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Tungstaarsirenes: Synthesis and Structure of η^2-Arsinocarbene Complexes of Tungsten $[(\eta^5\text{-}C_5H_5)(CO)_2\overline{W{=}C(R){-}As}Ph_2][PF_6]$[†]

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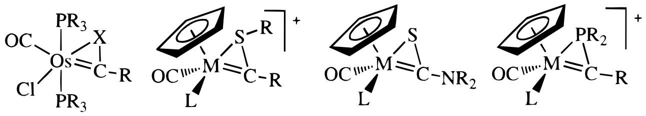
The reaction of the carbyne complexes $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CR$ (R = Me, Ph, Tol) with chlorodiphenylarsine, Ph_2AsCl, provides in the presence of thallium hexafluorophosphate the novel cationic η^2-arsinocarbene complexes $[(\eta^5\text{-}C_5H_5)(CO)_2\overline{W{=}C(R){-}As}Ph_2][PF_6]$ (**2a**−**c**) in high yields. The constitution of the new tungstaarsacyclopropene complexes was determined by spectroscopic investigation and, in the case of the 4-methylphenyl-substituted compound **2c**, additionally by X-ray single-crystal structure determination.

Introduction

The classification of transition-metal carbene and carbyne complexes[1−3] according to Fischer and Schrock can be followed from the electrophilic or nucleophilic behavior of the carbene/carbyne (alkylidene/alkylidyne) complexes. Besides the usual alkyl, aryl, amino, and alkoxy substituents for transition-metal carbene complexes $L_nM{=}CR^1R^2$ a large number of various combinations with heteroatoms of the group 14 to 17 of the periodic table has been established and characterized so far. The huge amount of acyclic carbene complexes is accompanied by only a few examples with a cyclic structure, as in $(\eta^5\text{-}C_5H_5)(CO)_{2-n}(PMe_3)_n\overline{M{=}C(R)N{=}NN}\text{-}(CH_2)_nCOOR$ (M = Mo, W; R = alkyl, aryl; *n* = 0, 1).[4] Further investigations have shown that with the heteroatoms phosphorus,[5−7] sulfur,[8−11] selenium,[9] and tellurium[9] even smaller ring systems could be formed.

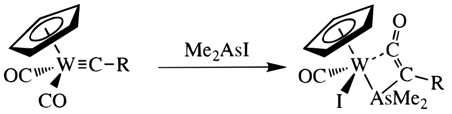
First attempts to synthesize η^2-arsinocarbene complexes—acyclic representatives are already known from the work of Fischer[12]—by treating $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CR$ with iododimethylarsine have failed. Unfortunately, the latter synthon undergoes a base-induced CC-coupling reaction, affording η^3-arsinoketene complexes.[13] In this respect, the reaction behavior of the haloarsines is similar to those known from the corresponding halophosphines. Subsequent efforts to dehalogenate the ketene complexes with $Tl[PF_6]$ or $Na[BPh_4]$ have not been successful. However, η^2-arsinocarbene complexes have been obtained in the reaction of $(\eta^5\text{-}C_5H_5)\text{-}(CO)_2W{\equiv}CR$ with Ph_2AsCl in the presence of convenient dehalogenating reagents such as $Tl[PF_6]$.



M = Mo, W; R = alkyl, aryl; L = CO, PR$_3$; X = S, Se, Te

Figure 1. Well-known cyclic transition-metal carbene complexes.

Scheme 1



Results and Discussion

The addition of chlorodiphenylarsine to the dicarbonyl cyclopentadienyl (alkyl/aryl)carbyne complexes of tungsten $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CR$ (**1a**−**c**; R = Me, Ph, Tol) generates in the presence of thallium hexafluorophosphate the first η^2-arsinocarbene complexes $[(\eta^5\text{-}C_5H_5\text{-}(CO)_2\overline{W{=}C(R){-}As}Ph_2][PF_6]$ (**2a**−**c**) in high yields.

The yellow diamagnetic compounds are soluble in dichloromethane or acetone. The constitution and structure of **2a**−**c** have been confirmed by elemental analysis, infrared, and ^1H, ^{13}C, and ^{31}P NMR spectroscopy and, in the case of **2c**, by an additional single-crystal X-ray analysis.

