New Borylene Complexes of the Type [μ-BX{(η^5-C_5H_4Me)Mn$(CO)_2$}$_2$]: Substitution Reactions at the Metal-Coordinated Borylene Moiety

Holger Braunschweig*[a] and Matthias Müller[b]

Institut für Anorganische Chemie der Technischen Hochschule[a],
Templergraben 55, D-52056 Aachen, Germany
E-mail: holger.braunschweig@ac.rwth-aachen.de

Chemical Crystallography Laboratory, University of Oxford[b],
9 Parks Road, Oxford OX1 3PD, UK

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The reaction of the air- and water-stable borylene complex [μ-$BNMe_2${(η^5-C_5H_4Me)Mn$(CO)_2$}$_2$] (**1a**) with a solution of HCl in Et_2O affords the corresponding chloroborylene complex [μ-Chloroborylenebis{dicarbonyl(η^5-methylcyclopentadienyl)manganese}(*Mn*–*Mn*)] (**2**). This compound easily undergoes further substitution reactions with protic reagents such as primary amines, alcohols and water at the metal coordinated borylene moiety with elimination of HCl, giving new products of the type [μ-BX{(η^5-C_5H_4Me)Mn$(CO)_2$}$_2$] (**3a**, **b**: X = NH*t*Bu, NHPh; **4a**, **b**: X = OMe, OEt; **5**: X = OH). All borylene complexes were isolated as crystalline solids in good yields and characterized by multinuclear NMR methods and IR spectroscopy in solution. In addition, the structure of **4b** in the crystalline state was determined by a single-crystal X-ray study.

Introduction

The first example of a structurally characterized transition metal complex showing a two-center two-electron bond between the metal and a threefold coordinated boryl moiety was reported in 1990. This compound, *fac*-[$IrH_2(PMe_3)_3(BC_8H_{14})$], was obtained from the reaction of [$IrH(PMe_3)_4$] with 9-borabicyclononane[1] by oxidative addition to the boron hydrogen bond to the iridium center with elimination of PMe_3. Since then a number of structurally authentic boryl complexes were described. The 1,2-dioxobenzo or "catechol" group as ligand to boron has had a privotal role in establishing these compounds, since most of them were obtained either by the reaction of an anionic transition metal complex with CatBCl (Cat = 1,2-$O_2C_6H_4$)[2a–d] or by oxidative addition of CatBH or Cat BBCat to a suitable transition metal center[3a–f]. There are only a few examples of such compounds with ligands other than the 1,2-dioxobenzo group at boron including the boryl complex [(Cp)Fe$(CO)_2BPh_2$][2a], the diborane(4)yl complexes [(Cp)M$(CO)_n${$B_2NMe_2)_2Cl$}] [(Cp)M$(CO)_n$ = (Cp)W$(CO)_3$, (Cp)Fe$(CO)_2$][4], and the η^1-borazine complex [{(C_5H_4Me)Fe$(CO)_2$}$_2ClB_3N_3H_3$][5].

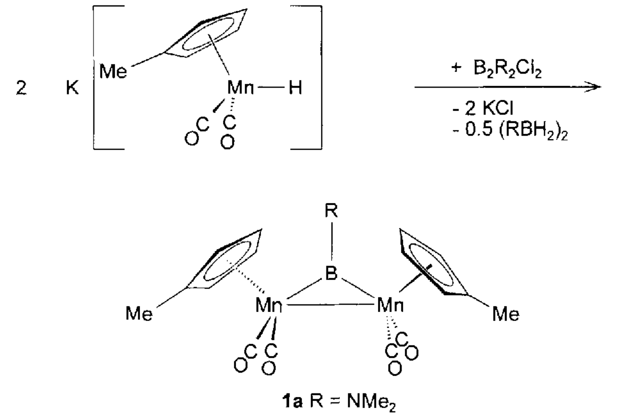
Despite the fact that there are some examples where transition-metal–boron bonds were calculated to be stronger than the corresponding metal–carbon bonds[6a,b], the metal-coordinated boryl group of such boryl complexes is easily cleaved in reactions with alcohols, secondary amines and dihydrogen. Likewise, the photochemically-induced activation of hydrocarbons by boryl complexes proceeds via splitting of the metal–boron bond under formation of metal-free boranes[2a,d;3e;7]. The preservation of a metal–boron linkage after such a reaction has not yet been reported.

