ELSEVIER

Journal of Organometallic Chemistry 498 (1995) 237–240

Journal of Organometallic Chemistry

# Synthesis, characterization and X-ray structure of $Rh_6(CO)_{10}(\mu_3\text{-}CO)_4(\eta^4\text{-}C_6H_8)$

Paul J. Dyson [a], Scott L. Ingham [b], Brian F.G. Johnson [b,*], Alexander J. Blake [b]

[a] *Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK*
[b] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK*

Received 20 January 1995

---

**Abstract**

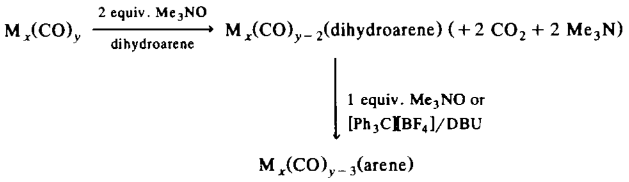
The reaction of the tetrahedral cluster $Rh_4(CO)_{12}$ with two molar equivalents of trimethylamine *N*-oxide in the presence of an excess of cyclohexa-1,3-diene affords the hexanuclear cluster $Rh_6(CO)_{10}(\mu_3\text{-}CO)_4(\eta^4\text{-}C_6H_8)$ (**1**). This new cluster was characterized by spectroscopy and in the solid-state by a single-crystal X-ray diffraction study, and shown to be based on the structure of $Rh_6(CO)_{12}(\mu_3\text{-}CO)_4$ with two terminal carbonyl ligands replaced by a an $\eta^4$-cyclohexadiene unit.

*Keywords:* Rhodium; Carbonyl; Cyclohexa-1,3-diene; Crystal structure

---

## 1. Introduction

In recent years organometallic cluster chemistry has flourished as a natural extension of traditional organometallic chemistry, with the clusters offering the possibility of multicentre bonding unavailable for mononuclear complexes. We have paid particular attention to the synthesis and characterization of clusters bearing unsaturated and aromatic $C_6$ rings, and this area of research has recently been reviewed. A diverse range of synthetic methods have been developed to make such clusters, and one systematic and widely applicable route to benzene clusters of ruthenium and osmium [1–4] involves treatment of the appropriate carbonyl cluster with two molar equivalents of the oxidative chemical activator trimethylamine *N*-oxide ($Me_3NO$) in the presence of a suitable dihydroarene, which results in coordination of the dihydroarene through both unsaturated bonds in the first instance. Treatment of this initial cluster either with one further aliquot of $Me_3NO$ or with $[Ph_3C][BF_4]$ followed by DBU (1,8-diazabicyclo[5.4.0]undeca-7-ene) results in the formation of the appropriate benzene cluster according to the equation below.



$$\begin{tikzcd} M_x(CO)_y \arrow[r, "2\text{ equiv. }Me_3NO", "\text{dihydroarene}"'] & M_x(CO)_{y-2}(\text{dihydroarene})\ (+2\ CO_2 + 2\ Me_3N) \arrow[d, "1\text{ equiv. }Me_3NO\text{ or}", "{[Ph_3C][BF_4]/DBU}"'] \\ & M_x(CO)_{y-3}(\text{arene}) \end{tikzcd}$$

This route has been successfully used for a number of clusters, including the ruthenium-carbido clusters $Ru_5C(CO)_{15}$ [1] and $Ru_6C(CO)_{17}$ [2] and the osmium-hydrido cluster $H_4Os_4(CO)_{12}$ [4]. The mechanisms involved in these reactions have been discussed in detail, and the dehydogenation of the ring has been clearly shown to involve the intermediacy of a cyclohexadienyl ($C_6H_7$) ring when $[Ph_3C][BF_4]$ and DBU are employed, and a similar two-step process has been proposed for $Me_3NO$, the driving force for the dehydrogenation in this case being the initial generation of a coordinatively unsaturated cluster unit by removal of a coordinated carbonyl ligand.

An attractive feature of this reaction compared with others is that the integrity of the cluster unit generally remains intact. We have now extended these studies,

---

* Corresponding author.

*SSDI* 0022-328X(95)05514-2

previously restricted to a selection of ruthenium and osmium clusters, to the tetranuclear clusters $M_4(CO)_{12}$ (M = Co and Rh), and find that the central cluster unit is modified during the reaction.

