Cs(1)$\cdots$Cl(2^{ii})	3.479 (2)	Cs(4)$\cdots$N(2^{ix})	3.535 (6)
Cs(2)$\cdots$O(1w)	2.99 (1)	Cs(4)$\cdots$N(3^{vii})	3.569 (6)
Cs(2)$\cdots$N(1)	3.200 (7)	Cs(4)$\cdots$N(4^x)	3.544 (7)
Cs(2)$\cdots$N(2^{iii})	3.167 (7)	Cs(4)$\cdots$N(4^{vii})	3.489 (7)
Cs(2)$\cdots$Cl(1^{iii})	3.752 (2)	Cs(4)$\cdots$Cl(1)	3.643 (2)
Cs(2)$\cdots$Cl(2^{iv})	3.428 (2)	Cs(4)$\cdots$Cl(2)	3.446 (2)
Cs(2)$\cdots$Cl(2^v)	3.428 (2)	Cs(4)$\cdots$Cl(2^{xi})	3.499 (2)
Cs(3)$\cdots$O(1w^{vi})	3.35 (1)	O(1w)$\cdots$N(4^i)	2.73 (1)*
Cs(3)$\cdots$N(2)	3.607 (5)	Cl(1)$\cdots$O(1w^{xii})	3.10 (1)*
Cs(3)$\cdots$N(3)	3.321 (5)		

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}-z$; (ii) $x, \frac{1}{2}-y, z$; (iii) $x, y, z-1$; (iv) $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$; (v) $\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$; (vi) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (vii) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (viii) $-x, 1-y, -z$; (ix) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; (x) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (xi) $1-x, 1-y, -z$; (xii) $x, y, 1+z$.

* Possible hydrogen bonds

The systematic absences ($0kl$, $k+l = 2n+1$; $hk0$, $h = 2n+1$) were consistent with space groups $Pn2_1a$ (No. 33) and $Pnma$ (No. 62); the latter was chosen on the basis of the statistical analysis of intensity distribution and confirmed by refinement. The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1990). A Fourier difference map calculated after all Cs, Cl, Fe, N and C atoms were located and refined showed a residual electron density peak of $3.7\,e\,\text{Å}^{-3}$, which was assigned to a water molecule of solvation. This O atom was refined isotropically, with an occupancy of 0.5 (see *Comment*). No satisfactory positions for the corresponding H atoms could be found.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993a). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993b). Program(s) used to solve structure: *SHELXS*86. Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Aquabis(2,2'-bipyridine)chloromanaganese(II) Perchlorate

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Abstract

The crystal structure of the title compound, $[MnCl(C_{10}H_8N_2)_2(H_2O)]ClO_4$, contains monomeric $[Mn(bpy)_2Cl(H_2O)]^+$ cations in which the Mn^{II} ion is surrounded by a pair of chelating bpy ligands (bpy = 2,2'-bipyridine) [Mn—N 2.235 (3)–2.291 (3) Å], an aqua ligand [Mn—O 2.167 (3) Å] and a chloro ligand [Mn—Cl 2.447 (1) Å] in a distorted octahedral environment. Adjacent cations are linked into dimers by pairs of Cl$\cdots$O hydrogen bonds [Cl$\cdots$O 3.137 (3) Å].

Comment

Manganese complexes have attracted considerable interest recently because of the frequent occurrence of such metal centers in biological systems (Wieghardt,

1989). Recently we have characterized an unusual dinuclear Mn^{II} complex bridged by a single carboxylato-O,O' group of betaine (bet, Me$_3$N$^+$CH$_2$CO$_2^-$), [Mn$_2$(bpy)$_4$(bet)(H$_2$O)$_2$](ClO$_4$)$_4$.2H$_2$O (bpy = 2,2'-bipyridine) (Chen & Mak, 1993). In our attempt to isolate an analogous Mn^{II} complex using pyridinioacetate (C$_5$H$_5$N$^+$CH$_2$CO$_2^-$) we obtained the monomeric Mn^{II} complex [Mn(bpy)$_2$Cl(H$_2$O)]ClO$_4$, (I).

