Metal complexes of acyclic diaminocarbenes: links between *N*-heterocyclic carbene (NHC)- and Fischer-carbene complexes ☆

Wolfgang A. Herrmann *, Karl Öfele, Denise v. Preysing, Eberhardt Herdtweck

Anorganisch-Chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, 85747 Garching, Germany

Dedicated to Professor Ernst Otto Fischer in great admiration of his scientific work as a pioneer of organometallic chemistry on the occasion of his 85th birthday

Abstract

Starting from free bis(diisopropylamino)carbene, only rhodium and iridium complexes could be synthesized with these carbene ligands so far. The formation of further carbene complexes of Group 18 metals failed, because of the high sensitivity of the free diaminocarbenes, as described by Alder. Here we report the synthesis of diaminocarbene complexes of Group 16 metals by reaction of several acyclic and cyclic carbenes—first synthesized by Alder—with hexacarbonyls of these metals. The reaction of bis(diisopropyl)aminocarbene with photolytically produced (ether)$Cr(CO)_5$ leads to a stable η^2-carbene complex, with one amino group of the carbene coordinated to the metal. The chemical and spectroscopic characteristics of this complex are described. The reaction of the same carbene with ethersubstituted $Mo(CO)_6$ resp. $W(CO)_6$ leads to unstable merely η^1-bonded complexes. In contrast to the bis(diisopropylamino)carbene, the reaction of the tetrahydropyrimidinocarbene, which was already isolated by Alder, with photolytically activated $Cr(CO)_6$ leads to a simply η^1-bonded complex; two of his CO ligands can be replaced with isonitrile even at ambient temperature. The analogous reaction of bis(*N*-piperidyl)carbene with photolytically activated $Cr(CO)_6$ leads to the formation of a tetracarbonylchromium complex with a completely novel chelating ligand. During all reactions of bis(diisopropylamino)carbene and tetrahydropyrimidinocarbene with the metal carbonyls their reduction to carbonyl metallates could be observed as side reaction.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Carbenes; Ruthenium and iridium complexes; Group 16 metal complexes

1. Introduction

For several time complexes of acyclic diaminocarbenes with different metals are already well-known; they were synthesized by means of the methods shown in Scheme 1.

Chatt reported their formation by addition of amines to isonitrile complexes [1] (Scheme 1a). According to this scheme corresponding diaminocarbene complexes of rhodium, palladium and also of mercury have been synthesized.

Another method is the deprotonation of tetrazolium ions with carbonylferrate, whereby a diaminocarbene complex is generated besides the expected tetrazolcarbene complex [2] (Scheme 1b).

☆ *N*-Heterocyclic carbenes, Part 35.

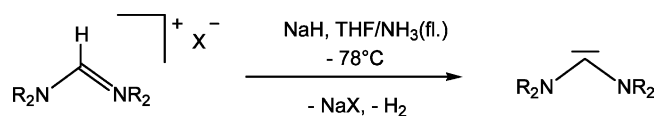* Corresponding author. Tel.: +49-89-289-13080; fax: +49-89-289-13473.

E-mail address: lit@arthur.anorg.chemie.tu.muenchen.de (W.A. Herrmann).
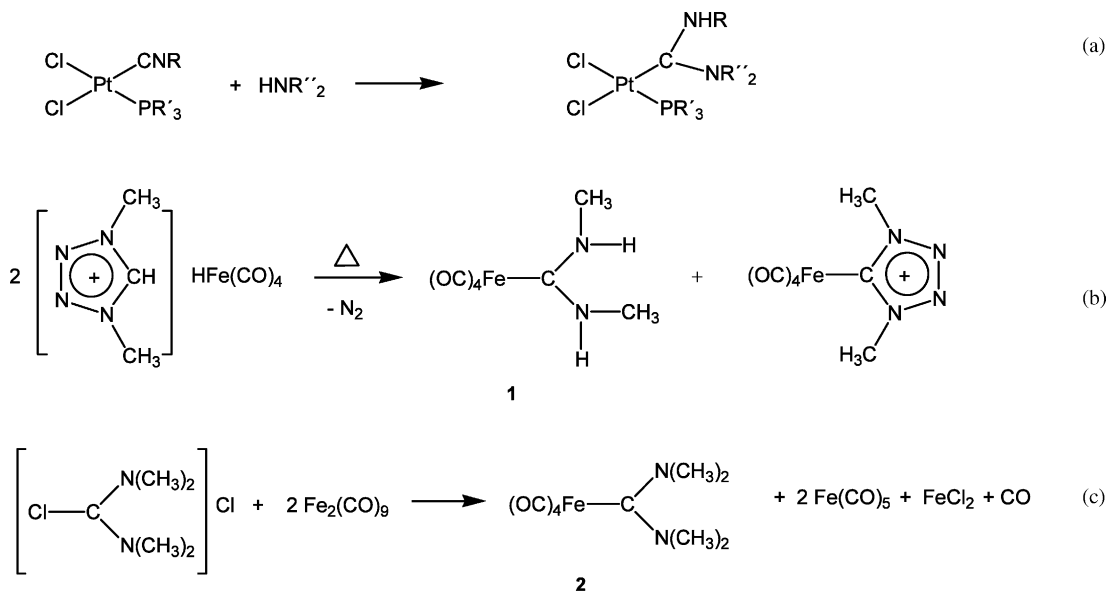
Scheme 1. Methods of synthesis for transition metal complexes with acyclic diaminocarbenes.

In both cases the carbenes contain at least one primary aminogroup.

W. Petz finally synthesized the bisdimethylaminocarbene complex **2** by reaction of chloroformamidinium chloride with $Fe_2(CO)_9$ [3] (Scheme 1c).

2. Results and discussion

2.1. Acyclic diaminocarbenes

R.W. Alder had succeeded for the first time, to isolate acyclic diaminocarbenes as more or less stable compounds by deprotonation of formamidinium salts with lithiumdiisopropylamide (LDA) [4] (Scheme 2). Therewith, possibilities to synthesize complexes with a diversity of metals opened. Similarly as with N-heterocyclic carbenes. The application of the three synthetic methods stated above is limited to few examples only. With the formation of free carbenes according to Alder, we expected more general synthetic methods enabling larger variations.

Scheme 3. Deprotonation of formamidinium salts in liquid NH_3.

Meanwhile the deprotonation of the formamidinium salts succeeded in our group also with NaH in liquid NH_3 at low temperatures (Scheme 3).

Due to the clearly recognizable ^{13}C-signals of the carbene carbon atoms the free bisdialkylaminocarbenes can be analyzed very well by means of NMR-spectroscopy and can be compared with the N-heterocyclic carbenes (Table 1).

It shows up that the carbene ^{13}C-signals of the acyclic diaminocarbenes occur in the same range as those of the saturated five-membered NHC, however, clearly differ from the high-field-shifted signals of the unsaturated NHC.
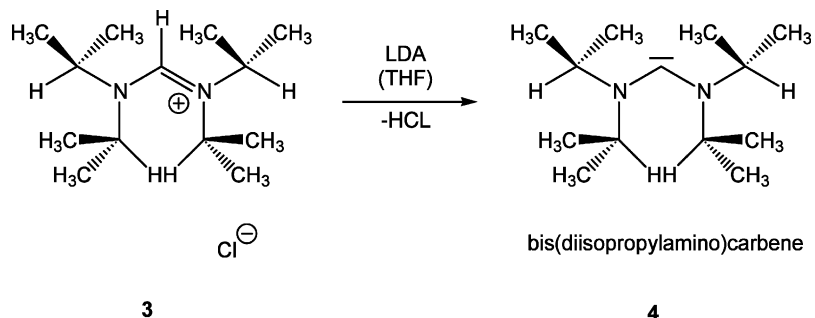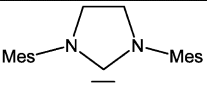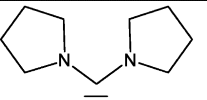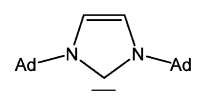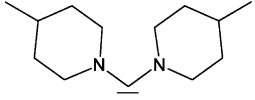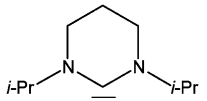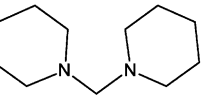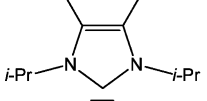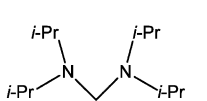
Scheme 2. Deprotonation of formamidinium salt **3** with LDA.

