3). A calculation of the methylene proton chemical shift difference in the solid using the McGlinchey method is in progress to compare that difference with the NMR experimental data.

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Acta Cryst. (1988). C**44**, 1391–1394

Structures of [*N*-(*p*-Methoxyphenyl)-2-(*p*-methoxyphenylimino)propylamino-*N*,*N*′]-dimethylaluminium (I) and Dimethyl[*N*-(*p*-tolyl)-2-(*p*-tolylimino)propylamino-*N*,*N*′]aluminium (II)

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(*Received* 9 *November* 1987; *accepted* 14 *April* 1988)

Abstract. $[Al(CH_3)_2(C_{17}H_{19}N_2O_2)]$ (I), $M_r = 340{\cdot}40$, triclinic, $P\bar{1}$, $a = 9{\cdot}844\,(1)$, $b = 10{\cdot}263\,(2)$, $c = 11{\cdot}317\,(1)$ Å, $\alpha = 74{\cdot}15\,(1)$, $\beta = 70{\cdot}14\,(1)$, $\gamma = 63{\cdot}70\,(1)°$, $V = 953{\cdot}8\,(3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}185$ g cm^{-3}, $\lambda(\text{Cu}\,K\alpha) = 1{\cdot}54184$ Å, $\mu = 9{\cdot}40$ cm^{-1}, $F(000) = 364$, $T = 298$ K. The structure has been refined to $R = 0{\cdot}0480$ for 3057 unique observed reflections with $I \geq 2{\cdot}5\sigma(I)$. $[Al(CH_3)_2(C_{17}H_{19}N_2)]$ (II), $M_r = 308{\cdot}40$, triclinic, $P\bar{1}$, $a = 9{\cdot}593\,(2)$, $b = 10{\cdot}135\,(1)$, $c = 11{\cdot}274\,(2)$ Å, $\alpha = 104{\cdot}88\,(5)$, $\beta = 109{\cdot}54\,(5)$, $\gamma = 102{\cdot}69\,(7)°$, $V = 940{\cdot}5\,(5)$ Å^3, $Z = 2$, $D_x = 1{\cdot}089$ g cm^{-3}, $\lambda(\text{Cu}\,K\alpha) = 1{\cdot}54184$ Å, $\mu = 8{\cdot}9$ cm^{-1}, $F(000) = 332$, $T = 298$ K. The structure has been refined to $R = 0{\cdot}0735$ for 1507 unique observed reflections with $I \geq 2{\cdot}5\sigma(I)$. Corresponding distances, angles and conformations of (I) and (II) are very similar. The phenyl ring at N(1) is coplanar with the five-membered aluminium ring in both compounds, whereas the phenyl ring at N(2) makes an angle of 78·1 (1)° for (I) and 69·9 (3)° for (II).

Introduction. Trialkylaluminium and dialkylzinc compounds react selectively with 1,4-dihetero-1,3-butadienes (*R*-DAB with *R* = alkyl, aryl) to give, after hydrolysis, interesting products such as 1-amino-2-iminoethanes and 1,2-diaminoethanes (Klerks, Stufkens, van Koten & Vrieze, 1979). Intermediate complexes have been obtained from the reactions of AlR_3 and ZnR_2 with $R{-}N{=}C(R')C(R''){=}N{-}R$ (Klerks, Stufkens, van Koten & Vrieze, 1979; Klerks, Jastrzebski, van Koten & Vrieze, 1982; Jastrzebski, Klerks, van Koten & Vrieze, 1981; van Koten, Jastrzebski & Vrieze, 1983) and with $R{-}N{=}C(R')C(R''){=}O$ (van Vliet, Jastrzebski, van Koten, Vrieze & Spek, 1983; van Vliet, van Koten, Rotteveel, Schrap, Vrieze, Kojič-Prodič, Spek & Duisenberg, 1986; van Vliet, van Koten & Buysingh, 1987; van Vliet, van Koten, de Keijser & Vrieze, 1987). In the course of our investigations with the *R*-DAB molecule as a bidentate ligand we decided to carry out crystal structure analyses on the two title compounds obtained from the reaction of *R*-DAB with trimethylaluminium.

