Organoaluminium and -Gallium Compounds with O-Oximato Substituents

Norbert W. Mitzel, Christian Lustig, and Markus Woski

Westfälische Wilhelms-Universität Münster, Institut für Anorganische und Analytische Chemie, Wilhelm-Klemm-Str. 8, D-48149 Münster, Germany

Reprint requests to Prof. Dr. N. W. Mitzel, Fax (+49)25183360 07.
E-mail: Mitzel@uni-muenster.de

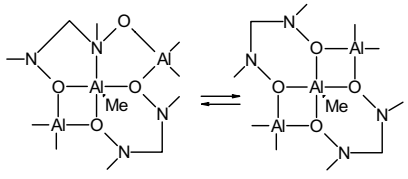
Z. Naturforsch. **58b**, 363–368 (2003); received February 24, 2003

The organoaluminium and -gallium acetonoximates (tBu$_2$MON=CMe$_2$)$_2$ (M = Al, Ga) have been prepared by the reaction of acetoneoxime with tri-*tert*-butylaluminium and -gallium. The compounds (Me$_2$MON=CMe$_2$)$_2$ (M = Al, Ga), described previously, were synthesized for comparison. All compounds have been characterised by NMR spectroscopy (^{1}H, ^{13}C, ^{27}Al), by mass spectrometry and elemental analyses. The crystal structures of the four compounds have been determined, and it was shown that all form dimers with six-membered M$_2$O$_2$N$_2$ rings by aggregation through the imino N atoms. The compounds (Me$_2$MON=CMe$_2$)$_2$ adopt boat conformations, whereas the compounds (tBu$_2$MON=CMe$_2$)$_2$ prefer chair conformations. Large differences in the M-O-N angles have been found between the methyl and the *tert*-butyl analogues.

Key words: Aluminium, Gallium, Oximates, Crystal Structure

Introduction

Organoaluminium and -gallium compounds containing ligands with donor functions in α- and β-position relative to the metal show a great variety of structural motifs, as was shown for hydrazides including Cowley's tetranuclear compound [Al$_4${NHNMe$_2$}$_8${NNMe$_2$}$_4$] with four Al$_2$N$_2$ rings and two three-membered AlNN units [1], [Et$_2$GaNHNPh$_2$]$_2$ which aggregates in Ga$_2$N$_2$ four-membered rings [2], and a few organoaluminium hydrazides prepared by Molter, Uhl and coworkers [3], part of which also show β-donor bonding leading to three-membered AlNN units. Peroxide derivatives of gallium organyls like [(tBu)$_2$GaO$O$$t$Bu]$_2$ with four-membered Ga$_2$O$_2$ rings have also recently been reported [4]. We have recently demonstrated the bis-hydroxylamine H$_2$C[N(Me)OH]$_2$ to react in two completely different modes with trimethylaluminium and -gallium [5]. With GaMe$_3$ heteronorbornane cages of the composition H$_2$C[N(Me)OGaMe$_2$]$_2$ with donor-acceptor bonds between Ga and the β-N atoms are formed (analogous to H$_2$C[N(Me)-CH$_2$GaMe$_2$]$_2$ [6]), which aggregate into endless chains linked by Ga$_2$O$_2$ rings. By contrast, AlMe$_3$ reacts with H$_2$C[N(Me)OH]$_2$ to give a trinuclear compound {H$_2$C[N(Me)O]$_2$}$_2$[AlMe$_2$]$_2$[AlMe], with an enormously flexible coordination behaviour. In solution at ambient temperature the central five-coordinate Al(Me) unit is dynamically bonded on time-average to all eight donor sites of the twelve-membered (ONCNOAl)$_2$ macro-cycle of the {H$_2$C[N(Me)O]$_2$}$_2$[AlMe$_2$]$_2$ unit (Scheme 1). In the solid state a rigid unsymmetrical binding mode with a central O$_3$NAl(Me) unit occurs, rather than a O$_4$Al(Me) core, as was found in the related but β-nitrogen-free trinuclear Al compounds of diols [7].

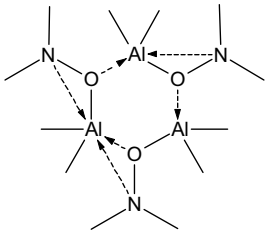


Scheme 1.

