N,N'-Bis(2,2-dimethylpropyl)benzimidazolin-2-ylidene: A Stable Nucleophilic Carbene Derived from Benzimidazole

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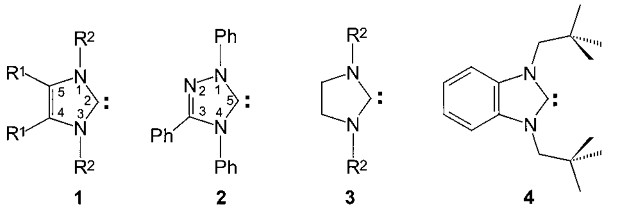
Dedicated to Professor Wolf-Peter Fehlhammer on the occasion of his 60th birthday

Abstract: N,N'-Dialkylated benzimidazol-2-thiones **6** can be prepared in a three-step procedure from *o*-phenylenediamine. Thione **6a** was reduced with sodium/potassium under desulfurization leading to carbene **4**. Compound **4** is the first stable free carbene derived from benzimidazole. It exhibits the topology of an unsaturated carbene including a short C4–C5 bond. Its ^{13}C NMR spectrum [$\delta(C2) = 231.47$] and selected structural parameters [angle N1-C2-N3 103.5(1)° and 104.2(1)°], however, correspond to those of saturated carbenes of the imidazolidin-2-ylidene type **3**. The observation that the unsaturated carbene **4** behaves like a saturated imidazolidin-2-ylidene is corroborated by the tendency of the sterically less bulky N,N'-dialkylated thione **6b** to yield the olefin **8** after reduction with Na/K. Carbene **4** can be coordinated to a $W(CO)_5$ fragment yielding the complex **9**, which contains a nonplanar carbene ring.

Keywords: carbenes · carbene complexes · NMR spectroscopy · tungsten

Introduction

Stable, N-heterocyclic carbenes, which were first proposed by Wanzlick about 40 years ago,[1] have been intensely studied[2] since the isolation and characterization of 1,3-bis(adamantyl)imidazolin-2-ylidene in 1991.[3] In the meantime, stable imidazolin-2-ylidenes (**1**),[4] triazol-5-ylidene (**2**),[5] imidazolidin-2-ylidenes (**3**),[6] (Figure 1) and other N,S-[7] and acyclic N,N′-stabilized carbenes[8] have been reported. Stable carbenes derived from annelated N-heterocyclic five-membered rings are hitherto unknown despite the successful stabilization of N,N'-dialkylated benzimidazolin-2-ylidenes[9] and benzoxazolin-2-ylidenes[10] in metal complexes. We report here the preparation and molecular structure of 1,3-bis(2,2-dimethylpropyl)benzimidazolin-2-ylidene (**4**) (Figure 1), which is the first stable free carbene derived from benzimidazole,[11] together with the crystal structure of its tungsten complex $[W(CO)_5(\mathbf{4})]$ **9**.



1a : $R^1 = H, R^2 = Adamantyl$
1b : $R^1 = H, R^2 = Me$
1c : $R^1 = H, R^2 = p$Tolyl
1d : $R^1 = H, R^2 = Mesityl$
1e : $R^1 = H, R^2 = p$-Cl-Ph
1f : $R^1 = R^2 = Me$
1g : $R^1 = Me, R^2 = Et$
1h : $R^1 = Me, R^2 = i$Prop

3a : $R^2 = Mesityl$
3b : $R^2 = t$Bu

Figure 1. Stable N-heterocyclic carbenes.

Results and Discussion

The synthesis of carbenes of type **4** containing an annelated N-heterocyclic five-membered ring by methods described by Arduengo et al.[4a,b] or Kuhn et al.[4c] is hampered by two factors; i) the deprotonation of sterically less bulky substituted N,N'-dialkylated benzimidazolium ions with strong bases like *n*BuLi, *t*BuLi, or NaH in THF, in contrast to the corresponding imidazolium ions, does not yield stable carbenes but instead C2–C2 connected olefins,[12] and ii) the preparation of bulky (*t*Bu, neopentyl) substituted N,N'-dialkylated benzimidazolium salts starting from benzimid-