Experimental. (I) A yellowish rod-shaped crystal (0·3 × 0·3 × 0·5 mm), mounted under nitrogen in a Lindemann-glass capillary, was used for data collection on an Enraf–Nonius CAD-4F diffractometer with

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for non-*H *atoms of compounds* (I) *and* (II), *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}†
Compound (I)				
Al	0·07554 (7)	0·70871 (6)	0·53692 (6)	0·0484 (2)
O(1)	−0·3327 (2)	0·7149 (2)	1·1626 (2)	0·0856 (8)
O(2)	0·3018 (2)	0·7636 (2)	−0·1208 (1)	0·0737 (6)
N(1)	−0·1315 (2)	0·7659 (2)	0·6336 (2)	0·0524 (5)
N(2)	−0·0173 (2)	0·7812 (2)	0·3903 (1)	0·0488 (5)
C(1)	0·2029 (3)	0·4983 (2)	0·5399 (2)	0·072 (1)
C(2)	0·1873 (3)	0·8280 (3)	0·5328 (2)	0·0663 (6)
C(3)	−0·2464 (2)	0·8341 (2)	0·5596 (2)	0·0518 (6)
C(4)	−0·1682 (2)	0·8376 (2)	0·4215 (2)	0·0497 (6)
C(5)	−0·2688 (3)	0·9036 (3)	0·3306 (2)	0·0635 (6)
C(6)	−0·4934 (3)	0·7574 (3)	1·2258 (2)	0·085 (1)
C(7)	0·3808 (4)	0·6288 (3)	−0·1719 (3)	0·087 (1)
C(11)	−0·1892 (2)	0·7590 (2)	0·7643 (2)	0·0503 (6)
C(12)	−0·0848 (3)	0·7009 (3)	0·8416 (2)	0·0615 (6)
C(13)	−0·1360 (3)	0·6894 (3)	0·9721 (2)	0·0659 (8)
C(14)	−0·2942 (3)	0·7357 (3)	1·0316 (2)	0·0621 (6)
C(15)	−0·3995 (3)	0·7941 (3)	0·9587 (2)	0·0621 (6)
C(16)	−0·3476 (2)	0·8056 (2)	0·8267 (2)	0·0577 (6)
C(21)	0·0676 (2)	0·7748 (2)	0·2582 (2)	0·0491 (6)
C(22)	0·0887 (3)	0·8975 (2)	0·1796 (2)	0·0582 (6)
C(23)	0·1686 (3)	0·8890 (2)	0·0541 (2)	0·0626 (6)
C(24)	0·2289 (2)	0·7580 (2)	0·0058 (2)	0·0564 (6)
C(25)	0·2113 (3)	0·6351 (2)	0·0854 (2)	0·0583 (6)
C(26)	0·1312 (3)	0·6432 (2)	0·2115 (2)	0·0570 (6)
Compound (II)				
Al	0·3518 (2)	0·2010 (2)	0·5601 (2)	0·0571 (6)
N(1)	0·4361 (6)	0·2787 (5)	0·4557 (5)	0·057 (2)
N(2)	0·5727 (6)	0·2748 (5)	0·6944 (5)	0·056 (2)
C(1)	0·2672 (9)	−0·0118 (7)	0·4986 (7)	0·087 (3)
C(2)	0·2312 (9)	0·3051 (8)	0·6308 (8)	0·092 (3)
C(3)	0·6043 (7)	0·3532 (7)	0·5208 (6)	0·059 (2)
C(4)	0·6682 (8)	0·3446 (6)	0·6595 (6)	0·055 (2)
C(5)	0·8427 (8)	0·4187 (8)	0·7396 (7)	0·079 (3)
C(6)	0·096 (1)	0·2017 (9)	−0·0974 (7)	0·096 (3)
C(7)	0·762 (1)	0·180 (1)	1·1974 (7)	0·097 (4)
C(11)	0·3610 (7)	0·2655 (6)	0·3238 (6)	0·051 (2)
C(12)	0·1971 (8)	0·1952 (7)	0·2570 (6)	0·064 (3)
C(13)	0·1139 (8)	0·1770 (8)	0·1235 (7)	0·069 (3)
C(14)	0·1885 (9)	0·2249 (7)	0·0501 (7)	0·065 (3)
C(15)	0·3492 (8)	0·2953 (7)	0·1154 (7)	0·063 (3)
C(16)	0·4342 (8)	0·3156 (6)	0·2484 (6)	0·062 (2)
C(21)	0·6247 (7)	0·2522 (7)	0·8216 (7)	0·056 (2)
C(22)	0·6769 (8)	0·3673 (7)	0·9432 (7)	0·073 (3)
C(23)	0·7204 (8)	0·3401 (8)	1·0621 (7)	0·075 (3)
C(24)	0·7137 (8)	0·2067 (8)	1·0651 (7)	0·067 (3)
C(25)	0·6605 (8)	0·0933 (8)	0·9437 (7)	0·077 (3)
C(26)	0·6161 (8)	0·1175 (7)	0·8233 (7)	0·071 (3)

