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Structural investigations of metalcarbonyl complexes with acyclic diamino carbenes ☆

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This paper is dedicated to Dr. Karl Öfele in great admiration of his scientific work as a pioneer in N-heterocyclic carbene (NHC) and carbonyl coordination chemistry and in appreciation of his role as a research mentor.

Abstract

Here, we report the synthesis of acyclic and cyclic aminocarbene substituted carbonyl complexes of group 6 metals. The reaction of bis(diisopropyl)aminocarbene with photolytically produced (ether)M(CO)$_5$ leads to unstable η^1-carbene complexes, which convert to η^2-carbene complexes; crystallographic data are presented for the tungsten complex, where one amino group of the carbene coordinates to the metal. The Mo and W η^2-complexes can be converted to an imine-complex under elimination of propene; characterized by chemical, spectroscopic and crystallographic data. DFT-calculations of a new bis(dialkyl)aminocarbene and the corresponding methylidene salt were performed and compared with the corresponding crystallographic data of the latter one. In a side-reaction during the reaction of (diethyl ether)Cr(CO)$_5$ with a free six-membered cyclic carbene a three-nuclear dianionic metal carbonyl *nido* complex $(C_{14}H_{10}Cr_3O_{12})^{2-}$ is formed, which could be characterized by spectroscopic and crystallographic data.
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Keywords: Acyclic carbene complexes; Group 6 carbonylcomplexes; Imine-carbonyl complex

1. Introduction

The discovery in 1968 when Öfele [1] and Wanzlick[2] synthesized for the first time N-heterocyclic carbene (NHC) complexes (Fig. 1), and the isolation of stable free carbenes, almost two decades later, by Arduengo [3,4] were landmarks for a large number of applications in synthesis and catalysis [5–7].

The preparation of these complexes was performed the first two decades via an in situ method, with the disadvantage of a small group of metal precursors suitable for complex synthesis [8–11]. For this synthesis only acidic dialkyl-azolium salts derived from imidazole, pyrazole, tri-

azole, thiazole, and tetrazole [12] could be used. With the possibility of isolating free carbenes a new era of the Öfele–Wanzlick carbene complexes was opened.

After the preparation of a free acyclic carbene **2a**, bis(diisopropylamino)carbene, by Alder et al. [13–15], the first metal-complexes of rhodium and iridium could be synthesized via the free carbene by Denk and Herrmann [16] (Fig. 2).

Complexes with acyclic diaminocarbenes have been synthesized before already by addition of amines to isonitrile complexes [17], the deprotonation of tetrazolium ions with carbonylferrate [9,18], and the reaction of tetramethylformamidinium dichloride with Fe$_2$(CO)$_9$ [19].

Carbonyl complexes of group six metals with stable "Alder"-diaminocarbenes have been studied to investigate the σ-donor/π-acceptor ability of these carbenes via the CO-stretching frequencies, and to compare them with known NHC-ligands. The reaction of acyclic diaminocarbenes with photolytically produced (diethyl ether)Cr(CO)$_5$
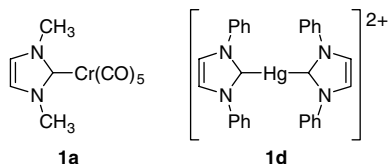
Fig. 1. First NHC complexes synthesized by Öfele (**1a**) and Wanzlick (**1d**).
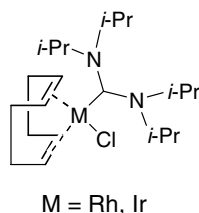

M = Rh, Ir

Fig. 2. First metal complex synthesized with a free acyclic carbene.

leads to the formation of a chelating diaminocarbene complex (**5a**), where the diaminocarbene is η^2-bonded to the metal (Scheme 1) [20].

In this interesting complex **5a** the lone pairs of the metal-coordinating nitrogen and the carbene atom contribute to donor stabilization of the Lewis-acidic metal center; a very short Cr–C–bond (1.920 Å) occurs because of the triangular chelating-coordination. A similar behaviour was observed recently in the Bertrand group, where a (amino)(phosphino)carbene is coordinated to rhodium. In this case the phosphorus atom and not the nitrogen is coordinated to the metal [21].

DFT-calculations of complex **4a** show a CO-bond energy of only 21.2 kcal/mol [22]; it is the smallest bond energy for such Cr(CO)$_5$L complexes to our knowledge. This behaviour is attributed to the high basic properties of the carbene ligand and its ability to stabilize the Cr(CO)$_4$L species (**5a**).

^{1}H NMR-studies show that the metal–nitrogen bond in complex **5a** can be cleaved easily, resulting in a fluctuating system at room temperature, where all alkyl substituents are equal. In complex **5a** one CO can be inserted into the metal–nitrogen bond to form reversibly the η^1-complex **4a**. At these reactions of acyclic carbenes with metal-hexacarbonyls some side-reactions were observed, which led to unstable products [23,24].

In this work, we report some studies on these reactions of the diaminocarbene complexes and the behaviour of the resulting products.

2. Results and discussion

2.1. X-ray structural results

Metal carbonyl complexes of molybdenum and tungsten show a more complicate behaviour at the reaction with free diamino carbenes, than the chromium carbonyl complex (Scheme 2). First results were presented from the Herrmann group recently [24,25].

In the reaction of photolytically produced THF-substituted pentacarbonyl complexes of molybdenum and tungsten with the free carbene **2a** at low temperature (−10 °C), the η^1-substituted-carbene pentacarbonyl complexes **4b**, and **4c** can be obtained for a short time (Scheme 2). These complexes undergo a rearrangement to the η^2-bonded complexes **5b** and **5c** by losing one CO as previously observed for complex **4a**. Suitable crystals for an X-ray diffraction analysis could be obtained from complex **5c** (Fig. 3). Crystal data and details of the structure determination are presented in Table 5.

The bis(diisopropylamino)carbene ligand in complex **5c** is η^2-coordinated to the tungsten with a short metal-carbon bond (2.072(3) Å) and a long metal–nitrogen bond (2.363(3) Å) (Fig. 3). As previously mentioned, the homologous chromium complex **5a** shows with 1.920(1) and 2.207(1) Å the same behaviour [20]. Also the N1–C5-bond with a bond length of 1.302(4) Å in complex **5c** shows the same π-bond characteristics as observed in the chromium complex **5a** (1.309(2) Å). The length of the N2–C5-bond is with 1.470(4) Å in the range of a single bond, similar to that in complex **5a** (1.457(2) Å). Because of the much longer metal–C5-, and metal–N2-bond the N2–W–C5-angle is with 38.0(1)° considerably 2.6° smaller as in the homologous chromium complex. In these complexes a π-electron delocalization over the N1–C5-metal bonds was proposed [20].

In contrast to the homologous chromium complex **5a** no dynamic fluctuation of the carbene ligand at room temperature was observed in the ^{1}H NMR-spectrum. Varying chemical shifts are obtained for the different N-alkyl groups in these complexes (**5b**, **5c**). In consequence, the metal–nitrogen bond must be stronger than in complex **5a**. By insertion of a carbonyl into the metal–nitrogen bond a rearrangement under elimination of propene occurs in the complexes **5b** and **5c** to form the imine complexes **6b** and **6c** (Scheme 2), which could be characterized by single crystal X-ray analysis (Fig. 4) (**6c** [26]).
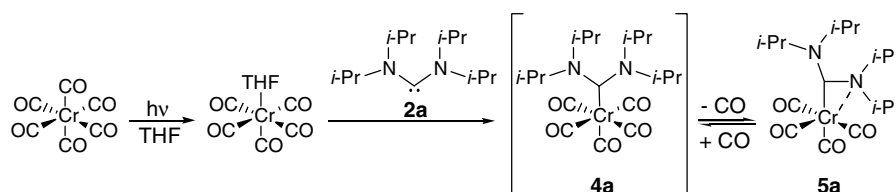
Scheme 1. Reaction of free bis(diisopropylamino)carbene with a pentacarbonylchromium complex.
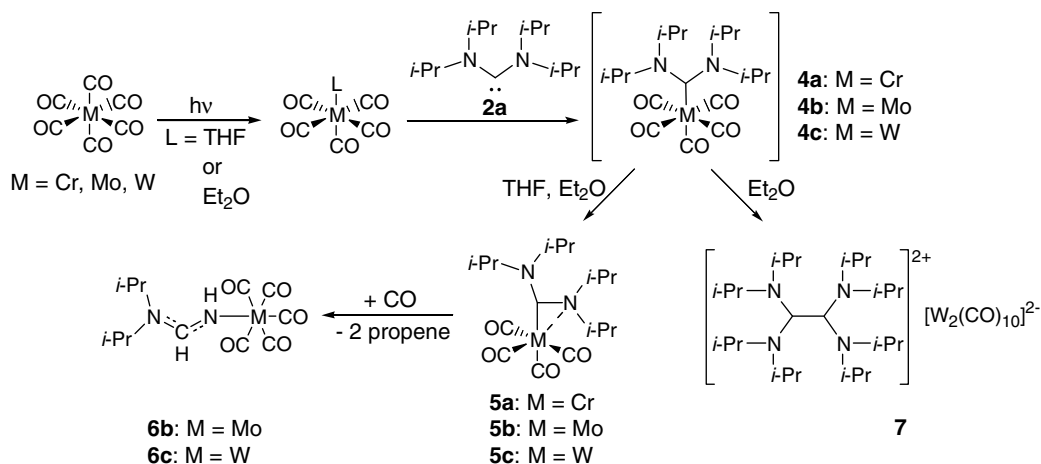
Scheme 2. Reaction mechanism for the formation of pentacarbonyl complexes of group 6 metals with a bis(diisopropylamino)carbene ligand.
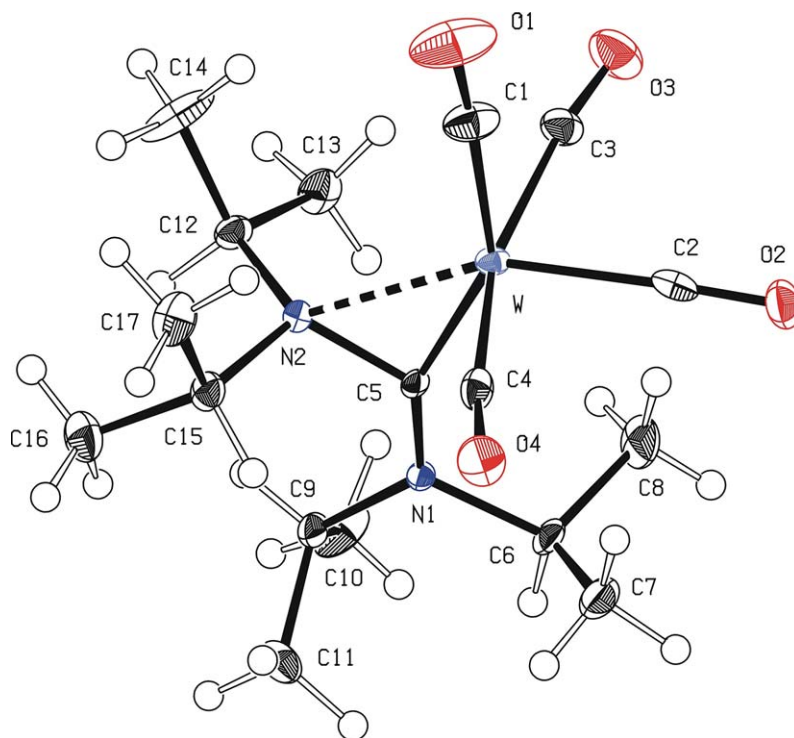

