

Platinum(II) and palladium(II) complexes with 1,2-dihydrobenzoxazol-2-ylidene ligands and molecular structure of *trans*-bis(1,2-dihydrobenzoxazol-2-ylidene) diiodo palladium¹

U. Kernbach^a, T. Lügger^b, F.E. Hahn^{b,*}, W.P. Fehlhammer^{a,2}

^a Deutsches Museum, Museumsinsel 1, D-80306 München, Germany

^b Institut für Anorganische und Analytische Chemie der Freien Universität, Fabeckstraße 34–36, D-14195 Berlin, Germany

Received 6 November 1996; accepted 15 December 1996

Abstract

2-Trimethylsiloxyphenyl isocyanide **1** reacts with $[MCl_2(NCPh)_2]$ ($M = Pd, Pt$) to yield homoleptic tetrakisocyanide complexes $[M(1)_4]Cl_2$. Subsequent hydrolysis of the Si–O bonds leads to intramolecular nucleophilic attack at the isocyanide carbon atom with formation of homoleptic complexes with four 1,2-dihydrobenzoxazol-2-ylidene ligands $[M(\overline{CN(H)C_6H_4-2-O})_4]X_2$ ($M = Pt, X = Cl, 2$; $M = Pt, X = BF_4, 3$; $M = Pd, X = Cl, 4$). Double deprotonation of **4** by ammonia yields the neutral complex $[Pd(\overline{CNC_6H_4-2-O})_2(\overline{CN(H)C_6H_4-2-O})_2]$ **5**. Under similar conditions, PdI_2 reacts with **1** even in excess to give only the diisocyanide complex *trans*- $[PdI_2(1)_2]$ **6** which upon Si–O bond cleavage yields the neutral dicarbene complex *trans*-bis(1,2-dihydrobenzoxazol-2-ylidene)diiodo palladium **7**. Complex **7** was shown by X-ray crystallography to contain a planar tetracoordinated palladium atom and two carbenoid benzoxazole rings which are rotated by about 80° relative to the palladium coordination plane. © 1997 Elsevier Science S.A.

Keywords: Carbene complexes; Palladium; Platinum; X-ray crystallography

1. Introduction

The addition of *N*- and *O*-nucleophiles to coordinated isocyanides is one of the most efficient synthetic approaches to carbene-rich metal complexes. While the first homoleptic tetracarbene complexes of palladium and platinum were obtained from tetra(methylisocyanide) metal precursors and methylamine [1], it was through intramolecular cyclization of functionalized isocyanides like $CN-CH_2CH_2-OH$ **A** that numerous new complexes with cyclic diheteroatom-stabilized carbene ligands have been prepared [2–4]. The first octahedral Co(III) and Rh(III) hexacarbene complexes **B**, for example, were obtained from simple salts such as $CoCl_2$ and $RhCl_3 \cdot 3H_2O$ respectively, and either 2-hydroxyethyl isocyanide [5] (Fig. 1) or trimethylsiloxyethyl isocyanide–KF [6] in water– O_2 .

Recently, the reactivity of the closely related aromatic 2-trimethylsiloxyphenyl isocyanide **1** [7] was investigated with various transition metals, showing some unexpected results [8–11]. After Si–O bond cleavage, coordinated **1** undergoes intramolecular cyclization even when coordinated to electron-rich transition metals [8,9] where normally $(d \rightarrow \pi^*)\pi$ backbonding from the metal to the isocyanide carbon prevents nucleophilic attack. Thus the open chain form is maintained in $[W(CO)_5(CN-CH_2CH_2-OH)]$ [2], while cleavage of the Si–O bond in $[W(CO)_5(1)]$ does not yield $[W(CO)_5(CNC_6H_4-2-OH)]$ but instead the carbene complex $[W(CO)_5(\overline{CN(H)C_6H_4-2-O})]$ [8]. The driving force for the carbene formation observed for complexes of **1** after Si–O bond hydrolysis has been attributed to the aromatic character of the five-membered ring incorporating the carbene carbon atom [8]. The reaction of **1** (even when used in excess) with PdI_2 and CoI_2 has been reported to yield *trans*- $[PdI_2(1)_2]$ and *trans*- $[CoI_2(1)_4]$ respectively [12]. In this contribution we report on the carbene complexes obtained after Si–O bond cleavage in palladium(II) and platinum(II) complexes of **1**.