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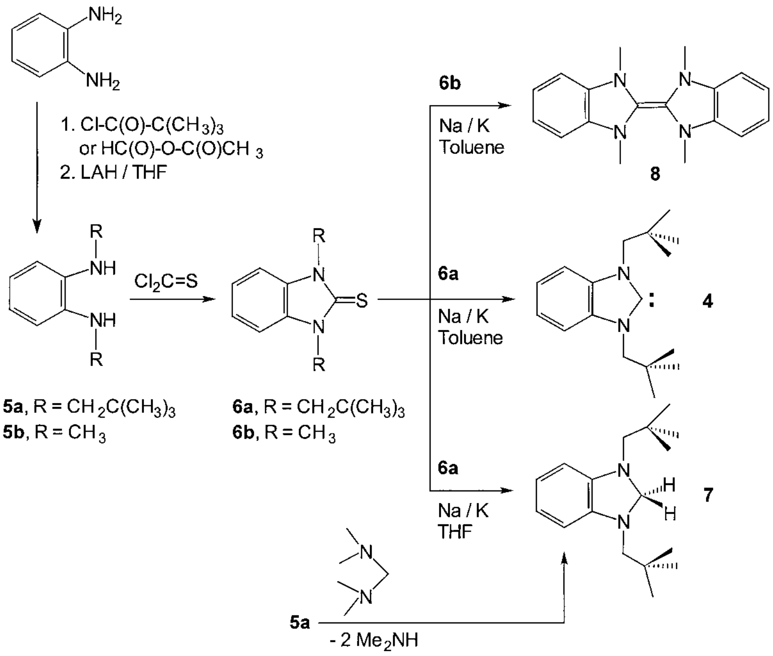
azole, which cannot dimerize after C2 deprotonation, proved unsuccessful to date.

For the synthesis of stable carbenes with a benzimidazole frame, a new synthetic strategy was developed which is outlined in Scheme 1. For the preparation of bulky substituted *o*-phenylenediamines of type **5** we used a procedure originally developed by Lappert et al. for the synthesis of N-heterocyclic stannylenes.[13] The dialkylated *o*-phenylenediamines *N,N'*-bis(2,2-dimethylpropyl)-1,2-diaminobenzene (**5a**) and *N,N'*-dimethyl-1,2-diaminobenzene (**5b**) were subsequently treated with thiophosgene to yield the thiones **6a** and **6b**, respectively.[4c]

The reduction of the thione **6a** with Na/K in THF (reaction time 20 days) leads, in contrast to the same reaction with non annelated imidazol-2-thiones,[4c] not to a carbene, but instead to the benzimidazoline **7**. Compound **7** was identified by NMR spectroscopy and by comparison with an authentic sample obtained by reaction of **5a** with bis(dimethylamino)methane. We assume, that during the relatively long reaction time of **6a** with Na/K in THF reduction of THF occurs, leading to hydrogenation of the intermediately formed carbene.



Scheme 1. Synthesis of **4**, **7**, and **8**.

Reduction of **6a** with Na/K in the more inert solvent toluene leads to carbene **4** in 60% yield. The reaction, which takes about 20 days, can be monitored by ^{13}C NMR spectroscopy: the resonance for the thione carbon atom ($\delta = 175.24$) vanishes and the low-field shifted resonance for the carbene carbon atom appears at $\delta = 231.47$.

Surprisingly, the resonance for the carbene carbon atom in **4** does not fall in the range normally observed for unsaturated N-heterocyclic carbenes of the imidazolin-2-ylidene type **1** (δC(2) ≈ 215), but is observed instead in the range typical for saturated N-heterocyclic carbenes of the imidazolidin-2-ylidene type **3** (δC(2) ≈ 240, Table 1). The deshielding of the carbene carbon atom in carbenes of type **3** relative to type **1** was attributed to the lack of aromatic stabilization in the saturated N-heterocyclic systems.[6] Carbene **4** exhibits an unsaturated N-heterocyclic five-membered ring containing formally 6π electrons, yet its ^{13}C NMR spectrum indicates that it behaves like a saturated derivative of the imidazolidin-2-ylidene type **3** which lacks aromatic stabilization.