Fig. 3. ORTEP [34] style plot of compound **5c** in the solid state. Atomic displacement ellipsoids for non-H atoms are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (°): W–N2 2.363(3), W–C5 2.072(3), N1–C5 1.302(4), N1–C6 1.503(4), N1–C9 1.497(4), N2–C5 1.470(4), N2–C12 1.514(4), N2–C15 1.522(4); N2–W–C5 38.0(1), W–C5–N1 153.6(2), W–C5–N2 81.8(2), N1–C5–N2 124.6(3), C6–N1–C9 115.4(2), C12–N2–C15 115.3(3), W–N2–C5 60.2(2), C3–W–C5 97.9(1).

The complexes **5b** and **5c** can be obtained by removing the solvent in vacuo to prevent an insertion of CO into the metal–nitrogen bond.

If carbene **2a** reacts with diethyl ether-tungstenpentacarbonyl, produced by irradiation of W(CO)$_6$ in diethyl ether as solvent, an anionic reduction product **7** [23], is formed in a side reaction besides complex **6c** (Scheme 2).

The postulated mechanism for the formation of complexes **6b** and **6c** as shown in Scheme 3 starts from tetracarbonyl complexes **5b** and **5c**, where a bis(diisopropylamino) carbene ligand is η^2-coordinated (**A**). This species can be

converted by insertion of a carbon monoxide to the η^1-coordinated complex **B** resp. **C**. Because of the high basic properties of the carbene ligand an H-shift occurs (**D**) under release of propene, yielding the mesomeric forms **E** and **F**. A similar reaction was obtained by Bertrand at free aminoalkyl- and aminophosphino-carbenes (Scheme 4) [21,27]. **F** converts to **H** by a second H-shift to the highly nucleophilic nitrogen. By a second release of propene the imine complex **I** is formed as the stable final product. The formation of propene during these conversions was proved by GC-analysis.
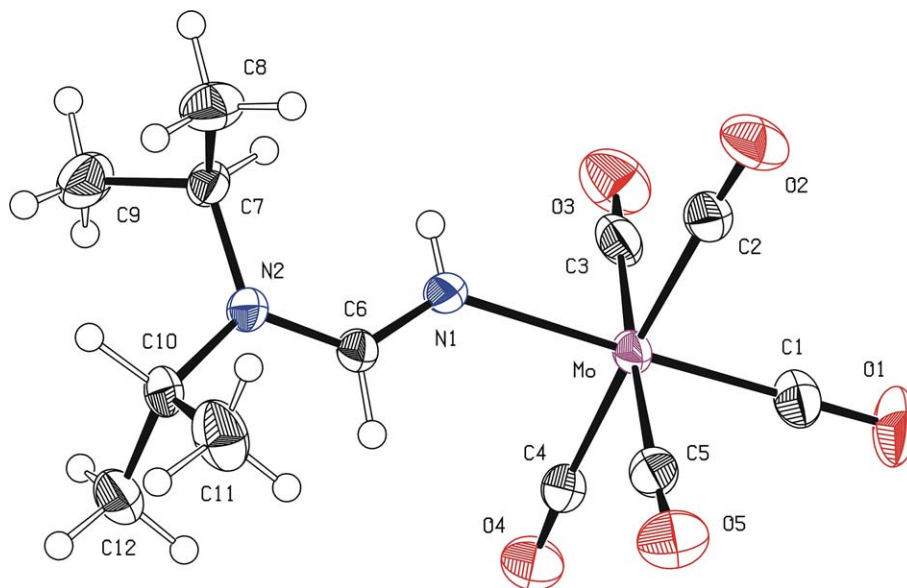
Fig. 4. ORTEP [34] style plot of compound **6b** in the solid state. Atomic displacement ellipsoids for non-H atoms are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (°): Mo–N1 2.252(2), Mo–C1 1.967(2), Mo–C3 2.037(2), Mo–C4 2.052(2), N1–C6 1.288(3), N2–C6 1.338(2), N2–C7 1.472(3), N2–C10 1.490(3); N1–Mo–C1 178.25(8), N1–Mo–C3 90.18(8), N1–Mo–C4 92.95(8), C1–Mo–C3 89.52(9), C2–Mo–C3 91.70(9), Mo–N1–C6 132.5(1), C7–N2–C10 118.7(2), N1–C6–N2 129.5(2).
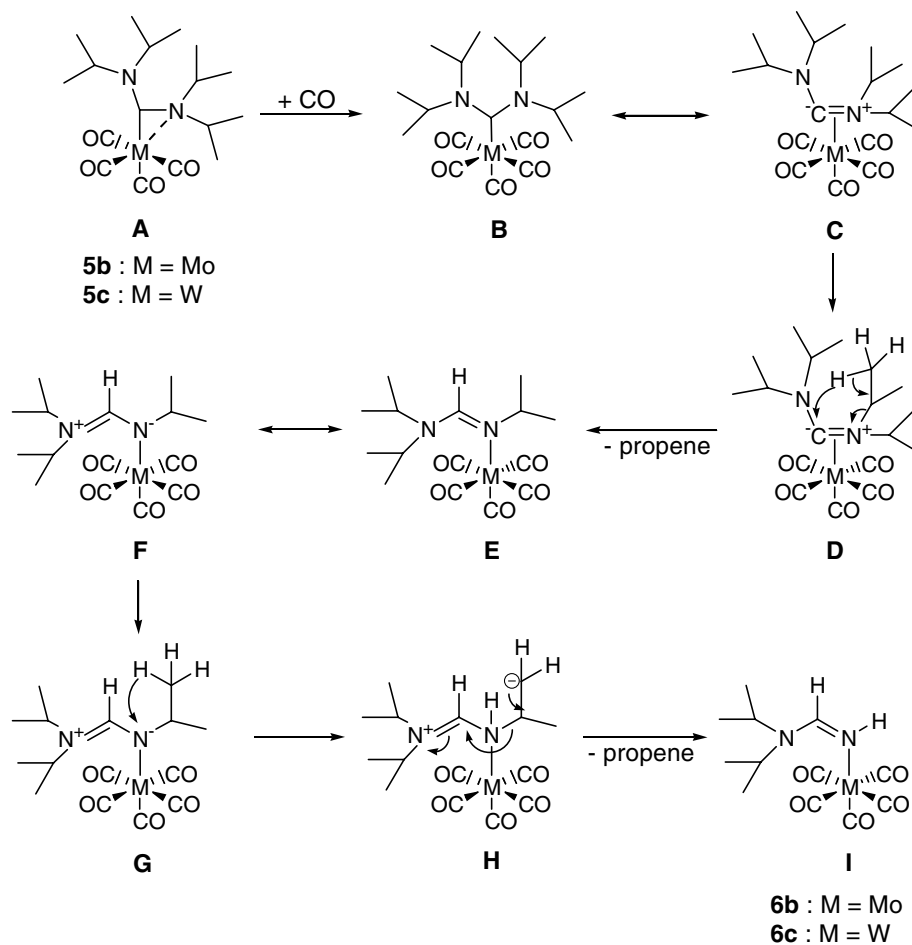
Scheme 3. Postulated mechanism for the formation of complexes **6b** and **6c**.
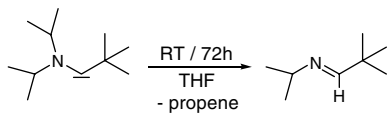
Scheme 4. Elimination of propene from an alkylamino carbene published by Bertrand.

Free carbenes may also react slowly with metal hexacarbonyls without previous photolytical activation [28,29]. In the case of the acyclic carbene **2a** (Scheme 5) only the imine complexes **6b** and **6c** could be obtained in low yields, in contrast to published experiments [23,25].

Yellow crystals of complex **6b**, suitable for a solid state X-ray diffraction study, were obtained by slow diffusion of *n*-pentane into a saturated THF solution (Fig. 4, Table 5).

The bond length N1–C6 (1.288(3) Å) is too long for a normal double bond and bond N2–C6 with 1.338(2) Å very short for a single bond. A hint for a sp^2-hybridisation at N2 and a π-delocalization over the planar backbone atoms C7, C10, N2, C6, N1 (max. deviation 0.03 Å) is the sum of the three angles (∼359.9°) spanned around the nitrogen atom N2, same as in the free carbene **2a** (∼359.7°) [13], instead of ∼320° for a nitrogen atom with optimal sp^3-hybridisation [30].

Elimination of propene from the carbene ligand should be suppressed if the nitrogen at the carbene center is involved in a rigid ring-system instead of bearing two independent alkyl groups. To realize this idea and to keep the same sterical bulkiness as in carbene **2a**, an acyclic carbene ligand with at least one 2,6-dimethylpiperidine group was synthesized [31]. The precursor diisopropyl(*cis*-2,6-dimethylpiperidin-1-ylmethylidene)ammonium dichlorophosphate (**3b**) was prepared in 36% yield analogous to the formamidinium salt **3a** [13], but without an additional

base. In contrast to the chloride salt **3a**, **3b** could be obtained as the dichlorophosphate salt (Scheme 6) [31].

