CHEMISTRY
A EUROPEAN JOURNAL

Spirocyclic Diaminocarbenes: Synthesis, Coordination Chemistry, and Investigation of Their Dimerization Behavior

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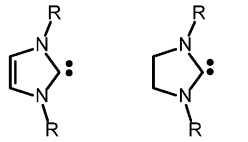
Abstract: Nonaromatic, "saturated", spirocyclic N-heterocyclic diaminocarbenes **11** can be obtained from spirocyclic imidazolidin-2-thiones **10** by reductive desulfurization with potassium. The unsymmetrically *N*,*N*′-substituted spirocyclic imidazolidin-2-thiones were obtained by reaction of ketimines **9** with lithium *N*-butyl-*N*-lithiomethyldithiocarbamate (**6**). ^{13}C NMR spectroscopy revealed that the unsymmetrically *N*,*N*′-substituted spirocyclic imidazolidin-2-ylidene **11a** undergoes a slow, acid-catalyzed dimerization to give the enetetramine **11a**=**11a**, which exists in two isomeric forms (*syn* and *anti*). This reaction is reversible under special circumstances. Carbenes of type **11** react with $[W(CO)_6]$ to yield air-stable carbene complexes of type $[W(\mathbf{11})(CO)_5]$ (**14**). The molecular structures of two derivatives **14a** and **14b** were established by X-ray crystallography and show clear distortion of the five-membered N-heterocyclic ring, caused by the spirocyclic molecular structure of the carbene ligands of type **11**.

Keywords: carbenes · dimerization · enetetramines · nitrogen heterocycles · tungsten

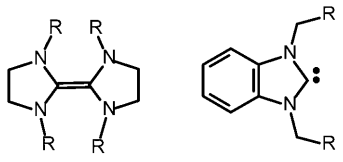
Introduction

The chemistry of N-heterocyclic carbenes has recently attracted much attention owing to the application of such ligands for the preparation of complexes with desirable properties in homogenous catalysis.[1] The characterization of the first stable N-heterocyclic carbene **1**[2] in 1991 and especially the preparation of the first stable nonaromatic ("saturated") N-heterocyclic carbenes of type **2**[3] in 1995 have initiated a renewed interest in the chemistry of stable carbenes.



1 **2**

Among others, this has also led to a reinvestigation of the diaminocarbene–enetetramine equilibrium for saturated carbenes of type **2**, which was postulated by Wanzlick about 40 years ago.[4] For carbenes of type **2**, the steric bulk of the *N*-alkyl or *N*-aryl substituents determines whether the carbene is stable as a monomer or if it dimerizes to an enetetramine of type **2**=**2**. Monomeric carbenes of type **2** are observed for bulky *N*-substituents like R = *t*Bu[5] or R = mesityl.[3] In contrast to this, less bulky *N*-substituted carbenes (R = Me, Et) dimerize at once.[5] Cross metathesis with symmetrically *N*,*N*′-substituted enetetramine of type **2**=**2** seemed to have proven convincingly that Wanzlick's equilibrium does not exist in the absence of catalysts.[6]



2=2 **3**

However, the existence of an equilibrium between the monomeric carbene and its dimeric dibenzotetraazafulvalene has been demonstrated for benzannulated carbenes of type **3**.[7] The dimerization behavior of these carbenes is again controlled by the steric bulk of the *N*-substituents.[7b]

In general, symmetrically substituted, saturated imidazolidin-2-ylidenes exist, depending of the steric bulk of the *N*,*N*′-substituents, either as monomeric carbenes **2** or as ene-

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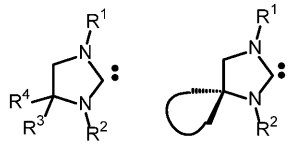
DOI: 10.1002/chem.200500306

tetramines **2**⇌**2**, and no equilibrium between these species has been reported.[8] In this situation we developed a synthetic pathway leading to unsymmetrically *N*,*N*′-substituted carbenes *rac*-**4**.[9] The two different *N* substituents allow the