[†] Dedicated to Professor Wolfgang Beck on the occasion of his 65th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

(1) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983.

(2) Engel, P. F.; Pfeffer, M. *Chem. Rev.* **1995**, *95*, 2281.

(3) Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schrock, R. R.; Schubert, U.; Weiss, K. *Carbyne Complexes*; VCH: Weinheim, Germany, 1988.

(4) Stegmair, C. M.; Schütt, W.; Ullrich, N.; Kiprof, P.; Ostermeier, J.; Kreissl, F. R. *J. Organomet. Chem.* **1994**, *447*, 251.

(5) Fischer, E. O.; Reitmeier, R.; Ackermann, K. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 411.

(6) Huy, N. H. T.; Fischer, J.; Mathey, F. *Organometallics* **1988**, *7*, 240.

(7) Lehotkay, Th.; Wurst, K.; Jaitner, P.; Kreissl, F. R. *J. Organomet. Chem.* **1996**, *523*, 105.

(8) Kreissl, F. R.; Schütt, W.; Stegmair, C. M.; Ullrich, N.; Keller, H.; Ostermeier, J.; Herdtweck, E. *Chem. Ber.* **1993**, *126*, 1609.

(9) Clark, G. R.; Cochrane, C. M. N.; Marsden, K.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1986**, *315*, 211.

(10) Kim, H. P.; Kim, S.; Jacobsen, R. A.; Angelici, R. J. *Organometallics* **1984**, *3*, 1124.

(11) Ogric, C.; Wurst, K.; Jaitner, P.; Kreissl, F. R. Unpublished results, 1996.

(12) (a) Schubert, U.; Fischer, E. O.; Wittmann, D. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 643. (b) Fischer, E. O.; Wittmann, D.; Himmelreich, D.; Schubert, U.; Ackermann, K. *Chem. Ber.* **1982**, *115*, 3141.

(13) Wolfgruber, M.; Stegmair, C. M.; Kreissl, F. R. *J. Organomet. Chem.* **1989**, *376*, 45.

S0276-7333(96)00993-4 CCC: $14.00

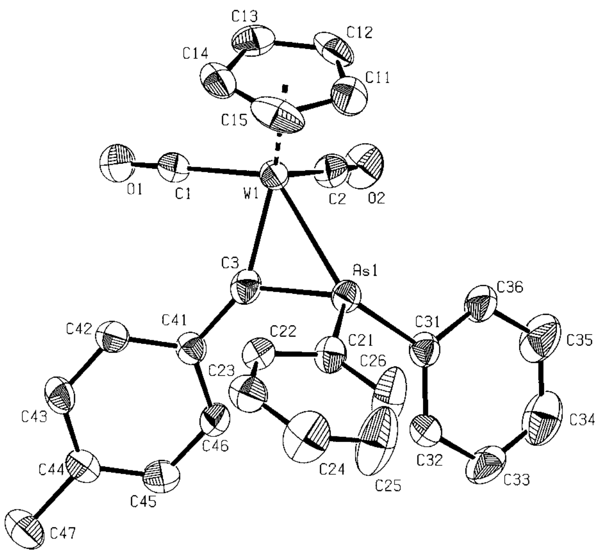
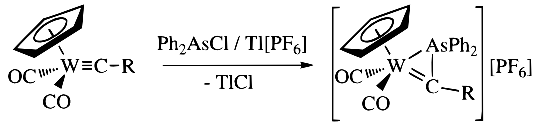


Figure 2. ORTEP plot for the molecular structure of **2c**. The thermal ellipsoids correspondent to 50% probability.