The only other organometallic AlON and GaON compounds reported previously were the hydroxylamine derivative Me$_2$AlONMe$_2$ [8] and the oximes Me$_2$AlON=CMe$_2$ and Me$_2$GaON=CMe$_2$ [9]. Weidlein's Me$_2$AlONMe$_2$ shows an interesting form of aggregation into trimers with an Al$_3$O$_3$ six-membered ring with the primary coordination mediated through the α-donors and with the three NMe$_2$ groups weakly bonded to only two of the Al centres, so that a compound with four-, five-

0932–0776/03/0500–0363 $06.00

and six-coordinate Al atoms in the same molecule results (Scheme 2).



Scheme 2.

$Me_2AlON{=}CMe_2$ and $Me_2GaON{=}CMe_2$ first prepared by K. Wade and co-workers have so far not been structurally characterized. In this contribution, we report on the crystal structures of these compounds and of two analogous compounds with increased sterical bulk at the metal centres, introduced by *tert*-butyl instead of methyl substituents.

Results

Equimolar amounts of trimethylaluminium or -gallium and acetoneoxime react at low temperatures in hexane or diethyl ether solution to give methane and the corresponding singly substituted (acetoneoximato)dimethylaluminium (**1**) and -gallium (**2**) [9].

$$2\ Me_3M + 2\ HON{=}CMe_2 \rightarrow (Me_2MON{=}CMe_2)_2 + 2\ CH_4 \qquad M = Al\ (\mathbf{1}),\ Ga \qquad (\mathbf{2})$$

These oximates can be isolated in good yields as colourless crystals after storage of the solutions at – 20 °C for one day. The solids are sensitive to hydrolysis by moist air.

Characterisation by spectroscopic methods was undertaken complementing the results of Wade *et al.* In the ^{1}H NMR and ^{13}C NMR spectra of **1** and **2** the metal bound methyl groups give only one signal indicating the flexibility of the six-membered ring dimers (see crystallographic part) at ambient temperature and the rapid interconversion of their conformations. The methyl groups of the oxime ligands in both, **1** and **2**, give different resonances due to their chemical and magnetical inequivalence. In the ^{27}Al NMR spectrum of **1** a broad signal appears at 149 ppm with a half width of 3000 Hz, which is indicative of a tetra-coordinate Al atom with low symmetry in its first coordination sphere.

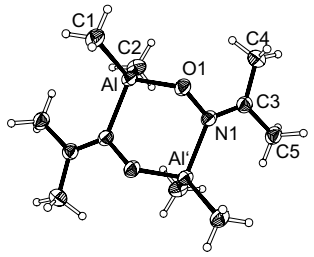


Fig. 1. Molecular structure of $(Me_2AlON{=}CMe_2)_2$ (**1**) as determined by low-temperature X-ray crystallography.

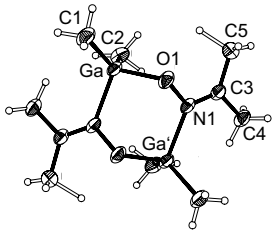


Fig. 2. Molecular structure of $(Me_2GaON{=}CMe_2)_2$ (**2**) as determined by low-temperature X-ray crystallography.

The results of the crystal structure determinations are shown in Fig. 1 and 2, and a selection of bond lengths and angles is listed in Table 1. **1** and **2** are isomorphous and crystallise in the monoclinic space group *C*2/*c* with eight monomer units in the cell. The monomers are aggregated into six-membered ring dimers through M-N donor-acceptor bonds. The M-N distances are 1.988(1) Å (M = Al,

Table 1. Selected bond lengths and angles [Å/°] of (2-propanoneoximato)dimethylaluminium und -gallium, **1** and **2**, as determined by low-temperature X-ray crystallography.

