

C(17)	0.4845 (2)	-0.2234 (2)	0.2472 (1)	0.060 (1)
C(18)	0.3793 (3)	-0.1903 (2)	0.2331 (1)	0.064 (1)
C(19)	0.3389 (2)	-0.1210 (2)	0.2574 (1)	0.055 (1)
C(20)	0.4079 (2)	-0.0838 (1)	0.2966 (1)	0.041 (1)

Table 2. Selected geometric parameters (Å, °)

Ni—N(1)	2.045 (2)	Ni—N(6)	2.051 (2)
Ni—N(4)	2.060 (2)	Ni—N(3)	2.142 (2)
Ni—O(1)	2.191 (2)	Ni—O(2)	2.200 (2)
N(1)—C(7)	1.329 (3)	N(1)—C(1)	1.401 (3)
C(1)—C(2)	1.390 (4)	C(1)—C(6)	1.393 (3)
C(2)—C(3)	1.377 (4)	C(3)—C(4)	1.390 (4)
C(4)—C(5)	1.366 (4)	C(5)—C(6)	1.382 (4)
C(6)—N(2)	1.378 (3)	N(2)—C(7)	1.343 (3)
C(7)—C(8)	1.483 (4)	C(8)—C(9)	1.517 (4)
C(9)—N(3)	1.485 (3)	N(3)—C(10)	1.477 (3)
C(10)—C(11)	1.498 (4)	C(11)—N(4)	1.477 (3)
N(4)—C(12)	1.470 (3)	C(12)—C(13)	1.514 (3)
C(13)—C(14)	1.488 (3)	C(14)—N(6)	1.329 (3)
C(14)—N(5)	1.337 (3)	C(15)—N(5)	1.377 (3)
C(15)—C(16)	1.384 (3)	C(15)—C(20)	1.396 (3)
C(16)—C(17)	1.364 (4)	C(17)—C(18)	1.393 (4)
C(18)—C(19)	1.373 (4)	C(19)—C(20)	1.389 (3)
C(20)—N(6)	1.401 (3)	N(7)—O(3)	1.221 (3)
N(7)—O(1)	1.263 (3)	N(7)—O(2)	1.269 (3)
N(8)—O(4)	1.223 (3)	N(8)—O(5)	1.229 (3)
N(8)—O(6)	1.258 (3)		
N(1)—Ni—N(6)	95.71 (8)	N(3)—C(9)—C(8)	112.0 (2)
N(6)—Ni—N(4)	92.63 (8)	C(10)—N(3)—Ni	106.5 (2)
N(6)—Ni—N(3)	174.33 (8)	N(3)—C(10)—C(11)	110.2 (2)
N(1)—Ni—O(1)	159.98 (7)	N(4)—C(11)—C(10)	108.4 (2)
N(4)—Ni—O(1)	93.34 (7)	C(12)—N(4)—Ni	115.8 (2)
N(1)—Ni—O(2)	101.85 (8)	N(4)—C(12)—C(13)	111.9 (2)
N(4)—Ni—O(2)	150.51 (7)	N(6)—C(14)—N(5)	112.1 (2)