In 1995 we isolated the first structurally characterized borylene complexes[8], and recently the synthesis of these compounds was significantly improved (Scheme 1)[9]. This paper describes a number of new borylene complexes of the type [η^5-C_5H_4Me)Mn$(CO)_2$}$_2$], which are obtained from the aminoborylene complex **1a** by substitution of the exocyclic boron-coordinated ligands with preservation of the central Mn_2B unit.

Results and Discussion

The aminoborylene complex [μ-$BNMe_2${(η^5-C_5H_4Me)-Mn$(CO)_2$}$_2$] (**1a**) is characterized by its high stability and

Scheme 1



1a R = NMe_2
1b R = CMe_3

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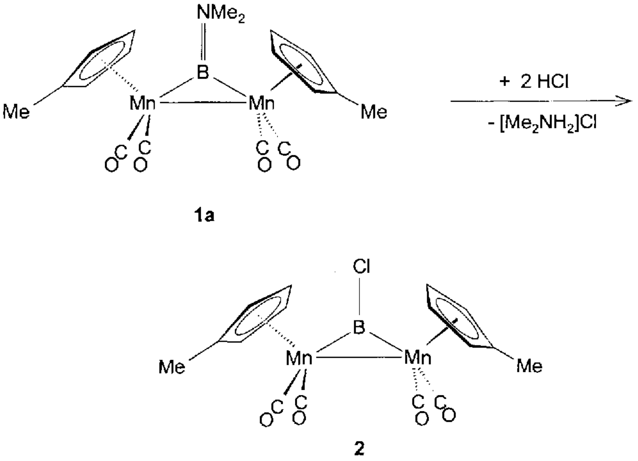
shows no reactivity towards protic reagents like alcohols, primary amines or even water. For example, this compound can be isolated in yield >60% from the aqueous phase after complete hydrolysis of the reaction mixture in air. With an excess of HCl disssolved in Et_2O, however, **1a** readily affords the corresponding chloroborylane complex [μ-BCl{(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$] (**2**) as a red crystalline solid in yields of up to 74% with formation of [Me_2NH_2]Cl (Scheme 2).

