Transition Metal Substituted Acyl Phosphanes and Phosphaalkenes, 36[◇]

Synthesis and Structure of the First Carbyne Complex Functionalized Zwitterionic α-Carbenium Phosphinates [Tp′(CO)$_2$M≡C−P(O)$_2$−C(NR$_2$)$_2$] (M = Mo, W; R = Me, Et)

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Oxidation of the phosphaalkenyl-substituted carbyne complexes [Tp′(CO)$_2$M≡C−P=C(NR$_2$)$_2$] (**1a**: M = Mo, R = Me; **1b**: M = W, R = Me; **2a**: M = Mo, R = Et; **2b**: M = W, R = Et) with molecular dioxygen cleanly affords the orange carbyne complexes [Tp′(CO)$_2$M≡C−P(O)$_2$C(NR$_2$)$_2$] [**3a**: M = Mo, R = Me; **3b**: M = W; R = Me; **4a**: M = Mo, R = Et; **4b**: M = W, R = Et; Tp′ = HB(3,5-Me$_2$HC$_3$N$_2$)$_3$], which are functionalized at the methylidyne carbon atom by an α-carbenium phosphinate moiety. The novel compounds have been characterized by IR, ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy. In addition, the molecular structure of **4a** has been determined by a single-crystal X-ray structure analysis.

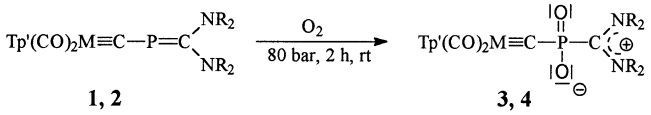
Introduction

In search for transition-metal complexes with terminal isophosphaalkyne ligands R−P≡C[2][3][4][5][6] we recently obtained phosphaalkenyl-substituted carbyne complexes of the type Tp′(CO)$_2$M≡C−P=C(NR$_2$)$_2$ (**1**, **2**)[1]. These molecules possess electrophilic and nucleophilic centres in close proximity which renders them promissing as precursors for a number of chemical transformations.

Herein we report on the facile oxidation of the phosphaalkenyl carbyne complexes **1**, **2** (M = Mo, W; R = Me, Et) with molecular dioxygen.

Results and Discussion

When crystalline samples of the phosphaalkenyl carbyne complexes **2a** and **2b** were exposed to air for two weeks, a color change from deep-red to orange-red took place. The same oxidation process could be achieved within 2 h using pure oxygen at a pressure of 80 bar. Similarly, compounds **1a** and **1b** were rapidly oxidized under O_2 pressure, whereas in air complete oxidation took about three weeks (eq. 1).



1, 2 **3, 4**

Tp′ = HB(3,5-Me$_2$HC$_3$N$_2$)$_3$
M = Mo **(a)**, W **(b)**
R = Me **(1, 3)**; R = Et **(2, 4)** (1)

Purification of the products was effected by column chromatography on silanized silica, using CH_2Cl_2 and ethanol as eluents, followed by crystallization of the orange-red powdery solids from a CH_2Cl_2/pentane mixture. Compared to the starting materials [**1a**: $\tilde{\nu}$(CO) = 1946, 1864 cm^{-1}; **1b**: 1935, 1848 cm^{-1}; **2a**: 1943, 1859 cm^{-1}; **2b**: 1933, 1845 cm^{-1}], the bands of the carbonyl stretching vibrations in the IR spectra of the products are significantly shifted to higher wavenumbers [**3a**: $\tilde{\nu}$(CO) = 2005, 1918 cm^{-1}; **3b**: 1987, 1893 cm^{-1}; **4a**: 2002, 1923 cm^{-1}; **4b**: 1989, 1894 cm^{-1}]. This observation is consistent with a decreased σ-donor/π-acceptor behavior of the novel organophosphorus carbyne ligands, compared with the phosphaalkenyl carbyne ligands in the precursors **1** and **2**. The PO_2 group of the carbenium phosphinate unit of the products gives rise to medium intensity bands at 1202−1205 and 1066−1068 cm^{-1}, which, by analogy with the IR data of numerous previously described phosphinates[7][8][9], are attributed to the asymmetric and symmetric PO_2 stretching vibrations.

