Complexes of Organoaluminium Compounds. Part 12.[1] Preparation, Nuclear Magnetic Resonance Spectra, and the Crystal and Molecular Structure of Bis(μ-isopropylamido-dimethylaluminium)

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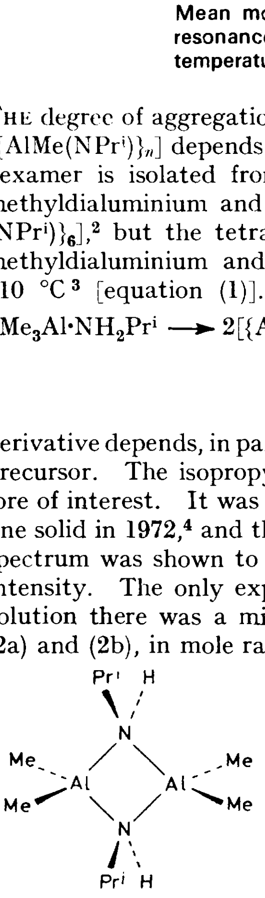
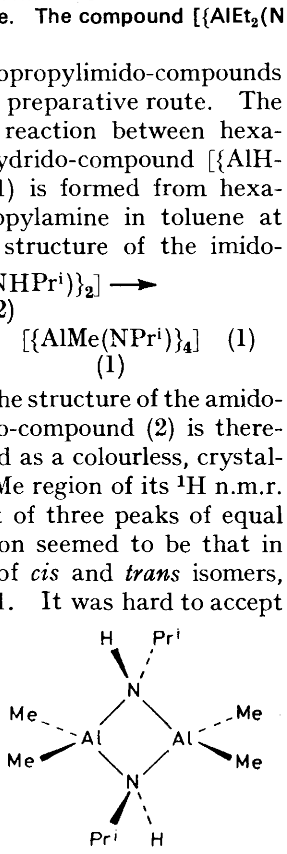
The title compound, $[\{AlMe_2(NHPr^i)\}_2]$, has been made from trimethylaluminium and isopropylamine. Crystals are triclinic with a = 858.6(3), b = 1 136.6(5), and c = 1 344.0(5) pm, α = 107.48(3), β = 90.52(2), γ = 99.21(3)°, and Z = 3. The structure determination (diffractometer data, 2 388 reflections, R = 0.078) shows that molecules have four-membered $(AlN)_2$ rings and that *cis* and *trans* isomers, mole ratio 2 : 1, crystallise together. Mean molecular parameters are: Al–N 195.2(9), Al–C 196.1(6), and N–C 149.7(8) pm. Nuclear magnetic resonance measurements show that the ratio of *cis* to *trans* isomers in solution is also close to 2 : 1 over a wide temperature range. The compound $[\{AlEt_2(NHPr^i)\}_3]$ has also been characterised.

THE degree of aggregation of isopropylimido-compounds $[\{AlMe(NPr^i)\}_n]$ depends on the preparative route. The hexamer is isolated from the reaction between hexamethyldialuminium and the hydrido-compound $[\{AlH(NPr^i)\}_6]$,[2] but the tetramer (1) is formed from hexamethyldialuminium and isopropylamine in toluene at 210 °C[3] [equation (1)]. The structure of the imido-derivative depends, in part, on the structure of the amido-precursor. The isopropylamido-compound (2) is therefore of interest. It was isolated as a colourless, crystalline solid in 1972,[4] and the Al–Me region of its ^1H n.m.r. spectrum was shown to consist of three peaks of equal intensity. The only explanation seemed to be that in solution there was a mixture of *cis* and *trans* isomers, (2a) and (2b), in mole ratio 2 : 1. It was hard to accept that this result arose fortuitously, so publication was withheld pending further investigations. We have now found *cis*- and *trans*-$[\{AlMe_2(NHPr^i)\}_2]$ in a 2 : 1 mole ratio in the solid state as well as in solution, and therefore describe our original preparation of this compound, and the related compound $[\{AlEt_2(NHPr^i)\}_3]$, (3), in detail.