Scheme 2

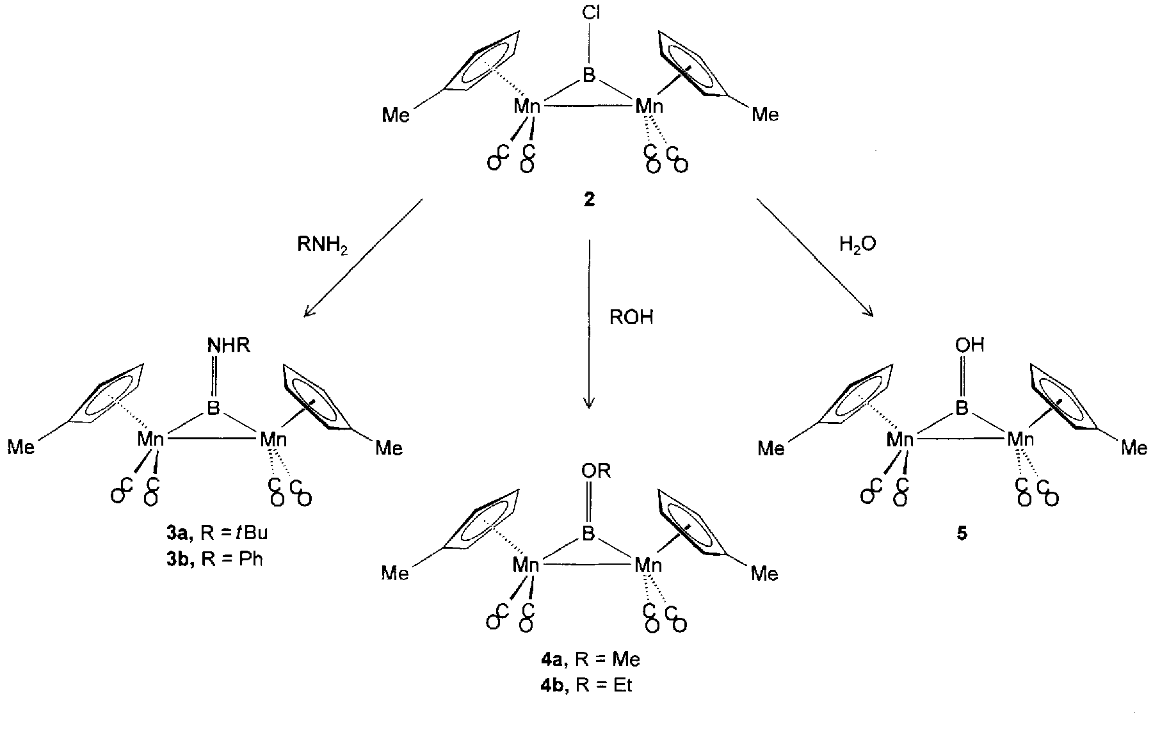


The solution structure of this compound has been derived from its NMR data. Due to less effective π-backbonding from chlorine to boron, the chloroborylene complex **2** exhibits a lowfield-shifted ^{11}B NMR signal with respect to the amino-substituted complex **1a** at δ = 133.5. In agreement with the known reactivity of amino- and chloroboranes, compound **2** is less stable towards air and water and displays a wider range of chemistry.

Treatment of [μ-BCl{(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$] (**2**) with two equivalents of a primary amine RNH_2 (R = *t*Bu, Ph; Scheme 3) yields the aminoborylene complexes [μ-BNHR{(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$] (**3a**, **b**) as orange and dark red crystals respectively, together with the corresponding ammoniumchlorides [RNH_3]Cl. In solution, both complexes show characteristic ^{1}H-NMR shifts for protons bound to nitrogen at δ = 5.33 and δ = 6.95 respectively. As expected, the ^{11}B-NMR signals for **3a**, **b** are found at about δ = 105, therefore in the same range as for [μ-BNMe$_2${(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$] (**1a**). Hence, the tendency of compounds **3a**, **b** to hydrolyse in solution at room temperature, after contact with traces of air or water, should be attributed to steric rather than electronic reasons, because all these aminoborylene complexes are expected to have similar BN-π-bonding components.

The reaction of [μ-BCl{(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$] (**2**) with alcohols, ROH (R = Me, Et), affords the alkoxoborylene complexes [μ-BOR{(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$] (**4a**, **b**), again as red, crystalline materials, with formation of HCl (Scheme 3). Almost quantitative yields of **4a**, **b** are obtained by simply dissolving **2** in the appropriate alcohol and evaporating the reaction mixture to dryness. Recrystallization of the crude materials from hexane affords analytically pure samples. These compounds show characteristic ^{11}B-NMR shifts in solution at about δ = 99 and 98, respectively, and no further spectroscopical pecularities are observed. The corresponding hydroxoborylene complex [μ-BOH{(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$] (**5**) is obtained in 81% yield by careful hydrolysis of [μ-BCl{(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$] (**2**) in

Scheme 3

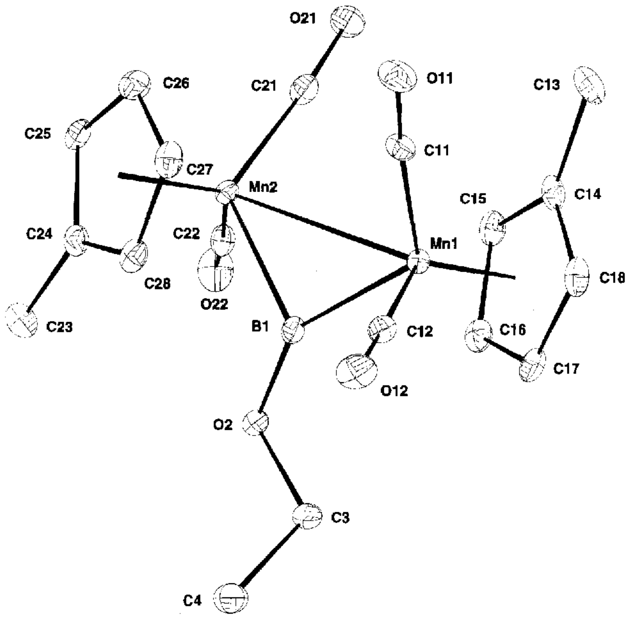


Et_2O. In contrast to **1a**, the chloroborylene complex **2** shows complete decomposition in water, hence it is necessary to carry out the hydrolysis in a suitable solvent. The solution ^{1}H-NMR spectrum of [μ-BOH{(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$] (**5**) contains a signal at $\delta = 6.18$ for the oxygen-bound proton, and the ^{11}B-NMR signal at $\delta = 101.6$ is in the expected range.