$(Me_2AlON{=}CMe_2)_2$ (**1**)		$(Me_2GaON{=}CMe_2)_2$ (**2**)	
Al-O	1.791(1)	Ga-O	1.898(2)
Al-N	1.988(1)	Ga-N	2.044(3)
Al-C1	1.956(1)	Ga-C1	1.962(3)
Al-C2	1.964(1)	Ga-C2	1.971(4)
N-O′	1.399(1)	N-O′	1.388(3)
N-C3	1.286(1)	N-C3	1.287(4)
Al-O-N′	120.2(1)	Ga-O-N′	117.1(2)
Al-N-O′	114.5(1)	Ga-N-O′	115.6(2)
C1-Al-C2	122.6(1)	C1-Ga-C2	127.6(2)
O-Al-N	99.6(1)	O-Ga-N	97.5(1)
C1-Al-O	107.7(1)	C1-Ga-O	105.6(1)
C2-Al-O	108.8(1)	C2-Ga-O	107.1(1)
C1-Al-N	108.7(1)	C1-Ga-N	107.4(1)
C2-Al-N	107.0(1)	C2-Ga-N	107.5(1)

1) and 2.044(3) Å (M = Ga, **2**), which is in the established range for Al-N and Ga-N donor-acceptor bonds.

The coordination geometry of the aluminium and gallium atoms is distorted tetrahedral. This is manifest from the strongly widened C-M-C angles [**1**: 122.6(1)°, **2**: 127.6(2)°], wheras the O-M-N angles are markedly compressed relative to an ideal tetrahedral angle [**1**: 99.6(3), **2**: 97.5(1)°]. In contrast to many other alkoxide complexes, the saturation of the coordination sphere in **1** and **2** is achieved by coordination to the nitrogen atoms and not to the oxygen atoms of the aggregation partner. This points to an increased hardness of the sp^2 imino nitrogen atom in the oximato substituents relative to the sp^3 amino nitrogen atom in hydroxylamines. Note that in the related (*N*,*N*-dimethylaminoxy)dimethylaluminium trimer, $(Me_2NOAlMe_2)_3$, the monomers are aggregated through the oxygen atoms [8].

The six-membered rings of **1** and **2** adopt a boat rather than the expected chair conformation, which was found in related compounds such as $Me_2MCH_2NMe_2$ (M = Al, Ga) [10]. The reason for this behaviour is not obvious.

In order to study the effect of steric bulk on the aggregation mode and the conformational behaviour of oximato-aluminium and -gallium compounds, we synthesized two compounds bearing *tert*-butyl groups at the metal atoms. For this purpose tri-*tert*-butyl-aluminium and -gallium were reacted with acetoneoxime in hexane. The reactions were conducted at low temperatures and proceeded with liberation of *iso*-butane. Crystalline samples of acetoneoximato-di-*tert*-butylaluminium (**3**) and -gallium (**3**) could be obtained upon cooling solutions to – 25 °C. The compounds are sensitive to moist air and decompose above 180 °C/230 °C without melting.

$$2\ (t\text{-Bu})_3M + 2\ HON{=}CMe_2 \rightarrow$$
$$((t\text{-Bu})_2MON{=}CMe_2)_2 + 2\ (t\text{-Bu})H \quad M = Al\ (\mathbf{3}),\ Ga \qquad (\mathbf{4})$$

The identity of both compounds was proven by elemental analyses, NMR spectroscopy (^1H, ^{13}C, ^{27}Al), mass spectrometry and single crystal X-ray diffraction.

Due to their chemical and magnetical inequivalence, the methyl groups of the oxime ligands give rise to two singlets in the ^1H NMR spectra of **3** (1.59, 1.66 ppm) and **4** (1.58, 1.76 ppm). In both compounds there is only one signal for the *tert*-butyl groups indicating their rotational dynamics and a rapid change between the conformations of the six-membered ring dimer-aggregates. Accordingly, the same pattern of signals is found in the ^{13}C NMR spectra.

The existence of aggregates is obvious for **1** from a resonance at 127 ppm in the ^{27}Al NMR spectrum with a half width of 3800 Hz, both values being typical for four-coordinate aluminium atoms as expected in oligomers.

In contrast to the pair **1** and **2**, compounds **3** and **4** are not isomorphous. Compound **3** crystallises in the monoclinic space group $P2_1/n$, whereas **4** was obtained in the form triclinic crystals, space group $P\bar{1}$. Otherwise the structures of both compounds are very similar as is depicted in Fig. 3 and 4 and found in the parameters listed in Table 2.