$$4Me_3Al{\cdot}NH_2Pr^i \longrightarrow \underset{(2)}{2[\{AlMe_2(NHPr^i)\}_2]} \longrightarrow \underset{(1)}{[\{AlMe(NPr^i)\}_4]} \quad (1)$$



(2a)



(2b)

EXPERIMENTAL

General methods have been indicated in earlier parts of this series.[5,6] For analysis, samples were hydrolysed by sulphuric acid (1 mol dm^{-3}). Methane and ethane were estimated by vacuum-line techniques, aluminium was determined gravimetrically, and isopropylamine by the semimicro Kjeldahl method.[7] Molecular weights were measured cryoscopically or ebullioscopically in benzene. In n.m.r. spectra, ^1H chemical shifts (relative intensities in parentheses) were measured relative to the solvent peak in toluene which was assumed to be at τ 7.67; ^{13}C shifts were measured in p.p.m. from C_6D_6.

Bis[isopropylamido(dimethyl)aluminium], (2).—The compounds $AlMe_3$ (2.42 g, 33.7 mmol) and NH_2Pr^i (33.7 mmol) were mixed at −196 °C and the mixture was warmed to 20 °C. The white product $Me_3Al{\cdot}NH_2Pr^i$, m.p. 38—40 °C, was heated for 3 h in an ethane atmosphere at 140 °C and the methane formed (33.5 mmol) was separated and identified (i.r. and gas–liquid chromatography) in the vacuum line. The residue was sublimed carefully at 10^{-3} Torr,† but only one product, m.p. 52—54 °C, was obtained [Found: Me, 26.0; Al, 22.4; $NHPr^i$, 50.6%. *M* (cryoscopic), 228, $C_{10}H_{28}Al_2N_2$ requires Me, 26.1; Al, 23.5; $NHPr^i$, 50.4%. *M*, 230]. I.r.: ν(N–H), 3 258 cm^{-1}. N.m.r.: ^1H τ 6.84 (1), two unequal septets [^3J(HCCH) 6.3 Hz], (CH); 8.90 (6), doublet, (C–CH_3); *ca.* 9.7 (1), very broad, (NH); 10.35 (2), 10.40 (2) (Al–CH_3, *cis* isomer); 10.45 (2) (Al–CH_3, *trans* isomer). ^{13}C (p.p.m.): 83.1 [$(CH_3)_2CH$], 101.2 [$(CH_3)_2$-CH], and 136.7, very broad, $AlCH_3$. The Al–Me region of the ^1H spectrum was recorded at various temperatures, and ratios of isomers were found from peak areas: *cis* : *trans* (°C), 2.11 : 1 (60), 2.05 : 1 (27), 1.97 : 1 (0), 1.86 : 1 (−30), 1.83 : 1 (−60). Hence ΔH for (2b) ⟶ (2a) = 848 J mol^{-1}.

Tris[diethyl(isopropylamido)aluminium], (3).—The compound NH_2Pr^i (28 mmol) was bled slowly from a vacuum line into a flask containing $AlEt_3$ (3.19 g, 28 mmol) at −78 °C. The resulting colourless liquid complex $Et_3Al{\cdot}NH_2Pr^i$ was heated to 80—100 °C for 5 h to give ethane (27 mmol) and a colourless *liquid* b.p. 78 °C (10^{-3} Torr). Yield after distillation: 75% [Found: Et, 39.8; Al, 18.9; $NHPr^i$, 40.3%. *M*(cryoscopic), 433; *M* (ebullioscopic), 343. $C_7H_{18}AlN$ requires Et, 40.6; Al, 18.9; $NHPr^i$, 40.6%. *M*(trimer), 429; *M*(dimer), 286]. I.r.: ν(N–H), 3 250 cm^{-1}. N.m.r.: ^1H τ *ca.* 7.2 (1) [$(CH_3)_2CH$]; 9.1 (9) [$(CH_3)_2CH$ + $AlCH_2CH_3$]; 9.6 (1), very broad, (NH); 10.3 (2) ($AlCH_2CH_3$). ^{13}C (p.p.m.): 83.3 [$(CH_3)_2CH$], 100.6 [$(CH_3)_2CH$], 118.4 ($AlCH_2CH_3$), 128.2, very broad, ($AlCH_2CH_3$). The resonances at τ 7.2, 9.1, and 10.3 all showed several overlapping multiplets and the ^1H-{^{13}C} resonances at 83.3 and 118.4 p.p.m. showed, besides the main peak, two weaker peaks with relative intensities 2 : 1.