O(1)—Ni—O(2)	58.59 (6)	N(5)—C(14)—C(13)	121.3 (2)
C(7)—N(1)—Ni	119.4 (2)	N(5)—C(15)—C(20)	105.2 (2)
C(2)—C(1)—C(6)	119.9 (2)	C(14)—N(5)—C(15)	108.6 (2)
C(6)—C(1)—N(1)	108.7 (2)	C(16)—C(17)—C(18)	121.3 (3)
C(2)—C(3)—C(4)	121.8 (3)	C(18)—C(19)—C(20)	117.4 (3)
C(4)—C(5)—C(6)	117.4 (3)	C(19)—C(20)—N(6)	131.0 (2)
N(2)—C(6)—C(1)	105.7 (2)	C(14)—N(6)—C(20)	105.3 (2)
C(7)—N(2)—C(6)	108.1 (2)	C(20)—N(6)—Ni	129.6 (2)
N(1)—C(7)—C(8)	124.6 (2)	O(3)—N(7)—O(2)	122.2 (2)
C(7)—C(8)—C(9)	110.8 (2)	N(7)—O(1)—Ni	92.8 (1)
C(10)—N(3)—C(9)	112.2 (2)	O(4)—N(8)—O(5)	121.0 (3)
C(9)—N(3)—Ni	121.0 (2)	O(5)—N(8)—O(6)	118.8 (2)
N(1)—Ni—N(4)	105.08 (8)	C(12)—N(4)—C(11)	111.6 (2)
N(1)—Ni—N(3)	89.34 (8)	C(11)—N(4)—Ni	104.6 (2)
N(4)—Ni—N(3)	83.52 (8)	C(14)—C(13)—C(12)	113.9 (2)
N(6)—Ni—O(1)	91.14 (7)	N(6)—C(14)—C(13)	126.6 (2)
N(3)—Ni—O(1)	84.94 (7)	N(5)—C(15)—C(16)	132.7 (2)
N(6)—Ni—O(2)	96.45 (7)	C(16)—C(15)—C(20)	122.1 (2)
N(3)—Ni—O(2)	85.01 (7)	C(17)—C(16)—C(15)	117.2 (3)
C(7)—N(1)—C(1)	105.5 (2)	C(19)—C(18)—C(17)	122.0 (3)
C(1)—N(1)—Ni	134.8 (2)	C(19)—C(20)—C(15)	120.0 (2)
C(2)—C(1)—N(1)	131.4 (2)	C(15)—C(20)—N(6)	108.9 (2)
C(3)—C(2)—C(1)	117.6 (3)	C(14)—N(6)—Ni	124.5 (2)
C(5)—C(4)—C(3)	121.1 (3)	O(3)—N(7)—O(1)	121.6 (3)
N(2)—C(6)—C(5)	132.1 (3)	O(1)—N(7)—O(2)	116.1 (2)
C(5)—C(6)—C(1)	122.2 (3)	N(7)—O(2)—Ni	92.3 (1)
N(1)—C(7)—N(2)	112.0 (2)	O(4)—N(8)—O(6)	120.2 (2)
N(2)—C(7)—C(8)	123.3 (2)		