The corresponding free carbene **2b** was prepared from **3b** according to the literature [13] (Scheme 7).

This acyclic carbene is stable against dimerisation, because of its bulky substituents at the nitrogens just as **2a** [15,32,33].

Crystals of **3b** suitable for X-ray diffraction were obtained from a concentrated THF solution (Fig. 5). Crystal data and details of the structure determination are presented in Table 5.

Compound **3b** crystallizes as an ionic pair in the space group $P2_1/n$. Cation and anion are bond together via a weak hydrogen bond C1–H11···O1. The N1–C1–N2 bond angle is in fact very similar to the bond angle reported for the *N,N,N′,N′*-tetraisopropylformamidinium chloride (133.2°) [13]. The bond lengths of N1–C1 and N2–C1 are with 1.318(2) and 1.325(2) Å nearly equal. Both nitrogen atoms in this salt are typically planar sp^2 configured. The torsion angles N1–C1–N2–C12 of −2.9(3)° and N2–C1–N1–C2 of 173.2(1)° suggest a widely delocalized π-system.

2.2. DFT-calculations

DFT calculations were performed for salt **3b** and the free carbene **2b** [35]. All calculations were performed using

Scheme 7. Preparation of the free carbene **2b**.
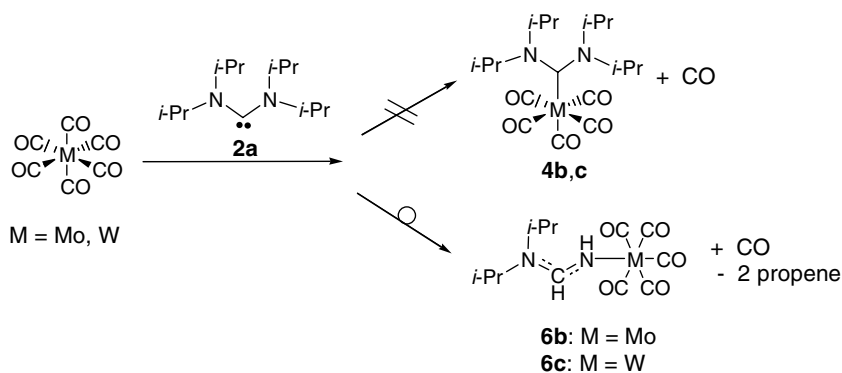
Scheme 5. Direct reaction of metalhexacarbonyls with a free diamino-carbene.

Scheme 6. Preparation of diisopropyl-(*cis*-2,6-dimethylpiperidin-1-ylmethylidene)ammoniumdichlorophosphate (**3b**).
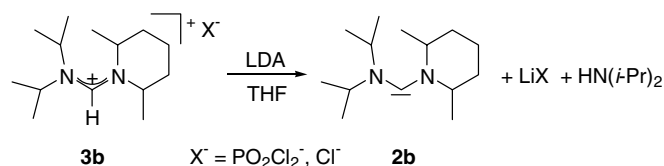
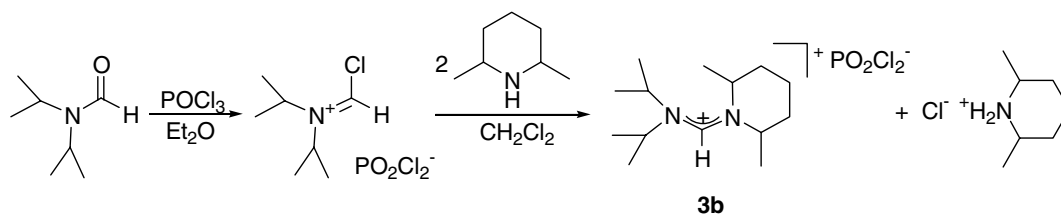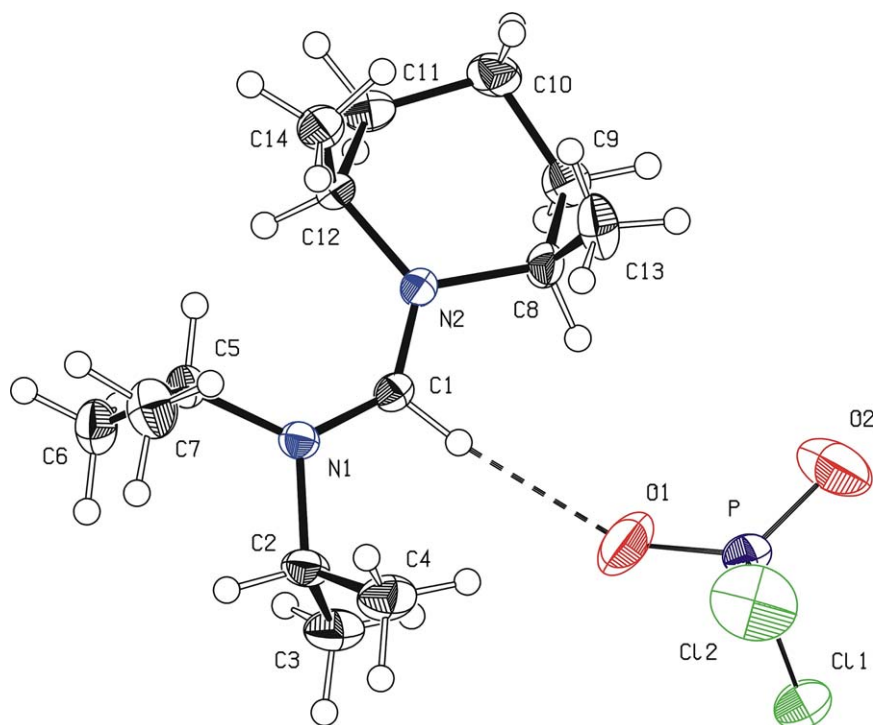Fig. 5. ORTEP [34] style plot of compound **3b** in the solid state. Atomic displacement ellipsoids for non-H atoms are drawn at the 50% probability level. Shown is the major part of the disordered PO_2Cl_2 anion (see Section 4.11). Selected bond lengths (Å), bond angles (°) and torsion angles (°): N1–C1 1.318(2), N1–C2 1.509(2), N1–C5 1.491(2), N2–C1 1.325(2), N2–C8 1.503(2), N2–C12 1.491(2); N1–C1–N2 133.3(1), C1–N1–C2 115.4(1), C1–N1–C5 129.1(1), C1–N2–C8 114.4(1), C1–N2–C12 125.3(1); N1–C1–N2–C12 −2.9(3), N2–C1–N1–C2 173.2(1). The hydrogen bond is characterized by C1–H11 0.96(2), O1···H11 2.35(2), C1···O1 3.292(2) and C1–H11···O1 166(1).

the GAUSSIAN03 program. Geometry optimizations and frequency calculations were performed with the DFT method using gradient corrected functionals according to Becke and for correlation, according to Lee et al. (B3LYP). For these calculations, the valence double-ζ basis set 6-31G(d) was used [36]. In Figs. 6 and 7 the optimized structures of **2b**, and **3b** are shown.

The calculated structure of salt **3b** correlates very well with the results of its X-ray analysis (Fig. 5) and previous published results in the literature [14,15] (see Table 1). The calculated structure of the free carbene **2b** is in agree-

ment with that of **2a** (Table 1). In the solid state structures of **3a** and **3b** no difference in the N1–C1–N2 angle was observed (Table 1). This agreement can be explained with nearly the same constitution of both salts. Also the C1–N bond distances in both salts are equal within esd's (1.316(3), 1.317(3) Å for **3a**; 1.318(2) Å and 1.325(2) Å for **3b**). In the free carbenes **2a** and **2b** a 12° smaller bond angle (N1–C1–N2) compared to the salts **3a** and **3b** was obtained [14].

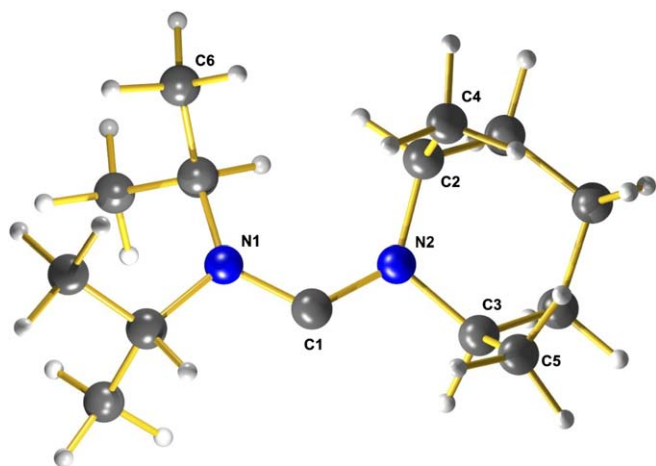The enlarged N1–C1–N2-angle of acyclic carbenes (circa 122°) compared to five-membered cyclic carbenes (circa
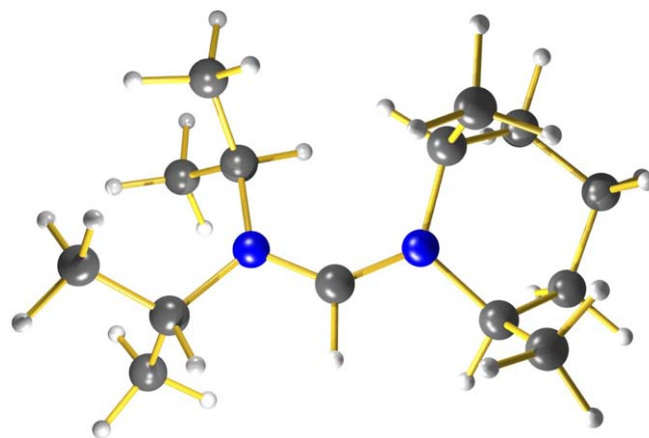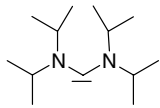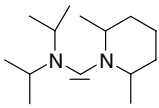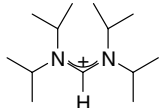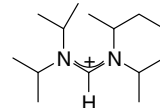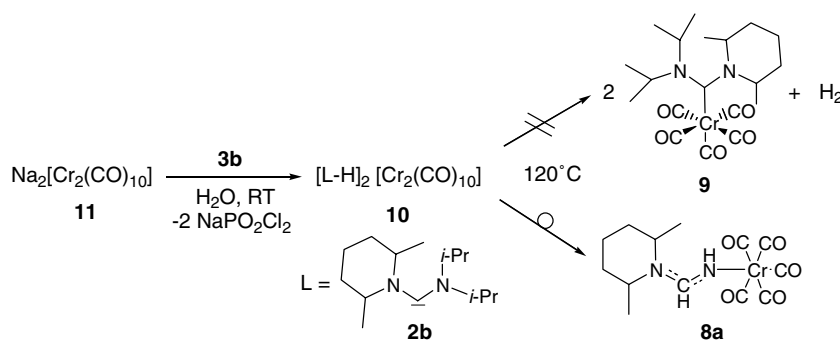

Fig. 6. DFT-optimized structure of **2b**.