Mass Spectra.—Details of the spectra of (2) and (3) are

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† Throughout this paper: 1 Torr = (101 325/760) Pa.

given in the Supplementary Publication (see below). Fragmentations are similar to those for other organoaluminium amides.[5,8] The most intense peaks correspond to loss of methyl or ethyl from the parent ions; thereafter, eliminations of even-electron fragments, *e.g.* CH_4, NH_2-Pr^i, C_3H_6, or C_2H_4, predominate.

Crystal Data.—$C_{10}H_{28}Al_2N_2$ (2), $M = 230.3$, Triclinic, $a = 858.6(3)$, $b = 1\,136.6(5)$, $c = 1\,344.0(5)$ pm, $\alpha = 107.48(3)$, $\beta = 90.52(2)$, $\gamma = 99.21(3)°$, $U = 1.232\,62$ nm^3, $Z = 3$, $D_c = 0.93$ g cm^{-3}, $F(000) = 384$, μ(Mo-K_α) = 1.58 cm^{-1}, space group $P\bar{1}$.

Crystallographic Measurements.—A crystal of approximate dimensions 0.3 × 0.2 × 0.2 mm was sealed in a Lindemann glass capillary. The crystal was shown to be triclinic by Weissenberg and precession photographs and data for refinement were collected using a Hilger and Watts Y290 four-circle diffractometer. Accurate cell dimensions were estimated from setting angles of 12 reflections (Mo-K_α radiation, $\lambda = 70.926$ pm, with a graphite-crystal monochromator). The intensities of 3 807 unique reflections with $2 < \theta < 20°$ were obtained by ω—2θ step scans and three standard reflections measured after every 100 showed no change during data collection. Corrections were made for Lorentz and polarisation effects but not for absorption. Data with $I < 3\sigma(I)$ were rejected leaving 2 388 reflections for use in the structure determination.

TABLE 1

Fractional atomic co-ordinates (× 10^4), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Al(3)	−1 339(2)	4 528(1)	9 314(1)
Al(1)	5 679(2)	1 902(1)	2 774(1)
Al(2)	3 106(2)	2 244(1)	4 033(1)
N(3)	930(5)	4 561(4)	9 189(3)
N(1)	3 429(5)	1 896(4)	2 541(3)
N(2)	5 403(5)	2 572(4)	4 254(3)
C(11)	6 155(9)	218(6)	2 425(6)
C(12)	6 988(10)	3 182(8)	2 282(6)
C(22)	2 296(10)	3 813(6)	4 554(6)
C(21)	2 184(8)	720(6)	4 362(6)
C(31)	−2 497(8)	2 844(5)	9 161(5)
C(10)	2 466(8)	809(5)	1 745(5)
C(101)	2 992(10)	727(7)	666(5)
C(102)	723(9)	891(7)	1 805(7)
C(20)	6 234(8)	2 113(6)	5 027(5)
C(201)	7 958(8)	2 425(8)	5 005(7)
C(202)	5 668(12)	2 661(8)	6 122(5)
C(30)	1 559(7)	3 386(5)	8 704(4)
C(302)	927(11)	2 795(8)	7 569(6)
C(301)	3 347(9)	3 621(8)	8 783(7)
C(32)	−2 035(9)	5 546(6)	8 499(6)

