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Tetra-μ-chloro-1:2κ^4*Cl*;1:3κ^4*Cl*-bis(4,4′-dimethyl-2,2′-bipyridine)-2κ^2*N*,3κ^2*N*-lithium(I)dipalladium(II) tetrakis(pentafluorophenyl)borate dichloromethane 1.196-solvate

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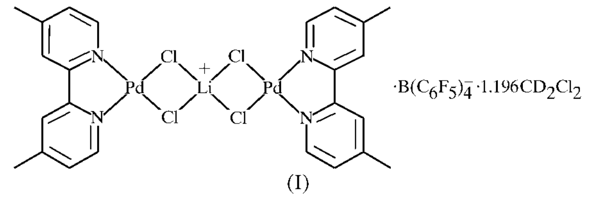
In the crystal structure of the title compound, $[LiPd_2Cl_4(C_{12}H_{12}N_2)_2](C_{24}F_{20}B)\cdot 1.196CD_2Cl_2$ or $[\{(Me_2bipy)PdCl_2\}_2(\mu\text{-}Li)]^+\cdot B(C_6F_5)_4^-\cdot 1.196CD_2Cl_2$ (Me_2bipy is 4,4′-dimethyl-2,2′-bipyridine), an Li^+ cation is stabilized by complexation with two $(Me_2bipy)PdCl_2$ units through weak Li—Cl interactions. This compound is thus a rare example of a complex that exhibits an arrested Cl^- abstraction.

Comment

The reaction of $(Me_2bipy)Pd(Me)Cl$ (Me_2bipy is 4,4′-dimethyl-2,2′-bipyridine) with $[Li(Et_2O)_{2.4}][B(C_6F_5)_4]$ (0.5 equivalents) in CD_2Cl_2 solution (296 K) quantitatively yields the dinuclear monocationic complex $[\{(Me_2bipy)PdMe\}_2(\mu\text{-}Cl)][B(C_6F_5)_4]$. The cation forms by initial Cl^- abstraction from $(Me_2bipy)Pd(Me)Cl$ to yield $[(Me_2bipy)PdMe]^+$, which is trapped by the remaining $(Me_2bipy)Pd(Me)Cl$ by Cl bridging (Shen & Jordan, 2003). LiCl is also formed. In an effort to generate the analogous $[(Me_2bipy)PdCl]^+$ and $[\{(Me_2bipy)PdCl\}_2(\mu\text{-}Cl)]^+$ cations, $(Me_2bipy)PdCl_2$ was treated with $[Li(Et_2O)_{2.4}][B(C_6F_5)_4]$ (1 equivalent) in CD_2Cl_2. Surprisingly, this reaction produced $[\{(Me_2bipy)PdCl_2\}_2(\mu\text{-}Li)]^+\cdot B(C_6F_5)_4^-$, which crystallized from the reaction mixture as a CD_2Cl_2 solvate, (I). The molecular structure of (I) has been determined by X-ray diffraction, and the results are presented here. There are no significant cation–anion or ion–solvent interactions present in the unit cell. The $[\{(Me_2bipy)PdCl_2\}_2(\mu\text{-}Li)]^+$ cation is shown in Fig. 1; the $B(C_6F_5)_4^-$ anion and CD_2Cl_2 molecules are normal and are not shown.

The cation comprises an Li^+ ion stabilized by complexation with two $(Me_2bipy)PdCl_2$ units, with each $(Me_2bipy)PdCl_2$ unit adopting a square-planar geometry. The sums of the angles about atoms Pd1 and Pd2 are 360.1 (2) and 360.0 (3)°, respectively. The Me_2bipy ligands are slightly twisted around the C5—C6 and C13—C22 bonds, such that the N1—C5—C6—N2 and N3—C13—C22—N4 angles are 2 (1) and 3 (1)°, respectively. The Pd—Cl distances [mean 2.304 (2) Å], Cl—Pd—Cl angles [mean 88.83 (7)°] and other geometric bond parameters in (I) (Table 1) are very similar to those in the neutral complex $(bipy)PdCl_2$ [Pd—Cl = 2.277 (3) and 2.317 (3) Å, and Cl—Pd—Cl = 89.89 (1)°; bipy is 2,2′-bipyridine; Canty *et al.*, 1992], which indicates that the presence of the Li^+ ion does not significantly perturb the structure of the $(Me_2bipy)PdCl_2$ units.



