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Preliminary Communication

Highly diastereoselective formation and structural characterization of [2+2] cycloadducts from the phosphenium complexes Cp(OC)$_2$M=P(Ph)(*o*-Tol) (M = Mo, W) and isocyanates [1]

Wolfgang Malisch [a,*], Christoph Hahner [a], Klaus Grün [a], Joachim Reising [a], Richard Goddard [b], Carl Krüger [b]

[a] *Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany*
[b] *Max-Planck-Institut für Kohleforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim a.d. Ruhr, Germany*

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Abstract

[2+2] Cycloaddition of the prostereogenic phosphenium complexes Cp(OC)$_2$M=P(*o*-Tol)Ph (M = Mo (**1a**), W (**1b**)) with the isocyanates RNCO (R = Et (**2a**), Ph (**2b**)) leads to the formation of the four-membered phosphametallacycles Cp(OC)$_2\overline{\text{M–P(o-Tol)(Ph)–C(O)–N}}$R (M = Mo, W; R = Et, Ph) (**3a–c**) with high diastereoselectivity. The X-ray crystal structure of Cp(OC)$_2\overline{\text{W–P(o-Tol)(Ph)–C(O)–N}}$Et (**3b**) reveals that the preferred diastereomer is characterized by a *syn* arrangement of the tolyl ligand and the cyclopentadienyl unit.

Keywords: Phosphenium complexes; Cycloaddition; Phosphametallacycle complexes; Crystal structures; Molybdenum complexes; Tungsten complexes; Isocyanate complexes

1. Introduction

The chemical behaviour of phosphenium metal complexes of the chromium group Cp(OC)$_2$M=PR$_2$ (M = Mo, W; R = alkyl, aryl) is determined by the high reactivity of the M=P bond [2]. It is the basis of diverse coupling reactions involving the phosphorus fragment via cycloaddition [3]. In this context high chemo- and regioselectivity has been observed in context with [2+2] cycloadditions involving isocyanates leading to four-membered phosphametallacycles. As this report demonstrates, phosphenium complexes in addition with a prostereogenic moiety undergo highly diastereoselective coupling with isocyanates.

2. Experimental

2.1. Syntheses

2.1.1. General information and instrumentation

^{1}H, ^{13}C, ^{31}P NMR spectra were obtained on Varian T60, Jeol FX90Q and Bruker AMX 400 spectrometers.

$\delta(^{31}P)$ chemical shifts were measured relative to external H$_3$PO$_4$ (85%). $\delta(^1H)/(^{13}C)$ are reported downfield from Me$_4$Si referenced to the residual proton signal (^{1}H) or natural abundance carbon signal of the solvent. Shifts downfield from the standard were assigned positive δ values. IR spectra were recorded on a Perkin-Elmer 283 grating spectrometer. The solutions were measured in NaCl cells with 0.1 mm path length with a resolution of about 2 cm^{-1}. Melting points: digital thermoanalysis (Du Pont 9000). Elemental analyses were performed in the microanalytical laboratory of the Institute of Anorganische Chemie Würzburg. The isocyanates RNCO (R = Et, Ph) were obtained commercially. All manipulations were performed under dry N$_2$. Solvents were rigorously dried with an appropriate drying agent, distilled before use and saturated with nitrogen.

2.1.2. Dicarbonyl(η^5-cyclopentadienyl)[1-(phenyl)-1-(ortho-tolyl)phosphino-N-(ethyl)formamidato-P,N] molybdenum(II) (3a)

The reaction of 226 mg (0.50 mmol) Cp(OC)$_2$[(*o*-Tol)(Ph)PH]MoCl and 51 mg (0.50 mmol) NEt$_3$ in 10 ml toluene leads to a solution of **1a**, which was combined with 36 mg (0.50 mmol) ethylisocyanate (**2a**) and stirred for 5 h at room temperature. The reaction mixture was reduced in vacuo to 2 ml and worked up by column chromatography (column 9×2 cm, alumina III, neutral, toluene). The eluate

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* Corresponding author.