Fig. 7. DFT-optimized structure of **3b**.

Table 1
Comparison of characteristic bond length and angles

Compound				
	2a [13]	**2b**	**3a** [14]	**3b**
Theo./*Exp*. N1–C1–N2 (°)	122.9/*121.0(5)*	123.2/–	132.7/*133.3(2)*	134.0/*133.3(1)*
Theo./*Exp*. N[*i*-Pr]₂–C1 (Å)	–/1.363(6) –/1.381(6)	1.359/– 1.362/– (ring)	–/1.316(3) –/1.317(3)	1.332/1.318(2) 1.329/*1.325(2)* (ring)

Scheme 8. Thermolysis of a bis(formamidinium)decacarbonyldichromium.

105°) has major consequences for the fundamental properties of these carbenes. The singlet–triplet (S–T) gap decreases sharply as the N–C–N angle increases, whereas the proton affinity (PA) increases. In consequence, the preparation of acyclic carbenes affords much stronger bases and the obtained carbenes are much more reactive as the cyclic carbenes [15].

The bis(dialkylamino)carbene ligand (**2a**) is mentioned in the literature with the biggest N1–C1–N2-angle (see Table 1), and with the largest chemical shift in the ¹³C NMR-spectroscopy for the carbene carbon with 255.5 ppm. The calculated N1–C1–N2-angle of carbene **2b** is larger than that of **2a** with the consequence of a higher proton affinity and reactivity of **2b**. In accordance with the larger N1–C1–N2-angle of carbene **2b** is its ¹³C-NMR shift of 258.9 ppm, the highest ever mentioned for acyclic diaminocarbenes.

2.3. Alternative synthesis of a complex with carbene (2b)

Pentacarbonyl NHC-complexes of Cr, Mo, and W can be prepared in good yields avoiding the use of free carbenes by reaction of dialkylazolium ions with anionic carbonyl-metalates [37]. We tried to apply this method also for the preparation of an acyclic diaminocarbene complex (**9**) (Scheme 8). The limiting factor for this method is the low acidity of the formamidinium cations, as well as the thermal instability of the desired carbene complexes.

When an aqueous solution of disodiumdecacarbonyldi-chromate (**11**) [Na₂Cr₂(CO)₁₀] at 0 °C was treated with the formamidinium salt **3b** or **3c**, a yellow precipitate of

10 was obtained. The azolium salt **3c** (diisopropyl(*cis*-2,6-dimethylpiperidin-1-ylmethylidene) hexafluorophosphate) was obtained by anion exchange of salt **3b** with NH₄PF₆. The product **10** was dried in high vacuum and heated in a Schlenk tube in vacuo to remove the decomposition products and Cr(CO)₆ by sublimation. However, from the residue only the imine-complex **8a** could be extracted in low yield. An analogous compound could not be generated from the η²-chromium carbene complex **5a** in contrast to the corresponding Mo-, and W-complexes **5b** and **5c**, which convert readily to the imine complexes **6b** and **6c**.

2.4. Spectroscopic results

In order to compare the σ-donor strength of the acyclic carbene ligand **2a** with that of NHC-ligands, the ν(CO)-stretching frequencies of their pentacarbonyl complexes (Fig. 8) have been considered (Table 2).
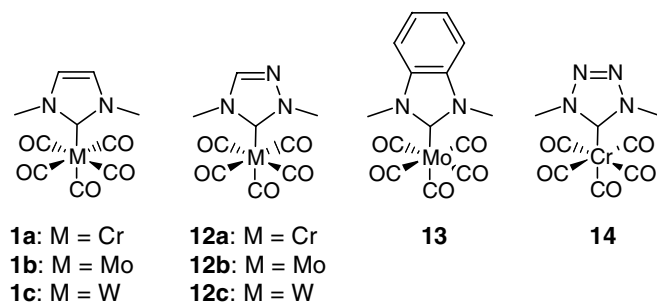

1a: M = Cr
1b: M = Mo
1c: M = W

12a: M = Cr
12b: M = Mo
12c: M = W

13

14

Fig. 8. In literature mentioned carbene substituted pentacarbonyl complexes.

Table 2
Comparison of the $v(CO)$-absorption frequencies of different carbene-pentacarbonyl complexes in THF

Metal	Complex	$A_1^{(2)}$ (cm^{-1})	E (cm^{-1})	$A_1^{(1)}$ (cm^{-1})
Cr	**4a**	2045.9	1923.4	–
	17 [23]	2050.2	1921.3	1899.9
	1a [28]	2056	1925	–
	12a [38]	2056	1923	–
	14 [39]	2063.5	1937.1	1907.5
Mo	**4b**	2057.8	1923.2	–
	1b [38]	2064	1930	1894
	12b [38]	2066	1931	1902
	13 [12]	2066	1934	–
W	**4c**	2056.2	1918.1	1892.3
	1c [28]	2062	1924	–
	12c [38]	2062	1919	–

Table 3
$v(CO)$-absorption frequencies of the imine-pentacarbonyl complexes in *n*-hexane

Metal	Complex	$A_1^{(2)}$ (cm^{-1})	E (cm^{-1})	$A_1^{(1)}$ (cm^{-1})
Cr	**8a**	2055.8	1933.3	1903.4
	15 [40]	2070	1936	1900
Mo	**6b**	2067.9	1932.9	1907.7
W	**6c**	2064.2	1927.8	1918.0

The $A_1^{(1)}$-frequencies of the carbonyl in *trans*-position to the carbene should show the biggest differences in IR-spectroscopy for different carbenes. In many cases the band of this frequency is hidden by the very strong E-band, and is not available for discussion. The complexes are ordered in Table 2 according to their diminishing σ-donor strength.

Table 2 indicates that the acyclic carbene **2a** is a stronger σ-donor than known NHC-ligands. The $A_1^{(2)}$-band in its complexes is at least eight wavenumbers smaller than in the imidazolinylidene complexes. This band is not so highly influenced by the donor ability of the carbene ligand such as the $A_1^{(1)}$-band.

In comparison of the received imine-pentacarbonyls in Table 3 with the carbene complexes shown in Table 2, the imine ligand shows a much weaker σ-donor ability than the carbene ligands, recognizable in the higher $A_1^{(1)}$-, and E-band, comparable to another nitrogen ligand in *N*-pyridinepentacarbonylchromium(0) (**15**) [40]. In this complex the frequency of the $A_1^{(1)}$-band is extremely high compared to the discussed complexes.

Table 4
$v(CO)$-absorption frequencies of the η²-carbene-tetracarbonyl complexes in diethyl ether

Complex	$v(CO)$ (cm^{-1})
5a [20]	2003.8, 1918.4, 1896.3, 1870.1
5b	2007.2, 1917.4, 1893.8, 1859.8
5c	2005.8, 1913.5, 1894.3, 1859.8

The IR-spectroscopic data of the η²-bonded carbene tetracarbonyl complexes of Mo, and W are in agreement with the corresponding Cr-complex [20] (see Table 4).

2.5. Preparation of a nido-Cr₃(CO)₁₀(OEt)₂ cluster

The free cyclic diamino carbene (**16**) [33], which in contrast to the carbenes **2a** and **2b** is stable against decomposition, does not coordinate η² to metal carbonyls due to its rigid N–C–N moiety.

Its η¹-complex **17** formed by reaction of photolytically produced (THF)Cr(CO)₅ with the free carbene **16** (Scheme 9) is highly unstable and decomposes to an indefinite product mixture. However, it could be stabilized by substitution of 2 carbonyls with isocyanide ligands [23].

If free carbene **16** reacts with photolytically generated [(diethyl ether)Cr(CO)₅] a red product insoluble in diethyl ether precipitates (Scheme 10). It can be recrystallized from acetone yielding dark brown crystal needles. Suitable crystals for X-ray diffraction were obtained overlaying a saturated acetone solution with diethyl ether at −20 °C. X-ray diffraction of these crystals showed the molecular structure of a completely novel chromium carbonyl complex **18**, consisting of a dianionic Cr₃(CO)₁₀(OEt)₂-cluster with two 1,3-diisopropyl-3,4,5,6-tetrahydropyrimidin-1-ium cations (Fig. 9, Table 5). This complex can be described as a *nido* tetrahedron. It may be formed by reductive cleavage of a coordinated diethyl ether by the free carbene under formation of the ethoxy-bridged structure **18**.