* Corresponding author.

¹ This paper is dedicated to Professor Dr. G. Huttner on the occasion of his 60th birthday.

² Also corresponding author.

2. Results and discussion

2.1. Homoleptic carbene complexes of palladium(II) and platinum(II)

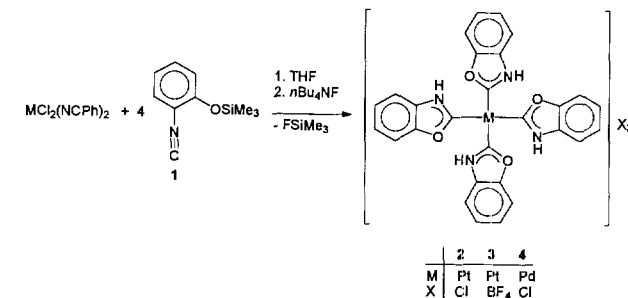
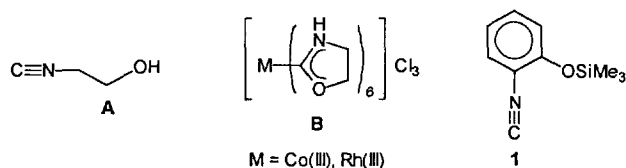
Tetra(oxazolidin-2-ylidene) palladium(II) and platinum(II) complexes have been obtained previously by the spontaneous cyclization of 2-hydroxyethyl isocyanide **A** in the presence of Pd(II) or Pt(II) salts [3]. No tetracarbene species was formed, however, by the analogous reaction with 2-trimethylsiloxyphenyl isocyanide and KF, i.e. under conditions where Si–O cleavage is known to occur readily. These findings may be explained by the fact that 2-hydroxyethyl isocyanide is a relatively stable compound, whereas free 2-hydroxyphenyl isocyanide is completely unstable rapidly forming benzoxazole instead of coordinating to the metal [7,8]. Thus it was clear that in order to circumvent this problem the two processes (i) isocyanide to metal coordination and (ii) desilylation–cyclization had to be carried out separately when **1** was used for carbene complex preparation.

In fact, the preparation of the homoleptic carbene complexes **2–4** in good yields was achieved by reaction of 4 equiv. of the *O*-silylated isocyanide **1** with [PdCl₂(NPh)₂] or [PtCl₂(NPh)₂] in THF with subsequent cleavage of the O–Si bonds with trace amounts of tetrabutylammonium fluoride (Scheme 1).

In the high frequency region, the IR spectra of **2–4** show the intense and structured $\nu(\text{NH})$ and $\nu(\text{CH})$ bands in the range 3500–2700 cm⁻¹. Strong absorptions at about 1440 cm⁻¹ were assigned to the asymmetric N–C–O stretching vibration.

The ¹H NMR spectra also confirm the presence of 1,2-dihydrobenzoxazol-2-ylidene ligands in **2–4**. Broad signals at about $\delta = 15$ ppm, which disappear upon addition of D₂O, confirm the presence of the exchangeable NH protons [8–11]. The ¹³C NMR chemical shift of the carbene carbon atom in complex **2** (188.5 ppm) appears at higher field than in the related aliphatic carbene ligands (196–204 ppm) [3]. The low solubility of complexes **3** and **4** prevented the recording of their ¹³C NMR spectra.

In the FAB MS spectra (positive ions) of **2–4** the strongest peaks correspond to the molecular ions [ML₄ – H]⁺ (L = 1,2-dihydrobenzoxazol-2-ylidene). Further



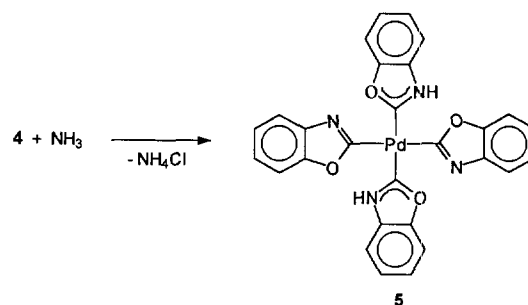
Scheme 1. Reactions of **1** with complexes [MCl₂(NPh)₂] (M = Pt, Pd).

peaks result from the successive loss of neutral carbene ligands L.

