A Facile, Palladium-Catalyzed Synthesis of 1,1′-Bi(bicyclo[1.1.1]pentanes)

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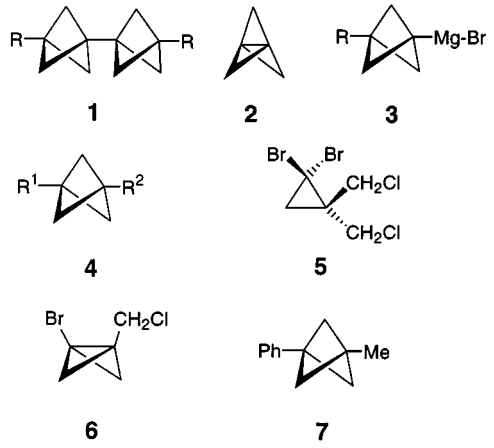
Symmetrically 3,3′-disubstituted 1,1′-bi(bicyclo[1.1.1]pentanes) were synthesized in a four-step procedure, using commercially available starting materials, in fair overall yields (51–60%). In this synthesis the final step is an unexpected bridgehead-to-bridgehead homocoupling of bicyclo[1.1.1]-pent-1-ylmagnesium halide catalyzed by palladium(II). Only 1.1 mol percent of bis(acetonitrile)palladium(II) chloride and two equivalents of bromomethane were necessary to accomplish this reaction. The bromomethane is essential to convert Pd^0 into Pd^{II}. The X-ray structure of the [2]staffane **1c** has been determined and shows a nonbonded C1–C3 distance of 1.907 Å in the bicyclo[1.1.1]pentyl subunit.

Introduction

Although a few methods have been developed for the synthesis of 1,1′-bi(bicyclo[1.1.1]pentanes) or [2]-staffanes **1** (for structures see Scheme 1)[1,2] a straightforward efficient synthetic route to **1** is still lacking. Recently, Michl and co-workers[3] published the results of a copper-mediated bridgehead-to-bridgehead coupling of 3-substituted bicyclo[1.1.1]pent-1-yllithium that yields some bi(bicyclo[1.1.1]pentanes) **1** in reasonable yields. However, attempts by the same authors to homocouple this compound with 50 mol percent of palladium or nickel reagents gave the staffanes **1** in yields of 26% and 38%, respectively.



Scheme 1

We have shown that alkyl or aryl Grignard reagents add to the [1.1.1]propellane **2** to give the bicyclo[1.1.1]pent-1-ylmagnesium halides **3**.[4,5] The bicyclo[1.1.1]pent-1-ylmagnesium halides **3** can be cross-coupled with bromoarenes using [dppf]$PdCl_2$ as the catalyst to afford the 1,3-disubstituted bicyclo[1.1.1]pentanes **4** in good yields.[6] Here we show that **3** can also be homocoupled to yield **1** by using a catalytic amount of bis(acetonitrile)palladium(II) chloride [$(CH_3CN)_2PdCl_2$]. The three steps were carried out in a one-pot reaction furnishing **1** with overall yields ranging from 51 to 60% (based on the Grignard reagent RMgX). Bromomethane, which is a by-product in the synthesis of [1.1.1]propellane **2**, and which is also present in the reaction mixture, acts as an oxidant for palladium(0).

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Results and Discussion

The Grignard reagents **3** were obtained by the addition of the corresponding organomagnesium halides to **2** as described previously.[4−6] The propellane **2** was generated from **5** with two equivalents of MeLi in ether.[7,8] The two equivalents of bromomethane that were formed from MeLi by lithium-bromine exchange with **5** and **6**, respectively, were not removed. The Grignard reagents **3** were then treated with 1.1 mol-% of [$PdCl_2(CH_3CN)_2$] and maintained for 48 hours at room temperature under an atmosphere of nitrogen. A conventional workup afforded the staffanes **1** in the isolated yields given in Table 1. The reactions leading to **1a**−**d** were performed in ether. The addition of the arylmagnesium halides to **2** with diethoxymethane (DEM) as the solvent has been found to give satisfactory results (reactions leading to **1e**−**g**).[5]

Table 1. Yields of **1** obtained from the palladium-catalyzed coupling reaction of **3**

1, **3**	R	Yields of **1** (%)
a	*tert*-Butyl	57
b	Cyclohexyl	51
c	Isopropyl	57
d	Cyclopentyl	60
e	Ph	53[a]
f	*p*-CH_3-C_6H_4	59
g	*p*-$Si(CH_3)_3$-C_6H_4	59

[a] By-product: 3-methyl-1-phenylbicyclo[1.1.1]pentane (**7**) (42%).