Scheme 2



1a-c **2a-c**

	a	b	c
R	Me	Ph	Tol

Table 1. Crystallographic Data for $[(\eta^5\text{-}C_5H_5)(CO)_2W{=}C(Tol){-}AsPh_2][PF_6]\cdot CH_2Cl_2$, 2c

Crystal Data	
chem formula	$C_{55}H_{46}As_2Cl_2F_{12}O_4P_2W_2$
fw	1649.3
color	yellow
cryst size (mm)	0.38 × 0.38 × 0.25
cryst syst	triclinic
space group	$P\bar{1}$
a (pm)	1169.1(1)
b (pm)	1334.8(1)
c (pm)	1948.2(2)
α (deg)	93.54(1)
β (deg)	106.60(1)
γ (deg)	94.72(1)
V (pm^3)	2892.0(5)
Z	2
T (K)	173
ρ_{calcd} (g cm^{-3})	1.894
μ (cm^{-1})	53.4
F(000)	1588
Data Collection	
λ (Å)	0.710 73
scan method	imaging plate
θ range (deg)	2.19–24.56
data collcd (h,k,l)	±13, ±15, ±22
Refinement[a]	
no. of rflns collcd	32066
no. of indep rflns	8926
no. of obsd rflns	8926 (all data)
R_{int}	0.0379
R1	0.0419
wR2	0.0861
GOF	1.086
$\Delta(\rho_{max/min})$ (e Å^{-3})	+1.09, −1.72

[a] $R1 = (||F_o| - |F_c||)/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(NO - NV)]^{1/2}$; w = SHELXL-93 weights.

The infrared spectra of **2a**−**c** in dichloromethane display in the ν_{CO} region two signals for the metal carbonyl ligands. In comparison to the starting compound the CO bonds are significantly stronger as a consequence of the diminished metal−carbonyl backdonation.

In the ^{13}C NMR spectra the significant chemical shifts of the carbene carbon atoms are found in the range of δ 257−266 ppm and coincide with those of comparable isostructural η^2-thio-[8] and η^2-phosphinocarbene complexes of tungsten.[7]

The existence of a tungstaarsirene has finally been proved by X-ray structure analysis. The title compound **2c** crystallizes from CH_2Cl_2/Et_2O as triclinic yellow crystals with two crystallographically independent molecules in the asymmetric unit (**2c** and **2c′**). Since these molecules show very similar geometry, only one of them, **2c**, is given in Figure 2. Crystal data are reported in Table 1, and selected bond distances and angles are summarized in Table 2. The complete set of structure data of **2c** is available on request (see the Supporting Information paragraph at the end of the paper).

The ORTEP plot of one cation shows the metal in a slightly distorted square pyramidal ligand sphere. The two carbonyl carbon atoms C(1) and C(2), the carbene carbon C(3), and the arsenic atom As(1) form the basis of the square pyramid with the cyclopentadienyl ligand in the apical position. Due to the dihedral angles W(1)−C(3)−As(1)−C(21) = 123.5(2)° and W(1)−C(3)−As(1)−C(31) = −117.2(2)° the two phenyl substituents of the AsPh$_2$ unit are oriented nearly symmetrically toward the W(1)−As(1)−C(3) plane. On the other hand, the two carbonyl ligands are in an asymmetric orientation with regard to the W(1)−As(1)−C(3) ring (C(1)−W(1)−C(3)−As(1) = 175.1(2)° and C(2)−W(1)−C(3)−As(1) = 87.5(2)°).

The W(1)−As(1) (249.7(6) pm) and As(1)-C(3) (192.3(5) pm) bond lengths within the tungstaarsacyclopropene ring are typical for single bonds and comparable to those of convenient reference compounds (e.g.: (η^5-$C_5H_5(CO)_2W{-}S{-}As(^tBu)_2$, W−As = 254.7 pm;[14] $(CO)_5W{-}AsPh_3$, W−As = 261.7 pm,[15] $(\eta^5\text{-}C_5H_5)(CO)_2W{-}As[Cr(CO)_5]{-}Cr(CO)_5$, W−As = 235.0 pm[16]). The W(1)−C(3) carbene bond distance is, at 196.8(6) pm, rather short and lies in the range of typical tungsten−carbon double bonds.[17] Similar W=C$_{carbene}$ units have been observed in comparable cyclic transition-metal carbene complexes (e.g.: $[(\eta^5\text{-}C_5H_5)(CO)_2W{=}C(Tol){-}PMe_2]^+$, W=C = 203.2 pm,[7] $[(\eta^5\text{-}C_5H_5(CO)_2W{=}C(Ph){-}SMe]^+$, W=C = 195.3 pm;[18] $(\eta^5\text{-}C_5H_5)(CO)_2W{=}C(Tol){-}NNNCO_2Me$, W=C = 209.5 pm.[19]

When the new η^2-arsinocarbene compounds **2a**−**c** are compared with the corresponding phosphorus homo-

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(14) Malisch, W.; Luksza, M. *Z. Naturforsch.* **1981**, *36B*, 1580.