## 2. Results and discussion

Two molar equivalents of $Me_3NO$ in dichloromethane were added dropwise to a solution of $Rh_4(CO)_{12}$ in dichloromethane containing an excess of cyclohexa-1,3-diene at 78°C. The solution was allowed to warm to room temperature during a short period, the reaction was then quenched by removal of the solvent and the products were isolated by chromatography on silica, with 20% dichloromethane–hexane as eluent. In addition to a small amount of unchanged starting material, a single product, the hexarhodium cluster $Rh_6(CO)_{10}(\mu_3\text{-}CO)_4(\eta^4\text{-}C_6H_8)$ (**1**), was isolated, in about 30% yield. From an analogous reaction of $Co_4(CO)_{12}$ with cyclohexa-1,3-diene, again a single major (yellow) product was isolated after the purification procedure; it was identified as the known dinuclear complex $Co_2(CO)_4(\eta^4\text{-}C_6H_8)_2$ **2** [5].

Compound **1** was characterized by spectroscopy, and in the solid-state by an X-ray diffraction study at 150 K. The infrared spectrum of **1** ($\nu_{CO}$) contains stretches typical of both terminal CO groups (2097, 2065 and 2033 $cm^{-1}$) and one at lower wavenumber (1793 $cm^{-1}$) indicative of the presence of bridging carbonyls. The $^1H$ NMR spectrum confirms the presence of the cyclohexa-1,3-diene ligand showing signals at $\delta$ 5.32, 4.56 and 1.24 ppm with relative intensities of 2 : 2 : 4. The first two of these signals are multiplets and come from the two pairs of C–H protons, whilst the third signal is a singlet that can be attributed to the protons of the aliphatic $-CH_2CH_2-$ portion of the ring. The mass spectrum indicates that the cluster nuclearity has increased, exhibiting a parent peak at 1089 u ($Rh_6(CO)_{14}(C_6H_8)$ = 1090 u).

Crystals of **1** of suitable quality for the X-ray diffraction analysis were grown from dichloromethane–hexane at −25°C during several weeks. The molecular structure of **1** is depicted in Fig. 1 together with pertinent bonding parameters. Fractional atomic coordinates are given in Table 1. The structure is closely related to those of the binary carbonyl cluster $Rh_6(CO)_{12}(\mu_3\text{-}CO)_4$ [6] and several derivatives of this compound [7,8]. It can be regarded as derived from the parent cluster by replacement of two terminal carbonyl ligands by an $\eta^4$-$C_6H_8$ ligand. The six Rh atoms form a regular octahedron, Rh–Rh bond lengths ranging from 2.715(3) to 2.817(2) Å (mean 2.77 Å) (cf. $Rh_6(CO)_{12}(\mu_3\text{-}CO)_4$, mean 2.78 Å) [6]. Except for Rh(2), which carries the cyclohexa-1,3-diene ligand, each Rh atom bears two terminal carbonyl groups. In addition, four $\mu_3$-carbonyl groups occupy alternate faces of the cluster octahedron in a manner reminiscent of the parent compound $Rh_6(CO)_{12}(\mu_3\text{-}CO)_4$. The $C_6H_8$ ligand is bonded to a single Rh atom (Rh(2)) in an $\eta^4$ fashion in which two bonds are comparatively short (mean 2.137(11) Å) and two slightly longer (mean 2.231(11)Å). The localized nature of the unsaturated bonds through which the diene coordinates is evident from their short length (1.38(2) and 1.40(2) Å versus a mean value of 1.50(2) Å for the remaining four C–C bonds).