The IR spectra of the new borylene complexes are very similar. The expected broad NH and OH bands of the amino- and hydroxoborylene complexes **3a**, **b**, and **5** are shown at respectively at $\tilde{\nu}$ = 3174, 3183 and 3649 cm^{-1}. In addition, all compounds exhibit three CO stretching frequencies each, being in the range between $\tilde{\nu}$ = 2025 and 1852 cm^{-1}. These results, together with the ^{11}B-NMR data, show that the structures of compounds **2**–**5** in solution are essentially the same, which is known for the aminoborylene complex [μ-BNMe$_2${(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$] (**1a**)[8].

An X-ray structure analysis was carried out for [μ-BOEt{(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$] (**4b**) as a representative of the new complexes, and the results demonstrate that this structural similarity extends to the solid state (Figure 1). Suitable crystals of complex **4b** were obtained from hexane at −30°C, and the compound crystallizes in the noncentrosymmetric space group $P2_12_12_1$. The center of the molecule, which adopts C_1 symmetry, consists of an almost isosceles triangle which is formed by the two manganese atoms and the boron atom, with distances between boron and manganese of 198.9(2) pm and 202.1(2) pm, and a distance between the two manganese atoms of 281.75(5) pm. These values, as well as the angle Mn1–B–Mn2 of 89.3(1)°, are almost identical to the corresponding data for [μ-BNMe$_2${(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$] (**1a**)[8]. The distance between boron and oxygen is 134.2(3) pm, which is in the expected range.

Figure 1. Molecular structure of **4b**



Selected bond lengths [pm] and angles [°]; Mn1–Mn2 281.75(5), Mn1–B1 198.8(2), Mn2–B1 202.1(2), B1–O2 134.2(3), Mn1–Lp1 177.1, Mn2–Lp2 176.8; Mn2–Mn1–B1 45.82(7), Mn1–Mn2–B1 44.86(7), Mn1–B1–Mn2 89.3(1), B(1)–O(2)–C(3) 125.6(2); Lp1 is the point crossed by the plumbline from Mn1 through the plane formed by the atoms C14 to C18.

Conclusions

This study presents the first reactions at metal-coordinated boron with preservation of the metal–boron linkage. It was achieved by reaction of the very stable [μ-BNMe$_2${(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$] (**1a**) with HCl, giving the more reactive chloroborylene complex [μ-BCl(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$] (**2**), and subsequent substitution of the boron-bound chlorine in **2** by primary amines, alcohols or water. All these borylene complexes of the type [μ-BX{(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$] (**2**: X = Cl; **3a**, **b**: X = NH*t*Bu, NHPh; **4a**, **b**: X = OMe, OEt; **5**: X = OH), which were obtained in good yields as hexane-soluble, high-melting crystalline solids, adopt the same constitution in solution and in the crystal as the parent aminoborylene complex **1a**, as proved by NMR, IR, and X-ray studies.

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Experimental Section

All manipulations were carried out in dry nitrogen atmosphere in Schlenk glassware. Solvents and reagents were dried by standard procedures, distilled and stored under nitrogen and molecular sieves. [μ-BNMe$_2${(η^5-C_5H_4Me)Mn(CO)$_2$}$_2$][9] was synthesized as described in the literature. – NMR: Varian Unity 500 at 499.843 (^{1}H, TMS as internal standard), 150.364 (^{11}B, $BF_3 \cdot OEt_2$ in C_6D_6 as external standard), 125.639 MHz (^{13}C{^{1}H}, APT, TMS as internal standard); all NMR spectra were recorded in C_6D_6 as solvent. – Elemental analyses (C, H, N): Carlo-Erba elemental analyzer, model 1106. – IR: Perkin-Elmer FT-IR 1720x.

