

(*trans*-Cinnamaldehyde)tris(2,6-diphenylphenoxy)aluminium**William Clegg,^{a*} Mark R. J. Elsegood,^{a†} Ronald Snaith^{b‡} and Andrew E. H. Wheatley^b**^aSchool of Natural Sciences (Chemistry), University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England, and ^bDepartment of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England† Current address: Chemistry Department, Loughborough University, Loughborough, Leicestershire LE11 3TU, England
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Key indicators

Single-crystal X-ray study

T = 160 K

Mean $\sigma(\text{C}-\text{C}) = 0.008 \text{ \AA}$

R factor = 0.068

wR factor = 0.228

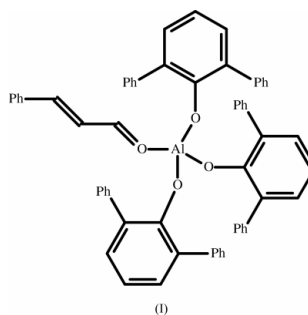
Data-to-parameter ratio = 10.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $[\text{Al}(\text{C}_{18}\text{H}_{13}\text{O})_3(\text{C}_9\text{H}_8\text{O})]$, crystallizes with three molecules in the asymmetric unit of the chiral trigonal space group $P3_2$. The three molecules have essentially the same geometry, and are related by non-crystallographic translation and other pseudosymmetry, all being in approximately the same orientation. Aluminium has a typical tetrahedral coordination. Al—O bond lengths range from 1.695 (3) to 1.716 (3) Å for the bulky substituted phenoxy ligands, and from 1.830 (4) to 1.841 (4) Å for the neutral *trans*-cinnamaldehyde ligands.

Comment

While soft organometallic reagents have frequently been employed to effect conjugate addition to α,β -unsaturated ketones, organolithium species have generally been found to be too nucleophilic for this purpose (Roux *et al.*, 1981). Oxophilic Lewis acids in general (see, for example, Volkman *et al.*, 1983; Yamamoto, 1986), and sterically congested organoaluminium species in particular (Maruoka & Yamamoto, 1985) have been developed in consequence. More recently, the organoaluminium species methylaluminium bis(di-2,6-*tert*-butyl-4-alkylphenoxy) (alkyl = Me or *t*Bu) have been found to aid conjugate addition to α,β -unsaturated ketones (Shreve *et al.*, 1988; Maruoka *et al.*, 1988). Lately, however, the regioselective conjugate addition of organolithium species to aromatic aldehydes has been effected by the employment of tris(di-2,6-*tert*-butylphenoxy)aluminium (Maruoka *et al.*, 1995); it is presumed (Maruoka *et al.*, 1994) that this reaction occurs *via* a 1:1 complex between the aldehyde and the organoaluminium species. Such adducts of aldehydes have not previously been structurally characterized, although they are known for ketones (Maruoka *et al.*, 1994). We report here the crystal structure of the 1:1 complex, (I), of *trans*-cinnamaldehyde and the related reagent tris(2,6-diphenylphenoxy)aluminium.



There are three independent molecules in the asymmetric unit, shown in Fig. 1. Differences between them are minor, consisting mainly of slightly different dihedral angles among