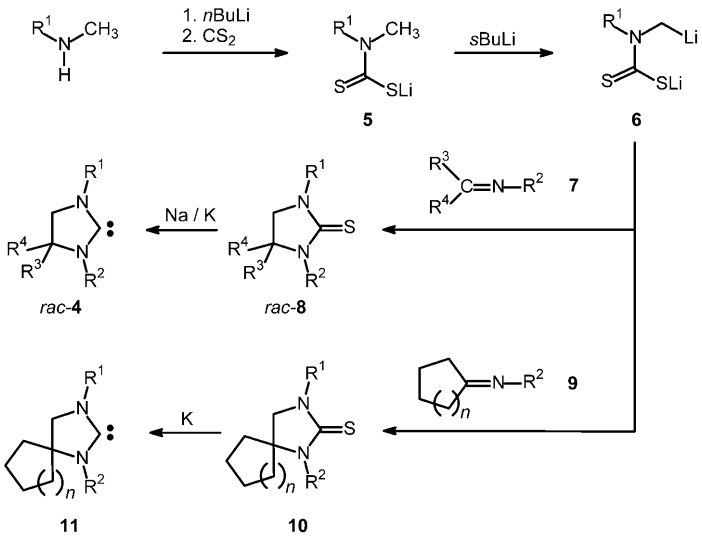


rac-**4** **11**

introduction of minute changes in the steric bulk and it was hoped, that an equilibrium between the monomeric carbene and its dimeric enetetramine could be observed for a certain set of *N*,*N*′ substituents. However, carbenes of type *rac*-**4** can only be obtained as a racemic mixtures. To overcome this problem we developed a synthesis for spirocyclic carbenes of type **11**, which contain no chiral carbon atoms. We report here on the preparation of carbenes of type **11** and on their coordination chemistry and dimerization behavior.

Results and Discussion

We have reported on a simple access to unsymmetrically substituted, saturated N-heterocyclic carbenes of type *rac*-**4**.[9] This synthesis (Scheme 1) proceeds via a racemic mixture of 4-substituted imidazolidin-2-thiones *rac*-**8** obtained from secondary amines and aldimines **7**. In the final reaction step the thiones were reductively desulfurized with a sodium/potassium alloy to give racemic mixtures of the unsymmetrically *N*,*N*′-substituted carbenes *rac*-**4**.



rac-**4a**, *rac*-**8a**: R^1 = *n*Bu, R^2 = *t*Bu, R^3 = *i*Pr, R^4 = H
rac-**4b**, *rac*-**8b**: R^1 = *n*Bu, R^2 = *i*Pr, R^3 = Et, R^4 = H
9a, **10a**, **11a**: *n* = 2, R^1 = *n*Bu, R^2 = *i*Pr
9b, **10b**, **11b**: *n* = 1, R^1 = *n*Bu, R^2 = *i*Bu

Scheme 1. Preparation of carbenes *rac*-**4** and spirocyclic carbenes **11**.

Our further studies were focused on the dimerization behavior of this type of N-heterocyclic carbene. Unfortunately, ^{1}H NMR spectra reveal complicated sets of resonance signals due to several proton couplings involving the N-heterocyclic ring and the substituents. Overlapping sets of signals therefore rendered ^{1}H NMR spectroscopy unsuitable for an investigation of the carbene–enetetramine equilibrium. ^{13}C NMR spectroscopy of less bulky substituted carbenes of type *rac*-**4** indicates slow dimerization of the imidazolidin-2-ylidenes in [D_8]THF under dry argon. For the unsymmetrically substituted carbene *rac*-**4a**, bearing at least one *N*-*tert*-butyl group, ^{13}C NMR spectroscopy proves the existence of a stable monomeric carbene (δ(C2) ≈ 240 ppm), which shows no tendency to dimerize.[9] Decreasing the steric demand of the bulky *N*-substituent from *tert*-butyl in *rac*-**4a** to isopropyl allows a slow dimerization of the resulting carbene *rac*-**4b** in [D_8]THF over weeks to give the corresponding olefin. Dimeric **4b**⇌**4b** exhibits several sets of signals in the ^{13}C NMR spectrum for the enantiomers and *syn* and *anti* isomers in the range of δ(C2) ≈ 126–129 ppm. To reduce the number of stereoisomers we extended the scope of the carbene synthesis to prepare spirocyclic unsymmetrically *N*,*N*′-substituted imidazolidin-2-ylidenes **11** (Scheme 1). Dimerization products of these carbenes can only exist as *syn* and *anti* isomers.

Synthesis of spirocyclic unsymmetrically *N*,*N*′-substituted imidazolidin-2-ylidenes (11): The preparation of carbenes of type **11** starts from lithium *N*-butyl-*N*-lithiomethyldithiocarbamate **6** and ketimines **9** (Scheme 1). The ketimines are synthesized by the proton-catalyzed reaction of cyclic ketones and primary amines to give **9** in isolated yields of about 80% after distillation.[10] Spirocyclic thiones **10a** and **10b** are prepared according to Ahlbrecht's one-pot procedure from **6** and ketimines **9a** or **9b**.[11] In a typical procedure *N*-butylmethylamine is deprotonated with *n*BuLi. After the addition of CS_2 the lithiumdithiocarbamate **5** is obtained, which is then converted into the strongly nucleophilic lithium *N*-lithiomethyldithiocarbamate **6** by a second deprotonation with *sec*-butyllithium. Compound **6** reacts even with less electrophilic ketimines of type **9** to give the spirocyclic thiones **10**. After purification by chromatography, thiones **10** are reductively desulfurized with potassium in refluxing THF[7c,12] giving carbenes **11** in yields of 80–90%.

