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Bis(η^5 -*tert*-butylcyclopentadienyl)dichloroniobium(IV)

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Abstract

The monomeric molecule of the title compound, $[\text{NbCl}_2(\text{C}_9\text{H}_{13})_2]$, is best described as a paramagnetic pseudo-tetrahedral complex of niobium(IV). The two *tert*-butylcyclopentadienyl ligands are asymmetrically bound

to the Nb atom [Nb—C bond-length range 2.394 (6)–2.470 (6) Å]. The asymmetry is accounted for in terms of the steric demand of the ^tBu groups and Cl ligands. Pseudo-tetrahedral geometry is completed by two Cl ligands [Nb—Cl 2.477 (2) and 2.483 (2) Å, Cl—Nb—Cl 84.15 (6)°].

Comment

Bis(cyclopentadienyl)metal complexes have been of interest for many years, finding applications in catalysis and organic synthesis. The use of alkyl-substituted cyclopentadienyl ligands, notably the pentamethylcyclopentadienyl ligand, has been shown to enhance the solubility and stability of metal complexes. The title complex, $[\text{NbCl}_2(\eta^5\text{-C}_9\text{H}_{13})_2]$ (1), is of interest since it represents a versatile precursor to a wide range of bis(*tert*-butylcyclopentadienyl)niobium(IV) compounds.

The Nb—Cl bond lengths and Cl—Nb—Cl bond angle are normal and comparable with other published data (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974; Lanfredi, Tiripicchio, Kapon & Reisner, 1990). The *tert*-butylcyclopentadienyl rings are bound in a staggered relative orientation. The Nb—ring-centroid distances are 2.103 and 2.094 Å and the intra-ring C—C distances do not differ significantly.

The crystal structures of $[\text{NbCl}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2]$ (2) (Lanfredi *et al.*, 1990), $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4\text{CMe}_3)_2]$ (3) (Howie, McQuillan, Thompson & Lock, 1986) and $[\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2]$ (4) (Antinolo *et al.*, 1987) have been determined previously. All have essentially the same staggered orientation of rings, with substituents positioned approximately perpendicular to the Cl—M—Cl bisector, as in Fig. 1. Relevant data for structures (1)–(4) are given in Table 3. The most striking change on moving from 16-electron zirconium(IV) to 17-electron niobium(IV) complexes is the reduction of the Cl—M—Cl angle. This has been observed previously in the unsubstituted $[\text{MCl}_2(\eta^5\text{-C}_5\text{H}_5)_2]$ analogues (Prout *et al.*, 1974) and is a consequence of the presence of an extra electron in a non-bonding but sterically significant orbital of approximate ' d_{z^2} ' description (Hoffmann & Lauher,

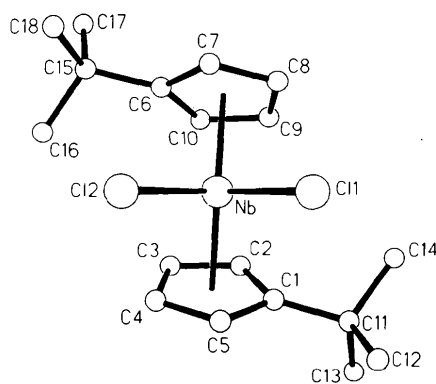


Fig. 1. Molecular structure of (1) without H atoms.

1976). There is a slight concomitant increase in the $M-X$ angle (X is the ring centroid). A slight decrease in the $M-X$ distance is observed on changing the metal from zirconium to niobium, presumably as a consequence of the reduction in covalent radius.