The H atoms of the CH and CH₂ groups were allowed to ride on their C atoms and were refined. The H atoms bonded to N atoms were located on a difference Fourier map at an advanced stage of anisotropic refinement and their coordinates refined.

Data collection: *SHELXTL-Plus* (Sheldrick, 1990). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Structure solution: *SHELXTL-Plus*. Structure refinement: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Preparation of material for publication: *SHELXTL-Plus* and *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1132). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Allyl)palladium(II) Complexes with Chiral Ligands. I. (Allyl)palladium(II) Complexes with Methylenebis(oxazoline) Ligands

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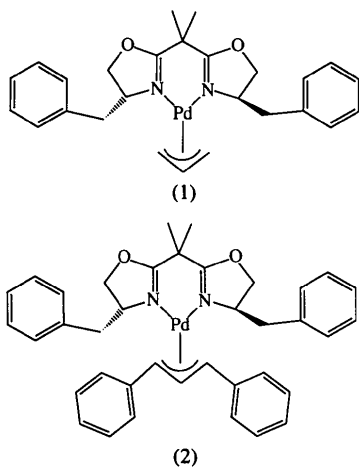
Abstract

The structures of two (allyl)palladium(II) bis(oxazoline) complexes containing (*R,R*)-2,2'-(1-methylethylidene)-bis(4-benzyl-4,5-dihydrooxazole) as a chiral ligand are

reported; $\{(\eta^3\text{-allyl})[(R,R)\text{-}2,2'\text{-}(1\text{-methyleneethylidene})\text{bis}(4\text{-benzyl-}4,5\text{-dihydrooxazole})]\text{palladium(II)}\}$ hexafluorophosphate, [Pd(C₂₃H₂₆N₂O₂)(C₃H₅)]PF₆, and [(R,R)-2,2'-(1-methyleneethylidene)bis(4-benzyl-4,5-dihydrooxazole)] $\{[\eta^3\text{-}(1,3\text{-diphenylallyl})]\text{palladium(II)}\}$ hexafluorophosphate, [Pd(C₂₃H₂₆N₂O₂)(C₁₅H₁₃)]PF₆. Complexes of this type are of interest as enantioselective catalysts for allylic substitution reactions. The structural data suggest a possible mechanism for the observed enantioselectivity of these catalysts.

Comment

Palladium complexes with chiral bis(oxazoline) and azasemicorin ligands have been found to be efficient catalysts for allylic substitution reactions (Leutenegger, Umbricht, Fahrni, von Matt & Pfaltz, 1992; Pfaltz, 1993). In the reaction of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate as nucleophile, enantiomeric excesses as high as 97% have been obtained. Here, we report the crystal structures of two (allyl)palladium(II) bis(oxazoline) complexes, (1) and (2), containing (R,R)-2,2'-(1-methyleneethylidene)bis(4-benzyl-4,5-dihydrooxazole) as a chiral ligand.



Compound (1), with an unsubstituted allyl ligand, shows the expected square-planar coordination geometry of the [PdC₂N₂] core and an almost planar conformation of the methylenebis(oxazoline) ligand framework. The structure of the corresponding 1,3-diphenylallyl complex, (2), which is postulated as an intermediate in the aforementioned allylic substitution reaction, is strikingly different. As a consequence of the steric repulsion between one of the allylic phenyl groups and the adjacent benzyl group at the oxazoline ring, the bis(oxazoline) ligand adopts a strongly distorted non-planar conformation. The deformation caused by the repulsive interaction between the chiral ligand and one of the allylic phenyl groups is also reflected in the bond lengths and bond angles of the [PdC₂N₂] core. One of the Pd—C bonds is significantly lengthened and its angle with the

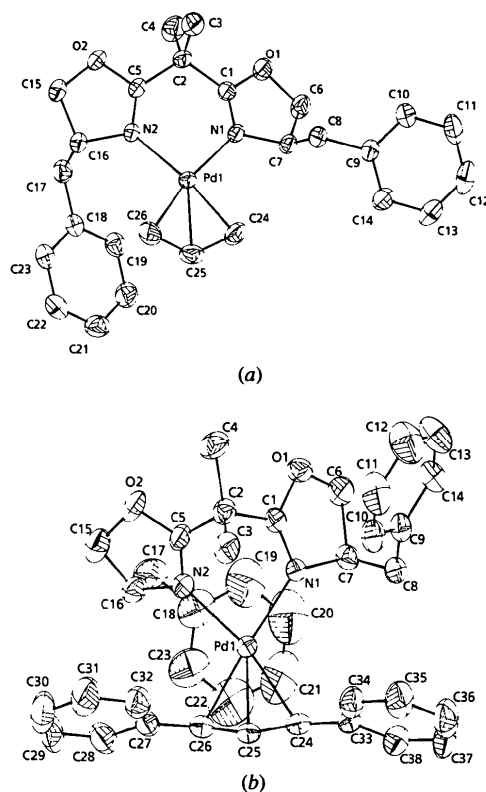


Fig. 1. View of the two bis(oxazoline) complexes of (a) compound (1) and (b) compound (2), showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level.

adjacent Pd—N bond is widened to 108°. (2) selectively reacts with dimethyl malonate at the allyl terminus that forms the longer bond to Pd (Pfaltz, 1993). This indicates that the release of strain associated with the cleavage of this bond may be one of the factors responsible for the observed selectivity in allylic nucleophilic substitution reactions.

