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}
Pt	0.20512 (2)	1/4	0.27906 (2)	0.02835 (7)
Re	−0.06524 (3)	1/4	0.13588 (3)	0.03849 (9)
P1	−0.0768 (1)	0.1274 (1)	0.2547 (1)	0.0465 (4)
P2	0.1842 (1)	0.0978 (1)	0.2991 (1)	0.0396 (4)
P3	0.4303 (2)	1/4	0.3357 (2)	0.0324 (3)
F1	−0.1812 (4)	0.0509 (3)	0.1895 (4)	0.081 (1)
F2	−0.1171 (3)	0.1427 (3)	0.3588 (3)	0.074 (1)
F3	0.1948 (3)	0.0273 (3)	0.2095 (3)	0.068 (1)
F4	0.2927 (3)	0.0548 (3)	0.4110 (3)	0.062 (1)
O1	−0.0208 (6)	0.3929 (4)	−0.0343 (4)	0.090 (2)
O2	−0.3645 (7)	1/4	−0.0020 (7)	0.101 (3)
N1	0.0550 (4)	0.0612 (3)	0.3166 (4)	0.048 (1)
C1	−0.0375 (6)	0.3433 (5)	0.0307 (5)	0.055 (2)
C2	−0.2516 (8)	1/4	0.0465 (8)	0.060 (3)
C3	0.0542 (7)	−0.0305 (5)	0.3742 (7)	0.085 (3)
C4	0.4725 (5)	0.3536 (4)	0.2712 (4)	0.042 (1)
C5	0.5493 (7)	0.4230 (5)	0.3395 (6)	0.061 (2)
C6	0.5700 (7)	0.5045 (5)	0.2896 (7)	0.076 (3)
C7	0.5103 (7)	0.5177 (5)	0.1713 (6)	0.082 (2)
C8	0.4295 (9)	0.4515 (6)	0.1013 (6)	0.105 (3)
C9	0.4096 (8)	0.3696 (6)	0.1506 (6)	0.084 (3)
C10	0.5377 (7)	1/4	0.4919 (6)	0.036 (2)
C11	0.4819 (7)	1/4	0.5731 (6)	0.050 (2)
C12	0.5623 (8)	1/4	0.6933 (7)	0.071 (4)
C13	0.694 (1)	1/4	0.7308 (8)	0.070 (3)
C14	0.7504 (8)	1/4	0.6507 (8)	0.056 (3)
C15	0.6742 (7)	1/4	0.5327 (7)	0.048 (2)
S	0.8586 (2)	3/4	0.3777 (2)	0.0489 (6)
F5	0.6504 (6)	3/4	0.1749 (7)	0.113 (3)
F6	0.8094 (6)	0.8243 (4)	0.1717 (4)	0.127 (2)
O3	0.8138 (4)	0.8342 (4)	0.4103 (4)	0.081 (2)
O4	0.9936 (5)	3/4	0.4007 (6)	0.064 (2)
C16	0.779 (1)	3/4	0.218 (1)	0.076 (4)

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

Pt—Re	2.818 (1)	Re—C1	1.975 (7)
Pt—P2	2.208 (1)	Re—C2	1.925 (9)
Pt—P3	2.336 (2)	O1—C1	1.144 (8)
Re—P1	2.323 (2)	O2—C2	1.16 (1)
Re—Pt—P2	86.13 (4)	P1—Re—P1^{i}	97.62 (8)
Re—Pt—P3	160.96 (6)	P1—Re—C1	172.0 (2)
P2—Pt—P2^{i}	158.77 (8)	P1—Re—C2	91.6 (2)
P2—Pt—P3	96.88 (4)	C1—Re—C2	93.2 (3)
Pt—Re—P1	86.15 (4)	Re—C1—O1	175.8 (6)
Pt—Re—C1	89.3 (2)	Re—C2—O2	177 (1)
Pt—Re—C2	176.6 (3)		

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

General procedures for crystal orientation and cell determination and refinement have been published (Mague & Lloyd, 1989). The choice between the possible space groups $P2_1$ and $P2_1/m$ was made on the basis of intensity statistics and the successful refinement in the latter. Most H atoms were seen in a difference map near the end of the refinement and all were included as fixed contributions in calculated positions (C—H = 0.95 Å) with isotropic displacement parameters 20% larger than those of the attached C atoms, and updated periodically. The structure was solved by Patterson and Fourier methods.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *MolEN CIF VAX*.