Complexes (1)–(4) show considerable variations in the $M-C$ bond lengths associated with the C₅H₄EMe₃ ($E = C, Si$) rings, represented graphically in Fig. 2. Such variations are not observed in the unsubstituted complexes, at least within the precision of their structures (Prout *et al.*, 1990). Complex (3) shows a simple parabolic curve, indicating that the substituted atom C1 and nearest ring neighbours C2 and C5 are furthest from the zirconium centre. This is attributable to steric repulsion between the ^tBu group and the nearest chloride ligand (approximate Cl...H distance 2.9 Å, based on the calculated H-atom positions). The shortest Zr...H contact is greater than 4 Å, indicating that steric interaction between the ^tBu group

and the Zr atom is minimal. Fig. 2 clearly demonstrates that the asymmetry in the [(η^5 -C₅H₄EMe₃)M] moiety is ameliorated when the ^tBu substituent is replaced with an SiMe₃ substituent: the Zr—C bond lengths are much more equivalent in (4). The longer Si—C bonds hold the methyl groups further away from the chloride ligand and steric repulsion is minimized. There may also be some orbital overlap of the Si d orbitals with the appropriate ring orbitals, which is at a maximum when the SiMe₃ substituent is not bent away from the metal.

The niobium complexes (1) and (2), while showing broadly similar features, also exhibit notable differences (Fig. 2). The ring substituent again levers the ring away from the metal. Surprisingly, there seems to be a tendency for C5 to move closer towards the metal, in spite of the shorter $M-X$ distance and the closing of the Cl— M —C1 angle. However, these factors act to bring C11 and C12 somewhat closer to the C8—H8 and C4—H4 bonds, respectively. Thus, the Nb—C4 and Nb—C8 bonds are now considerably longer than the other Nb—C bonds, in comparison with the zirconium analogue (3), as a consequence of the steric demands of the nearest chloride ligand. The resultant effect is that the *tert*-butylcyclopentadienyl ligands in (1) bond in a ‘butterfly’ fashion, with the C1/C6 and C4/C8 ‘wings’ pushed away from the Nb atom. Steric repulsions between the chloride ligand and the ring and substituent are the important factors governing the molecular geometry. This distortion may be enhanced by replacing Nb with the smaller metal Mo and is likely to have consequences on the subsequent chemistry of such complexes. An investigation of the chemistry of (1) is currently under way.

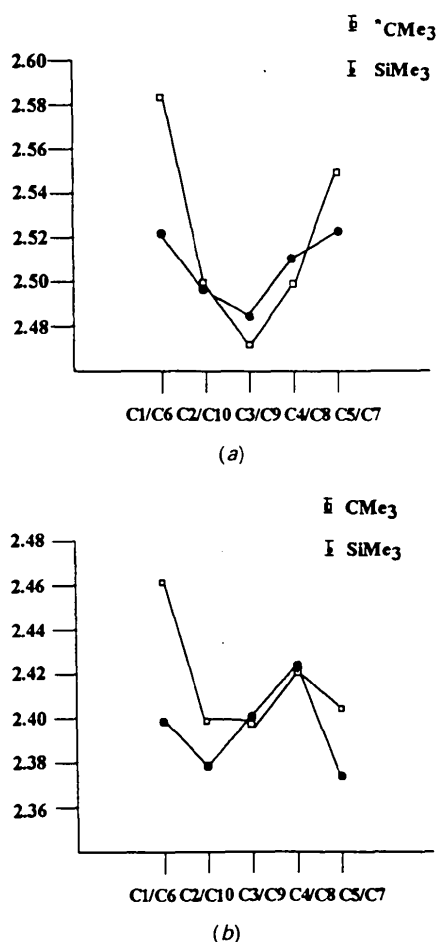


Fig. 2. The variation in $M-C$ bond lengths in (1)–(4): (a) $M = Zr$; (b) $M = Nb$. The points on each graph are given as the average of the two $M-C$ bond lengths specified, with atom numbering as in Fig. 1. Bond-length e.s.d. values are indicated by the vertical error bar on the key to each diagram.