Both compounds are dimers with six-membered $M_2N_2O_2$ rings. Like compounds **1** and **2**, the *tert*-butyl compounds **3** and **4** form N-M donor-acceptor bonds [**3**: 1.990(1), **4**: 2.054(1) Å], which shows that the bulk of the *tert*-butyl groups is not sufficient to change the aggregation mode. However, the conformation of the *tert*-butyl compounds deviates from that of the methyl substituted ones, as **3** and **4** adopt chair conformations. Despite con-

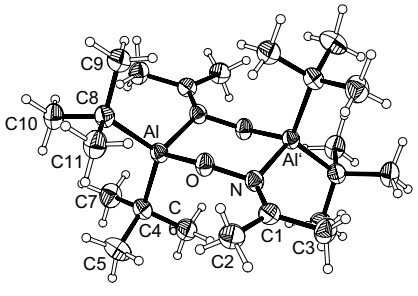


Fig. 3. Molecular structure of $(t\text{Bu}_2\text{AlON}{=}\text{CMe}_2)_2$ (**3**) as determined by low-temperature X-ray crystallography.

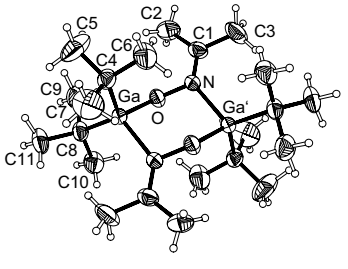


Fig. 4. Molecular structure of $(t\text{Bu}_2\text{AlON}{=}\text{CMe}_2)_2$ (**4**) as determined by low-temperature X-ray crystallography.

Table 2. Selected bond lengths and angles [Å/°] of (2-propanoneoximato)di-*tert*butylaluminium und -gallium, **3** and **4**, as determined by low-temperature X-ray crystallography.

(t-$Bu_2AlON{=}CMe_2)_2$ (**3**)		(t-$Bu_2GaON{=}CMe_2)_2$ (**4**)	
Al-O	1.779(1)	Ga-O	1.898(1)
Al-N′	1.990(1)	Ga-N′	2.054(1)
Al-C4	1.990(1)	Ga-C4	2.000(2)
Al-C8	2.011(1)	Ga-C8	2.013(2)
N-O′	1.375(1)	N-O′	1.381(2)
N-C1	1.284(1)	N-C1	1.280(2)
Al-O-N	133.4(1)	Ga-O-N	126.1(1)
Al-N-O′	111.2(1)	Ga-N′-O′	109.8(1)
C4-Al-C8	119.9(1)	C4-Ga-C8	122.8(1)
O-Al-N′	99.5(1)	O-Ga-N′	95.3(1)
C4-Al-O	114.8(1)	C4-Ga-O	115.0(1)
C8-Al-O	100.9(1)	C8-Ga-O	98.9(1)
C4-Al-N′	103.7(1)	C4-Ga-N′	103.5(1)
C8-Al-N′	116.6(1)	C8-Ga-N′	118.3(1)

formational changes, the bond lengths N-O, M-N and N-O in **1** and **3** as well as in **2** and **4** are similar.

While steric bulk and conformational changes seem not to exert a pronounced effect on bond lengths, the bond angles are found to be quite dependent on these changes.

The angles O-Al-N′ in **1** and **3** are almost identical, while the angles O-Ga-N′ in **2** and **4** differ only by 2°. The C-M-C angles are surprisingly smaller in **3** and **4** than in **1** and **2**, even though the alkyl groups in **3** and **4** are larger and thus should repel each other more strongly. The magnitudes of the C-M-O and C-M-N′ angles can also not be explained by solely taking the steric bulk of the *tert*-butyl groups into account.

The largest changes in bond angles are found to occur in the valence angles at oxygen. The Al-O-N angle is widened by 13° on going from **1** to **3** and by 9° between **2** and **4**. This points to strongly ionic contributions to the metal oxygen bonds, which are therefore not strictly bound to orientation preferences as would result from a pure hybrid orbital picture.

The coordination of the nitrogen donor atom is trigonal planar in all four compounds. There is a markedly widened M-N-C angle (**1**: 129.5(1) , **2**: 128.1(2), **3**: 132.5(1), **4**: 134.2(1)°) in all compounds, whereas the C-N-O and M-N-O angles are always less than 120°.

