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A Tetrahedral Titanium(IV) Amido Aryloxide Compound $[\mathrm{Ti(OC_6H_3{}^tBu_2\text{-}2,6)_2(NMe_2)_2}]$

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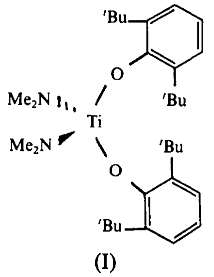
Abstract

In the compound bis(2,6-di-*tert*-butylphenoxy)bis(dimethylamido)titanium, $[\mathrm{Ti(C_2H_6N)_2(C_{14}H_{21}O)_2}]$, a distorted tetrahedral geometry is adopted around the Ti metal center by two aryloxide O atoms and two N atoms of the dialkylamido groups. Ti—O(aryloxide) = 1.808 (2), 1.828 (2) Å; Ti—N(amido) = 1.892 (3), 1.885 (3) Å.

Comment

The reaction of protic reagents with early transition-metal dialkylamido compounds is a very convenient route to new derivatives of these metals *via* elimination of secondary amines (Thomas, 1961; Lappert, Power, Sanger & Srivastava, 1980). We report here the isolation and structural characterization of a mixed amido aryloxide compound of titanium(IV) $[\mathrm{Ti(OC_6H_3{}^tBu_2\text{-}2,6)_2(NMe_2)_2}]$, (I), containing the sterically demanding 2,6-di-*tert*-butylphenoxide ligand.



(I)

A view of the molecule is shown in Fig. 1. The molecule can be seen to adopt a distorted tetrahedral geometry about the Ti atom. The distortion from idealized geometry is due to the N(3)—Ti—N(4) angle of 98.5 (1)° being smaller than the O(1)—Ti—O(2) angle of 113.1 (1)°. The Ti—N distances of 1.892 (3) and 1.885 (3) Å are shorter than a single bond length of 1.96 Å estimated from the sum of the covalent radii (Sutton, 1958). This decrease can be attributed to N-atom-*p* to metal-*d* π bonding. The Ti—O(aryloxide) distances of 1.808 (2) and 1.828 (2) Å and large Ti—O—Ar angles of 174.6 (2) and 177.1 (2)° are well within observed values for *M*—O—Ar (*M* = Zr, Ti) groups (Smith, Fanwick & Rothwell, 1990).

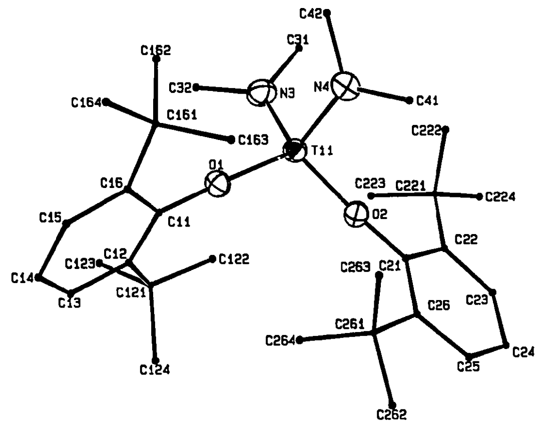


Fig. 1. A view of the molecule emphasizing the central coordination sphere. Displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

The title compound bears a close resemblance to the compound $[\mathrm{Ti(OC_6H_2{}^tBu_3\text{-}2,4,6)_2(NMe_2)_2}]$ reported by Jones, Hefner & Wright (1984). However, an interesting feature of the title compound is the fact that one of the *tert*-butyl methyl groups makes a close contact with the metal center; Ti···C(122) = 3.325 (8) Å. Previous work has shown that the *tert*-butyl groups of 2,6-di-*tert*-butylphenoxide and related ligands sometimes adopt a ground-state structure in which one of the substituent methyl groups points directly at the metal center (Fanwick, Ogilvy & Rothwell, 1987). The fact that a close contact is observed for the 2,6-di-*tert*-butylphenoxide complex (Fig. 1) but not the related 4-butyl derivative implies that this effect is simply due to packing forces and is not a consequence of an *agostic* interaction (Brookhart & Green, 1983) between the unique methyl group and the high-valence metal center.