(I)
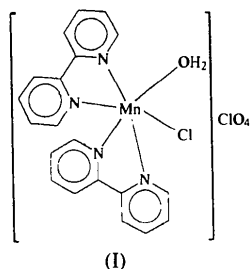
The crystal structure of the title compound consists of discrete [Mn(bpy)$_2$Cl(H$_2$O)]$^+$ cations and perchlorate anions. As illustrated in Fig. 1, the Mn^{II} ion in each cation is in a distorted octahedral environment, coordinated by a pair of cis-related chealting bpy ligands, one aqua ligand and one chloro ligand. The structure of the cation is analogous to those of [Mn(bpy)$_2$Cl$_2$] (Lumme & Lindell, 1988) and [Mn(bpy)$_2$(NCS)$_2$] (Veidis, Dockum, Charron, Reiff & Brennan, 1981), in which pairs of bpy ligands are also cis related, but is markedly different from those of some other [M(bpy)$_2$L$_2$]$^{n+}$ species, such as [Ru(bpy)$_2$(MeCN)$_2$]$^{2+}$ (Cordes, Durham, Pennington, Kurtz & Allen, 1992) and [Ru(bpy)$_2$(H$_2$O)(OH)]$^+$ (Endres, Keller, Moroni, Nöthe & Dong, 1978), in which the two bpy ligands are trans related. In the coordination sphere of the title complex, the most distorted angle of the octahedron is N(1)—Mn(1)—N(1) [71.8 (1)°], which results from the constraints imposed by the chelating bpy ligand. The Mn—N bonds have lengths ranging from 2.235 (3) to 2.291 (3) Å, while the Mn—O bond has a length of 2.167 (3) Å and the Mn—Cl bond has a length of 2.447 (1) Å. The shortest Mn—N bond, Mn(1)—N(3) [2.235 (3) Å], and the longest bond, Mn(1)—N(1) [2.291 (3) Å], are trans to the Mn—O and Mn(1)—Cl bonds, respectively. This fact demonstrates clearly that the negatively charged chloro ligand has a greater trans effect than the neutral aqua ligand. Similarly, the Mn—N bonds trans to the Cl$^-$ or NCS$^-$ ligands are significantly longer than the remaining Mn—N bonds in the analogous chloride (Lumme & Lindell, 1988) and isothiocyanate complexes (Veidis et al., 1981), by about 0.08 and 0.03 Å, respectively.

Hydrogen bonding plays an important role in consolidating the crystal structure. Each pair of adjacent [Mn(bpy)$_2$Cl(H$_2$O)]$^+$ cations related by an inversion center are linked by a pair of intermolecular hydrogen bonds between the aqua and chloro ligands, resulting

in a dimeric structure. The hydrogen-bond distance O(1)···Cl(1^i) of 3.137 (3) Å is comparable to those found for the O···Cl hydrogen bonds of 3.07–3.29 Å in several other compounds (Chen & Mak, 1990a,b, 1991) [symmetry code: (i) $-x$, $1 - y$, $-z$].
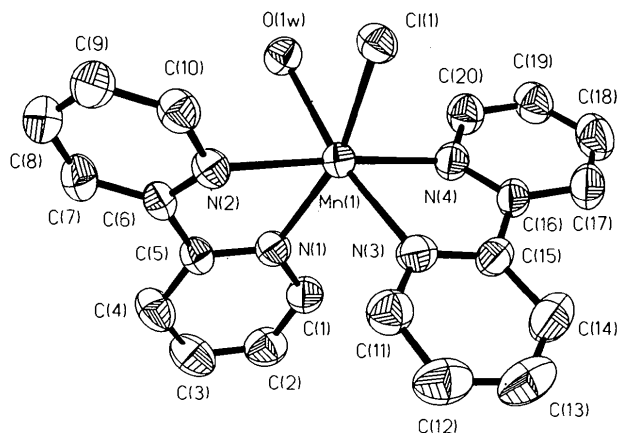

Fig. 1. A perspective view showing the structure of the [Mn(bpy)$_2$Cl(H$_2$O)]$^+$ cation and the atom-numbering scheme, drawn using ORTEP (Johnson, 1965). Displacement ellipsoids are shown at the 50% probability level.