[1] Part 34 of the series; for Part 33 see Ref. [1].

of the red zone was evaporated in vacuo and the remaining **3a** recrystallized from 7 ml pentane. Yield 229 mg (94%); orange microcrystalline powder; m.p. 132 °C. Diastereomeric ratio: 96/4 (determined by the integration of the ^{31}P NMR signals). Main diastereomer: ^{1}H NMR (CDCl$_3$, 400.1 MHz): δ 8.13–7.10 (m, 9H, C$_6$H$_4$/C$_6$H$_5$); 5.40 (s, 5H, C$_5$H$_5$); 3.50 (m, 1H, CH^{a}H^{b}); 2.02 (m, 1H, CH$^{a}H^{b}$); 2.39 (s, 3H, CH$_3$); 1.01 (dd, ^{3}J(H^{a}CCH) = ^{3}J(H^{b}CCH) = 7.2 Hz, 3H, CH$_2$CH_3) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 100.6 MHz): δ 255.5 (d, ^{2}J(PWC) = 18.3 Hz, *cis*-CO); 237.5 (s, *trans*-CO); 174.9 (d, ^{1}J(PC) = 58.3 Hz, PC=O); 142.9 (d, ^{2}J(PCC) = 9.5 Hz, C-2); 133.0 (d, ^{2}J(PCC) = 11.4 Hz, C-2/6); 132.5 (d, ^{4}J(PCCCC) = 1.8 Hz, C-4); 132.3 (d, ^{3}J(PCCC) = 6.1 Hz, C-5); 132.1 (d, ^{2}J(PCC) = 8.0 Hz, C-6); 131.5 (d, ^{4}J(PCCCC) = 2.9 Hz, C-4); 131.0 (d, ^{1}J(PC) = 36.2 Hz, C-1); 129.7 (d, ^{3}J(PCCC) = 11.2 Hz, C-3/5); 128.6 (d, ^{1}J(PC) = 39.0 Hz, C-1); 127.2 (d, ^{3}J(PCCC) = 7.8 Hz, C-3); 95.7 (s, C$_5$H$_5$); 45.9 (d, ^{3}J(PCCC) = 18.8 Hz, CH$_2$); 21.6 (d, ^{3}J(PCCC) = 7.7 Hz, 2-CH$_3$); 14.9 (s, CH$_2$CH_3) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$, 162.0 MHz): δ 11.3 ppm. IR (Toluol): ν(CO) 1958 (vs), 1877 (vs); ν(C(O)) 1642 cm^{-1}. Minor diastereomer: ^{1}H NMR (CDCl$_3$, 400.1 MHz): δ 5.61 (s, 5H, C$_5$H$_5$); 2.30 (s, 3H, CH$_3$); 0.86 (dd, ^{3}J(H^{a}CCH) = ^{3}J(H^{b}CCH) = 7.2 Hz, 3H, CH$_2$CH_3) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 162.0 MHz): δ 95.2 (s, C$_5$H$_5$) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$, 162.0 MHz): δ 7.7 ppm. *Anal.* Calc. for C$_{23}$H$_{22}$MoNO$_3$P (487.35): C, 56.69; H, 4.55; N, 2.87. Found: C, 56.97; H, 4.56; N, 2.74%.

*2.1.3. Dicarbonyl(η^5-cyclopentadienyl)[1-(phenyl)-1-(ortho-tolyl)phosphino-N-(ethyl)formamidato-P,N] tungsten(II) (**3b**)*