The ^{13}C{^{1}H}-NMR spectra of **3a**, **b** and **4a**, **b** are especially interesting in the low field region, where doublets are observed at δ = 298.7−314.4 for the metal-bound carbon atoms of the carbyne ligands. In the ^{13}C{^{1}H}-NMR spectra of the starting materials, the corresponding resonances are observed at considerably lower field [**1a**: δ = 337 (d, $^1J_{PC}$ = 111.3 Hz); **1b**: 318.3 (d, $^1J_{PC}$ = 101.2 Hz); **2a**: 338.8 (d, $^1J_{PC}$ = 115.6 Hz); **2b**: 319.0 (d, $^1J_{PC}$ = 108.3 Hz)]. More remarkable is the dramatic decrease in the carbon-phosphorus coupling constants from the aforementioned values in **1**, **2a**, **b** to $^1J_{PC}$ = 28.2−54.0 Hz in the products. These observations can be explained in terms of a decreased

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electron transfer from the organophosphorus ligand to the metal and a decreased 3s orbital contribution in the C−P bond. Doublets at δ = 178.3−181.9 ($^1J_{PC}$ = 91.9−98.1 Hz) are assigned to the tricoordinate carbon atom of the [PC(NMe$_2$)$_2$] moiety of **3a**, **b** and **4a**, **b**. The oxidation of **1**, **2a**, **b** is accompanied by a considerable upfield shift of the resonance of this carbon atom [Δδ = 17.7−24.4], whereas the coupling constants $^1J_{PC}$ remain almost unaffected. The decreased donor capacity of the novel organophosphorus ligands in **3a**, **b** and **4a**, **b** is also reflected in the chemical shifts of the carbonyl carbon atoms, which are shifted from δ = 228.1−230.7 in **1**, **2a**, **b** to δ = 225.9−227.3 in the oxidation products.

The $^{31}P\{^1H\}$-NMR spectra of **3a**, **b** and **4a**, **b** display singlets (δ = −6.85 to +7.0) at higher fields compared to those of the precursors (δ = 49.0−65.9). Interestingly, in the tungsten derivatives **3b** and **4b**, the coupling constants $^2J_{PW}$ = 152.9 and 151.7 Hz clearly exceed the values measured from the spectra of **1b** ($^2J_{PW}$ = 51.4 Hz) and **2b** ($^2J_{PW}$ = 61.6 Hz). The ^{31}P-chemical shifts of our products may be compared to the ^{31}P-NMR data of $(Me_4Sb)^+(O_2PH_2)^-$ (δ = +1.70 in CH_2Cl_2) or $(Me_4Sb)^+(O_2PMe_2)^-$ (δ = −24.50 in CH_2Cl_2)[10].

The mass spectra (LSIMS) show the peaks of the molecular ions of **3a**, **b** and **4a**, **b** as parent ion peaks, underlining the fact that two oxygen atoms are added at the phosphorus centre of the starting materials.

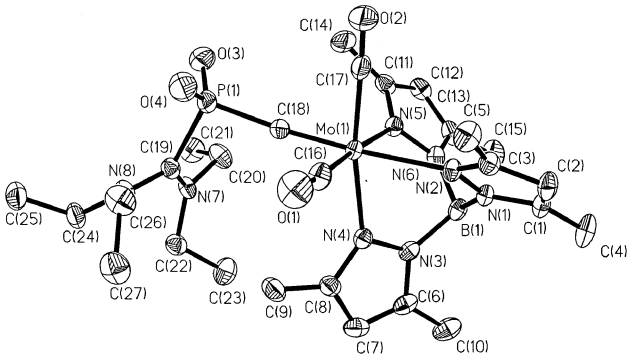
X-ray Structural Analysis of 4a

Single crystals of **4a** were grown from CH_2Cl_2/hexane at 5°C. The results of the structural determination are shown in Figure 1. Selected bond lengths and angles for the complex are given in the caption. Crystalline **4a** consists of monomeric molecules with distorted octahedral geometry. The bond angles between the organophosphorus ligand and the two carbonyl ligands [C(16)−Mo(1)−C(18) = 82.91(14)°; C(17)−Mo(1)−C(18) = 83.53(13)°] are more acute than those in **2b** [85.5(3)°; 88.1(3)°][1]. The angles between the nitrogen donor atoms N(2), N(4) and N(5) of the Tp′ ligand are comparable in **4a** [79.96(9)−83.68(9)°] and **2b** [80.3(2)−82.9(2)°], and are markedly smaller than the ideal 90°. The metal atom lies in the plane defined by the carbon atoms C(5), C(9), and C(14) (deviation 0.083 Å). The most interesting structural feature of the molecule is the geometry of the organophosphorus ligand. The bond length Mo(1)−C(18) of 1.813(3) Å compares well with the corresponding bond length in Tp′(CO)$_2$Mo≡C−S−C$_6$H$_4$NO$_2$-*p* [1.801(4) Å][11], hence this bond has to be regarded as a metal−carbon triple bond.