Experimental

The title compound was obtained in high yield (*ca* 90%) by reaction of $[\mathrm{Ti(NMe_2)_4}]$ (Bradley & Thomas, 1960) with 2,6-di-*tert*-butylphenol in benzene. Crystals of the compound were obtained from a hexane solution.

Crystal data

$[\mathrm{Ti(C_2H_6N)_2(C_{14}H_{21}O)_2}]$
M_r = 546.70
Monoclinic
$P2_1/n$
a = 15.318 (8) Å
b = 11.906 (2) Å
c = 19.163 (9) Å
β = 111.30 (2)°

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 19–22°
μ = 0.285 mm^{-1}
T = 201 K
Block

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$V = 3256$ (4) Å^3
$Z = 4$
$D_x = 1.115$ Mg m^{-3}

0.43 × 0.36 × 0.35 mm
Orange

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: empirical
$T_{\min} = 0.66$, $T_{\max} = 1.00$
4504 measured reflections
4504 independent reflections

3401 observed reflections $[F > 3\sigma(F)]$
$\theta_{\max} = 22.5°$
$h = -16 \rightarrow 15$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 83.3 min
intensity variation: <5%

Refinement

Refinement on F
$R = 0.056$
$wR = 0.074$
$S = 2.160$
3401 reflections
334 parameters
H-atom parameters not refined

$w = 1/[\sigma^2F + (0.02F)^2 + 1 - F]$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.99$ e Å^{-3}
$\Delta\rho_{\min} = -0.83$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{\rm eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$B_{\rm eq}$
Ti(1)	0.54253 (4)	0.05321 (5)	0.74536 (3)	1.87 (1)
O(1)	0.5604 (2)	0.1989 (2)	0.7735 (1)	1.98 (5)
O(2)	0.4197 (2)	0.0189 (2)	0.6932 (1)	1.94 (5)
N(3)	0.6429 (2)	0.0344 (3)	0.7111 (2)	2.80 (8)
N(4)	0.5749 (2)	−0.0606 (3)	0.8188 (2)	2.73 (8)
C(11)	0.5694 (2)	0.3099 (3)	0.7923 (2)	1.95 (8)
C(12)	0.5368 (2)	0.3929 (3)	0.7367 (2)	1.91 (8)
C(13)	0.5439 (3)	0.5035 (3)	0.7607 (2)	2.59 (9)
C(14)	0.5813 (3)	0.5325 (3)	0.8350 (2)	3.0 (1)
C(15)	0.6163 (3)	0.4506 (4)	0.8881 (2)	3.1 (1)
C(16)	0.6133 (3)	0.3384 (3)	0.8692 (2)	2.49 (9)
C(21)	0.3281 (2)	−0.0150 (3)	0.6587 (2)	1.72 (8)
C(22)	0.3071 (3)	−0.0960 (3)	0.6019 (2)	2.09 (8)
C(23)	0.2130 (3)	−0.1288 (3)	0.5690 (2)	2.9 (1)
C(24)	0.1450 (3)	−0.0861 (4)	0.5914 (2)	3.5 (1)
C(25)	0.1672 (3)	−0.0077 (4)	0.6471 (2)	3.0 (1)
C(26)	0.2581 (2)	0.0316 (3)	0.6826 (2)	2.12 (8)
C(31)	0.6716 (3)	−0.0730 (4)	0.6886 (3)	4.6 (1)
C(32)	0.7046 (3)	0.1231 (4)	0.7034 (2)	3.9 (1)
C(41)	0.5090 (4)	−0.1249 (4)	0.8417 (3)	4.6 (1)
C(42)	0.6704 (3)	−0.0928 (4)	0.8659 (3)	4.6 (1)
C(121)	0.4970 (3)	0.3780 (3)	0.6502 (2)	2.37 (9)
C(122)	0.4804 (3)	0.2588 (3)	0.6193 (2)	2.75 (9)
C(123)	0.5671 (3)	0.4316 (4)	0.6192 (2)	4.3 (1)
C(124)	0.4026 (3)	0.4398 (4)	0.6171 (3)	3.9 (1)
C(161)	0.6601 (3)	0.2511 (4)	0.9297 (2)	3.4 (1)
C(162)	0.7363 (3)	0.1897 (4)	0.9117 (3)	4.2 (1)
C(163)	0.5877 (4)	0.1695 (4)	0.9390 (2)	4.6 (1)
C(164)	0.7081 (5)	0.3061 (5)	1.0070 (3)	6.4 (2)
C(221)	0.3808 (3)	−0.1490 (3)	0.5758 (2)	2.62 (9)
C(222)	0.4517 (3)	−0.2151 (3)	0.6393 (2)	3.2 (1)
C(223)	0.4302 (3)	−0.0599 (4)	0.5453 (2)	3.5 (1)
C(224)	0.3378 (3)	−0.2335 (4)	0.5116 (2)	4.4 (1)
C(261)	0.2749 (3)	0.1213 (3)	0.7439 (2)	2.65 (9)
C(262)	0.1844 (4)	0.1643 (6)	0.7495 (4)	8.0 (2)
C(263)	0.3373 (5)	0.0771 (6)	0.8192 (3)	6.6 (2)
C(264)	0.3196 (4)	0.2250 (4)	0.7251 (3)	5.0 (1)