We have determined the molecular structure of thione **10a** by X-ray diffraction (Figure 1).[13] Crystals of **10a** were obtained from a saturated solution of the thione in hexane upon storage at room temperature. The bond parameters for **10a** (Table 1) fall in the range described previously for equivalent parameters in benzimidazol-2-thiones.[14] The difference in steric bulk of the *N*,*N*′-substituents manifests itself in two different S-C1-N angles (S-C1-N1 123.8(2)°, S-C1-N2 127.3(2)°).

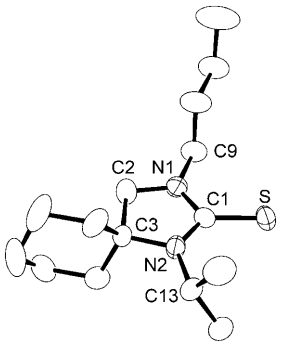


Figure 1. Molecular structure of thione **10a** with the crystallographic numbering scheme.

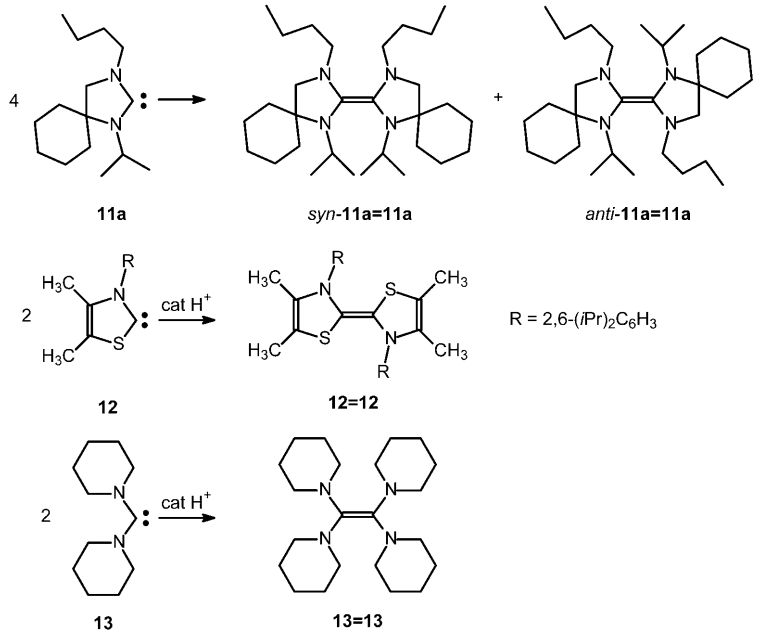
Table 1. Selected bond lengths [Å] and angles [°] for compounds **10a**, **14a**, and **14b**.

	10a	**14a**	**14b**
W(S)–C1	1.678(2)	2.295(2)	2.285(2)
W–CO_{cis}	–	2.028(2)–2.045(3)	2.020(3)–2.045(3)
W–CO_{trans}	–	2.005(3)	2.000(3)
N1–C1	1.351(3)	1.357(3)	1.349(3)
N1–C2	1.430(3)	1.463(3)	1.463(3)
N1–C9(C8)	1.452(3)	1.457(3)	1.457(3)
N2–C1	1.343(3)	1.351(3)	1.359(3)
N2–C3	1.488(3)	1.502(3)	1.487(3)
N2–C13(C12)	1.475(3)	1.476(3)	1.456(3)
C2–C3	1.533(3)	1.526(3)	1.516(4)
W(S)-C1-N1	123.8(2)	124.8(2)	124.9(2)
W(S)-C1-N2	127.3(2)	127.9(2)	128.1(2)
N1-C1-N2	108.9(2)	107.2(2)	106.3(2)
C1-N1-C2	112.6(2)	111.4(2)	112.1(2)
C1-N1-C9(C8)	125.4(2)	126.8(2)	129.3(2)
C2-N1-C9(C8)	121.9(2)	117.8(2)	117.6(2)
C1-N2-C3	112.2(2)	112.1(2)	111.7(2)
C1-N2-C13(C12)	127.1(2)	122.8(2)	127.0(2)
C3-N2-C13(C12)	120.7(2)	125.1(2)	120.2(2)
N1-C2-C3	104.6(2)	102.1(2)	101.9(2)
N2-C3-C2	101.3(2)	99.4(2)	99.2(2)

