

Table 2. Deviations (Å) from least-squares planes

	Plane (1)	Plane (2)	Plane (3)
C(1)	0.0512	0.0670*	0.0851*
C(2)	-0.0017	0.0289	0.0356*
C(3)	-0.0647	-0.0273	-0.0373*
C(4)	-0.0346	-0.0033	-0.0214*
C(5)	-0.0104	0.0069	-0.0024
C(6)	-0.0134	-0.0031	0.0046
N(1)	0.0042	0.0133	-0.0006
N(2)	-0.0160	-0.0185	-0.0049
N(3)	-0.0010	0.0382*	0.0030*
N(4)	-0.0002	0.0378*	0.0514*
O(1)	0.0068	0.0032	0.0033
O(2)	-0.0457	-0.0583*	-0.0310*
O(3)	-0.0617	-0.0105*	-0.0529*
O(4)	0.1327	0.1661*	0.1240*
O(5)	0.0850	0.1172*	0.1457*
O(6)	-0.0302	0.0200*	0.0248*

Plane (1): $3.076(15)X + 8.953(51)Y - 1.974(70)Z = 4.6485(137)$

Plane (2): $3.012(8)X + 8.950(36)Y - 2.017(64)Z = 4.5650(79)$

Plane (3): $3.036(5)X + 8.990(39)Y - 1.895(48)Z = 4.6106(61)$

* Deviations for atoms which did not contribute to the best-plane calculation.

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Structure of 4-*tert*-Butyl-2,6-dimethylacetophenone–Iron(III) Chloride (1/1)

BY H. VAN KONINGSVELD

Laboratory of Applied Physics, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands

AND J. J. SCHEELE AND J. C. JANSEN

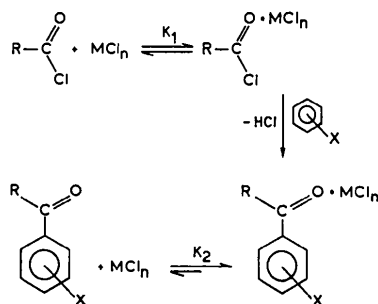
Laboratory of Organic Chemistry, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

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Abstract. $C_{14}H_{20}O.FeCl_3$, $M_r = 366.52$, triclinic, $P\bar{1}$, $a = 9.309(1)$, $b = 9.387(1)$, $c = 10.159(2)$ Å, $\alpha = 89.03(2)$, $\beta = 91.39(2)$, $\gamma = 95.19(1)^\circ$, $V = 883.7$ Å³, $Z = 2$, $D_x = 1.32$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 1.314$ mm⁻¹, $F(000) = 378$, $T = 210(2)$ K, $R = 0.034$ for 2360 observed reflections. The Fe^{III} atom is tetrahedrally coordinated by three Cl atoms [average Fe–Cl bond length 2.164(1) Å] and the O atom [Fe–O bond length 1.958(2) Å]. Another symmetry-

related Cl atom is at 3.845(1) Å from Fe. The acetyl group is rotated 43.7(5)° out of the aromatic ring plane. The *tert*-butyl group adopts a position deviating ~30° from the energetically most favourable position, in which a C–C bond of the *tert*-butyl group lies in the aromatic ring plane. The packing in the crystal is mainly governed by a weak Fe...Cl contact and by van der Waals interactions between the aromatic ring and the *tert*-butyl groups from neighbouring molecules.

Introduction. Friedel–Crafts acylations generally require a stoichiometric amount of catalyst (MCl_n with $M = Fe, Sn, Al$ etc.) because of poisoning of the Lewis-acid catalyst by relatively strong complexation with the ketone product (K_2) versus the acyl chloride reactant (K_1).



Experiments indicate that alkyl-substituted benzenes, delivering *o*-alkylacetophenones upon acylation, favour the formation of free-product ketone. The carbonyl group in these ketones is rotated out of the plane of the benzene ring. The less-conjugated system probably weakens the M – O interaction.

During our research we were able to crystallize a complex of 4-*tert*-butyl-2,6-dimethylacetophenone and $FeCl_3$. In order to study the product ketone–catalyst interaction the crystal structure analysis was started. To our knowledge this is the first carbonyl– $FeCl_3$ complex studied thus far.

Experimental. Very deliquescent crystals grown from 4-*tert*-butyl-2,6-dimethylacetophenone and iron(III) trichloride in a mixture (75:25) of carbon tetrachloride and petroleum ether at 278 K. Life time of crystals in open air: 10–30 s. Crystal, approximate size 0.25 × 0.27 × 0.30 mm, enclosed in glass capillary containing dry paraffin oil. Cooled to 210 K by cold N₂ gas stream. Exact temperature of crystal unknown because part of oil at room temperature. Enraf–Nonius CAD-4 diffractometer with graphite monochromator, lattice parameters from 25 reflections ($15 < \theta < 20^\circ$). Data collected to $\theta_{max} = 25.0^\circ$ ($h: -11$ to $10, k: -11$ to $11, l: 0$ to 12), $\omega/2\theta$ scan, scan width $(0.80 + 0.35 \tan \theta)^\circ$, max. counting time 240 s or time spent to obtain 2% accuracy. 3090 independent reflections, 2360 with $I > 2.0\sigma(I)$. Three reference reflections measured every 2 h of X-ray exposure time; slow intensity decrease amounting to 8% at end of measurements, correction applied. Lorentz and polarization corrections (none for extinction or absorption) applied. Structure solved by Patterson and Fourier techniques; function minimized during refinement $\sum w(F_o - F_c)^2$, with $w = 1/\sigma^2(F_o)$; H atoms located from difference map. Cascaded full-matrix refinement ($FeCl_3, t$ -Bu, rest of molecule) with fixed isotropic H atoms converged at $R = 0.034$,