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Tris(1,2-dimethoxyethane)lithium 1,1,4,4-Tetraphenyl-1,3-butadiene Radical Anion

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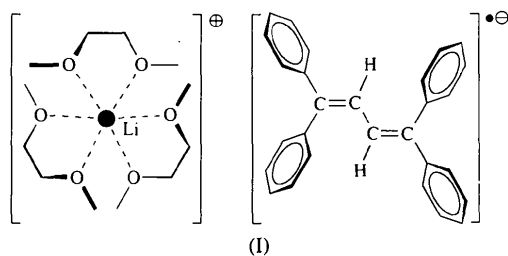
Abstract

The crystal structure of $[Li(C_4H_{10}O_2)_3](C_{28}H_{22})$ has been determined at 100 K. The structure of the radical anion displays a slightly distorted butadiene skeleton with reversed bond order compared to the neutral 1,1,4,4-tetraphenyl-1,3-butadiene molecule. The Li countercation is hexacoordinated by three dimethoxyethane molecules forming a solvent-separated ion pair.

Comment

The multiple reduction of unsaturated hydrocarbon molecules yields anionic intermediates with variably distorted molecular skeletons depending on their negative charge (Bock *et al.*, 1992; Schade & von Schleyer, 1988; Setzer & von Schleyer, 1985). These structural changes, as well as the structures of numerous organometallic compounds, can be predicted by quantum-mechanical calculations (Bock *et al.*, 1992; Schade & von Schleyer, 1988), which provide additional insight into the properties and reactivity of the compounds. Furthermore, because most organometallic compounds, which are typically obtained from solution, contain solvent and/or chelating ligands, it seems reasonable to assume that the complexes in the solid state represent the species in solution to a large extent. Therefore, these structures allow an insight into the complex multi-dimensional network of electron transfer and contact ion formation, as well as aggregation and solvation equilibria during the redox reactions. These organometallic structures can be discussed with regard to solvent effects, charge delocalization and the structures of their anions. We report here the crystal structure of a novel 1,1,4,4-tetraphenyl-1,3-butadiene radical anion (Fig. 1), which crystallizes as a solvent-separated ion pair from dimethoxyethane solution, (I).

(I)

Due to its bidentate nature, dimethoxyethane is a powerful solvating agent and forms predominantly solvent-separated complexes. In addition, the negative charge of radical anions of unsaturated hydrocarbons is delocalized over the whole π system and formation of contact ion pairs is therefore suppressed (Bock, Näther, Arad, John & Havlas, 1994). To our knowledge, pyrene–sodium–dimethyl ether is the only example of an alkali metal radical anion of an unsaturated hydrocarbon that forms contact ion pairs in the solid state (Jost, Adam, Enkelmann & Müllen, 1992).

One-electron reduction of 1,1,4,4-tetraphenyl-1,3-butadiene to its radical anion leads to nearly reversed bond lengths in the butadiene skeleton and formally to the formation of a butene system with highly delocalized charge. The terminal C—C bonds are elongated from 1.36 Å in the neutral molecule (Bock, Näther & Ruppert, 1992) to an average value of 1.413 (5) Å in the radical anion, whereas the central C—C bond is shortened from 1.44 Å to an average value of 1.391 (5) Å. The structure of the radical anion is therefore between
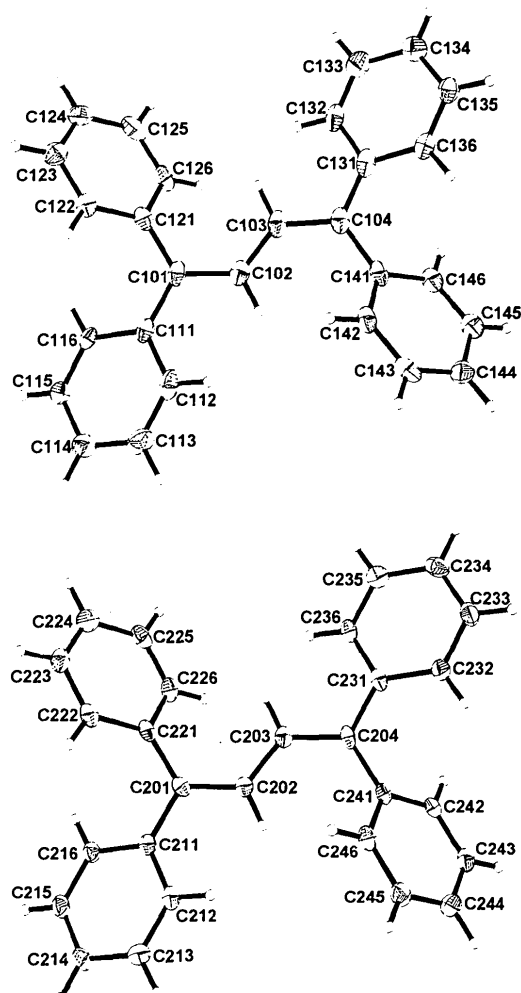