Table 2. *Selected geometric parameters* (Å, °)

Ti(1)—O(1)	1.808 (2)	Ti(1)—N(3)	1.892 (3)
Ti(1)—O(2)	1.828 (2)	Ti(1)—N(4)	1.885 (3)
O(1)—Ti(1)—O(2)	113.1 (1)	O(2)—Ti(1)—N(4)	100.8 (1)
O(1)—Ti(1)—N(3)	99.4 (1)	N(3)—Ti(1)—N(4)	98.5 (1)
O(1)—Ti(1)—N(4)	119.8 (1)	Ti(1)—O(1)—C(11)	177.1 (2)
O(2)—Ti(1)—N(3)	126.1 (1)	Ti(1)—O(2)—C(21)	174.6 (2)

The structure was solved using *SHELXS*86 (Sheldrick, 1985). The remaining atoms were located in succeeding difference Fourier syntheses. H atoms were located and includeded in the structure-factor calculations but their positions were not refined. The structure was refined by full-matrix least squares where the function minimized was $\sum w(|F_o|-|F_c|)^2$ and the weight, w, was as defined by the Killean & Lawrence (1969) method with terms of 0.020 and 1.0. Anomalous-dispersion effects were included in F_c (Ibers & Hamilton, 1964); the values for f' and f'' were those of Cromer (1974). There were eight correlation coefficients greater than 0.50. The highest correlation coefficient was 0.53 between parameters 277 and 279. The highest peak in the final difference Fourier map had a height of 0.99 e Å^{-3} with an estimated error based on ΔF (Cruickshank, 1949) of 0.07. Plots of $\sum w(|F_o|-|F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. All calculations were performed on a VAX computer using *MolEN* (Fair, 1990).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71773 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1069]

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[Mo{P(Ph)$_2$OC$_6$H$_3$(Ph)(η^6-Ph)}(CO)$_2$]

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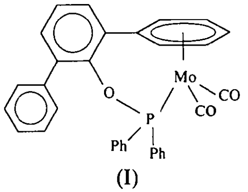
Abstract

Dicarbonyl[(2-η^6-phenyl-6-phenylphenoxy)diphenylphosphine-*P*]molybdenum contains a new phosphine ligand bound to Mo through the O atom and *via* an η^6-arene interaction. A 'three-legged-piano-stool' geometry is present with Mo—P = 2.354 (1) Å, Mo—C(carbonyl) = 1.942 (4) and 1.944 (5) Å and Mo—C(aryl) = 2.295 (4)–2.339 (4) Å.