Prepared as described for **3a** from 330 mg (0.61 mmol) Cp(OC)$_2$[(*o*-Tol)(Ph)PH]WCl, 62 mg (0.61 mmol) NEt$_3$ and 43 mg (0.61 mmol) ethylisocyanate (**2a**) in 10 ml toluene after 7 h stirring. Yield 305 mg (87%); orange microcrystalline powder; m.p. 182 °C. Diastereomeric ratio 96/4 (determined by the integration of the ^{31}P NMR signals). Main diastereomer: ^{1}H NMR (CDCl$_3$, 400.1 MHz): δ 7.96–7.11 (m, 9H, C$_6$H$_4$/C$_6$H$_5$); 5.16 (s, 5H, C$_5$H$_5$); 3.41 (m, 1H, CH^{a}H^{b}), 2.87 (m, 1H, CH$^{a}H^{b}$); 2.16 (s, 3H, CH$_3$); 0.93 (dd, ^{3}J(H^{a}CCH) = ^{3}J(H^{b}CCH) = 7.1 Hz, 3H, CH$_2$CH_3) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 100.6 MHz): δ 246.3 (d, ^{2}J(PWC) = 20.5 Hz, ^{1}J(WC) = 134.2 Hz, *cis*-CO); 237.1 (d, ^{2}J(PWC) = 4.1 Hz, ^{1}J(WC) = 169.1 Hz, *trans*-CO); 177.9 (d, ^{1}J(PC) = 58.9 Hz, PC=O); 141.6 (d, ^{2}J(PCC) = 9.6 Hz, C-2); 132.7 (d, ^{2}J(PCC) = 12.2 Hz, C-2/6); 131.6 (d, ^{4}J(PCCCC) = 2.1 Hz, C-4); 131.5 (d, ^{3}J(PCCC) = 5.9 Hz, C-5); 131.2 (d, ^{2}J(PCC) = 8.3 Hz, C-6); 131.0 (d, ^{4}J(PCCCC) = 3.2 Hz, C-4); 129.1 (d, ^{3}J(PCCC) = 11.5 Hz, C-3/5); 128.8 (d, ^{1}J(PC) = 42.1 Hz, C-1); 126.6 (d, ^{3}J(PCCC) = 8.4 Hz, C-3); 125.4 (d, ^{1}J(PC) = 44.2 Hz, C-1); 92.9 (s, C$_5$H$_5$); 46.3 (d ^{3}J(PCCC) = 19.2 Hz, CH$_2$); 21.5 (d, ^{3}J(PCCC) = 7.3 Hz, 2-CH$_3$); 14.5 (s, CH$_2$CH_3) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$, 162.0 MHz): δ −10.9 (s, ^{1}J(WP) = 240.1 Hz) ppm. IR (Toluol): ν(CO) 1944 (vs), 1861 (vs); ν(P–C(O)) 1649 cm^{-1}. Minor diastereomer: ^{31}P{^{1}H} NMR (CDCl$_3$, 162.0 MHz): δ −15.5 (s, ^{1}J(WP) = 234.1 Hz) ppm. *Anal.* Calc. for C$_{23}$H$_{22}$NO$_3$PW (575.26): C, 48.02; H, 3.85; N, 2.43. Found: C, 48.38; H, 3.99; N, 2.43%.

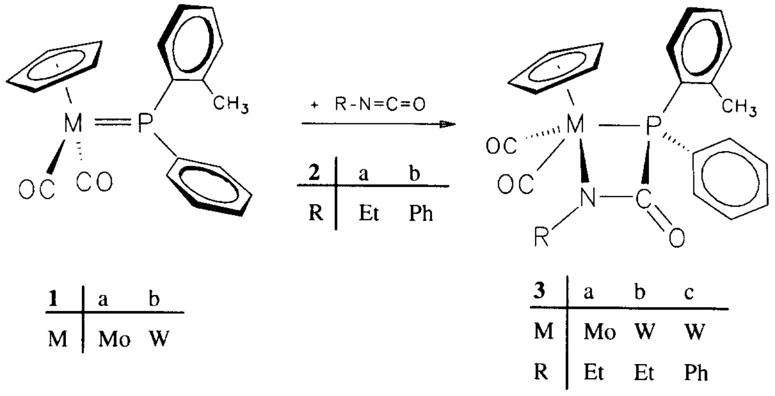
2.1.4. Dicarbonyl(η^5-cyclopentadienyl)[1-(phenyl)-1-(ortho-tolyl)phosphino-N-(phenyl)formamidato-P,N] tungsten(II) (3c)