Fig. 1. A view of the independent molecules of the 1,1,4,4-tetraphenyl-1,3-butadiene radical anion showing the labelling of the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level.

that of the neutral molecule and that of the dianion of 1,1,4,4-tetraphenyl-1,3-butadiene (Bock, Näther, Ruppert & Havlas, 1992; Bock, Näther & Ruppert, 1992). The dianion leads to the complete formation of a butene-1,4-diyl system with a terminal C—C bond length of 1.46 Å and a central C—C bond length of 1.36 Å, allowing a maximum separation of the negative charges. The butadiene skeleton is planar within experimental error and the Ph—C—Ph groups are twisted between 10 and 13°. The *ipso* angles of the phenyl substituents are reduced by the adjacent carbanionic charges to 115.4 (4)°. The average C—Ph bond length of 1.468 (5) Å is significantly longer than those found in the dianion, showing that the negative charge is localized predominantly in the butadiene π system.

The coordination spheres of the Li countercations are distorted octahedra (Fig. 2), with Li···O distances

between 2.049 (7) and 2.225 (7) Å. The steric repulsion between the donor ligands significantly increases these Li···O distances, as becomes evident on comparison with those in tetrahedrally ether-solvated Li complexes, such as Li(thf)$_4$ in [Li(thf)$_4$][Li{C(SiMe$_3$)$_2$}$_2$] (Eaborn, Hitchcock, Smith & Sullivan, 1983). In contrast to the hexacoordinate Li ion in the title compound, the bidentate ligand *N,N*-tetramethylethylenediamine forms only tetracoordinate Li complexes (Jonas, Pörschke,

Krüger & Tsay, 1976); this is mainly due to the steric bulkiness of this solvent compared with dimethoxyethane.

In summary, the structure of the title compound provides an illustrative example of the increasing distortion of organic molecules caused by multiple reduction. Whereas the insertion of one electron leads only to small structural changes, two-electron reduction perturbs the molecular skeletons dramatically.
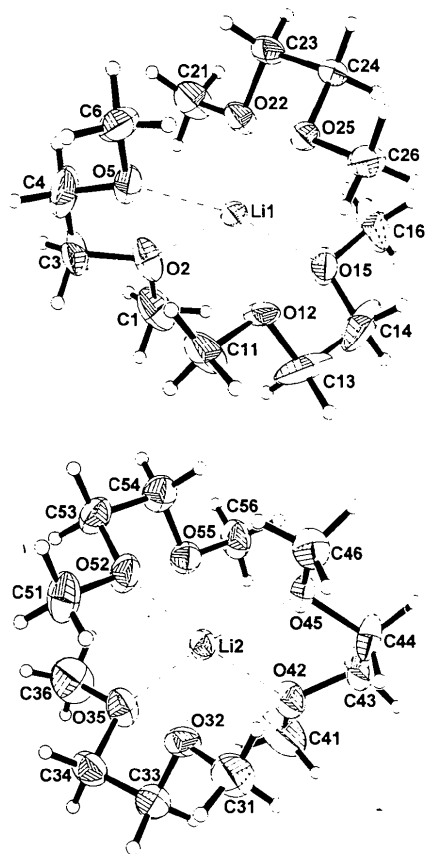
Experimental

The title compound was prepared by adding 100 mg (14.4 mmol) of carefully cleaned pieces of lithium metal to a mixture of 300 mg (0.84 mmol) of 1,1,4,4-tetraphenyl-1,3-butadiene in 10 ml of absolute dimethoxyethane under argon in a carefully dried Schlenk trap. After short ultrasonic activation, the solution became dark blue and extremely air and moisture sensitive crystals grew within 1 d.