The formation of **1e** was accompanied by 3-methyl-1-phenylbicyclo[1.1.1]pentane (**7**) in 28% yield. It is unlikely that this by-product is formed by the methylation of the Grignard reagent **3e** with bromomethane. In a control experiment, a solution of **3e**, which also contained bromo-

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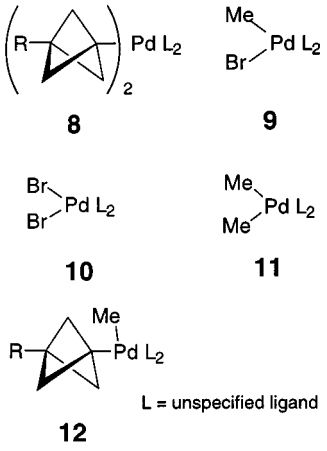
methane, was maintained for six days at room temperature. An aqueous workup afforded 1-phenylbicyclo[1.1.1]pentane as the sole product. Inspection of the NMR spectra of the crude products of **1a**−**d** and **1f** and **1g** showed the presence of trace impurities of the corresponding 3-methylbicyclo-[1.1.1]pentanes **4** (R^1 as indicated in Table 1).

The essential role of the bromomethane in this reaction was shown by initially removing the bromomethane and the ether solvent in vacuo. The residual Grignard reagent **3a** was then dissolved in pure anhydrous ether, 1.1 mol-% of $[PdCl_2(CH_3CN)_2]$ was added and after 48 hours a standard workup yielded the crude product. The ^1H NMR spectrum of the product showed that **1a** was not present. In a second experiment, a bromomethane-free solution of **3a** was charged with two equivalents of bromomethane and again maintained for two days at room temperature. In this case **1a** was isolated in a yield of 54%.

Concerning the mechanism of this reaction, the precursor of **1** should be the bis(organo)palladium complex **8**, which decomposes to **1** and Pd^0. Oxidative addition of bromomethane to Pd^0 would lead to **9**. We propose that **9** undergoes a symmetrization reaction leading to **10** and **11** (see Scheme 2). Structurally related gold or platinum compounds are known to show this type of reaction.[9] Transmetallation of **10** with the Grignard reagent **3** will furnish the intermediate **8**, whereas **11** is expected to decompose to ethane and Pd^0. Obviously, the symmetrization process of **9** should be considerably faster than the transmetallation of **9** to give **12**, the decomposition of which would lead to 3-methylbicyclo[1.1.1]pentanes of type **7**.



Scheme 2

The rate-determining steps in our postulated mechanism will strongly depend on the ligand L of the palladium catalyst. We have therefore investigated the influence of the catalyst on the yield of **1a** for the reaction of **3a** and bromomethane. The results are summarized in Table 2.

Remarkably, the presence of triphenylphosphane inhibited the reaction completely (entry 2, Table 2), presumably because the decomposition of the triphenylphosphane complex of **11** is rather slow at 20 °C.[9c] There is no significant difference between a Pd^{II} or a Pd^0 catalyst and even palladium on charcoal (entry 4, Table 2) is able to catalyze the reaction satisfactorily. The use of a nickel or platinum catalyst proved to be ineffective.

Table 2. Yields of **1a** from **3a** with different catalysts

Entry	Catalyst[a]	% Yield[b] of **1a**
1	$PdCl_2(CH_3CN)_2$	63
2	$PdCl_2(PPh_3)_2$	−
3	$Pd(dba)_2$	47
4	Pd/C	41
5	$NiCl_2$	−
6	$(NH_4)_2PtCl_6$	traces[c]

[a] Conditions: **3a** (16.8 mmol), catalyst (0.18 mmol), diethyl ether (25 mL), 72 h at 20 °C. − [b] Isolated yields. − [c] Determined by ^1H NMR spectroscopy.