Prepared as described for **3a** from 350 mg (0.65 mmol) Cp(OC)$_2$[(*o*-Tol)(Ph)PH]WCl, 66 mg (0.65 mmol) NEt$_3$ and 77 mg (0.65 mmol) phenylisocyanate (**2b**) in 10 ml toluene after 72 h stirring. The reaction mixture was reduced under vacuo to 2 ml, filtered, evaporated to dryness and the residue recrystallized from 5 ml pentane. Yield 295 mg (73%); orange crystals; m.p. 212 °C. ^{1}H NMR ([D$_6$]-acetone, 400.1 MHz): δ 8.17–6.92 (m, 14H, C$_6$H$_4$/C$_6$H$_5$/N(C$_6$H$_5$)); 5.50 (s, 5H, C$_5$H$_5$); 2.43 (s, 3H, CH$_3$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]-acetone, 100.6 MHz): δ 246.4 (d, ^{2}J(PWC) = 20.6 Hz, *cis*-CO); 238.8 (d, ^{2}J(PWC) = 4.1 Hz, *trans*-CO); 175.9 (d, ^{1}J(PC) = 60.1 Hz, PC=O); 148.0 (d, ^{3}J(PCCC) = 24.0 Hz, *ipso*-N(C$_6$H$_5$)); 141.8 (d, ^{2}J(PCC) = 10.1 Hz, C-2); 132.2 (d, ^{2}J(PCC) = 11.8 Hz, C-2/6); 131.7 (d, ^{3}J(PCCC) = 8.3 Hz, C-5); 131.5 (s, C-4); 130.6 (d, ^{3}J(PCCC) = 5.9 Hz, C-3); 129.5 (d, ^{3}J(PCCC) = 11.2 Hz, C-3/5); 129.3 (d, ^{2}J(PCC) = 12.5 Hz, C-6); 128.7 (s, C-4); 128.3 (s, *o*-N(C$_6$H$_5$)); 127.7 (d, ^{1}J(PC) = 44.5 Hz, C-1); 125.9 (s, *m*-N(C$_6$H$_5$)); 125.7 (d, ^{1}J(PC) = 45.6 Hz, C-1); 123.8 (s, *p*-N(C$_6$H$_5$)); 94.2 (s, C$_5$H$_5$); 21.2 (d, ^{3}J(PCCC) = 7.2 Hz, 2-CH$_3$) ppm. ^{31}P{^{1}H} NMR ([D$_6$]-acetone, 162.0 MHz): δ −8.3 (s, ^{1}J(WP) = 250.8 Hz) ppm. IR (CH$_2$Cl$_2$): ν(CO) 1950 (vs), 1863 (vs); ν(C(O)) 1639 cm^{-1}. *Anal.* Calc. for C$_{27}$H$_{22}$NO$_3$PW (623.30): C, 52.03; H, 3.56; N, 2.25. Found: C, 52.32; H, 3.81; N, 2.24%.

*2.2. X-ray crystal structure determination of **3b***

An orange crystal of complex **3b** was isolated from a mixture of trichloromethane/pentane.

Molecular formula C$_{23}$H$_{22}$NO$_3$PW, formula weight 575.3, crystal size 0.06×0.19×0.33 mm, a = 8.025(1), b = 14.595(1), c = 18.468(1) Å, V = 2163.4 Å^3, T = 293 K, orthorhombic, space group $P2_12_12_1$ (No. 19), D_{calc} = 1.77 g cm^{-3}, μ = 55.5 cm^{-1}, Z = 4, Enraf-Nonius CAD4 diffractometer, λ = 0.71069 Å, scan mode ω–2θ, 2830 measured reflections (+h, +k, +l), $(\sin\theta/\lambda)_{\max}$ = 0.65 Å^{-1}, analytical absorption correction (min. 1.405, max. 2.588), 2804 independent reflections, 2433 observed reflections ($I \geq 2\sigma(I)$) for 263 parameters, structure solved by heavy atom method, H atom positions calculated, absolute configuration determined (x = −0.02), R = 0.034, R_{w} = 0.033, residual electron density 1.04 e Å^{-3}. Atomic positional parameters and equivalent thermal parameters are given in Table 1. See also Section 5. Computer programmes used: data reduction: DATAP [4]; structure solution: SHELXS-



Scheme 1.

