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

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A novel method for the detection of synthetically useful pentacarbonyl chromium and tungsten carbene complexes by electrospray ionization Fourier transform ion cyclotron resonance (ESI-FTICR) mass spectrometry is presented which utilizes the addition of CN^- anions to the electrophilic carbene carbon. This method is nondestructive, provided the ionization proceeds under soft conditions. The scope and limitations of this method are examined by utilizing different types of carbene complexes. Depending on the α-CH acidity of the carbene complexes, $[M - H]^-$ anions can be observed either in competition with the CN^- adducts or as the only ions, even in the presence of cyanide. Secondary aminocarbene complexes exclusively form $[M - H]^-$ anions by deprotonation of the NH moiety. The ions under study have been mass-selected and subjected to collision-induced decay (CID) experiments in order to examine their fragmentation reactions. CO loss is not the only observable process. Most prominently, 1,2-eliminations and a retro-aldol reaction within a sugar carbene complex compete with decarbonylation and thus have rather low activation barriers. Some reactions can be attributed to coordinatively unsaturated chromium atoms formed through preceding CO losses.

Introduction

Chromium carbene complexes are well-known and widely used reagents for organic synthesis.[1] They have been used for the synthesis of a number of natural products such as peptides, vitamins, antibiotics, steroids, and alkaloids[2] as well as for the preparation of cyclophanes,[3] dendritic molecules,[4] and axial[5] or helical chiral[6] frameworks. In these cases, readily accessible aryl- or vinylcarbene chromium complexes serve as starting materials for the [3 + 2 + 1]-benzannulation reaction with alkynes, providing a straightforward approach to densely functionalized benzenoids and fused arenes regioselectively labeled with a $Cr(CO)_3$ fragment. These arene−$Cr(CO)_3$ complexes are interesting reagents for haptotropic metal migration experiments[7] or for asymmetric syntheses due to their planar chirality.[8] The manifold chiral information readily available in customary carbohydrates provides an attractive approach to a versatile chiral modification of metal carbenes which may be applied to either metal-mediated stereoselective organic synthesis via sugar auxiliaries or to carbohydrate synthesis via organometallic methodologies.[9] Additionally, some sugar derivatives have

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(1) (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983. (b) Hegedus, L. S. *Tetrahedron* **1997**, *53*, 4105. (c) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 5, p 1065. (d) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12, p 549. (e) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271. (f) Dötz, K. H.; Tomuschat, P. *Chem. Soc. Rev.* **1999**, *28*, 187. (g) Barluenga, J.; Fañañas, F. J. *Tetrahedron* **2000**, *56*, 4597. (h) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 4124. (i) de Meijere, A.; Schirmer, H.; Duetsch, M. *Angew. Chem.* **2000**, *112*, 4124; *Angew. Chem., Int. Ed.* **2000**, *39*, 3964. (j) Dötz, K. H.; Minatti, A. In *Transition Metals for Organic Synthesis*, 2nd ed.; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Vol. 1, p 397. (k) Dötz, K. H., Ed. *Metal Carbenes in Organic Synthesis*; Topics in Organometallic Chemistry 13; Springer: Heidelberg, Germany, 2004.

(2) (a) Dötz, K. H. *Angew. Chem.* **1984**, *96*, 573; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (b) Dötz, K. H.; Stendel, J., Jr. In *Modern Arene Chemistry*; Astruc, D., Ed.; Wiley-VCH: Weinheim, Germany, 2002; p 250.

(3) (a) Longen, A.; Nieger, M.; Airola, K.; Dötz, K. H. *Organometallics* **1998**, *17*, 1538. (b) Dötz, K. H.; Gerhardt, A. *J. Organomet. Chem.* **1999**, *578*, 223. (c) Wang, H.; Wulff, W. D. *J. Am. Chem. Soc.* **2000**, *122*, 9862. (d) Dötz, K. H.; Mittenzwey, S. *Eur. J. Org. Chem.* **2002**, 39.

(4) Quast, L.; Nieger, M.; Dötz, K. H. *Organometallics* **2000**, *19*, 2179.

(5) (a) Tomuschat, P.; Kröner, L.; Steckhan, E.; Nieger, M.; Dötz, K. H. *Chem. Eur. J.* **1999**, *5*, 700. (b) Fogel, L.; Hsung, R. P.; Wulff, W. D.; Sommer, R. G.; Rheingold, A. L. *J. Am. Chem. Soc.* **2001**, *123*, 5580.

(6) (a) Schneider, J. F.; Nieger, M.; Nättinen, K.; Dötz, K. H. *Synthesis* **2005**, 1109. (b) Schneider, J. F.; Nieger, M.; Nättinen, K.; Lewall, B.; Niecke, E.; Dötz, K. H. *Eur. J. Org. Chem.* **2005**, 1541.

(7) (a) Oprunenko, Y. F. *Russ. Chem. Rev.* **2000**, *69*, 683. (b) Jahr, H. C.; Nieger, M.; Dötz, K. H. *Chem. Commun.* **2003**, 2866. (c) Dötz, K. H.; Szesni, N.; Nieger, M.; Nättinen, K. *J. Organomet. Chem.* **2003**, *671*, 58. (d) Zabalov, M. V.; Gloriozov, I. P.; Oprunenko, Y. F.; Lemenovskii, D. A. *Russ. Chem. Bull., Int. Ed.* **2003**, *52*, 1567. (e) Dötz, K. H.; Jahr, H. C. *Chem. Rec.* **2004**, *4*, 61. (f) Jahr, H. C.; Nieger, M.; Dötz, K. H. *Chem. Eur. J.,* in press. (g) Stendel, J., Jr.; Nieger, M.; Müller, S.; Ketrat, S.; Dolg, M.; Dötz, K. H. *Organometallics*, in press.