Table 1. Selected spectroscopic and geometric parameters for N-heterocyclic carbenes.[a]

Carbene	^{13}C NMR [δ]	Angle	Ref.
C2	N1-C2-N3		
1a	211.4	102.2(2)	3
1b	215.2	–	4a
1c	215.8	101.2(1)	4a
1d	219.7	101.4(2)	4a
1e	216.3	101.7(1)	4a
1f	213.7	101.5(1)	4a, 4b
1g	211.1	–	4c
1h	205.9	–	4c
2	214.6	100.6(2)	5
3a	244.5	104.7(3)	6a
3b	238.2	106.44(9)	6b
4	231.5	103.5(1), 104.3(1)	this study
9	198.9	103(1), 103(1)	this study

[a] The numbering scheme for carbenes is illustrated in Figure 1.

Further evidence for an unusual electronic situation in **4** is furnished by the X-ray crystal structure analysis of crystals of **4**. The asymmetric unit contains two, within experimental error, identical, enantiomeric, C_2-chiral molecules of **4** (Figure 2). The geometric parameters of the five-membered ring in **4** are typical for imidazolin-2-ylidenes of type **1**. One notheworthy exception is the enlarged N1-C2-N3 angle (103.5(1)° and 104.3(1)°) in **4** (Table 1), which falls in the range normally observed for saturated N-heterocyclic carbenes of type **3**. The ^{13}C NMR spectra and the N1-C2-N3 angle of **4** indicate that the unsaturated carbene **4** actually behaves like a saturated N-heterocyclic carbene of type **3**. The main difference between **4** and saturated carbenes of type **3** is the length of the C–C bond in the five-membered ring. Saturated carbenes possess a C–C single bond [*d*(C–C) 1.505(6) Å for **3a**, 1.512(2) Å for **3b**], while **4** exhibits the topology of an unsaturated five-membered ring with a C–C double bond. The long C–C single bond in carbenes of type **3** has been used to explain the widening of the N1-C2-N3 angle in saturated carbenes relative to their unsaturated analogues.[6a] Since **4** exhibits a C–C double bond in the five-membered ring and still shows an enlarged N1-C2-N3 angle

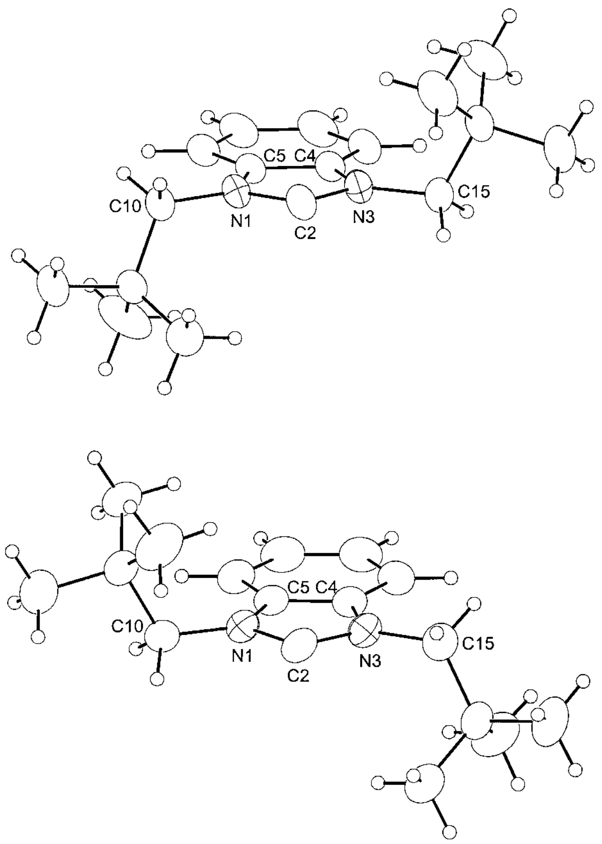


Figure 2. ORTEP plot of the two crystallographically independent molecules of **4** in the asymmetric unit (molecule A top, molecule B bottom). Selected bond lengths [Å] and angles [°] for molecule A [molecule B]: N1–C2 1.361(2) [1.360(2)], N1–C5 1.397(2) [1.394(2)], N1–C10 1.458(2) [1.458(2)], N3–C2 1.374(2) [1.368(2)], N3–C4 1.388(2) [1.397(2)], N3–C15 1.456(2) [1.457(2)], C4–C5 1.395(2) [1.386(2)]; C2-N1-C5, 112.80(12) [111.99(14)], C2-N1-C10 122.32(14) [123.1(2)], C5-N1-C10 124.88(13) [124.89(14)], C2-N3-C4 112.36(13) [111.83(14)], C2-N3-C15 121.61(14) [122.4(2)], C4-N3-C15 125.94(14) [125.8(2)], N1-C2-N3 103.49(13) [104.26(14)].

relative to unsaturated N-heterocyclic carbenes, this explanation now appears less satisfactory.