The valence angle at the *sp*-hybridized methylidene carbon atom Mo(1)−C(18)−P(1) of 166.8(2)° shows only slight deviation from linearity, as was also found for the corresponding valence angle W−C−P in **2b** [167.9(4)°] and for that in the ion [Tp′(CO)$_2$W≡C−PMe$_2$Ph]$^+$ [168.1(5)°][12]. However, unlike in **2b**, the bonds between the phosphorus atom and carbon atoms C(18) [P(1)−C(18) = 1.788(3) Å] and C(19) [P(1)−C(19) = 1.909(3) Å] differ significantly. The standard value for a P−C single bond is 1.85 Å[13]. The tetracoordinate phosphorus atom can be considered as being part of a phosphinate unit $[R^1R^2PO_2]^-$. The phosphorus−oxygen atomic distances differ in length [1.496(3) and 1.467(3) Å] and are shorter than the P−O bond lengths in the hypophosphite ion (1.51 Å)[14].

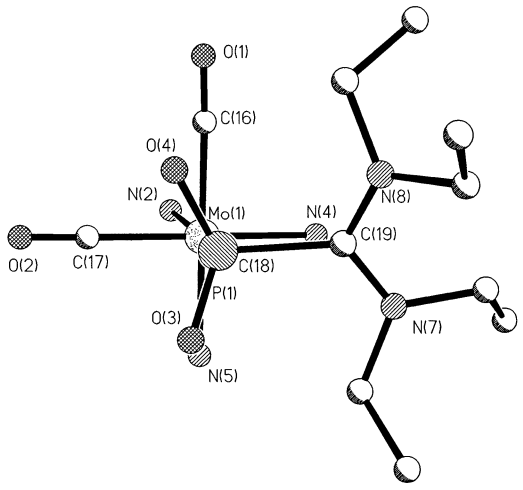
The fourth substituent at the phosphorus atom is a trigonal-planar bis(diethylamino)carbenium unit [sum of bond angles at C(19) = 359.9(2)°]. Accordingly, the carbon−nitrogen bond lengths N(7)−C(19) [1.333(4) Å] and N(8)−C(19) [1.347(4) Å] are shortened compared to the calculated value of a $C_{sp^2}-N_{sp^2}$ single bond [1.450 Å][15].

Figure 1. Molecular structure of **4a**[a]



[a] Selected bond lengths [C] and bond angles [°]: Mo(1)−C(18) 1.813(3), Mo(1)−C(16) 2.004(3), Mo(1)−C(17) 2.000(3), Mo(1)−N(2) 2.326(2), Mo(1)−N(4) 2.227(2), Mo(1)−N(5) 2.219(2), P(1)−O(3) 1.496(3), P(1)−O(4) 1.467(3), P(1)−C(18) 1.788(3), P(1)−C(19) 1.909(3), O(1)−C(16) 1.147(4), O(2)−C(17) 1.139(4), N(7)−C(19) 1.333(4), N(8)−C(19) 1.347(4); C(16)−Mo(1)−C(18) 82.91(14), C(17)−Mo(1)−C(18) 83.53(13), C(16)−Mo(1)−C(17) 87.54(14), C(16)−Mo(1)−N(5) 175.87(11), C(16)−Mo(1)−N(4) 94.70(12), C(17)−Mo(1)−N(4) 170.26(11), N(4)−Mo(1)−N(5) 83.68(9), N(2)−Mo(1)−N(4) 79.96(9), N(2)−Mo(1)−N(5) 82.84(9), N(2)−Mo(1)−C(18) 172.93(12), Mo(1)−C(18)−P(1) 166.8(2), C(18)−P(1)−O(3) 110.81(15), C(18)−P(1)−O(4) 111.03(15), C(18)−P(1)−C(19) 98.57(14), C(19)−P(1)−O(3) 105.24(14), C(19)−P(1)−O(4) 109.94(15), O(3)−P(1)−O(4) 119.10(16), P(1)−C(19)−N(7) 120.4(2), P(1)−C(19)−N(8) 119.4(2), N(7)−C(19)−N(8) 120.1(3).