(I)

The geometry at the Li^+ cation is distorted tetrahedral. The Cl—Li—Cl angles associated with the four-membered $LiCl_2Pd$ rings are acute [Cl1—Li1—Cl2 = 86.8 (5)° and Cl3—Li1—Cl4 = 87.0 (5)°] and the other Cl—Li—Cl angles are correspondingly larger [115.2 (6)–133.4 (7)°]. The angle between the Li—Cl1—Cl2 and Li—Cl3—Cl4 planes is 79.04 (8)°. The Li—Cl distances are nearly equal [mean 2.35 (2) Å] and are approximately equal to the sum of the ionic radii of Li and Cl (0.60 and 1.81 Å, respectively; Huheey *et al.*, 1993). These data indicate that the Li—Cl interactions are quite weak.

There are numerous examples of $L_mMCl_2LiL'_n$ complexes (L and L' are ancillary ligands) in which the L_mMCl_2 units coordinate in a bidentate fashion to Li^+ ions *via* the Cl ligands, and many of these complexes have been structurally characterized. However, most examples contain early transition metals, *f*-block metals or anionic $[L_nMCl_2]^-$ units. Notable examples include $[(Me_3Si)_2C_5H_3]_2YbCl_2Li(THF)_2$ (THF is tetrahydrofuran; Chan *et al.*, 2000; Hitchcock *et al.*, 2000), $(C_5Me_5)(C_4H_4BN^iPr_2)ZrCl\cdot LiCl(Et_2O)_2$ (Quan *et al.*, 1994), $[Me_2N(indenyl)]_2TiCl\cdot LiCl(THF)_2$ (Greidanus *et al.*, 2001) and [2,4-bis(2,6-diisopropylphenylimido)pentanate]$FeCl_2Li(THF)_2$ (Smith *et al.*, 2001). Complex (I) is a rare example of a complex in which a neutral late-transition-metal L_2MCl_2 unit coordinates to an Li^+ ion.

Compound (I) is also a rare example of a complex that exhibits an arrested Cl^- abstraction. The more electrophilic character of $[(Me_2bipy)PdCl]^+$ compared with that of $[(Me_2bipy)PdMe]^+$ prevents complete Cl^- abstraction by Li^+.

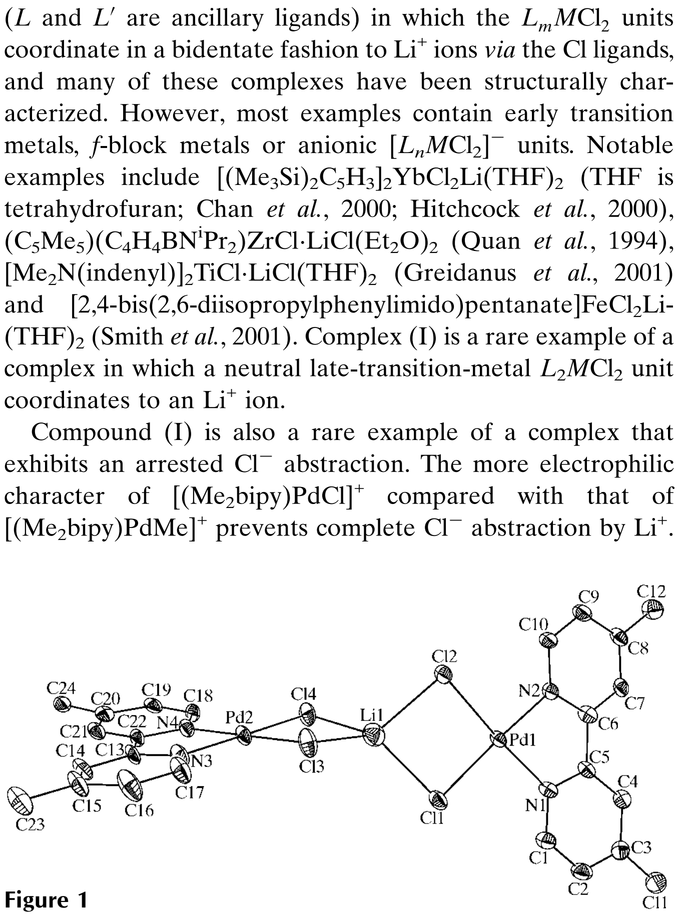


Figure 1
A view of the cation of complex (I), with displacement ellipsoids shown at the 50% probability level. H atoms have been omitted for clarity.

