



## BIS(ARYLIMIDO) COMPLEXES OF CHROMIUM(VI)\*

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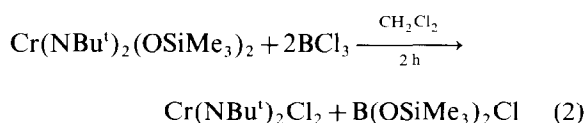
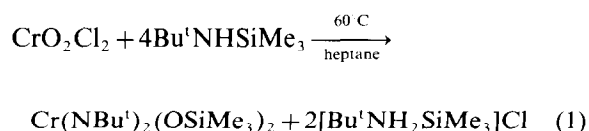
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**Abstract**—A synthetic entry into bis(arylimido) chromium(VI) chemistry is described.  $\text{Cr}(\text{NAr})_2(\text{NHBu}^t)\text{Cl}$  (**1**;  $\text{Ar} = 2,6\text{-Pr}_2\text{C}_6\text{H}_3$ ) may be obtained (1) by treatment of  $\text{Cr}(\text{NBU}^t)_2\text{Cl}_2$  with two equivalents of 2,6-diisopropylaniline in pentane, or (2) via the reaction of  $\text{Cr}(\text{NBU}^t)_2\text{Cl}_2$  with two equivalents of  $\text{LiNHAr}$  in  $\text{Et}_2\text{O}$ . An X-ray structure determination on **1** reveals a pseudo-tetrahedral coordination geometry with  $\text{Cr}-\text{N}$  distances of 1.643(3) and 1.654(4) Å for the imido groups and 1.813(3) Å for the tert-butylamido ligand; the substituents of the amide are orientated perpendicular to the  $\text{Cl}-\text{Cr}-\text{N}(\text{amido})$  plane. Compound **1** is readily converted to  $\text{Cr}(\text{NAr})_2\text{Cl}_2$  (**2**) by treatment with excess  $\text{BCl}_3$  in dichloromethane.

The synthetic entry into bis(imido) chromium(VI) chemistry established by Nugent and Harlow<sup>1</sup> involves the treatment of  $\text{CrO}_2\text{Cl}_2$  with  $\text{Bu}^t\text{NH}-\text{SiMe}_3$  to give  $\text{Cr}(\text{NBU}^t)_2(\text{OSiMe}_3)_2$  [eq. (1)], a reaction that to date has proved specific to the tert-butylimido system.<sup>2</sup> Wilkinson and co-workers<sup>3</sup> subsequently showed that  $\text{Cr}(\text{NBU}^t)_2(\text{OSiMe}_3)_2$  can be converted to  $\text{Cr}(\text{NBU}^t)_2\text{Cl}_2$  by reaction with  $\text{BCl}_3$  [eq. (2)], and the dichloride has been used to access several bis(tert-butylimido) chromium derivatives.



Schaverien and co-workers<sup>2</sup> have employed the five-coordinate pyridine adduct,  $\text{Cr}(\text{NBU}^t)_2\text{Br}_2(\text{py})$ , to prepare a number of alkyl derivatives of the type  $\text{Cr}(\text{NBU}^t)_2\text{R}_2$ , where  $\text{R} = \text{CH}_2\text{CMe}_3$ ,  $\text{CH}_2\text{SiMe}_3$ ,  $\text{CH}_2\text{CMe}_2\text{Ph}$ , and  $\text{R}_2 = o\text{-(CH}_2\text{SiMe}_3)_2\text{C}_6\text{H}_4$ . With few exceptions, the dialkyls are oils, which leads to difficulties with their handling and manipulation.

In general, arylimido ligands often lend favourable solubility and crystallinity characteristics to imido complexes and in some cases may confer enhanced stability on their derivatives. The development of a synthetic entry into the bis(arylimido) chromium system remained, therefore, an important objective. A potential entry using chromate as a starting material, analogous to the route employed for the synthesis of bis(imido) molybdenum complexes, affords reduced chromium

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products that do not contain imido ligands.<sup>4</sup> In recent work on bis(imido) molybdenum systems, we have exploited proton transfer between a free aniline and tert-butylimido ligands to access arylimido derivatives.<sup>5,6</sup> Here, we take advantage of this proton transfer methodology to prepare bis(arylimido) chromium(VI) complexes on a useful scale, thereby opening up the bis(arylimido) chromium system to development.