(8) (a) Berger, A.; Djukic, J.-P.; Michon, C. *Coord. Chem. Rev.* **2002**, *225*, 215. (b) Rose-Munch, F.; Rose, E. In *Modern Arene Chemistry*; Astruc, D., Ed.; Wiley-VCH: Weinheim, Germany, 2002, p 368. (c) Schmalz, H. G.; Dehmel, F. In *Transition Metals for Organic Synthesis*, 2nd ed.; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Vol. 1, p 601. (d) Muniz, K. *Top. Organomet. Chem.* **2004**, *7*, 205.

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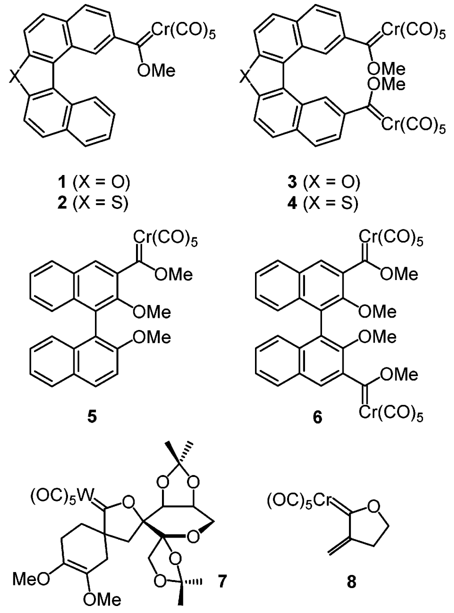
proven to be organometallic gelators.[10] Despite their synthetic importance, it is still a considerable challenge to characterize these compounds by mass spectrometry. While small derivatives could be successfully ionized by electron ionization (EI)[11] or chemical ionization in the positive (PCI) or negative mode (NCI),[12] such an approach is difficult for larger, synthetically more useful derivatives, because the samples must be vaporized before ionization. Due to their thermolability, decomposition often occurs in the inlet system. In addition, carbon monoxide losses are prominent in the EI mass spectra and often dramatically reduce the intensity of the desired molecular ion. Other ionization methods such as fast atom bombardment (FAB), field desorption (FD), or matrix-assisted laser desorption ionization (MALDI) can be applied to larger chromium carbene complexes,[4,6,13] but all suffer from pronounced carbon monoxide losses. Consequently, electrospray ionization (ESI) would be the method of choice, due to its intrinsic softness.[14] However, the ionization of neutral metal carbenes in solution such as those under study here may cause a problem. Recent progress in this direction was made by Martínez-Álvarez and co-workers,[15] who demonstrated electron-transfer processes to occur during the electrospray ionization of some Fischer-type carbene complexes, when hydroquinone or tetrathiofulvalene was added to the sample solution. However, carbene complexes bearing an aromatic system directly conjugated with the carbene center did not give any useful results. The carbene complexes under study here either bear aliphatic groups attached to the carbene carbon or directly conjugated aryl substituents and, thus, require a complementary ionization protocol.

Here, we discuss the scope and limitations of an ionization procedure which utilizes the electrophilicity of the carbene carbon in the metal carbene fragment which is isolobal to carbonyl groups.[16] Addition of nucleophiles[17] such as cyanide (CN^-) provides the charge necessary for the detection of intact species in the negative ESI mode of the Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. Depending on the acidity of the carbene complexes, we were also able to detect $[M - H]^-$ anions. Mass-selected parent ions were furthermore subjected to collision-induced dissociation (CID) experiments in order to investigate their fragmentation reactions. Interestingly, several reactions were detected that can compete with the almost ubiquitous consecutive losses of carbon monoxide and must thus be energetically quite favorable.

Chart 1. Mono and Bis Chromium and Tungsten Carbene Complexes That Do Not Bear Any Acidic Positions Which Could Be Deprotonated during the Negative Ion Electrospray Ionization[a]



[a] Also, they do not have particularly basic positions which could be cationized in the positive mode.

Results and Discussion

1. Negative Ion ESI-FTICR Mass Spectra of Chromium and Tungsten Carbene Complexes. All our attempts to electrospray ionize carbene complexes **1**–**8** depicted in Chart 1 from different solvents by attaching a proton or a cation failed. In the negative ion mode (Figure 1a), **1**–**6** gave low-intensity signals, which could be attributed to the loss of a methyl group, presumably that of the methoxycarbene moiety, which yields an acylmetalate anion well stabilized through conjugation with the carbene center. However, the finding that a small signal was observed for $[M + CN]^-$, when acetonitrile containing a trace of cyanide as an impurity was used as the spray solvent, prompted us to run the experiment again with the same sample to which a small amount[18] of KCN was added. Indeed, intense signals for the cyanide adducts of all six carbene complexes were found (Figure 1b). The same approach also worked nicely for the other carbene complexes shown in Chart 1, including the tungsten carbene complex **7** and the α,β-unsaturated carbene complex **8** (see the Supporting Information).