Table 1
^{13}C-NMR shifts of the carbene carbon atoms in different free carbenes

carbene	δ (carbene-C-atom)	carbene	δ (carbene-C-atom)
5	244.5 ppm [5]	**9**	241.86 ppm
6	211.4 ppm [5]	**10**	237.3 ppm
7	237.4 ppm [6]	**11**	236.8 ppm [7]
8	206.8 ppm [6]	**12**	255.5 ppm [4]

The free carbenes **7** [6], **11** [7] and **12** [4] were characterized for the first time by Alder; **9** and **10** in our group. The carbenes **5**, **6** and **12** are characterized also by means of X-ray structure analysis. It shows up that the NCN angle of bis(diisopropylamino)carbene **12** with 121.0° [4] is clearly expanded compared to the saturated *N*-heterocyclic carbene **5** with 104.7° [5a] and still more compared to the unsaturated 1,3-diadamantylimidazolin-2-ylidene **6** with 102.2°, which was isolated by Arduengo et al. [5b].
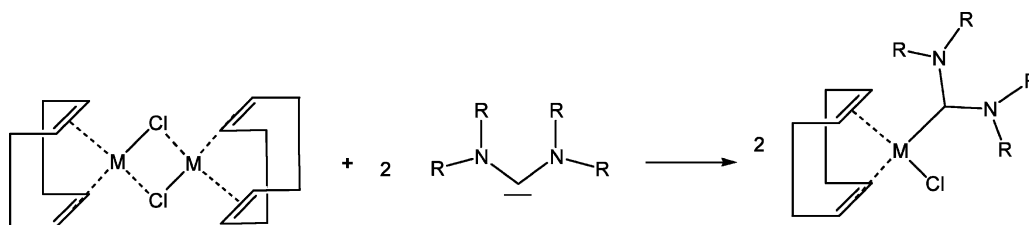
M = Rh; R = *iso*-propyl [8], NR$_2$= piperidyl, pyrrolidyl, 4-methyl-piperidyl
M = Ir; R = *iso*-propyl [8]

Scheme 4. Synthesis of transition metal complexes via free bis(dialkylamino)carbenes.
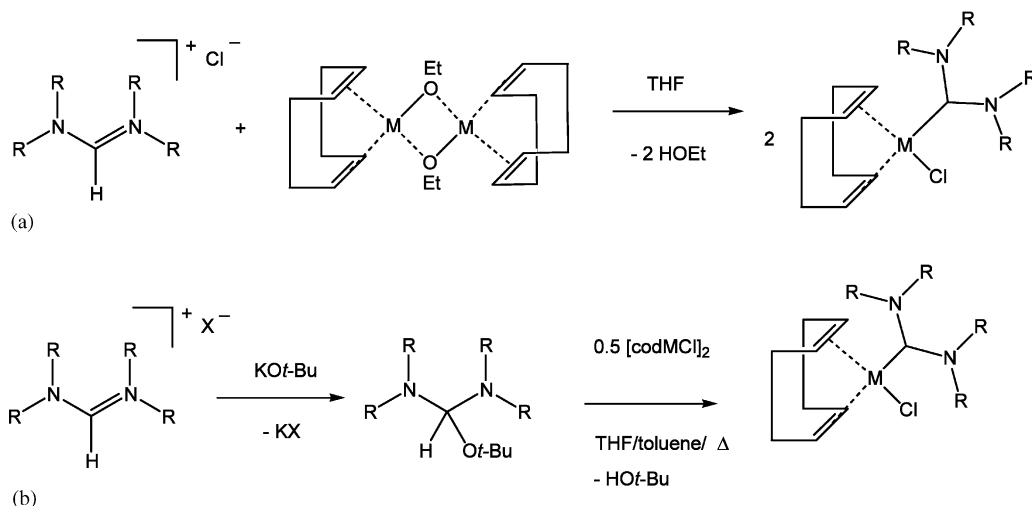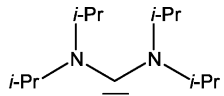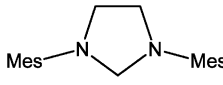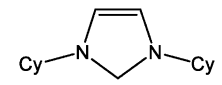
M = Rh; R = *iso*-propyl [8], NR$_2$= piperidyl, pyrrolidyl, 4-methyl-piperidyl
M = Ir; R = *iso*-propyl [8]

Scheme 5. Synthesis of transitionmetal complexes.

Table 2
ν(CO)vibrations of complexes of the type *cis*-(CO)$_2$Rh(carbene)Cl [8].

carbene	12	5	4
ν(CO) I [cm^{-1}]	2057	2081	2076
ν(CO) II [cm^{-1}]	1984	1996	2006

2.2. Diaminocarbene complexes of rhodium and iridium

The synthesis of monocarbene rhodium(I) and -iridium(I) complexes succeeded for the first time by reaction of free diaminocarbenes with the corresponding COD-metalchlorides (Scheme 4) [8]. In contrast to similar reactions with NHC, even a large excess of diaminocarbene does not lead to the formation of dicarbene complexes, probably due to the space requirement of the acyclic carbenes with their widened NCN angle.

The formation of the desired complexes succeeds substantially better than via free carbenes through in situ deprotonation of the formamidinium salts with ethoxy-bridged COD-metal complexes (Scheme 5a) or by reaction of formamidinium alcoholate adducts with metalprecursors under elimination of alcohol (Scheme 5b).

An important characteristic of the carbene ligands in catalytically active metal complexes is their strong electron donating effect. On the basis of ν(CO)vibrations of *cis*-dicarbonyl carbene rhodium complexes (Table 2), which are easily accessible by exchange of the COD ligand against CO (Scheme 6), it is recogniz-

carbene = **4, 5, 12**
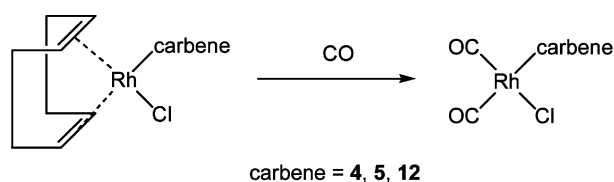
Scheme 6. Synthesis of *cis*-dicarbonylcarbene rhodium complexes.
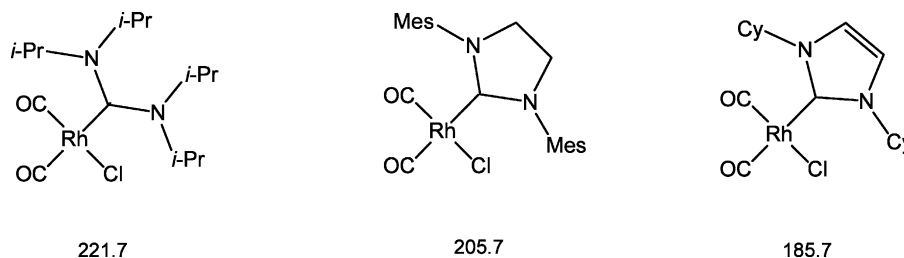
Fig. 1. Shifts of the ^{13}C-NMR signals of the carbene carbon atoms in different carbene complexes in ppm.
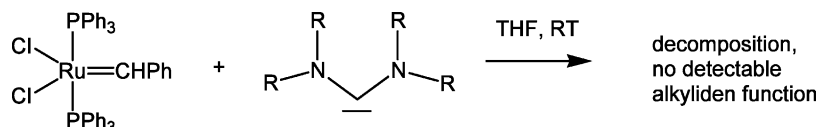
Scheme 7. Synthesis attempt for Grubbs analogous ruthenium-complexes with acyclic carbenes as ligands.

able that acyclic diaminocarbenes possess clearly stronger electron donating effects as both unsaturated and saturated NHC ligands (Table 2) [8].