Experimental

Crystal data

[NbCl₂(C₉H₁₃)₂]
 $M_r = 406.20$
 Orthorhombic
 $P2_12_12_1$
 $a = 10.383$ (2) Å
 $b = 12.906$ (3) Å
 $c = 13.327$ (3) Å
 $V = 1785.9$ (7) Å³
 $Z = 4$
 $D_x = 1.511$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 31 reflections
 $\theta = 10.02 - 12.42^\circ$
 $\mu = 0.965$ mm⁻¹
 $T = 160.0$ (10) K
 Block
 $0.31 \times 0.15 \times 0.08$ mm
 Orange

Data collection

Stoe Siemens diffractometer
 ω/θ scans
 Absorption correction:
 empirical
 $T_{\min} = 0.65$, $T_{\max} = 0.84$
 3567 measured reflections
 2418 independent reflections
 1858 observed reflections
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0795$ (on F^2)
 $\theta_{\text{max}} = 25.00^\circ$
 $h = -11 \rightarrow 12$
 $k = -15 \rightarrow 15$
 $l = -15 \rightarrow 15$
 5 standard reflections
 frequency: 60 min
 intensity variation: 2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0324$
 $wR(F^2) = 0.0831$ (all data)
 $S = 1.053$ (all data)
 2418 reflections
 191 parameters
 H atoms constrained
 Calculated weights
 $w = 1/[\sigma^2(F_o^2) + (0.0353P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.61 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.03 \text{ e } \text{Å}^{-3}$

Extinction correction:
SHELXL93 (Sheldrick, 1993)
 Extinction coefficient:
 0.0010 (4)
 Atomic scattering factors
 from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
 Absolute configuration:
 Flack (1983); $x = 0.16$ (9)

C10—C6—C15	125.9 (5)	C18—C15—C17	108.7 (5)
C7—C6—C15	127.8 (5)	C6—C15—C16	111.3 (5)
C8—C7—C6	109.4 (5)	C18—C15—C16	109.3 (6)
C7—C8—C9	108.2 (6)	C17—C15—C16	109.0 (5)
C8—C9—C10	106.7 (5)		

Table 3. Summary of crystallographic data (Å , $^\circ$) for (1)–(4)

X is the ligand ring centroid.

Complex	Mean M—Cl	Mean M—X	Cl—M—Cl	X—M—X
(1)	2.480	2.099	84.2	131.0
(2)	2.461	2.079	84.8	131.7
(3)	2.457	2.218	94.3	128.7
(4)	2.490	2.204	93.7	129.1

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)
$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Nb	0.24255 (6)	0.47524 (4)	0.41620 (3)	0.0163 (2)
Cl1	0.3378 (2)	0.37676 (13)	0.55742 (10)	0.0291 (10)
Cl2	0.1064 (2)	0.55441 (12)	0.54875 (11)	0.0273 (8)
C1	0.1911 (6)	0.3035 (5)	0.3449 (4)	0.021 (3)
C2	0.1973 (6)	0.3769 (4)	0.2672 (4)	0.021 (3)
C3	0.0966 (6)	0.4517 (5)	0.2779 (4)	0.023 (3)
C4	0.0286 (6)	0.4234 (5)	0.3640 (5)	0.028 (3)
C5	0.0879 (6)	0.3362 (4)	0.4077 (5)	0.024 (3)
C6	0.3078 (6)	0.6523 (5)	0.3733 (4)	0.021 (3)
C7	0.3871 (6)	0.6163 (5)	0.4529 (5)	0.026 (3)
C8	0.4642 (5)	0.5340 (5)	0.4183 (5)	0.028 (3)
C9	0.4298 (6)	0.5128 (5)	0.3179 (4)	0.023 (3)
C10	0.3345 (6)	0.5860 (4)	0.2911 (4)	0.019 (4)
C11	0.2662 (7)	0.2034 (4)	0.3484 (4)	0.024 (4)
C12	0.2430 (8)	0.1445 (4)	0.4478 (5)	0.039 (4)
C13	0.2206 (8)	0.1359 (5)	0.2604 (5)	0.042 (5)
C14	0.4124 (7)	0.2230 (5)	0.3363 (5)	0.034 (4)
C15	0.2294 (8)	0.7515 (4)	0.3692 (4)	0.027 (5)
C16	0.0900 (7)	0.7304 (5)	0.3330 (5)	0.027 (4)
C17	0.2964 (8)	0.8246 (5)	0.2938 (5)	0.041 (5)
C18	0.2252 (8)	0.8048 (5)	0.4722 (5)	0.038 (5)