Experimental

A mixture of MnCl$_2$.4H$_2$O (0.4 g, 2.0 mmol) and bpy (0.31 g, 2.0 mmol) was dissolved in warm distilled water (10 ml, 333 K). To the yellowish solution, pyridinioacetate (0.270 g, 2.0 mmol) (Chen & Mak, 1991) was added and the solution was stirred for 15 min. After addition of an aqueous solution (2 ml) of sodium perchlorate (0.3 g), the resulting solution was allowed to stand in air overnight and a yellow precipitate was deposited. Recrystallization of the raw product yielded the title complex (0.37 g). FT-IR data (cm^{-1}): 3200–3600 (w, br), 3103 (w), 3059 (m), 3028 (w), 1637 (w), 1596 (vs), 1565 (s), 1475 (s), 1438 (vs), 1316 (s), 1156 (s), 1110 (s), 1053 (s), 1013 (s), 906 (w), 772 (vs), 735 (s), 649 (s), 625 (m), 414 (m).

Crystal data

[MnCl(C$_{10}$H$_8$N$_2$)$_2$(H$_2$O)]- ClO$_4$	Mo $K\alpha$ radiation
M_r = 520.23	λ = 0.71073 Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
a = 8.903 (2) Å	θ = 10.5–14°
b = 9.594 (2) Å	μ = 0.843 mm^{-1}
c = 14.175 (3) Å	T = 302 K
α = 79.15 (2)°	Polyhedral
β = 84.86 (1)°	0.42 × 0.34 × 0.18 mm
γ = 76.05 (3)°	Yellow
V = 1152.8 (4) Å^3	
Z = 2	
D_x = 1.499 Mg m^{-3}	

Data collection

Siemens P4 diffractometer	$\theta_{max} = 25°$
ω scans	$h = 0 \rightarrow 10$
Absorption correction:	$k = -10 \rightarrow 11$
empirical	$l = -17 \rightarrow 18$
$T_{min} = 0.790$, $T_{max} = 0.947$	2 standard reflections monitored every 125 reflections
4098 measured reflections	
4098 independent reflections	intensity decay: 1.1%
2998 observed reflections $[I > 2\sigma(I)]$	

Refinement

Refinement on F	$w = 1/[\sigma^2(F_o) + 0.002|F_o|^2]$
$R = 0.0486$	$(\Delta/\sigma)_{max} = 0.002$
$wR = 0.0688$	$\Delta\rho_{max} = 0.79$ e Å^{-3}
$S = 1.18$	$\Delta\rho_{min} = -0.51$ e Å^{-3}
2998 reflections	Atomic scattering factors
285 parameters	from *International Tables*
H-atom parameters not refined	*for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

U_{iso} for O(1) to O(4′), $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* a_i.a_j$ for all others.