The strength of the σ-donor properties of the carbene ligands—as specified by v(CO)vibrations—is confirmed by the shift of the ^{13}C-signals of the carbene carbon atoms (Table 1) in the complexes 12, 4 and 5 indicated in Table 2, since the chemical shift correlates directly with the electronic situation at the considered atom. The signal of the diaminocarbene complexes appears at clearly deeper field than the corresponding signals of the NHC complexes (Fig. 1) [8].

The increased reactivity of the acyclic carbenes compared to the N-heterocyclic carbenes already mentioned by Alder, in particular their inclination to rapid dimerization, proved in consequence as a clear handicap attempting to link acyclic carbenes to other metals.

The stronger σ-donating effect of the diaminocarbenes should affect favourably Grubbs analogous ruthenium carbene complexes, which are assigned as metathese catalysts.

However, it was not possible so far to substitute phosphane ligands in a Grubbs catalyst by isolated diaminocarbenes—similarly to the NHC complexes (Scheme 7). No alkylidene unit could be detected in the reaction products; obviously the free carbene reacts under attack at the alkylidene ligand. Also the method for the in situ deprotonation of formamidinium salts with t-BuOK in presence of Grubbs catalyst as well as reactions of the latter with a formamidinium alcoholate adduct according to Scheme 5b, led basically to decomposition products [9].

2.3. Reactions of acyclic diaminocarbenes with metalcarbonyls

For comparison of acyclic diaminocarbene ligands with NHC ligands on the one hand and with Fischer carbenes on the other hand, carbene carbonyl complexes with metals of the chromium group seemed particularly very appropriate indeed, since corresponding coordination compounds both with Fischer carbenes and with N-heterocyclic carbenes are well-known in large diversity and easily accessible via their metal hexacarbonyls [10].

Therefore, NHC complexes can be generated by heating metal hexacarbonyles for 2 h at 60 °C together with free carbene in THF under CO elimination (Scheme 8a). With acyclic diaminocarbenes, which are substantially more sensitive and more reactive a synthetic way via photolytically proven ether substituted carbonyl complexes should be pursued (Scheme 8b).

The reaction of bis(diisopropylamino)carbene with photolytic produced with (ether)Cr(CO)$_5$ leads in relatively smooth reaction, in contrast to the NHC, to a η^2-bonded complex 13 in 49% yield (Scheme 9), which is clearly characterized both by spectroscopic measurements and by X-ray structure analysis [11].

A similar η^2-bonded complex with a aminophosphino carbene ligand had been obtained from E.O. Fischer in
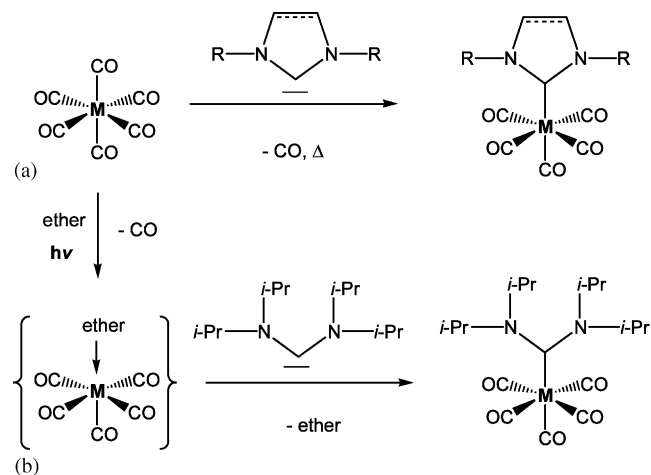
Scheme 8. Synthesis of carbene complexes of the type M(CO)$_5$L.
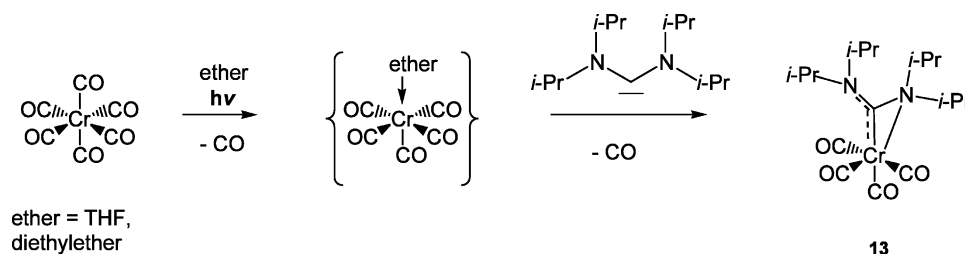
Scheme 9. Formation of η^2-bonded carbene complex of chromium.
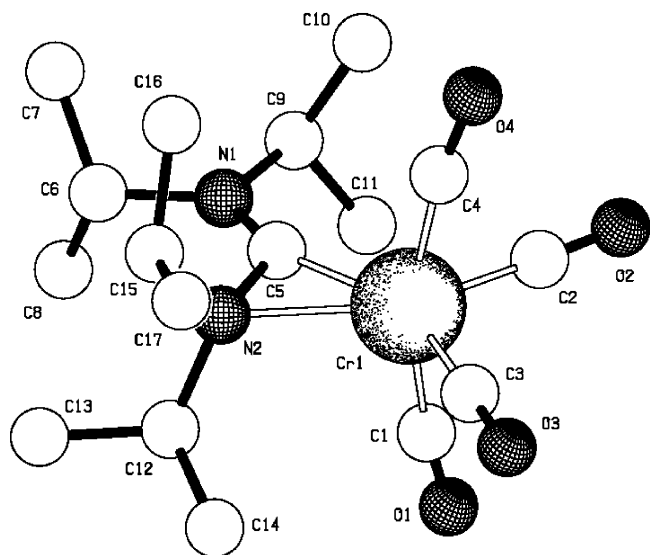
Fig. 2. PLUTON style plot of the solid state structure of compound 13.

1983 for the first time. This metallacyclic carbene complex 14 (Scheme 10) represents a transition state within the carbene–carbyne rearrangement according to data of the authors, the phosphino group still bonding to the carbene carbon atom whereby its coordination to the metal atom and the elimination of the *trans* ligand already takes place [12].

The formation of 14 is based on a rather complicated reaction, while the creation of the η^2-diaminocarbene complex 13 runs very easily.

With respect to the molecule of the η^2-bonded diaminocarbene complex 13 one can differentiate two strong bonds: a strong Cr–C bond (1.920 Å) and a weak Cr–N bond (2.207 Å). The nitrogen bound to the metal shows trigonal pyramidal configuration and has thus

sp^3-hybridisation, while the not bound nitrogen is planar and obtains thus sp^2-hybridisation.