Table 2. Selected geometric parameters (Å , $^\circ$)

Nb—C9	2.394 (6)	C2—C3	1.429 (9)
Nb—C10	2.395 (6)	C3—C4	1.396 (9)
Nb—C2	2.403 (5)	C4—C5	1.410 (8)
Nb—C3	2.405 (6)	C6—C10	1.418 (8)
Nb—C7	2.409 (6)	C6—C7	1.421 (8)
Nb—C5	2.411 (6)	C6—C15	1.517 (8)
Nb—C4	2.422 (6)	C7—C8	1.408 (9)
Nb—C8	2.424 (6)	C8—C9	1.411 (8)
Nb—C6	2.451 (6)	C9—C10	1.414 (8)
Nb—C1	2.470 (6)	C11—C13	1.536 (8)
Nb—C11	2.477 (2)	C11—C12	1.547 (8)
Nb—C12	2.483 (2)	C11—C14	1.547 (10)
C1—C2	1.404 (8)	C15—C18	1.536 (8)
C1—C5	1.423 (8)	C15—C17	1.544 (9)
C1—C11	1.510 (8)	C15—C16	1.551 (10)
C11—Nb—C12	84.15 (6)	C9—C10—C6	110.2 (5)
C2—C1—C5	105.6 (6)	C1—C11—C13	107.6 (5)
C2—C1—C11	125.2 (5)	C1—C11—C12	111.5 (6)
C5—C1—C11	128.6 (5)	C13—C11—C12	109.1 (5)
C1—C2—C3	110.4 (6)	C1—C11—C14	111.3 (5)
C4—C3—C2	106.0 (5)	C13—C11—C14	108.4 (6)
C3—C4—C5	109.1 (6)	C12—C11—C14	108.8 (6)
C4—C5—C1	108.8 (5)	C6—C15—C18	111.2 (5)
C10—C6—C7	105.4 (5)	C6—C15—C17	107.3 (6)

The compound was synthesized by the reaction of *tert*-butylcyclopentadienyllithium with $[\text{NbCl}_4(\text{OC}_4\text{H}_8)_2]$ in 1,2-dimethoxyethane at 273 K under an argon atmosphere [a modification of the preparation described by Broussier, Normand & Gautheron (1978)]. A single crystal suitable for X-ray diffraction was grown by slow diffusion of hexane into a dichloromethane solution. A molecular ion was observed in the mass spectrum at $m/e = 405$, with an isotope pattern appropriate for a complex containing two chloride ligands. Chemical analysis figures were acceptable.

The absolute structure determination is based on the enantiomorph polarity parameter method of Flack (1983); the data comprise a complete set of Friedel pairs. H atoms were constrained: cyclopentadiene C—H = 0.94 Å on ring-angle external bisector, $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$; methyl C—H = 0.99 Å, H—C—H = 109.5°, staggered conformations, $U(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. Data collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93* and local programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71463 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1065]

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Structures of the Indium Trihalide Bisphosphine Complexes [InBr₃(PMe₂Ph)₂] and [InI₃(PMePh₂)₂]

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Abstract

Both title compounds, tribromobis(dimethylphenylphosphine)indium and triiodobis(methyldiphenylphosphine)indium, contain indium(III) in a trigonal bipyramidal environment, with axial phosphine and equatorial halide ligands. In—P bonds are *ca* 0.1 Å longer in the triiodide compound; this probably results mainly from the larger size of the phosphines in this compound, although the effect of changing the halide cannot be assessed from the limited data available. Deviations of angles from ideal trigonal bipyramidal values are statistically significant but no larger than those commonly observed for this type of geometry.