Fig. 2. Coordination of the dimethoxyethane-solvated lithium countercations showing the labelling of the non-H atoms in the two independent complexes. Displacement ellipsoids are drawn at the 50% probability level.
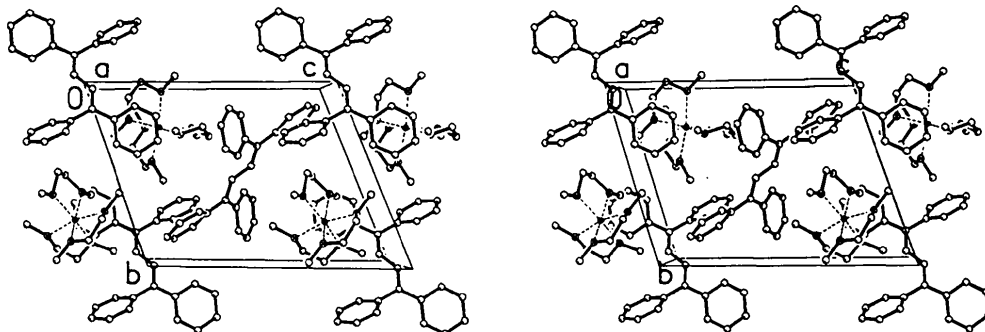
Crystal data

[Li(C₄H₁₀O₂)₃](C₂₈H₂₂)	Mo $K\alpha$ radiation
$M_r = 635.8$	$\lambda = 0.7107$ Å
Triclinic	Cell parameters from 22
$P\bar{1}$	reflections
$a = 12.160\,(5)$ Å	$\theta = 10.50$–$22.00°$
$b = 12.482\,(5)$ Å	$\mu = 0.075$ mm^{-1}
$c = 14.755\,(5)$ Å	$T = 100$ K
$\alpha = 68.172\,(5)°$	Block
$\beta = 80.307\,(5)°$	$0.50 \times 0.30 \times 0.30$ mm
$\gamma = 61.792\,(5)°$	Dark blue
$V = 1832.0\,(12)$ Å^3	
$Z = 2$	
$D_x = 1.153$ Mg m^{-3}	

Data collection

Stoe AED II diffractometer	$\theta_{max} = 24.53°$
$2\theta/\omega$ scans	$h = 0 \rightarrow 14$
Absorption correction:	$k = -12 \rightarrow 14$
none	$l = -16 \rightarrow 17$
6409 measured reflections	4 standard reflections
6409 independent reflections	frequency: 120 min
5256 observed reflections	intensity decay: none
[$I > 2\sigma(I)$]	

Fig. 3. Packing of the four independent molecules in the *bc* plane.

Refinement

Refinement on F^2

$R(F) = 0.0433$

$wR(F^2) = 0.1289$

$S = 1.043$

6409 reflections

859 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0892P)^2 + 0.3469P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.508$ e Å^{-3}