Figure 2. View along the vector P(1)−C(18)−Mo(1); only the ligating atoms N(2), N(4) and N(5) of the tripod are drawn for clarity



The valence angle C(18)−P(1)−C(19) of 98.57(14)° is significantly compressed, compared with the corresponding C−P−C angle in **2b** [105.7(3)°]. The remarkably long interatomic distance P(1)−C(19) [1.909(3) Å] between the phosphinato and carbenium centres is surprising. It is conceivable that the positively charged carbon atom and the positively polarized phosphorus centre repel each other. The diaminocarbenium unit is oriented towards the tripod ligand in such a way that the bonds P(1)−C(19) and Mo(1)−N(4) are eclipsed (Figure 2).

The *trans*-influence of the methylidyne ligand is reflected in the Mo(1)−N(2) bond length of 2.326(2) Å, which significantly exceeds the lengths of the other two Mo−N bonds [2.219(2) and 2.227(2) Å], which are *trans*-oriented with respect to the carbonyl ligands.

Experimental Section

Unless stated otherwise, standard inert-atmosphere techniques were used for the manipulation of all reagents and reaction products. − Infrared spectra were recorded on a Bruker FT-IR IFS66 spectrometer. − ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were recorded in CD_2Cl_2 solution on Bruker AC 100 and Bruker AM Avance DRX 500 instruments. Standards: $SiMe_4$ (^{1}H, ^{13}C), external 85% H_3PO_4 (^{31}P). − Elemental analyses were performed in the Microanalytical Laboratory of the University of Bielefeld and in the Microanalytical Laboratory, H. Kolbe, Mülheim, Germany. − Mass spectra (LSIMS) (matrix: *p*-nitrobenzyl alcohol) were obtained with a Varian MAT-CH5-DF spectrometer.

The precursors [Tp′(CO)$_2$M≡C−P=C(NR$_2$)$_2$] (**1a**: M = Mo, R = Me; **1b**: W, Me; **2a**: Mo, Et; **2b**: W, Et) were synthesized according to literature procedures[1]. Dioxygen was taken from a cylinder. Silanized silica gel (Merck) was purchased commercially.

[Tp′(CO)$_2$Mo≡C−P(O)$_2$C(NMe$_2$)$_2$] (**3a**): A solution of [Tp′(CO)$_2$Mo≡C−P=C(NMe$_2$)$_2$] (**1a**) (0.80 g, 1.35 mmol) in 15 ml of dichloromethane was treated with dioxygen in an autoclave at 20°C and 80 bar for 3 h. Thereafter, the ^{31}P{^{1}H}-NMR spectrum of the solution displayed a singlet at δ = −6.8. The solvent and volatile components were then removed in vacuo (ca. 0.1 Torr), and the yellow-brown residue was chromatographed on silanized silica 60 (column: *l* = 15 cm, *d* = 2 cm). Elution with *n*-hexane (300 ml) afforded a yellow fraction, which was discarded. The column was developed with 200 ml of CH_2Cl_2. An orange-red zone was then eluted with ethanol (100 ml) and this fraction was concentrated to dryness. The powdery, ochre residue was dissolved in 25 ml of a CH_2Cl_2/hexane mixture (1:2), and the solution was stored for 7 days at −5°C. Orange-red needles of **3a** separated (0.55 g, 65.3%). − IR (KBr): $\tilde{\nu}$ = 2551 cm^{-1} w [ν(BH)], 2005 vs, 1918 vs [ν(CO)], 1202 m [ν_{as}(PO$_2$)], 1067 m [ν_s(PO$_2$)]. − ^{1}H NMR: δ = 2.36 (s, 3 H, Tp′CH$_3$), 2.41 (s, 3 H, Tp′CH$_3$), 2.64 (s, 6 H, Tp′CH$_3$), 2.78 (s, 6 H, Tp′CH$_3$), 3.42 (s, 12 H, NCH$_3$), 5.80 (s, 1 H, Tp′-H), 5.95 (s, 2 H, Tp′-H). − ^{13}C{^{1}H} NMR: δ = 12.3 (s, Tp′*C*H$_3$), 13.9 (s, Tp′*C*H$_3$), 15.7 (s, Tp′*C*H$_3$), 38.1 (s, NCH$_3$), 106.0 (s, Tp′*C*H), 144.9 (s, Tp′*C*CH$_3$), 145.5 (s, Tp′*C*CH$_3$), 150.8 (s, Tp′*C*CH$_3$), 178.3 (d, $^{1}J_{PC}$ = 93.2 Hz, PCN$_2$), 226.5 (s, CO), 312.6 (d, $^{1}J_{PC}$ = 30.3 Hz, Mo≡C). − ^{31}P{^{1}H} NMR: δ = −6.85 (s). − MS: *m/z* = 626 [M$^+$] (^{98}Mo), 570 [M$^+$ − 2 CO] (^{98}Mo). − $C_{23}H_{34}BMoN_8O_4P$ (624.31): calcd. C 44.25, H 5.49, N 17.95; found C 42.20, H 5.52, N 17.19. Solid samples retained varying amounts of CH_2Cl_2 despite prolonged drying in vacuo.