Dimerization behavior of the spirocyclic unsymmetrically *N,N′*-substituted diaminocarbene 11a: A ^{13}C NMR spectrum of **11a** in [D_8]THF recorded immediately after preparation of the carbene clearly indicates the presence of the imidazolidin-2-ylidene (δ(C2) = 236.0 ppm). No signals due to the presence of the dimeric enetetramine **11a**=**11a** were observed. However, storage of **11a** under dry argon for several weeks leads to the slow, but complete conversion of **11a** into the electron-rich olefin **11a**=**11a**. Due to the formation of *syn* and *anti* isomers of **11a**=**11a** (Scheme 2), two resonance signals with different intensities were detected (δ(C2) = 130.0 ppm and 128.6 ppm). Removal of the solvent and heating of olefin **11a**=**11a** under dry argon (130 °C, 16 h) leads to partial reformation of the carbene **11a**, which coexists with the olefin **11a**=**11a** as indicated by ^{13}C NMR spectroscopy.

The dimerization of different types of N-heteroyclic carbenes has been reported previously. Arduengo et al. isolated the thiazol-2-ylidene **12**, which is stable as a monomer in the absence of a protic catalyst (Brønsted or Lewis acid).[15] Addition of a small amount of the corresponding thiazolium salt as a catalyst leads to the formation of the dimeric derivative **12**=**12** (Scheme 2). Alder et al. prepared the bis(*N*-piperidyl)-carbene **13**, which undergoes an extraordinary slow dimerization to the olefin **13**=**13**.[16a] The dimerization can be initiated by the protonated carbene **13H$^+$** and is first-order with respect to the carbene.[16b]

In both cases the dissociation of the olefin back to the carbene was not clearly observed. Precisely this reversible dissociation of electron-rich olefins **2**=**2** was proposed by Wanzlick more than 40 years ago.[4] However, this proposal was rejected based on the absence of cross metathesis products when different, symmetrically *N,N′*-substituted olefins were heated together.[6] The diaminocarbene–enetetramine equilibrium postulated by Wanzlick is unequivocally established if both the carbene and the corresponding enetetramine are detected together in the absence of protic or electrophilic catalysts in solution. Denk et al. observed the rapid formation of mixed olefins in metathesis experiments starting from olefins of type **2**=**2** by NMR spectroscopy.[17] However, these experiments, as the authors noticed, do not conclusively establish the existence of the Wanzlick equilibrium, because the formation of mixed enetetramines could also be rationalized by a [2+2] cycloaddition/[2+2] cycloreversion



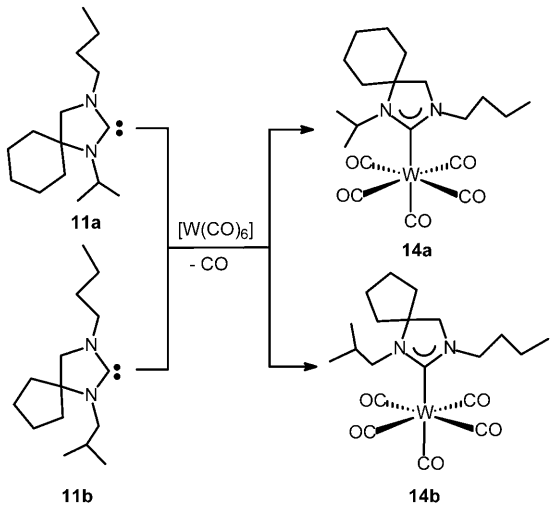
Scheme 2. Dimerization of diaminocarbenes.

reaction mechanism. The equilibrium between carbene and olefin at room temperature was established for benzannulated carbenes **3** (R = *i*Bu),[7b] which have spectroscopic and structural properties typical for saturated carbenes of type **2**.[7c] Potassium hydride was added to the mixture to exclude the presence of protons as a catalyst for the formation of the equilibrium.

To establish the type of equilibrium between carbenes **11** and their dimeric enetetramines **11**=**11**, the dimerization reaction was studied under rigorous exclusion of protic catalysts in solution. For this experiment a 2.5 M solution of the carbene **11a** in [D_8]THF was stored over sodium/potassium alloy under argon. Under these conditions no dimerization of **11a** to give enetetramine **11a**=**11a** was observed over weeks at room temperature. These experiments indicate that a protic catalyst is necessary to initiate the dimerization process of N-heterocyclic carbenes of type **2**. Our findings are identical to those of Alder et al., who found that the attack of the acyclic carbene **13** by the protonated carbene **13H$^+$** initiates the dimerization process, finally leading to the enetetramine **13**=**13**.[16] A review summarizing these findings on the dimerization behavior of N-heterocyclic carbenes has recently appeared.[8]

Coordination chemistry of spirocyclic diaminocarbenes: To get structural information about the carbene ligands **11a** and **11b**, these spirocyclic carbene ligands were coordinated to a $W(CO)_5$ unit to give the air-stable complexes **14a** and **14b**, respectively (Scheme 3). Complexes of type **14** were obtained by heating carbenes **11** with an equimolar amount of [$W(CO)_6$] in toluene under reflux for 2 h. The molecular structures of **14a** and **14b** were determined by X-ray diffraction.[13] Both **14a** and **14b** contain a tungsten atom surrounded in an octahedral fashion by five CO and one carbene ligand (Figure 2). Selected bond lengths and angles for **14a** and **14b** are summarized in Table 1.