As adducts with some other background anions (nitrate, chloride, or even weakly coordinating tetrafluo-

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(9) (a) Duthaler, R. O.; Hafner, A. *Chem. Rev.* **1992**, *92*, 807. (b) Dötz, K. H.; Straub, W.; Ehlenz, R.; Peseke, K.; Meisel, R. *Angew. Chem.* **1995**, *107*, 2023; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1856. (c) Dötz, K. H.; Ehlenz, R. *Chem. Eur. J.* **1997**, *6*, 1751. (d) Dötz, K. H.; Jäkel, C.; Haase, W.-C. *J. Organomet. Chem.* **2001**, *617–618*, 119. (e) Janes, E.; Nieger, M.; Saarenketo, P.; Dötz, K. H. *Eur. J. Org. Chem.* **2003**, 2276. (f) Jäkel, C.; Dötz, K. H. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1107.

(10) Bühler, G.; Feiters, M. C.; Nolte, R. J. M.; Dötz, K. H. *Angew. Chem.* **2003**, *115*, 2599; *Angew. Chem., Int. Ed.* **2003**, *42*, 2494.

(11) (a) Müller, J.; Connor, J. A. *Chem. Ber.* **1969**, *102*, 1148. (b) Fischer, E. O.; Leupold, M.; Kreiter, C. G.; Müller, J. *Chem. Ber.* **1972**, *105*, 1150.

(12) Careri, M.; Mangia, A.; Manini, P.; Predieri, G.; Licandro, E.; Papagni, A. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 51.

(13) (a) Dötz, K. H.; Tomuschat, P.; Nieger, M. *Chem. Ber./Recl.* **1997**, *130*, 1605. (b) Janes, E.; Dötz, K. H. *J. Organomet. Chem.* **2003**, *669*, 1.

(14) (a) Fenn, J. B.; Mann, M.; Meng, C. K.; Wong, S. F.; Whitehouse, C. M. *Mass Spectrom. Rev.* **1990**, *9*, 37. (b) Kebarle, P.; Tang, L. *Anal. Chem.* **1993**, *65*, 972A. (c) Gaskell, S. J. *J. Mass Spectrom.* **1997**, *32*, 677.

(15) (a) Sierra, M. A.; Gómez-Gallego, M.; Mancheño, M. J.; Martínez-Alvarez, R.; Ramírez-Lopez, P.; Kayali, N.; González, A. *J. Mass Spectrom.* **2003**, *38*, 151. (b) Martínez-Álvarez, R.; Gómez-Gallego, M.; Fernández, I.; Mancheño, M. J.; Sierra, M. A. *Organometallics* **2004**, *23*, 4647.

(16) (a) Hoffmann, R. *Angew. Chem.* **1982**, *94*, 725; *Angew. Chem., Int. Ed.* **1982**, *21*, 711. (b) Stone, F. G. A. *Angew. Chem.* **1984**, *96*, 85; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89.

(17) (a) Barluenga, J.; Flórez, J.; Fañanáz, F. J. *J. Organomet. Chem.* **2001**, *624*, 5. (b) Bernasconi, C. F.; Ali, M. *Organometallics* **2004**, *23*, 6134.

(18) Larger amounts of salts added to the solution result in pronounced formation of salt clusters $(KCN)_nCN^-$. The addition of 1–2 equiv of KCN gave the best results.

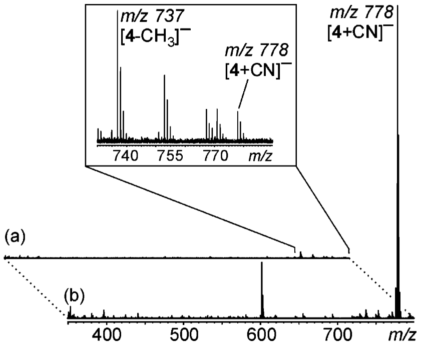


Figure 1. ESI mass spectra of **4** (a) before and (b) after the addition of KCN to the sample solution. Note that traces of cyanide are present in acetonitrile which lead to a low-intensity signal for the cyanide complex [**4** + CN]$^-$. Also, a small signal is observed for [**4** − CH$_3$]$^-$. Both spectra are recorded under comparable conditions and are shown on the same intensity scale.

roborate) were observed for **7** as well, we tested a selection of nucleophiles, i.e., cyanate, thiocyanate, and methoxide with chromium carbene complex **6** as a representative example. Indeed, addition of these nucleophiles to the carbene carbon atom is observed, but cyanide works best and provides the highest intensities. The addition of methoxide as the nucleophile leads to fast decomposition of the carbene complexes and gives rise to more intense fragments appearing in the mass spectrum.

One remarkable feature of this approach is that a nondestructive ionization of **1**−**8** is achieved under soft ionization conditions. The CO losses typically observed with other ionization techniques are hardly visible within the noise. When harsher conditions are applied, for example by inducing collisions with residual gas in the instrument's ESI source, these CO losses become more pronounced. Consequently, our ionization technique may be useful for synthetic chemists facing the problem of analytically characterizing chromium and tungsten carbene complexes by mass spectrometry. One disadvantage—at least from the perspective of a gas-phase chemist—is that nucleophile addition alters the carbene center and thus prohibits the examination of the gas-phase chemistry of the unaltered metal carbene moiety.