Structure Solution and Refinement.—After initial data processing with University of Sussex crystallographic computer programs, the SHELX system of G. M. Sheldrick was used for structure solution and refinement, with atomic scattering factors from ref. 9. The centrosymmetrical space group was confirmed by the subsequent successful refinement. The *E* map obtained by the direct methods program revealed aluminium and nitrogen atoms and some of the carbon atoms. The remaining carbon atoms were found from the next map. Hydrogen atoms, except those on N(1), N(2), N(3), C(10), C(20), and C(30), were visible on a difference-Fourier map and were included at idealised positions but not refined. Full-matrix least-squares refinement, with anisotropic temperature factors for non-hydrogen atoms, and a weighting scheme defined as $w = 0.084\,5/[\sigma^2(F) + 0.138(F)^2]$ was continued until the maximum parameter shift-to-error was <0.25, with $R = 0.078$, $R' = 0.116$. A final difference-Fourier map was everywhere $\leqslant 0.45$ e Å^{-3} (1 Å = 100 pm). Final fractional co-ordinates are given in Table 1. Fractional co-ordinates for hydrogen atoms, temperature factors, torsional angles, observed structure amplitudes, and calculated structure factors are given in Supplementary Publication No. SUP 22945 (16 pp.).*

RESULTS AND DISCUSSION

The *X*-ray study of crystalline $[\{AlMe_2(NHPr^i)\}_2]$ indicates an asymmetric unit of $1\frac{1}{2}$ molecules. Thus, two thirds of the molecules [(2a), Figure 1] occupy general positions and have no crystallographically required symmetry, though the molecular parameters (Table 2) indicate that the symmetry is close to C_{2v}.

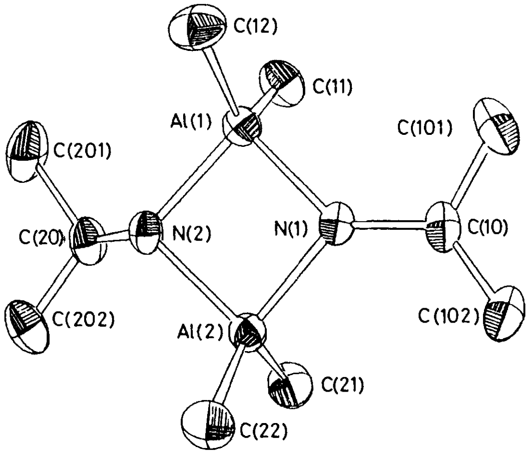

FIGURE 1 The molecular structure of *cis*-$[\{AlMe_2(NHPr^i)\}_2]$, (2a)

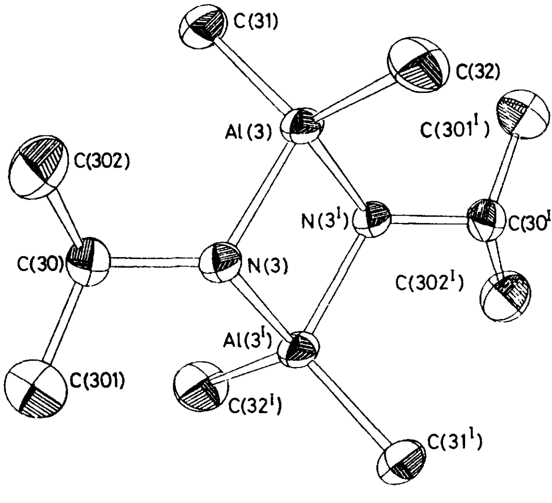

FIGURE 2 The molecular structure of *trans*-$[\{AlMe_2(NHPr^i)\}_2]$, (2b)

One third of the molecules [(2b), Figure 2] have crystallographic symmetry C_i, but the non-bonding distances in Table 2 show that the true symmetry is greater and approximately C_{2h}. All the molecules have four-

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

membered rings of alternate aluminium and nitrogen atoms; the isopropyl groups are *cis* in (2a) and *trans* in (2b). The Al–N, Al–C, and N–C bond distances in (2a) are not significantly different from the corresponding distances in (2b) and are similar to those in the dimers $[\{AlMe_2(NMe_2)\}_2]$, (4),[10,11] and $[\{AlX_2(NMe_2)\}_2]$ (X = Cl,[12,13] Br, or I [13]), or the trimers $[\{AlMe_2(NHMe)\}_3]$ [10] and $[\{AlMe_2(NH_2)\}_3]$.[14] The N–Al–N and Al–N–Al angles in (2a), (2b), and (4) are also similar.