X-ray Structure of 1c

The structure of compound **1c** (Figure 1) has been determined by X-ray diffraction analysis. The bridgehead-to-bridgehead distance C−C3 in **1c** is 1.9068(21) Å and is typical for bicyclo[1.1.1]pentanes. The distance between the two bicyclo[1.1.1]pentyl cages is 1.5002(27) Å and this is significantly shorter than the bond distance between two tertiary carbon atoms in other compounds, such as 1,1′-bi(adamantane) (1.58 Å),[10] but is in agreement with structurally related molecules.[1,11,12]

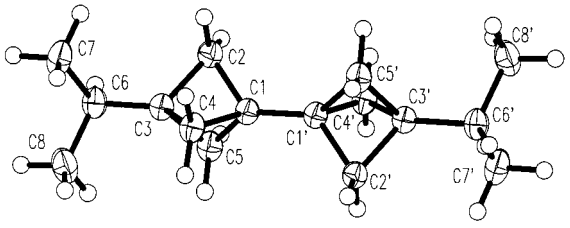


Figure 1. ORTEP Plot of **1c** (50% probability ellipsoids); selected bond lengths [Å] and angles [°]: C1−C3 1.907(3); C1−C2 1.552(3); C1−C1′ 1.500(3); C3−C6 1.525(3); C1−C2−C3 75.43(10); C2−C3−C4 87.23(12); C2−C3−C5 85.62(11)

Experimental Section

General: 1,1-Dibromo-2,2-bis(chloromethyl)cyclopropane (**5**) and [1.1.1]propellane (**2**) were prepared by literature methods.[7,8] Methyllithium in DEM was purchased from Chemetall AG. 3-Chloro-2-(chloromethyl)-1-propene, *tert*-butylmagnesium chloride and cyclopentylmagnesium bromide were purchased from Aldrich; isopropylmagnesium chloride and cyclohexylmagnesium chloride were purchased from Fluka. All the reactions were carried out under an atmosphere of nitrogen. Melting points were determined on a Büchi 530 and are uncorrected. ^1H (at 300 MHz) and ^{13}C NMR spectra (at 75 MHz) were measured in $CDCl_3$ on a Bruker DPX300 with TMS as an internal standard. IR spectra were recorded on a Perkin−Elmer 881 spectrometer. MS spectra were taken on a MSI Concept 1H. Elemental analyses were carried out by the Analytisches Labor des Instituts für Chemie der Humboldt-Universität zu Berlin.

General Procedure for the Preparation of 3a−g

a) Preparation of the Grignard Reagents 3a−d: 1,1-Dibromo-2,2-bis(chloromethyl)cyclopropane (**5**) was reacted with 2.00 equiv. of MeLi[7,8] to yield the [1.1.1]propellane **2** (in an assumed yield of

70%, based on **5**). To a solution of [1.1.1]propellane **2** in diethyl ether was added the Grignard reagent (0.95 equivalents based on **2**; **a**: *tert*-butylmagnesium chloride; **b**: cyclohexylmagnesium chloride; **c**: 2-propylmagnesium chloride, **d**: cyclopentylmagnesium chloride) at 0 °C and the solution was stirred for 48 h at room temperature. After this time, the propellane **2** had disappeared and the Grignard reagents **3a−d** had formed quantitatively.

b) Preparation of the Grignard Reagents 3e−g: 1,1-Dibromo-2,2-bis(chloromethyl)cyclopropane (**5**) was reacted with 2.00 equiv. of MeLi[7,8] to yield the [1.1.1]propellane **2** (in an assumed yield of 70%, based on **5**). To a solution of the [1.1.1]propellane **2** in diethoxymethane was added the Grignard reagent [0.95 equiv. based on **2**; **e**: phenylmagnesium bromide; **f**: *p*-methylphenylmagnesium bromide; **g**: *p*-(trimethylsilyl)phenylmagnesium bromide] at 0 °C and the solution was stirred for 6 days at room temperature. After this time the propellane **2** had disappeared and the Grignard reagents **3e−g** had formed quantitatively.