2.2. Reaction of the tetracarbene complex **4** with NH₃

Addition of an aqueous solution of NH₃ to a solution of tetra(1,2-oxazolidin-2-ylidene)dichloro palladium(II) in water or methanol resulted in a white solid which was spectroscopically analyzed as the neutral [Pt(CNCH₂CH₂O)₂(CN(H)CH₂CH₂O)₂] [13]. Transformation of this reaction to the new unsaturated tetracarbene complex **4** gives an analogous result. Two of the four ligands can be deprotonated with ammonia and the resulting insoluble white solid [Pd(CNC₆H₄-2-O)₂(CN(H)C₆H₄-2-O)₂] **5** precipitates from the reaction solution (Scheme 2). After deprotonation, all four ligands remain coordinated via carbon atoms. Complex **5** can be reprotonated with mineral acids, giving back the starting compound **4**. The coexistence of protonated and deprotonated 1,2-dihydrobenzoxazol-2-ylidene species in the same ligand sphere has been demonstrated previously for an iron complex [11].

The removal of two protons causes a change in the IR spectrum of **5** when compared to **4**. It can be assumed, that hydrogen bridges of the type N–H...Cl exist in **4** as reported for the palladium complex with four oxazolin-2-ylidene ligands [3]. No anions are present in **5**, which rules out the possibility of this type of a hydrogen bond. As a consequence, in the IR spectrum of **5** the $\nu(\text{NH})$ and $\nu(\text{CH})$ band pattern of **4** ranging



Scheme 2. Deprotonation of complex **4** (the trans geometry was assumed for **5** but has not yet been confirmed experimentally).

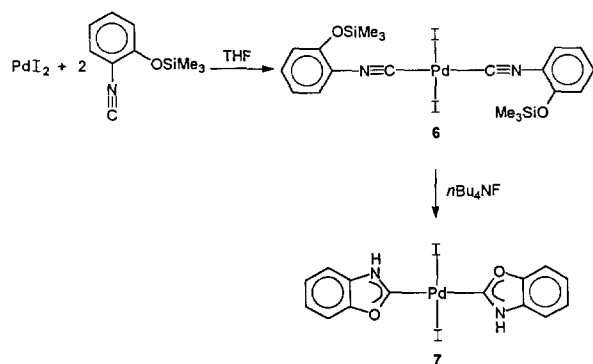
Fig. 1. Functionalized isocyanides and intramolecular cyclization of **A** giving complex **B**.

from 2700 to 3500 cm^{-1} is absent. Instead, strong hydrogen bonds between the NH and O groups of the five-membered rings are possible. These can be of intermolecular or, in case of coplanarity of the carbene ligands with the Pd coordination plane, of intramolecular nature [14]. Weak but broad bands, centered at about 2550 cm^{-1} , are assigned to intra- and intermolecular hydrogen bonds of the remaining NH groups with nitrogen or oxygen atoms of the benzoxazol-2-yl ligands. The strong absorption for the asymmetric N–C–O stretching vibration appears around 1440 cm^{-1} as a split band due to the presence of two different five-membered ring systems. Low energy $\nu(\text{NH})$ absorptions have been observed in the IR spectra for NH groups engaged in strong hydrogen bonds [15].

2.3. Reaction of **1** with palladium diiodide

Even when applied in excess, **1** reacts with PdI_2 in acetonitrile to give only the diisocyanide complex $\text{trans-}[\text{PdI}_2(\mathbf{1})_2]$ **6** [12]. If this reaction is carried out in THF followed by addition of $n\text{-Bu}_4\text{NF}$ i.e. under conditions which favor Si–O bond cleavage, complex **6** cannot be isolated and the reaction product is the neutral carbene complex $\text{trans-bis}(1,2\text{-dihydro-benzoxazol-2-ylidene})\text{diiodo palladium(II)}$ **7** (Scheme 3). This complex crystallizes from DMF as $7 \cdot 4\text{DMF}$. Its molecular structure has been established by X-ray diffraction. Fig. 2 shows an ORTEP drawing of one molecule of **7**.