† $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

Ni-filtered Cu $K\alpha$ radiation. Cell constants were obtained by least-squares fitting of four alternative settings of six reflections in the range $23{\cdot}3 < \theta < 29{\cdot}6°$, with the 'set 4' method of de Boer & Duisenberg (1984). The intensity data of 7699 reflections were collected within the complete reflection sphere ($-12 \le h \le 12$, $-12 \le k \le 12$ and $-13 \le l \le 13$; $2\theta_{max} = 140°$). Averaging of equivalent reflections and applying $I > 2{\cdot}5\sigma(I)$ resulted in 3057 independent reflections ($R_{int} = 0{\cdot}057$). Scan mode ω–2θ with $\Delta\omega = (0{\cdot}55 + 0{\cdot}15\tan\theta)°$. Three reference reflections (100, 020, 002) were measured every hour and showed no significant variation.

(II) A red rod-shaped crystal (0·6 × 0·2 × 0·2 mm), mounted under nitrogen in a Lindemann-glass capillary, was used for data collection on an Enraf–Nonius CAD-4F diffractometer with Ni-filtered Cu $K\alpha$ radiation. Cell constants were obtained by least-squares fitting of the setting angles of 25 reflections in the range $12{\cdot}6 < \theta < 20{\cdot}4°$. The intensity data of 3373 observed reflections were collected within one half of the reflection sphere ($-11 \le h \le 11$, $-11 \le k \le 12$, $-13 \le l \le 0$; $2\theta_{max} = 140°$). Scan mode ω–2θ with $\Delta\omega = (0{\cdot}55 + 0{\cdot}15\tan\theta)°$. Three reference reflections ($1\bar{3}0$,$\bar{1}01$,$\bar{1}02$), measured every hour, showed a considerable, systematic decay of 60% during 65 h of X-ray exposure. After correction for decay 1507 reflections resulted with $I > 2{\cdot}5\sigma(I)$.