Compound **18** crystallizes in the orthorhombic space group *Pnma*. This structure consists of a scalene triangle of chromium atoms. Two edges of the triangle are bridged by carbon monoxide ligands. Two triply bridging ethoxy groups lie above and below the plane defined by the three chromium atoms. The anion and cations are well separated, and no unusually short interatomic contacts are observed. Through the middle of the triangle passes a mirror plane. The terminal chromium atoms are coordinated to three terminal carbon monoxides. The middle chromium has two terminal coordinated carbon monoxides. The terminal chromium atoms are bridged by μ₂-CO molecules to the third chromium. In this case the chromium atoms show a heptahedral coordination. The observed Cr–Cr distances (2.6589(9) Å) are compatible with the presence of Cr–Cr single bonds. Bond distances corresponding to Cr–Cr single bonds have been observed in several previously reported chromium carbonyl derivatives, for example:
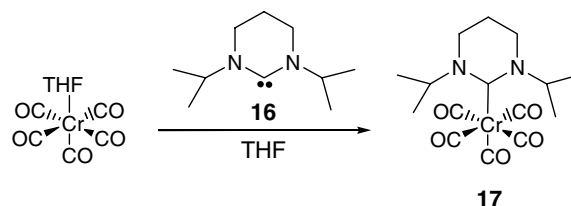
Scheme 9. Synthesis of the carbene substituted pentacarbonyl complex **17**.
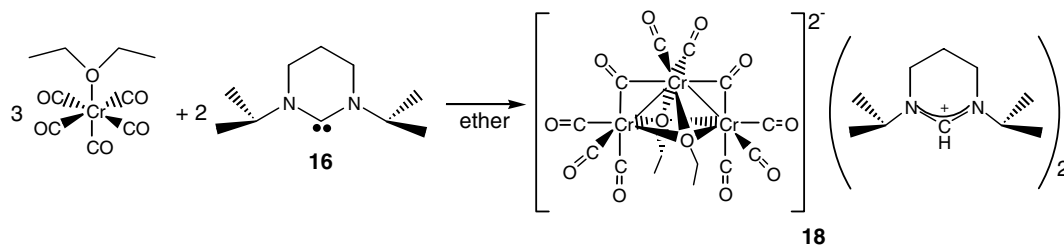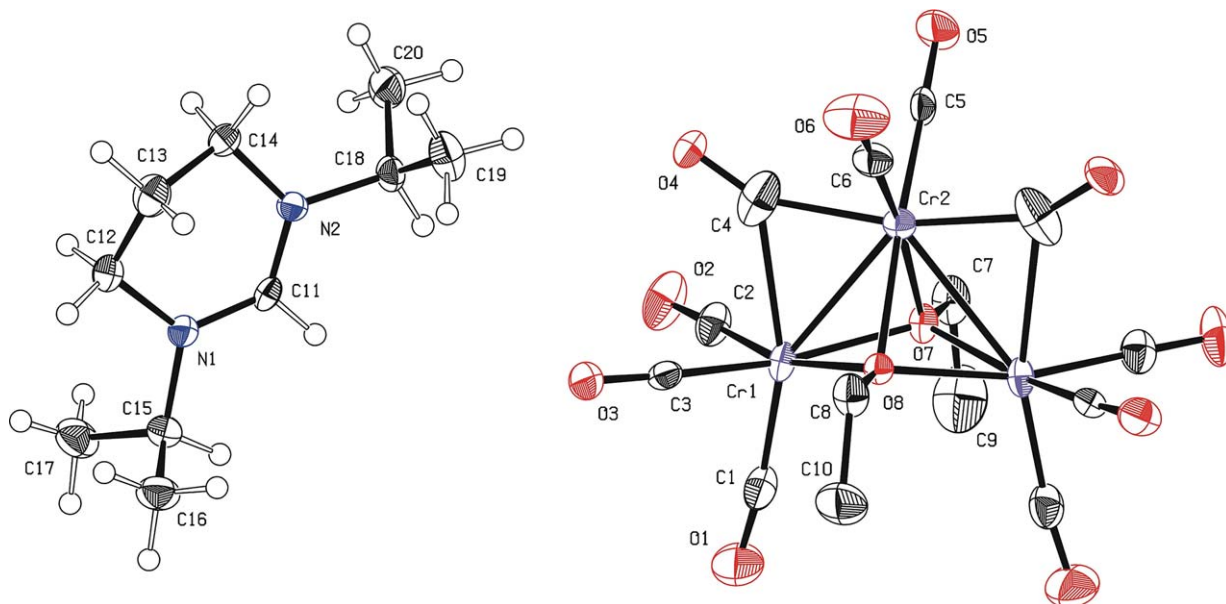
Scheme 10. Preparation of a Cr₃-carbonyl complex.

Fig. 9. ORTEP [34] style plots of the dianionic and cationic part of compound **18** · (C₃H₆O) in the solid state. Atomic displacement ellipsoids for non-H atoms are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (°): Cr1–Cr2 2.6589(9), Cr1···Cr1′ 3.3574(9), Cr1–O7 2.058(2), Cr1–O8 2.066(2), Cr1–C1 1.842(4), Cr1–C2 1.825(4), Cr1–C3 1.802(4), Cr1–C4 2.320(5), Cr2–O7 2.083(4), Cr2–O8 2.074(3), Cr2–C4 1.981(4), Cr2–C5 1.827(6), Cr2–C6 1.834(6), O7–C7 1.426(7), O8–C8 1.427(6), N1–C11 1.318(5), N1–C12 1.472(5), N1–C15 1.482(5), N2–C11 1.302(5), N2–C14 1.470(5), N2–C18 1.494(5); Cr1–Cr2–Cr1′ 78.30(3), Cr2–Cr1–O7 50.46(10), Cr2–Cr1–O8 50.17(9), O7–Cr1–O8 67.8(1), Cr1–Cr2–O7 49.63(5), Cr1–Cr2–O8 49.91(6), Cr1–O7–Cr1′ 109.3(2), Cr1–O7–Cr2 79.9(1), Cr1–O8–Cr1′ 108.7(2), Cr1–O8–Cr2 79.9(1), Cr1–C4–Cr2 75.9(2), N1–C11–N2 125.8(3), C11–N1–C12 119.8(3), C11–N1–C15 119.9(3), C11–N2–C14 120.5(3), C14–N2–C18 119.7(3). Symmetry operation to equivalent atom positions: x, 0.5 − y, z.

[PPN]₂[μ₂-CO₃(CO)₉Cr₃(μ₄-S)Cr(CO)₅] (2.850(9) Å) [41], [PPN]₂[(CO)₁₂Cr₃S] (∼2.840 Å) [42], [η⁵-C₅H₅Cr(CO)₂-P(OCH₃)₃]₂ (3.343(1) Å) [43], [η⁵-C₅H₅Cr(CO)₃]₂ (3.281(1) Å) [44], [η⁵-C₅Me₅Cr(CO)₃]₂ (3.311(1) Å) [45], Cr₂(CO)₈(μ-CO)₂ (2.677 Å) [46]. Clearly, the Cr–Cr distances in **18** fall within the range observed for Cr–Cr single bonds.

This interpretation also formally satisfies the 18-electron requirement of each chromium atom, where the μ₃-OC₂H₅ groups are normally considered to be a five-electron donor. Analogous complexes are the neutral manganese complexes Mn₃(CO)₉(μ-OC₂H₅)(μ₃-OC₂H₅)₂ and Mn₃(CO)₈(PMe₂Ph)(μ-OC₂H₅)(μ₃-OC₂H₅)₂ [47] and the tungsten complex [Me₄N]₃[W₃(CO)₉(μ-OC₂H₅)(μ₃-OC₂H₅)₂] [48]. The both latter complexes have essentially the same structural features as **18**. But these quite unsymmetrical molecules were formulated to contain only one metal–metal bond in contrast to the chromium complex.

The ¹³C NMR spectrum of complex **18** shows four CO-signals. Two signals for the six terminal-coordinated carbonyl groups at Cr¹, Cr¹′ (231.8 and 231.7 ppm), one signal for both two terminal CO ligands at Cr² (210.0 ppm), and one signal for the two μ-bridged ones (206.0 ppm). The two tetrahydropyrimidinium cations show no unexpected signals in the ¹³C NMR.

3. Conclusion

We present the synthesis of metastable η²-carbene-substituted pentacarbonylcomplexes of molybdenum and tungsten using the acyclic carbene bis(diisopropylamino)carbene. In contrast to the analogous stable η²-chromium complex the new complexes convert in a CO-atmosphere under elimination of propene to an imine species. To avoid this conversion the acyclic carbene ligand should have two cyclic amino groups to form a stable η²-species. The reaction of a 6-membered cyclic diaminocarbene with photolytically activated group 6-metalcarbonyls dependents on the used ether: while using THF the η¹-carbene complex (**17**) is formed; in diethyl ether a proton

Table 5
Crystallographic Data for **3b**, **5c**, **6b**, and **18** · (C$_3$H$_6$O)

	3b	**5c**	**6b**	**18** · (C$_3$H$_6$O)
Formula	C$_{14}$H$_{29}$Cl$_2$N$_2$O$_2$P	C$_{17}$H$_{28}$N$_2$O$_4$W	C$_{12}$H$_{16}$MoN$_2$O$_5$	C$_{37}$H$_{58}$Cr$_3$N$_4$O$_{13}$
F_w	359.26	508.25	364.21	922.87
Color/habit	Colorless/fragment	Orange/fragment	Yellow/fragment	Dark brown/needle
Crystal dimensions (mm^3)	0.36 × 0.41 × 0.61	0.46 × 0.51 × 0.51	0.13 × 0.25 × 0.33	0.08 × 0.15 × 0.76
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$Pnma$ (no. 62)
a (Å)	7.7567(1)	8.3062(1)	10.3169(1)	10.7228(1)
b (Å)	15.2084(2)	18.0840(2)	6.0477(1)	21.6801(2)
c (Å)	15.8115(2)	13.1936(1)	24.9984(2)	18.9619(2)
β (°)	93.8948(5)	95.8951(5)	89.9363(6)	90
V (Å^3)	1860.93(4)	1971.32(4)	1559.74(3)	4408.10(7)
Z	4	4	4	4
T (K)	173	123	123	123
D_{calc} (g cm^{-3})	1.282	1.713	1.551	1.391
μ (mm^{-1})	0.440	5.881	0.859	0.790
$F(000)$	768	1000	736	1936
θ Range (°)	1.86–25.35	1.92–25.38	2.56–25.33	1.88–22.72
Index ranges (h,k,l)	±9,±18,±19	±10,±21,±15	±12,±7,±30	±11,±23,±20
Number of reflections collected	43491	20759	31016	99297
Number of independent reflections/R_{int}	3416/0.042	3599/0.041	2851/0.033	3057/0.073
Number of observed reflections ($I > 2\sigma(I)$)	3022	3335	2607	2963
Number of data/restraints/parameters	3416/0/325	3599/0/330	2851/0/245	3057/0/296
R_1/wR_2 ($I > 2\sigma(I)$)[a]	0.0319/0.0771	0.0202/0.0481	0.0222/0.0481	0.0520/0.1081
R_1/wR_2 (all data)[a]	0.0380/0.0803	0.0232/0.0492	0.0256/0.0494	0.0544/0.1093
GOF (on F^2)[a]	1.039	1.102	1.053	1.307
Largest difference peak and hole (e Å^{-3})	+0.32/−0.23	+1.39/−1.03	+0.47/−0.44	+0.36/−0.50

[a] $R_1 = \sum(\|F_o\| - \|F_c\|)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; GOF $= \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

transfer from the ether substituted carbonyl to the carbene occurs and the anionic ethoxy-metalcarbonyl *nido* cluster (**18**) is formed.

