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Oxidative Addition of α-Bromoglycine to Palladium(0) and Platinum(0) Complexes: α-Metallated Amino Acids as Models for Intermediates in the Metal-Catalyzed Hydrogenation of Dehydroamino Acids☆

Bernd Kayser, Christopher Missling, Jörg Knizek[2], Heinrich Nöth[2], Wolfgang Beck*

Institut für Anorganische Chemie der Ludwig-Maximilians-Universität,
Meiserstraße 1, D-80333 München, Germany

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Oxidative addition of methyl *N*-benzoyl-2-bromoglycinate to bis(dibenzylideneacetone)palladium, in the presence of 2,2′-bipyridyl, and to $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ gives the α-metallated glycine esters **1a** and **2a**. Abstraction of bromide from **1a**, **2a**, using $AgSbF_6$ or $AgBF_4$, affords the cationic C,O-chelate complexes $[(bpy)Pd{-}CH(CO_2Me)NHC(Ph)O]^+$ (**1b**,**c**) and $[(Ph_3P)_2Pt{-}CH(CO_2Me)NHC(Ph)O]^+$ (**2b**), respectively, featuring coordination of the amide O atom. The complexes **1b** and **2b** have been characterized by X-ray diffraction.

α-Haloglycine esters are valuable synthons for the synthesis of modified α-amino acids[3]. Recently, we used these compounds for the introduction of α-amino acid residues into organometallic systems[4], giving products that may find application in the labelling of amino acids and peptides, a growing field in bioinorganic chemistry[5]. α-Metallated amino acids are intermediates in the asymmetric hydrogenation of dehydroamino acids and have been detected as such by Halpern et al.[6] and Brown et al.[7] by means of NMR spectroscopy.

Structures of α-metallated amino acids have been reported by Vahrenkamp et al.[8] and by ourselves[4b]. Recently, Bergens et al.[9] characterized a C,O-bound intermediate in the hydrogenation of methyl α-acetamidocinnamate, derived from a $(BINAP)(H)Ru^{II}$ catalyst.

The easy access to α-metallated amino acids by oxidative addition of methyl *N*-benzoyl-2-bromoglycinate to $Me_2Pt(bpy)$ (bpy = 2,2′-bipyridyl)[4b] prompted us to search for square-planar complexes with the halide and the *C*-bound α-amino acid in a *cis* configuration. Abstraction of halide from these should yield simple models for intermediates in the hydrogenation of dehydroamino acids, with coordination of the amide O atom.

The oxidative addition of organic halides to zerovalent palladium and platinum complexes[10], e.g. to $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$[11] or to $(dba)_2Pd$ (dba = dibenzylideneacetone)[12] is a general method for the synthesis of σ-bonded organometallic complexes.

Results and Discussion

The reactions of methyl *N*-benzoyl-2-bromoglycinate with $(dba)_2Pd$ in the presence of bpy, and with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ yielded the α-metallated complexes **1a** and **2a**, respectively, in good yields. The compounds were found to be light-sensitive and relatively unstable in air and towards organic solvents. Abstraction of bromide from **1a**, **2a**, using $AgSbF_6$ or $AgBF_4$, led to coordination of the amide group, thereby affording the stable C,O-chelate complexes **1b**,**c** and **2b**.

The IR spectra of **1a** and **2a** show typical ester and amide absorptions at 1715 and 1640 cm^{-1}. The shift of the carbonyl ester band to lower wavenumbers ($\tilde{\nu} \approx 30\ cm^{-1}$) compared with the corresponding band in α-amino acid esters has been observed previously[4b]. The lower wavenumber of the amide absorption in **1b**,**c** and **2b** (1600 cm^{-1}) is characteristic of a coordinated amide group. The ^{1}H-NMR spectrum of **1a** exhibits a doublet due to the CH proton, as expected, while that of complex **1c** features a broad singlet.

The signal of the Pt−CH proton in **2a** appears as a pseudo-quadruplet with satellites due to ^{195}Pt−C−H coupling. In the ^{1}H-NMR spectrum of **2b**, a doublet of triplets is observed for the α-CH proton due to *cis* and *trans* ^{31}P−Pt−C−H coupling.

The ^{13}C-NMR spectra of **1c** and **2b** show the expected resonances. Two ^{31}P-NMR signals for the two non-equivalent P atoms are observed for **2b**. Their ^1J(Pt−P) values differ significantly because of the different *trans* influence of the strong C and weak O donors, similar to the situation in $(Ph_3P)_2Pt{-}C(H)(CO_2R)C(O)O$[13].