[μ-Chloroborylene-bis{dicarbonyl(η^5-methylcyclopentadienyl)-manganese}(Mn–Mn) (**2**): 0.92 g (2.11 mmol) of **1a** was dissolved in Et_2O (50 ml) at ambient temp. and 10 ml of a 1.0 M solution of HCl in Et_2O was added dropwise. After stirring for 20 h the solution was filtered and 0.66 g (74%) of the product was obtained from the filtrate at −30°C as a red crystalline solid, m.p. 113°C. – ^{1}H NMR δ = 1.74 (s, 6H, 2 Me), 3.92 (broad, 8H, 2 C_5H_4). – ^{11}B NMR: δ = 133.5. – ^{13}C NMR: δ = 13.07 (Me), 81.91, 82.05, 86.57, 87.12, 103.09 (C_5H_4). – IR (hexane): $\tilde{\nu}$ = 1969 cm^{-1}, 1941, 1912 (C=O). – $C_{16}H_{14}BClMn_2O_4$ (426.42): calcd. C 45.07, H 3.31; found C 44.54, H 3.36.

[μ-(tert-Butylamino)borylene-bis{dicarbonyl(η^5-methylcyclopentadienyl)manganese}(Mn–Mn) (**3a**): To a solution of 0.47 g (1.10 mmol) **2** in benzene (50 ml), neat *tert*-butylamine (0.24 ml, 2.26 mmol) was added at ambient temp. After stirring for 3 days, all volatiles were removed under high vacuum and the solid residue was extracted with 25 ml hexane. 0.33 g (65%) of the product was obtained from the filtrate at −30°C as an orange crystalline solid, m.p. 96°C. – ^{1}H NMR δ = 1.29 (s, 9H, CMe$_3$), 1.88 (s, 6H, 2 Me), 4.16 (broad, 8H, 2 C_5H_4), 5.33 (s, 1H, NH). – ^{11}B NMR: δ = 102.4. – ^{13}C NMR: δ = 13.48 (Me), 32.23 [NC(CH$_3$)$_3$], 54.12 (NC), 83.02, 84.23, 86.14, 87.40, 101.18 (C_5H_4), 234.23 and 236.64 (CO). – IR (toluene): $\tilde{\nu}$ = 3174 cm^{-1} (NH), 1932, 1921, 1852 (C=O). – $C_{20}H_{24}BMn_2NO_4$ (463.11): calcd. C 51.87, H 5.22, N 3.02; found C 51.35, H 4.99, N 2.82.

[μ-(Phenylamino)borylene-bis{dicarbonyl(η^5-methylcyclopentadienyl)manganese}(Mn−Mn) (**3b**): As described for **3a**, the reaction of 1.02 g (2.39 mmol) **2** with 0.45 ml (4.78 mmol) phenylamine in 40 ml benzene afforded 0.74 g (64%) of the product as a red crystalline solid, m.p. 152°C (decomp.). − ^{1}H NMR $\delta = 1.77$ (s, 6H, 2 Me), 4.12 (broad, 8H, 2 C_5H_4), 6.95 (s, 1H, NH), 7.20 (broad, 5H, C_6H_5). − ^{11}B NMR: $\delta = 107.6$. − ^{13}C NMR: $\delta = 13.48$ (Me), 82.70, 84.28, 85.59, 86.63, 101.77 (C_5H_4), 122.16, 123.88, 129.48 (C_6H_5), 231.11, 233.24 (CO). − IR (hexane): $\tilde{\nu} = 3183$ cm^{-1} (NH), 2025, 1943, 1927 (C=O). − $C_{22}H_{20}BMn_2NO_4$ (483.10): calcd. C 54.70, H 4.17, N 2.90; found C 54.34, H 4.36, N 3.05.

[μ-Methoxoborylene-bis{dicarbonyl(μ^5-methylcyclopentadienyl)manganese}(Mn−Mn) (**4a**): 0.35 g (0.82 mmol) **2** was dissolved in 40 ml methanol and stirred for 2 h at ambient temp. All volatiles were removed under high vacuum and recrystallization of the solid residue from 20 ml hexane gave 0.32 g (92%) of the product as a red crystalline solid, m.p. 106°C. − ^{1}H NMR $\delta = 1.82$ (s, 6H, 2 Me), 3.78 (s, 3H, OMe), 4.10 (broad, 8H, 2 C_5H_4). − ^{11}B NMR: $\delta = 98.9$. − ^{13}C NMR: $\delta = 13.35$ (Me), 59.45 (OMe), 82.07, 84.34, 86.63, 101.75 (C_5H_4), 229.54, 232.82 (CO). − IR (hexane): $\tilde{\nu} = 1978$ cm^{-1}, 1930, 1900 (C=O). − $C_{17}H_{17}BMn_2O_5$ (422.01): calcd. C 48.38, H 4.06; found C 48.18, H 4.21.