The plane that is spanned by the atoms C6, N1 and C9 is coplanar to the metallacycle, which stands perpendicularly to the plane of the three CO ligands C^{1}O^1, C^{2}O^2 and C^{4}O^4.

One imagines the Cr–N–C triangle perpendicularly to the indication level in Fig. 2.

The N(1)–C(5)–N(2)–angle amounts to 125°, is thus expanded in relation to the appropriate angle of the free carbene; the distance C(5)–N(1) is clearly shorter with 1.309 Å than the distance between C(5)–N(2) with 1.457 Å; the bond between carbene carbon and the not-coordinated nitrogen atom possesses thus a clear double bond character. The v(CO) vibrations in the IR spectra appear at 2003.8, 1918.4, 1896.3 and 1870.1 cm^{-1} corresponding to an octahedral *cis*-M(CO)$_4$ fragment with approximately C_{2v} symmetry.

The relatively weak character of the Cr–N bond shows in its easily reversibly splitting, e.g. by CO under formation of a η^1-bonded complex 15 (Scheme 11).

Thereby, working at ambient temperature and atmospheric pressure, an IR-spectroscopically proven equilibrium has been detected between the η^2-bound complex 13 and the η^1-bound complex 15, with v(CO) frequencies at 2066.2 (w, CO); 1915 (st, CO); 1897.4 (m, CO) cm^{-1} in hexane.

The attempt, to realize a carbene–carbyne rearrangement discussed by E.O. Fischer at the complex 14, by reaction of the η^2-complex 13 with methyliodide at −20 °C did not succeed (Scheme 12). The educt complex 13 turned out to be completely inert under these conditions.

The result of a X-ray structure analysis shown in Fig. 2 and shows the η^2-bonded complex 13 in a frozen condition. The NMR spectra at ambient temperature
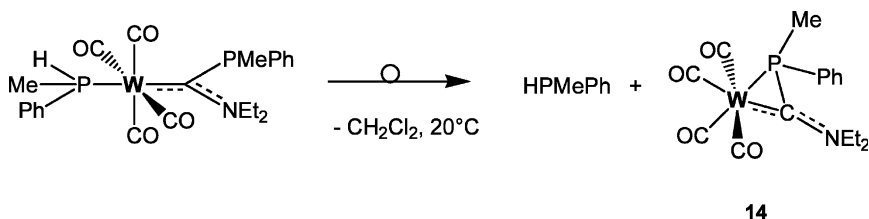
Scheme 10. Generation of the metallacyclic Fischer carbene complex 14.
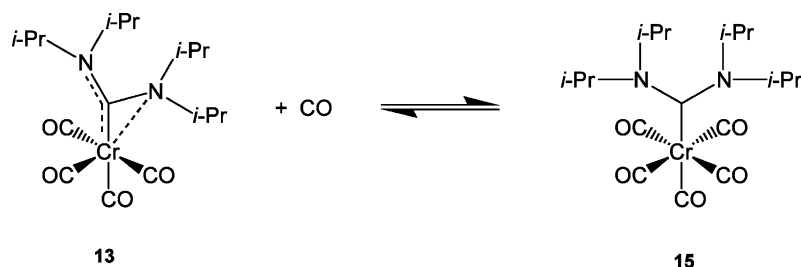
Scheme 11. Reversible CO accumulation to the η^2-bonded complex 13.

(Fig. 3a) in CD_2Cl_2 shows basically only one broad signal for the –CH– resp. –CH$_3$– protons of the isopropyl groups, which is not in agreement with the different amino groups, which are clearly recognizable in the X-ray structure analysis.

Not until low temperature the signals split up (Fig. 3b). One recognizes altogether three methyl signals and three signals of CH protons. The two CH$_3$ signals at 1.125 and 1.597 ppm correspond in the 'frozen' molecule to the methyl protons of the amino group which is not bound to the metal and whose isopropyl substituents are—due to the prevented rotation—in different surroundings; accordingly two CH signals arise at 4.02 and 4.14 ppm.

The signals at 1.239 ppm (CH$_3$) and 3.07 ppm (CH) are not split and twice as intensively as the other CH$_3$ resp. CH signals, corresponding to the isopropyl protons of the amino group coordinating to the metal.

At ambient temperature a rapidly fluctuating structure in the molecule is thus present. At the coalescence temperature at 283 K the free activation enthalpy $\Delta G^\ddagger$ is calculated to 53.06 kJ mol^{-1}.

Scheme 13 introduces a possible rearrangement mechanism of complex 13. After opening of the weak metal–nitrogen bond a rotation around 180° of the carbene ligand takes place. The fivefold coordinated transition state could be stabilized by the solvent.

In contrast to Cr(CO)$_6$, the reaction of higher homologes Mo(CO)$_6$ and W(CO)$_6$ with bis(diisopropyl)-aminocarbene leads to η^1-bonded complexes 16 and 17 (Scheme 14).

Probably because of the larger metal–ligand distances no three-membered metallacyclus can be formed in this reaction like with the chromium. Therein, the diamino-carbene differs from the aminophosphino carbene in the Fischer η^2-tungsten complex mentioned above.

Both η^1-bonded complexes 16 and 17 are very unstable and eliminate very easily CO under decomposition. This may happen, e.g. during removal of the solvent. Only in CO atmosphere they are restrictedly manageable. The v(CO) vibrations of both molecules with 2067.9 (w), 1932.6 (st), 1907.5 (m) for the molybdenum complex 18 and with 2056.0 (w), 1918.1 (st), 1892.3 (m) for the tungsten complex 19 clearly prove the existence of pentacarbonyl complexes.

During the reaction of the free 1,3-diisopropyl-3,4,5,6-tetrahydropyrimide-2-ylidene 7 with photolytically produced (ether)Cr(CO)$_5$ only a η^1-bonded complex 18 is formed, as well is form (Scheme 15) and no three-membered metallacycle. Although the NCN angle of the tetrahydropyrimidino carbene 7 with 116.2° differs not too much of that of the bis(diisopropylamino)carbene 12 with 121°, here was formed surprisingly no η^2-bonded complex, which is possibly to be ascribed to the fact that the rigid sixmembered ring opposes an expansion of the NCN angle when forming a η^2-complex. Analogous Mo and W complexes have been synthesised by Lappert and co-workers [13,14] from the reaction of corresponding methyl substituted 'dimeric carbenes' (electron-rich olefins) with Mo– and W–hexacarbonyl.