Experimental

Compound (1)

Crystal data

[Pd(C₂₃H₂₆N₂O₂)(C₃H₅)]-PF₆

M_r = 654.91

Triclinic

*P*1

a = 9.1706 (41) Å

b = 9.3871 (73) Å

c = 9.5577 (27) Å

α = 112.988 (57)°

β = 113.552 (22)°

γ = 93.402 (51)°

V = 671.34 (78) Å³

Z = 1

D_x = 1.620 Mg m⁻³

D_m = 1.62 Mg m⁻³

D_m measured by flotation

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 25

reflections

θ = 2–28°

μ = 0.8063 mm⁻¹

T = 250 K

Prism

0.4 × 0.2 × 0.2 mm

Yellow

Data collection

Four-circle Enraf–Nonius
CAD-4 diffractometer
equipped with Oxford
Cryostream cooling
device
 $\theta/2\theta$ scans
Absorption correction:
refined from ΔF
(DIFABS; Walker &
Stuart, 1983)
 $T_{\min} = 0.93$, $T_{\max} = 1.00$
3424 measured reflections
3418 independent reflections

3418 observed reflections
[$F > 3.0\sigma(F)$]
 $R_{\text{int}} = 0$ (six independent
reflections were rejected
by the data reduction
process)
 $\theta_{\max} = 28^\circ$
 $h = -12 \rightarrow 12$
 $k = -12 \rightarrow 12$
 $l = 0 \rightarrow 12$
4 standard reflections
frequency: 60 min
intensity decay: 0.4%

Refinement

Refinement on F
 $R = 0.0176$
 $wR = 0.0206$
 $S = 1.0996$
3418 reflections
385 parameters
Only coordinates of allyl H
atoms refined, remaining
H-atom parameters not
refined
Chebychev weighting
(Carruthers & Watkin,
1979)
 $(\Delta/\sigma)_{\max} = 0.04$

$\Delta\rho_{\max} = 0.68 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.45 \text{ e } \text{\AA}^{-3}$
Extinction correction:
Larson (1970)
Extinction coefficient: 30 (3)
Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV, Table
2.2B)
Absolute configuration:
known from the chosen
educts; additionally
determined by refining
the enantiopole parameter

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (1)

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

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Pd1	0.5001 (3)	0.4958 (3)	0.5007 (3)	0.02460 (3)
N1	0.5202 (4)	0.5148 (4)	0.7317 (4)	0.0260 (4)
N2	0.4122 (4)	0.2476 (4)	0.3987 (4)	0.0265 (4)
O1	0.5007 (4)	0.4414 (4)	0.9197 (4)	0.0351 (4)
O2	0.3937 (4)	0.0108 (4)	0.3985 (4)	0.0374 (4)
C1	0.5010 (4)	0.4015 (4)	0.7683 (4)	0.0287 (4)
C2	0.4911 (4)	0.2279 (4)	0.6739 (4)	0.0289 (7)
C3	0.3779 (5)	0.1254 (5)	0.7003 (5)	0.0433 (4)
C4	0.6675 (5)	0.2081 (5)	0.7491 (5)	0.0447 (4)
C5	0.4316 (4)	0.1707 (4)	0.4855 (4)	0.0291 (4)
C6	0.4975 (5)	0.6085 (4)	0.9846 (4)	0.0360 (6)
C7	0.5535 (4)	0.6669 (4)	0.8821 (4)	0.0285 (4)
C8	0.7356 (4)	0.7520 (4)	0.9783 (4)	0.0329 (4)
C9	0.7703 (4)	0.9116 (4)	1.1251 (4)	0.0330 (4)
C10	0.8406 (5)	0.9341 (5)	1.2921 (4)	0.0455 (5)
C11	0.8667 (6)	1.0816 (5)	1.4254 (5)	0.0544 (7)
C12	0.8255 (6)	1.2064 (5)	1.3906 (5)	0.0520 (7)
C13	0.7545 (6)	1.1845 (5)	1.2260 (6)	0.0493 (7)
C14	0.7281 (5)	1.0392 (4)	1.0940 (5)	0.0414 (4)
C15	0.3629 (5)	-0.0240 (4)	0.2258 (4)	0.0405 (6)
C16	0.3316 (4)	0.1298 (4)	0.2149 (4)	0.0329 (4)
C17	0.1491 (4)	0.1242 (4)	0.1302 (4)	0.0377 (4)
C18	0.1152 (4)	0.2610 (4)	0.0883 (4)	0.0331 (4)
C19	0.0829 (4)	0.3924 (5)	0.1921 (4)	0.0388 (4)
C20	0.0566 (5)	0.5186 (5)	0.1524 (5)	0.0449 (4)
C21	0.0639 (5)	0.5156 (5)	0.0097 (5)	0.0442 (5)
C22	0.0956 (4)	0.3846 (5)	-0.0950 (4)	0.0410 (5)
C23	0.1197 (4)	0.2578 (4)	-0.0566 (4)	0.0371 (4)
C24	0.5889 (7)	0.7371 (5)	0.5662 (6)	0.0426 (7)