(15) Aroney, M. J.; Murray, I. E.; Davies, S.; Hambley, T. W. *J. Chem. Soc., Dalton Trans.* **1994**, 2827.

(16) Huttner, G.; Sigwarth, B.; von Seyerl, J.; Zsolnai, L. *Chem. Ber.* **1982**, *115*, 2035.

(17) Schubert, U. In *Transition Metal Carbene Complexes*; Dötz, K. H.; Fischer, H., Hofmann, P., Kreissl, F. R., Schubert, U., Weiss, K. Eds.; Verlag Chemie: Weinheim, Germany, 1983.

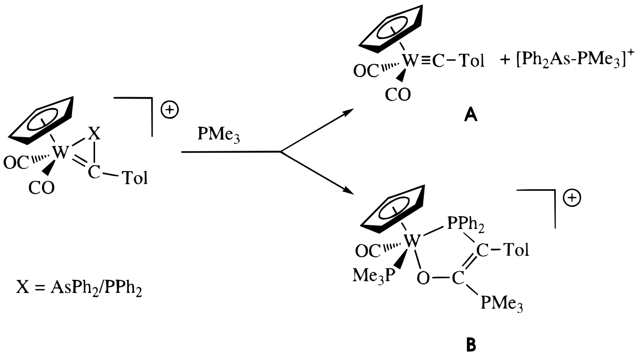
(18) Ullrich, N.; Stegmair, C. M.; Keller, H.; Herdtweck, E.; Kreissl, F. R. *Z. Naturforsch.* **1990**, *45B*, 921.

(19) Lehotkay, Th.; Kreissl, F. R. Unpublished results, 1996.

Table 2. Selected Bond Distances and Angles for 2c

Bond Distances (pm)			
As(1)−C(3)	192.3(5)	W(1)−C(1)	201.8(6)
As(1)−C(21)	193.8(6)	W(1)−C(2)	202.0(6)
As(1)−C(31)	192.1(6)	O(1)−C(1)	112.2(7)
W(1)−As(1)	249.7(6)	O(2)−C(2)	112.7(7)
W(1)−C(3)	197.8(6)	C(3)−C(41)	146.4(8)
Bond Angles (deg)			
As(1)−W(1)−C(3)	49.28(16)	C(1)−W(1)−C(2)	88.6(2)
As(1)−C(3)−W(1)	79.9(2)	C(21)−As(1)−C(31)	107.2(2)
W(1)−As(1)−C(21)	125.97(17)	C(3)−As(1)−C(21)	106.2(2)
W(1)−As(1)−C(31)	126.76(17)	C(3)−As(1)−C(31)	116.4(2)
W(1)−As(1)−C(3)	50.87(17)		
Torsion Angles			
C(1)−W(1)−C(3)−As(1)	175.1(2)	C(2)−W(1)−C(3)−As(1)	87.5(2)
C(1)−W(1)−C(3)−C(41)	−7.9(9)	C(2)−W(1)−C(3)−C(41)	−95.4(9)
W(1)−C(3)−As(1)−C(21)	123.5(2)	W(1)−C(3)−As(1)−C(31)	−117.2(2)

Scheme 3



logues, differences are evident in the less pronounced thermal stability as well as in the reaction behavior toward trimethylphosphine. Thus, in the case of **2c** cleavage of the $AsPh_2$ unit is observed (**A**), providing the original carbyne complex **1c**. In contrast, the η^2-phosphinocarbene complex $[(\eta^2\text{-}C_5H_5)(CO)_2W{=}C(Tol){-}As\text{-}Ph_2][PF_6]$ leads to a tungstaphosphaoxacyclopentene complex[19] (**B**).