Complex 18 is very unstable, too, and eliminates very easily CO under decomposition like the molybdenum and tungsten complexes 16 and 17. According to this, rapid substitution of up to two CO ligands by isonitrile takes place at ambient temperature generating the stable facial configured tricarbonyl complex 19 (Scheme 16). In contrary the same attempt with triphenyl phosphane
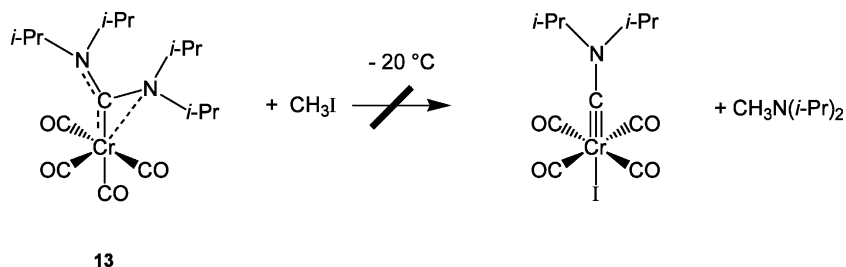
Scheme 12. Attempt of the synthesis of a carbyne complex.
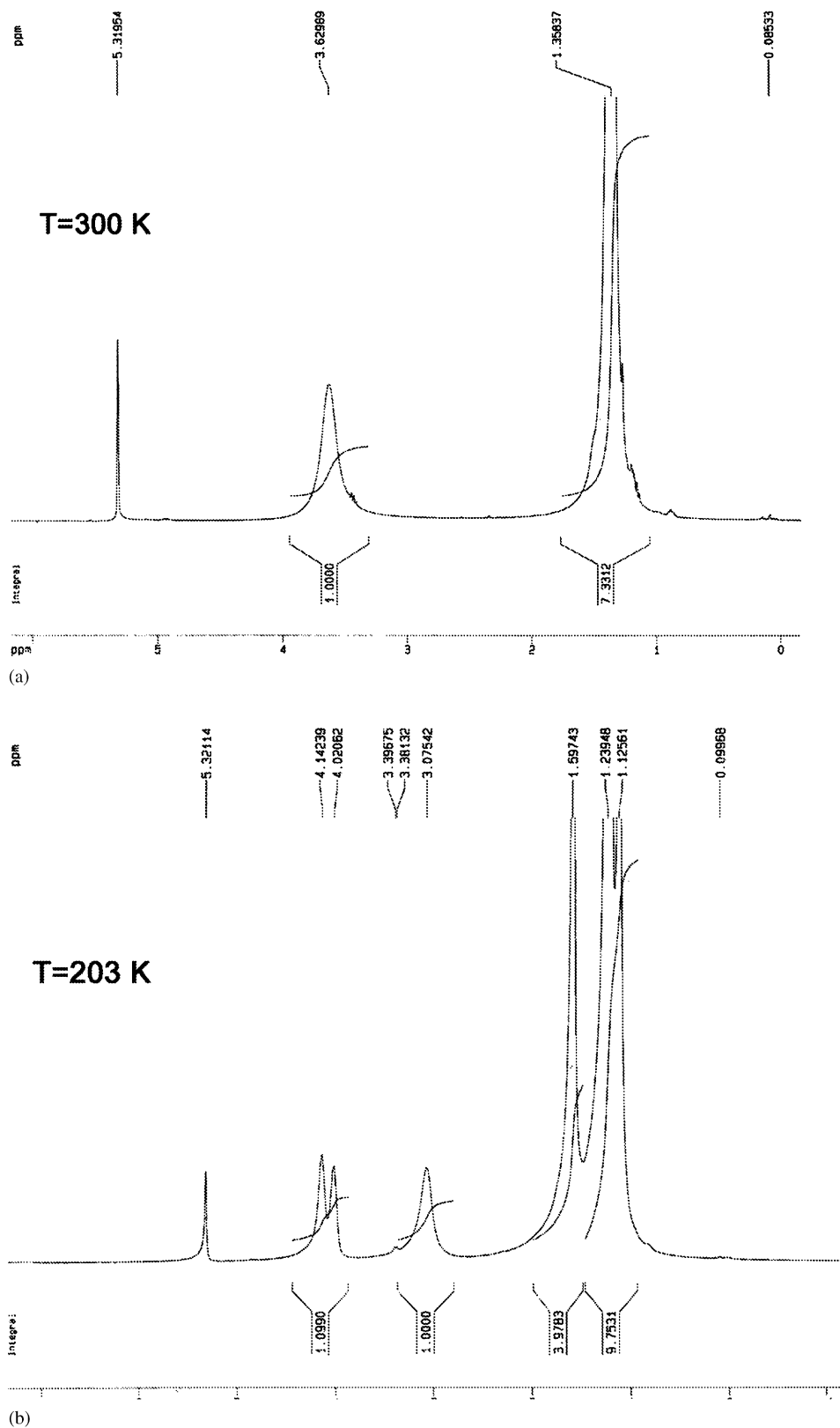
Fig. 3. Temperature dependent ^{1}H-NMR spectra of the η^2-bonded carbonyl chromium complex 13.
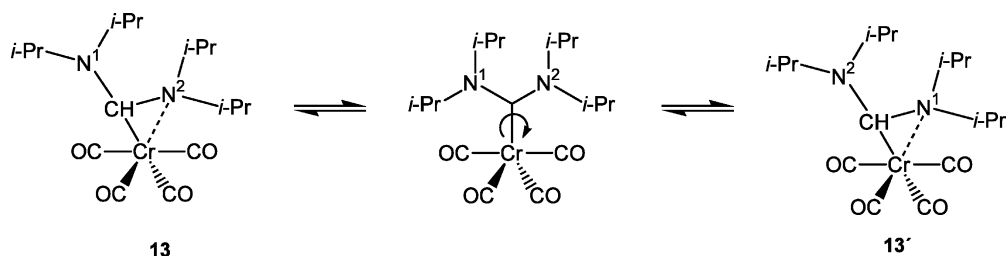
Scheme 13. Possible mechanism of fluctuation in the complex **13**.
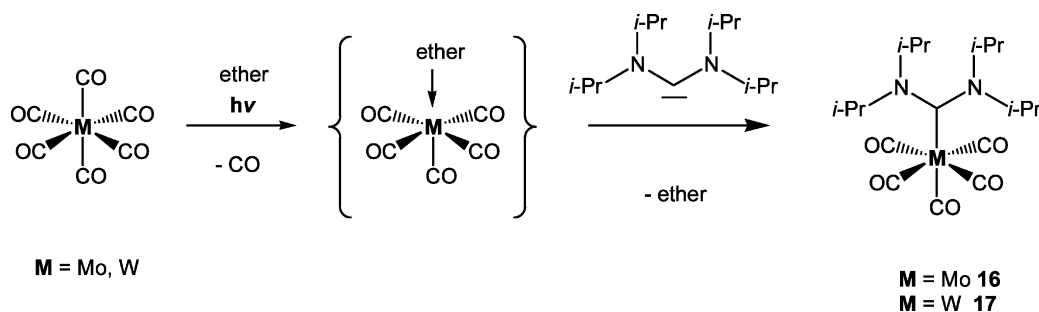
Scheme 14. Reaction of bis(diisopropylamino)carbene with Mo(CO)$_6$ and W(CO)$_6$.

leads to decomposition and elimination of CO. The reason may be the sterical handicap of the entrance of the bulky phosphane. This substitution behavior shows a clear difference between cyclic and acyclic carbenes. With similar pentacarbonyl imidazolinylidene chromium complexes the substitution of CO takes place only at higher temperature and substantially more slowly [15].

In contrast to the latter and similar to the diaminocarbene complex **18** CO substitution in Fischer carbene complexes by neutral donor ligands takes place clearly eased [16].

Both complexes **18** and **19** are proven by means of IR spectrometry, **19** furthermore by NMR spectroscopy and elemental analysis.

Diaminocarbenes may act as reducing agents for metal–hexacarbonyls too. During the reaction of carbenes **7** and **12** with irradiated hexacarbonyls of chromium, molybdenum and tungsten saltlike byproducts can be observed besides the carbene complexes containing carbonyl metallate anions. At the reaction of bis(diisopropylamino)carbene with W(CO)$_6$ this byproduct could be isolated and characterized as the decacarbonyl tungstate **20** (Scheme 17). This behaviour corresponds to the reducing capacity of electron-rich olefins—'dimeric carbenes', which are able to reduce metal carbonyl compounds forming stable dications of the type **20** as observed by Lappert and co-workers [13,17].