Complex **7** is a trans configured dicarbene complex. The palladium atom resides on a crystallographic inversion center. This causes the C1–Pd–C1* and I–Pd–I* angles to be 180°, while the C1–Pd–I angle (80.86(8)°) differs significantly from 90°, indicating the distortion of the square planar coordination geometry. The ylidene ligands themselves are almost planar with a maximum deviation from the least-squares plane of 0.03 Å, but are rotated by 80.22(8)° against the Pd–I–C1 plane. The Pd–C distance of 2.173(3) Å is significantly longer than in the tetracarbene complex $[\text{Pd}(\text{CN}(\text{H})\text{CH}_2\text{CH}_2\text{O})_4]\text{Cl}_2$ (2.022(2) Å and 2.018(2) Å



Scheme 3. Synthesis of complexes **6** and **7**.

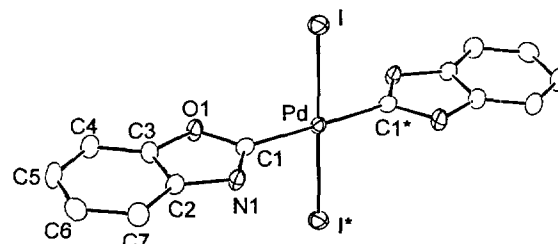
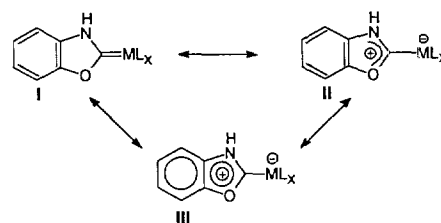


Fig. 2. Molecular structure of **7** in $7 \cdot 4\text{DMF}$ (hydrogen atoms are omitted for clarity). Atom Pd resides on a crystallographic inversion center. Starred atoms represent transformed coordinates of the type $(-x, 1-y, -z)$. Selected bond distances (Å) and angles (deg): Pd–I 2.8106(2), Pd–C1 2.173(3), O1–C1 1.256(3), O1–C3 1.497(4), N1–C1 1.279(4), N1–C2 1.493(4), C2–C3 1.195(4), I–Pd–C1 80.86(8), C1–O1–C3 116.6(2), C1–N1–C2 119.8(2), Pd–C1–O1 127.4(2), Pd–C1–N1 136.0(2), O1–C1–N1 96.6(3), N1–C2–C3 100.5(3), O1–C3–C2 106.5(3).

[3]) and is best described as a single bond. It is also longer than the Pd–C separation found in complexes with N,N -substituted carbene ligands [16,17]. At first glance this is surprising as it has been shown that the $\text{W}-\text{C}_{(\text{carbene})}$ separation in pentacarbonyl(1,2-dihydrobenzoxazol-2-ylidene) tungsten is shorter than in the corresponding imidazol-2-ylidene complex [18]. The short Pd–C distance in $\text{cis-}[\text{PdI}_2(\text{CN}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)]$ [17] can, however, be explained with the weak trans influence of the halogen atoms trans to the N,N -substituted carbene ligands, while in $7 \cdot 4\text{DMF}$ the carbene ligands are oriented trans to each other. A comparison of the Pd– $\text{C}_{(\text{carbene})}$ distance in $7 \cdot 4\text{DMF}$ with the Pd– $\text{C}_{(\text{isocyanide})}$ distance (1.968(11) Å) in **6** [12] confirms the weak ability of the 1,2-dihydrobenzoxazol-2-ylidene ligand to act as a π -acceptor.

The most important structural feature of $7 \cdot 4\text{DMF}$ is the lack of aromaticity in the metal-coordinated heterocycle. In complexes of the type $[\text{M}(\text{CO})_5(\text{CN}(\text{H})\text{C}_6\text{H}_4-2\text{O})]$ ($\text{M} = \text{W}, \text{Fe}$) [8–11], practically identical bond lengths (around 1.365(5) Å) [8–11] within the carbenoid five-membered ring indicate a strong contribution from the mesomeric structure **III** (Scheme 4). This uniformity of bond lengths cannot be detected in the five-membered rings of $7 \cdot 4\text{DMF}$. Quite contrarily, the bond parameters clearly show a break-up of the 6π electron system of the five-membered ring



Scheme 4. Resonance structures for (1,2-dihydrobenzoxazol-2-ylidene)metal complexes.

into two sections. The MC(O)N carbene moiety (O1–C1 1.256(3) Å, N1–C1 1.279(4) Å) is separated by two significantly longer O–C and N–C single bonds (O1–C3 1.497(4) Å, N1–C2 1.493(4) Å) from the benzene ring. This structural feature has earlier been found in *N,N*-heterocyclic carbene ligands [19].