General Procedure for the Palladium-Catalyzed Reaction: $[PdCl_2(CH_3CN)_2]$ (1.1 mol-%, based on **2**) was added to a solution of **3a−g**. The solution turned brown and was then stirred for 48 h at room temperature. For the workup, aqueous NH_4Cl was added, the organic layer was separated and the aqueous layer was extracted with pentane (2 × 50 mL). The combined organic layers were washed twice with water, dried with $MgSO_4$, and the solvent removed in vacuo. The crude coupling product **1** was purified by flash chromatography with silica gel using pentane as the solvent. The yields of **1** are based on the Grignard reagent RMgX, which amounted to 64−67% of the starting tetrahalide **5**.

3,3′-Di-*tert*-butyl-1,1′-bi(bicyclo[1.1.1]pentane) (1a): a) 3a and $[PdCl_2(CH_3CN)_2]$: The general procedures for the preparation of **3a** from **5** and the subsequent reaction of **3a** with $[PdCl_2(CH_3CN)_2]$ were followed. Tetrahalide **5** (5.00 g, 16.8 mmol) was converted into **3a** and then reacted with $[PdCl_2(CH_3CN)_2]$ to yield a crude product. A standard workup and purification yielded **1a** (778 mg, 57%) as a colorless solid, m.p. 180 °C. − ^{1}H NMR: δ = 0.80 (s, 18 H), 1.35 (s, 12 H). − ^{13}C NMR: δ = 25.9 (q, 6 C), 29.4 (s, 2 C), 36.3 (s, 2 C), 46.5 (s, 2 C) 45.2 (t, 6 C). − IR (KBr): $\tilde{\nu}$ = 2958, 2953, 2927, 2902, 2864, 1358, 1210, 697 cm^{-1}. − MS (EI): *m*/*z* (%) = 133 (38), 119 (28), 105 (33), 91 (46), 83 (27), 67 (22), 57 (100), 55 (52), 41 (77). − $C_{18}H_{30}$ (246.4): calcd. C 87.73, H 12.27; found C 87.56, H 11.92.

b) 3a and $[PdCl_2(CH_3CN)_2]$ without Bromomethane: Tetrahalide **5** (5.00 g, 16.8 mmol) was reacted with methyllithium (1.4 M, 24.0 mL, 33.6 mmol) and then with *tert*-butylmagnesium chloride (2.0 M in diethyl ether, 5.40 mL, 10.80 mmol) to yield a solution of **3a**. The volatile materials were removed in vacuo and anhydrous diethyl ether was added. This solution was then charged with $[PdCl_2(CH_3CN)_2]$ (50 mg, 0.19 mmol). A standard workup and purification of the crude product yielded only traces of **1a** (as determined by ^{1}H NMR spectroscopy).

c) 3a, Purified, and $[PdCl_2(CH_3CN)_2]$ with Bromomethane: Tetrahalide **5** (5.00 g, 16.8 mmol), methyllithium (24.00 mL, 33.6 mmol) and *tert*-butylmagnesium chloride (2.0 M in diethyl ether, 5.40 mL,10.80 mmol) were treated according to the procedure described in b). The volatile materials were removed in vacuo and the residue was dissolved in anhydrous diethyl ether to yield a solution of **3a**. Bromomethane (about 5 mL) and $[PdCl_2(CH_3CN)_2]$ (50 mg, 0.19 mmol) were added to the solution of **3a** and the reaction mixture was maintained at room temperature for 48 h. A standard workup and purification yielded **1a** (739 mg, 54%)

d) 3a and Several Catalysts: Individual solutions of **3a** in ether, prepared by the procedure described in a) were charged with bis(dibenzylideneacetone)palladium(0) [$Pd(dba)_2$, 115 mg, 0.20 mmol], palladium (10%) on charcoal (180 mg), bis(triphenylphosphane)-palladium dichloride [$(Ph_3P)_2PdCl_2$, 126 mg, 0.18 mmol], $NiCl_2$ (23 mg, 0.18 mmol), or ammonium hexachloroplatinate [$(NH_4)_2PtCl_6$, 64 mg, 0.14 mmol]. After 72 h at room temperature a standard workup afforded **1a** in the yields given in Table 2.