[μ-Ethoxoborylene-bis{dicarbonyl(η^5-methylcyclopentadienyl)manganese}(Mn−Mn) (**4a**): As described for **4a** 0.45 g (1.05 mmol) **2** was dissolved in 40 ml methanol and 0.43 g (94%) of the product was obtained as a red crystalline solid, m.p. 105°C. − ^{1}H NMR $\delta = 1.24$ (br, 3H, Me of OEt), 1.84 (s, 6H, 2 Me), 3.99−4.21 (br, 10H, 2 C_5H_4 and OCH_2). − ^{11}B NMR: $\delta = 97.6$. − ^{13}C NMR: $\delta = 13.35$ (Me), 16.98 (Me of OEt), 68.85 (OCH_2), 82.48, 84.05, 84.02, 85.93, 101.62 (C_5H_4), 229.71, 235.41 (CO). − IR (hexane): $\tilde{\nu} = 1978$ cm^{-1}, 1937, 1910 (C=O). − $C_{18}H_{19}BMn_2O_5$ (436.04): calcd. C 49.58, H 4.39; found C 49.50, H 4.31.

[μ-Hydroxoborylene-bis{dicarbonyl(η^5-methylcyclopentadienyl)manganese}(Mn−Mn) (**5**): 0.65 g (1.53 mmol) **2** was dissolved in 40 ml Et_2O and 0.10 ml (7.55 mmol) water was added. The mixture was stirred for 6 h at ambient temp. and all volatiles were removed under high vacuum. The solid residue was treated with 30 ml Et_2O, filtered and cooled to −30°C. 0.51 g (81%) of the product was obtained as a red crystalline solid, m.p. 112°C. − ^{1}H NMR $\delta =$ 1.77 (s, 6H, 2 Me), 4.08 (br, 8H, 2 C_5H_4), 6.18 (s, 1H, OH). − ^{11}B NMR: $\delta = 101.6$. − ^{13}C NMR: $\delta = 13.36$ (Me), 81.90, 82.06, 84.46, 101.49 (C_5H_4), 230.44, 232.99 (CO). − IR (toluene): $\tilde{\nu} =$ 3649 cm^{-1} (OH), 2018, 1969, 1926 (C=O). − $C_{16}H_{15}BMn_2O_5$ (407.98): calcd. C 47.10, H 3.71; found C 46.58, H 3.52.

Crystal Data of **4b**: $C_{18}H_{19}BMnO_5$, $M = 436.01$ g mol^{-1}, unit cell dimensions $a = 8.111(1)$ Å, $b = 14.051(1)$ Å, $c = 15.697(1)$ Å, $V = 1786.9$ Å^3, $P2_12_12_1$, $Z = 4$, $D_{\text{calcd.}} = 1.62$ g cm^{-3}, $\mu = 13.8$ cm^{-1}, crystal size [mm] 0.26 × 0.18 × 0.16. The data were collected at 150 K on an Enraf-Nonius DIP2020 image plate diffractometer with graphite-monochromated Mo−K_α radiation, $\lambda = 0.71069$ Å. 13829 reflections were measured ($1 < \Theta < 26°$, $+h$, $+k$, $+l$). Friedel's pairs were merged and 2045 unique reflections were obtained giving 1999 reflections with $I > 3\sigma(I)$. The image were processed with DENZO and SCALEPACK programs[10]. Corrections for Lorentz and polarisation effects but not for absorption, extinction or anomalous scattering were performed. Direct methods and fullmatrix least-squares refinement were applied. All non-hydrogen atoms were refined in anisotropic- and all hydrogen atoms in isotropic approximation. Restraints were used for the C23-methyl group (all H−C−H angles equal, all H−C−C angles equal). 2005 observations for 311 refined parameters resulted in an observations/refined parameters ratio of 6.5. Chebyshev weighting scheme[11] with parameters 1.36, 0.401, 1.19 was applied. Refinement on F converged at $R = 0.026$, $R_w = 0.024$, GOF = 1.15 with residual electron densities of −0.30 and 0.32 e Å^3. Refinement using unmerged Friedel's pairs resulted in a Flack parameter[12] of 0.50 (18), indicating merohedral twinning. Therefore the determination of the absolute configuration by taking into account anomalous scattering contributions was impossible. All crystallographic calculations were carried out using the CRYSTALS program package[13]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 100345. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: Int. code +44(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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