Table 1
Atomic positional and equivalent thermal parameters

Atom	x	y	z	B_{eq} (Å)
W	0.26271(2)	0.08403(2)	0.58808(1)	1.977(4)
P	0.4450(1)	0.1823(1)	0.67101(8)	2.11(3)
O1	0.0991(4)	0.2647(5)	0.4673(3)	4.8(1)
O2	0.1539(4)	0.2724(5)	0.6757(3)	4.9(1)
O3	0.5809(3)	0.2116(4)	0.5738(2)	3.6(1)
N	0.3943(4)	0.1278(4)	0.5346(2)	2.4(1)
C1	0.1634(5)	0.1987(6)	0.5105(3)	3.0(1)
C2	0.1937(5)	0.2007(6)	0.6438(3)	2.9(1)
C3	0.2233(6)	−0.0846(6)	0.6553(4)	3.9(1)
C4	0.3251(6)	−0.1175(6)	0.6420(4)	4.4(2)
C5	0.2990(6)	−0.1316(6)	0.5612(4)	4.2(2)
C6	0.1808(6)	−0.1053(6)	0.5266(3)	3.5(1)
C7	0.1340(5)	−0.0772(6)	0.5853(4)	3.7(1)
C8	0.3850(5)	0.1182(6)	0.4518(3)	3.3(1)
C9	0.3610(7)	0.2434(8)	0.4109(4)	5.0(2)
C10	0.4906(5)	0.1754(5)	0.5831(3)	2.5(1)
C11	0.5403(4)	0.0828(6)	0.7456(3)	2.5(1)
C12	0.5103(5)	0.0453(6)	0.8100(3)	2.7(1)
C13	0.5852(6)	−0.0359(6)	0.8624(4)	3.6(1)
C14	0.6867(6)	−0.0788(7)	0.8542(4)	4.3(2)
C15	0.7164(6)	−0.0402(7)	0.7918(4)	4.5(2)
C16	0.6444(5)	0.0401(7)	0.7373(4)	3.6(1)
C17	0.4026(5)	0.0924(7)	0.8246(3)	3.4(1)
C18	0.4723(4)	0.3443(6)	0.7086(3)	2.5(1)
C19	0.4277(5)	0.4517(6)	0.6642(4)	3.4(1)
C20	0.4572(6)	0.5695(6)	0.6981(4)	4.6(2)
C21	0.5279(6)	0.5845(7)	0.7728(4)	4.7(2)
C22	0.5712(5)	0.4795(7)	0.8161(4)	3.8(1)
C23	0.5433(5)	0.3595(6)	0.7842(3)	2.9(1)

86 [4]; structure refinement: GFMLX, a modified version of ORFLS [4]; molecular diagram (50% thermal ellipsoids): ORTEP [5]. Computer: VAX 4000-3000. Scattering factors from Ref. [6].

3. Discussion

In context with our efforts to use the phosphenium group in complexes of the type $\mathrm{Cp(OC)_2M{=}PR_2}$ for coupling reactions under the stereocontrol of the metal fragment we have now focussed our interest on the phosphenium complexes **1a,b**, characterized by the prostereogenic organophosphorus unit. Reaction of **1a,b** with the isocyanates **2a,b** leads to a controlled [2+2] addition via the N=C double bond, to give the four-membered phosphametallacycles **3a–c**, in which the electrophilic carbon of the isocyanate is bonded to the phosphorus, while the nitrogen is coordinated to the metal atom (Scheme 1).

The chemo- and regioselectivity of cycloaddition follows from the spectroscopic data of **3a–c**, especially the ^{13}C NMR resonance of the P–*C*=O carbon giving rise to a doublet due to the coupling with the phosphorus (^1J(PC) = 58.3–60.1 Hz). The reaction time increases considerably on going from ethylisocyanate (**2a**) (5–7 h) to phenylisocyanate (**2b**) (72 h). For that reason the molybdenum phosphenium complex