C25†	0.4885 (5)	0.6604 (5)	0.3993 (6)	0.0379 (8)
C26	0.5098 (6)	0.5210 (6)	0.2937 (6)	0.0412 (8)
C125‡	0.611 (1)	0.641 (1)	0.426 (1)	0.036 (2)
P1	0.0943 (3)	0.7244 (3)	0.6606 (3)	0.0416 (1)
F1	0.2439 (5)	0.8409 (5)	0.8425 (4)	0.0717 (8)
F2	0.2051 (5)	0.7440 (5)	0.5762 (5)	0.0751 (8)
F3	0.1580 (5)	0.5739 (5)	0.6691 (6)	0.085 (1)
F4	-0.0132 (5)	0.7047 (6)	0.7477 (5)	0.091 (1)
F5	-0.0538 (4)	0.6106 (4)	0.4773 (4)	0.0697 (4)
F6	0.0284 (5)	0.8711 (4)	0.6489 (5)	0.0812 (7)

† Occupancy 0.74 (1).

‡ Occupancy 0.26 (1).

Table 2. Selected geometric parameters (\AA , $^\circ$) for (1)

Pd1—N1	2.075 (3)	Pd1—C24	2.110 (4)
Pd1—N2	2.099 (3)	Pd1—C26	2.117 (4)
N2—Pd1—N1	87.6 (1)	C26—Pd1—N2	102.8 (1)
C24—Pd1—N1	101.3 (1)	C26—Pd1—C24	68.2 (2)

Compound (2)**Crystal data**

[Pd(C₂₃H₂₆N₂O₂)(C₁₅H₁₃)]-
PF₆
 $M_r = 807.102$
Orthorhombic
 $P2_12_12_1$
 $a = 12.6087$ (25) \AA
 $b = 15.2262$ (192) \AA
 $c = 18.5205$ (70) \AA
 $V = 3555.61$ (4.76) \AA^3
 $Z = 4$
 $D_x = 1.508 \text{ Mg m}^{-3}$
 $D_m = 1.51 \text{ Mg m}^{-3}$
 D_m measured by flotation

Mo $K\alpha$ radiation
 $\lambda = 0.71069 \text{ \AA}$
Cell parameters from 25
reflections
 $\theta = 2-28^\circ$
 $\mu = 0.6239 \text{ mm}^{-1}$
 $T = 250 \text{ K}$
Prism
 $0.4 \times 0.3 \times 0.3 \text{ mm}$
Yellow

Data collection

Four-circle Enraf–Nonius
CAD-4 diffractometer
equipped with Oxford
Cryostream cooling device
 $\theta/2\theta$ scans
Absorption correction:
spherical
 $T_{\min} = 0.98$, $T_{\max} = 1.00$
4683 measured reflections
4683 independent reflections