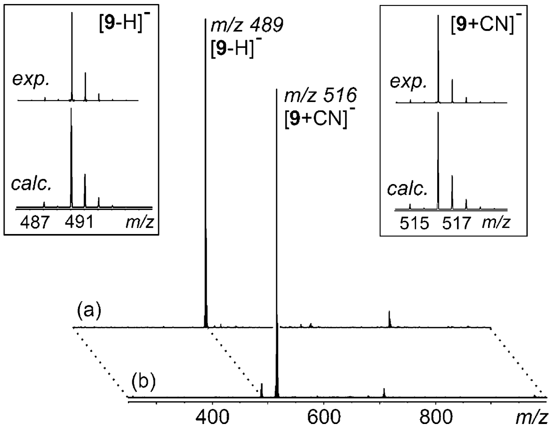
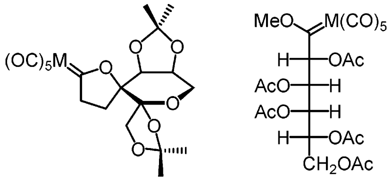


Figure 2. Negative ion ESI mass spectra of **9** sprayed from an acetonitrile solution (a) before and (b) after the addition of KCN. An almost complete switching of the ionization mode is observed. While deprotonation gives rise to intense signals in the absence of cyanide, the cyanide adduct is much greater in intensity, when KCN is added. The insets show the experimental and calculated isotope patterns for the two major signals.

Chart 2. Chromium and Tungsten Carbene Complexes with α-Acidic Protons as the Only Acidic Position at Which Deprotonation Is Possible



9 (M = Cr)
10 (M = W)

11 (M = Cr)
12 (M = W)

To investigate the scope and limitations of this novel approach to the ionization of chromium and tungsten carbene complexes, structurally different carbene complexes were tested (Chart 2). All four samples **9**−**12** differ from those discussed above by the presence of α-acidic CH moieties.[19] Figure 2 depicts the ESI mass spectra obtained before and after addition of KCN to a solution of **9** in acetonitrile. Clearly, a signal for the deprotonated carbene complex [**9** − H]$^-$ is visible in both spectra. However, upon addition of cyanide, the CN$^-$ adduct is much more intense than the deprotonated species. Similar results are obtained for the corresponding tungsten complex **10**. This situation changes for **11** and **12** (see the Supporting Information), which even after addition of cyanide exclusively show the signal for the deprotonated compound [M − H]$^-$. Apparently, deprotonation at the α-position is facilitated by the presence of the more electronegative *O*-acetyl group, which inductively stabilizes the anion.

The last category of samples are the aminocarbene complexes **13**−**21**, shown in Chart 3. Two effects can be expected to govern the ionization in the negative mode. On one hand, the amino substituent reduces the electrophilicity significantly, due to the resonance delocalization from nitrogen to the carbene carbon. This is in line with the significant upfield shift of the carbene carbon atom of amino- versus alkoxycarbene complexes in the ^{13}C NMR spectra.[20] On the other hand, the NH proton is much more acidic than those located at the α-carbon atoms of **9**−**12**. Consequently, one would expect the deprotonated complexes [M − H]$^-$ to dominate the negative ion ESI mass spectra. This is indeed observed for all compounds in Chart 3. Addition of cyanide does not have a detectable effect on the mass spectra.

The deprotected sugar carbene complexes **20** and **21** represent particular examples, since they are known to form gels in dichloromethane, chloroform, benzene, toluene, and mixtures of these solvents.[10] Consequently, they are expected to have a strong tendency to form

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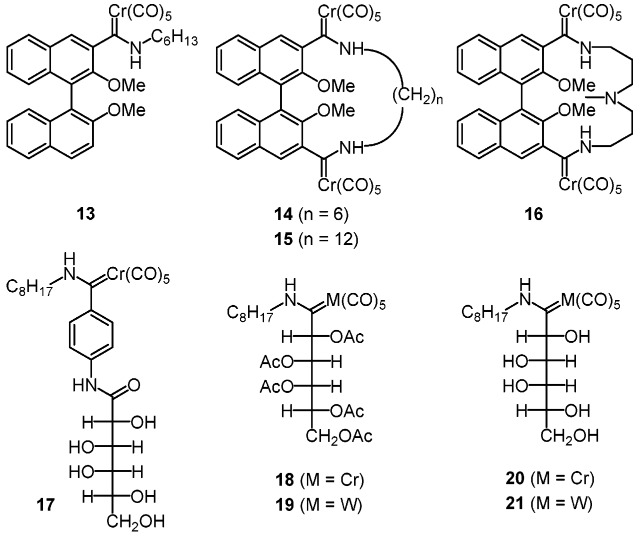
(19) (a) Kreiter, C. G. *Angew. Chem.* **1968**, *80*, 402; *Angew. Chem., Int. Ed.* **1968**, *7*, 390. (b) Casey, C. P.; Andersson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230. (c) Bernasconi, C. F. *Chem. Soc. Rev.* **1997**, *26*, 299. (d) Bernasconi, C. F.; Leyes, A. E.; Ragains, M. L.; Shi, Y.; Wang, H.; Wulff, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 8632.

(20) (a) Kreiter, C. G.; Formacek, V. *Angew. Chem.* **1972**, *84*, 155; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 141. (b) Zaragoza Dörwald, F. *Metal Carbenes in Organic Synthesis*; Wiley: New York, 1999.

Chart 3. Chromium and Tungsten Amino Carbene Complexes with Their Acidic NH in the α-Position Relative to the Carbene Center



aggregates resulting mainly from multiple hydrogen bonding. In marked contrast to their O-protected analogues **18** and **19**, such aggregates are indeed observed in the mass spectra (Figure 3). Although the dimer $[M_2 - H]^-$ (M = monomer) gives rise to the most intense signal by far in the mass spectrum, three series of clusters are observed with different charge states: singly charged $[M_n - H]^-$ ($n = 1-6$), doubly charged $[M_n - 2H]^{2-}$ ($n = 8-14$), and triply charged $[M_n - 3H]^{3-}$ ($n = 16-20$).