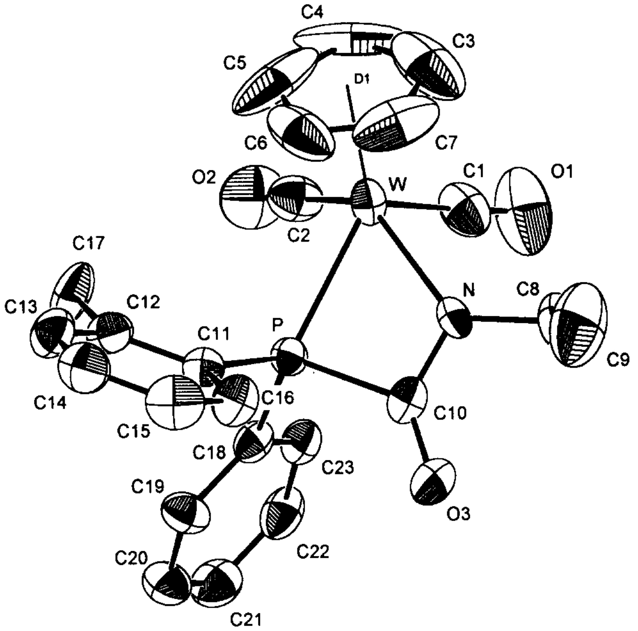


Fig. 1. Molecular structure of $\mathrm{Cp(OC)_2\overline{W{-}P(\textit{o}\text{-}Tol)(Ph){-}C(O){-}N}Et}$ (**3b**). Selected bond lengths (Å), bond angles and torsion angles (°): W–P 2.444(2), W–N 2.185(7), P–C10 1.80(8), N–C10 1.33(1), N–C8 1.49(1), C10–O3 1.22(1); P–W–N 63.6(2), P–C10–N 98.2(5), P–C10–O3 129.7(7), O3–C10–N 131.9(8), W–P–C10 85.4(3), W–N–C10 112.7(5), C8–N–C10 116.6(7), W–N–C8 129.7(6); W–P–C10–N 357, W–N–C10–O3 189, O3–C10–N–C8 359.

1b decomposes before the coupling reaction with phenylisocyanate **2b** occurs. The diastereoselectivity of the [2+2] cycloaddition is extremely high. It most likely derives from a preference for the phosphenium conformation. Diastereomer ratios estimated from the ^{31}P NMR spectrum amount to 96:4 for **3a,b**, while in the case of the phenyl-substituted phosphametallacycle **3c** no indication for the formation of a second diastereomerically related pair of enantiomers is obtained from the NMR spectra. An X-ray analysis of **3b** reveals that the main isomer adopts a structure with the phenyl substituent at the phosphorus *anti* to the Cp ligand at the metal (Fig. 1).

The four-membered metallacycle is only slightly folded (torsion angle W–P–C10–N 357°) and is characterized by the planarity of the coordination at C10 and N (sum of angles 360°). This finding in the latter case, the short C10–N distance of 1.33(1) Å and the torsion angle O3–C10–N–C8 (359°) indicates delocalization of the non-bonding electron pair on the nitrogen atom.

4. Conclusions

This report demonstrates extremely high chemo-, regio- and stereoselectivity of the cycloaddition of prostereogenic phosphenium complexes with organoisocyanates. This finding motivates further investigations concerning stereocontrolled coupling reactions via cycloaddition involving heteroallenes.

5. Supplementary material

Atomic coordinates, bond length and angles, and thermal parameters for **3b** have been deposited at the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany.

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References

[1] W. Malisch, C. Hahner, K. Grün, J. Reising and O. Fey, *Chem. Ber.*, submitted for publication.

[2] W. Malisch, M. Märkl, S. Amann, U. Hirth and M. Schmeußer, *Phosphorus Sulfur, 49/50* (1990) 441.

[3] A. Spörl, K. Hindahl, A. Fried, H. Pfister and W. Malisch, in H. Werner, A.G. Griesbeck, W. Adam, G. Bringmann and W. Kiefer (eds.), *Selective Reactions of Metal-Activated Molecules,* Vieweg, Braunschweig, Germany, 1992, p. 195.

[4] P. Coppens, L. Leiserowitz and D. Rabinovich, *Acta Crystallogr., 18* (1965) 1035; G.M. Sheldrick, *Acta Crystallogr., Sect. A, 46* (1990) 468; W.R. Busing, K.O. Martin and H.A. Levy, *Rep. ORNL-TM-305,* Oak Ridge National Laboratory, Oak Ridge, TN, USA, 1962.

[5] C.K. Johnson, *Rep. ORNL-5138,* Oak Ridge National Laboratory, Oak Ridge, TN, USA, 1976.

[6] *International Tables for X-Ray Crystallography,* Vol. C, Kluwer, Dordrecht, Netherlands, 1992, Tables 4.2.6.8 and 6.1.1.4.