Cationic alkyl- or acyl$(bpy)Pd^{II}$ complexes readily react with CO, isonitriles, alkenes or allenes[14]. Surprisingly, **1a** does not undergo insertion of CO, ethylene or allene at atmospheric pressure. Treatment with *tert*-butylisonitrile leads only to coordination of the isonitrile {$\tilde{\nu} = 2222\ cm^{-1}$ [ν(CN)]} and no insertion product could be detected.

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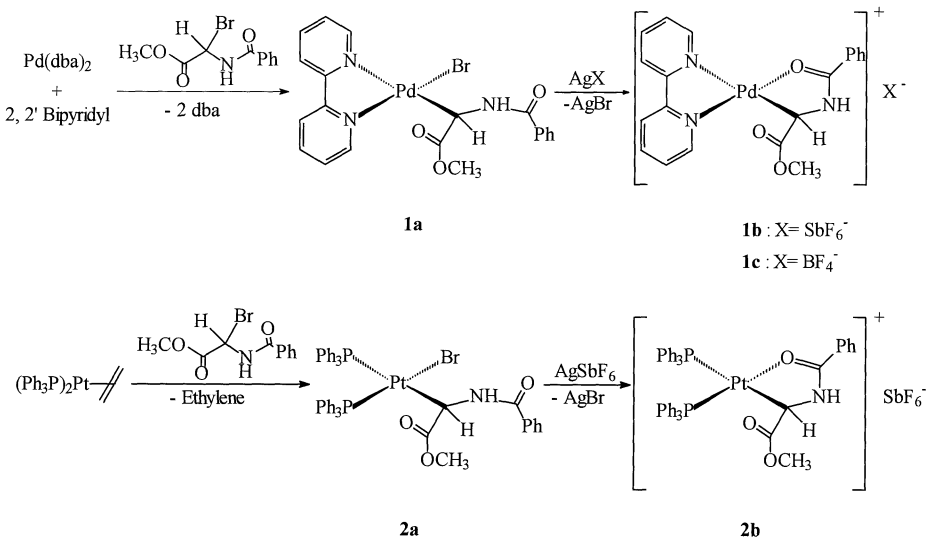
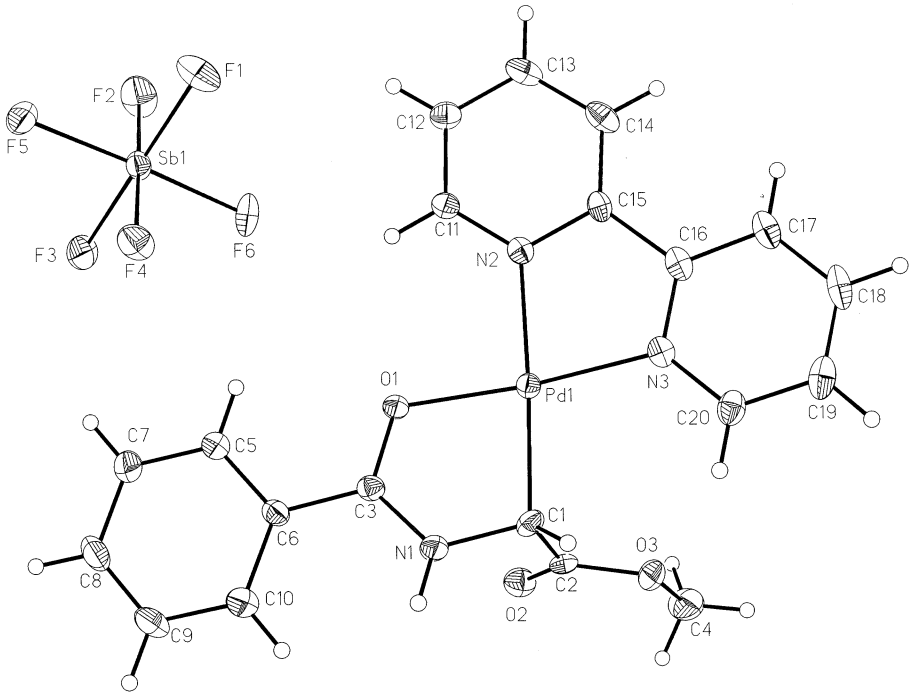


Figure 1. Molecular structure of **1b**[a]