## RESULTS AND DISCUSSION

Treatment of  $\text{Cr}(\text{NBU}^t)_2\text{Cl}_2$  with two equivalents of 2,6-diisopropylaniline proceeds smoothly to afford the bis(arylimido) complex,  $\text{Cr}(\text{NAr})_2(\text{NHBu}^t)\text{Cl}$  (**1**;  $\text{Ar} = 2,6\text{-Pr}_i^2\text{C}_6\text{H}_3$ ), in 60% isolated yield.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra reveal resonances attributable to inequivalent imido ligands, a consequence of the local  $C_1$  symmetry arising from the amido hydrogen and  $\text{Bu}^t$  substituents orientating towards the imido groups. A characteristic high frequency signal is found at  $\delta$  11.84 for the nitrogen-bound proton of the tert-butylamido ligand. A plausible mechanism for the formation of **1**, involving intermediate five-coordinate aniline adducts and amido species, is shown in Scheme 1. Whilst there is good precedent for the viability of these intermediates, it should be recognized that we have not been able to observe them directly, and therefore a pathway involving direct proton transfer from the aniline to the imido nitrogen cannot be excluded.  $\text{Bu}^t\text{NH}_3\text{Cl}$  is, however, the sole by-product of the reaction. We have also found that **1** can be accessed, albeit in lower yield, by treatment of  $\text{Cr}(\text{NBU}^t)_2\text{Cl}_2$  with two equivalents of  $\text{LiNHAr}$  in diethyl ether.

Crystals of **1** suitable for an X-ray structure determination were grown from a saturated pentane solution at  $-30^\circ\text{C}$ . The molecular structure is shown in Fig. 1 and selected bond lengths and angles are collected in Table 1. The molecule is pseudo-tetrahedral with inter-ligand angles in the range  $106\text{--}112^\circ$ . The  $\text{ArN}=\text{Cr}=\text{NAr}$  angle of  $109.3(2)^\circ$  is somewhat smaller than for bis(tert-butylimido) analogues ( $114\text{--}116^\circ$ ),<sup>3,7</sup> a reflection of the greater steric flexibility of the aryl substituent. The  $\text{Cr}=\text{N}-\text{Ar}$  angles of  $157.0(3)^\circ$  and  $159.4(3)^\circ$  lie at the low end of the range typically observed for bis(imido) complexes containing quasi-linear imido ligands<sup>6</sup> and the  $\text{Cr}=\text{NAr}$  bond lengths of  $1.643(3)$  and  $1.654(4)$  Å are longer than for tert-butylimido derivatives ( $1.58\text{--}1.63$  Å),<sup>7</sup> a consequence of  $\pi$ -bonding between the imido nitrogen and the *ipso*-carbon of the aryl substituent which leads to a reduction in the  $\text{M}-\text{N}$   $\pi$ -bond order.

The  $\text{Cr}-\text{N}(\text{amide})$  distance of  $1.813(3)$  Å compares with values for molybdenum and tungsten tert-butylamides of  $1.93\text{--}2.05$  Å.<sup>1,8,9</sup> The shorter distance in the chromium complex is not fully compensated by the smaller ionic radius for chromium ( $0.52$  Å) compared with molybdenum and tungsten ( $0.62$  Å) and therefore may also reflect stronger  $\pi$ -bonding between the amido nitrogen and the chromium centre.

A convenient way of illustrating the orientation of the amide ligand in a pseudo-tetrahedral complex is using a representation<sup>10</sup> of the type shown in Fig. 2, in which the molecule is viewed along the amide-metal axis with the two imido ligands and chloride defining a plane beneath the metal. The orientation of the amido substituent is such as to allow the donor *p*-orbital of the amide ligand to lie in the  $\text{Cr}-\text{N}(1)-\text{Cl}$  plane; this is consistent with the two imido ligands dominating the  $\pi$ -donor bonding to the metal<sup>10</sup> and is related to the orientational constraints seen in bent metallocene compounds.