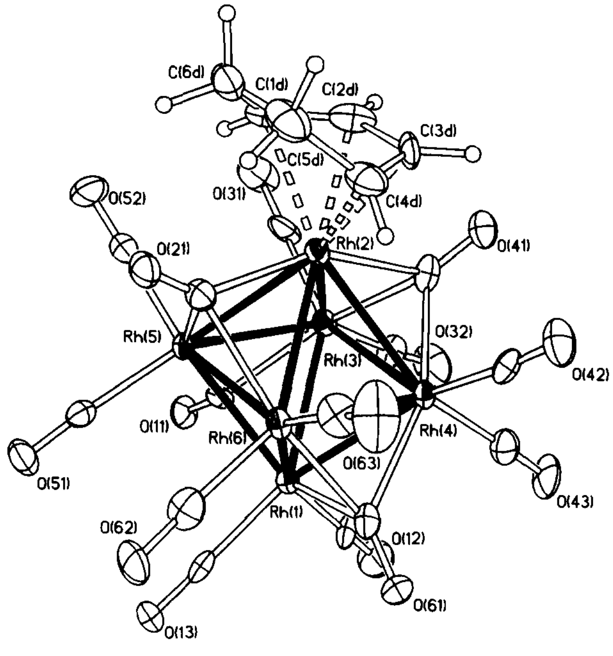


Fig. 1. Molecular structure of **1** in the solid-state. Principal bond distances (Å) include. Rh(1)–Rh(3) 2.752(2), Rh(1)–Rh(4) 2.747(3), Rh(1)–Rh(5) 2.751(3), Rh(1)–Rh(6) 2.750(2), Rh(2)–Rh(3) 2.817(2), Rh(2)–Rh(4) 2.803(3), Rh(2)–Rh(5) 2.775(3), Rh(2)–Rh(6) 2.776(2), Rh(3)–Rh(4) 2.779(2), Rh(3)–Rh(5) 2.715(3), Rh(4)–Rh(6) 2.709(3), Rh(5)–Rh(6) 2.777(2), Rh(2)–C(1d) 2.245(11), Rh(2)–C(2d) 2.138(11), Rh(2)–C(3d) 2.136(10), Rh(2)–C(4d) 2.216(11), C(1d)–C(2d) 1.38(2), C(2d)–C(3d) 1.44(2), C(3d)–C(4d) 1.40(2), C(4d)–C(5d) 1.48(2), C(5d)–C(6d) 1.53(2), C(6d)–C(1d) 1.53(2), mean Rh–C(terminal CO) 1.910, mean C–O(terminal) 1.125, mean Rh–C(bridging CO) 2.186, mean C–O(bridging) 1.160.

Recognition of the mechanism by which cluster **1** is produced from $Rh_4(CO)_{12}$ is complicated by the fact that the cluster nuclearity changes from four to six. Such an increase is are not entirely unexpected for rhodium species [9]. It appears that the coordinatively unsaturated cluster intermediates produced by reaction with $Me_3NO$ are not stable, and undergo a degree of fragmentation, followed by recombination, to afford the octahedral cluster product, during which sequence the cyclohexa-1,3-diene is introduced into the cluster system. A similar reaction has been observed when a mixture of $Rh_4(CO)_{12}$ with other dienes (cycloocta-1,5-diene, norbornadiene, cyclohexa-1,4-diene and 2,3-dimethylbuta-1,3-diene) in *n*-hexane was heated for sev-

Table 1
Atomic coordinates and equivalent isotropic displacement parameters (Å$^2$) for **1**. $U$(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor

| | $x$ | $y$ | $z$ | $U$(eq) |
|---|---|---|---|---|
| Rh(1) | 0.73744(8) | 0.65526(8) | 0.28220(4) | 0.0169(2) |
| Rh(2) | 0.36193(8) | 0.98561(8) | 0.26386(4) | 0.0168(2) |
| Rh(3) | 0.45654(8) | 0.69491(8) | 0.23928(4) | 0.0174(2) |
| Rh(4) | 0.60555(8) | 0.89349(8) | 0.16064(4) | 0.0168(2) |
| Rh(5) | 0.49838(8) | 0.74173(8) | 0.38425(4) | 0.0175(2) |
| Rh(6) | 0.64786(8) | 0.93952(8) | 0.30538(4) | 0.0181(2) |
| O(11) | 0.5978(8) | 0.4137(8) | 0.3749(4) | 0.026(2) |
| O(12) | 0.8862(9) | 0.4317(9) | 0.1791(5) | 0.040(2) |
| O(13) | 0.9604(8) | 0.5140(9) | 0.4169(4) | 0.037(2) |
| O(21) | 0.3975(8) | 1.0492(8) | 0.4268(4) | 0.028(2) |
| O(31) | 0.1638(9) | 0.6482(10) | 0.2981(5) | 0.051(2) |
| O(32) | 0.5265(10) | 0.5149(9) | 0.1100(5) | 0.046(2) |
| O(41) | 0.3143(8) | 0.9306(7) | 0.0913(4) | 0.028(2) |
| O(42) | 0.5454(9) | 1.2120(9) | 0.0648(5) | 0.038(2) |
| O(43) | 0.7527(9) | 0.7411(9) | 0.0238(4) | 0.040(2) |
| O(51) | 0.6776(8) | 0.6341(8) | 0.5364(4) | 0.031(2) |
| O(52) | 0.2118(9) | 0.7209(9) | 0.4725(5) | 0.044(2) |
| O(61) | 0.9268(8) | 0.8577(8) | 0.1969(4) | 0.026(2) |
| O(62) | 0.8583(9) | 0.8860(11) | 0.4383(5) | 0.048(2) |
| O(63) | 0.6556(12) | 1.2531(10) | 0.2409(5) | 0.056(3) |
| C(11) | 0.5793(11) | 0.5362(13) | 0.3418(6) | 0.026(2) |
| C(12) | 0.8343(12) | 0.5175(12) | 0.2157(6) | 0.024(2) |
| C(13) | 0.8797(11) | 0.5666(11) | 0.3670(6) | 0.022(2) |
| C(21) | 0.4344(11) | 0.9870(11) | 0.3753(6) | 0.024(2) |
| C(31) | 0.2750(12) | 0.6655(12) | 0.2739(7) | 0.030(3) |
| C(32) | 0.5023(11) | 0.5764(11) | 0.1598(7) | 0.025(2) |
| C(41) | 0.3898(12) | 0.8905(11) | 0.1485(6) | 0.023(2) |
| C(42) | 0.5730(11) | 1.0921(12) | 0.1005(6) | 0.024(2) |
| C(43) | 0.6973(12) | 0.8001(12) | 0.0727(7) | 0.028(3) |
| C(51) | 0.6086(11) | 0.6761(11) | 0.4822(6) | 0.021(2) |
| C(52) | 0.3181(12) | 0.7274(12) | 0.4392(6) | 0.027(2) |
| C(61) | 0.8130(12) | 0.8456(10) | 0.2202(6) | 0.022(2) |
| C(62) | 0.7788(13) | 0.9046(12) | 0.3905(7) | 0.031(3) |
| C(63) | 0.6474(13) | 1.1375(13) | 0.2645(7) | 0.033(3) |
| C(1D) | 0.1277(11) | 1.0479(13) | 0.3121(7) | 0.034(3) |
| C(2D) | 0.1371(11) | 1.0678(12) | 0.2287(8) | 0.035(3) |
| C(3D) | 0.2139(11) | 1.1693(11) | 0.1858(6) | 0.024(2) |
| C(4D) | 0.2748(12) | 1.2312(12) | 0.2337(7) | 0.033(3) |
| C(5D) | 0.1883(13) | 1.2812(12) | 0.3049(7) | 0.041(3) |
| C(6D) | 0.1025(14) | 1.178(2) | 0.3518(7) | 0.048(4) |
| C(1S) | 0.860(2) | 1.260(2) | −0.0378(10) | 0.077(5) |
| Cl(1S) | 0.8577(6) | 1.4331(6) | −0.0747(5) | 0.143(3) |
| Cl(2S) | 0.9183(5) | 1.1700(6) | 0.0562(3) | 0.0862(14) |

eral hours, yielding products formulated as $Rh_6(CO)_{14}$(diene) [5].

In contrast to other systems in which the coordinated hexadiene may be "dehydrogenated" to form a benzene ring, a process which also requires the loss of one further CO ligand, it has not proved possible to bring about a similar transformation in **1**.