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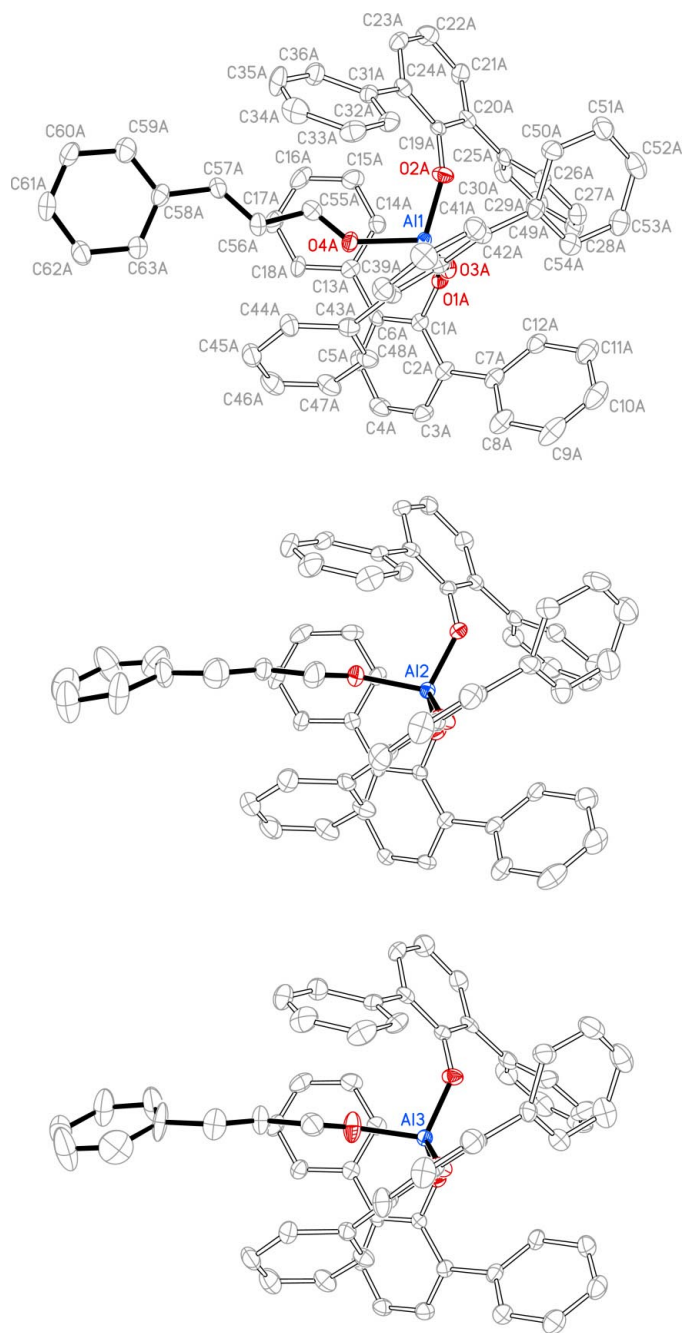


Figure 1

The structure of the three independent molecules of (I), shown with 50% probability ellipsoids. The view direction is the same for all three molecules. Only one molecule is labelled in full; the others follow a similar scheme. H atoms have been omitted.

aromatic ring planes within the aryloxy ligands and somewhat different orientations of the cinnamaldehyde ligand. Dihedral angles between the central and outer rings for the nine independent aryloxy ligands range from 36.3 (2) to 52.4 (2)°. Those between the cinnamaldehyde phenyl ring and its corresponding chain substituent are 18.3 (5), 19.6 (5) and 22.6 (5)° in the three independent molecules.

Aluminium has a typical tetrahedral coordination, the range of O—Al—O bond angles being 104.31 (15)–

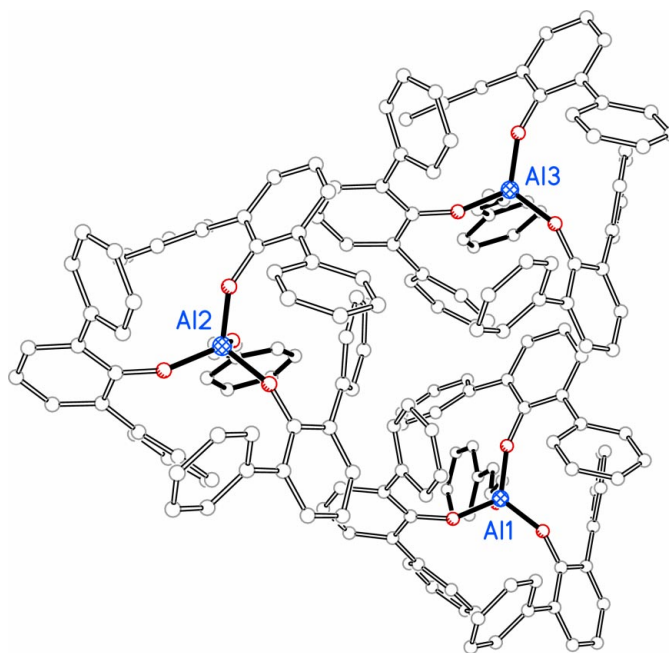


Figure 2

The three molecules in the asymmetric unit, seen down the *c* axis, showing the pseudosymmetry. H atoms have been omitted.