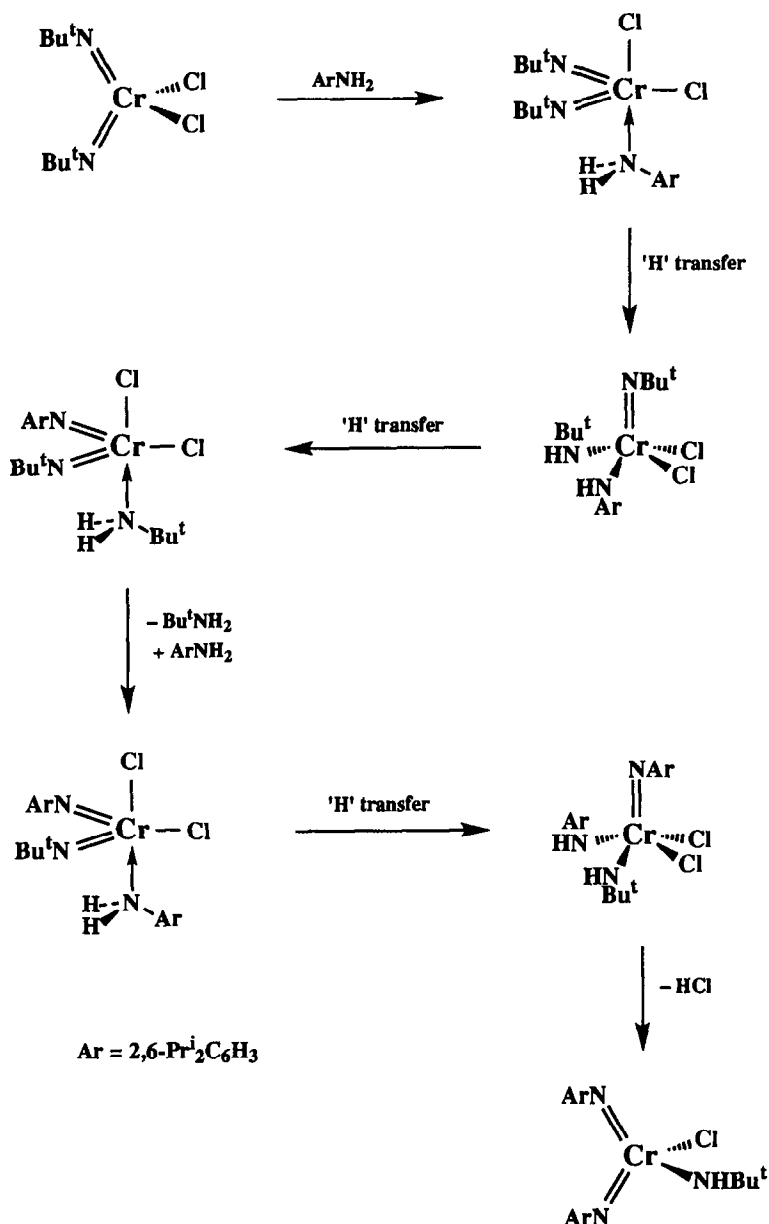
The mono-amido complex **1** may be converted to  $\text{Cr}(\text{NAr})_2\text{Cl}_2$  (**2**) via a procedure analogous to that described for the conversion of  $\text{Cr}(\text{NBU}^t)_2(\text{OSiMe}_3)_2$  to  $\text{Cr}(\text{NBU}^t)_2\text{Cl}_2$ .<sup>3</sup> We have also found that it is possible to synthesize **2** in a "one-pot" reaction from  $\text{Cr}(\text{NBU}^t)_2\text{Cl}_2$  without isolation of the intermediate **1**.

The synthetic procedures described herein allow a convenient entry point for developing the derivative chemistry of the bis(2,6-diisopropylphenylimido)chromium system, procedures that should be extendable to other arylimido derivatives.

## EXPERIMENTAL

### General

All manipulations were carried out under dry nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glovebox. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Durham. NMR spectra were recorded on a Varian VXR 400 S spectrometer at  $400.0$  MHz ( $^1\text{H}$ ) and  $100.6$  MHz ( $^{13}\text{C}$ ); chemical shifts are referenced to the residual protio impurity of the deuterated solvent; IR spectra (Nujol mulls, CsI windows), Perkin-Elmer 577 and 457 grating spectrophotometers; mass spectra, VG 7070E [70 eV (*ca*  $1.12 \times 10^{17}$  J),  $100$   $\mu\text{A}$  emission].  $\text{Cr}(\text{NBU}^t)_2\text{Cl}_2$  was synthesized via the procedure described by Wil-



Scheme 1. A plausible mechanism for the formation of 1.

kinson and co-workers,<sup>3</sup> but employing heptane as solvent. CrO<sub>2</sub>Cl<sub>2</sub>, BCl<sub>3</sub> (1.0 M solution in heptane) and 2,6-diisopropylaniline were purchased from Aldrich Chemical Co.; the aniline was distilled under dinitrogen prior to use. All other chemicals were obtained commercially and used as received unless stated otherwise.