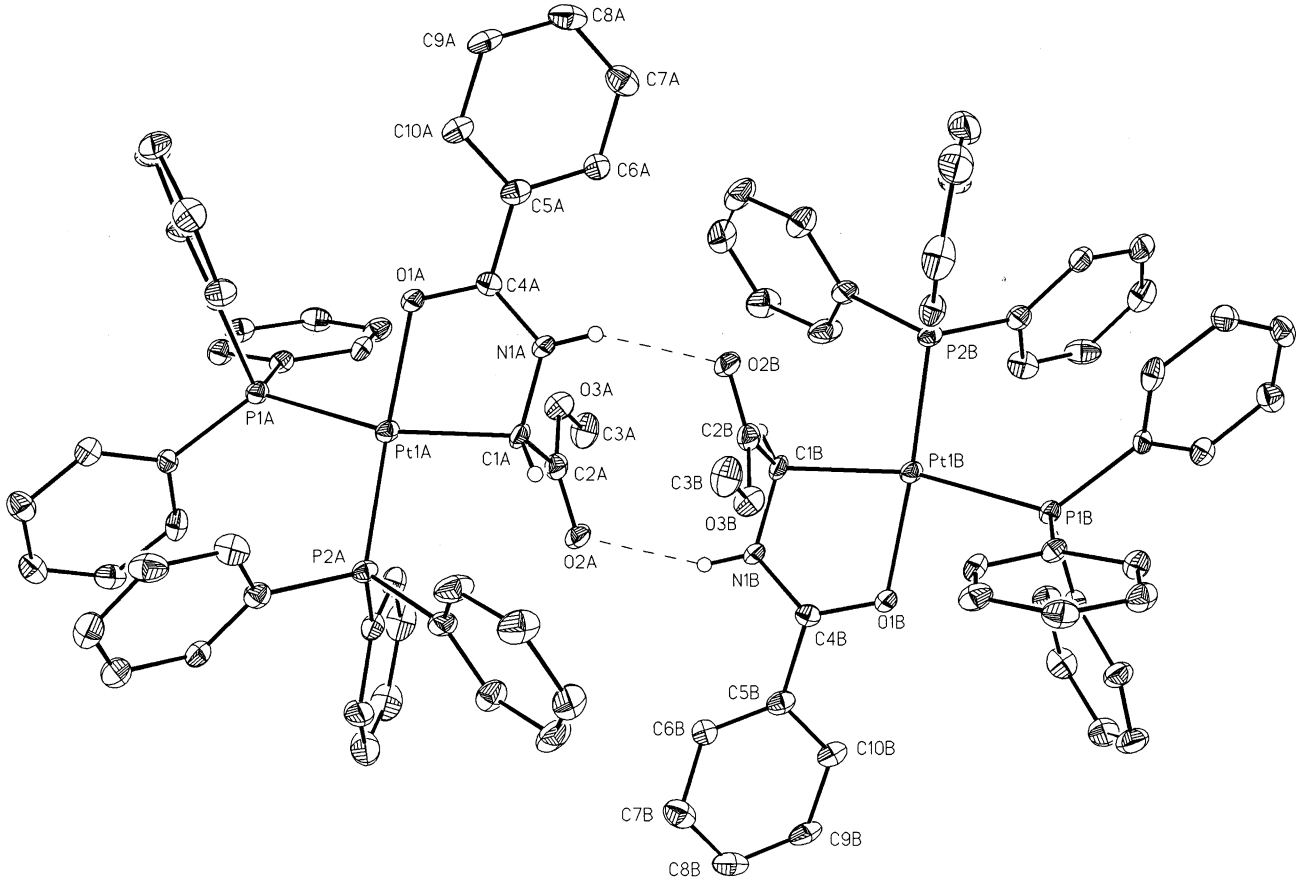
[a] Selected bond lengths [pm] and angles [°]: Pd1−N2 205.2(5), Pd1−N3 201.9(5), Pd1−O1 201.3(4), Pd1−C1 203.3(6), O1−C3 127.5(7), C3−N1 132.2(8), N1−C1 146.0(8); N2−Pd−N3 80.0(2), O1−Pd1−C1 82.4(2), Pd1−C1−N1 104.2(4), Pd1−O1−C3 113.4(4).

