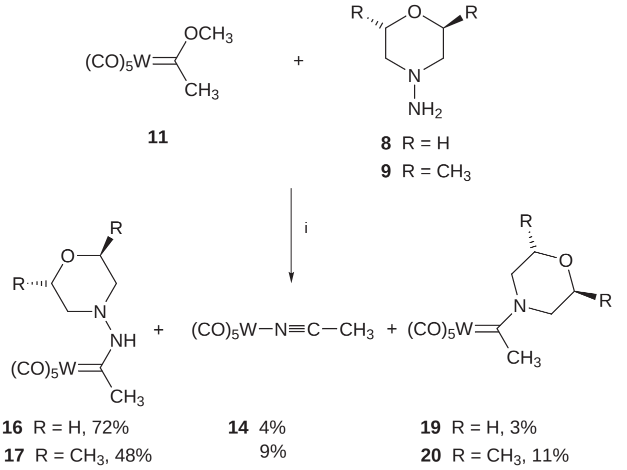
Hydrazine		(*Z*)-Hydrazinocarbene **15–18** (% yield)	Yield of **14** (%)
5		—	52
7		**15** (34)	42
8		**16** (34)	50
9		**17** (6)	74
10		**18** (28)	41

[a] *Reagents and conditions*: i, THF, −78 °C, 30 min.

Table 2 Hydrazinolysis in the presence of LiCl



Complex	LiCl (equiv.)	*T*/°C	Time	Hydrazinocarbene (% yield, *E* : *Z*)	Aminocarbene (% yield)
4	—	−78	5 min	21 (18, 7 : 3)	23 (40)
4	2	−78 → −20	15 h	21 (73, 4 : 6)	23 (7)
13	—	−78	5 min	22 (30, 1 : 1)	24 (35)
13	2	−78 → −20	15 h	22 (80, 1.3 : 1)	23 (13)



Scheme 1 *Reagents and conditions*: i, LiCl (2 equiv.), THF, −40 °C, 3 h.

reduced. As a result of the decrease in reaction rates, the amines produced in the N–N bond breaking step can compete with the hydrazine in the reaction with **11** affording the aminocarbenes **19** and **20** (Scheme 1).

Even in the presence of LiCl, only the (*Z*)-isomer of the hydrazinocarbenes **16** and **17** was formed. In a typical procedure, LiCl (0.0999 g, 2.47 mmol) was dissolved in anhydrous THF (3 ml) and hydrazine **8** (0.115 ml, 1.19 mmol.) was added under N$_2$ at the same temperature, thus generating a white slurry to which a 3 ml THF solution of **11** (0.412 g, 1.08 mmol.) was added dropwise over 5 min at −78 °C. After 2 h at −78 °C, the temperature was raised and kept at −40 °C for a further 3 h. Standard work-up followed by purification by flash chromatography [eluent: Et$_2$O–light petroleum (6 : 4) then Et$_2$O] gave the hydrazinocarbene **16**.§

The hydrazinolysis reaction was then extended to the 1,2-dimethylhydrazine **12** which was reacted with the chromium(0) carbenes **4** and **13** (Table 2). When the free hydrazine was used, the expected hydrazinocarbenes **21** (*E/Z* = 7 : 3) and **22** (*E/Z* = 1 : 1) were obtained in 18 and 30% yield respectively, as well as the methyl(amino)carbene complexes **23** and **24** (yields of 40 and 35%, respectively). Also in this case, the presence of 2 equiv. of LiCl in the reaction mixture greatly increased the yields of hydrazinocarbenes **21** and **22** (see Table 2), thus demonstrating a general and important effect of the presence of this salt in the reaction medium. The reaction was carried out starting from a commercially available dihydrochloride salt of the 1,2-dimethylhydrazine (0.328 g, 2.46 mmol) suspended in anhydrous THF (20 ml), and treated under nitrogen at 0 °C with a stoichiometric amount of Bu^{n}Li (1.4 M *n*-hexane solution, 3.5 ml, 4.92 mmol) (Table 2).