#### Preparation of Cr(N-2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>(NHBu<sup>t</sup>)Cl

*Procedure A.* A solution of H<sub>2</sub>N-2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub> (356 μl, 1.89 mmol) in pentane (20 cm<sup>3</sup>) was added dropwise over 10 min to a stirred solution of Cr(NBu<sup>t</sup>)<sub>2</sub>Cl<sub>2</sub> (0.25 g, 0.94 mmol) in pentane (70

cm<sup>3</sup>) at -78°C. The mixture was allowed to warm to room temperature, during which the colour gradually changed from black to red. The mixture was stirred at ambient temperature for a further 18 h, after which the volatile components were removed under reduced pressure. Extraction of the resultant red oily residue with pentane (50 cm<sup>3</sup>) followed by concentration and cooling of the filtrate to ca -30°C afforded dark red crystals of Cr(N-2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>(NHBu<sup>t</sup>)Cl. Yield 0.288 g (60%).

*Procedure B.* Cr(NBu<sup>t</sup>)<sub>2</sub>Cl<sub>2</sub> (0.25 g, 0.94 mmol) was dissolved in diethyl ether (30 cm<sup>3</sup>) and cooled in a dry-ice/acetone slush bath. This solution was then added dropwise over 10 min to a cold (-78°C)

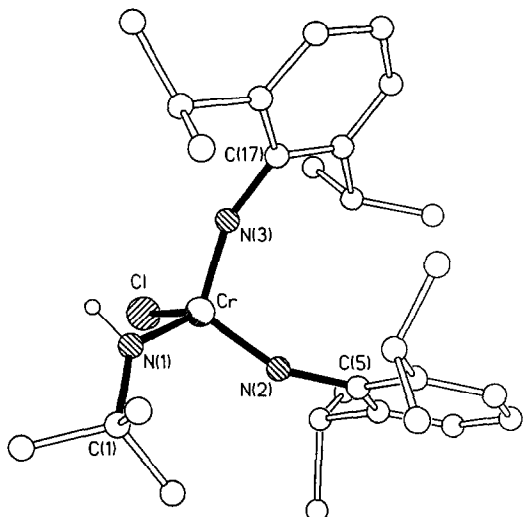


Fig. 1. Molecular structure of **1** without hydrogen atoms and disorder, and with key atoms labelled.

(m, 6H,  $C_6H_3$ ), 3.97 [sept (br), 2H,  $CHMe_2$ ], 3.81 [sept (br), 2H,  $CHMe_2$ ], 1.28 (s, 9H,  $CMe_3$ ), 1.22–0.99 (m, 12H,  $CHMe_2$ ).  $^{13}C$  NMR (100 MHz,  $C_6D_6$ ):  $\delta$  161.0, 160.0 (*ipso*- $C_6H_3$ ), 146.5, 145.4 (*o*- $C_6H_3$ ), 123.1 (d,  $^1J_{CH} = 154.0$  Hz, *m*- $C_6H_3$ ), 122.8 (d,  $^1J_{CH} = 154.7$  Hz, *m*- $C_6H_3$ ), \* 64.5 ( $CMe_3$ ), 32.4 (q,  $^1J_{CH} = 125.7$  Hz,  $CMe_3$ ), 29.3 (d,  $^1J_{CH} = 124.4$  Hz,  $CHMe_2$ ), 28.4 (d,  $^1J_{CH} = 126.7$  Hz,  $CHMe_2$ ), 24.7, 23.8, 23.3, 23.1 (overlapping quartet resonances,  $CHMe_2$ ). \**p*- $C_6H_3$  resonances obscured by  $C_6D_6$  signal. MS (EI<sup>+</sup>, *m/z*,  $^{35}Cl$ ): 509 [M]<sup>+</sup>, 437 [M – NHBu<sup>t</sup> + H], 262 [Cr(NAr)Cl]<sup>+</sup>. IR (Nujol, CsI,  $cm^{-1}$ ): 3225w, 1579w, 1260s, 1198m(br), 1096s(br), 1056m, 1018s(br), 983m, 932w, 795s, 760m, 749s, 703m, 636w, 526w, 250s, 230m.