To accommodate the steric requirements of the *N2*-substituents the W-C1-N2 angles (127.9(2)° for **14a** and



Scheme 3. Preparation of carbene complexes **14a** and **14b**.

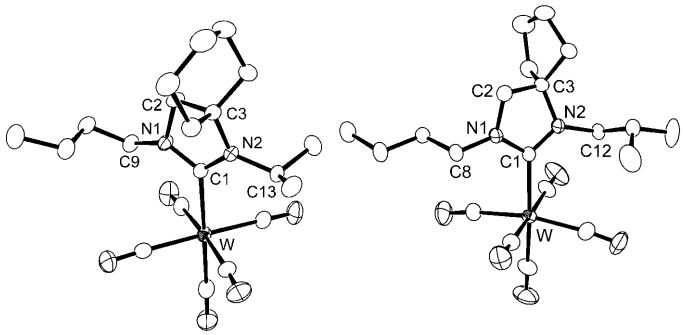


Figure 2. Molecular structures of complexes **14a** (left) and **14b** (right) with the crystallographic numbering scheme. Hydrogen atoms have been omitted for clarity.

128.1(2)° for **14b**) are slightly larger than the W-C1-N1 angles (124.8(2)° for **14a** and 124.9(2)° for **14b**). A similar observation was made for complexes with the unsymmetrically substituted N-heterocyclic carbenes of type *rac*-**4**.[9] The carbene ligand acts as a strong σ donor and leads to a shortening of the $W-CO_{trans}$ bond compared to the $W-CO_{cis}$ bonds in both complexes (Table 1).

The W–C1 bond lengths in **14a** (2.295(2) Å) and **14b** (2.285(2) Å) compare well to equivalent parameters in tungsten complexes with benzannulated N-heterocyclic carbene ligands.[7c,18] The steric demand of the cyclohexyl ring (**14a**) and the cyclopentyl ring (**14b**) lead to a distortion of the angles at the spirocyclic carbon atom C3.

Conclusion

We have prepared a novel type of N-heterocyclic carbene **11** with a spirocyclic molecular structure. These carbene ligands are easily accessible in a two-step reaction sequence starting from ketimines and secondary amines. We have demonstrated the slow dimerization of **11a** to **11a**=**11a** in [D_8]THF and the coexistence of both carbene and corresponding enetetramine over several weeks in solution. Under special circumstances the dimerization is reversible and the cleavage of the enetetramine giving the monomeric carbene is observed. This reversible reaction was once postulated by Wanzlick for carbenes of type **2** in the absence of electrophilic catalysts.[4] We found that even the dimerization of the monomeric carbene requires acid catalysis. Under rigorous exclusion of protic catalysts we observed no dimerization of carbene **11a**. In addition, carbene complexes [W(**11**)$(CO)_5$] have been prepared and structurally characterized. The molecular structures reveal the strong σ-donating properties of carbene ligands **11** and a distortion of the five-membered N-heterocyclic ring owing to the spirocyclic carbon atom.

Experimental Section

General: All operations were carried out in an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by stan-

dard methods and freshly distilled prior to use. NMR spectra were recorded on Bruker AC 200 (200 MHz) or Bruker AMX 400 (400 MHz) spectrometers and are reported relative to TMS as an internal standard. IR spectra were recorded on a Bruker Vector 22 infrared spectrometer. Mass spectra (EI) were measured on a Varian MAT 212 instrument. Correct elemental analyses (C, H, N) were obtained for all compounds using a Vario EL III elemental analyzer at the Westfälische Wilhelms-Universität Münster .

***N*-(Cyclohexylidene)isopropylamine (9a)**: This compound was prepared as reported.[10] ^{1}H and ^{13}C NMR data for **9a** match those reported there.