4183 observed reflections
[$F > 3.0\sigma(F)$]
 $\theta_{\max} = 28^\circ$
 $h = 0 \rightarrow 16$
 $k = 0 \rightarrow 20$
 $l = 0 \rightarrow 24$
4 standard reflections
frequency: 60 min
intensity decay: 0.7%

Refinement**Refinement on F**

$R = 0.0309$
 $wR = 0.0183$
 $S = 1.1326$
4183 reflections
451 parameters
H-atom parameters not
refined
Chebychev weighting
(Carruthers & Watkin,
1979)

$(\Delta/\sigma)_{\max} = 0.17$
 $\Delta\rho_{\max} = 0.64 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.46 \text{ e } \text{\AA}^{-3}$

Extinction correction:

Larson (1970)
Extinction coefficient: 58 (2)
Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV, Table
2.2B)
Absolute configuration:
known from the chosen
educts; additionally
determined by refining
the enantiopole parameter

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (2)
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U _{eq}
Pd1	0.02848 (2)	0.96547 (2)	0.88343 (1)	0.02770 (3)
N1	-0.0989 (2)	1.0493 (2)	0.9144 (1)	0.0284 (3)
C1	-0.0825 (3)	1.1310 (2)	0.9216 (2)	0.0303 (3)
C2	0.0074 (2)	1.1822 (2)	0.8880 (2)	0.0344 (3)
C3	0.0103 (3)	1.1676 (2)	0.8056 (2)	0.0411 (3)
C4	-0.0027 (3)	1.2806 (2)	0.9031 (2)	0.0467 (4)
C5	0.1076 (3)	1.1449 (2)	0.9196 (2)	0.0353 (3)
N2	0.1253 (2)	1.0635 (2)	0.9291 (2)	0.0354 (3)
O1	-0.1469 (2)	1.1747 (2)	0.9661 (1)	0.0367 (3)
C6	-0.2114 (3)	1.1076 (3)	1.0018 (2)	0.0390 (3)
C7	-0.1985 (2)	1.0280 (2)	0.9532 (2)	0.0318 (3)
C8	-0.2910 (3)	1.0146 (2)	0.9001 (2)	0.0359 (3)
C9	-0.3254 (2)	1.0970 (2)	0.8634 (2)	0.0373 (3)
C10	-0.2753 (3)	1.1271 (3)	0.8014 (2)	0.0453 (3)
C11	-0.3048 (4)	1.2063 (3)	0.7709 (3)	0.0607 (4)
C12	-0.3836 (4)	1.2557 (3)	0.8020 (3)	0.0717 (4)
C13	-0.4355 (4)	1.2253 (3)	0.8622 (3)	0.0655 (4)
C14	-0.4077 (3)	1.1465 (3)	0.8922 (2)	0.0507 (3)
O2	0.1833 (2)	1.2005 (2)	0.9413 (2)	0.0496 (4)
C15	0.2731 (4)	1.1459 (3)	0.9601 (3)	0.0640 (4)
C16	0.2250 (3)	1.0564 (3)	0.9713 (3)	0.0457 (3)
C17	0.1951 (4)	1.0349 (4)	1.0503 (2)	0.0538 (3)
C18	0.1258 (4)	0.9577 (3)	1.0575 (2)	0.0599 (3)
C19	0.0220 (4)	0.9673 (4)	1.0786 (3)	0.0964 (3)
C20	-0.0424 (5)	0.8936 (4)	1.0826 (4)	0.1145 (4)
C21	-0.0006 (5)	0.8131 (4)	1.0626 (4)	0.1011 (4)
C22	0.1029 (5)	0.8037 (4)	1.0452 (4)	0.1060 (4)
C23	0.1666 (4)	0.8758 (3)	1.0428 (3)	0.0825 (4)
C24	-0.0388 (3)	0.8478 (2)	0.8359 (2)	0.0367 (3)
C25	0.0573 (3)	0.8714 (2)	0.8029 (2)	0.0353 (3)
C26	0.1477 (3)	0.8785 (2)	0.8464 (2)	0.0379 (3)
C27	0.2477 (3)	0.9189 (2)	0.8216 (2)	0.0397 (3)
C28	0.3416 (3)	0.8967 (3)	0.8565 (2)	0.0535 (3)
C29	0.4357 (3)	0.9359 (4)	0.8371 (3)	0.0608 (4)
C30	0.4364 (3)	0.9986 (4)	0.7834 (3)	0.0678 (4)
C31	0.3437 (3)	1.0227 (4)	0.7490 (2)	0.0657 (4)
C32	0.2495 (3)	0.9827 (3)	0.7678 (2)	0.0493 (3)
C33	-0.1413 (3)	0.8488 (2)	0.7987 (2)	0.0362 (3)
C34	-0.1608 (3)	0.9069 (3)	0.7426 (2)	0.0449 (3)
C35	-0.2582 (3)	0.9082 (3)	0.7085 (2)	0.0551 (4)
C36	-0.3359 (3)	0.8494 (4)	0.7287 (3)	0.0655 (4)
C37	-0.3163 (3)	0.7898 (3)	0.7830 (3)	0.0634 (4)
C38	-0.2197 (3)	0.7906 (3)	0.8189 (3)	0.0533 (4)
P1	0.5246 (1)	0.93473 (8)	0.08382 (6)	0.0585 (2)
F1	0.5871 (4)	0.8874 (3)	0.1444 (2)	0.1458 (4)
F2	0.4633 (3)	0.9876 (3)	0.1429 (2)	0.1039 (4)
F3	0.6113 (3)	1.0072 (3)	0.0811 (2)	0.0928 (4)
F4	0.5865 (4)	0.8856 (3)	0.0233 (2)	0.1211 (4)
F5	0.4625 (3)	0.9848 (3)	0.0236 (2)	0.1302 (4)
F6	0.4380 (4)	0.8631 (3)	0.0857 (3)	0.1382 (4)