3,3′-Dicyclohexyl-1,1′-bi(bicyclo[1.1.1]pentane) (1b): Tetrahalide **5** (5.00 g, 16.8 mmol) was converted into **3b** which, following the standard procedure, gave rise to **1b** (850 mg, 51%) as a colorless solid, m.p. 222 °C. − ^{1}H NMR: δ = 0.70−1.75 (m, 22 H), 1.33 (s, 12 H). − ^{13}C NMR: δ = 26.2 (t, 2 C), 26.4 (t, 4 C), 29.3 (t, 4 C), 38.3 (d, 2 C), 38.2 (s, 2 C), 42.2 (s, 2 C), 46.6 (t, 6 C). − IR (KBr): $\tilde{\nu}$ = 2957, 2956, 2920, 2903, 2864, 2850, 1445, 1203 cm^{-1}. − MS (EI): *m*/*z* (%) = 215 (10), 133 (50), 121 (30), 105 (62), 93 (60), 91 (64), 81 (50), 67 (87), 55 (100), 41 (84). − $C_{22}H_{34}$ (298.5): calcd. C 88.52, H 11.48; found C 88.17, H 11.54.

3,3′-Diisopropyl-1,1′-bi(bicyclo[1.1.1]pentane) (1c): Tetrahalide **5** (5.00 g, 16.8 mmol) was converted into **3c** which, following the standard procedure, gave rise to **1c** (700 mg, 57%) as a colorless solid, m.p. 35 °C. − ^{1}H NMR: δ = 0.79 (d, 12 H), 1.34 (s, 12 H), 1.62 (sp, 2 H). − ^{13}C NMR: δ = 18.8 (q, 4 C), 28.6 (d, 2 C), 37.9 (s, 2 C), 43.3 (s, 2 C), 46.3 (t, 6 C). − IR (KBr): $\tilde{\nu}$ = 2956, 2904, 2868, 1465, 1363, 1274, 1202, 893 cm^{-1}. − MS (EI): *m*/*z* (%) = 133 (28), 119 (65), 105 (58), 93 (64), 91 (100), 79 (54), 69 (66), 55 (50), 41 (94). − $C_{16}H_{26}$ (218.4): calcd. C 88.00, H 12.00; found C 87.98, H 11.67.

3,3′-Dicyclopentyl-1,1′-bi(bicyclo[1.1.1]pentane) (1d): Tetrahalide **5** (5.00 g, 16.8 mmol) was converted into **3d** which, following the standard procedure, gave rise to **1d** (910 mg, 60%) as a colorless solid, m.p. 122 °C. − ^{1}H NMR: δ = 1.20 (m, 4 H), 1.35 (s, 12 H), 1.51 (m, 12 H), 1.86 (m, 2 H). − ^{13}C NMR: δ = 25.7 (t, 4 C), 29.0 (t, 4 C), 39.0 (d, 2 C), 40.5 (s, 2 C), 41.2 (s, 2 C), 47.3 (t, 6 C). − IR (KBr): $\tilde{\nu}$ = 2954, 2901, 2863, 1445, 1270, 1199 cm^{-1}. − MS (EI): *m*/*z* (%) = 159 (11), 145 (18), 133 (30), 119 (65), 105 (38), 93 (50), 91 (100), 79 (59), 55 (33), 41 (97). − $C_{20}H_{30}$ (270.5): calcd. C 88.82, H 11.18; found C 88.42, H 10.85.

3,3′-Diphenyl-1,1′-bi(bicyclo[1.1.1]pentane) (1e) and 3-Methyl-1-phenylbicyclo[1.1.1]pentane (7): Tetrahalide **5** (5.00 g, 16.8 mmol) was converted into **3e** which, following the standard procedure, gave rise to a mixture of **1d** (850 mg, 53%; the analytical data match the previously published data[2]) and **7** (750 mg, 42%) as a colorless liquid, b.p. 80−85 °C (0.1 Torr). − ^{1}H NMR: δ = 1.27 (s, 3 H), 1.93 (s, 6 H), 7.25 (m, 5 H). − ^{13}C NMR: δ = 18.2 (q), 35.3 (s), 38.68 (s), 53.89 (t, 3 C), 126.0 (d, 1 C), 128.0 (d, 5 C), 141.5 (s). − IR (KBr): $\tilde{\nu}$ = 2958, 2918, 2905, 2865, 1277, 1153, 739 cm^{-1}. − MS (EI): *m*/*z* (%) = 154 (37), 91 (48), 77 (50), 55 (38), 43 (76), 41 (53), 39 (78), 29 (74), 18 (100). − $C_{12}H_{14}$ (158.2): calcd. C 91.08, H 8.92; found C 90.98, H 8.70.