The preference for oxygen as the donor site used for aggregation as in $Me_2AlONMe_2$ [9] and in the trinuclear $\{H_2C[N(Me)O]_2\}_2[AlMe_2]_2[AlMe]$ [5] cannot be found in the oximates discussed in this paper. These present compounds are thus more similar to the heteronorbornane $H_2C[N(Me)\text{-}OGaMe_2]_2$, which saturates the coordination sphere of its metal atoms by bonding to the softer nitrogen centres [5]. Further investigations on hydroxylamine derivatives of aluminium- and galliumalkyls are necessary to get a deeper insight into coordinative preferences in compounds with donor centres in α- and β-position relative to the metal.

Experimental Section

The preparation of **1** and **2** was analogous to the reported literature procedure [10]. New spectroscopic data are listed here:

(Acetoneoximato)dimethylaluminium (**1**)

M. p. 71 °C. – ^{1}H NMR (400.05 MHz, C_6D_6): δ =– 0.48 (s, 6H, AlC$\underline{H}_3$), 1.40 (s, 3H, CC$\underline{H}_3$), 1.75 (s, 3H, CC$\underline{H}_3$). – ^{13}C NMR (100.64 MHz, C_6D_6): δ = – 10.0 [q, $^1J_{CH}$ = 113.2 Hz, Al($\underline{C}H_3)_2$], 17.3 (q q, $^1J_{CH}$ = 126.5 Hz, $^3J_{CH}$ = 3.2 Hz,C$\underline{C}H_3$), 20.8 (q q, $^1J_{CH}$ = 128.9 Hz, $^3J_{CH}$ = 3.2 Hz, C$\underline{C}H_3$), 161.4 [sep, $^2J_{CH}$ = 6.4 Hz, $\underline{C}(CH_3)_2$]. – ^{27}Al NMR (104.05 MHz, C_6D_6): δ = 149 (s, $\nu_{1/2}$ = 3000 Hz).

(Acetoneoximato)dimethylgallium (**2**)

M. p. 90 °C. – ^{1}H NMR (400.05 MHz, C_6D_6): δ = 0.02 (s, 6H, GaC$\underline{H}_3$), 1.45 (s, 3H, CC$\underline{H}_3$), 1.67 (s, 3H, CC$\underline{H}_3$). – ^{13}C NMR (100.64 MHz, C_6D_6): δ = – 6.7 [q, $^1J_{CH}$ = 113.0 Hz, Ga($\underline{C}H_3)_2$], 16.9 (q q, $^1J_{CH}$ = 125.9 Hz, $^3J_{CH}$ = 3.2 Hz, C$\underline{C}H_3$), 20.7 (q q, $^1J_{CH}$ = 128.8 Hz, $^3J_{CH}$ = 3.2 Hz, C$\underline{C}H_3$), 160.9 [sep, $^2J_{CH}$ = 6.4 Hz, $\underline{C}(CH_3)_2$].

Acetoneoximato-di-tert-butylaluminium (**3**)

A solution of tri-*tert*-butylaluminium (0.883 g, 5 mmol) in hexane (40 mL) was slowly added to acetoneoxime (0.365 g, 5 mmol) in hexane (25 ml) at – 78 °C. The mixture was allowed to warm to ambient temperature and was stirred overnight. The solution was separated from the precipitate by a filtration cannula. Storage at – 25 °C afforded colourless crystals of **3** after 5 d. Yield 1.08 g (51%). ^{1}H NMR (400.05 MHz, C_6D_6): δ = 1.19 (s, 18H, Al(C($C\underline{H}_3)_3$), 1.59 (s, 3H, NC($C\underline{H}_3)_2$), 1.66 (s, 3H, NC($C\underline{H}_3)_2$). – ^{13}C {^{1}H} NMR (100.64 MHz, C_6D_6): δ = 15.8 (s, Al$\underline{C}(CH_3)_3$), 17.9 (s, N=C($\underline{C}H_3$)), 21.5 (s, N=C($\underline{C}H_3$)), 31.2 (s, Al(C($\underline{C}H_3)_3$), 166.6 (s, N=$\underline{C}(CH_3)_2$). – ^{27}Al NMR