Crystal Structure Determinations of 1b and 2b

Crystals suitable for structure determination by X-ray diffraction were obtained by liquid-liquid diffusion of diethyl ether into an acetone solution of **1b** at room temperature and from a dichloromethane solution of **2b** layered with *n*-pentane. The unit cell of **1b** was found to contain the α*S* and α*R* enantiomers (at C1), with a parallel arrangement of the molecules and pairs of enantiomers (with a center of symmetry, Pd···Pd 427 pm) in the lattice. As expected on the basis of the spectroscopic data, the amino acid is coordinated to the Pd atom through the α-carbon atom and the amide group (Figure 1).

The palladium center in **1b** has a square-planar environment with Pd−N distances (203−205 pm) similar to those reported for related complexes[12][15]. The Pd−C distance [203.3(6) pm] compares well with values found for other sp^3 carbon atoms *trans* to an sp^2 nitrogen atom[15]. The acyl CO bond length [127.5(7) pm] is typical for a carbonyl group, although the CO absorption in the IR spectrum (1602 cm^{-1}) is suggestive of more single-bond character. The α-carbon atom is approximately tetrahedrally coordinated, with the largest deviation from ideal geometry being manifested in the N−C−Pd angle (104°). The chelate ring is almost planar and has a (small) O−C−N−C torsion angle of 11.7°.

Figure 2. Structure of **2b**[a]



[a] Selected bond lengths [pm] and angles [°]: Pt1−P1 232.8(2), Pt1−P2 223.3(2), Pt1−O1 208.9(4), Pt1−C1 210.0(6), O1−C4 128.1(7), C4−N1 130.9(8), N1−C1 146.0(8); P1−Pt1−P2 99.91(6), C1−Pt1−O1 80.8(2), Pt1−C1−N1 104.4(4), Pt1−O1−C4 112.1(4).

A similar structure is found for **2b**. The two P atoms in **2b** are seen to deviate from the coordination plane by 18° and 3.4°, respectively. The Pt−α-C bond length [210.0(6) pm] is comparable to that found in other platinum(II) complexes with Pt−α-alkyl bonds[16].

Interestingly, pairs of enantiomers α*S* and α*R* are found in the crystal (Figure 2), which are linked through two hydrogen bonds between the amino and the carbonyl groups of the methyl ester (N−H···O 286 pm).

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Experimental Section

General: All reactions were carried out in dry solvents under argon. − NMR: Jeol GSX 270 (^{1}H 270.0; ^{13}C 100.4; ^{31}P 109.3 MHz) with tetramethylsilane as internal standard; H_3PO_4 (85%) as external standard. − IR: 5ZDX FT-IR. − $(dba)_2Pd$[18], (η^2-ethylene)$(Ph_3P)_2Pt$[19] and methyl *N*-benzoyl-2-bromoglycinate[3b] were prepared according to literature procedures. $AgBF_4$ and $AgSbF_6$ were purchased from Aldrich and stored in the dark under argon.

(bpy)[CH(NHCOPh)(CO$_2$Me)]PdBr (**1a**): To a solution of 173 mg (0.3 mmol) of $(dba)_2Pd$ in 10 ml of benzene, 47 mg (0.3 mmol) of 2,2′-bipyridyl and 82 mg (0.3 mmol) of methyl *N*-benzoyl-2-bromoglycinate were added. The mixture was stirred for 1 h

Table 1. Details of the crystal structure determinations[17]

	1b	**2b**
Formula	$C_{20}H_{18}F_6N_3O_3PdSb$	$C_{46}H_{40}F_6NO_3P_2PtSb$
M_r	690.52	1147.57
Crystal system	monoclinic	triclinic
Space group	*P*2(1)/*c*	*P*$\bar{1}$
a [Å]	8.422(2)	11.9029(1)
b [Å]	18.357(4)	12.4852(1)
c [Å]	14.958(3)	16.3340(1)
α [°]	90°	94.012(1)
β [°]	105.643(9)	92.620(1)
γ [°]	90°	114.292(1)
V [Å^3]	2227.0(9)	2199.64(3)
Z	4	2
$\rho_{calcd.}$ [gcm^{-3}]	2.060	1.733
μ [mm^{-1}]	2.099	3.930
Crystal size	0.2 × 0.15 × 0.12	0.3 × 0.3 × 0.2
2θ range [°]	3.6−58.8	3.6−58.8
Index range	±*h*, ±*k*, ±*l*	±*h*, ±*k*, ±*l*
Collected reflns.	6146	13135
Independent reflns. [R_{int} (%)]	4281 [2.45]	7027 [3.21]
Max./min. transmissions	0.727/0.606	0.710/0.497
Parameters	307	596
*R*1/*wR*2 [*F* > 4σ(*F*)]	0.0488/0.0914	0.0424/0.1039
GoF	1.368	1.139
Largest diff. peak and hole [eÅ^{-3}]	0.445/−0.502	1.685/−2.364