Experimental Section

Standard inert-atmosphere techniques were used for the manipulation of all reagents and reaction products. Infrared spectra were recorded on a Perkin-Elmer FT-IR 1600 spectrometer. ^1H, ^{13}C, and ^{31}P NMR spectra were taken in $CDCl_3$ and CD_2Cl_2 on a JEOL JNM-GX 270 (^1H, 270.27 MHz; ^{13}C, 67.94 MHz; ^{31}P, 109.37 MHz) spectrometer. The spectral standard for ^{31}P NMR was 85% H_3PO_4. Mass spectra were recorded on a Finnigan MAT 90 spectrometer with FAB techniques (nitrobenzyl alcohol (NBA) matrix, molecular mass relative to ^{184}W). The starting materials **1a**−**c** as well as Ph_2AsCl were prepared according to the literature. $Tl[PF_6]$ was a commercial product from Strem Chemicals.

Preparation of $[(\eta^5\text{-}C_5H_5)(CO)_2W{=}C(Me){-}AsPh_2]][PF_6]$ (2a). To a solution of 0.36 g (1.08 mmol) of **1a** in 20 mL of diethyl ether was added successively stoichiometric amounts of thallium hexafluorophosphate (0.38 g) and chlorodiphenylarsine (0.19 mL) at −20 °C. The suspension was warmed to room temperature and stirred for 18 h. Then the yellow solid was isolated by filtration and washed several times with 10 mL of diethyl ether. The crude product was redissolved in dichloromethane, and insoluble thallium chloride was removed by filtration. Recrystallization from CH_2Cl_2/Et_2O/pentane provided a brownish yellow solid: yield 0.49 g (64%). Anal. Calcd for $C_{21}H_{18}AsF_6O_2PW$: C, 35.72; H, 2.57; W, 26.04. Found: C, 36.40; H, 2.84; W, 26.45. IR (CH_2Cl_2): ν_{CO} 2064 vs, 2007 vs cm^{-1}. MS (FAB): *m/e* 561 $[M]^+$, 533 $[M - CO]^+$. ^1H NMR (CD_2Cl_2, 270 MHz): δ 7.54−7.31 (m, 10H, C_6H_5), 6.12 (s, 5H, C_5H_5), 2.84 (s, 3H, CH_3) ^{13}C NMR ($CDCl_3$, 68 MHz): δ 266.4 (s, $J(^{183}W-^{13}C) = 66.2$ Hz, W=C), 202.9 (s, $J(^{183}W-^{13}C) = 171.9$ Hz, W−CO), 134.7−127.3 (m, C_6H_5), 94.4 (s, C_5H_5), 34.2 (s, CH_3).

Preparation of $[(\eta^5\text{-}C_5H_5)(CO)_2W{=}C(Ph){-}AsPh_2]][PF_6]$ (2b). This compound was prepared analogously to **2a**, using 0.41 g (1.04 mmol) of **1b** in 20 mL of diethyl ether by addition of equimolar amounts of thallium hexafluorophosphate (0.36 g) and chlorodiphenylarsine (0.19 mL). A yellow solid was isolated: yield 0.71 g (89%). Anal. Calcd for $C_{26}H_{20}AsF_6O_2PW$: C, 40.65; H, 2.62; W, 23.93. Found: C, 39.82; H, 2.69 W, 24.11. IR (CH_2Cl_2): ν_{CO} 2065 vs, 2007 vs cm^{-1}. MS (FAB): *m/e* 623 $[M]^+$, 595 $[M - CO]^+$. ^1H NMR (CD_2Cl_2, 270 MHz): δ 7.66−7.14 (m, 15H, C_6H_5), 6.17 (s, 5H, C_5H_5). ^{13}C NMR (CD_2Cl_2, 68 MHz): δ 258.4 (s, W=C), 203.6 (s, W−CO), 134.7−126.9 (m, C_6H_5), 94.3 (s, C_5H_5).