$wR = 0.033, S = 3.62$ for 233 parameters; $(\Delta/\sigma)_{max} = 0.52$; highest peak in final difference map $0.38 e \text{ \AA}^{-3}$. All calculations performed with XRAY72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972); atomic scattering factors for C, O, Cl and Fe from Cromer & Mann (1968), those for H from Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections (Fe, Cl) from *International Tables for X-ray Crystallography* (1974).

Table 1. Fractional coordinates ($\times 10^4$) and U_{eq} values ($\text{\AA}^2 \times 10^3$) for non-hydrogen atoms

	$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$			
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Fe	1890.2 (4)	1258.1 (4)	1277.6 (4)	36.9 (2)
Cl(1)	3992.5 (9)	1787.6 (9)	2204.4 (8)	57.7 (3)
Cl(2)	174.0 (9)	2096.9 (11)	2331.7 (8)	66.7 (4)
Cl(3)	1540.4 (11)	-1012.7 (8)	923.1 (9)	65.7 (4)
O(1)	2009 (2)	2280 (2)	9582 (2)	37.2 (6)
C(1)	2620 (3)	3210 (3)	7498 (3)	29.6 (8)
C(2)	2686 (3)	4684 (3)	7787 (3)	33.5 (8)
C(3)	2737 (3)	5650 (3)	6748 (3)	33.1 (8)
C(4)	2679 (3)	5240 (3)	5436 (2)	28.7 (8)
C(5)	2552 (3)	3787 (3)	5187 (3)	32.3 (8)
C(6)	2516 (3)	2766 (3)	6182 (3)	32.6 (8)
C(7)	2648 (3)	6338 (3)	4305 (3)	33.6 (8)
C(8)	1073 (4)	6578 (6)	4041 (5)	86 (2)
C(9)	3334 (5)	5830 (4)	3080 (4)	58 (1)
C(10)	3477 (6)	7760 (4)	4691 (4)	74 (2)
C(11)	2713 (3)	2164 (3)	8572 (3)	34.5 (8)
C(12)	3734 (5)	1035 (4)	8511 (4)	68 (2)
C(13)	2767 (5)	5254 (4)	9176 (3)	58 (1)
C(14)	2252 (5)	1217 (3)	5800 (4)	54 (1)

Table 2. Bond lengths (\AA), bond angles ($^\circ$) and some torsion angles ($^\circ$) involving non-H atoms

Fe–Cl(1)	2.171 (1)	C(3)–C(4)	1.392 (4)
Fe–Cl(2)	2.158 (1)	C(4)–C(5)	1.386 (4)
Fe–Cl(3)	2.162 (1)	C(4)–C(7)	1.531 (4)
Fe–O(1)	1.958 (2)	C(5)–C(6)	1.380 (4)
		C(6)–C(14)	1.508 (4)
C(1)–C(2)	1.415 (4)	C(7)–C(8)	1.520 (5)
C(1)–C(6)	1.406 (4)	C(7)–C(9)	1.516 (5)
C(1)–C(11)	1.461 (4)	C(7)–C(10)	1.532 (5)
C(2)–C(3)	1.379 (4)	C(11)–C(12)	1.489 (5)
C(2)–C(13)	1.516 (4)	C(11)–O(1)	1.243 (3)
Cl(1)–Fe–Cl(2)	112.42 (4)	C(3)–C(4)–C(7)	121.8 (2)
Cl(1)–Fe–Cl(3)	110.66 (4)	C(5)–C(4)–C(7)	120.8 (2)
Cl(1)–Fe–O(1)	103.92 (6)	C(6)–C(5)–C(4)	122.4 (2)
Cl(2)–Fe–Cl(3)	113.73 (4)	C(1)–C(6)–C(5)	119.1 (2)
Cl(2)–Fe–O(1)	106.65 (6)	C(1)–C(6)–C(14)	123.0 (2)
Cl(3)–Fe–O(1)	108.85 (6)	C(5)–C(6)–C(14)	117.8 (3)
C(11)–O(1)–Fe	134.2 (2)	C(4)–C(7)–C(8)	106.7 (3)
C(2)–C(1)–C(6)	119.9 (2)	C(4)–C(7)–C(9)	111.8 (2)
C(2)–C(1)–C(11)	119.5 (2)	C(4)–C(7)–C(10)	110.9 (2)
C(6)–C(1)–C(11)	120.5 (2)	C(8)–C(7)–C(9)	111.1 (3)
C(1)–C(2)–C(3)	118.0 (2)	C(8)–C(7)–C(10)	109.0 (3)
C(1)–C(2)–C(13)	123.4 (2)	C(9)–C(7)–C(10)	107.2 (3)
C(3)–C(2)–C(13)	118.5 (2)	C(1)–C(11)–C(12)	120.5 (3)
C(2)–C(3)–C(4)	123.1 (2)	C(1)–C(11)–O(1)	119.6 (2)
C(3)–C(4)–C(5)	117.3 (2)	C(12)–C(11)–O(1)	119.7 (3)
C(2)C(1)C(11)O(1)	44.4 (4)	C(3)C(4)C(7)C(10)	31.0 (4)
C(3)C(4)C(7)C(8)	87.6 (4)	C(5)C(4)C(7)C(9)	29.3 (4)