$\Delta\rho_{min} = -0.248$ e Å^{-3}

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
Li1	0.5034 (6)	0.7659 (6)	0.7707 (5)	0.0258 (14)
C1	0.5782 (6)	0.9883 (6)	0.6416 (4)	0.0601 (15)
O2	0.5985 (3)	0.8809 (3)	0.7267 (2)	0.0478 (8)
C3	0.6637 (5)	0.8721 (6)	0.8012 (5)	0.062 (2)
C4	0.6918 (5)	0.7556 (7)	0.8827 (5)	0.061 (2)
O5	0.5972 (3)	0.7190 (3)	0.9017 (3)	0.0531 (9)
C6	0.6131 (5)	0.6131 (5)	0.9881 (4)	0.0517 (13)
C11	0.3247 (5)	0.9438 (6)	0.8812 (5)	0.068 (2)
O12	0.3357 (3)	0.8969 (3)	0.8047 (3)	0.0403 (7)
C13	0.2641 (5)	0.9952 (5)	0.7201 (5)	0.071 (2)
C14	0.2685 (5)	0.9335 (7)	0.6509 (5)	0.075 (2)
O15	0.3946 (3)	0.8580 (3)	0.6326 (2)	0.0445 (8)
C16	0.4083 (8)	0.7938 (7)	0.5645 (4)	0.078 (2)
C21	0.7604 (5)	0.6157 (5)	0.6777 (4)	0.0526 (14)
O22	0.6416 (3)	0.6239 (3)	0.7156 (2)	0.0402 (8)
C23	0.6471 (4)	0.4994 (4)	0.7680 (3)	0.0348 (10)
C24	0.5167 (4)	0.5158 (4)	0.7901 (3)	0.0295 (9)
O25	0.4560 (2)	0.6111 (2)	0.8369 (2)	0.0276 (6)
C26	0.3334 (4)	0.6258 (4)	0.8677 (4)	0.0394 (11)
Li2	−0.5170 (6)	−0.7567 (7)	−0.7546 (5)	0.0289 (14)
C31	−0.2912 (5)	−0.7334 (6)	−0.6960 (4)	0.0560 (14)
O32	−0.4137 (3)	−0.7163 (3)	−0.6803 (2)	0.0326 (6)
C33	−0.4379 (5)	−0.7599 (5)	−0.5783 (4)	0.0452 (12)
C34	−0.5792 (5)	−0.7091 (5)	−0.5616 (4)	0.0441 (11)
O35	−0.6220 (3)	−0.7555 (3)	−0.6178 (2)	0.0432 (8)
C36	−0.7511 (5)	−0.7175 (7)	−0.6033 (5)	0.069 (2)
C41	−0.4336 (8)	−1.0530 (5)	−0.6139 (4)	0.076 (2)
O42	−0.4049 (3)	−0.9615 (3)	−0.6947 (2)	0.0418 (8)
C43	−0.3298 (6)	−1.0138 (5)	−0.7649 (4)	0.0570 (15)
C44	−0.2934 (4)	−0.9225 (4)	−0.8388 (4)	0.0470 (12)
O45	−0.3946 (3)	−0.7972 (3)	−0.8700 (2)	0.0338 (7)
C46	−0.3660 (5)	−0.7086 (4)	−0.9495 (3)	0.0411 (11)
C51	−0.6232 (5)	−0.4564 (4)	−0.8130 (4)	0.0491 (13)
O52	−0.6152 (3)	−0.5620 (3)	−0.8334 (2)	0.0397 (7)
C53	−0.7348 (4)	−0.5324 (4)	−0.8647 (4)	0.0412 (11)
C54	−0.7169 (4)	−0.6452 (4)	−0.8920 (4)	0.0423 (11)
O55	−0.6685 (3)	−0.7575 (3)	−0.8104 (3)	0.0381 (7)
C56	−0.6610 (5)	−0.8652 (5)	−0.8290 (4)	0.0480 (12)
C101	0.5909 (4)	0.3487 (3)	0.6133 (3)	0.0239 (8)
C102	0.4854 (4)	0.4601 (4)	0.5628 (3)	0.0254 (8)
C103	0.4750 (4)	0.5367 (4)	0.4660 (3)	0.0279 (9)
C104	0.3733 (4)	0.6516 (4)	0.4126 (3)	0.0246 (8)
C111	0.5767 (3)	0.2704 (3)	0.7120 (3)	0.0211 (8)
C112	0.4610 (4)	0.2739 (4)	0.7511 (3)	0.0336 (10)
C113	0.4462 (4)	0.2088 (4)	0.8482 (3)	0.0356 (10)
C114	0.5497 (4)	0.1309 (4)	0.9117 (3)	0.0341 (10)