TABLE 2

Intramolecular bond lengths (pm) and angles (°) with estimated standard deviations in parentheses and selected intramolecular contact distances (pm)

(*a*) Distances			
Al(1)–N(1)	195.3(5)	Al(2)–C(22)	195.2(8)
Al(1)–N(2)	193.6(4)	N(1)–C(10)	148.9(6)
Al(2)–N(1)	195.6(4)	N(2)–C(20)	151.4(9)
Al(2)–N(2)	195.0(5)	C(10)–C(101)	150.4(10)
Al(1)–C(11)	194.0(7)	C(10)–C(102)	151.5(10)
Al(1)–C(12)	197.1(9)	C(20)–C(201)	146.9(10)
Al(2)–C(21)	196.2(8)	C(20)–C(202)	153.3(9)
Al(1) · · · Al(2)	280.0	N(1) · · · N(2)	268.6
Al(1) · · · C(101)	342.8	N(2) · · · C(11)	320.2
Al(1) · · · C(201)	340.9	N(2) · · · C(21)	322.8
Al(2) · · · C(102)	341.0	N(1) · · · C(12)	323.9
Al(2) · · · C(202)	342.0	N(1) · · · C(22)	319.4
N(1) · · · C(11)	322.5	N(2) · · · C(12)	319.8
N(1) · · · C(21)	323.7	N(2) · · · C(22)	318.6
Al(3)–N(3)	195.2(4)	N(3)–C(30)	148.8(7)
Al(3)–N(3$^{\mathrm{I}}$)*	196.5(5)	C(30)–C(301)	151.3(10)
Al(3)–C(31)	196.2(6)	C(30)–C(302)	152.5(9)
Al(3)–C(32)	196.6(9)		
Al(3) · · · Al(3$^{\mathrm{I}}$)	278.9	N(3) · · · N(3$^{\mathrm{I}}$)	275.0
Al(3) · · · C(302)	342.0	N(3) · · · C(31)	325.3
Al(3) · · · C(301$^{\mathrm{I}}$)	345.7	N(3$^{\mathrm{I}}$) · · · C(32)	328.2
Al(3) · · · C(30)	299.7	N(3) · · · C(32)	317.6
Al(3$^{\mathrm{I}}$) · · · C(30)	301.8	N(3$^{\mathrm{I}}$) · · · C(31)	319.0
(*b*) Angles			
N(1)–Al(1)–N(2)	87.4(2)	N(1)–Al(2)–N(2)	86.9(2)
Al(1)–N(1)–Al(2)	91.5(2)	Al(1)–N(2)–Al(2)	92.2(2)
C(11)–Al(1)–N(1)	111.9(2)	C(21)–Al(2)–N(1)	111.4(2)
C(12)–Al(1)–N(1)	111.2(3)	C(22)–Al(2)–N(1)	109.6(3)
C(11)–Al(1)–N(2)	111.4(3)	C(21)–Al(2)–N(2)	111.2(3)
C(12)–Al(1)–N(2)	109.8(3)	C(22)–Al(2)–N(2)	109.5(3)
C(10)–N(1)–Al(1)	119.2(4)	C(20)–N(2)–Al(1)	119.8(3)
C(10)–N(1)–Al(2)	121.5(4)	C(20)–N(2)–Al(2)	121.7(4)
C(101)–C(10)–C(102)	110.8(7)	C(201)–C(20)–C(202)	111.7(6)
C(101)–C(10)–N(1)	110.8(5)	C(201)–C(20)–N(2)	110.9(6)
C(102)–C(10)–N(1)	110.7(5)	C(202)–C(20)–N(2)	109.5(6)
N(3)–Al(3)–N(3$^{\mathrm{I}}$)	89.2(2)	Al(3)–N(3)–Al(3$^{\mathrm{I}}$)	90.8(2)
C(31)–Al(3)–N(3)	112.5(2)	C(30)–N(3)–Al(3)	120.6(3)
C(32)–Al(3)–N(3)	108.3(3)	C(30)–N(3)–Al(3$^{\mathrm{I}}$)	121.3(3)
C(31)–Al(3)–N(3$^{\mathrm{I}}$)	108.6(2)	C(301)–C(30)–C(302)	110.9(6)
C(32)–Al(3)–N(3$^{\mathrm{I}}$)	113.3(3)	C(301)–C(30)–N(3)	111.1(5)
C(32)–Al(3)–C(31)	120.6(3)	C(302)–C(30)–N(3)	110.7(6)