The assumption that stable, unsaturated carbenes derived from benzimidazole exhibit properties comparable to those of saturated imidazolin-2-ylidenes of type **3** is also corroborated by the reactivity of the *N,N'*-dimethyl-substituted derivative of **4** (Scheme 1). Wanzlick[1] noted more than 30 years ago that saturated carbenes of type **3** dimerize rapidly to the corresponding olefins if the substituents at the nitrogen atoms allow this geometrically, an observation which was only recently confirmed.[6b] This dimerization is not observed for unsaturated carbenes of type **1**. It can, however, be enforced by geometric constraints.[14] No tendency for dimerization was observed for **4**, which we attribute to the steric bulk at the nitrogen atoms. However, reduction of the *N,N'*-dimethyl-substituted thione **6b** with Na/K leads not to a carbene, but instead to the olefin **8**. The same product was obtained by Lappert et al. upon deprotonation of *N,N'*-dimethylbenzimidazolium iodide with NaH.[12a] In both cases, the rapid dimerization of the most likely intermediately formed carbene is typical for saturated N-heterocyclic carbenes of the imidazolidin-2-ylidene type **3**. We take this as a confirmation of our proposal that unsaturated carbenes derived from benzimidazole exhibit the topology of an unsaturated N-heterocyclic carbene but show spectroscopic and structural properties and the reactivity of carbenes with a saturated N-heterocyclic ring.

Not only carbene **4** itself, but also its metal complexes show remarkable properties. Reaction of **4** with $[W(CO)_5(thf)]$ leads to the air-stable complex $[W(CO)_5(\mathbf{4})]$ **9**. The X-ray structure analysis of crystals of **9** (Figure 3) shows that the ligand **4** has to undergo a conformational change with the loss of the C_2-chirality for coordination. In coordinated **4** both neopentyl groups are positioned on the same side of the N-heterocycle. This minimizes the steric interaction with the CO groups at the tungsten atom. However, two of the C2-W-C_{cis} angles (C20, C21) are still larger than 90°, while the other two C2-W-C_{cis} angles (C22, C23) are smaller than 90°. The carbene carbon atom (C2) does not reside in the plane of the N-heterocyclic ring but is shifted from that plane by 0.207(11) Å (molecule A) or 0.190(11) Å (molecule B) towards the side of the ring, which is not occupied by the neopentyl groups. This geometric situation allows **4** to coordinate tightly to the $W(CO)_5$ fragment inspite of the steric bulk at the nitrogen atoms. This is also confirmed by the W–C2 distances of 2.27(1) Å (molecule A) and 2.29(1) Å (molecule B), which are in the typical range of $W(CO)_5$ complexes with N-heterocyclic carbenes.[15]