C115	0.6650 (4)	0.1217 (4)	0.8747 (3)	0.0246 (8)
C116	0.6793 (4)	0.1888 (3)	0.7789 (3)	0.0195 (8)
C121	0.7163 (3)	0.3117 (3)	0.5690 (3)	0.0221 (8)
C122	0.8021 (3)	0.1808 (3)	0.5824 (3)	0.0210 (8)
C123	0.9191 (4)	0.1465 (4)	0.5423 (3)	0.0289 (9)
C124	0.9573 (4)	0.2400 (4)	0.4845 (3)	0.0325 (10)
C125	0.8753 (4)	0.3688 (4)	0.4707 (3)	0.0331 (10)
C126	0.7583 (4)	0.4043 (4)	0.5126 (3)	0.0283 (9)
C131	0.3981 (4)	0.7249 (4)	0.3158 (3)	0.0256 (9)
C132	0.5196 (4)	0.7164 (4)	0.2853 (3)	0.0303 (9)
C133	0.5435 (4)	0.7798 (4)	0.1905 (3)	0.0334 (10)
C134	0.4501 (4)	0.8570 (4)	0.1207 (3)	0.0327 (10)
C135	0.3303 (4)	0.8694 (4)	0.1475 (3)	0.0285 (9)
C136	0.3056 (4)	0.8045 (4)	0.2421 (3)	0.0241 (8)
C141	0.2447 (4)	0.6943 (4)	0.4498 (3)	0.0237 (8)
C142	0.1960 (4)	0.6089 (4)	0.5059 (3)	0.0256 (9)
C143	0.0728 (4)	0.6511 (4)	0.5356 (3)	0.0303 (9)
C144	−0.0089 (4)	0.7816 (4)	0.5093 (3)	0.0301 (9)
C145	0.0363 (4)	0.8698 (4)	0.4546 (3)	0.0297 (9)
C146	0.1598 (4)	0.8276 (4)	0.4268 (3)	0.0261 (9)
C201	0.0000 (3)	0.1529 (3)	−0.0035 (3)	0.0171 (7)
C202	−0.0105 (3)	0.0382 (3)	0.0261 (3)	0.0167 (7)
C203	0.0089 (3)	−0.0407 (3)	−0.0282 (3)	0.0184 (7)
C204	−0.0068 (3)	−0.1549 (3)	0.0012 (3)	0.0184 (8)
C211	−0.0089 (3)	0.2105 (3)	0.0701 (3)	0.0175 (7)
C212	0.0200 (3)	0.1365 (3)	0.1694 (3)	0.0212 (8)
C213	0.0080 (4)	0.1917 (4)	0.2385 (3)	0.0262 (8)
C214	−0.0324 (4)	0.3244 (4)	0.2119 (3)	0.0271 (9)
C215	−0.0619 (4)	0.3990 (4)	0.1145 (3)	0.0243 (8)
C216	−0.0500 (3)	0.3443 (3)	0.0448 (3)	0.0192 (8)
C221	0.0160 (3)	0.2202 (3)	−0.1068 (3)	0.0169 (7)
C222	0.0977 (3)	0.2787 (3)	−0.1376 (3)	0.0205 (8)
C223	0.1171 (3)	0.3343 (3)	−0.2345 (3)	0.0237 (8)
C224	0.0572 (4)	0.3334 (4)	−0.3068 (3)	0.0279 (9)
C225	−0.0256 (4)	0.2797 (3)	−0.2792 (3)	0.0243 (8)
C226	−0.0463 (3)	0.2255 (3)	−0.1810 (3)	0.0222 (8)
C231	−0.0002 (3)	−0.2091 (3)	−0.0732 (3)	0.0176 (7)
C232	0.0289 (3)	−0.3405 (3)	−0.0491 (3)	0.0213 (8)
C233	0.0434 (4)	−0.3953 (4)	−0.1193 (3)	0.0258 (8)
C234	0.0291 (4)	−0.3220 (4)	−0.2173 (3)	0.0268 (9)
C235	−0.0015 (4)	−0.1920 (4)	−0.2435 (3)	0.0251 (8)
C236	−0.0168 (3)	−0.1366 (3)	−0.1739 (3)	0.0204 (8)
C241	−0.0233 (3)	−0.2210 (3)	0.1043 (3)	0.0165 (7)
C242	−0.1054 (3)	−0.2775 (3)	0.1353 (3)	0.0177 (7)
C243	−0.1165 (3)	−0.3413 (3)	0.2335 (3)	0.0229 (8)
C244	−0.0500 (4)	−0.3478 (4)	0.3044 (3)	0.0274 (9)
C245	0.0314 (4)	−0.2922 (4)	0.2758 (3)	0.0258 (9)
C246	0.0449 (3)	−0.2316 (3)	0.1782 (3)	0.0207 (8)