Finally, it should briefly be mentioned that the presence of a free tertiary amine in **16** also permits an ionization of this compound in the positive mode by spraying it from MeOH solution. Protonation of the amino nitrogen atom provides the necessary charge, which is located remote from the carbene center. This method could be developed into an ionization technique which would allow the chemist to circumvent one of the disadvantages of our approach as discussed above and to investigate the gas-phase chemistry of carbene complexes without any alteration at the carbene carbon. As expected, protonation of the carbene-centered nitrogen atom in the ESI process is hampered by its reduced basicity resulting from N−C π bonding.

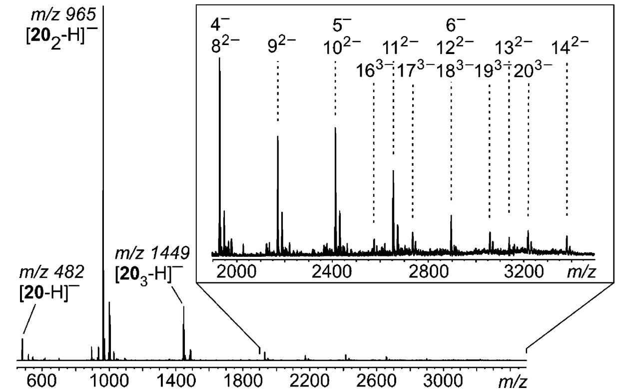


Figure 3. Negative ESI mass spectrum of **20** showing the formation of large clusters up to the triply charged 20-mer. For clarity, the labels in the inset provide the number of monomers incorporated in the ions together with their charge state as a superscript.

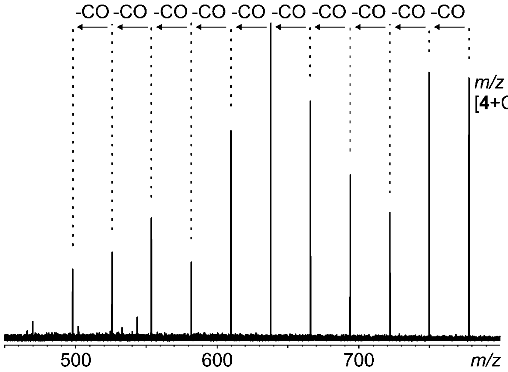


Figure 4. MS/MS spectrum of mass-selected $[\mathbf{4} + CN]^-$ which was collided with argon as the collision gas. Up to 10 consecutive losses of carbon monoxide are observed.

2. The Fragmentation Patterns: Collision-Induced Decay (CID) Experiments. On the basis of experiences with ionization methods other than ESI, which give rise to intense signals for a series of CO losses in the mass spectra, one would expect the carbon monoxide expulsion to be the dominating fragmentation reaction with which no other reaction can efficiently compete. Overall, this expectation is confirmed by the experiments to be discussed in this section, but a closer look shows that there is more to learn from the collision-induced fragmentation reactions of chromium and tungsten carbene complexes. For an examination of the fragmentation mechanisms, the monoisotopic parent ions of interest were mass-selected in the FT-ICR cell and then collided with argon in order to increase the internal energy of the ions and provoke their decomposition. It should be noted that, due to the chromium isotopes, the monoisotopic and thus most intense signal in the isotope pattern predominantly contains ions which bear a ^{52}Cr and exclusively ^{1}H, ^{12}C, ^{14}N, and ^{16}O. Nevertheless, a very small population of ions incorporating ^{50}Cr contain contributions of, for example, ^{13}C. The abundance of these ions, however, is so small that all fragments due to their decomposition will vanish within the noise.

As expected, for the cyanide adducts of mono- and biscarbene complexes **1**−**4**, only carbon monoxide losses are observed. Figure 4 shows the CID mass spectrum of $[\mathbf{4} + CN]^-$ as a representative example. Irrespective of the addition of CN^- to one of the carbene centers, a series of up to 10 CO molecules are cleaved from the complex without any other fragmentation products observed. One implication is that even a Cr atom which is coordinatively highly unsaturated after several CO losses does not induce further fragmentation reactions within the backbone of the ion under study. Of course, one needs to consider that each leaving CO molecule takes part of the internal energy of the ions with it, reducing the probability of consecutive reactions. On the other hand, however, collision-induced activation leads to a broad, non-Boltzmann distribution of internal energies within an ion population. Consequently, other fragmentation reactions in addition to CO losses would not be completely unexpected.

The picture changes significantly when we look at the tandem mass spectra of mass-selected and collisionally activated $[\mathbf{6} + CN]^-$ and $[\mathbf{14} - H]^-$ (Figure 5 and the

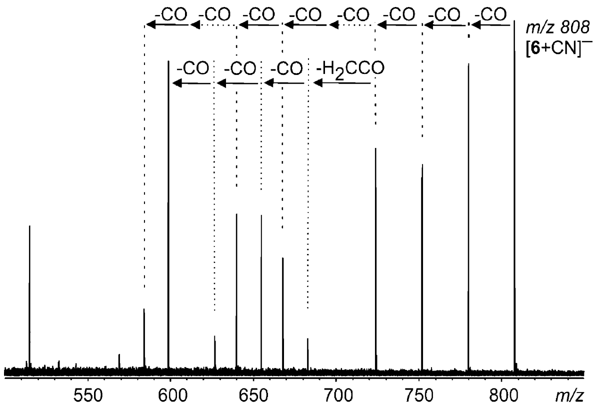
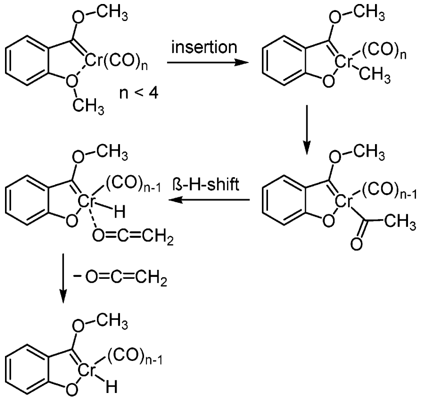


Figure 5. MS/MS spectrum (CID) of mass-selected [**6** + CN]$^-$. A second fragmentation channel competes with the CO losses and involves the formation of the neutral ketene $CH_2{=}C{=}O$.