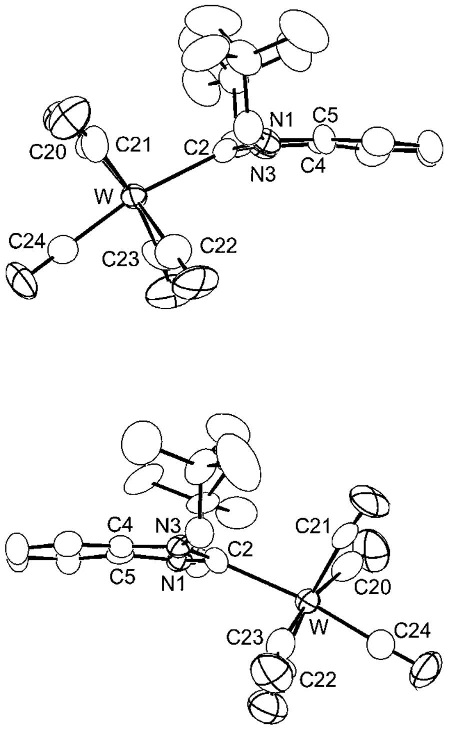


Figure 3. ORTEP plot of the two crystallographically independent molecules of **9** in the asymmetric unit (molecule A top, molecule B bottom). Selected bond length [Å] and angles [°] for molecule A [molecule B]: W–C2 2.27(1) [2.29(1)], N1–C2 1.42(2) [1.38(2)], N1–C5 1.37(2) [1.40(2)], N3–C2 1.33(2) [1.36(2)], N3–C4 1.39(2) [1.39(2)], C4–C5 1.35(2) [1.36(2)]; N1-C2-N3 103(1) [1.03(1)].

Experimental Section

General remarks: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 or Bruker AM 250 spectrometer. Elemental analyses were obtained with a Vario EL Elemental Analyzer at the Freie Universität Berlin. Mass spectra (EI, 70 eV) were taken on a Finnigan MAT 112 spectrometer. Air-sensitive compounds were prepared and handled under argon by Schlenk techniques. All solvents used were rigorously dried (typically over Na or Na/K and benzophenone) and freshly distilled prior to use. X-ray data sets were collected on a Siemens SMART CCD area detector system at 293(2) K (in a sealed capillary for air-sensitive **4**) or on a CAD-4 counter diffractometer at 298(2) K (for air-stable **9**).The programs used were Siemens SHELXL-97 UNIX Version, Release 97-1 for **4** and MolEN for **9**. Molecular structure plots were generated with ORTEP. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-408863 and CSD-59646.

***N,N*-Bis(2,2-dimethylpropyl)-1,2-diaminobenzene (5a):** The compound was prepared according to the method described by Lappert et al.[13] Colorless oil. ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 6.80$ (m, 2H, Ar-H), 6.65 (m, 2H, Ar-H), 3.40 (s, 2H, NH), 2.81 (s, 4H, CH$_2$), 1.05 (s, 18H, CH$_3$); ^{13}C NMR (62.9 MHz, CDCl$_3$): $\delta = 138.33$, 119.15, 112.09 (Ar-C), 56.41 (CH$_2$), 31.44 (*C*Me$_3$), 27.81 (CH$_3$).

***N,N'*-Dimethyl-1,2-diaminobenzene (5b):** The compound was prepared as reported in ref. [16]. Colorless crystals (m.p. 22–24 °C). ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 6.83$ (m, 2H, Ar-H), 6.59 (m, 2H, Ar-H), 3.20 (s, 2H, NH), 2.63 (s, 6H, CH$_3$); ^{13}C NMR (62.9 MHz, CDCl$_3$): $\delta = 137.94$, 118.59, 109.97 (Ar-C), 30.61 (CH$_3$).

***N,N'*-Bis(2,2-dimethylpropyl)-benzimidazolin-2-thione (6a):** A stirred solution of **5a** (1.2 g, 4.83 mmol) in THF (60 mL) was treated with triethylamine (5.4 mL, 38.7 mmol). The solution was cooled to −15 °C and thiophosgene (0.55 mL, 7.21 mmol) was added dropwise under formation of a yellow precipitate. The solution was allowed to warm to room temperature and stirred for another 14 h. Subsequently the solvent was removed and the dark orange residue was extracted with diethyl ether (8 × 10 mL). The solvent was removed and the oily product was purified by column chromatography (SiO$_2$, hexane/ethyl acetate, 10:1, v:v). Yield 1.23 g (89%) of a colorless oil. ^{1}H NMR (250 MHz, [D$_8$] THF): $\delta = 7.44$ (m, 2H, Ar-H), 7.26 (m, 2H, Ar-H), 4.40 (s, 4H, CH$_2$), 1.22 (s, 18H, CH$_3$); ^{13}C NMR (62.9 MHz, [D$_8$] THF): $\delta = 175.24$ (C=S), 134.37, 122.77, 111.05 (Ar-C), 55.43 (CH$_2$), 36.24 (*C*Me$_3$), 29.60 (CH$_3$).