Treatment of **1** with $Me_3NO$ results in decomposition, whereas treatment with $[Ph_3C][BF_4]$ has no apparent effect on the cluster. Thermal and photochemical methods result in the degradation of **1** and the formation of intractable decomposition material. This resistance of the cluster to undergo conversion to the potential product $Rh_6(CO)_{13}(\eta^6\text{-}C_6H_6)$ can be rationalized by inspection of the carbonyl ligand topology in **1**. This is such that, because of the carbonyl arrangement, it is difficult to envisage replacement of three CO ligands by the tridentate arene. Each rhodium atom only carries two terminal CO groups and shares two face-bridging CO groups, and so no simple $Rh(CO)_3$ unit is available for replacement by the ring. The observation that a tetrarhodium complex is not formed in this reaction is less easy to understand, since there appears to be an ideal coordination site for both cyclohexa-1,3-diene and benzene. In the analogous cobalt system, arene clusters of formula $Co_4(CO)_9(\eta^6\text{-}C_6H_6)$ are known, having been prepared by thermolysis of $Co_2(CO)_8$ or $Co_4(CO)_{12}$, either directly in the arene used as solvent or in *n*-hexane containing an excess of the arene [10]. So far, all attempts to prepare a rhodium derivative by either of these reactions have proved unsuccessful. As for the rhodium complex $Co_4(CO)_{12}$ does not afford $Co_4(CO)_{10}(\eta^4\text{-}C_6H_8)$ on reaction with $Me_3NO$ and cyclohexa-1,3-diene; this is perhaps even less easy to understand given that the benzene cluster $Co_4(CO)_9(\eta^6\text{-}C_6H_6)$ is known. Instead, the dicobalt complex **2** is produced.

## 3. Experimental

Reactions were carried out with the exclusion of air in solvents distilled under nitrogen. During subsequent work-up no precautions were taken to exclude air. IR spectra were recorded on a Perkin-Elmer 1710 series Fourier transform IR instrument in $CH_2Cl_2$ using NaCl cells (0.5 mm path length). Positive-ion fast atom bombardment (FAB) mass spectra were obtained using a Kratos MS50TC spectrometer, calibrated with CsI. $^1$H NMR spectra were recorded in $CDCl_3$ on a Bruker 250 B.MHz instrument, using internal TMS as reference. The clusters $Rh_4(CO)_{12}$ was purchased from Strem Chemicals and cyclohexa-1,3-diene from Aldrich Chemicals. The $Me_3NO$ was sublimed prior to use.

### *3.1. Reaction of $Rh_4(CO)_{12}$ with cyclohexa-1,3-diene and $Me_3NO$: preparation of $Rh_6(CO)_{10}(\mu_3\text{-}CO)_4(\eta^4\text{-}C_6H_8)$ (1)*

A solution of $Rh_4(CO)_{12}$ (80 mg) and cyclohexa-1,3-diene (1.5 ml) in dichloromethane (20 ml) was cooled in a dry ice–acetone bath (−78°C) and, $Me_3NO$ (17 mg, 2.1 mol equiv.) in dichloromethane (5 ml) was added dropwise. The mixture was allowed to warm to room temperature during 20 min, and the solvent was then removed in vacuo. The residue was dissolved in a minimum amount of dichloromethane and subjected to TLC with dichloromethane–hexane (1 : 4, v/v) as eluent. The major brown band eluted was characterized as $Rh_6(CO)_{10}(\mu_3\text{-}CO)_4(\eta^4\text{-}C_6H_8)$ (**1**) (19 mg). Spectroscopic data for **1**: $\nu_{CO}(CH_2Cl_2)$ 2097 (m), 2065 (vs) 2033 (w), 1793 (s) $cm^{-1}$; $^1H$ NMR ($CDCl_3$), $\delta$ 5.32 (m, 2H), 4.56 (m, 2H), 1.24 (s, 4H) ppm; positive-ion FAB mass spectrum $M^+ = 1089$ (Calc. 1090) u.