Scheme 1. Proposed Mechanism for the Formation of Neutral Ketene from [6 + CN]$^-$ or [14 − H]$^-$ [a]



[a] Parts of these anions not taking part in the reaction are omitted for clarity.

Supporting Information). Both anions liberate neutral ketene molecules, as confirmed by the exact mass differences. A comparison with the monocarbene complex **5** shows that there is no ketene loss observed, so that it most likely is the still intact chromium carbene moiety which induces the ketene loss. Apparently, the $Cr(CO)_5$ moiety becomes less reactive when the cyanide is attached. Interestingly, the ketene loss is observed only after three and two preceding CO losses, respectively, indicating that it cannot proceed in the presence of a coordinatively saturated Cr atom. This reaction involves the methoxy group attached to the aromatic ring at the carbene center. If this group is absent, as in **3** and **4**, no ketene loss is observed. Vice versa, the presence of a methoxy group on the carbene center is not required, since the aminocarbene complex **14** also gives rise to a ketene loss.

A reasonable mechanism taking into account these conclusions from the experiments is shown in Scheme 1. It begins with an insertion of the coordinatively unsaturated chromium atom into the $H_3C{-}O$ bond of the aryl-centered methoxy group. This is expected to be energetically quite favorable, in view of the oxophilicity of chromium. The insertion of the metal into the C−O bond is also likely favored by a coordination to the methoxy oxygen atom. Tetracarbonyl chromium carbene chelates with their coordinative O−Cr bond readily form upon decarbonylation of their pentacarbonyl precursors and have been isolated and characterized by X-ray crystallography, providing evidence for such structures.[21] Transfer of the methyl group to one of the carbonyl ligands generates an acetyl group which can easily be converted to the ketene by a β-hydrogen atom transfer to the metal. Loss of the weakly coordinated ketene competes with additional decarbonylation, as observed in the CID mass spectra. This mechanism is in agreement with the fact that it is not observed as long as more than three CO ligands are attached to the metal center.[22] For the time being, the structure of the final product ions remains unclear, because further rearrangements cannot be excluded in a CID experiment like that performed here.

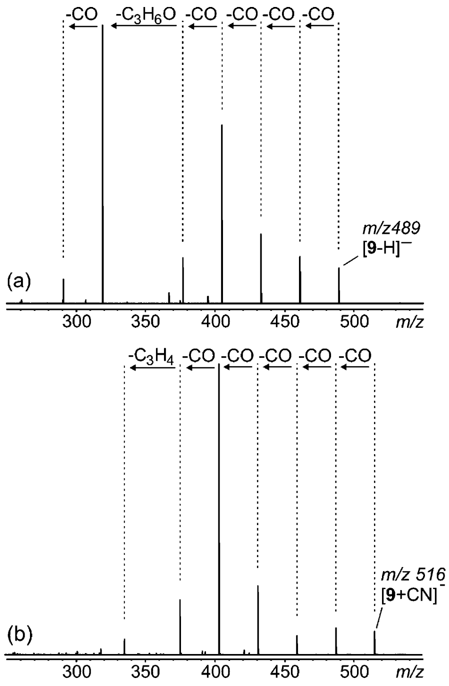


Figure 6. MS/MS spectrum (CID) of mass-selected (a) [**9** − H]$^-$ and (b) [**9** + CN]$^-$. Different fragmentation channels are observed that compete with CO losses.

While the cyanide adduct of **6** and deprotonated **14** fragment through qualitatively similar reactions, there is a slight difference in the fragmentation patterns of [**9** − H]$^-$ and [**9** + CN]$^-$ (Figure 6). Still, CO losses dominate the spectrum, but in addition to these, [**9** − H]$^-$ reveals the expulsion of C_3H_6O, which we ascribe to two consecutive 1,2-elimination reactions within the isopropylidene protecting groups of the sugar moieties. For this reaction several possibilities exist, as shown in Scheme 2. In contrast, [**9** + CN]$^-$ liberates allene, presumably also from the isopropylidene groups. The differences in the fragmentation patterns of the two anions differing with respect to their ionization indicate that the metal carbonyl fragment is involved in at least one of the two reactions at the isopropylidene groups. This assumption is supported by the fact that the allene loss from [**9** + CN]$^-$ is only observed after liberating all