To our great surprise the reaction of bis-*N*-piperidylaminocarbene **11** with Cr(CO)$_6$ followed a quite different pattern: the reaction of this carbene with

(ether)Cr(CO)$_5$ yielded in reproducible manner in the formation of tetracarbonyl chromium complex **22** besides (piperidine)Cr(CO)$_5$ **21** (Scheme 18). The completely novel chelating ligand probably originates via fragmentation, rearrangement and recombination from the originally used diaminocarbene. Compound **22** could be characterized by X-ray structure analysis and **21** by IR spectra and elemental analysis. There are two

Scheme 15. Synthesis of the η^1-bonded carbene pentacarbonyl chromium complex **18**.

Cr–N bonds with different lengths: a larger one to the

Scheme 16. CO substitution by isonitrile in η^1-diaminocarbene complex **18**.

Scheme 17. Reduction of irradiated $W(CO)_6$ by bis(diisopropylamino)carbene.

sp^3-hybridisized N(2) and a shorter one to the sp^2-hybridisized N(1). K.H. Dötz generated a complex with a similar amine–imine (*N,N*)-chelating ligand on the basis of a Fischer carbene complex [18].

We are not able to explain at this time how this new ligand, which still shows certain structural components of the carbene, was generated. The result of a X-ray structure analysis of complex **21** is represented in Fig. 4.

3. Conclusions

Acyclic diaminocarbenes can be isolated similarly as the NHC in substance. Although acyclic diaminocarbenes exhibit a clearly larger N–C–N angle than the fivemembered saturated NHC, the characteristic ^{13}C-signals of the carbene carbon atoms lie in the same region, however, they differ clearly, compared to the high field shifted ^{13}C-signals of unsaturated NHC signals.

Free bis(diisopropylamino)carbene reacts with $Cr(CO)_6$ under formation of a η^2-complex **13**, in which the carbene is a component of a threemembered N–Cr–C metallacycle. A comparable tetracarbonyl complex was only known for tungsten with a phosphinoaminocarbene ligand, so far. The relatively weak coordination of the nitrogen in this threemembered ring shows up once in the easy replacement by CO and on the other hand in the fluctuation of the molecule in solution at ambient temperature. The transformation to a carbyne complex by electrophilic elimination of an amino group does not succeed.

The same carbene reacts with $Mo(CO)_6$ and $W(CO)_6$ to regular η^1-carbene pentacarbonyl complexes **16** and

17, which are very unstable in contrast to the η^2-chromium complex and decompose even at ambient temperature under CO cleavage, without the prove of a formation of a corresponding η^2-complex.

Tetrahydropyrimidinocarbene **7**, whose N–C–N moiety is very similar to that of bis(diisopropylamino)carbene **12**, forms with $Cr(CO)_6$ an unstable simply η^1-bonded carbene complex **18**. The destabilization of the CO ligands in *cis* position shows up in the extremely easy substitution of the ligands by isonitrile. Into this context, pentacarbonyl complexes with acyclic diaminocarbenes (including **7**) show a similar behavior like Fischer carbene complexes, in which the CO substitution with donor ligands is likewise disburdened, while the substitution at corresponding five-membered NHC complexes is substantially more slowly. To what extent the coordination behavior of the acyclic diaminocarbene deviating from the five-membered NHC is due to the larger N–C–N angle, must be scrutinized by further analysis.

The observed reducing capability of diaminocarbenes towards metal–organic compounds may interfere seriously with their application in direct formation of metal carbene complexes.

The reaction of bis(*N*-piperidyl)carbene with $Cr(CO)_6$ performs clearly deviating from the usual schemes. Besides several partly not yet identified products here was developed the tetracarbonyl complex **22** with a novel chelating ligand, whose generation is the subject of further experiments.

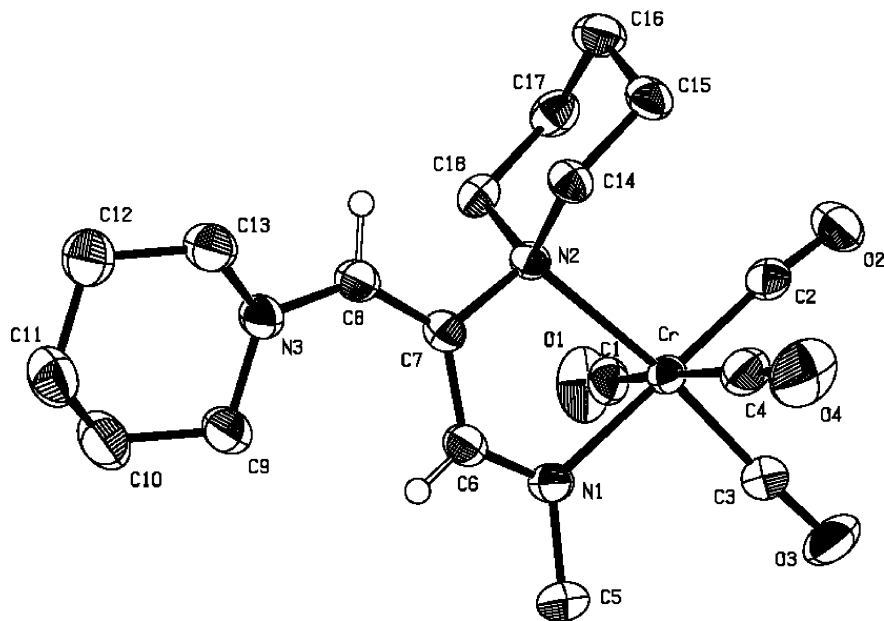Scheme 18. Reaction of bis(piperidyl)carbene with $Cr(CO)_6$.

Fig. 4. ORTEP style plot of the solid state structure of compound **22**. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity, except those located at C6 and C8.

4. Experimental

4.1. General

All reactions were performed by standard Schlenk techniques in an oxygen-free Ar or nitrogen atmosphere. Solvents were dried by standard methods and distilled under nitrogen. Infrared spectra were recorded in a Perkin–Elmer 1600 series FT-IR spectrometer, and the ^{1}H- and ^{13}C-NMR spectra at 400 and 100.54 MHz, respectively, in a FT JEOL GX 400 instrument. Elemental analyses were performed in the microanalytical laboratory of the TU München.

4.2. Tetracarbonyl{bis(diisopropylamino)carbene}-chromium (13)

A solution of 390 mg $Cr(CO)_6$ (1.77 mmol) in 150 ml diethylether was irradiated with a 150-W Hg high pressure immerging lamp while stirring for 1 h at −15 °C, then 1/2 h at slowly rising temperature up to 0 °C. After switching off the lamp ca. 380 mg (ca. 1.8 mmol) bis(diisopropylamino)carbene, dissolved in 30 ml hexane was transferred rapidly to the orange solution while vigorous stirring. The solution darkened and became cloudy. After stirring for 15 min the solvent was removed in vacuo and excessive $Cr(CO)_6$ sublimed off the partial crystalline brown–yellow residue, in high vacuo at 30 °C. The residue was extracted with 3 × 20 ml diethylether, the extracts were filtered and the orange filtrate evaporated in vacuo. After recrystallization from diethylether–hexane dark-yellow crystals were produced. Yield: 330 mg, 49%. ^{1}H-NMR (400.13 MHz,

C_6D_6): $\delta = 0.942$ (br, CH_3, 24H), 2.961 (br, CH, 4H). IR (hexane, cm^{-1}): $\nu = 2003.8$ (m, CO), 1918.4 (w, CO), 1896.3 (s, CO), 1870.1 (m, CO). Anal. Calc. for $C_{17}H_{28}CrN_2O_4$: C, 54.24; H, 7.50; N, 7.44. Found: C, 54.85; H, 7.39; N, 6.94%.

