

Mass Spectrometric Detection and Fragmentation Patterns of Chromium and Tungsten Carbene Complexes

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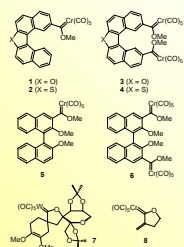
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Introduction

Fischer carbene complexes are useful compounds in organic syntheses. Due to this importance, their mass spectrometric characterization is necessary for the synthetic chemist. During the ionization of these compounds, the following problems arise:

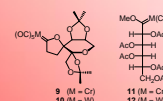
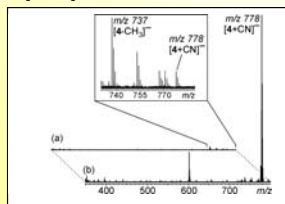
- Most ionization methods (EI, FAB, MALDI) are limited to a small group of compounds or give bad results in most cases.
- Most ionization methods are too harsh – the molecule ion peak is detected only with negligible intensity, fragments dominate the spectra.
- ESI – known as one of the softest ionization methods – requires the presence of a charge and can thus cause problems with uncharged molecules that do not have an easy-to-charge site.

Here we discuss two complementary methods for the ionization of Fischer carbene complexes: non acidic carbene complexes – a deprotonation is not possible in the ESI-process – can be ionized by attaching a good nucleophile like cyanide to the electrophilic carbene center, acidic carbene complexes can be ionized by deprotonation. In addition to the CO losses typical for these compounds, some other fragmentation reactions can be observed in the gas phase.



Carbene complexes 1-8 bear no acidic protons, so they can't be ionized by deprotonation during the ESI process. In this case, adding a small amount of KCN to the sample solution leads to ionization through nucleophilic attack of the cyanide anion to the electrophilic carbene carbon atom. Spectrum (a) sprayed from an acetonitrile solution shows the negative mode ESI mass spectrum of 4 before addition of KCN. Here, signals with low intensities can be observed for the $[M-CH_3]$ - and for the $[M+CN]$ -anion.

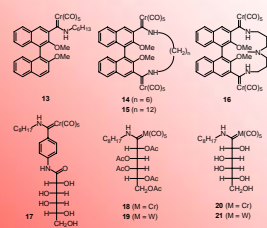
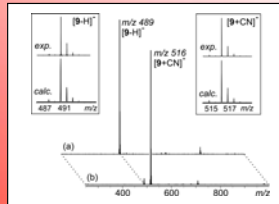
After the addition of KCN, a large signal for the $[M+CN]$ -anion at $m/z = 778$ is observed (spectrum (b)). This method works also for the α,β -unsaturated carbene complex 8.



The sugar-substituted chromium and tungsten complexes 9-12 contain acidic protons in the α -position to the carbene center. Ionization by deprotonation is possible in the ESI ion source.

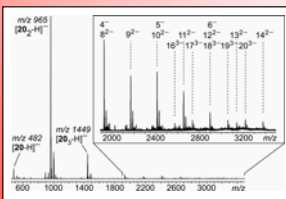
The ESI mass spectrum of 9 (spectrum (a)) shows a signal for the deprotonated complex. After addition of KCN, the spectrum changes completely (spectrum (b)): only a small signal for the $[M-H]$ -anion at $m/z = 489$, but a large signal for the $[M+CN]$ -anion at $m/z = 516$ can be detected.

Complexes 11 and 12 behave completely different. Here addition of KCN doesn't change the observed spectrum: in both cases the deprotonated species leads to signals with large intensities.



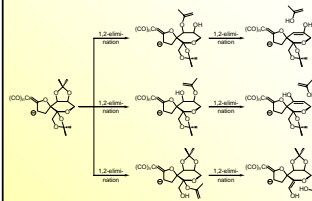
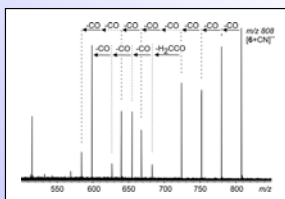
Amino carbene complexes 13-21 can be easily deprotonated and ionized in the ESI ion source. Additionally, complexes 17, 20, and 21 bear acidic OH protons which can be deprotonated during the ionization. Protonation at the carbene nitrogen atom is not possible due to the delocalization of the N-centered lone pair.