	x	y	z	U_{iso}/U_{eq}
Mn(1)	0.03061 (7)	0.26577 (6)	0.17750 (4)	0.0419 (2)
Cl(1)	0.1904 (1)	0.3214 (1)	0.0320 (1)	0.052 (1)
O(1W)	−0.0892 (3)	0.4927 (3)	0.1685 (2)	0.062 (1)
N(1)	−0.0710 (4)	0.2216 (4)	0.3316 (2)	0.061 (1)
N(2)	0.1989 (4)	0.2963 (3)	0.2787 (2)	0.056 (1)
C(1)	−0.1962 (5)	0.1665 (5)	0.3548 (3)	0.083 (1)
C(2)	−0.2570 (5)	0.1438 (5)	0.4495 (4)	0.110 (1)
C(3)	−0.1817 (6)	0.1811 (6)	0.5177 (4)	0.135 (1)
C(4)	−0.0518 (5)	0.2316 (6)	0.4961 (3)	0.109 (1)
C(5)	0.0037 (5)	0.2536 (4)	0.4001 (3)	0.070 (1)
C(6)	0.1455 (5)	0.3056 (4)	0.3685 (3)	0.065 (1)
C(7)	0.2233 (5)	0.3619 (5)	0.4290 (3)	0.100 (1)
C(8)	0.3546 (5)	0.4076 (5)	0.3948 (4)	0.108 (1)
C(9)	0.4120 (5)	0.3939 (5)	0.3041 (4)	0.086 (1)
C(10)	0.3298 (4)	0.3386 (4)	0.2481 (3)	0.070 (1)
N(3)	0.0858 (3)	0.0260 (3)	0.1770 (2)	0.044 (1)
N(4)	−0.1671 (3)	0.2191 (3)	0.1086 (2)	0.044 (1)
C(11)	0.2136 (4)	−0.0670 (4)	0.2123 (3)	0.055 (1)
C(12)	0.2428 (4)	−0.2138 (4)	0.2148 (3)	0.067 (1)
C(13)	0.1357 (5)	−0.2685 (4)	0.1772 (4)	0.075 (1)
C(14)	0.0055 (4)	−0.1738 (4)	0.1388 (4)	0.060 (1)
C(15)	−0.0182 (4)	−0.0284 (3)	0.1402 (3)	0.041 (1)
C(16)	−0.1567 (4)	0.0801 (3)	0.1000 (3)	0.041 (1)
C(17)	−0.2682 (4)	0.0410 (4)	0.0543 (3)	0.060 (1)
C(18)	−0.3921 (4)	0.1480 (4)	0.0175 (3)	0.071 (1)
C(19)	−0.4020 (4)	0.2881 (4)	0.0268 (3)	0.069 (1)
C(20)	−0.2899 (4)	0.3207 (4)	0.0721 (3)	0.058 (1)
Cl(2)	0.6553 (2)	0.7406 (2)	0.3107 (1)	0.079 (1)
O(1)†	0.5216 (5)	0.7597 (6)	0.3708 (4)	0.093 (1)
O(2)†	0.7440 (6)	0.8342 (6)	0.3342 (5)	0.122 (1)
O(3)†	0.7527 (6)	0.5996 (5)	0.3354 (5)	0.117 (1)
O(4)†	0.6221 (6)	0.7871 (5)	0.2127 (4)	0.082 (1)
O(1′)†	0.8090 (5)	0.6647 (6)	0.3305 (5)	0.100 (1)
O(2′)†	0.6332 (6)	0.7076 (6)	0.2186 (4)	0.108 (1)
O(3′)†	0.6272 (7)	0.8880 (6)	0.3144 (6)	0.235 (1)
O(4′)†	0.5483 (6)	0.6736 (6)	0.3738 (4)	0.103 (1)

† Site occupancy = 0.5.

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

Mn(1)—Cl(1)	2.447 (1)	Mn(1)—O(1W)	2.167 (3)
Mn(1)—N(1)	2.291 (3)	Mn(1)—N(2)	2.268 (4)
Mn(1)—N(3)	2.235 (3)	Mn(1)—N(4)	2.259 (3)