Comment

Previous work by our group has shown that the molecule 2,6-diphenylphenol can react with Mo(CO)$_6$ to produce the complex [Mo(HOC$_6$H$_3$Ph-η^6-Ph)(CO)$_3$] (Kerschner, Torres, Fanwick & Rothwell, 1989) in which the metal is π bonded to one of the substituent arene rings of the aryl alcohol. The phenolic group remains unreacted. As an extension of this work we have synthesized the new phosphine ligand (2,6-diphenylphenoxy)diphenylphosphine, [P(Ph)$_2$OC$_6$H$_3$(Ph)$_2$]. In this case the initial coordination of the P atom to the metal should allow chelation *via* an η^6 interaction with either the central phenoxy ring or with one of the substituent aryl rings. We report here the structure of the product (I) obtained on reacting this ligand with [Mo(CO)$_6$] in which chelation occurs to one of the substituent rings.



(I)

A view of the molecule is given in Fig. 1. The molecule can be seen to adopt a 'three-legged-piano-stool' geometry about the metal center. The presence of the chelate ring between the donor P atom and the η^6-bonded arene ring does not appear to distort the geometry from that typical for the ubiquitous [(η^6-arene)M(L)$_3$] (M = Cr, Mo, W) class of compounds. The Mo—C(arene) distances fall in the narrow range of 2.295 (4) Å to the *ipso* C atom to 2.339 (4) Å to C(123). These distances are typical of molybdenum η^6-arene complexes of this type (Kerschner, Torres, Fanwick & Rothwell, 1989).

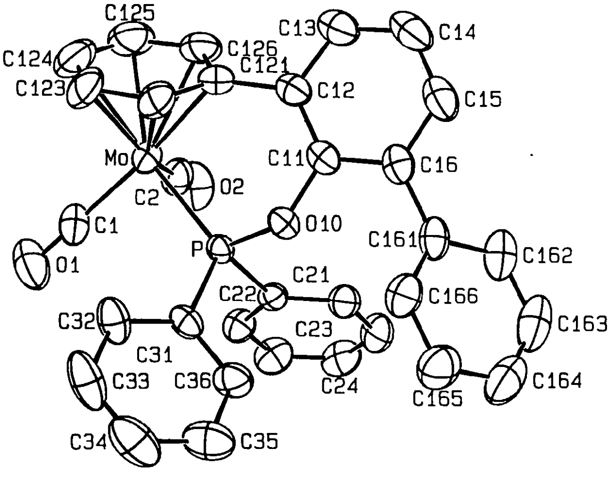


Fig. 1. A view of the molecule emphasizing the central coordination sphere. Displacement ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity.

Experimental

[Mo(CO)$_2${P(Ph)$_2$OC$_6$H$_3$(Ph)$_2$}] was obtained in low yield by refluxing a mixture of [Mo(CO)$_6$] (0.61 g, 2.3 mmol) and [P(Ph)$_2$OC$_6$H$_3$(Ph)$_2$] (1.00 g, 2.33 mmol) in octane for 9 h. The resulting crude product was recrystallized from a chloroform solution layered with hexane.

Crystal data

[Mo($C_{30}H_{23}OP$)(CO)$_2$]
M_r = 581.45
Orthorhombic
Pbca
a = 8.942 (2) Å
b = 20.445 (2) Å
c = 28.448 (4) Å
V = 5200 (2) Å^3
Z = 8
D_x = 1.488 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 19–23°
μ = 0.583 mm^{-1}
T = 293 K
Needle
0.46 × 0.38 × 0.22 mm
Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer

2629 observed reflections [$F > 3\sigma(F)$]

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