Comment

Phosphine complexes of the *p*-block elements have been known for many years and the subject has been reviewed (Levason & McAuliffe, 1976), but the number of compounds which have been structurally characterized remains small. For the specific example of indium(III) halides (*X* = halogen), the following types of complex have been proposed on the basis of analytical and spectroscopic data: [InX₃(PR₃)_{*n*}] (*n* = 1, 2, 3), [InX₂(PR₃)_{*n*}]⁺ (*n* = 2, 4) and [In(PR₃)₄]³⁺ (Carty & Tuck, 1975). However, the only compounds to have been structurally characterized are the 1:1 adducts [InI₃(PPhPh₂)] (1) and [InI₃(PH^{*t*}Bu₂)] (2) (Alcock, Degnan, Howarth & Wallbridge, 1992), and the 2:1 adducts [InCl₃(PPh₃)₂] (3) (Veidis & Palenik, 1969), [InCl₃(PMe₃)₂] (4) and [(InI₃)₂(Ph₂PCH₂CH₂PPh₂)₃] (5) (Degnan, Alcock, Roe & Wallbridge, 1992). In the former set of complexes,

the indium adopts a tetrahedral geometry, while in the latter set the geometry is trigonal bipyramidal with *trans* axial phosphines. In (5), one diphosphine ligand bridges the two indium centres, whereas the other two are monodentate. Also worth mentioning is the related 1:1 gallium complex [GaCl₃(PMe₃)] (Carter, Jugie, Enjalbert & Galy, 1978). We report here the structures of the two indium trihalide bisphosphine adducts [InBr₃(PMe₂Ph)₂] (6) and [InI₃(PMePh₂)₂] (7).

The indium centre in both molecules adopts a trigonal bipyramidal geometry with the phosphine ligands *trans* in the axial sites. The In—P bond distances in (6) are 2.614 (3) and 2.622 (3) Å, but are *ca* 0.1 Å longer in (7) at 2.712 (3) and 2.719 (3) Å. We note that in (5), the In—P bond distances are longer still at 2.798 (3) and 2.819 (2) Å, whereas those in (4) are 2.575 (3) and 2.576 (3) Å, the shortest bonds between InX₃ and PR₃ in any structure to date; in (3) the relevant bond lengths are 2.701 and 2.723 Å. Clearly, the wide range of observed values reflects the large variation in the size of the phosphines, but the nature of the halide is also likely to be important. Additional structures in which the phosphine is varied while the halide is kept constant, and structures of complexes of different indium(III) halides with the same phosphine, would allow the various factors to be delineated more clearly. The In—P bond lengths in the tetrahedral complexes (1) and (2) are 2.598 (mean of two independent molecules)

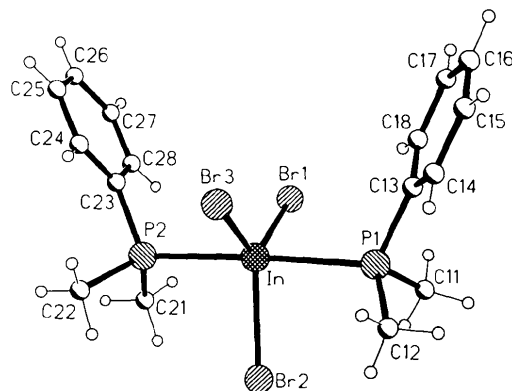


Fig. 1. Molecular structure of (6).

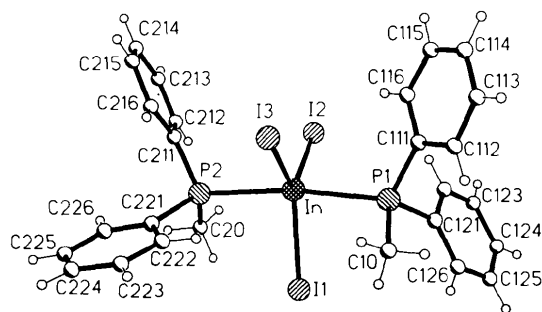


Fig. 2. Molecular structure of (7).