The space groups of (I) and (II) were assumed to be $P\bar{1}$, which was confirmed by the refinement. The structures were solved using direct methods (*SHELXS*86, Sheldrick, 1986) and subsequent Fourier analysis. Blocked full-matrix least-squares refinement on F. All H atoms were introduced at calculated positions with C—H = 1·0 Å, and refined riding on their carrier atoms with a general isotropic thermal parameter for (I). For (II) two different overall isotropic thermal parameters were calculated: one for the methyl H atoms, and one for the remaining H atoms. In the final cycles of the refinement positional and individual anisotropic thermal parameters for the non-H atoms, positional parameters for H atoms, their overall isotropic thermal parameter and an overall scale factor were varied. For (I) the final R value was 0·0451, $wR = 0{\cdot}0639$, $w = 1/[\sigma^2(F_o) + 0{\cdot}000073(F_o)^2]$, $S = 2{\cdot}98$ and the overall isotropic thermal parameter for the H atoms was 0·098 (3) Å^2; for (II) $R = 0{\cdot}0735$, $wR = 0{\cdot}0944$, $w = 1/[\sigma^2(F_o) + 0{\cdot}002172(F_o)^2]$, $S = 1{\cdot}39$, $U(H_{ring}) = 0{\cdot}074$ (7), $U(H_{rest}) = 0{\cdot}18$ (1) Å^2. An empirical extinction parameter (0·0183) was applied in the last stages of the refinement of (I). The relatively high R value of (II) must be ascribed to the poor quality of the crystal and the large decay of diffracting power during data collection. The average and max. shift/e.s.d. ratios in the final cycles were 0·007 and 0·017 (I) and 0·056 and 1·205 (II), respectively. Final residual electron density $-0{\cdot}24 < \rho < 0{\cdot}31$ e Å^{-3} (I) and $-0{\cdot}26 < \rho < 0{\cdot}36$ e Å^{-3} (II). The scattering factors for non-H atoms were taken from Cromer & Mann (1968), those for H atoms from Stewart, Davidson & Simpson (1965); anomalous-dispersion factors from Cromer & Liberman (1970). Calculations were performed with *SHELX*76 (refinement) (Sheldrick, 1976) and the *EUCLID* package (geometric calculations and illustrations) (Spek, 1982).

Discussion. The final atomic coordinates and equivalent isotropic thermal parameters of the non-H atoms of complexes (I) and (II) are given in Table 1.* Selected bond distances and angles are listed in Table 2.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and the complete internal geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44969 (51 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°)

	(I)	(II)
Al—N(1)	1·863 (2)	1·869 (6)
Al—N(2)	1·973 (2)	1·979 (6)
Al—C(1)	1·956 (2)	1·969 (8)
Al—C(2)	1·960 (3)	1·951 (9)
O(1)—C(14)	1·380 (3)	—
O(1)—C(6)	1·412 (4)	—
O(2)—C(24)	1·365 (2)	—
O(2)—C(7)	1·425 (3)	—
N(1)—C(3)	1·447 (3)	1·449 (9)
N(1)—C(11)	1·387 (3)	1·374 (8)
N(2)—C(4)	1·288 (3)	1·262 (9)
N(2)—C(21)	1·447 (2)	1·449 (8)
C(3)—C(4)	1·488 (3)	1·510 (9)
C(4)—C(5)	1·488 (4)	1·51 (1)
C(6)—C(14)	—	1·53 (1)
C(7)—C(24)	—	1·52 (1)
N(1)—Al—N(2)	84·7 (1)	84·3 (3)
N(1)—Al—C(1)	117·9 (1)	116·8 (3)
N(1)—Al—C(2)	115·9 (1)	115·0 (3)
N(2)—Al—C(1)	108·9 (1)	110·6 (3)
N(2)—Al—C(2)	110·0 (1)	109·7 (3)
C(1)—Al—C(2)	114·8 (1)	115·8 (4)
C(14)—O(1)—C(6)	117·1 (2)	—
C(24)—O(2)—C(7)	117·5 (2)	—
Al—N(1)—C(3)	114·3 (2)	114·9 (4)
Al—N(1)—C(11)	129·2 (2)	128·3 (5)
C(3)—N(1)—C(11)	116·5 (2)	116·7 (6)
Al—N(2)—C(4)	113·5 (1)	113·8 (4)
Al—N(2)—C(21)	126·3 (2)	124·6 (5)
C(4)—N(2)—C(21)	120·2 (2)	121·6 (6)
N(1)—C(3)—C(4)	110·6 (2)	109·2 (6)
N(2)—C(4)—C(3)	116·8 (2)	117·6 (6)
N(2)—C(4)—C(5)	125·1 (2)	127·3 (6)
C(3)—C(4)—C(5)	118·1 (2)	115·0 (6)
N(1)—C(11)—C(12)	119·6 (2)	118·6 (6)
N(1)—C(11)—C(16)	124·2 (2)	125·1 (6)
C(13)—C(14)—O(1)	116·0 (3)	—
O(1)—C(14)—C(15)	125·1 (3)	—
N(2)—C(21)—C(22)	120·8 (2)	120·5 (6)
N(2)—C(21)—C(26)	119·2 (2)	120·1 (6)
C(23)—C(24)—O(2)	115·4 (2)	—
O(2)—C(24)—C(25)	125·1 (2)	—
Phenyl rings $(\mathrm{C-C})_{\mathrm{av}}$		
C(11)···C(16)	1·39 (1)	1·39 (1)
C(21)···C(26)	1·382 (5)	1·38 (2)
Phenyl rings $(\angle\mathrm{C-C-C})_{\mathrm{av}}$		
C(11)···C(16)	120 (2)	120 (2)
C(21)···C(26)	120·0 (3)	120 (2)