3,3′-Bis(4-methylphenyl)-1,1′-bi(bicyclo[1.1.1]pentane) (1f): Tetrahalide **5** (5.00 g, 16.8 mmol) was converted into **3f** which, following the standard procedure, afforded **1f** (1.04 g, 59%) as a colorless solid, m.p. 214 °C: ^{1}H NMR: δ = 1.90 (s, 12 H) 2.32 (s, 6 H) 7.15 (s, 8 H). − ^{13}C NMR: δ = 21.1 (q, 2 C), 38.2 (s, 2 C), 40.5 (s, 2 C), 51.1 (t, 6 C) 125.9 (d, 4 C), 128.8 (d, 4 C), 135.8 (s, 2 C), 138.6 (s, 2 C). − IR (KBr): $\tilde{\nu}$ = 2992, 2964, 2918, 1904, 2867, 2851, 1520, 1443, 1333, 1208, 1110, 823 cm^{-1}. − MS (EI): *m*/*z* (%) = 314 [M$^+$] (1), 299 (15), 209 (39), 196 (95), 183 (49), 181 (61), 167 (50), 115 (57), 105 (100), 91 (64), 51 (17). − $C_{24}H_{26}$ (314.5): calcd. C 91.67, H 8.33; found C 91.43, H 8.16.

3,3′-Bis[3-(trimethylsilyl)phenyl]-1,1′-bi(bicyclo[1.1.1]pentane) (1g): Tetrahalide **5** (5.00 g, 16.8 mmol) was converted into **3g** which, fol-

Table 3. Crystal data and structure refinement for compound **1c**

	1c
Empirical formula	$C_{16}H_{26}$
M_r	218.37
a [Å]	12.119(3)
b [Å]	5.805(2)
c [Å]	10.248(2)
α [°]	90
β [°]	91.16(3)
γ [°]	90
Z	2
D_x [Mg/cm^3]	1.006
Crystal system	monoclinic
Space group	$P2_1/c$
Crystal size [mm]	0.57 × 0.38 × 0.15
θ range [°]	3.36−25.24
Reflections measured	4252
Independent reflections	1243
μ [mm^{-1}]	0.056
Max./min. transmission	0.9917/0.9690
Parameters	126
F(000)	244
GoF	0.979
Max./min Δρ [e Å^{-3}]	0.225/−0.172
$R1$[a]	0.0482
$wR2$[b]	0.1335

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for reflections with $I > 2\sigma(I)$. − [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_c^2)^2]\}^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and a and b were constants set by the program.

lowing the standard procedure, afforded **1g** (1.41 g, 59%) as a colorless solid, m.p. 252 °C. − ^{1}H NMR: δ = 0.25 (s, 18 H), 1.93 (s, 12 H) 7.24 (d, 4 H), 7.46 (d, 4 H). − ^{13}C NMR: δ = −1.1 (q, 6 C), 38.3 (s, 2 C), 40.7 (s, 2 C), 51.1 (t, 6 C), 125.5 (d, 4 C), 133.2 (d, 4 C), 138.1 (s, 2 C), 124.0 (s, 2 C). − IR (KBr): $\tilde{\nu}$ = 3030, 3014, 2961, 2904, 2867, 1601, 1389, 1246, 1208, 1117, 1064, 852, 754 cm^{-1}. − MS (EI): m/z (%) = 430 [M$^+$] (1), 416 (27), 254 (46), 239 (32), 225 (26), 200 (40), 167 (7), 73 (100). − $C_{28}H_{38}Si_2$ (430.8): calcd. C 78.07, H 8.89; found C 77.87, H 8.84.

X-ray Crystal Structure Determination of 1c: The crystal data of **1c** are given in Table 3. Measurements were carried out on a STOE Imaging Plate Diffraction System at 180 K using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Unit cell parameters were determined from a least-squares analysis of 1243 reflections (6.72° < 2θ < 50.48°). Intensities were measured by -oscillation scans. The structure was solved by direct methods and refined anisotropically on F^2 (SHELX-97).[13] Hydrogen atoms were isotropically included into the full-matrix least-squares refinement.[14]

Acknowledgments

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[14] Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crytallographic Data Centre as supplementary publication no. CCDC-151584. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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