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

Li1—O12	2.049 (7)	C101—C111	1.457 (6)
Li1—O22	2.103 (7)	C101—C121	1.480 (5)
Li1—O2	2.108 (7)	C102—C103	1.379 (6)
Li1—O25	2.116 (7)	C103—C104	1.420 (5)
Li1—O5	2.156 (8)	C104—C131	1.453 (6)
Li1—O15	2.225 (7)	C104—C141	1.474 (6)
Li2—O52	2.075 (8)	C201—C202	1.395 (5)
Li2—O45	2.110 (7)	C201—C221	1.473 (5)
Li2—O32	2.123 (7)	C201—C211	1.475 (5)
Li2—O55	2.146 (7)	C202—C203	1.403 (4)
Li2—O42	2.146 (7)	C203—C204	1.423 (4)
Li2—O35	2.200 (8)	C204—C231	1.462 (5)
C101—C102	1.413 (5)	C204—C241	1.468 (5)
O2—Li1—O5	76.0 (3)	C103—C104—C131	117.8 (4)
O12—Li1—O15	77.4 (2)	C103—C104—C141	122.4 (4)
O22—Li1—O25	78.3 (2)	C131—C104—C141	119.7 (3)
O32—Li2—O35	78.9 (2)	C202—C201—C221	121.8 (3)
O45—Li2—O42	77.5 (2)	C202—C201—C211	119.2 (3)
O52—Li2—O55	79.6 (3)	C221—C201—C211	119.0 (3)
C102—C101—C111	119.4 (3)	C201—C202—C203	128.9 (3)
C102—C101—C121	121.4 (3)	C202—C203—C204	128.7 (3)
C111—C101—C121	119.1 (3)	C203—C204—C231	118.5 (3)
C103—C102—C101	128.5 (4)	C203—C204—C241	121.2 (3)
C102—C103—C104	130.9 (4)	C231—C204—C241	120.3 (3)
O2—C3—C4—O5	−37.0 (7)	O32—C33—C34—O35	57.4 (5)
O12—C13—C14—O15	−54.6 (6)	O42—C43—C44—O45	−44.2 (7)
O22—C23—C24—O25	−52.6 (4)	O52—C53—C54—O55	57.6 (5)

Data were corrected for Lorentz and polarization effects. The C, O and Li atoms were refined with anisotropic displacement parameters. All H atoms were located from a difference map, but refined with fixed individual isotropic displacement parameters [for aromatic and methylene H atoms $U(H) =$

1.2U_{eq}(C), for methyl H atoms U(H) = 1.5U_{eq}(C)] using a riding model with C—H(methylene) = 0.99, C—H(aromatic) = 0.95 and C—H(methyl) = 0.98 Å. For each methyl group, the torsion angle H—C—O—C was refined.

Due to the negligible anomalous dispersion, the absolute structure could not be determined. The Flack (1983) absolute-structure parameter converged to x = −0.5 (1). Origin restraints were generated automatically by the program of Flack & Schwarzenbach (1988). The structure contains two nearly centrosymmetric radical anion molecules and two solvent-separated lithium countercations, each surrounded by three dimethoxyethane molecules (Fig. 3). The coordination spheres of both lithium cations differ significantly in their Li· · ·O distances, as do the torsion angles of the solvent molecules. The structure cannot be successfully refined in the centrosymmetric space group $P\bar{1}$. The reciprocal space was thoroughly but unsuccessfully scanned for reflections that might give a hint of a superstructure.

Data collection: *DIF*4 (Stoe & Cie, 1988a). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988b). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXL*93 *CIFTAB*.

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mer,*trans*-[Bis(2-diphenylphosphinoethyl)(*n*-propyl)amine-*N*,*P*,*P*']dichloro(triphenylphosphine)ruthenium(II) 0.5-Dichloromethane Solvate

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Abstract

The structure consists of discrete neutral molecules of [RuCl2(PPh3)(PNP)] [PNP = CH3CH2CH2N(CH2CH2PPh2)2] and dichloromethane solvent molecules. In the molecular structure of the complex a Ru^{II} metal centre is pseudo-octahedrally coordinated by a meridional tridentate PNP ligand, by two Cl ligands *trans* to each other, and by a triphenylphosphine ligand. The latter ligand is *trans* to the N-atom donor of the aminodiphosphine.

Comment

As part of our effort to control the chemo-, regio-, stereo- and enantioselectivity of organometallic reactions, we have recently prepared a number of transition metal complexes containing aminodiphosphine ligands of the general formula RN(CH*R'*CH2P*R''*2)2 [*R* and *R'* are (chiral) alkyl groups, *R''* is an aryl or cycloalkyl group] (Bianchini, Innocenti, Masi, Peruzzini & Zanobini, 1992; Bianchini *et al.*, 1990; Bianchini, Farnetti *et al.*, 1995). These ligands offer significant advantages over linear and tripodal polyphosphines in homogeneous catalytic reactions assisted by transition metal complexes, since the concomitant presence in the ligand framework of both hard and soft donor atoms provides easy access to coordination vacancies at the metal centre by different mechanisms.

In this paper we report the crystal structure of the title complex, *mer*,*trans*-[RuCl2(PPh3)(PNP)], (I), which represents the key compound for studying the organometallic chemistry of the (PNP)Ru^{II} sys-