Preparation of $[(\eta^5\text{-}C_5H_5)(CO)_2W{=}C(Tol){-}AsPh_2][PF_6]$ (2c). By the method used for **2a**, 0.41 g (1.00 mmol) of **1c**, 0.35 g of thallium hexafluorophosphate, and 0.18 mL of chlorodiphenylarsine yielded 0.70 g (90%) of a yellow product. Anal. Calcd for $C_{27}H_{22}AsF_6O_2PW$: C, 41.46; H, 2.83; W, 23.50. Found: C, 41.30; H, 2.77; W, 23.67. IR (CH_2Cl_2): ν_{CO} 2060 vs, 2002 vs cm^{-1}. MS (FAB): *m/e* 637 $[M]^+$, 609 $[M - CO]^+$. ^1H NMR ($CDCl_3$, 270 MHz): δ 7.60−7.12 (m, 14H, $C_6H_{4/5}$), 6.12 (s, 5H, C_5H_5), 2.29 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 68 MHz): δ 257.8 (s, W=C), 204.4 (s, $J(^{183}W-^{13}C) = 167.3$ Hz, W−CO), 145.4−127.7 (m, $C_6H_{4/5}$), 94.1 (s, C_5H_5), 21.7 (s, CH_3).

X-Ray Single Crystal Structure Determination of 2c. Suitable crystals were grown from dichloromethane/diethyl ether at −30 °C. Crystal data together with details of the data collection and structure refinement are listed in Table 1. Preliminary examination and data collection were carried out on an imaging plate diffraction system (IPDS; Stoe & Cie) equipped with a rotating anode (ENRAF-Nonius FR591; 50 kV; 80 mA; 4.0 kW) and graphite monochromated Mo Kα radiation. The data collection was performed at 173 ± 1 K within the θ range $2.19° < \theta < 24.56°$ with an exposure time of 3 min/image (oscillating scan modus from $\varphi = 0.0°$ to 360° with $\Delta\varphi = 1°$[20]). A total of 32 066 reflections were collected, from which 8926 independent reflections remained and were used for all calculations. Data were corrected for Lorentz and polarization effects, intensity decay, and/or absorption effects.[21] The unit cell parameters were obtained by least-squares refinements of 1999 reflections with the program Cell.[21] The structure was solved by direct methods and refined with standard difference Fourier techniques. All "heavy atoms" of the asymmetric unit were anisotropically refined. All hydrogen atoms were calculated in ideal positions (riding model).

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(20) Schütt, W.; Herdtweck, E.; Hahn, F.; Kreissl, F. R. *J. Organomet. Chem.* **1993**, *443*, C33 and references cited therein.

(21) IPDS Operating System Version 2.7; Stoe & Cie GmbH, Darmstadt, Germany, 1996.

Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with SHELXL-93 weighting scheme and stopped at shift/error <0.005. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the ref 22. All calculations were performed on a DEC 3000 AXP workstation with the *STRUX-V* system,[23] including the programs PLATON-92, PLUTON-92, SIR-92, and SHELXL-93.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for the support of this work.

Supporting Information Available: Tables of crystallographic and structure refinement data, atomic coordinates and isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates (11 pages). Ordering information is given on any current masthead page. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlichtechnische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Germany, on quoting the depository number CSD-406444, the names of the authors, and the journal citation.

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(22) Wilson, A. J. C., Ed. *International Tables for Crystallography*; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. C, Tables 6.1.1.4 (p 500), 4.2.6.8 (p 219), and 4.2.4.2 (p 193).

(23) (a) Artus, G.; Scherer, W.; Priermeier, T.; Herdtweck, E. STRUX-V, a Program System To Handle X-ray Data; TU München, München, Germany, 1994. (b) Spek, A. L. PLATON-92-PLUTON-92, An Integrated Tool for the Analysis of the Results of a Single Crystal Structure Determination. *Acta Crystallogr.* **1990**, *A46*, C34. (c) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. SIR-92; University of Bari, Bari, Italy, 1992. (d) Sheldrick, G. M. SHELXL-93; University of Göttingen, Göttingen, Germany, 1993.