In conclusion, carbene complexes of tungsten(0) and chromium(0) **16**, **17**, **21** and **22** were synthesized in satisfactory to good yields by means of the hydrazinolysis reaction carried out in the presence of 2 equiv. of LiCl. It is likely that hydrazine/LiCl aggregates are involved as the reactive species. To the best of our knowledge, nothing has yet been reported in the literature concerning the use of stable aggregates between hydrazines and LiCl for synthetic purposes.[6]

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Notes and references

† Only the (*Z*)-rotamers were observed. The lack of isolation of any of the (*E*)-rotamers of **15**–**18** means that they are not formed at all or, if formed, they are unstable and immediately give the W(CO)$_5$·NCCH$_3$ as postulated by Fischer (ref. 3).

‡ To a THF solution of LiCl (2 equiv.), the hydrazine **8** (1 equiv.) was added at room temperature. The resulting white solid was isolated and used for the hydrazinolysis of complex **11**, affording the hydrazino complex **16** in the same yield as that shown in Scheme 1 (72%). The structure of the above lithium aggregate is under investigation.

§ *Selected data* for (*Z*)-**16**: yellow solid, mp 112 °C (from CH$_2$Cl$_2$–pentane); ν_{max}(Nujol)/cm^{-1} 3161 (NH), 2060 (CO$_{trans}$) 1960–1880 (CO$_{cis}$); δ_H(300 MHz, CDCl$_3$) 2.92–3.03 (m, 7 H, Cr=CCH$_3$ + NCH$_2$), 3.87–3.92 (m, 4 H, OCH$_2$), 8.50 (br s, 1 H, NH); δ_C(75 MHz, CDCl$_3$) 42 (q, CH$_3$), 55 (t, NCH$_2$), 56.2 (t, CH$_2$), 65 (t, OCH$_2$) 198 (s, CO$_{cis}$), 204 (s, CO$_{trans}$), 253 (s, C=W); *m/z* (EI) 452 [M$^+$] (Calc. for C$_{11}$H$_{12}$N$_2$O$_6$W: C, 29.2, H, 2.7; N, 6.2%. Found, C, 29.50; H, 2.88; N, 6.07%). For (*E*)-**21**: light yellow solid, mp 79–80 °C (from CH$_2$Cl$_2$–pentane); ν_{max}(Nujol)/cm^{-1} 3334 (NH), 2054 (CO$_{trans}$), 1917–1803 (CO$_{cis}$); δ_H(300 MHz, CDCl$_3$) 2.71 (d, 3 H, *J* 6.2, NHC*H*$_3$) 2.78 (s, 3H, Cr=CCH$_3$), 3.96 (s, 3 H, Cr=CNCH$_3$), 4.36 (q, 1 H, *J* 6.2, N*H*CH$_3$); δ_C(75 MHz, CDCl$_3$) 36.2 (NHCH$_3$) 37.2 (Cr=C*C*H$_3$), 48.4 (NCH$_3$), 217.8 (s, 2CO$_{cis}$), 223.4 (s, CO$_{trans}$), 265.2 (s, C=Cr) (Calc. for C$_9$H$_{10}$CrN$_2$O$_5$: C, 38.86, H, 3.62, N, 10.07. Found: C, 38.93; H, 3.39; N, 9.95%). For (*Z*)-**21**: yellow solid, mp 95–96 °C (from EtOAc–pentane); ν_{max}(Nujol)/cm^{-1} 3321 (NH), 2054 (CO$_{trans}$), 1917–1803 (CO$_{cis}$), δ_H(300 MHz, CDCl$_3$) 2.61 (s, 3H, Cr=CCH$_3$), 2.82 (d, 3 H, *J* 6.3, NHC*H*$_3$), 3.41 (s, 3 H, Cr=CNCH$_3$), 6.10 (q, 1 H, *J* 6.3, N*H*CH$_3$); δ_C(75 MHz, CDCl$_3$) 36.7 (NHCH$_3$) 37.6 (Cr=C*C*H$_3$), 39.1 (NCH$_3$), 217.1 (s, 2CO$_{cis}$), 222.7 (s, CO$_{trans}$), 258.9 (s, C=Cr) (Calc. for C$_9$H$_{10}$CrN$_2$O$_5$: C, 38.86, H, 3.62; N, 10.07. Found: C, 38.79; H, 3.60; N, 10.26%).

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