114.51 (16)°. Angles at O atoms are generally rather wide, ranging from 136.6 (3) to 153.3 (3)° for the aryloxy ligands and from 137.3 (3) to 145.4 (5)° for cinnamaldehyde, presumably because of the steric congestion. The only other reported structure of a complex of the type Al(*R*CHO)(OR')₃ has the same aryloxy ligands, together with benzaldehyde, and here the angles at oxygen are similar: 136.1, 144.1, 149.6, and 135.7°; the structure has not been published in a journal, but is deposited in the Cambridge Structural Database (CSD refcode QULSUQ; Saito *et al.*, 2001). The CSD (Allen, 2002) contains only three other complexes of aluminium with aldehyde ligands (Power *et al.*, 1990; Ko *et al.*, 2000; Liu *et al.*, 2002). Al—O(aldehyde) distances range from 1.856 to 2.018 Å, because Al is variously four- or five-coordinate; Al—O—C angles at the aldehyde O atom lie within the relatively small range 127.1–135.7°.

Ignoring the cinnamaldehyde ligand, each of the independent molecules has approximate threefold rotation symmetry, with the aromatic substituents arranged like three propeller blades; in each case, the approximate rotation axis lies along the crystallographic *c* axis (Fig. 2). Indeed, the structure has a high degree of pseudosymmetry. The three independent molecules have very similar orientations, the main differences being in the disposition of the cinnamaldehyde ligand. Moreover, the cluster of three molecules shown in Fig. 2 has approximate 3₂ screw-axis symmetry within itself (and continuing to clusters related by genuine crystallographic symmetry), the approximate screw translation being one-ninth of the unit cell *c* axis. Propellers are chiral, and all the molecules in the crystal structure have the same chirality. The space group itself is one of an enantiomorphous pair (together with its opposite hand, *P*3₁), and the chirality of this particular

crystal has been established by refinement of the Flack (1983) parameter. It is likely, however, that the sample as a whole is racemic, consisting of crystals of opposite chirality in equal amounts.

Experimental

Trimethylaluminium (0.25 ml, 0.5 mmol) was added to 2,6-diphenylphenol (0.370 g, 1.5 mmol) in CH_2Cl_2 (4 ml) at room temperature. The resultant yellow solution was stirred for 10 min, then *trans*-cinnamaldehyde (0.06 ml, 0.5 mmol) was added, affording an orange suspension. Further addition of CH_2Cl_2 (10 ml) resulted in nearly complete dissolution. After filtering, the orange solution was stored at room temperature for 2 d, and orange blocks of the 1:1 title adduct were formed. Yield 0.110 g (25%); m.p. 549–550 K. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.68–6.88 (*m*, 44H, Ar), 6.70 (*d*, 1H, $^3J_{\text{HH}} = 15.9$ Hz, CHPh), 6.30 (*d*, 1H, $^3J_{\text{HH}} = 8.5$ Hz, OCH), 6.35 (*dd*, 1H, $^3J_{\text{HH}} = 15.9$ and 8.5 Hz, OCCH).