4.3. Pentacarbonyl-[bis(diisopropylamino)carbene]molybdenum(0) (16)

Similarly to the formation of **16**, a solution of 445 mg $Mo(CO)_6$ (1.69 mmol) was irradiated in 150 ml diethylether. The yielding yellow solution was mixed with a solution of 531 mg bis(diisopropylamino)carbene (2.5 mmol) in 20 ml hexane at 0 °C. After stirring the yellow solution at ambient temperature for 30 min, the solvent was removed in a CO stream at ambient temperature. Unreacted hexacarbonyl was sublimated from the yellow crystalline residue at 30 °C in high vacuo. The product was dissolved in 30 ml diethylether under CO atmosphere and then filtered (D4). The yellow filtrate was concentrated to a few milliliters in a CO stream. After layered with 10 ml hexane and leaving in the refrigerator under CO atmosphere, pale-yellow crystals were formed which were recrystallized again from ether–hexane. Yield: 190 mg, 25%, ^{13}C{^{1}H}-NMR ($(CH_3)_2CO$, 25 °C): $\delta = 213.32$ (s, NCN), 201.94 (W–CO), 158.32(W(CO)$_4$), 45.9 (br, $CH(CH_3)_2$), 23.85 (br, CH(CH_3)$_2$). ^{13}C{^{1}H}-NMR (CDCl$_3$, 25 °C): $\delta = 213.48$ (s, NCN), 201.0 (W–CO), 157.56 (W(CO)$_4$), 46.1 (br, $CH(CH_3)_2$), 21.92 (br, CH(CH_3)$_2$). IR (hexan, cm^{-1}): $\nu = 2067.9$ (w, CO), 1932.6 (s, CO), 1907.5 (m, CO).

4.3.1. Pentacarbonyl-[bis(diisopropylamino)carbene]tungsten(0) (17)

Similarly to the formation of **17**, 545 mg W(CO)$_6$ (1.55 mmol) was irradiated in 150 ml diethylether and the yellow solution was mixed with 510 mg carbene (2.4 mmol), which was dissolved in 30 ml hexane. The colour of the reaction mixture first lightened easily, after some minutes a strong brownish turbidity was formed. After removal of the solvent in a CO stream and sublimation of unreacted hexacarbonyl in high vacuo, the dark-yellow crystalline residue was extracted with 3×10 ml diethylether under CO atmosphere. The yellow extracts were then filtered (D4) and the collected filtrates were concentrated to a few milliliters in a CO stream. After layered with 10 ml hexane, nearly colourless, pale-yellow crystals were formed under CO atmosphere in the refrigerator, which were again cleaned from a brown, oily contamination by crystallization from ether–hexane. Yield: 200 mg, 25%; IR (hexane, cm^{-1}): $v = 2066.2$ (w, CO), 1915 (st, CO), 1897.4 (m, CO).

4.3.2. Formation of decacarbonylditungstate (20)

The brownish-yellow ether insoluble part of the reaction product was dissolved in 10 ml acetone and the orange solution filtered (D4). After concentration in vacuo to 4 ml, 10 ml of diethylether was added while avoiding rapid mixing. After leaving overnight in the refrigerator orange crystals were formed. Yield 500 mg, 58%. IR (CH$_2$Cl$_2$, cm^{-1}): $v = 1942$ (w, CO), 1890 (vst, CO), 1838 (w, CO), 1745 (m, CO). Anal. Calc. for C$_{36}$H$_{56}$N$_4$O$_{10}$W$_2$: C, 40.31; H, 5.26; N, 5.22; W, 34.28. Found: C, 39.11; H, 5.36; N, 5.04; W, 33.56%.

4.4. Pentacarbonyl-(N,N′-diisopropyl-3,4,5,6-tetrahydropyrimidinocarbene)chromium(0) (18)

A solution of 360 mg Cr(CO)$_6$ (1.64 mmol) in 150 ml diethylether was irradiated with vigorous stirring under argon atmosphere with a 150-W Hg high pressure immerging lamp. The temperature was held first at $-20\,°C$, increased after 30 min to $-10\,°C$ and then another further 30 min to $0\,°C$. After a total of 1 and 1/2 h of irradiation a slow argon stream was led through the solution for 10 min and the lamp was switched off. The generation of the free carbene succeeded by mixing 440 mg (N,N-diisopropyl-3,4,5,6-tetrahydro-pyrimidinium)BF$_4$ (1.72 mmol), 65 mg t-BuOK (0.58 mmol) and 751 mg NaH (31.3 mmol) under argon in a Schlenk tube with 20 ml THF and stirring at ambient temperature for 2 h. After removal of the solvent in vacuo, the colourless crystalline product was extracted twice with 15 ml hexane each, the pale-yellow solution filtered in a predried Schlenk tube and concentrated in vacuo to ca. 15 ml.

After completion of the photolysis of Cr(CO)$_6$ the carbene solution (ca. 0.7 mmol) was transferred im-mediately with vigorous stirring into the irradiation vessel with the orange solution of the (ether)Cr(CO)$_5$ complex. The colour of the solution lightened up and a brownish precipitation separated. The solution was stirred vigorously at ambient temperature for 30 min. From the reaction solution the solvent was completely removed in a CO stream. Unreacted Cr(CO)$_6$ was sublimated by $30\,°C$ in high vacuo. The brown–yellow residue was extracted twice in CO atmosphere with 15 ml diethylether each. The yellow solution was filtered (D4) and concentrated to a few milliliters in a CO stream. After layered with hexane light yellow crystals were received, which were purified by recrystallizing from hexane–ether in CO atmosphere. Yield: 110 mg [44% according to the carbene]. ^{13}C{^{1}H}-NMR (CD$_2$Cl$_2$, 25 °C): $\delta = 324.01$ (s, NCN), 224.01 (Cr–CO), 217.65, 215.82, 212.10, 125.00 (Cr(CO)$_4$), 59.20, 40.77 (s, CH$_2$), 22.04, 20.77 (s, CH(CH$_3$)$_2$). IR (hexane, cm^{-1}): $v = 2050.2$ (m, CO), 1921.3 (s, CO), 1890.9 (w).

4.5. Reaction of 18 with t-butylisonitril to form complex 19

Compound **18** (100 mg, 0.28 mmol) was dissolved at ambient temperature in 20 ml hexane and the yellowish solution mixed while stirring with 0.2 ml t-butylisonitril (1.9 mmol). The solution suddenly turned citrus and after a few minutes a fine crystalline yellow precipitate was formed. After 30 min in the refrigerator the crystallization was complete. The product was collected and washed with 5 ml hexane twice and dried in vacuo. Citrus crystals of bis(t-butylisonitril)tricarbonyl(N,N′-diisopropyl-3,4,5,6-tetrahydropyrimidinocarbene)–chromium(0) (**19**) were collected. Yield: 120 mg, 91% of the theory. IR (ether, cm^{-1}): $v = 2107.4$ (w, CN), 1918.3 (w, CO), 1890.1 (s, CO), 1867.9 (m, CO). EA for C$_{23}$H$_{38}$CrN$_4$O$_3$ (470.57 g mol^{-1}): Anal. Found: C, 58.29; H, 8.21; N, 11.74; Cr, 10.87, Calc.: C, 58.71; H, 8.14; N, 11.91; Cr, 11.05%.