***N,N'*-Dimethylbenzimidazolin-2-thione (6b):** Compound **6b** was synthesized from **5b** (0.87 g, 6.4 mmol), triethylamine (7.12 mL, 51.1 mmol), and thiophosgene (0.73 mL, 9.6 mmol) as described for **6a**. Column chromatography (SiO$_2$, hexane/ethyl acetate, 8:1, v:v) yielded 0.93 g (82%) of **6b** as white powder. ^{1}H NMR (250 MHz, [D$_8$] THF): $\delta = 7.15$ (m, 4H, Ar-H), 3.68 (s, 6H, CH$_3$); ^{13}C NMR (62.9 MHz, [D$_8$] THF): $\delta = 171.64$ (C=S), 133.32 123.15, 109.36 (Ar-C), 31.17 (CH$_3$).

***N,N'*-Bis(2,2-dimethylpropyl)-benzimidazoline (7):** Compound **7** was initially obtained by Na/K reduction of **6a** in THF over a reaction time of 20 days. An authentic sample of **7** was synthesized by heating a mixture of **5a** (0.62 g, 2.5 mmol) and bis(dimethylamino)methane (1.0 g, 9.8 mmol) in diethylether (40 mL) in the presence of a trace (0.03 g) of *p*-toluenesulfonic acid under reflux for 6 h. After standard workup 0.19 g (88%) of a yellow solid was obtained. ^{1}H NMR (250 MHz, C$_6$D$_6$): $\delta = 6.81$ (m, 2H, Ar-H), 6.38 (m, 2H, Ar-H), 4.54 (s, 2H, N-CH$_2$-N), 2.53 (s, 4H, CH$_2$), 0.86 (s, 18H, CH$_3$); ^{13}C NMR (62.9 MHz, C$_6$D$_6$): $\delta = 143.67$, 118.92, 105.47 (Ar-C), 83.19 (N-C-N), 64.19 (CH$_2$), 33.66 (*C*Me$_3$), 27.91 (CH$_3$).

***N,N'*-Bis(2,2-dimethylpropyl)-benzimidazolin-2-ylidene (4):** Sodium (0.08 g, 3.5 mmol) and potassium (0.28 g, 7.2 mmol) were melted together under vacuum. The resulting alloy was cooled to 0 °C and treated with a solution of **6a** (0.31 g, 1.07 mmol) in dry toluene (30 mL). The mixture was stirred for 20 days at room temperature. The cloudy solution was then filtered and the solvent was removed under reduced pressure. Analytically pure **4** was obtained as a colorless oil, which crystallized over a period of one week upon standing. Yield 0.21 g (76%), m.p. 26 °C. ^{1}H NMR (250 MHz, [D$_8$]THF): $\delta = 6.95$ (m, 4H, Ar-H), 3.98 (s, 4H, CH$_2$), 1.01 (s, 18H, CH$_3$); ^{13}C NMR (62.9 MHz, [D$_8$]THF): $\delta = 231.47$ (N-C-N), 136.39, 120.77, 110.82 (Ar-C), 58.74 (CH$_2$), 33.82 (*C*Me$_3$), 28.49 (CH$_3$).

Tetramethyltetraazafulvalene (8): Sodium (0.17 g, 7.4 mmol) and potassium (0.58 g, 14.9 mmol) were melted under vacuum. The resulting alloy was cooled to 0 °C and treated with a solution of **6b** (0.43 g, 2.41 mmol) in dry toluene (40 mL). The mixture was stirred for 20 days at room temperature. The cloudy solution was then filtered and the solvent was removed under reduced pressure yielding pure **8** (0.29 g, 83%) as a colorless oil, which crystallized over a period of two days. ^{1}H NMR (250 MHz, C$_6$D$_6$): $\delta = 6.86$ (m, 4H, Ar-H), 6.47 (m, 4H, Ar-H), 2.73 (s, 12H, CH$_3$); ^{13}C NMR (62.9 MHz,C$_6$D$_6$): $\delta = 143.61$ (Ar-C), 124.42 (N-C-N) 121.04, 108.59 (Ar-C), 35.98 (CH$_3$); MS (EI) *m/z* (%): 292 (10) [M^+], 147 (100).