* Symmetry operation I: $-x, 1-y, 2-z$.

Several bond angles and non-bonded contacts show intramolecular steric interactions. In the *cis* isomer, (2a), the $(AlN)_2$ ring is folded at the Al · · · Al line, with a dihedral angle of 15.5°. In the *trans* isomer, the $AlMe_2$ groups are twisted away from the perpendicular plane bisecting the $(AlN)_2$ ring along the Al · · · Al line. These distortions are accommodated so that bond angles at aluminium and nitrogen are about the same in the two isomers. A wide range of CAlC angles has been observed in other dimethylaluminium derivatives;[15] the values found here for (2a) and (2b) are similar to those in $[\{AlMe_2(N{=}CMe_2)\}_2]$,[16] but a little larger than those in $[\{AlMe_2(NMe_2)\}_2]$, (4), and $[\{AlMe_2(NHMe)\}_3]$. This may indicate that in the last two species the $AlMe_2$ group is strongly compressed. There are no intermolecular distances significantly shorter than the sum of the van der Waals radii.

The structure of $[\{AlMe_2(NHPr^i)\}_2]$ is remarkably similar to that of $[(AlMe_2Ph)_2]$, which also crystallises in space group $P\bar{1}$, with one third of the molecules having symmetry D_{2h} and two thirds lying at general positions with symmetry C_{2v}. The $(AlC)_2$ ring is folded about the Al · · · Al line with a dihedral angle of 14°.[17] A careful study of intramolecular H · · · H distances in this case suggested that folding produced little increase in repulsion energy. Folded four-membered rings have also been reported in $[Al_2(C_3H_5)_6]$ (dihedral angle 32°) [18] and $[\{AlEtBr(NHBu^t)\}_2]$.[19]

The elucidation of the crystal structure of $[\{AlMe_2(NHPr^i)\}_2]$ explains several puzzling features of the original preparative work,[4] *e.g.* the ^1H n.m.r. spectrum, and the failure to separate *cis* and *trans* isomers, as achieved for $[\{AlMe_2(NHMe)\}_3]$.[5,10] It is evident that the isomers (2a) and (2b) persist in hydrocarbon solution, and that the ratio of concentrations is close to 2 : 1 over a wide temperature range. If this ratio represents an equilibrium constant, the enthalpy of interconversion is small. However, the alternative explanation, that the isomers are kinetically stable, *i.e.* that they are formed in 2 : 1 mole ratio and subsequently interconvert only slowly, cannot be completely ruled out. On heating, the concentrations of both isomers fall at the same rate with formation of the tetramer $[\{AlMe(NMe)\}_4]$, (1), which, apart from methane, is the only product detected. This reaction is being studied further.

It is still not clear why the ethyl derivative (3) is trimeric rather than dimeric in benzene at 5 °C. Both the ^1H and ^{13}C n.m.r. spectra suggest that there may be *cis* and *trans* isomers in solution, as found previously for $[\{AlMe_2(NHMe)\}_3]$ [5] and $[\{AlEt_2(NHMe)\}_3]$,[8] but, with the resolution so far available, quantitative determination of the proportions has not been possible. There is some evidence that trimers are converted to dimers in boiling benzene; the only peaks observed in the mass spectrum are from fragmentation of dimers.