[Tp′(CO)$_2$W≡C−P(O)$_2$C(NMe$_2$)$_2$] (**3b**): Analogously to the preparation of **3a**, a sample of 0.49 g (58.5%) of orange-red **3b** was obtained by the oxidation of 0.80 g (1.18 mmol) of **1b**. − IR (KBr): $\tilde{\nu}$ = 2551 cm^{-1} w [ν(BH)], 1987 vs [ν(CO)], 1893 vs [ν(CO)], 1202 m [ν_{as}(PO$_2$)], 1067 m [ν_s(PO$_2$)]. − ^{1}H NMR: δ = 2.35 (s, 3 H, Tp′CH$_3$), 2.38 (s, 3 H, Tp′CH$_3$), 2.41 (s, 6 H, Tp′CH$_3$), 2.66 (s, 6 H, Tp′CH$_3$), 3.41 (s, 12 H, NCH$_3$), 5.82 (s, 1 H, Tp′-H), 5.99 (s, 2 H, Tp′-H). − ^{13}C{^{1}H} NMR: δ = 12.6 (s, Tp′*C*H$_3$), 15.0 (s, Tp′*C*H$_3$), 16.9 (s, Tp′*C*H$_3$), 45.1 (s, NCH$_3$), 106.8 (s, Tp′*C*H), 145.4 (s, Tp′*C*CH$_3$), 146.2 (s, Tp′*C*CH$_3$), 152.2 (s, Tp′*C*CH$_3$), 152.4 (s, Tp′*C*CH$_3$), 179.4 (d, $^{1}J_{PC}$ = 91.9 Hz, PCN$_2$), 225.9 (s, CO), 298.7 (d, $^{1}J_{PC}$ = 46.2 Hz, W≡C). − ^{31}P{^{1}H} NMR: δ = 6.6 ($^{2}J_{PW}$ = 152.9 Hz). − MS: *m/z* = 713 [M$^+$], 656 [M$^+$ − 2 CO]. − $C_{23}H_{34}BN_8O_4PW$ (712.22): calcd. C 38.78, H 4.81, N 15.73; found C 38.39, H 4.78, N 15.66.

[Tp′(CO)$_2$Mo≡C−P(O)$_2$C(NEt$_2$)$_2$] (**4a**): As described above, a sample of **2a** (0.90 g, 1.39 mmol) was converted into orange-red **4a** by treatment with molecular dioxygen (yield: 0.67 g, 70.8%). − IR (KBr): $\tilde{\nu}$ = 2551 cm^{-1} w [ν(BH)], 2002 vs [ν(CO)], 1923 vs [ν(CO)], 1203 m [ν_{as}(PO$_2$)], 1066 m [ν_s(PO$_2$)]. − ^{1}H NMR: δ = 1.27 (t, $^{3}J_{HH}$ = 7.1 Hz, 12 H, CH$_2$C*H*$_3$), 2.31 (s, 6 H, Tp′CH$_3$), 2.37 (s, 6 H, Tp′CH$_3$), 2.62 (s, 6 H, Tp′CH$_3$), 3.89 (q, $^{3}J_{HH}$ = 7.1 Hz, 8 H, C*H*$_2$CH$_3$), 5.75 (s, 1 H, Tp′-H), 5.89 (s, 2 H, Tp′-H). − ^{13}C{^{1}H} NMR: δ = 12.9 (s, Tp′*C*H$_3$), 13.9 (s, NCH$_2$*C*H$_3$), 14.5 (s, Tp′*C*H$_3$), 16.4 (s, Tp′*C*H$_3$), 48.1 (s, N*C*H$_2$CH$_3$), 106.6 (s, Tp′*C*H), 145.3 (s, Tp′*C*CH$_3$), 145.9 (s, Tp′*C*CH$_3$), 151.4 (s, Tp′*C*CH$_3$), 181.0 (d, $^{1}J_{PC}$ = 95.3 Hz, PCN$_2$), 227.3 (s, CO), 314.4 (d, $^{1}J_{PC}$ = 28.2 Hz, Mo≡C). − ^{31}P{^{1}H} NMR: δ = −6.51 (s). − MS: *m/z* = 682 [M$^+$] (^{98}Mo), 626 [M$^+$ − 2 CO] (^{98}Mo). − $C_{27}H_{42}BMoN_8O_4P$ (680.42): calcd. C 47.66, H 6.22, N 16.47; found C 46.20, H 6.21, N 15.99. Solid samples retained varying amounts of CH_2Cl_2 despite prolonged drying in vacuo.