4. Experimental

4.1. General comments

The free carbenes **2a** and **2b** [13,31], and the free carbene **16** [33] were prepared according to the literature. All experiments were carried out under dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under nitrogen. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a JEOL-JMX-GX 270 or 400 MHz spectrometer at room temperature and referenced to the residual ^{1}H and ^{13}C signals of the solvents or 85% H$_3$PO$_4$ as an external standard (^{31}P). NMR multiplicities are abbreviated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br., broad signal. Coupling constants J are given in Hz. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. Mass spectra were performed at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 spectrometer using the CI or FAB technique. IR spectra were recorded using a Jasco FT-IR 460 spectrometer. GC–MS spectra were measured on a Hewlett-Packard gas chromatograph GC 5890A equipped with a mass selective detector MS 5970B. Melting points were measured with a Büchi melting point apparatus system (Dr. Tottoli).

4.2. Diisopropyl(cis-2,6-dimethylpiperidin-1-ylmethylidene)ammonium dichlorophosphate (3b)

A solution of 3.2 ml (34.5 mmol) POCl$_3$ in 20 ml diethyl ether was added to a solution of 5 ml (34.5 mmol) diisopropylformamide dissolved in 50 ml diethyl ether. After stirring the combined solutions for 1 h at room temperature, the precipitate was collected by filtration. The residue was washed twice with 20 ml diethyl ether and dissolved in 30 ml dichloromethane. After cooling to −30 °C *cis*-2,6-dimethylpiperidine (4.6 ml, 34.2 mmol) was added and stirred for 45 min at 25 °C. To this solution 100 ml diethyl ether were added to precipitate a colorless crystalline product. The raw substance was extracted with acetone, and the product precipitated by adding diethyl ether to the acetone solution. The white hydroscopic product **2b** was dried in vacuo. Yield: 4.400 g (12.3 mmol, 36%). ^{1}H NMR (270 MHz, CDCl$_3$): δ = 8.06 (1H, s, NC*H*N), 4.34 (2H, s, C*H*(CH$_3$)$_2$), 4.11 (1H, br. s, NC*H*(CH$_3$)CH$_2$), 3.86 (1H, br. s, NC*H*(CH$_3$)CH$_2$), 1.88 (2H, m, CH(CH$_3$)C*H$_2$*CH$_2$), 1.69 (2H, d, $^3J_{HH}$ = 8.7 Hz, CH$_2$C*H$_2$*CH$_2$), 1.59 (2H, m), 1.45 (12H, d, $^3J_{HH}$ = 6.9 Hz, CH(C*H$_3$*)$_2$), 1.40 (6H, d, $^3J_{HH}$ = 6.2 Hz, NCH(C*H$_3$*)). ^{13}C\{^{1}H\} NMR (67.8 MHz, CDCl$_3$): δ = 154.4 (N*C*HN), 55.4 (*C*(CH$_3$)$_2$), 51.2 (N*C*HCH$_3$), 30.2 (C(HCH$_3$)*C*H$_2$CH$_2$), 22.9, 22.0, 12.5 (*C*H$_3$). MS (FAB) *m/z* (%): 225.2 (100, [M$^+$]), 181.2 (5), 112.1 (2, [((CH$_3$)$_2$CH)$_2$NC]). Anal. Calc. for C$_{14}$H$_{29}$N$_2$-PO$_2$Cl$_2$ (359.26): C, 46.80; H, 8.14; N, 7.80; P, 8.62; Cl, 19.74. Found: C, 46.91; H, 8.24; N, 7.76; P, 8.11; Cl, 19.71%.

4.3. Diisopropyl(cis-2,6-dimethylpiperidin-1-ylmethylidene)hexafluorophosphate (3c)

A solution of 163 mg (1.0 mmol) NH_4PF_6 in 5 ml water was added to a solution of 250 mg (0.7 mmol) diisopropyl(*cis*-2,6-dimethylpiperidin-1-ylmethylidene)ammonium dichlorophosphate (**3b**) in 5 ml water. A colorless product precipitated and was washed with 5 ml water and dried in vacuo. Yield: 252 mg (0.68 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.45$ (1H, s, NC*H*N), 4.13 (2H, t, $^3J_{HH} = 6.9$ Hz, C*H*(CH$_3$)$_2$), 4.11 (2H, br. s, NC*H*(CH$_3$)CH$_2$), 1.95 (2H, m, CH(CH$_3$)C*H*$_2$CH$_2$), 1.84 (2H, m), 1.70 (2H, d, $^3J_{HH} = 14.8$ Hz, CH$_2$C*H*$_2$CH$_2$), 1.45 (6H, d, $^3J_{HH} = 7.2$ Hz, CH(C*H*$_3$)$_2$), 1.39 (12H, d, $^3J_{HH} = 6.4$ Hz, NCH(C*H*$_3$)). ^{13}C{^{1}H} NMR (67.8 MHz, $CDCl_3$): $\delta = 153.0$ (N*C*HN), 54.5 (*C*H(CH$_3$)$_2$), 51.5 (N*C*HCH$_3$), 30.0 (C(HCH$_3$)*C*H$_2$CH$_2$), 21.9, 22.0, 12.5 (*C*H$_3$). ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$): $\delta = -143.7$ (sept., $J = 713$ Hz).

4.4. Diisopropylamine-cis-2,6-dimethyl-N-piperidylmethylidene (2b)

Yield: 189 mg (0.84 mmol, 63%). m.p. 37 °C. ^{1}H NMR (270 MHz, C_6D_6): $\delta = 4.22$ (2H, sept., $^3J_{HH} = 4.7$ Hz, C*H*(CH$_3$)$_2$), 3.73 (2H, br. s, NC*H*(CH$_3$)CH$_2$), 1.68 (4H, d, $^3J_{HH} = 5.9$ Hz), 1.36 (2H, m), 1.24 (12H, s, CH(C*H*$_3$)$_2$), 1.21 (6H, s, NCH(C*H*$_3$)). ^{13}C{^{1}H} NMR (67.8 MHz, C_6D_6): $\delta = 258.9$ (N*C*N), 56.2 (*C*(CH$_3$)$_2$), 49.3 (N*C*HCH$_3$), 31.8 (C(HCH$_3$)*C*H$_2$CH$_2$), 24.2, 23.0, 14.6 (*C*H$_3$).

4.5. General procedure for the preparation of complexes 4b and 4c

A solution of 1.55 mmol M(CO)$_6$, (M = Cr, Mo, W) in 150 ml THF was irradiated with a 150-W Hg high-pressure immerging lamp while stirring for 1 h at −15 °C, then 1 h at slowly rising temperature up to −5 °C. After switching off the lamp 2 mmol fresh sublimated carbene, dissolved in 30 ml THF, was transferred to the carbonyl solution with vigorous stirring. The solution darkened rapidly to orange. After stirring for 30 min the solvent was removed by a stream of carbon monoxide. The residue was dried for 1 h at 2×10^{-3} mbar. The products were extracted with *n*-hexane from the residue.

4.5.1. Pentacarbonyl[bis(diisopropylamino)carbene]-molybdenum(0) (4b)
IR (THF, cm^{-1}): $\nu = 2057.8$ (w, CO), 1923.2 (s, CO). The colorless compound rearranges to complex **5b** within 30 min.

4.5.2. Pentacarbonyl[bis(diisopropylamino)carbene]-tungsten(0) (4c)
^{1}H NMR (270 MHz, C_6D_6): $\delta = 2.86$ (4H, m, C*H*(CH$_3$)$_2$), 0.86 (24H, br. d, $^3J_{HH} = 5.2$ Hz, C*H*$_3$). IR (THF, cm^{-1}): $\nu = 2056.2$ (m, CO), 1918.1 (s, CO), 1892.3

(w, CO). The light yellow compound rearranges to complex **5b** within 1 h.

4.6. General procedure for the preparation of complexes 5b and 5c

The complexes **5b** and **5c** can be obtained from a *n*-hexane solution of complexes **4b**, respectively **4c** during 30–60 min at room temperature. The insoluble compounds **5b** and **5c** precipitate from the *n*-hexane solution.

4.6.1. Tetracarbonyl[bis(diisopropylamino)carbene]-molybdenum(0) (5b)
Yield: 163 mg (0.388 mmol, 25%) of yellow crystals soluble in diethyl ether. This yellow compound decomposes very easily under formation of complex **6b**. ^{1}H NMR (270 MHz, C_6D_6): $\delta = 4.68$ (2H, sept., $^3J_{HH} = 6.8$ Hz, C*H*(CH$_3$)$_2$), 2.86 (2H, sept., $^3J_{HH} = 7.0$ Hz, C*H*(CH$_3$)$_2$), 0.98 (12H, d, $^3J_{HH} = 6.8$ Hz, CH(C*H*$_3$)$_2$), 0.94 (12H, d, $^3J_{HH} = 7.2$ Hz, CH(C*H*$_3$)$_2$). IR (diethyl ether, cm^{-1}): $\nu = 2007.2$ (w, CO), 1917.4 (s, CO), 1893.8 (m, CO), 1859.8 (m, CO).

4.6.2. Tetracarbonyl[bis(diisopropylamino)carbene]-tungsten(0) (5c)
Yield: 265 mg (0.496 mmol, 32%) of orange crystals soluble in diethyl ether. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 4.73$ (2H, sept., $^3J_{HH} = 7.0$ Hz, C*H*(CH$_3$)$_2$), 2.82 (2H, sept., $^3J_{HH} = 7.0$ Hz, C*H*(CH$_3$)$_2$), 1.00 (12H, d, $^3J_{HH} = 7.2$ Hz, CH(C*H*$_3$)$_2$), 0.94 (12H, d, $^3J_{HH} = 7.2$ Hz, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (67.8 MHz, C_6D_6): $\delta = 220.7$ (N*C*N), 211.5 (*C*O), 199.7 (*C*O), 58.4 (N*C*HN), 56.1 (br., N*C*HN), 23.4 (*C*H$_3$), 22.4 (br., *C*H$_3$). IR (diethyl ether, cm^{-1}): $\nu = 2005.8$ (w, CO), 1913.5 (s, CO), 1894.3 (m, CO), 1859.8 (m, CO).