***N*-(Cyclopentylidene)isobutylamine (9b)**: Cyclopentanone (8.41 g, 0.1 mol) and isobutylamine (10.97 g, 0.15 mol) were combined while stirring at 0 °C. Concentrated HCl (0.05 g) was added dropwise under formation of some white smoke. After a short while the resulting solution became clear again and was stirred for 16 h at ambient temperature under an argon atmosphere. Subsequently solid NaOH (2.0 g) was added and the reaction mixture was stirred for an additional 2 h. The aqueous phase was removed, fresh NaOH (0.5 g) was added to the organic layer and the mixture was distilled (45–47 °C, 1.0 mbar) giving pure **9b** (11.14 g, 80 %) as colorless liquid. ^{1}H, ^{13}C NMR and IR data for **9b** were in agreement with those previously reported using a different synthesis.[19]

1-Butyl-3-isopropyl-1,3-diazaspiro[4.5]decane-2-thione (10a): This compound was prepared according to the method described by Ahlbrecht et al.[11] However, the crude reaction product was not distilled, but purified by column chromatography (SiO_2, hexane/EtOAc, 10:1, v/v) to give **10a** as a yellow solid. Yield: 45 %. ^{1}H and ^{13}C NMR data match those reported.[11] MS (70 eV, EI): *m*/*z* (%): 268 (63) $[M]^+$, 253 (11) $[M-CH_3]^+$.

1-Butyl-3-isobutyl-1,3-diazaspiro[4.4]nonane-2-thione (10b): A solution of *N*-butylmethylamine (0.872 g, 10.0 mmol) in THF (15 mL) was treated at 0 °C with *n*BuLi (2.5 M in hexane, 4.2 mL, 10.5 mmol). The reaction mixture was allowed to warm to room temperature, was stirred at this temperature for 30 min, and was subsequently again cooled to 0 °C. CS_2 (0.761 g, 10.0 mmol) was added, and the mixture was stirred for 30 min at 0 °C and then cooled to −78 °C. At this temperature *s*BuLi (1.3 M in pentane, 8.1 mL, 10.5 mmol) was added dropwise. The resulting yellow suspension of **6** was stirred at −25(±5) °C for 4 h. The reaction mixture was again cooled to −78 °C and ketimine **9b** (1.393 g, 10.0 mmol) was added. The resulting solution was stirred at −10(±5) °C for 2 h. Subsequently the reaction mixture was allowed to warm up to 0 °C and water (20 mL) was added. The aqueous phase was separated and the organic phase was washed with a saturated aqueous solution of NaCl (2×10 mL). The combined aqueous phases were extracted with diethyl ether (3×10 mL). The combined organic phases were dried over $MgSO_4$. After filtration, the solvent was removed in vacuo, and the residue was purified by column chromatography (SiO_2, hexane/EtOAc, 10:1, v/v) to give **10b** as a yellow solid (1.074 g, 40 %). ^{1}H NMR (200.1 MHz, $CDCl_3$): $\delta = 0.84$ (t, J = 7.2 Hz, 3H; CH_2CH_3), 1.15–1.68 (m, 18H; $CH(CH_3)_2$, $NCH_2CH_2CH_2CH_3$, $(CH_2)_4$ ring), 2.22 (m, 1H; $CH(CH_3)_2$), 3.09 (d, J = 7.4 Hz, 2H; $NCH_2CH(CH_3)_2$), 3.17 (s, 2H; NCH_2C_{spiro}), 3.52 ppm (t, J = 7.4 Hz, 2H; $NCH_2CH_2CH_2CH_3$); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 13.6$, 19.6 (CH_2CH_3, $CH(CH_3)_2$), 20.0, 22.1, 27.8, 29.2, 33.7 ($CH_2CH_2CH_2CH_3$, $(CH_2)_4$ ring, $CH_2CH(CH_3)_2$), 46.8, 50.7, 59.5 (NCH_2), 70.7 (C_{spiro}), 182.9 ppm (CS); MS (70 eV, EI): *m*/*z* (%): 268 (69) $[M]^+$, 225 (47), 179 (100).

1-Butyl-3-isopropyl-1,3-diazaspiro[4.5]decane-2-ylidene (11a): Potassium (0.489 g, 12.5 mmol) was added at 0 °C to a solution of **10a** (1.342 g, 5.0 mmol) in THF (25 mL). The reaction mixture was heated under reflux for 4 h and then cooled to room temperature. After filtration over Celite the solvent was removed to give **11a** as colorless oil (1.040 g, 88 %). ^{1}H NMR (200.1 MHz, [D$_8$]THF): $\delta = 0.91$ (t, J = 7.0 Hz, 3H; CH_2CH_3), 1.25 (d, J = 6.8 Hz, 6H; $CH(CH_3)_2$), 1.36–1.67 (m, 14H; $CH_2CH_2CH_2CH_3$, $(CH_2)_5$ ring), 3.18 (s, 2H; NCH_2C_{spiro}), 3.32–3.39 ppm (m, 3H; $CH(CH_3)_2$, $NCH_2CH_2CH_2CH_3$); ^{13}C NMR (50.3 MHz, [D$_8$]THF): $\delta = 14.8$, 20.8 (CH_2CH_3, $CH(CH_3)_2$), 25.0, 26.1, 26.8 ($(CH_2)_5$ ring), 31.8, 36.4 ($NCH_2CH_2CH_2CH_3$), 44.9, 51.2, 59.3 (NCH_2, $NCH(CH_3)_2$), 70.3 (C_{spiro}), 236.0 ppm (NCN).