N(1)—C(1)	1.335 (6)	N(1)—C(5)	1.344 (6)
N(2)—C(6)	1.330 (5)	N(2)—C(10)	1.336 (5)
C(1)—C(2)	1.400 (7)	C(2)—C(3)	1.370 (8)
C(3)—C(4)	1.348 (8)	C(4)—C(5)	1.402 (6)
C(5)—C(6)	1.469 (6)	C(6)—C(7)	1.402 (7)
C(7)—C(8)	1.363 (7)	C(8)—C(9)	1.359 (7)
C(9)—C(10)	1.377 (7)	N(3)—C(11)	1.336 (4)
N(3)—C(5)	1.350 (5)	N(4)—C(16)	1.342 (5)
N(4)—C(20)	1.346 (4)	C(11)—C(12)	1.364 (5)
C(12)—C(13)	1.380 (7)	C(13)—C(14)	1.373 (5)
C(14)—C(15)	1.364 (5)	C(15)—C(16)	1.488 (4)
C(16)—C(17)	1.390 (6)	C(17)—C(18)	1.378 (5)
C(18)—C(19)	1.355 (6)	C(19)—C(20)	1.360 (6)
		O(1W)···Cl(1ⁱ)	3.137 (3)
		O(1W)···O(3ⁱⁱ)	2.872 (3)
		O(1W)···O(1′ⁱⁱ)	3.025 (3)
Cl(1)—Mn(1)—O(1W)	91.7 (1)	Cl(1)—Mn(1)—N(1)	166.4 (1)
O(1W)—Mn(1)—N(1)	88.8 (1)	Cl(1)—Mn(1)—N(2)	94.6 (1)
O(1W)—Mn(1)—N(2)	90.1 (1)	N(1)—Mn(1)—N(2)	71.8 (1)
Cl(1)—Mn(1)—N(3)	94.6 (1)	O(1W)—Mn(1)—N(3)	163.2 (1)
N(1)—Mn(1)—N(3)	88.7 (1)	N(2)—Mn(1)—N(3)	104.9 (1)
Cl(1)—Mn(1)—N(4)	98.7 (1)	O(1W)—Mn(1)—N(4)	90.7 (1)
N(1)—Mn(1)—N(4)	94.9 (1)	N(2)—Mn(1)—N(4)	166.7 (1)
N(3)—Mn(1)—N(4)	73.0 (1)	Mn(1)—N(1)—C(1)	123.6 (3)
Mn(1)—N(1)—C(5)	116.1 (3)	C(1)—N(1)—C(5)	120.3 (4)
Mn(1)—N(2)—C(6)	116.5 (3)	Mn(1)—N(2)—C(10)	123.0 (3)
C(6)—N(2)—C(10)	118.6 (4)	N(1)—C(1)—C(2)	122.0 (5)
C(1)—C(2)—C(3)	116.6 (5)	C(2)—C(3)—C(4)	122.1 (5)
C(3)—C(4)—C(5)	119.0 (5)	N(1)—C(5)—C(4)	119.8 (4)
N(1)—C(5)—C(6)	116.5 (3)	C(4)—C(5)—C(6)	123.7 (4)
N(2)—C(6)—C(5)	116.7 (4)	N(2)—C(6)—C(7)	120.6 (4)
C(5)—C(6)—C(7)	122.7 (4)	C(6)—C(7)—C(8)	119.4 (5)
C(7)—C(8)—C(9)	120.1 (5)	C(8)—C(9)—C(10)	117.7 (4)
N(2)—C(10)—C(9)	123.5 (4)	Mn(1)—N(3)—C(11)	124.1 (3)
Mn(1)—N(3)—C(15)	117.7 (2)	C(11)—N(3)—C(15)	118.1 (3)
Mn(1)—N(4)—C(16)	117.0 (2)	Mn(1)—N(4)—C(20)	124.9 (3)
C(16)—N(4)—C(20)	118.0 (3)	N(3)—C(11)—C(12)	123.4 (4)
C(11)—C(12)—C(13)	118.1 (3)	C(12)—C(13)—C(14)	119.1 (4)
C(13)—C(14)—C(15)	119.9 (4)	N(3)—C(15)—C(14)	121.4 (3)
N(3)—C(15)—C(16)	115.9 (3)	C(14)—C(15)—C(16)	122.7 (4)
N(4)—C(16)—C(15)	116.3 (3)	N(4)—C(16)—C(17)	121.5 (3)
C(15)—C(16)—C(17)	122.2 (3)	C(16)—C(17)—C(18)	118.8 (4)
C(17)—C(18)—C(19)	119.4 (4)	C(18)—C(19)—C(20)	119.6 (3)
N(4)—C(20)—C(19)	122.7 (4)	O(1W)—H(1WA)···Cl(1ⁱ)	177.6 (4)
		O(1W)—H(1WB)···O(3ⁱⁱ)	152.8 (4)
		O(1W)—H(1WB)···O(1′ⁱⁱ)	142.2 (4)

Symmetry codes: (i) $-x, 1 - y, -z$; (ii) $x - 1, y, z$.

All calculations were carried out using the *SHELXTL/PC* program package (Sheldrick, 1990). Refinement was by full-matrix least-squares methods.

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[Ru(η^5-C$_5$H$_5$)(η^4-C$_5$H$_4$O){As(CH$_3$)$_3$}]PF$_6$ and [Ru(η^5-C$_5$H$_5$)(η^4-C$_5$H$_4$O)-{As(C$_6$H$_5$)$_3$}]PF$_6$

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Abstract

As part of studies on the syntheses and chemical reactions of ruthenium η^5-cyclopentadienyl-η^4-cyclopentadienone complexes, the crystal structures of the two title compounds, (η^4-cyclopentadienone)(η^5-cyclopentadienyl)(trimethylarsine)ruthenium hexafluorophosphate and (η^4-cyclopentadienone)(η^5-cyclopentadienyl)(triphenylarsine)ruthenium hexafluorophosphate, have been determined from single-crystal X-ray diffraction data. The metal complexes of the two title compounds are both of a bent-sandwich type, but differ somewhat in conformation. The cyclopentadienone moieties of both compounds are distinctly puckered at the C(2) and C(4) atoms, and the C=O groups are bent away from the Ru atom. Ru—C bond lengths vary from 2.137 (4) to 2.248 (4) Å in (I), and from 2.159 (4) to 2.271 (4) Å in (II). Ru—As bond lengths are 2.491 (1) Å in (I) and 2.512 (1) Å in (II).