In summary, the strong tendency of the aromatic isocyanide ligand **1** to form ylidene complexes by intramolecular cyclization after Si–O bond cleavage when attached to Pd(II) or Pt(II) has been demonstrated. The driving force for the generation of even homoleptic tetracarbene complexes is a consequence of the activation of the coordinated isocyanide carbon atom by the metal center towards nucleophilic attack of the oxygen atom in ortho position. Aromatization of the resulting ylidene ligands, which was observed with electron-rich transition metal fragments, is not necessary for the stabilization of the coordinated 1,2-dihydrobenzoxazol-2-ylidenes.

3. Experimental

3.1. Preparation of tetra(1,2-dihydrobenzoxazol-2-ylidene)dichloro platinum(II) **2**

To a solution of 1.0 g (2.15 mmol) of [PtCl₂(NCPPh)₂] [20] in 25 ml of THF was added 4.1 g (21.0 mmol) of 2-trimethylsilyloxyphenyl isocyanide **1** [7] at 0°C. The mixture was stirred at room temperature for 2 h. After the addition of 2 ml of an aqueous THF solution containing 0.020 g of *n*-tetrabutylammonium fluoride and stirring at room temperature for several hours a colorless solid had precipitated. The precipitate was separated by filtration, washed with small amounts of THF and diethyl ether and dried in vacuo to give 1.14 g (72%) of **2**. M.p. 250°C (dec.). Anal. Calc. for C₂₈H₂₀Cl₂N₄O₄Pt (*M* = 741.05): C, 45.34; H, 2.72; N, 7.56. Found: C, 45.08; H, 2.85; N, 7.78. ¹H NMR (250 MHz, CD₃OD): δ 7.80–7.40 (m, 4 H, Ar-H). ¹³C{¹H} NMR (62.9 MHz, CD₃OD): δ 188.5 (carbene-C); 152.9, 131.2, 128.0, 114.9, 112.9 (Ar-C). IR (KBr, cm⁻¹): ν 3410 (s, br, NH); 2800 (vs, br, CH); 1438 (vs, N–C–O). MS (FAB, positive ions): *m/z* 670 ([PtL₄ – H]⁺, 100%); 551 ([PtL₃ – H]⁺, 38); 433 ([PtL₂ – H]⁺, 38); 314 ([PtL – H]⁺, 36).

3.2. Preparation of tetra(1,2-dihydrobenzoxazol-2-ylidene)platinum(II)bis(tetrafluoroborate) **3**

Addition of 5 equiv. of a saturated solution of NaBF₄ in water–methanol (1:1) to a solution of **2** in methanol resulted in a colorless precipitate which was separated by filtration and dried in vacuo to give **3**. M.p. 209°C (dec.). Anal. Calc. for C₂₈H₂₀B₂F₈N₄O₄Pt (*M* = 845.06): C, 39.79; H, 2.38; N, 6.63. Found: C, 38.32;

H, 2.84; N, 6.60. ¹H NMR (250 MHz, DMSO-*d*₆): δ 7.80–7.25 (m, 4 H, Ar-H); 15.00 (s, 1 H, NH). IR (KBr, cm⁻¹): ν 3300 (s, br, NH); 2850 (s, br, CH); 1438 (vs, N–C–O); 1150, 1000 (vs, BF₄). MS (FAB, positive ions): *m/z* 758 ([PtL₄ – BF₄]⁺, 7%); 670 ([PtL₄ – H]⁺, 100); 551 ([PtL₃ – H]⁺, 47); 433 ([PtL₂ – H]⁺, 52); 314 ([PtL – H]⁺, 62).