(104.05 MHz, C_6D_6): δ = 127 ($\nu_{1/2}$ = 3800 Hz). – MS (CI): *m/z* = 400 (M^+ –Me), 355 (M^+–Me–^{t}Bu), 314 (M^+–2^{t}Bu), 255 (M^+–3^{t}Bu), 214 (M^+–3^{t}Bu–CMe_2), 172 (^{t}Bu$_2$AlON$^+$), 117 (M^+–4^{t}Bu–2 CMe_2). – $C_{22}H_{48}N_2O_2Al_2$ (426.58) calcd. C 61.9, H 11.3, N 6.6; found C 56.2, H 10.3, N 6.0. Large deviations in the carbon contents from the calculated values are frequently observed for organoaluminium compounds due to carbide formation. Decomposition of the compound occurs above 180 °C without melting.

Acetoneoximato-di-tert-*butylgallium* (**4**)

A solution of acetoneoxime (0.365 g, 5 mmol) in hexane (25 ml) was slowly added to a solution of tri-*tert*-butylgallium (1.203 g, 5 mmol) in hexane (30 ml) at – 78 °C. After allowing the mixture to warm to ambient temperature a clear solution resulted from which the product crystallised upon cooling to – 25 °C. Yield 0.48 g (1.89 mmol, 38%) of colourless crystals, which are sensitive to hydrolysis. ^{1}H NMR (400.05 MHz, C_6D_6): δ = 1.27 (s, 18H, Ga(C(C$\underline{H}_3$)$_3$)$_3$), 1.58, (s, 3H, NC(C$\underline{H}_3$)$_2$), 1.76 (s, 3H, NC(C$\underline{H}_3$)$_2$). – ^{13}C {^{1}H} NMR (100.64 MHz, C_6D_6): δ = 17.4, (s, N=C(C$\underline{H}_3$)$_2$), 21.9 (s, N=C(C$\underline{H}_3$)$_2$), 24.5 (s, Ga(C$\underline{(CH_3)_3}$), 31.3 (s, Ga(C(C$\underline{H}_3$)$_3$), 162.2 (s, N=C$\underline{(CH_3)_2}$). – MS (CI): *m/z* = 455 (M^+–^{t}Bu), 400 (M^+–2 ^{t}Bu), 340 (M^+–3 ^{t}Bu), 285 (M^+–4 ^{t}Bu), 142 ($GaONMe_2^+$). – $C_{22}H_{48}N_2O_2Ga_2$ (512.08): calcd. C 51.6, H 9.5, N 5.5, found C 51.5, H 9.4, N 5.4. Decomposition above 230 °C without melting.

Crystal structure determinations

Single crystals of compounds **1**, **2**, **3** and **4** were mounted under inert perfluoropolyether at the tip of a glass fiber and cooled in the cryostream of the diffractometer. Data were collected on a Nonius Turbo-CAD4 diffractometer for **1** and **2** and a Nonius DIP 2020 for **3** and **4**. Both diffractometers were operated with monochromatic Mo-K_α radiation (λ = 0.71073 Å). No absorption corrections were applied for **1** and **2**, while the scattering intensities of **3** and **4** were corrected by the program SCALEPACK [12]. The structure solutions were carried out using direct methods and the refinements of the structure were undertaken with the program SHELXTL 5.01 [13]. Non-hydrogen atoms were refined with anisotropic thermal displacement parameters, hydrogen atoms isotropically. Further details of data collection and refinement are listed in Table 3. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre

Table 3. Data for the single-crystal X-ray diffraction experiments.