### 3.2. Structural characterization

Crystals of **1** suitable for X-ray analysis were grown from dichloromethane–hexane at −25°C during several weeks. The crystals were unstable when separated from the mother liquor and were therefore mounted in a droplet of mineral oil and data were collected at low temperature. Crystal data: $C_{20}H_8O_{14}Rh_6 \cdot CH_2Cl_2$, $M = 1174.65$ (including solvate), triclinic, space group $P\bar{1}$, $a = 9.606(7)$, $b = 9.805(7)$, $c = 17.01(2)$ Å, $\alpha = 75.41(7)$, $\beta = 83.53(7)$, $\gamma = 70.76(5)°$, $U = 1464(2)$ Å$^3$ (by least-squares refinement of the $2\theta$ values from 12 reflections measured at $\pm\omega$ ($2\theta = 22$–$26°$, $\lambda = 0.71073$ Å)), $Z = 2$, $F(000) = 1104$, $D_c = 2.666$ mg m$^{-3}$, $T = 150$ K, red crystals, $0.19 \times 0.27 \times 0.43$ mm, $\mu$(Mo $K\alpha$) = 3.553 mm$^{-1}$. Intensity data were measured on a Stoë Stadi-4 diffractometer to a maximum value for $\theta$ of 22.5°. A total of 4199 reflections were measured within the range $-10 \le h \le 10, -10 \le k \le 10, 0 \le l \le 18$ and avaraged to yield 3807 unique reflections ($R_{int} = 0.0280$) of which 3084 were judged as significant by the criterion that $F_{obs}^2 > 2\sigma(F_{obs}^2)$. Absorption corrections were applied by the use of semi-empirical $\psi$ scans (minimum and maximum transmission coefficients 0.445 and 0.540, respectively). Corrections for Lorentz and polarization effects were applied. Structure solution was by a combination of direct methods and Fourier techniques [11,12]. Hydrogen atoms were placed in calculated positions and refined using a riding model. Anisotropic thermal motion was assumed for all non-hydrogen atoms. Full matrix least-squares refinement on $F_{obs}^2$ for 3796 data, 388 parameters converged to $wR2 = 0.1075$ (all data), conventional $R1 = 0.0354$ (observed data), $(\Delta/\sigma)_{max} = 0.001$, GOF = 1.139. The function minimized was $\Sigma w(F_{obs}^2 - F_{calc}^2)^2$, $w = 1/(\sigma^2(F_{obs}^2) + (0.0283P)^2 + 20.87P)$, where $P = (F_{obs}^2 + 2F_{calc}^2)/3$ and $\sigma$ was obtained from counting statistics. A final difference electron density Fourier synthesis revealed maximum and minimum residual electron density peaks of 1.921 and −1.292 e Å$^{-3}$, respectively, which were located in close proximity to the Rh atoms. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and a full list of bond lengths and angles.

## Acknowledgement

We thank the EPSRC for financial support.

## References

[1] D. Braga, F. Grepioni, P. Sabatino, P.J. Dyson, B.F.G. Johnson, J. Lewis, P.J. Bailey, P.R. Raithby and D. Stalke, *J. Chem. Soc., Dalton Trans.*, (1993) 985.

[2] P.J. Dyson, B.F.G. Johnson, J. Lewis, M. Martinelli, D. Braga and F. Grepioni, *J. Am. Chem. Soc.*, 115 (1993) 9062.

[3] A.J. Blake, P.J. Dyson, B.F.G. Johnson, C.M. Martin, J.G.M. Nairn, E. parasini and J. Lewis, *J. Chem. Soc., Dalton Trans.*, (1993) 981.

[4] B.F.G. Johnson, A.J. Blake, C.M. Martin, D. Braga, E. Parisini and H. Chen, *J. Chem. Soc., Dalton Trans.*, (1994) 2167.

[5] T. Kitamura and T. Joh, *J. Organomet. Chem.*, 65 (1974) 235.

[6] E.R. Corey, L.F. Dahl and W. Beck, *Inorg. Phys. Theor.*, (1963) 1202.

[7] S.P. Tunik, A.V. Vlasov, N.I. Gorshkov, G.L. Starova, A.B. Nikol'skii, M.I. Rybinskaya, A.S. Batsanov and Y.T. Struchkov, *J. Organomet. Chem.*, 433 (1992) 189.

[8] G. Ciani, M. Manassero and V.G. Albano, *J. Chem. Soc., Dalton Trans.*, (1981) 515.

[9] P. Chini, G. Longoni and V.G. Albano, *Adv. Organomet. Chem.*, 14 (1976) 285.

[10] I.U. Khand, G.R. Knox, P.L. Pauson and W.E. Watts, *J. Chem. Soc., Perkin Trans.*, (1973) 975.

[11] G.M. Sheldrick, *SHELXTL-PLUS, 1992, Release 4.2 for Siemens Crystallographic Research Systems*, Siemens Analytical X-ray Instruments Madison, WI, 1992.

[12] G.M. Sheldrick, *SHELXL-93, Program for Structure Refinement*, University of Göttingen, Göttingen, 1993.