3.3. Preparation of tetra(1,2-dihydrobenzoxazol-2-ylidene) palladium(II)dichloride **4**

Compound **4** was synthesized in analogy to the procedure described for **2** with an isolated yield of 75% by starting from 1.0 g (2.60 mmol) of [PdCl₂(NCPPh)₂] [20] in 25 ml of THF and 5.0 g (26.0 mmol) of 2-trimethylsilyloxyphenyl isocyanide. M.p. 245°C (dec.). Anal. Calc. for C₂₈H₂₀Cl₂N₄O₄Pd (*M* = 651.98): C, 51.56; H, 3.09; N, 8.59. Found: C, 51.17; H, 2.88; N, 8.33. ¹H NMR (250 MHz, DMSO-*d*₆): δ 7.95–7.20 (m, 4 H, Ar-H), 15.15 (s, 1 H, NH). IR (KBr, cm⁻¹): ν 3300 (s, br, NH); 2950 (s, br, CH); 1441 (vs, N–C–O).

3.4. Preparation of di(benzoxazol-2-yl)-bis(1,2-dihydrobenzoxazol-2-ylidene) palladium(II) **5**

To a solution of 5 ml of NH₃ in water was added 20 ml of a solution of **4** (ca. 1.0 g) in methanol. The white solid which precipitated spontaneously was collected and washed with small amounts of water, ethanol and diethyl ether and dried in vacuo. M.p. 280°C (dec.). Anal. Calc. for C₂₈H₁₈N₄O₄Pd (*M* = 580.03): C, 57.93; H, 3.13; N, 9.66. Found: C, 56.62; H, 3.26; N, 9.23. IR (KBr, cm⁻¹): ν 3056 (vw, CH); 2550 (w, NH); 1428, 1443 (s, N–C–O). MS (FAB, positive ions): *m/z* 581 ([PdL₂L'₂ + H]⁺, 0.5%); 461 ([PdL₂L']⁺, 0.7); 344 ([PdLL']⁺, 1.7); L = 1,2-dihydrobenzoxazol-2-ylidene, L' = benzoxazol-2-yl ligand.

3.5. Preparation of trans-bis(1,2-dihydrobenzoxazol-2-ylidene)diiodo palladium(II) **7**

To a suspension of 1.0 g (2.8 mmol) of PdI₂ in 25 ml of THF was added 4.0 g (24.0 mmol) of 2-trimethylsilyloxyphenyl isocyanide at 0°C. The mixture rapidly turned into a clear orange solution. Then 2 ml of an aqueous THF solution containing 20 mg of *n*-tetrabutylammonium fluoride was added. After stirring at room temperature for several hours a yellow solid had precipitated, which was filtered off and washed with small amounts of THF and diethyl ether. The resulting light yellow solid was recrystallized from acetone to give 1.08 g (65%) of **7**. M.p. 153°C (dec.). Anal. Calc. for C₁₄H₁₀I₂N₂O₂Pd (*M* = 597.78): C, 28.10; H, 1.69; N, 4.68. Found: C, 28.71; H, 2.08; N, 4.75. ¹H NMR (250 MHz, DMSO-*d*₆): δ 8.05–7.35 (m, 4 H, Ar-H); 15.15 (s, 1 H, NH). IR (KBr, cm⁻¹): ν 3265 (vs, NH);

3000 (s, br, CH) 1419 (vs, N–C–O). MS (FAB, positive ions): m/z 471 ($[\text{PdL}_2\text{I}]^+$, 4%); 344 ($[\text{PdL}_2]^+$, 2).

3.6. X-ray structure determination³

Crystals of $7 \cdot 4\text{DMF}$ were grown from a DMF solution at -10°C . Selected crystallographic details: size of data crystal $0.32 \times 0.25 \times 0.18 \text{ mm}^3$, formula $\text{C}_{26}\text{H}_{38}\text{I}_2\text{N}_6\text{O}_6\text{Pd}$, $M = 890.84 \text{ amu}$, triclinic, space group $\bar{1}$, $a = 8.946(4)$, $b = 9.886(2)$, $c = 9.894(2) \text{ \AA}$, $\alpha = 80.21(2)$, $\beta = 72.82(3)$, $\gamma = 83.52(3)^\circ$, $V = 822(1) \text{ \AA}^3$, $Z = 1$, $\rho_{\text{exp}} = 1.81$, $\rho_{\text{calc}} = 1.800 \text{ g cm}^{-3}$, Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$, graphite monochromator), $\mu(\text{Mo K}\alpha) = 24.59 \text{ cm}^{-1}$. 3248 symmetry-independent diffraction data were measured at $-100(2)^\circ\text{C}$ in the 2θ range $2\text{--}50^\circ$. Structure solution with Patterson and refinement with Fourier methods, refinement of positional parameters of all non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms on calculated positions ($d(\text{C–H}) = 0.95 \text{ \AA}$, $d(\text{N–H}) = 0.87 \text{ \AA}$ [21]) with $B_{\text{eq}(\text{H})} = 1.3 B_{\text{eq}(\text{C})}$. $R = 0.037$, $R_w = 0.062$ for 3093 absorption corrected (7ψ -scans) structure factors $F_o^2 \geq 3\sigma(F_o^2)$ and 188 refined parameters. Neutral atomic scattering factors were used and all scattering factors were corrected for anomalous dispersion [22]. All calculations were carried out with the MOLEN program package [23].