at room temp., during the course of which a yellow-green powder precipitated. The precipitate was separated by centrifugation, washed with diethyl ether (2 × 10 ml), and dried in vacuo. Yield 128 mg (80%), yellow-green powder, m.p. 164°C. – IR (KBr): $\tilde{\nu}$ = 3407 cm^{-1} m (NH), 1716 s (CO_2), 1633 s (NCO). – ^1H NMR ($CDCl_3$): δ = 3.74 (s, 3 H, CH_3), 5.32 (d, ^3J = 9.2 Hz, 1 H, CH), 7.36–7.49 (m, 4 H, NH, C_6H_5), 7.57–7.74 (m, 2 H, bpy), 7.86–8.21 (m, 6 H, bpy, C_6H_5), 9.25 (d, ^3J = 3.94 Hz, 1 H, *o*-bpy), 9.35 (d, ^3J = 5.4 Hz, 1 H, *o*-bpy). – $C_{20}H_{18}N_3O_3BrPd \cdot 0.5C_6H_6$ (573.8): calcd. C 48.15, H 3.69, N 7.32; found C 47.97, H 3.71, N 7.26.

[CH(NHCOPh)(CO$_2$Me)](PPh$_3$)$_2$PtBr (**2a**): To a solution of 224 mg (0.3 mmol) of (η^2-ethylene)($Ph_3P)_2Pt$ in 10 ml of benzene, 82 mg (0.3 mmol) of methyl *N*-benzoyl-2-bromoglycinate was added. Gas evolution was observed and the yellow solution was stirred for 1 h. A white residue was separated by centrifugation, the volatiles were evaporated from the supernatant solution, and the residue was washed with pentane (3 × 15 ml). Yield 268 mg (90%), white powder, m.p. 104°C (decomp.). – IR (KBr): $\tilde{\nu}$ = 3413 cm^{-1} m (NH), 1713 s (CO_2), 1647 s (NCO), 280 m (PtBr). – ^1H NMR (C_6D_6): δ = 3.78 (s, 3 H, CH_3), 5.44 (pseudo-q, $^3J_{PH}$ = 9.7 Hz, $^2J_{PtH}$ = 93.6 Hz, 1 H, CH), 6.94–8.74 (m, 36 H, NH, C_6H_5, PPh_3). – ^{31}P NMR (C_6D_6): δ = 17.90 (d, $^2J_{PP}$ = 16.5 Hz, $^1J_{PtP}$ = 1902.9 Hz), 20.45 (d, $^2J_{PP}$ = 16.5 Hz, $^1J_{PtP}$ = 4481.5 Hz). – $C_{46}H_{40}NO_3BrP_2Pt$ (991.8): calcd. C 55.71, H 4.07, N 1.41; found C 55.51, H 4.76, N 1.75.

General Procedure for the Abstraction of Bromide from **1a** and **2a**: To a solution of 160 mg (0.3 mmol) of **1a** [or 297 mg (0.3 mmol) of **2a**] in 10 ml of acetone, a solution of 58 mg (0.3 mmol) of $AgBF_4$ or 103 mg (0.3 mmol) of $AgSbF_6$ in 5 ml of acetone was added. Reaction was indicated by the rapid precipitation of AgBr; the suspension was stirred for 1 h in the dark at room temp. and then the precipitate was separated by centrifugation. The colorless/yellow solution was concentrated in vacuo and the residue was washed with diethyl ether (**1b**,**c**) or pentane (**2b**) (2 × 15 ml) and dried in vacuo.