The mass spectrum of complex 20 which is known as a good gelator for organic solvents shows a series of large clusters up to a triply charged icosamer.



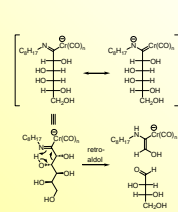
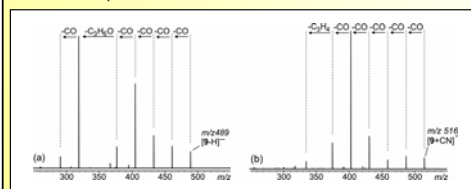
To study the fragmentation patterns of these compounds in the gas phase, we performed CID experiments with mass selected parent ions and argon as collision gas. While the unfunctionalized carbene complexes 1-4 show only the typical losses of the carbonyl ligands, complex 6 which bears a methoxy group attached to the ortho position of the aromatic system shows a second fragmentation reaction: one ketene molecule can be liberated by the mechanism shown here.

This reaction can only happen with bis-carbene complex 6, because an intact carbene fragment is necessary.

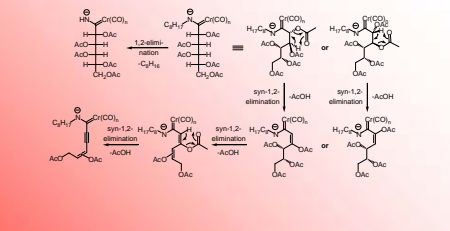
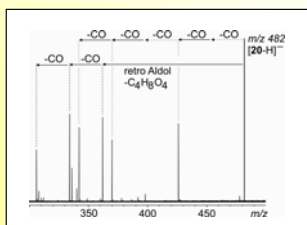


In the MS/MS-spectrum the cyanide adduct of 6 shows the loss of allene after the cleavage of all five CO-ligands.

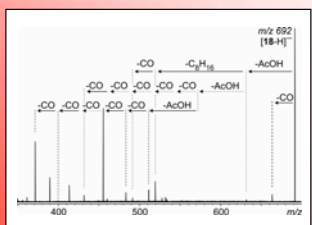
In contrast, the deprotonated complex 6 with the isopropylidene protection groups reveals competition of the decarbonylation with the repulsion of one 2-propenol molecule which is ascribed by two consecutive 1,2-eliminations.



Besides the usual series of CO losses, in the CID experiment another fragment with $\Delta m = 120$ mass units is formed directly from the parent ion $[20-H]^+$. This fragment corresponds to a retro-aldol reaction which splits the sugar backbone. It can proceed through a six-membered transition structure and is energetically favored by the formation of the strong C=O double bond in the neutral fragment.



Deprotonated 18 yields neutral octene and acetic acid through 1,2-elimination reactions. The expulsion of acetic acid molecules leads to ions with side chains conjugated with the carbene moiety.



Conclusion

- Non-acidic carbene complexes can be ionized by addition of good nucleophiles like cyanide which add to the carbene center (in analogy to the isolobal carbonyl groups).
- Acidic carbene complexes can be ionized by addition of nucleophiles or by deprotonation depending on the carbene complex backbone.
- Not only CO losses are observed in MS/MS experiments: processes like the retro-aldol reaction and the loss of ketene or enols compete with the decarbonylation.
- These processes must thus have lower or comparable barriers as compared to those of the CO losses.
- The fragmentation pattern depends significantly on the structural details of the carbene complex backbone.

[1] T. Weilandt, E. Graeff, J. F. Schneider, A. W. Koch, F. A. Zschoche, K. H. Dötz, C. A. Schalley, *Organometallics* 2005, 24, 3671.

Acknowledgement

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