Perspective views of the two compounds with the adopted atomic numbering are shown in Fig. 1.

The structures of both compounds (I) and (II) show unambiguously that the initially formed 1:1 addition products formed in the 1:2 reaction of Me_6Al_2 with *R*-DAB undergo a subsequent hydrogen shift. The relocation of the C=N double bond that accompanies this hydrogen shift is reflected by the short C(4)—N(2) distance of 1·288 (3) and 1·262 (9) Å for compounds (I) and (II), respectively. These distances are comparable to those found in 1,4-dichlorohexyl-1,4-diaza-1,3-butadiene, *viz* 1·258 (3) Å (Keijsper, van der Poel, Polm, van Koten, Vrieze, Seignette, Varenhorst & Stam, 1983).

The phenyl ring on N(1) is in the same plane as that of the five-membered aluminium ring. As a result, conjugation is possible between the free electron pair in a *p*-type orbital on N(1) and the π electrons of the phenyl ring. This is not possible for the phenyl ring on N(2), since this ring is twisted 78·1 (1) and 69·9 (3)° for (I) and (II), respectively, out of the plane of the metal ring system, owing to steric hindrance caused by the methyl group on C(4). Therefore, the N(1)—C(11) distance is significantly shortened in comparison to the N(2)—C(21) bond where no conjugation occurs: N(1)—C(11) = 1·387 (3) Å for (I) and 1·374 (8) Å for (II); N(2)—C(21) = 1·447 (2) and 1·449 (8) Å for (I) and (II), respectively.

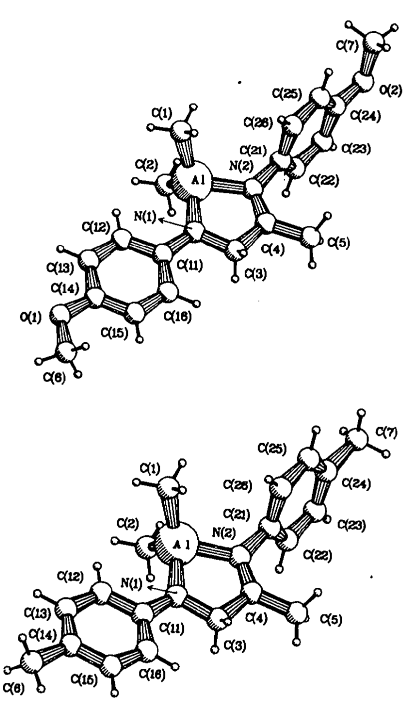

Fig. 1. Perspective views with atomic numbering of compounds (I) (top) and (II) (bottom).

The electron pair on N(2) is involved in a coordination bond to aluminium, whereas the Al—N(1) bond is more covalent in character as is reflected by the fact that the Al—N(2) bond [1·973 (2) Å for (I) and 1·979 (6) Å for (II)] is longer than the Al—N(1) bond [1·863 (2) Å for (I) and 1·869 (6) Å for (II)].

We wish to thank Mr M. Serné for the preparation of the compounds and Mr J. Jastrzebski for helpful discussions.

