
Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1336). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$[Li_2(\mu_3\text{-}{}^tBu_2P)(\mu_2\text{-}{}^tBu_2P)(thf)]_2$: a Redetermination

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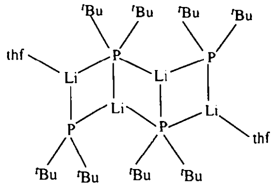
Abstract

The crystal structure of the title compound as its *n*-hexane solvate, bis(μ_3-di-*tert*-butylphosphino)-1:2:3κ^3P;2:3:4κ^3P-bis(μ_2-di-*tert*-butylphosphino)-1:2κ^2P;3:4κ^2P-bis(tetrahydrofuran)-1κO;4κO-tetralithium, $[Li_4(C_8H_{18}P)_4(C_4H_8O)_2].C_6H_{14}$, has been redetermined to improved precision using diffractometer data collected at 213 K, resulting in more accurate bond distances and angles with reduced standard deviations. Furthermore, the relatively high R values (R = 0.10, wR = 0.13) of the previous structure determination at room temperature [Jones, Stuart & Wright (1983). *J. Am. Chem. Soc.* **105**, 7459–7460] were caused by the omission of the molecule of solvent *n*-hexane, which was not localized; the inclusion of this solvent molecule reduced the R value to 0.0552.

Comment

Lithium diorganophosphides are useful transfer agents for $-PR_2$ groups. In contrast to the corresponding amido derivatives of the alkaline metals, relatively little information has been published on the related diorganophosphides (Hey, Hitchcock, Lappert & Rai, 1987). These synthetically important reagents are also of interest with respect to their solid-state structures (Bartlett, Olmstead & Power, 1986).

We have recently reported the synthesis and X-ray crystal structure determination of two formally four-coordinate lanthanide phosphido species, trivalent $({}^tBu_2P)_2La[(\mu\text{-}P^tBu_2)_2Li(thf)]$ and divalent $Yb[(\mu\text{-}P^tBu_2)_2Li(thf)]_2$ (Rabe, Riede & Schier, 1996). In our attempted synthesis of the lanthanum complex, we isolated the title compound, (I), as its *n*-hexane solvate.



(I)

The single-crystal X-ray structure determination of the title compound at room temperature has been published previously (Jones, Stuart & Wright, 1983). However, the presence of an *n*-hexane molecule in the unit cell was not reported although *n*-hexane was used for crystallization. Relatively high R and wR values of 0.0982 and 0.1312 were found. These, according to the authors, were the result of substantial thermal motion, especially of the coordinated thf molecules. Furthermore, a strikingly low calculated density of 0.842 g cm^{-3} was determined for the title complex. These two points lead us to believe that both samples are identical. The authors were planning to collect a low-temperature data set in order to resolve this. However, to the best of our knowledge, this low-temperature determination has not yet been reported.

Whereas the relatively high U_{eq} values of the thf C atoms in our data set are the result of slight disorder of this ligand, the values for the hexane C atoms (C5–C7) in the same range (Table 1) might be indicative of site-occupancy factors of less than 1 for the solvent molecule. This would be in accordance with our findings and the observation of Jones, Stuart & Wright (1983) that the crystals were found to rapidly crumble to a white powder in the absence of either hexane or tetrahydrofuran vapour at room temperature. Thus, it is very likely that the solvent molecule, which shows substantial

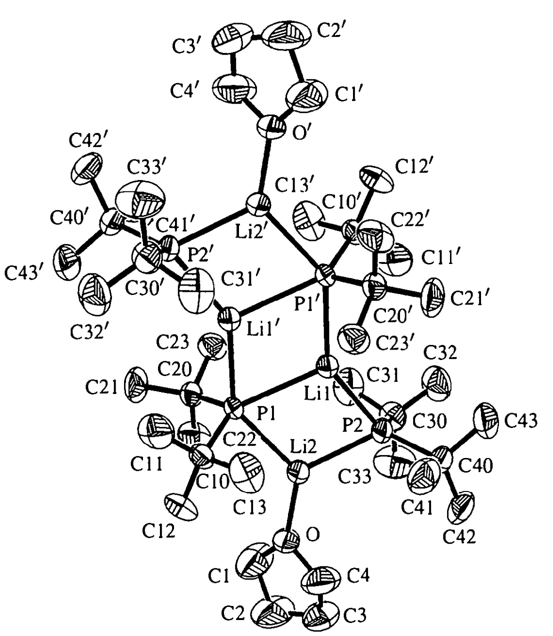


Fig. 1. Molecular structure of the title compound showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