4.7. Pentacarbonyl[N-(C-diisopropylamin)imin]-molybdenum(0) (6b)

Compound **6b** could be obtained by bubbling a CO-stream through a solution of complex **4b** or **5b** in THF for 50 min. After removing the solvent in vacuo the yellow product was obtained by extraction of the residue with *n*-hexane. Yield: 255 mg (0.70 mmol, 42%). ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 7.08$ (1H, d, $^3J_{HH} = 19.6$ Hz, NC*H*N), 4.95 (1H, br. s, N*H*), 3.67 (2H, br. s, C*H*(CH$_3$)$_2$), 1.22 (12H, d, $^3J_{HH} = 6.9$ Hz, C*H*$_3$). ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.05$ (1H, d, $^3J_{HH} = 19.6$ Hz, NC*H*N), 4.89 (1H, br. d, $^3J_{HH} = 16.9$ Hz, N*H*), 3.64 (2H, sept., $^3J_{HH} = 6.8$ Hz, C*H*(CH$_3$)$_2$), 1.22 (12H, d, $^3J_{HH} = 6.8$ Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (67.8 MHz, $CDCl_3$): $\delta = 213.5$ (*trans*-CO), 204.7 (*cis*-CO), 157.6 (N*C*HN), 46.0 (N*C*H(CH$_3$)$_2$), 21.6 (*C*H$_3$). ^{1}H NMR (400 MHz, acetone-d_6): $\delta = 7.27$ (1H, d, $^3J_{HH} = 19.4$ Hz, NC*H*N), 5.93 (1H, br. d, $^3J_{HH} = 13.3$ Hz, N*H*), 3.89 (2H, br. s, C*H*(CH$_3$)$_2$), 1.20 (12H, d, $^3J_{HH} = 6.7$ Hz, C*H*$_3$). ^{13}C{^{1}H}NMR (100.5 MHz, acetone-d_6): $\delta = 213.9$ (*trans*-CO), 206.0 (*cis*-CO),

158.3 (N*C*HN), 45.9 (N*C*H(CH$_3$)$_2$), 29.6 (*C*H$_3$). ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 6.88$ (1H, d, $^3J_{HH} = 19.4$ Hz, NC*H*N), 4.95 (1H, br. d, $^3J_{HH} = 15.7$ Hz, N*H*), 2.55 (2H, br. s, C*H*(CH$_3$)$_2$), 0.42 (12H, d, $^3J_{HH} = 5.6$ Hz, C*H$_3$*). ^{13}C{^{1}H} NMR (100.5 MHz, C$_6$D$_6$): $\delta = 213.6$ (*trans*-CO), 205.2 (*cis*-CO), 157.4 (N*C*HN), 45.4 (N*C*H(CH$_3$)$_2$), 20.3 (*C*H$_3$). MS (FAB): *m/z* (%): 338.1 (4, [M$^+$ − CO]), 310.1 (4, [M$^+$ − (2 CO)]), 280.1 (1, [M$^+$ − (3 CO)]), 225.3 (100, [M$^+$ − (5 CO)]). *Anal.* Calc. for C$_{12}$H$_{16}$N$_2$O$_5$Mo (364.21): C, 39.57; H, 4.43; N, 7.69. Found: C, 39.59; H, 4.77; N, 7.70%. IR (*n*-hexane, cm^{-1}): $\nu = 2067.9$ (w, CO), 1932.9 (s, CO), 1908.8 (w, CO).

4.8. Pentacarbonyl[N-(C-diisopropylamine)imine]tungsten (0) (6c)

Complex **6c** was prepared analogous to complex **6b** from compound **4c** or **5c** in 48.1% (337 mg, 0.75 mmol) yield as an orange product. ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 8.13$ (1H, d, $^3J_{HH} = 13.2$ Hz, NC*H*N), 5.45 (1H, d, $^3J_{HH} = 13.2$ Hz, N*H*), 3.28 (2H, br., C*H*(CH$_3$)$_2$), 0.83 (12H, d, $^3J_{HH} = 6.4$ Hz, C*H$_3$*). ^{13}C{^{1}H} NMR (100.5 MHz, C$_6$D$_6$): $\delta = 216.9$ (*trans*-CO), 200.8 (*cis*-CO), 160.8 (N*C*HN), 43.8 (N*C*H(CH$_3$)$_2$), 22.5 (*C*H$_3$). IR (*n*-hexane, cm^{-1}): $\nu = 2064.2$ (w, CO), 1927.8 (s, CO), 1918.0 (w, CO).

4.9. Pentacarbonyl[N-(C-(cis-2,6-dimethyl-N-piperidyl)imine)]chromium(0) (8a)

To a solution of 0.5 g (1.16 mmol) Na$_2$Cr$_2$(CO)$_{10}$ in 15 ml H$_2$O, 1.0 g (2.78 mmol) of compound **3b** and 300 mg NaH$_2$PO$_4$ dissolved each in 10 ml H$_2$O are added at 0 °C. The yellow product was filtrated and dried in vacuo and heated in vacuo at 130 °C to obtain small amounts of a yellow product at a −80 °C cold sublimation finger. Yield: 15 mg. IR (*n*-hexane, cm^{-1}): $\nu = 2055.8$ (m, CO), 1933.3 (s, CO), 1903.4.

4.10. Compound 18

A solution of 1.55 mmol Cr(CO)$_6$ in 150 ml diethyl ether was irradiated with a 150-W Hg high-pressure immerging lamp while stirring for 1 h at −15 °C, then 1 h at slowly rising temperature up to −5 °C. After switching off the lamp 2 mmol fresh sublimated carbene **16**, dissolved in 30 ml diethyl ether, was transferred to the carbonyl solution with vigorous stirring. The solution darkened rapidly to red. A dark red precipitate occurs in the solution and was filtered, washed with 20 ml diethyl ether and dried for 4 h at 2×10^{-3} mbar. The product was recrystallized from an acetone/diethyl ether solution to obtain the product in 56% yield.

^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 8.14$ (2H, d, $^3J_{HH} = 13.2$ Hz, NC*H*N), 4.04 (4H, sept., C*H*(CH$_3$)$_2$), 3.60 (4H, br., OC*H$_2$*CH$_3$), 3.54 (8H, br. s, NC*H$_2$*), 2.18 (4H, br., C*H$_2$*), 1.60 (6H, t, $J = 6.8$ Hz, OCH$_2$C*H$_3$*), 1.37

(24H, br., C*H$_3$*). ^{1}H NMR (400 MHz, acetone-d_6): $\delta = 8.14$ (2H, br., NC*H*N), 4.04 (4H, sept., $J = 6.8$ Hz, C*H*(CH$_3$)$_2$), 3.62 (4H, br., OC*H$_2$*CH$_3$), 3.54 (8H, t, $J = 5.6$ Hz, NC*H$_2$*), 2.18 (4H, quin., $J = 5.2$ Hz, C*H$_2$*), 1.78 (6H, m, OCH$_2$C*H$_3$*), 1.35 (24H, d, $J = 6.4$ Hz, C*H$_3$*). ^{13}C{^{1}H} NMR (100.5 MHz, acetone-d_6): $\delta = 231.8$ (4 CO), 231.7 (2 CO), 210.0 (2 CO), 206.0 (μ-CO), 151.8 (N*C*HN), 69.2 (O*C*H$_2$), 57.8 (N*C*H(CH$_3$)$_2$), 40.1 (N*C*H$_2$), 21.3, 20.4, 20.0 (*C*H$_3$). IR (CH$_2$Cl$_2$, cm^{-1}): $\nu = 2979.5$ (s), 2936.1, 2879.2, 2030.7 (w, CO), 1936.2 (m), 1913.0, 1885.1 (s), 1677.8 (s). IR (KBr, cm^{-1}): $\nu = 2975$ (s), 2938, 2879, 2029 (w, CO), 1966, 1936 (m), 1910, 1877, 1704 (sh), 1678 (vs).

4.11. Single crystal X-ray structure determination of compounds 3b, 5c, 6b, and 18 · (C$_3$H$_6$O)

4.11.1. General

Crystal data and details of the structure determination are presented in Table 5. Suitable single-crystals for the X-ray diffraction study were grown with standard cooling techniques. Crystals were 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 (NONIUS, MACH3, κ-CCD) at the window of a rotating anode (NONIUS, FR591) and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained by full-matrix least-squares refinements during the scaling procedure. Data collection were performed at low temperatures (OXFORD CRYOSYSTEMS). Each crystal was measured with a couple of data sets in rotation scan modus with either $\Delta\varphi/\Delta\omega = 1.0°$ or 2.0°. Intensities were integrated and the raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure for latent decay and absorption effects. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err <0.002. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*. All calculations were performed on an Intel Pentium II PC with the STRUX-V system, including the programs PLATON, SIR92, SIR97, and SHELXL-97 [49]. *Specials*: **3b**: A disorder over two positions (0.896(3):0.104(3)) of the PO$_2$Cl$_2$ anion could be resolved clearly. All hydrogen positions could be located from difference Fourier syntheses and were allowed to refine freely. **5c**: All hydrogen positions could be located from difference Fourier syntheses and were allowed to refine freely. Small extinction effects were corrected with the SHELXL-97 procedure with $\varepsilon = 0.0060(2)$. **6b**: All hydrogen positions could be located from difference Fourier

syntheses and were allowed to refine freely. **18 · (C$_3$H$_6$O)**: All hydrogen atoms were placed in calculated positions and refined using a riding model, with C–H distances of (0.95, 0.98, 0.99, 1.00) Å and $U_{\text{iso(H)}} = 1.2 U_{\text{eq(C)}}$ or $1.5 U_{\text{eq(C)}}$.

5. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary Publication Nos. CCDC-296019 (**3b**), CCDC-296020 (**5c**), CCDC-296021 (**6b**), and CCDC-296022 [**18 · (C$_3$H$_6$O)**]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

References

[1] K. Öfele, J. Organomet. Chem. 12 (1968) P42.
[2] H.W. Wanzlick, H.J. Schönherr, Angew. Chem. 80 (1968) 154;
Angew. Chem. Int. Ed. Engl. 7 (1968) 141.
[3] (a) A.J. Arduengo III, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361;
(b) D.A. Dixon, A.J. Arduengo III, J. Phys. Chem. 95 (1991) 4180;
(c) A.J. Arduengo III, H.V.R. Dias, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 114 (1992) 5530.
[4] A.J. Arduengo III, H.V.R. Dias, J.C. Calabrese, F. Davidson, Organometallics 12 (1993) 3405.
[5] (a) M.F. Lappert, P.L. Pye, G.M. McLaughlin, J. Chem. Soc., Dalton Trans. (1977) 1272;
(b) M.F. Lappert, P.L. Pye, J. Chem. Soc., Dalton Trans. (1977) 1283;
(c) M.F. Lappert, P.L. Pye, J. Chem. Soc., Dalton Trans. (1977) 2172;
(d) B. Cetinkaya, P. Dixneuf, M.F. Lappert, J. Chem. Soc., Dalton Trans. (1974) 1827;
(e) M.F. Lappert, J. Organomet. Chem. 358 (1988) 185.
[6] (a) W.A. Herrmann, P.W. Roesky, M. Elison, G.R.J. Artus, K. Öfele, Organometallics 14 (1995) 1085;
(b) W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R.J. Artus, Angew. Chem. 107 (1995) 2602;
Angew. Chem. Int. Ed. Engl. 34 (1995) 2371;
(c) W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R.J. Artus, Chem. Eur. J. 2 (1996) 772.
[7] (a) For reviews see: W.A. Herrmann, C. Köcher, Angew. Chem. 109 (1997) 2256;
Angew. Chem. Int. Ed. Engl. 36 (1997) 2162;
(b) T. Weskamp, V.P.W. Böhm, W.A. Herrmann, J. Organomet. Chem. 600 (2000) 12;
(c) W.A. Herrmann, Angew. Chem. 114 (2002) 1343;
Angew. Chem. Int. Ed. Engl. 41 (2002) 1290;
(d) W.A. Herrmann, T. Weskamp, V.P.W. Böhm, Adv. Organometal. Chem. 48 (2002) 1;
(e) B. Cornils, W.A. Herrmann, J. Catal. 216 (2003) 23.
[8] K. Öfele, M. Herberhold, Angew. Chem. 82 (1970) 775;
Angew. Chem. Int. Ed. Engl. 9 (1970) 739.
[9] K. Öfele, C.G. Kreiter, Chem. Ber. 105 (1972) 529.
[10] K. Öfele, M. Herberhold, Z. Naturforsch. b 28 (1973) 306.
[11] C.G. Kreiter, K. Öfele, G. Wieser, Chem. Ber. 109 (1976) 1749.
[12] K. Öfele, E. Roos, M. Herberhold, Z. Naturforsch., B: Anorg. Chem., Org. Chem. B 31 (1976) 1070.
[13] R.W. Alder, P.R. Allen, M. Murray, A.G. Orpen, Angew. Chem. 108 (1996) 1211;
Angew. Chem. Int. Ed. Engl. 35 (1996) 1121.
[14] (a) R.W. Alder, M.E. Blake, S. Bufali, C.P. Butts, A.G. Orpen, J. Schütz, S.J. Williams, J. Chem. Soc., Perkin Trans. 1 (2001) 1586;
(b) R.W. Alder, M.E. Blake, L. Chaker, J.N. Harvey, F. Paolini, J. Schütz, Angew. Chem. 116 (2004) 6020;
Angew. Chem. Int. Ed. 43 (2004) 5896.
[15] D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand, Chem. Rev. 100 (2000) 39.
[16] (a) K. Denk, P. Sirsch, W.A. Herrmann, J. Organomet. Chem. 649 (2002) 219;
(b) W.A. Herrmann, K. Denk, German Patent DE 10148722 A1, 2003;
W.A. Herrmann, K. Denk, European Patent EP 1300410 A2, 2003.
[17] E.M. Badley, J. Chatt, R.L. Richards, G.A. Sim, J. Chem. Soc., Chem. Commun. (1968) 1322.
[18] J. Müller, K. Öfele, G. Krebs, J. Organomet. Chem. 82 (1974) 383.
[19] W. Petz, Angew. Chem. 87 (1975) 288;
Angew. Chem. Int. Ed. Engl. 14 (1975) 367.
[20] M. Tafipolsky, W. Scherer, K. Öfele, G. Artus, B. Pedersen, W.A. Herrmann, G.S. McGrady, J. Am. Chem. Soc. 124 (2002) 5865.
[21] (a) N. Merceron-Saffon, H. Gornitzka, A. Baceiredo, G. Bertrand, J. Organomet. Chem. 689 (2004) 1431;
(b) Y. Canac, S. Conejero, B. Donnadieu, W.W. Schoeller, G. Bertrand, J. Am. Chem. Soc. 127 (2005) 7312.
[22] M.-T. Lee, C.-H. Hu, Organometallics 23 (2004) 976.
[23] W.A. Herrmann, K. Öfele, D. von Preysing, E. Herdtweck, J. Organomet. Chem. 684 (2003) 235.
[24] W.A. Herrmann, D. von Preysing, G.D. Frey, K. Öfele, E. Herdtweck, in: Abstracts of Papers of the American Chemical Society National Meeting, vol. 229, INOR 598, 2004.
[25] K. Denk, Ph.D. Thesis, Technische Universität München, 2002, ISBN 3-934767-64-8.
[26] G.D. Frey, Ph.D. Thesis, Technische Universität München, 2005, ISBN 3-89963-186-2.
[27] N. Merceron, K. Miqueu, A. Baceiredo, G. Bertrand, J. Am. Chem. Soc. 124 (2002) 6806.
[28] (a) K. Öfele, W.A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, W. Scherer, J. Mink, J. Organomet. Chem. 459 (1993) 177;
(b) W.A. Herrmann, K. Öfele, M. Elison, F.E. Kühn, P.W. Roesky, J. Organomet. Chem. 480 (1994) C7.
[29] (a) W.A. Herrmann, L.J. Gooßen, C. Köcher, G.R.J. Artus, Angew. Chem. 108 (1996) 2980;
Angew. Chem. Int. Ed. Engl. 35 (1996) 2805;
(b) W.A. Herrmann, C. Köcher, L.J. Gooßen, G.R.J. Artus, Chem. Eur. J. 2 (1996) 1627.
[30] A.F. Holleman, E. Wiberg, Holleman-Wiberg – Lehrbuch der Anorganischen Chemie, 101 ed., Walter de Gruyter & Co., Berlin, New York, 1995.
[31] G.D. Frey, W.A. Herrmann, J. Organomet. Chem. 690 (2005) 5876.
[32] R.W. Alder, M.E. Blake, J.M. Oliva, J. Phys. Chem. A 103 (1999) 11200.
[33] R.W. Alder, M.E. Blake, J. Chem. Soc., Chem. Comm. (1997) 1513.
[34] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2001.
[35] We thank Dr. T. Bannenberg for the calculations of the DFT-structures.
[36] The calculations were carried out using the GAUSSIAN 03 program package at the B3LYP/6-31G*-optimized geometry for the ligands, using the B3LYP method, together with the 6-31G* basis C.T. Lee, W.T. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785;

Both structures were verified to be minima at the indicated point group by a subsequent frequency calculation. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN 03, Revision A.1, Gaussian, Inc., Pittsburgh, PA, 2003.

[37] K. Ackermann, P. Hofmann, F.H. Köhler, H. Kratzer, H. Krist, K. Öfele, H.R. Schmidt, Z. Naturforsch. 38B (1983) 1313.
[38] E. Roos, Ph.D. Thesis, Technische Universität München, 1976.
[39] G.D. Frey, K. Öfele, H.G. Krist, E. Herdtweck, W.A. Herrmann, Inorg. Chim. Acta 359, in press.
[40] R.E. Dessy, L. Wieczorek, J. Am. Chem. Soc. 91 (1969) 4963.
[41] M. Hoefler, K.-F. Tebbe, H. Veit, N.E. Weiler, J. Am. Chem. Soc. 105 (1983) 6338.
[42] D.J. Darensbourg, D.J. Zalewski, K.M. Sanchez, T. Delord, Inorg. Chem. 27 (1988) 821.
[43] L.-Y. Goh, M.J. D'Aniello, S. Slater, E.L. Muetterties, I. Tavanaiepour, M.I. Chang, M.F. Friedrich, V.W. Day, Inorg. Chem. 18 (1979) 192.
[44] R.D. Adams, D.E. Collins, F.A. Cotton, J. Am. Chem. Soc. 96 (1974) 749.
[45] (a) T.J. Jaeger, M.C. Baird, Organometallics 7 (1988) 2075;
(b) W.C. Watkins, T. Jaeger, C.E. Kidd, S. Fortier, M.C. Baird, G. Kiss, G.C. Roper, C.D. Hoff, J. Am. Chem. Soc. 114 (1992) 907.
[46] R.B. King, Y. Xie, H.F. Schaefer, N. Richardson, S. Li, Inorg. Chim. Acta 358 (2005) 1442.
[47] (a) E.W. Abel, G. Farrow, I.D.H. Towle, J. Chem. Soc., Dalton Tran. (1979) 71;
(b) E.W. Abel, I.D.H. Towle, S.T. Cameron, R.E. Cordes, J. Chem. Soc., Chem. Commun. (1977) 385.
[48] J.E. Ellis, G.L. Rochford, Organometallics 1 (1982) 682.
[49] (a) Data Collection Software for Nonius κ-CCD devices, Delft, The Netherlands, 2001;
(b) Z. Otwinowski, W. Minor, Meth Enzymol 276 (1997) 307ff;
(c) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. 27 (1994) 435–436;
(d) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, M.C. Burla, G. Polidori, M. Camalli, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115–119;
(e) A.J.C. Wilson (Ed.), International Tables for Crystallography, Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2, vol. C, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992;
(f) G.M. Sheldrick, SHELXL-97, Universität Göttingen, Göttingen, Germany, 1998.
[50] G.D. Frey, J. Schütz, W.A. Herrmann, J. Organomet. Chem. 691 (2006) in press, doi:10.1016/j.jorganchem.2006.01.018.