no	**1**	**2**	**3**	**4**
formula	$C_5H_{12}NOAl$	$C_5H_{12}NOGa$	$C_{11}H_{24}NOAl$	$C_{11}H_{24}NOGa$
M_r	129.14	171.88	213.29	256.03
T [K]	168(2)	168(2)	143(2)	143(2)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	*C*2/*c*	*C*2/*c*	$P2_1/n$	$P\bar{1}$
a [Å]	11.9207(4)	11.9146(8)	8.3045(2)	8.0136(2)
b [Å]	8.4227(2)	8.5899(5)	9.8405(2)	9.2978(2)
c [Å]	16.6389(5)	16.5321(15)	16.7912(5)	11.1873(3)
α [°]	90	90	90	67.1676(9)
β [°]	110.3111(16)	110.350(6)	104.0972(10)	70.9182(10)
γ [°]	90	90	90	66.8016(16)
V [Å^3]	1566.74(8)	1568.4(2)	1330.86(6)	691.06(3)
Z, D_{calc} [g cm^{-3}]	8, 1.095	8, 1.439	4, 1.065	2, 1.230
Crystal size [mm]	0.5 × 0.4 × 0.4	0.4 × 0.3 × 0.25	0.5 × 0.3 × 0.3	0.5 × 0.3 × 0.3
$Refl_{collected/unique}$	2351/2351	2450/1729	61810/4411	33181/4203
R_{int}	–	0.073	0.050	0.047
θ_{max}	30.4	27.0	31.6	31.7
Completeness [%]	99.2	99.7	99.1	89.5
Data/parameters	2351/121	1729/121	4411/223	4203/224
Extinction coeff.	–	–	–	0.039(6)
R_1/wR_2 ($I > 2\sigma(I)$)	0.0345/0.0985	0.0381/0.1008	0.0472/0.1208	0.0320/0.0752
R_1/wR_2 (all data)	0.0357/0.0989	0.0448/0.1057	0.0577/0.1280	0.0372/0.0782
$\Delta\varrho_{fin}$ [eÅ^{-3}]	0.238/– 0.248	1.125/– 1.029	0.442/– 0.255	0.289/– 0.475

as supplementary publication no. CCDC-204067 (**1**), CCDC-204068 (**2**) CCDC-204070 (**3**) and CCDC-204069 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie.

[1] J. S. Silverman, C. D. Abernethy, R. A. Jones, A. H. Cowley, J. Chem. Soc., Chem. Commun. 1645 (1999).
[2] D. A. Neumayer, A. H. Cowley, A. Decken, R. A. Jones, V. Lakhotia, J. G. Eckerdt, Inorg. Chem. **34**, 4698 (1995).
[3] W. Uhl, J. Molter, B. Neumüller, Eur. J. Inorg. Chem. 1510 (2001); W. Uhl, J. Molter, R. Koch, Eur. J. Inorg. Chem. 2021 (1999); d) W. Uhl, J. Molter, R. Koch, Eur. J. Inorg. Chem. 2255 (2000); f) W. Uhl, J. Molter, B. Neumüller, Organometallics **19**, 4422 (2000); g) W. Uhl, J. Molter, B. Neumüller, Inorg. Chem. **20**, 2011 (2001); h) W. Uhl, J. Molter, B. Neumüller, Chem. Eur. J. **7**, 1510 (2001).
[4] M. B. Power, W. M. Cleaver, A. W. Apblett, A. R. Barron, J. W. Ziller, Polyhedron **11**, 477 (1992).
[5] N. W. Mitzel, C. Lustig, Angew. Chem. **113**, 4521 (2001); Angew. Chem. Int. Ed. **113**, 4390 (2001).
[6] C. Lustig, N. W. Mitzel, Chem. Commun. 1393 (2000).
[7] W. Ziemkowska, S. Pasynkiewicz, J. Organomet. Chem. **508**, 243 (1996); J. Lewinski, J. Zachara J. Organomet. Chem. **560**, 89 (1998); W. Ziemkowska, S. Pasynkiewicz, T. Glowiak, J. Organomet. Chem. **562**, 3 (1998).
[8] H. D. Hausen, G. Schmöger, W. Schwarz, J. Organomet. Chem. **153**, 271 (1978).
[9] J. R. Jennings, K. Wade, J. Chem. Soc. A 1333 (1967).
[10] a) C. Lustig, N. W. Mitzel, Organometallics **21**, 3471 (202); b) C. Lustig, N. W. Mitzel, Organometallics **22**, 242 (2003).
[11] Z. Otwinowski, W. Minor, Methods Enzymol. **276**, 307(1976).
[12] SHELXTL 5.01, Siemens Analytical X-Ray Instrumentation Inc. Madison, WI (1995).