1-Butyl-3-isobutyl-1,3-diazaspiro[4.4]nonane-2-ylidene (11b): Compound **11b** was synthesized from **10b** (0.805 g, 3 mmol) and potassium (0.293 g, 7.5 mmol) in THF (15 mL) as described for **11a**. Compound **11b** (0.581 g, 82 %) was obtained as pale yellow oil. ^{1}H NMR (200.1 MHz, [D$_8$]THF): $\delta = 0.80$–0.92 (m, 9H; CH_2CH_3, $CH(CH_3)_2$), 1.28–1.66 (m, 12H; $NCH_2CH_2CH_2CH_3$, $(CH_2)_4$ ring), 1.99 (m, 1H; $CH(CH_3)_2$), 3.08 (d, J = 7.0 Hz, 2H; $NCH_2CH(CH_3)_2$), 3.30–3.46 ppm (m, 4H; NCH_2); ^{13}C NMR (50.3 MHz, [D$_8$]THF): $\delta = 13.8$, 19.9 (CH_2CH_3, $CH(CH_3)_2$), 23.7, 30.0, 31.4, 32.1, 35.6 ($CH_2CH_2CH_2CH_3$, $(CH_2)_4$ ring, $CH_2CH(CH_3)_2$), 52.7, 54.1, 60.4 (NCH_2), 70.5 (C_{spiro}), 239.9 ppm (NCN).

Pentacarbonyl(1-butyl-3-isopropyl-1,3-diazaspiro[4.5]decane-2-ylidene)-tungsten(0) (14a): In a glove box hexacarbonyltungsten (0.704 g, 2.0 mmol) was added to a solution of **11a** (0.473 g, 2.0 mmol) in toluene (20 mL). The resulting mixture was refluxed for 2 h and then cooled to room temperature. After removal of the solvent, residual hexacarbonyltungsten was removed by sublimation and the crude product was purified by column chromatography (SiO_2, hexane/diethyl ether, 10:1, v/v). Yield: 0.840 g (75 %) of a pale yellow solid. ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta =$ 0.96 (t, J = 7.2 Hz, 3H; CH_2CH_3), 1.40 (d, J = 7.2 Hz, 6H; $CH(CH_3)_2$), 1.51–2.02 (m, 14H; $CH_2CH_2CH_2CH_3$, $(CH_2)_5$ ring), 3.33 (s, 2H; NCH_2C_{spiro}), 3.71 (t, J = 7.6 Hz, 2H; $NCH_2CH_2CH_2CH_3$), 5.26 ppm (sept, J = 7.2 Hz, 1H, $CH(CH_3)_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 14.0$ (CH_2CH_3), 19.9 ($CH(CH_3)_2$), 23.6, 24.1, 24.9 ($(CH_2)_5$ ring), 30.7 ($NCH_2CH_2CH_2CH_3$), 35.5 ($NCH_2CH_2CH_2CH_3$), 53.4 ($NCH_2CH_2CH_2CH_3$), 55.5 ($NCH(CH_3)_2$), 59.0 (NCH_2C_{spiro}), 68.5 (C_{spiro}), 198.7 (CO_{cis}), 201.7 (CO_{trans}), 207.6 ppm (NCN); MS (70 eV, EI): *m*/*z* (%): 560 (26) $[M]^+$, 532 (18) $[M-CO]^+$, 504 (64) $[M-2\,CO]^+$, 472 (100); IR (KBr pellet): $\nu = 2058$, 1958, 1891 cm^{-1} (vs, CO).

Pentacarbonyl(1-butyl-3-isobutyl-1,3-diazaspiro[4.4]nonane-2-ylidene)-tungsten(0) (14b): Compound **14b** was prepared from **11b** (0.473 g, 2 mmol) and hexacarbonyltungsten (0.704 g, 2 mmol) in toluene (20 mL) as described for **14a**. Compound **14b** (0.795 g, 71 %) was obtained as pale yellow solid. ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 0.96$ (m, 9H; CH_2CH_3, $CH(CH_3)_2$), 1.35 (m, 2H; CH_2CH_3), 1.57–1.79 (m, 10H; $CH_2CH_2CH_2CH_3$, $(CH_2)_4$ ring), 2.06 (m, 1H; $CH(CH_3)_2$), 3.23 (s, 2H; NCH_2C_{spiro}), 3.47 (d, J = 7.8 Hz, 2H; NCH_2CH), 3.74 ppm (t, J = 8.4 Hz, 2H; $NCH_2CH_2CH_2CH_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 13.9$ (CH_2CH_3), 19.3, 19.8 ($CH(CH_3)_2$), 22.1, 28.6, 29.7 (CH_2CH_3, $(CH_2)_4$ ring), 30.4, 34.3 ($CH_2CH_2CH_2CH_3$, $CH_2CH(CH_3)_2$), 53.4 ($NCH_2CH_2CH_2CH_3$), 54.8 (NCH_2CH), 61.1 (NCH_2C_{spiro}), 73.6 (NCH_2C_{spiro}), 198.7 (CO_{cis}), 200.5 (CO_{trans}), 209.7 ppm (NCN); MS (70 eV, EI): *m*/*z* (%): 560 (7) $[M]^+$, 532 (4) $[M-CO]^+$, 504 (15) $[M-2\,CO]^+$, 472 (23), 442 (25), 414 (16), 140 (100); IR (KBr pellet): $\nu = 2059$, 1925, 1886 cm^{-1} (vs, CO).