#### Preparation of $Cr(N-2,6-Pr^i_2C_6H_3)_2Cl_2$

Boron trichloride (1.0  $cm^3$ , 1 M solution in heptane) was added dropwise via syringe to an ice-

Table 1. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **1**

Cr—N(2)	1.643(3)	Cr—N(3)	1.654(4)
Cr—N(1)	1.813(3)	Cr—Cl	2.247(2)
N(1)—C(1)	1.479(6)	N(2)—C(5)	1.392(5)
N(3)—C(17)	1.380(5)		
N(2)—Cr—N(3)	109.3(2)	N(2)—Cr—N(1)	110.1(2)
N(3)—Cr—N(1)	110.6(2)	N(2)—Cr—Cl	108.63(13)
N(3)—Cr—Cl	106.18(13)	N(1)—Cr—Cl	111.96(13)
C(1)—N(1)—Cr	136.7(3)	C(5)—N(2)—Cr	157.0(3)
C(17)—N(3)—Cr	159.4(3)		

solution of  $LiNH-2,6-Pr^i_2C_6H_3$  (0.346 g, 2.08 mmol) in diethyl ether (30  $cm^3$ ). The mixture was allowed to warm to room temperature and stirred for 18 h. The resultant red solution was filtered from the white precipitate and the volatile components were removed under reduced pressure to give a red oily solid. Extraction with pentane (50  $cm^3$ ) followed by concentration and cooling of the filtrate to *ca*  $-30^\circ C$  afforded  $Cr(N-2,6-Pr^i_2C_6H_3)_2(NHBu^t)Cl$ . Yield 0.125 g (26%).

Found: C, 66.0; H, 9.0; N, 8.0. Calc. for  $C_{28}H_{44}N_3ClCr$ : C, 65.9; H, 8.7; N, 8.2%.  $^1H$  NMR (400 MHz,  $C_6D_6$ ):  $\delta$ , 11.84 (s, 1H,  $NHBu^t$ ), 6.88

cooled solution of  $Cr(N-2,6-Pr^i_2C_6H_3)_2(NHBu^t)Cl$  (0.43 g, 0.84 mmol) in  $CH_2Cl_2$  (50  $cm^3$ ). The mixture was allowed to warm to room temperature and stirred for a further 3 h. The volatile components were then removed under reduced pressure to give a red oily solid which was washed with cold pentane ( $2 \times 5$   $cm^3$ ) and dried *in vacuo*. The solid was sublimed at  $80^\circ C$  ( $5 \times 10^{-2}$  Torr) on to a dry-ice/acetone probe to give analytically pure  $Cr(N-2,6-Pr^i_2C_6H_3)_2Cl_2$ . Yield 0.30 g (75%).

$Cr(N-2,6-Pr^i_2C_6H_3)_2Cl_2$  can also be prepared in a “one-pot” reaction by direct treatment of the oily residue obtained from the preparation of **1** with

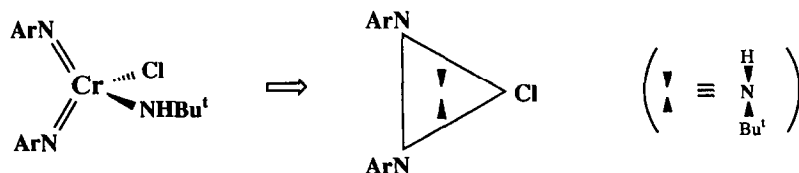


Fig. 2. A triad representation of **1**.