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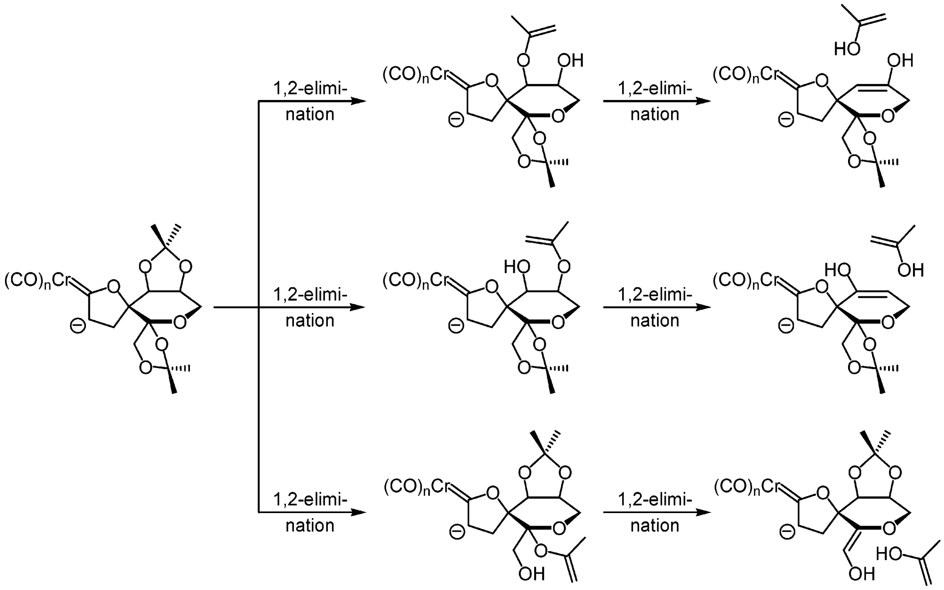
(21) (a) Dötz, K. H.; Sturm, W.; Popall, M.; Riede, J. *J. Organomet. Chem.* **1984**, *277*, 267. (b) Gräff, E. Dissertation, Universität Bonn, 2004.

(22) Dötz, K. H.; Popall, M.; Müller, G. *J. Organomet. Chem.* **1987**, *334*, 57.

Scheme 2. Proposed Mechanism for the Loss of Neutral 2-Propenol from [9 − H]$^-$ [a]



[a] Three different pathways give rise to isobaric product ions. Rearrangements of the enols to the corresponding keto isomers are energy-demanding in the gas phase. However, such isomerizations cannot be thoroughly ruled out.

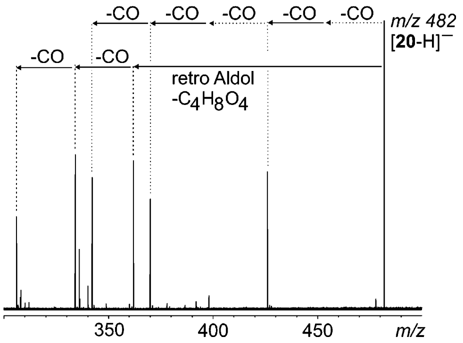
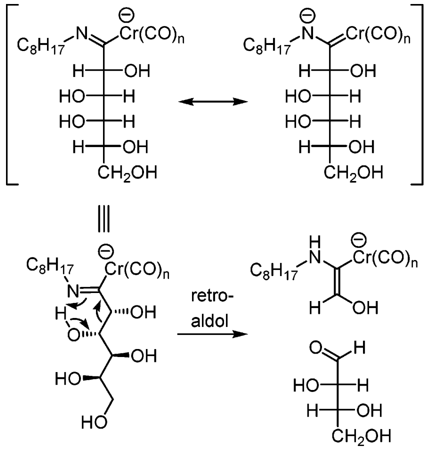


Figure 7. MS/MS spectrum (CID) of mass-selected [**20** − H]$^-$. A retro-aldol reaction is observed which splits the sugar backbone.

five carbonyl ligands from the chromium atom. Also, allene is energetically not too favorable, and its generation may be favored by the formation of two donative Cr−O bonds with the resulting diol product. Unfortunately, the quite low intensities of the precursor and product ions render further experiments aimed at elucidating their structures impossible and prevent us from providing a final answer here. More importantly, both reactions involve 1,2-eliminations, and we will see in the following section that 1,2-elimination reactions represent a common theme in the fragmentation of the sugar carbene complexes as well. This is due to the fact that they are not too energy demanding and thus can compete with the CO losses.

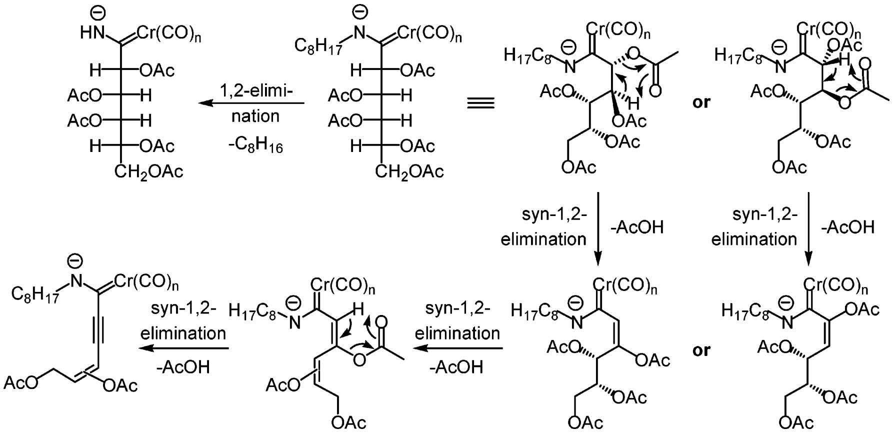
The last part of this article is devoted to the acyclic sugar carbene complexes and their derivatives. The CID mass spectrum of [**20** − H]$^-$ reveals that, besides the usual series of CO losses, another fragment is formed directly from the parent ion with $\Delta m = 120$ mass units (Figure 7). This fragment corresponds to a retro-aldol reaction which splits the sugar backbone, as shown in Scheme 3. It may 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.