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft and the International NRW Graduate School of Chemistry Münster for financial support.

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[13] X-ray crystal structure analysis for **10a**: formula $C_{15}H_{28}N_2S$, $M_r=268.45$, colorless crystal, $0.40\times0.30\times0.10$ mm, $a=8.796(1)$, $b=13.005(1)$, $c=14.192(1)$ Å, $V=1623.5(3)$ Å^3, $\rho_{calcd}=1.098$ g cm^{-3}, $\mu=1.647$ mm^{-1}, empirical absorption correction ($0.599\le T\le0.853$), $Z=4$, orthorhombic, space group $P2_12_12_1$ (no. 19), $\lambda=1.54178$ Å, $T=223$ K, $\omega/2\theta$ scans, 1898 reflections collected ($-h$, $+k$, $+l$), $[(\sin\theta)/\lambda]=0.62$ Å^{-1}, 1898 independent and 1743 observed reflections [$I\ge2\sigma(I)$], 166 refined parameters, $R=0.042$, $wR^2=0.116$, max/min residual electron density 0.16/−0.24 e Å^{-3}, Flack parameter −0.02(3), hydrogen atoms calculated and refined as riding atoms. X-ray crystal structure analysis for **14a**: formula $C_{20}H_{28}N_2O_5W$, $M_r=560.29$, colorless crystal $0.30\times0.30\times0.30$ mm, $a=9.594(1)$, $b=10.072(1)$, $c=12.814(1)$ Å, $\alpha=94.85(1)$, $\beta=104.52(1)$, $\gamma=113.29(1)°$, $V=1077.3(2)$ Å^3, $\rho_{calcd}=1.727$ g cm^{-3}, $\mu=53.93$ cm^{-1}, empirical absorption correction ($0.295\le T\le0.295$), $Z=2$, triclinic, space group $P\bar{1}$, (no. 2), $\lambda=0.71073$ Å, $T=198$ K, ω and ϕ scans, 11716 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]=0.66$ Å^{-1}, 5085 independent ($R_{int}=0.039$) and 4916 observed reflections [$I\ge2\sigma(I)$], 257 refined parameters, $R=0.018$, $wR^2=0.044$, max/min residual electron density 0.57/−1.14 e Å^{-3}, hydrogen atoms calculated and refined as riding atoms. X-ray crystal structure analysis for **14b**: formula $C_{20}H_{28}N_2O_5W$, $M_r=560.29$, yellow crystal $0.40\times0.35\times0.10$ mm, $a=12.316(1)$, $b=11.576(1)$, $c=15.766(1)$ Å, $\beta=94.50(1)°$, $V=2240.8(3)$ Å^3, $\rho_{calcd}=1.661$ g cm^{-3}, $\mu=51.85$ cm^{-1}, empirical absorption correction ($0.231\le T\le0.625$), $Z=4$, monoclinic, space group $P2_1/n$ (no. 14), $\lambda=0.71073$ Å, $T=198$ K, ω and ϕ scans, 13978 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]=0.68$ Å^{-1}, 5645 independent ($R_{int}=0.031$) and 5137 observed reflections [$I\ge2\sigma(I)$], 257 refined parameters, $R=0.025$, $wR^2=0.063$, max/min residual electron density 0.91/−1.22 e Å^{-3}, hydrogen atoms calculated and refined as riding atoms. Data sets were collected with Enraf-Nonius CAD4 and Nonius KappaCCD diffractometers, the later one equipped with a rotating anode generator. Programs used: absorption correction for CCD data SORTAV[20] and Denzo,[21] structure solution SHELXS-97,[22] structure refinement SHELXL-97.[23] CCDC-265622 (**10a**), CCDC-265621 (**14a**), and CCDC-265620 (**14b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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Received: March 18, 2005
Published online: June 30, 2005