Initiation of Polymerization.—The compounds $[\{AlEt_2(NHPr^i)\}_2]$ and $[\{AlEt_2(NMe_2)\}_2]$ [20] were examined as initiators for the polymerization of methyl methacrylate, acetaldehyde, and n-butyraldehyde. Polymerisation of methyl methacrylate occurred over the temperature range 35—80 °C; below 35 °C the rate of polymerization was immeasurably small. The i.r. spectrum of the polymer proved that the ethylenic bond was the site of polymerization, and all the evidence from i.r. spectroscopy, *X*-ray studies, and differential scanning calorimetry was consistent with the polymer being amorphous. Because of the known low ceiling temperatures for polymerization of aldehydes, all experiments were carried out below −40 °C, mostly at −78 °C. The i.r. spectra of the polymers clearly demonstrated that reaction took place through the carbonyl function to yield a product with an alternating carbon–oxygen backbone. Evidence of crystallinity from i.r. frequencies was confirmed by *X*-ray studies and by solubility measurements. The crystallinity of the polyacetaldehyde was $>95\%$. Details of our polymerization experiments will be published elsewhere.

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REFERENCES

[1] Part 11, S. Amirkhalili, P. B. Hitchcock, J. D. Smith, and J. G. Stamper, *J. Chem. Soc., Dalton Trans.*, 1980, 2493.

[2] S. Cucinella, T. Salvatori, C. Busetto, and M. Cesari, *J. Organomet. Chem.*, 1976, **121**, 137.

[3] G. Del Piero, M. Cesari, G. Dozzi, and A. Mazzei, *J. Organomet. Chem.*, 1977, **129**, 281.

[4] J. Z. Nyathi, B.Sc. Thesis, University of Sussex, 1973.

[5] K. J. Alford, K. Gosling, and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 1972, 2203.

[6] S. Amirkhalili, P. B. Hitchcock, and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 1979, 1206.

[7] J. A. Barnard and R. Chayen, 'Modern Methods of Chemical Analysis,' McGraw-Hill, London, 1965, p. 26.

[8] K. Gosling, J. D. Smith, and D. H. W. Wharmby, *J. Chem. Soc. A*, 1969, 1738.

[9] D. T. Cromer and J. B. Mann, *Acta Crystallogr.*, 1968, **A24**, 321; R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175; D. T. Cromer and D. Liberman, *ibid.*, 1970, **53**, 1891.

[10] G. M. McLaughlin, G. A. Sim, and J. D. Smith, *J. Chem. Soc., Dalton Trans.*, 1972, 2197.

[11] A. Hess, A. Hinderer, and S. Steinhauser, *Z. Anorg. Allg. Chem.*, 1970, **377**, 1.

[12] A. Ahmed, W. Schwarz, and H. Hess, *Acta Crystallogr.*, 1977, **B33**, 3574; *Z. Naturforsch., Teil B*, 1978, **33**. 43.

[13] T. C. Bartke A. Haaland, and D. P. Novak, *Acta Chem. Scand., Ser. A*, 1975, **29**, 273.

[14] K. N. Semenenko, E. B. Lobkovskii, and A. L. Dorosinskii, *J. Struct. Chem.* (*Eng. Transl.*), 1972, **13**, 696.

[15] M. T. Barlow, A. J. Downs, P. D. P. Thomas, and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1979, 1793.

[16] J. F. Malone and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1972, 2649.

[17] S. K. Seale and J. L. Atwood, *J. Organomet. Chem.*, 1974, **73**, 27.

[18] J. W. Moore, D. A. Sanders, P. A. Scherr, M. D. Glick, and J. P. Oliver, *J. Am. Chem. Soc.*, 1971, **93**, 1035.

[19] R. E. Bowen and K. Gosling, *J. Chem. Soc., Dalton Trans.*, 1974, 964.

[20] K. Ziegler, B.P. 799,823/1958.