***N,N'*-Bis(2,2-dimethylpropyl)-benzimidazolin-2-ylidene-pentacarbonyltungsten (9):** A solution of [W(CO)$_6$] (1.41 g, 4.0 mmol) in THF (100 mL) was irridiated (mercury-vapor lamp) for 5 h at room temperature. Then a solution of **4** (0.42 g, 1.63 mmol) was added dropwise. After the mixture had been stirred at room temperature overnight, the solvent was removed and the residue was purified by column chromatography (SiO$_2$, hexane/dichlormethane 6:1, v:v). Yield 0.81 g (85%, relative to **4**) of pale yellow crystals. ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 7.40$ (m, 2H, Ar-H), 7.14 (m, 2H, Ar-H), 4.51 (s, 4H, CH$_2$), 0.98 (s, 18H, CH$_3$); ^{13}C NMR (62.9 MHz, CDCl$_3$): $\delta = 200.47$ (*trans*-CO), 198.25 (*cis*-CO), 196.86 (N-C-N), 135.45, 122.30, 112.65 (Ar-C), 60.30 (CH$_2$), 34.72 (*C*Me$_3$) 29.08 (CH$_3$).

X-ray structure analysis of *N,N*-Bis(2,2-dimethylpropyl)-benzimidazolin-2-ylidene (4): Suitable crystals of **4** were obtained by stripping the solvent from a solution of the compound in toluene. The oily product crystallizes upon standing for one week. The crystals melt at 26 °C. The data crystal was mounted in a glass capillary. Compound **4** crystallizes with two independent molecules in the asymmetric unit. Formula C$_{17}$H$_{26}$N$_2$, Mr = 258.40, 0.84 × 0.53 × 0.45 mm^3, $a = 10.1057(3)$, $b = 10.6191(4)$, $c = 16.7234(6)$ Å, $\alpha = 77.50(1)$, $\beta = 73.72(1)$, $\gamma = 73.452(1)^\circ$, $V = 1633.0(1)$ Å^3, $\rho_{\text{calcd}} = 1.051$ g cm^{-3}, $\mu(\text{Mo}_{K\alpha}) = 0.061$ mm^{-1}, $Z = 4$, triclinic, space group $P\bar{1}$ (no. 2), Mo$_{K\alpha}$ radiation = 0.71073 Å, $T = 293(2)$ K, ω scans, 12060 refelctions collected, 2Θ range 4.04–51.46°, 5238 independent and 3864 observed reflections [$I > 2(I)$], 343 refined parameters (refinement on F^2), $R = 0.0534$, $wR^2 = 0.1472$, max. (min.) residual electron density 0.215 (−0.179) e Å^{-3}, hydrogen atoms on calculated positions.

X-ray structure analysis of 9: Suitable crystals of **9** were grown by evaporation of a CH$_2$Cl$_2$/hexane (5:1, v:v) solution. The crystals are air-stable. Compound **9** crystallizes with two independent molecules in the asymmetric unit. Formula C$_{22}$H$_{26}$N$_2$O$_5$W, $M_r = 582.31$, 0.4 × 0.2 × 0.2 mm^3, $a = 7.030(2)$, $b = 39.552(14)$, $c = 17.160(9)$ Å, $\beta = 101.50(3)^\circ$, $V = 4676(6)$ Å^3, $\rho_{\text{calcd}} = 1.654$ g cm^{-3}, $\mu(\text{Mo}_{K\alpha}) = 5.078$ mm^{-1}, $Z = 8$, monoclinic, space group *Cc* (no. 9), Mo$_{K\alpha}$ radiation = 0.71073 Å, $T = 298(2)$ K, ω scans, 6495 unique reflections collected, 2Θ range 2.0–46.0°, 4922 observed reflections [$F^2 > 3(F^2)$], 539 refined parameters (refinement on F), $R = 0.0371$, $wR^2 = 0.0410$, max. (min.) residual electron density 1.82 (−0.39) e Å^{-3}, hydrogen atoms on calculated positions.

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[11] During the preparation of this manuscript we became aware, that Prof. M. Lappert, University of Sussex at Brighton had prepared **4** in the same manner as we did and stopped his efforts to crystallize the carbene, when he became aware of our work. See also Organometallic Chemistry in the South Pacific, 24–28.1.1999, Book of Abstracts, L21

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