Scheme 3. Retro-Aldol Reaction Occurring in the Collision-Induced Decay of Mass-Selected [20 − H]$^-$, Likely Proceeding in a Concerted Fashion through a Six-Membered Transition Structure



The *O*-acetyl-protected sugar carbene complex **18** does not have any OH groups which would make a retro-aldol reaction feasible; consequently, a different fragmentation pattern is observed (Figure 8). A 1,2-elimination may proceed next to the deprotonated nitrogen atom (Scheme 4), yielding an octene molecule as the neutral product. In addition, up to three subsequent losses of acetic acid have been observed, which mechanistically most likely proceed in a concerted syn fashion in analogy to ester pyrolysis. Two regioisomers can be formed in each of the first two elimination steps, as indicated in Scheme 4, if one assumes that the resulting double bonds are formed in conjugation to the already existing π system of the carbene. The third expulsion of acetic acid must then generate a triple bond. Since this can only occur in a syn-periplanar transition structure, when the acetyl group and the proton at the double bond are cis to each other, it would be interesting to study other stereoisomers of the sugar derivative. The final anion to be discussed here is [**11** − H]$^-$ (see the Supporting Information). Interestingly, carbon monox-

Scheme 4. Fragmentation of O-Acetylated [18 − H]⁻ by 1,2-Elimination of the N-Centered Side Chain or by Sequences of 1,2-Elimination Reactions Giving Rise to Acetic Acid Concomitant with Unsaturated Products with π Bonds Conjugated to the Carbene [a]



[a] The first step can proceed in two directions, yielding two different regioisomers as shown. Similarly, two pathways are feasible for the second 1,2-elimination so that a total of four different regioisomers can be formed. For simplicity, only one of them is shown.

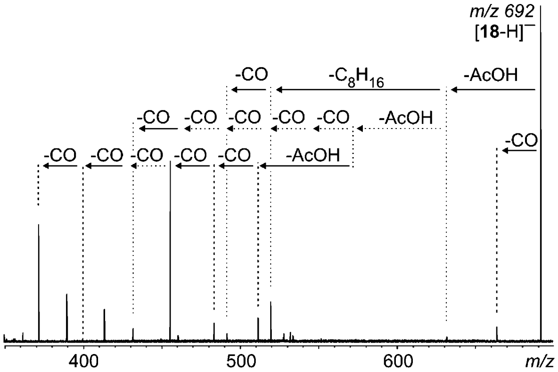


Figure 8. MS/MS spectrum (CID) of mass-selected [**18** − H]⁻. 1,2-Eliminations of acetic acid molecules and octene from the N-centered side chain compete with the CO losses. Dotted arrows represent losses that are not observed as peaks, although consecutive fragmentation reactions are found. This is possible, when a slow reaction precedes a much faster one.

ide losses are completely absent and only the consecutive losses of two acetic acid molecules are observed, which likely proceed through the same mechanism as discussed in Scheme 4.

So far, we have focused the discussion on chromium carbenes. Therefore, it should finally be noted that the chromium and tungsten carbene complexes examined in this study behave quite similarly. One of the most significant differences is the less pronounced CO loss observed for the tungsten carbene complexes. This is in line with a higher M−CO bond dissociation energy for tungsten as compared to chromium. The other reactions are observed for the tungsten complexes as well, in particular the retro-aldol reaction, which represents the major reaction channel in the decomposition of [**21** − H]⁻.

Conclusions

In this contribution, we report a novel mass spectrometric protocol for the ionization of chromium and tungsten carbene complexes by negative ion electrospray ionization, which is potentially useful not only for the mass spectrometrist but also for synthetic chemists using metal carbene complexes as synthetic intermediates. The addition of negatively charged nucleophiles such as cyanide to the electrophilic carbene carbon is utilized to provide the charge to carbene complexes that cannot be charged otherwise. The carbene complexes can then be ionized without inducing significant fragmentation. Carbene complexes bearing α-CH acidic carbene side chains can also be observed as deprotonated species [M − H]⁻. In some cases, cyanide addition competes with deprotonation, when KCN is added; in other cases, deprotonation prevails. In particular, for aminocarbene complexes, deprotonation is easily accomplished at the nitrogen atom, while cyanide addition is hampered due to the reduced electrophilicity at the electronically more saturated carbene carbon. These results underline the isolobal relationship between Fischer-type carbene complexes and carbonyl compounds such as amides and esters. Consequently, nucleophile addition and deprotonation are highly complementary ways to ionize carbene complexes in the negative mode. The softness of ESI mass spectrometry can be seen in the mass spectra of sugar carbene complexes that are known from solution phase to form gels. In the mass spectra quite large hydrogen-bonded assemblies up to the triply charged 20-mer can be observed.

The most important aspect of the CID experiments with mass-selected parent ions is that carbon monoxide losses are not always the most prominent fragmentation reactions. Several collision-induced fragmentations have been observed which can compete with the CO losses and therefore must have quite low activation barriers. One of these is a retro-aldol reaction within the carbohydrate backbone of a sugar carbene complex; another reaction channel corresponds to 1,2-elimination reactions that likely proceed in a concerted manner in analogy to ester pyrolysis and generate conjugated product ions. The presence of the quite weakly bound CO ligands is consequently not a disadvantage. On the contrary, the analysis of the fragmentations benefits from the competition with the CO losses. Energetically demanding reactions do not occur, and all reactions able to compete with the expulsion of carbon monoxide must be energetically quite favorable. Thus, the CO ligands represent a qualitative probe for the barrier height of the fragmentation reactions observed.

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Supporting Information Available: Text and figures giving selected mass spectra of other compounds discussed in detail in the text and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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