Comment

Cyclopentadienone in the free state is a highly unstable molecule which dimerizes rapidly but can be stabilized by coordination with transition metals. The accessibility of such complexes is limited, however, since they can be obtained only *via* reactions on certain precursor complexes. The syntheses and reactions of two Ru complexes containing unsubstituted cyclopentadienyl (CP) and cyclopentadienone (CPD), [Ru(η^5-C$_5$H$_5$)(η^4-C$_5$H$_4$O)]$_2$(PF$_6$)$_2$ (Kirchner & Taube, 1991) and [Ru(η^5-C$_5$H$_5$)(η^4-C$_5$H$_4$O)(CH$_3$CN)]PF$_6$ (Kirchner, Taube, Scott & Willett, 1993), have been described recently. It was shown that these complexes react with various nucleophiles by substitution on either the metal centre, the CP or the CDP ligand, thus yielding a range of new complexes. While the nucleophiles P(CH$_3$)$_3$ and P(C$_6$H$_5$)$_3$ were found to attack the two complexes by substitution on the CP or CPD ligands (Kirchner, Mereiter, Schmid & Taube, 1993), the corresponding arsines displayed ligand substitution on the metal centre.

A view of the metal complex (I) is shown in Fig. 1. The two C$_5$ rings adopt a staggered conformation in which the cyclopentadienone molecule is oriented so that its C=O group is almost coplanar with the Ru—As bond, as can be seen from the dihedral angle As—Ru—C(6)—O of 0.7 (4)°. This and the specific orientation of the As(CH$_3$)$_3$ ligand cause complex (I) to have nearly mirror symmetry, where Ru, As, C(3), C(6), O and C(11) are approximately in the same plane (0.037 Å r.m.s. deviation of these atoms from the corresponding least-squares plane), while the remaining atoms of the complex lie on either side. In comparison with (I), the triphenylarsine compound (II) (Tables 3 and 4) is less symmetric. Here, the configuration of the two C$_5$ rings lies between staggered and eclipsed, and the bulky As(C$_6$H$_5$)$_3$ group is rotated by *ca* 30° about the Ru—As bond in comparison to the As(CH$_3$)$_3$ group (Fig. 1).

(I) L = AsMe$_3$
(II) L = AsPh$_3$
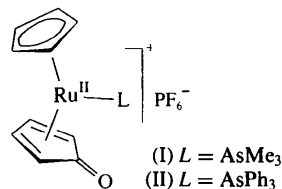
Bond lengths and angles of the Ru complexes in (I) and (II) are similar and agree with the values observed in the related compounds Ru(CP)(CPD)Br, [Ru(CP)(CPD)(CH$_3$CN)]PF$_6$ and [Ru(CP)(CPD){P-(OC$_6$H$_5$)$_3$}]PF$_6$ (Smith, Kwan, Taube, Bino & Cohen, 1984; Kirchner, Mereiter, Schmid & Taube, 1993; Kirchner, Taube, Scott & Willett, 1993). Selected mean bond lengths for (I) and (II), respectively, are: ⟨Ru—C$_{CP}$⟩ 2.203 (3), 2.203 (5) Å; ⟨Ru—C$_{CPD}$⟩ 2.194 (4), 2.214 (4) Å; ⟨C—C⟩$_{CP}$ 1.410 (5), 1.397 (8) Å; ⟨C—C⟩$_{CPD}$ = 1.429 (6), 1.431 (6) Å. The CPD molecules of both compounds display typical behaviour: in their butadiene part [C(7)–C(10)] they exhibit a short–long–short pattern of C—C bond lengths with overall mean values of 1.395 (6) Å (short) and 1.415 (7) Å (long); the CPD molecules are distinctly puckered at the atoms