[Tp′(CO)$_2$W≡C−P(O)$_2$C(NEt$_2$)$_2$] (**4b**): As described above, 0.65 g (77.9%) of orange-red **4b** was prepared by oxidation of 0.80 g (1.09 mmol) of **2b** with dioxygen at 80 bar. − IR (KBr): $\tilde{\nu}$ = 2552 cm^{-1} w [ν(B−H)], 1989 vs [ν(CO)], 1894 vs [ν(CO)], 1205 m [ν_{as}(PO$_2$)], 1068 m [ν_s(PO$_2$)]. − ^{1}H NMR: δ = 1.30 (t, $^{3}J_{HH}$ = 6.8 Hz, 12 H, CH$_2$C*H*$_3$), 2.34 (s, 3 H, Tp′CH$_3$), 2.37 (s, 3 H, Tp′CH$_3$), 2.40 (s, 6 H, Tp′CH$_3$), 2.69 (s, 6 H, Tp′CH$_3$), 3.92 (q, $^{3}J_{HH}$ = 6.8 Hz, 8 H, C*H*$_2$CH$_3$), 5.81 (s, 1 H, Tp′-H), 5.97 (s, 2 H, Tp′-H). − ^{13}C{^{1}H} NMR: δ = 12.7 (s, Tp′*C*H$_3$), 13.9 (s, NCH$_2$*C*H$_3$), 15.0 (s, Tp′*C*H$_3$), 17.1 (s, Tp′*C*H$_3$), 47.9 (s, N*C*H$_2$CH$_3$), 106.8 (s, Tp′*C*H), 145.4 (s, Tp′*C*CH$_3$), 146.2 (s, Tp′*C*CH$_3$), 152.5 (s, Tp′*C*CH$_3$), 181.9 (d, $^{1}J_{PC}$ = 98.1 Hz, PCN$_2$), 226.5 (s, CO), 299.9 (d, $^{1}J_{PC}$ = 54.0 Hz, W≡C). − ^{31}P{^{1}H} NMR: δ = 7.0 (s, $^{2}J_{WP}$ = 151.7 Hz). − MS: *m/z* = 769 [MH$^+$], 712 [M$^+$ − 2 CO]. − $C_{27}H_{42}BN_8O_4PW$ (768.33): calcd. C 42.21, H 5.51, N 14.58; found C 41.91, H 5.51, N 14.35.

X-ray Crystal Structure Determination of **4a**: Single crystals of **4a** were grown from CH_2Cl_2/hexane at 5°C. A red crystal with the approximate dimensions 0.1 × 0.15 × 0.3 mm^3 was examined with a Siemens SMART CCD area detector system with three axis geometry using Mo-K_α radiation at 173 K. Crystal data and refinement details: Cell dimensions *a* = 16.8674(9), *b* = 15.8355(8), *c* = 13.6762(7) Å, β = 102.9790(10)°, *V* = 3559.6(3) Å^3, *Z* = 4, d_{calcd} = 1.428 g cm^{-3}, μ = 0.608 mm^{-1}, space group $P2_1/c$, data collection of 7737 unique intensities ($2\theta_{max}$ = 54°), semiempirical absorption correction from equivalents, structure solution by direct methods and anisotropic refinement with full-matrix least-squares methods on F^2 for all non-hydrogen atoms, programs used: Siemens SHELXTL-PLUS, SHELXL-97, R_F = 0.0478 for 6115 reflections with $I > 2\ \sigma(I)$, wR_F^2 = 0.0965 for all data, largest diff. peak 0.775 eÅ^{-3}.[16]

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[16] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100859. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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