$\text{CrCl}_3$  according to the procedure outlined above. Found: C, 60.5; H, 7.4; N, 5.9. Calc. for  $\text{C}_{24}\text{H}_{34}\text{N}_2\text{Cl}_2\text{Cr}$ : C, 60.9; H, 7.2; N, 5.9%.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  6.75 (m, 6H,  $\text{C}_6\text{H}_3$ ), 3.81 (sept,  $^3J_{\text{HH}} = 6.7$  Hz, 4H,  $\text{CHMe}_2$ ), 1.02 (d,  $^3J_{\text{HH}} = 6.7$  Hz, 24H,  $\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  162.9 (s, *ipso*- $\text{C}_6\text{H}_3$ ), 149.1 (s, *o*- $\text{C}_6\text{H}_3$ ), 132.2 (d,  $^1J_{\text{CH}} = 160.8$  Hz, *p*- $\text{C}_6\text{H}_3$ ), 123.2 (d,  $^1J_{\text{CH}} = 160.0$  Hz, *m*- $\text{C}_6\text{H}_3$ ), 29.4 (d,  $^1J_{\text{CH}} = 127.8$  Hz,  $\text{CHMe}_2$ ), 23.8 (q,  $^1J_{\text{CH}} = 125.9$  Hz,  $\text{CHMe}_2$ ). MS (EI<sup>+</sup>, *m/z*,  $^{35}\text{Cl}$ ): 473 [M]<sup>+</sup>, 437 [M-Cl]<sup>+</sup>, 402 [M-2Cl]<sup>+</sup>, 262 [Cr(NAr)Cl]<sup>+</sup>. IR (Nujol, CsI,  $\text{cm}^{-1}$ ): 2360w, 1579m, 1342m, 1259s, 1222w, 1179w, 1142w, 1096m(br), 1057m, 1019m(br), 931w, 799s, 753m, 600w, 523w, 427m, 250s, 220s.

#### *X-ray crystallography for 1*

*Crystal data.*  $\text{C}_{28}\text{H}_{44}\text{ClCrN}_3$ ,  $M = 510.11$ , triclinic, space group  $P\bar{1}$ ,  $a = 11.483$  (6),  $b = 11.634$  (6),  $c = 12.426$  (6) Å,  $\alpha = 81.91$ ,  $\beta = 71.16$ ,  $\gamma = 68.16$  (2)°,  $U = 1458.0$  (13) Å<sup>3</sup> at 160 K (Mo- $K_\alpha$  radiation,  $\lambda = 0.71073$  Å),  $Z = 2$ ,  $D_c = 1.162$  g cm<sup>-3</sup>,  $\mu = 0.503$  mm<sup>-1</sup>,  $F(000) = 548$ .

Data collection and processing: crystal size 0.31 × 0.16 × 0.12 mm, Stoe-Siemens diffractometer with Cryostream cooler,<sup>11</sup> cell parameters from 2 $\theta$  values (17–22°) of 40 reflections measured at  $\pm\omega$ , intensities from  $\omega$ - $\theta$  scans, 2 $\theta$  range 5–45°, index ranges  $h$ -11 to 12,  $k$ -12 to 12,  $l$ -10 to 13, together with some Friedel opposites; corrections for 16% intensity decay of five standard reflections, semi-empirical absorption corrections,<sup>12</sup> transmission 0.876–0.983; 4448 measured reflections, 3793 unique data,  $R_{\text{int}} = 0.086$  on  $F^2$ .

Structure solution and refinement:<sup>12</sup> Patterson and difference syntheses, hydrogen atoms riding with  $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ; full-matrix least-squares refinement on  $F^2$  for all unique data, with weighting  $w^{-1} = \sigma^2(F_0^2) + (0.0653P)^2$ , where  $P = (F_0^2 + 2F_c^2)/3$ , anisotropic displacement parameters for all non-hydrogen atoms; extinction effects negligible; two-fold disorder for one isopropyl group with refined occupancy factors 0.47: 0.53(3); all shifts < 0.001 times corresponding parameter e.s.d.; final difference map between +0.700 and -0.469 e Å<sup>-3</sup>. For 322 parameters,  $R_w = 2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_c^2)^2]^{1/2} = 0.1333$  for all

data, conventional  $R = 0.0430$  for unweighted  $F$  values of 2318 reflections having  $F_0^2 > 2\sigma(F_0^2)$ , goodness of fit = 1.018 on  $F^2$ .

Atomic coordinates, complete bond lengths and angles, and displacement parameters have been deposited as supplementary material at the Cambridge Crystallographic Data Centre.

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