[(bpy)Pd–CH(CO$_2$Me)NHC(Ph)O]$^+$ BF$_4^-$ (**1c**): Yield 154 mg (95%), colorless powder, m.p. 193°C (decomp.). – IR (KBr): $\tilde{\nu}$ = 3410 cm^{-1} m (NH), 1707 s (CO_2), 1602 s (NCO), 1083 (BF_4^-). – ^1H NMR ($CDCl_3$ + DMSO): δ = 3.33 (s, 3 H, CH_3), 4.57 (s, 1 H, CH), 7.14–7.43 (m, 5 H, Ph, bpy), 7.71 (d, ^3J = 7.6 Hz, 2 H, Ph), 7.92 (pseudo-q, ^3J = 7.7 Hz, 2 H, bpy), 8.01–8.11 (m, 2 H, bpy), 8.43 (d, ^3J = 5.5 Hz, 1 H, bpy), 8.71 (d, ^3J = 5.2 Hz, 1 H, bpy), 9.77 (s, 1 H, NH). – ^{13}C NMR ($CDCl_3$ + DMSO): δ = 50.86, 51.25 (CH, CH_3), 122.30, 122.98, 126.64, 126.71, 126.73, 127.77, 128.07, 132.89, 140.07, 140.44, 147.62, 152.66, 152.71, 155.72 (bpy, Ph), 173.90, 178.63 (CO_2, NCO). – $C_{20}H_{18}BF_4N_3O_3Pd$ (541.6): calcd. C 44.35, H 3.35, N 7.76; found C 43.89, H 3.17, N 7.61.

[(Ph$_3$P)$_2$Pt–CH(CO$_2$Me)NHC(Ph)O]$^+$ SbF$_6^-$ (**2b**): Yield 309 mg (90%), colorless powder, m.p. 158°C (decomp.). – IR (KBr): $\tilde{\nu}$ = 3437 cm^{-1} m (NH), 1709 m (CO_2), 1607 m (NCO), 1098 (SbF_6^-). – ^1H NMR ($CDCl_3$): δ = 3.27 (s, 3 H, CH_3), 5.44 (dt, $^3J_{(PH)trans}$ = 9.9 Hz, $^3J_{(PH)cis}$ = 2.1 Hz, $^3J_{HH}$ = 2.1 Hz, $^2J_{PtH}$ = 46.8 Hz, 1 H, CH), 7.00–7.71 (m, 35 H, PPh_3, Ph), 8.24 (pd, $^4J_{PH}$ = 6.5 Hz, $^3J_{HH}$ = 2.1 Hz, 1 H, NH). – ^{13}C NMR ($CDCl_3$): δ = 50.62 (CH_3), 62.82 (dd, $^2J_{(PC)trans}$ = 81.8 Hz, $^2J_{(PC)cis}$ = 3.6 Hz, CH), 127.57–134.87 (m, 42 C, PPh_3, Ph), 173.64 (d, $^3J_{(PC)trans}$ = 4.7 Hz, CO_2), 180.78 (dd, $^3J_{(PC)trans}$ = 10.6 Hz, $^3J_{(PC)cis}$ = 3.4 Hz, NCO). – ^{31}P NMR ($CDCl_3$): δ = 8.33 (d, $^2J_{PP}$ = 19.8 Hz, $^1J_{PtP}$ = 4223.1 Hz), 22.87 (d, $^2J_{PP}$ = 19.8 Hz, $^1J_{PtP}$ = 2243.5 Hz). – $C_{46}H_{40}F_6NO_3P_2PtSb$ (1147.6): calcd. C 48.14, H 3.51, N 1.22; found C 48.53, H 3.89, N 1.24.

Crystal Structure Determinations: A suitable single crystal of **1b** or **2b** was mounted on a glass fibre with perfluoroether oil. After cooling to –80°C, the crystal was optically centered on a Siemens P4 four-circle diffractometer equipped with a CCD area detector. The dimensions of the unit cell were determined from the observed reflections (> 10 σ) in 4 × 15 frames with different ψ and χ orientations. Data collection was performed with 10-s exposures at two different χ settings with Δψ intervals of 0.3° (altogether 1296 frames). Data reduction was performed with the program SAINT of Siemens Analytical Instruments, and a semiempirical absorption correction was applied. The structures were solved by the heavy-atom method and successive Fourier synthesis using the SHELX-93 program (G.W. Sheldrick, University of Göttingen). All non-hydrogen atoms were refined anisotropically. H atoms bound to carbon atoms were placed in calculated positions and refined with a riding model. *N*-bonded H atoms were located in the difference Fourier synthesis and were freely refined with a fixed isotropic N. Selected crystallographic data and data relating to the structure solutions and refinement are summarized in Table 1.

☆ Dedicated to Professor *Wolfgang Herrmann*, as a mark of friendship and respect, on the occasion of his 50th birthday.

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[17] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100822. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambrige CB2 1EZ, U.K. [Fax: (internat.) + 44 (0)1223 336033; e-mail: deposit@ccdc.cam.ac.uk].
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