4.6. Reaction of bispiperidylcarbene (11) with irradiated hexacarbonylchromium

Cr(CO)$_6$ (400 mg, 1.82 mmol) in 160 ml ether was irradiated as in Section 4.2. At $0\,°C$ a solution of the carbene {formed according to Alder from 622 mg formamidinium salt (2.5 mmol)} in 30 ml hexane was added to the orange solution while vigorously stirring. A slight bathochromic shift occurred. After the removal of the solvent in vacuo the remaining Cr(CO)$_6$ was sublimed from the red–brown residue at $30\,°C$ in high vacuum. The raw product was extracted at ambient temperature with 4×20 ml hexane and the solvent removed from the orange solution at ambient temperature in vacuo. The partial crystalline orange residue (155 mg) was mixed with 40 ml hexane and purified by

Table 4
Crystal data and summary of intensity data collection and structure refinement of compound **22**

	22
Formula	$C_{18}H_{25}CrN_3O_4$
Formula weight	399.41
Color/shape	Orange fragment
Space group	$P2_1/c$ (no. 14)
Unit cell dimensions	
a (Å)	12.1981(1)
b (Å)	11.5558(1)
c (Å)	14.0913(1)
β (°)	104.6024(3)
V (Å^3)	1922.13(3)
Z	4
ρ_{calc} (g·cm^{-3})	1.380
μ (mm^{-1})	0.623
Diffractometer	Nonius kappaCCD
λ (Å), Mo–K$_\alpha$	0.71073
T (K)	173
Reflections integrated	41620
Independent reflections (all data)	3508
Observed reflections ($I > 2\sigma(I)$)	3313
Parameters refined	335
R_1 (observed/all data)	0.0284/0.0307
wR_2 (observed/all data)	0.0752/0.0768
GOF (observed/all data)	1.086/1.086

chromatography. A citrus product was eluted with hexane–ether (2:1). After removal of the solvent, yellow crystals of **21**, which were easily soluble in hexane, were formed. Yield 80 mg. IR (hexane, cm^{-1}): $v = 2065.9$ (m, CO), 1932.8 (vst, CO), 1916.3 (s, CO), 1900 (sh, CO), 1876.8 (w, CO). Anal. Found: C, 43.48; H, 4.11; Cr, 18.42; N, 4.93. Calc. for $C_{10}H_{11}CrNO_5$: C, 43.33; H, 4.00; Cr, 18.76; N, 5.05%.

The hexane-insoluble reaction product was extracted three times with 20 ml diethylether, the extracts were filtered and the clear orange filtrate was concentrated in vacuo to 5 ml. After layered with 10 ml hexane a few well-shaped orange crystals of **22** were formed. Yield ca. 20 mg.

Table 3
Characteristic bond lengths (Å) and bond angles (°) for compound **22**

Bond lengths

Cr–N1	2.0798(14)	C5–N1	1.467(2)
Cr–N2	2.3231(13)	C6–N1	1.282(2)
Cr–C1	1.898(2)	C6–C7	1.424(2)
Cr–C2	1.838(2)	C7–N2	1.491(2)
Cr–C3	1.822(2)	C7–C8	1.369(2)
Cr–C4	1.907(2)	C8–N3	1.354(2)

Bond angles

N1–Cr–N2	76.69(5)	C6–C7–N2	114.8(1)
C5–N1–Cr	122.93(12)	C6–C7–C8	127.6(2)
C5–N1–C6	117.7(2)	C7–N2–Cr	107.28(9)
N1–C6–C7	121.8(2)	C7–C8–N3	133.8(2)

4.7. Structure determination of compound **22**

Crystal data and details of the structure determination are presented in Table 4. Table 3 summarizes selected bond distances and bond angles. Suitable single crystals for the X-ray diffraction study were grown from a concentrated solution of **22** in diethylether layered with hexane. A clear orange fragment ($0.38 \times 0.46 \times 0.56$ mm^3) was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed and sealed. Preliminary examination and data collection were carried out on an area detecting system (κCCD; Nonius) at the window of a rotating anode (Nonius; Fr951) and graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 3697 reflections. Data collection were performed at 173 K within a Θ-range of $1.73 < \Theta < 25.36°$. Nine sets were measured in rotation scan modus with $\Delta\varphi/\Delta\Omega = 1.0°$. A total number of 41 620 intensities were integrated. Raw data were corrected for Lorentz, polarization, decay and absorption effects. After merging ($R_{int} = 0.035$) a sum of 3508 independent reflections remained and were used for all calculations. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found in the difference Fourier maps and refined freely. Full-matrix least-squares refinements with 335 parameters were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with SHELXL-97 weighting scheme and stopped at shift/err < 0.001. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography. All calculations were performed on an Intel Pentium II PC, with the STRUX-V system, including the programs PLATON, SIR-92 and SHELXL-97 [19].

5. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 213534 for compound **22**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam. ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

References

[1] E.M. Badley, J. Chatt, R.L. Richards, G.A. Sim, J. Chem. Soc., Chem. Commun. (1969) 1322.

[2] K. Öfele, C.G. Kreiter, Chem. Ber. 105 (1972) 529.

[3] W. Petz, Angew. Chem. 87 (1975) 288.

[4] R.W. Alder, P.R. Allen, M. Murray, A.G. Oprgen, Angew. Chem. 108 (1996) 1211.

[5] (a) A.J. Arduengo, III, J.R. Goerlich, W.J. Marshall, J. Am. Chem. Soc. 117 (1995) 11027;
(b) A.J. Arduengo, III, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.

[6] R.W. Alder, M.E. Blake, C. Bortolotti, S. Bufali, C.P. Butts, E. Linehan, J.M. Oliva, A.G. Orpen, M.J. Quayle, J. Chem. Soc., Chem. Commun. (1999) 241.

[7] R.W. Alder, M.E. Blake, J. Chem. Soc., Chem. Commun. (1997) 1513.

[8] K. Denk, P. Sirsch, W.A. Herrmann, J. Organomet. Chem. 649 (2002) 219.

[9] K. Denk, Dissertation, Technische Universität München, 2002.

[10] (a) E.O. Fischer, Pure Appl. Chem. 30 (1972) 353;
(b) J. Müller, K. Öfele, G. Krebs, J. Organomet. Chem. 82 (1974) 383.

[11] M. Tafipolsky, W. Scherer, K. Öfele, G. Artus, B. Pedersen, W.A. Herrmann, G.S. McGrady, J. Am. Chem. Soc. 124 (2002) 5865.

[12] E.O. Fischer, R. Reitmeier, K. Ackermann, Angew. Chem. 95 (1983) 419.

[13] M.F. Lappert, P.L. Pye, G.M. McLaughlin, J. Chem. Soc., Dalton Trans. (1977) 1272.

[14] M.F. Lappert, P.L. Pye, J. Chem. Soc., Dalton Trans. (1977) 1283.

[15] C.G. Kreiter, K. Öfele, G.P. Wieser, Chem. Ber. 109 (1976) 1749.

[16] H. Werner, H. Rascher, Helv. Chim. Acta 51 (1968) 1765.

[17] M.F. Lappert, J. Organomet. Chem. 358 (1988) 185.

[18] K.H. Dötz, A. Rau, K. Harms, J. Organomet. Chem. 439 (1992) 263.

[19] (a) L.A. Strater, Data Collection Software for Nonius κCCD devices, Delft, The Netherlands, 1997.;
(b) Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307ff;
(c) A.J.C. Wilson (Ed.), International Tables for Crystallography, vol. C, Tables 6.1.1.4 (pp. 500–502), 4.2.6.8 (pp. 219–222), and 4.2.4.2 (pp. 193–199), Kluwer Academic Publisher, Dordrecht, The Netherlands, 1992.;
(d) G. Artus, W. Scherer, T. Priermeier, E. Herdtweck, STRUX-V: A Program System to Handle X-ray Data, TU München, Garching, Germany, 1997.;
(e) A.L. Spek, PLATON: A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1999.;
(f) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, SIR92, J. Appl. Crystallogr. 27 (1994) 435–436;
(g) G.M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, Germany, 1998.