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Experimental

A valved NMR tube was charged with $(Me_2bipy)PdCl_2$ (5.0 mg, 0.016 mmol) and $[Li(Et_2O)_{2.4}][B(C_6F_5)_4]$ (13.5 mg, 0.016 mmol), and CD_2Cl_2 (0.5 ml) was added by vacuum transfer. The NMR tube was warmed briefly to 296 K, vigorously shaken to form a pale-yellow slurry and then heated at 333 K to form a clear pale-yellow solution. The mixture was cooled to 296 K and pale-yellow plate-shaped crystals formed overnight.

Crystal data

$[LiPd_2Cl_4(C_{12}H_{12}N_2)_2](C_{24}F_{20}B)\cdot$-
1.196CD_2Cl_2
M_r = 1513.06
Monoclinic, $P2/c$
a = 22.361 (6) Å
b = 7.939 (2) Å
c = 31.754 (9) Å
β = 98.621 (5)°
V = 5573 (3) Å^3
Z = 4

D_x = 1.806 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 27 015 reflections
θ = 1.7–25.0°
μ = 1.06 mm^{-1}
T = 100 (2) K
Plate, pale yellow
0.40 × 0.16 × 0.10 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.676, T_{max} = 0.901
27 015 measured reflections

9813 independent reflections
8967 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 25.0°
$h = -19 \rightarrow 26$
$k = -9 \rightarrow 9$
$l = -37 \rightarrow 36$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.076
$wR(F^2)$ = 0.182
S = 1.25
9813 reflections
782 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0574P)^2 + 46.4907P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.005
$\Delta\rho_{max}$ = 1.82 e Å^{-3}
$\Delta\rho_{min}$ = −1.38 e Å^{-3}

All H atoms were placed at idealized positions and were allowed to ride on their parent atoms. The CD_2Cl_2 molecules were considered to be partially occupied on the basis of their large displacement parameters. Thus the occupancies of the atoms were taken to be equal for each molecule and these values were refined as free variables. The resulting occupancies were 0.559 and 0.637. The $B(C_6F_5)_4^-$ anions lie on twofold axes and there are two half-anions in the asymmetric unit. Some elongated ellipsoids exist in the structure of this anion, which indicates that either it is thermally mobile or has slight positional disorder. However, the Li-bridged dinuclear monocation does not show elongated ellipsoids, which suggests that the elongation is a feature of the anion and not of the overall structure. Therefore, the anion was treated not as a rigid body but in the same way as the rest of the structure.

Table 1
Selected geometric parameters (Å, °).

Cl1—Pd1	2.306 (2)	Cl3—Li1	2.35 (2)
Cl2—Pd1	2.313 (2)	Cl4—Li1	2.34 (2)
Cl3—Pd2	2.292 (2)	N1—Pd1	2.004 (6)
Cl4—Pd2	2.306 (2)	N2—Pd1	2.018 (6)
Cl1—Li1	2.35 (2)	N3—Pd2	2.024 (6)
Cl2—Li1	2.35 (2)	N4—Pd2	2.010 (6)
Cl4—Li1—Cl3	87.0 (5)	N2—Pd1—Cl2	95.7 (2)
Cl2—Li1—Cl1	86.8 (5)	N3—Pd2—Cl3	94.8 (2)
N1—Pd1—N2	80.7 (2)	N4—Pd2—Cl3	175.4 (2)
N3—Pd2—N4	81.0 (3)	N4—Pd2—Cl4	95.2 (2)
N1—Pd1—Cl1	95.0 (2)	Cl1—Pd1—Cl2	88.69 (7)
N2—Pd1—Cl1	174.4 (2)	Cl3—Pd2—Cl4	88.97 (7)
N1—Pd1—Cl2	176.1 (2)		

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1023). Services for accessing these data are described at the back of the journal.

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