Acknowledgements

Financial support of this work by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft and the BMBW (Graduiertenkolleg Synthese und Strukturaufklärung niedermolekularer Verbindungen) is gratefully acknowledged.

³ Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-59365 and the journal citation.

References

- [1] J.S. Miller, A.L. Balch, *Inorg. Chem.* 11 (1972) 2069.
- [2] K. Bartel, W.P. Fehlhammer, *Angew. Chem.* 86 (1974) 588; *Angew. Chem. Int. Ed. Engl.* 13 (1974) 599.
- [3] W.P. Fehlhammer, K. Bartel, B. Weinberger, U. Plaia, *Chem. Ber.* 118 (1985) 2220.
- [4] W.P. Fehlhammer, K. Bartel, U. Plaia, A. Vökl, A.T. Liu, *Chem. Ber.* 118 (1985) 2235.
- [5] U. Plaia, H. Stolzenberg, W.P. Fehlhammer, *J. Am. Chem. Soc.* 107 (1985) 2171.
- [6] H. Hoffmeister, Dissertation, FU Berlin, 1989.
- [7] P. Jutzli, U. Gilge, *J. Organomet. Chem.* 246 (1983) 159.
- [8] F.E. Hahn, M. Tamm, *J. Organomet. Chem.* 456 (1993) C11.
- [9] F.E. Hahn, M. Tamm, *J. Chem. Soc. Chem. Commun.* (1993) 842.
- [10] (a) F.E. Hahn, M. Tamm, T. Lügger, *Angew. Chem.* 106 (1994) 1419; *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1356. (b) F.E. Hahn, M. Tamm, *Organometallics* 14 (1995) 2597. (c) M. Tamm, T. Lügger, F.E. Hahn, *Organometallics* 15 (1996) 1251.
- [11] F.E. Hahn, M. Tamm, *J. Chem. Soc. Chem. Commun.* (1995) 569.
- [12] F.E. Hahn, T. Lügger, *J. Organomet. Chem.* 481 (1994) 189.
- [13] K. Bartel, Dissertation, Ludwig-Maximilians-Universität München, 1976.
- [14] U. Kernbach, W.P. Fehlhammer, *Inorg. Chim. Acta* 235 (1995) 299.
- [15] E. Bär, J. Fuchs, D. Rieger, F. Aquilar-Parilla, H.-H. Limbach, W.P. Fehlhammer, *Angew. Chem.* 103 (1991) 88; *Angew. Chem. Int. Ed. Engl.* 30 (1991) 88.
- [16] W.M. Butler, J.H. Enemark, *Inorg. Chem.* 10 (1971) 2416.
- [17] 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.
- [18] M. Tamm, A. Grzegorzewski, F.E. Hahn, *J. Organomet. Chem.* 501 (1995) 309.
- [19] W.P. Fehlhammer, T. Bliß, J. Fuchs, G. Holzmann, *Z. Naturforsch. Teil B:* 47 (1992) 79.
- [20] W.P. Fehlhammer, W.A. Herrmann, K. Öfele, in: G. Brauer (Ed.), *Handbuch der Präparativen Anorganischen Chemie*, Ferdinand Enke, Stuttgart, 1981.
- [21] M.R. Churchill, *Inorg. Chem.* 12 (1973) 1213.
- [22] *International Tables for X-Ray Crystallography*, vol. IV, Kynoch, Birmingham, UK, 1974, Tables 2.2B and 2.3.1.
- [23] MOLEN: Molecular Structure Solution Procedures, Program Descriptions, Enraf–Nonius, Delft, Netherlands, 1990.