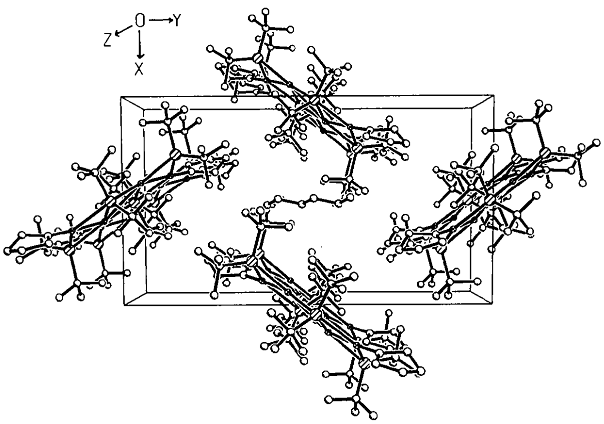


Fig. 2. Packing diagram of (I).*n*-hexane.

thermal motion even at 213 K, could not be located at room temperature. Attempts to resolve the disorder of the tetrahydrofuran molecule and to refine the site occupancy factors of the hexane molecule were not carried out. Nevertheless, the calculations using low-temperature data confirm the overall structure of the title compound (Fig. 1). The final *R* factor of 0.0552 and the improved e.s.d.'s for derived parameters indicate a more precise structure determination than the earlier study. Fig. 2 shows a packing diagram with the *n*-hexane solvent molecule in the centre of the unit cell.

Experimental

Colourless crystals were obtained from a hexane solution at 243 K. ^{1}H NMR (C_6D_6, 400 MHz, 293 K): δ 1.28 (*m*, 4H), 1.65 (*s*, 56H), 3.65 p.p.m. (*m*, 4H). ^{13}C NMR (C_6D_6, 100.4 MHz, 293 K): δ 25.2 (thf), 32.0 (CH_3—C), 36.7 (CH_3—C), 68.9 p.p.m. (thf). ^{31}P NMR (C_6D_6, 161.7 MHz, 293 K): δ 12.6 p.p.m. (*s*, $\nu_{1/2}$ = 255 Hz). ^{7}Li NMR (C_6D_6, 104.9 MHz, 293 K): δ 3.4 p.p.m. (*s*, $\nu_{1/2}$ = 58 Hz).

Crystal data

$[Li_4(C_8H_{18}P)_4(C_4H_8O)_2].C_6H_{14}$
$M_r = 838.98$
Monoclinic
$P2_1/n$
$a = 11.533\ (3)$ Å
$b = 20.585\ (6)$ Å
$c = 12.217\ (2)$ Å
$\beta = 97.20\ (2)°$
$V = 2877.5$ Å^3
$Z = 2$
$D_x = 0.968$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15–19°$
$\mu = 0.16$ mm^{-1}
$T = 213$ K
Prism
0.50 × 0.35 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
6059 measured reflections
5759 independent reflections
5740 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0351$
$\theta_{max} = 27°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 26$
$l = -15 \rightarrow 15$
3 standard reflections frequency: 90 min intensity decay: 1.5%

Refinement

Refinement on F^2
$R(F) = 0.0552$
$wR(F^2) = 0.1216$
$S = 1.004$
5740 reflections
253 parameters
H atoms riding
$w = 1/[\sigma^2(F) + 0.0001F^2]$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.358$ e Å^{-3}
$\Delta\rho_{min} = -0.307$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
P(1)	0.50280 (7)	0.02005 (4)	0.82926 (6)	0.0337 (2)
P(2)	0.27123 (8)	0.14202 (4)	0.95240 (7)	0.0422 (2)
C(10)	0.6393 (3)	0.0567 (2)	0.7831 (2)	0.0438 (8)
C(11)	0.7438 (3)	0.0110 (2)	0.7950 (4)	0.0819 (13)
C(12)	0.6226 (3)	0.0822 (2)	0.6651 (3)	0.0682 (11)
C(13)	0.6676 (4)	0.1139 (2)	0.8601 (3)	0.0827 (13)
C(20)	0.4341 (3)	−0.0429 (2)	0.7282 (2)	0.0444 (8)
C(21)	0.5219 (4)	−0.0888 (2)	0.6852 (3)	0.0761 (12)
C(22)	0.3582 (3)	−0.0123 (2)	0.6302 (3)	0.0678 (11)
C(23)	0.3546 (3)	−0.0826 (2)	0.7929 (3)	0.0601 (10)
C(30)	0.1124 (3)	0.1198 (2)	0.9149 (3)	0.0555 (9)
C(31)	0.1152 (4)	0.0497 (2)	0.8744 (4)	0.0809 (13)
C(32)	0.0410 (4)	0.1190 (2)	1.0110 (4)	0.0822 (13)
C(33)	0.0504 (4)	0.1605 (3)	0.8215 (4)	0.100 (2)
C(40)	0.2887 (3)	0.2222 (2)	1.0277 (3)	0.0556 (9)
C(41)	0.4184 (4)	0.2354 (2)	1.0380 (4)	0.0805 (13)
C(42)	0.2240 (5)	0.2782 (2)	0.9668 (4)	0.089 (2)