Table 4. Selected geometric parameters (Å, °) for (2)

Pd1—N1	2.130 (3)	Pd1—C24	2.169 (3)
Pd1—N2	2.105 (3)	Pd1—C26	2.118 (3)
N2—Pd1—N1	84.5 (1)	C26—Pd1—N2	99.3 (1)
C24—Pd1—N1	108.0 (1)	C26—Pd1—C24	68.3 (1)

For compound (1), the origin has been fixed using polar axes restraints (Flack & Schwarzenbach, 1988). The allyl group of compound (1) is disordered; the position of the central C atom was split and the occupancies of the two alternative positions were refined holding the sum equal to 1.

For both compounds, data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CRYSTALS* (Watkin, 1990); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *CRYSTALS*.

Lists of anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1124). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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fac- and *mer*-Dipyridiniomethane Trichlorotrifluoroosmate(IV), *fac*- and *mer*-[(C₅H₅N)₂CH₂][OsCl₃F₃]

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Abstract

The structures of *fac*-*N,N'*-methylenedipyridinium trichlorotrifluoroosmate(IV), (I), and *mer*-*N,N'*-methylenedipyridinium trichlorotrifluoroosmate(IV), (II), *fac*- and *mer*-[(C₅H₅N)₂CH₂][OsCl₃F₃], have been determined by single-crystal X-ray diffraction at room temperature. The complex anions are completely ordered. The Os—F distances in (I) are equal to within 3 e.s.d.'s, as are the Os—Cl distances. The mean Os—F distance of 1.948 Å and Os—Cl distance of 2.3199 Å are typical for bonds altered in length by the *trans* influence. The asymmetric Cl—Os—F coordination axis in (II) has a longer Os—F distance [1.976 (3) Å] and a shorter Os—Cl distance [2.2782 (13) Å] than the symmetric F—Os—F and Cl—Os—Cl axes, which have mean bond lengths of 1.944 and 2.307 Å, respectively.