Discussion. Positional and isotropic thermal parameters are given in Table 1. Bond lengths and bond angles are listed in Table 2. An *ORTEP* drawing of the molecule is shown in Fig. 1.*

The Fe^{III} atom is tetrahedrally coordinated by three Cl atoms and the one O atom. The Fe—Cl bond lengths observed in the vapour phase of dimeric FeCl₃ (Wertz & Kruh, 1969) are 2.17 and 2.29 Å (no standard deviations given) for distances of Fe to the symmetrically bridging and terminal Cl atoms, respectively. The asymmetrical 'bridge' in the title compound has Fe—Cl distances of 2.162 (1) and 3.845 (1) Å, indicating no dimeric coupling although the geometry is still that of a typical halo-bridged species. The terminal Fe—Cl distances [2.171 (1) and 2.158 (1) Å] are not essentially different from the shorter bridging Fe—Cl distance. The *t*-Bu group adopts a rotational orientation deviating about 30° from the energetically most favourable position, as found for *tert*-butylbenzene (Beckhaus, 1983), in which one C—C bond of the *t*-Bu group is in the plane of the ring. The observed energetically unfavourable orientation might be stabilized by the energy gain through van der Waals interactions between the aromatic ring and *t*-Bu groups from neighbouring molecules. The *ortho* methyl substituents force the acetyl group to rotate out of the aromatic ring plane. The torsion angle C(2)C(1)—C(11)O(1) is 44.4 (4)°.

With the search fragment Fe—O=C in the Cambridge Crystallographic Database, the Fe—O bond length in the 16 examples varies from 1.981 to 2.221 Å (CCDB; Allen *et al.*, 1979).† The observed Fe—O distance of 1.958 (2) Å is therefore short. However, no examples of FeCl₃—carbonyl coordination bond lengths were found and the comparison may not be valid. Therefore, the question whether the out-of-plane rotation of the acetyl group leads to a weakening of the Fe—O bond or not remains open. In other words, it is not possible to say whether the observed Fe—O distance points to less poisoning of the Lewis-acid catalyst by the product ketone or not. It is planned to continue our research by X-ray analysis of the ligand itself and of coordination compounds containing unsubstituted acetophenones and FeCl₃.

The Fe...Cl contact and the van der Waals interactions between the aromatic ring and *t*-Bu groups from neighbouring molecules govern the packing, as shown in Fig. 2.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond lengths and bond angles involving H atoms and REFCODES of Fe—O=C fragment hits of the Cambridge Crystallographic Database have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42509 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† REFCODES are listed in the deposited material.

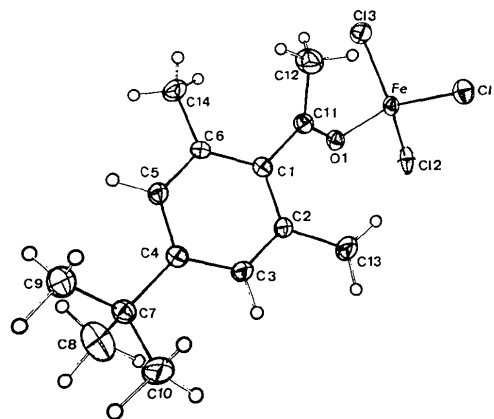


Fig. 1. *ORTEP* plot (Johnson, 1965) of the title compound showing the numbering of the atoms. Boundary surfaces are drawn at the 50% probability level.

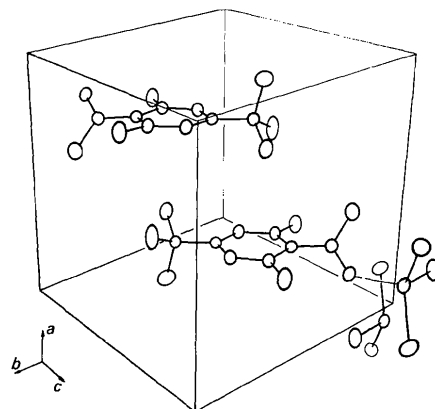


Fig. 2. Packing of the molecules in the crystal.

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