Crystal data

$[\text{Al}(\text{C}_{18}\text{H}_{13}\text{O})_3(\text{C}_9\text{H}_8\text{O})]$
 $M_r = 894.99$
 Trigonal, $P3_2$
 $a = 15.7741$ (10) Å
 $c = 49.394$ (5) Å
 $V = 10643.7$ (14) Å³
 $Z = 9$
 $D_x = 1.257$ Mg m⁻³

Cu $K\alpha$ radiation
 Cell parameters from 62 reflections
 $\theta = 21.1$ – 25.0°
 $\mu = 0.77$ mm⁻¹
 $T = 160$ (2) K
 Cuboid, orange
 $0.46 \times 0.46 \times 0.46$ mm

Data collection

Stoe–Siemens four-circle diffractometer
 ω/θ scans with on-line profile fitting (Clegg, 1981)
 Absorption correction: ψ scan (*SHELXTL*; Sheldrick, 2001)
 $T_{\text{min}} = 0.50$, $T_{\text{max}} = 0.70$
 19969 measured reflections
 19761 independent reflections

11027 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$
 $\theta_{\text{max}} = 67.6^\circ$
 $h = -15 \rightarrow 16$
 $k = -18 \rightarrow 18$
 $l = -57 \rightarrow 54$
 5 standard reflections
 frequency: 60 min
 intensity decay: 3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.068$
 $wR(F^2) = 0.228$
 $S = 1.02$
 19761 reflections
 1838 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.1038P)^2 + 10.8079P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.010$
 $\Delta\rho_{\text{max}} = 0.68$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.34$ e Å⁻³
 Extinction correction: *SHELXTL*
 Extinction coefficient: 0.000066 (15)
 Absolute structure: Flack (1983),
 7342 Friedel pairs
 Flack parameter = 0.00 (4)

H atoms were positioned geometrically and refined as riding, with C–H = 0.95 Å and with $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *DIF4* (Stoe & Cie, 1988); cell refinement: *DIF4*; data reduction: local programs; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

Table 1

Selected geometric parameters (Å, °).

Al1–O1A	1.716 (3)	O1B–C1B	1.347 (5)
Al1–O2A	1.695 (3)	O2B–C19B	1.349 (5)
Al1–O3A	1.707 (3)	O3B–C37B	1.347 (5)
Al1–O4A	1.841 (4)	O4B–C55B	1.165 (8)
O1A–C1A	1.352 (5)	Al3–O1C	1.700 (3)
O2A–C19A	1.336 (5)	Al3–O2C	1.715 (3)
O3A–C37A	1.347 (5)	Al3–O3C	1.705 (3)
O4A–C55A	1.245 (6)	Al3–O4C	1.834 (4)
Al2–O1B	1.698 (3)	O1C–C1C	1.336 (5)
Al2–O2B	1.708 (3)	O2C–C19C	1.343 (5)
Al2–O3B	1.703 (3)	O3C–C37C	1.340 (5)
Al2–O4B	1.830 (4)	O4C–C55C	1.203 (7)
O1A–Al1–O2A	114.51 (16)	O3B–Al2–O4B	108.97 (18)
O1A–Al1–O3A	110.47 (16)	Al2–O1B–C1B	145.1 (3)
O1A–Al1–O4A	106.13 (16)	Al2–O2B–C19B	136.8 (3)
O2A–Al1–O3A	112.80 (17)	Al2–O3B–C37B	149.5 (3)
O2A–Al1–O4A	107.84 (17)	Al2–O4B–C55B	145.4 (5)
O3A–Al1–O4A	104.31 (15)	O1C–Al3–O2C	111.56 (16)
Al1–O1A–C1A	136.6 (3)	O1C–Al3–O3C	114.11 (17)
Al1–O2A–C19A	153.3 (3)	O1C–Al3–O4C	108.20 (18)
Al1–O3A–C37A	141.1 (3)	O2C–Al3–O3C	111.44 (16)
Al1–O4A–C55A	137.3 (3)	O2C–Al3–O4C	105.07 (16)
O1B–Al2–O2B	110.73 (16)	O3C–Al3–O4C	105.83 (18)
O1B–Al2–O3B	113.25 (17)	Al3–O1C–C1C	149.6 (3)
O1B–Al2–O4B	104.29 (17)	Al3–O2C–C19C	139.8 (3)
O2B–Al2–O3B	113.21 (16)	Al3–O3C–C37C	140.5 (3)
O2B–Al2–O4B	105.71 (17)	Al3–O4C–C55C	140.8 (5)

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