C(43)	0.2532 (4)	0.2201 (2)	1.1448 (3)	0.0791 (13)
Li(1)	0.4079 (4)	0.0508 (2)	1.0092 (4)	0.0389 (11)
Li(2)	0.3685 (5)	0.1192 (2)	0.7879 (4)	0.0458 (13)
O	0.3464 (2)	0.17102 (11)	0.6556 (2)	0.0628 (7)
C(1)	0.3127 (6)	0.1589 (2)	0.5445 (3)	0.126 (2)
C(2)	0.2827 (6)	0.2216 (3)	0.4890 (4)	0.119 (2)
C(3)	0.2777 (5)	0.2673 (2)	0.5770 (5)	0.104 (2)
C(4)	0.3502 (7)	0.2393 (2)	0.6696 (4)	0.125 (2)
C(5)	1.0170 (6)	0.1122 (3)	0.3281 (5)	0.128 (2)
C(6)	0.9882 (6)	0.0817 (3)	0.4301 (6)	0.135 (2)
C(7)	1.0140 (5)	0.0159 (3)	0.4474 (4)	0.110 (2)

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

P(1)—C(10)	1.894 (3)	P(2)—C(40)	1.888 (4)
P(1)—C(20)	1.894 (3)	P(2)—Li(1)	2.493 (5)
P(1)—Li(1)	2.652 (5)	P(2)—Li(1)	2.466 (5)
P(1)—Li(2)	2.574 (5)	Li(2)—O	1.926 (5)
P(1)—Li(1)′	2.564 (5)	Li(1)···Li(2)	3.031 (7)
P(2)—C(30)	1.888 (4)	Li(1)···Li(1′)	3.010 (9)
P(2)—Li(2)—P(1)	108.4 (2)	P(1′)—Li(1)—P(1)	109.5 (2)
O—Li(2)—P(1)	128.1 (2)	P(1′)—Li(1)—P(2)	145.2 (2)
P(2)—Li(1)—P(1)	105.2 (2)		

All H atoms were placed in calculated idealized positions and allowed to ride on their corresponding C atoms with fixed isotropic contributions [U_{iso}(fix) = 0.08 or 0.15 Å^2].

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *SDP-Plus* (Enraf–Nonius, 1988); *CADSHEL* (Kopf & Rübcke, 1993). Program(s) used to solve structure: *SHELXTL-Plus* (Siemens, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: local programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1099). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Pentacarbonyl[tris(2-methoxyphenyl)phosphine-*P*]chromium and its Molybdenum Analogue

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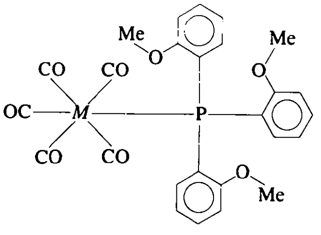
Abstract

In the title compounds, $[Cr(C_{21}H_{21}O_3P)(CO)_5]$ and $[Mo(C_{21}H_{21}O_3P)(CO)_5]$, the *M*—C bond lengths for the *cis*-carbonyl ligands (with respect to the phosphine) are longer than that observed for the *trans*-carbonyl group. The chromium compound has short intermolecular O···O contacts. The two crystal structures are not isomorphous and crystallize in triclinic and monoclinic systems, respectively.

Comment

There have been numerous X-ray structure determinations of phosphine-substituted metal carbonyls. Despite this, we have determined the structures of the complexes $[M(CO)_5(L)]$, where *M* is Cr [compound (1)] or Mo [compound (2)], and *L* is tris(2-methoxyphenyl)phosphine, in order to study the bonding characteristics of the phosphine ligand and the effects of the methoxy substituents on the stereochemistry of the complexes.



(1) M = Cr
(2) M = Co

(I)

The compounds have the expected octahedral geometry in which one carbonyl is *trans* and the remaining four are *cis* with respect to the phosphine ligand. The Cr—P distance of 2.457 (1) Å is longer than those observed in $[Cr(CO)_5(PPh_3)]$, (3), of 2.422 Å,

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