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Acta Cryst. (1988). C**44**, 1394–1397

Tricarbonyl[η^4-(méthoxy-4 phényl)-7 méthyl-3 octatriène-2,4,6 oate d'éthyle (tout-*E*)]fer

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(*Reçu le* 22 *septembre* 1987, *accepté le* 7 *avril* 1988)

Abstract. [$Fe(CO)_3(C_{18}H_{22}O_3)$], $M_r = 426{\cdot}3$, monoclinic, $P2_1/c$, $a = 16{\cdot}018\ (4)$, $b = 16{\cdot}749\ (4)$, $c = 7{\cdot}738\ (2)$ Å, $\beta = 91{\cdot}06\ (2)°$, $V = 2076\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}364$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}755$ mm^{-1}, $F(000) = 888$, $T = 295\ (1)$ K, $R = 0{\cdot}038$ for 2039 independent observed reflections. The molecule contains a butadiene chain bonded to the Fe atom. The geometry of the butadiene—Fe(CO)$_3$ group is in good agreement with that of the same group in other complexes. The Fe—C(carbonyl) distances are identical within the experimental error [from 1·781 (4) to 1·785 (4) Å] whilst the Fe—C(butadiene) distances fall in the range 2·055 (4)–2·166 (4) Å. The C—C bond lengths of the butadiene chain [1·408 (6)–1·425 (6) Å] indicate a complete delocalization of the π electrons which are partly conjugated with those of the ethylenic bond and with those of the carboxylate group. Each atom of the ethoxy group shows very high thermal motion. The cohesion of the structure is due to van der Waals interactions.

Introduction. On a reconnu récemment à l'acide rétinoïque et aux rétinoïdes des propriétés anticancéreuses (Sporn, Roberts & Goodman, 1984; Cunliffe & Miller, 1984; Nugent & Clark, 1985). Dans le but de déterminer les modifications susceptibles de renforcer ou d'atténuer l'activité pharmacologique, nous avons préparé des analogues structuraux, les aryl-7 méthyl-3 octatriène-2,4,6 oates d'alkyle et étudié leur activité antipapillomateuse (Ducrey, 1985).

Une méthode de préparation de ces composés met en jeu une réaction de Wittig entre l'(aryl-1 éthylidène)-1 triphénylphosphorane (synthon C_2) et le méthyl-3 oxo-6 hexadiène-2,4 oate d'alkyle (synthon C_6) dont la stéréochimie tout-*E* est conservée au cours de la réaction grâce à la fixation d'un groupement fertricarbonyle. Dans l'étape terminale, ce dernier est éliminé par les méthodes classiques (*N*-oxyde de triéthylamine, méthanol). La réaction de Wittig peut conduire aux deux stéréoisomères (2*E*, 4*E*, 6*E*) et (2*E*, 4*E*, 6*Z*). Les spectres de RMN de ^{1}H à 270 MHz et de ^{13}C ne permettent pas d'identifier l'isomère obtenu. C'est la raison pour laquelle l'étude structurale d'un composé intermédiaire, le tricarbonyl[η^4-(méthoxy-4 phényl)-7 méthyl-3 octatriène-2,4,6 oate d'éthyle (tout-*E*)]fer, a été entreprise. Les cristaux utilisés sont issus de l'évaporation d'une solution dans l'éther diisopropylique.

Partie expérimentale. Cristal en forme de plaquette: 0,05 × 0,27 × 0,42 mm. Dimensions de la maille déterminées sur monocristal avec 25 réflexions telles que $6{,}52 \leq \theta \leq 17{,}84°$. Diffractomètre Enraf–Nonius CAD-4. $0{,}039 \leq (\sin\theta)/\lambda \leq 0{,}550$ Å^{-1}; $-17 \leq h \leq 17$, $0 \leq k \leq 18$, $0 \leq l \leq 8$. Balayage $\theta/2\theta$ d'amplitude $s(°) = 0{,}80 + 0{,}35\,\text{tg}\,\theta$. Réflexions de contrôle: $\bar{4}12$, 0,10,0

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