

Fig. 3. Packing arrangement of the molecules viewed down *a*.

It can be observed that the conformation of the unsubstituted pyrrolidine ring in (II) may be considered intermediate between the conformation of the ring in (IV) and that in (III), perhaps closer to the conformation in (IV) which has an envelope-like form with C(4) at the flap. Therefore the five structures seem to represent five phases of the pseudorotation of the pyrrolidine ring in the sequence (IV)→(II)→(III)→(V)→(I) or, to stress the influence of the methyl substituents, (IV)←(II)→(III)→(V)→(I).

The shortest intermolecular contact [3.46 (2) Å], observed between N and Cl(2)[ $\frac{1}{2}+x$ ,  $\frac{1}{2}-y$ ,  $-z$ ], is probably due to an N—H...Cl hydrogen bond. The packing arrangement is shown in Fig. 3.

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#### References

- AMBUEHL, J., PREGOSIN, P. S., VENANZI, L. M., CONSIGLIO, G., BACHECHI, F. & ZAMBONELLI, L. (1979). *J. Organomet. Chem.* **181**, 255–269.
- BACHECHI, F., MURA, P. & ZAMBONELLI, L. (1980). *Acta Cryst.* **B36**, 2604–2608.
- BACHECHI, F., ZAMBONELLI, L. & MARCOTRIGIANO, G. (1977). *J. Cryst. Mol. Struct.* **7**, 11–20.
- CERRINI, S. & SPAGNA, R. (1977). 4th Eur. Crystallogr. Meet., Oxford. Abstracts, p. 7.
- CHATT, J. & VENANZI, L. M. (1955). *J. Chem. Soc.* pp. 3858–3864.
- COTTIN, H. (1966). *Bull. Soc. Chim. Fr.* p. 2731.
- International Tables for X-ray Crystallography* (1974). Vol. IV, Tables 2.2B and 2.3.1 Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- MCCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). *Acta Cryst.* **A31**, 245–249.
- NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- SPAGNA, R. & ZAMBONELLI, L. (1971). *J. Chem. Soc. A*, pp. 2544–2549.

*Acta Cryst.* (1985). **C41**, 838–840

## (Hexafluoroacetylacetonato-*O,O'*)(1-hydroxy-2,2,6,6-tetramethylpiperidinato-*O,N*)palladium(II), [Pd(C<sub>5</sub>HF<sub>6</sub>O<sub>2</sub>)(C<sub>9</sub>H<sub>18</sub>NO)], a Metal Complex Containing a Reduced Nitroxyl Radical

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**Abstract.**  $M_r = 469.7$ , monoclinic,  $P2_1/n$ ,  $a = 7.875$  (3),  $b = 20.511$  (8),  $c = 11.655$  (3) Å,  $\beta = 105.67$  (3)°,  $V = 1812$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.722$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 1.08$  mm<sup>-1</sup>,  $F(000) = 936$ ,  $T = 297$  K, final  $R = 0.042$  for 2498 observed reflections. The Pd atom is bound to a chelating hexafluoroacetylacetonato ligand and to a reduced nitroxyl radical coordinated in an  $\eta^2$  fashion through its N and O atoms. Principal bond distances include Pd—O(F<sub>6</sub>acac) = 2.058 (4), 2.078 (4), Pd—O(nitroxyl) = 2.009 (4), Pd—N = 1.985 (4), N—O = 1.346 (5) Å.

**Introduction.** The title compound was prepared in the course of exploratory studies of the reactions of stable nitroxyl radicals with transition-metal complexes containing a strongly Lewis-acidic metal center. Previous studies in this series have yielded examples of various types of interactions of the nitroxyl group, including metal coordination of the nitroxyl radical through O (Dickman & Doedens, 1981; Porter, Dickman & Doedens, 1983; Porter & Doedens, 1985), bidentate N,O binding of the reduced radical (Dickman & Doedens, 1982), hydrogen bonding to coordinated water (Dickman & Doedens, 1983), and formation of a co-crystallized solid with no specific interactions involving the nitroxyl group (Porter & Doedens, 1984). We

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Table 1. Atomic parameters

	x	y	z	$U_{eq}(\text{\AA}^2 \times 10^3)^*$
Pd	0.10791 (6)	0.13875 (2)	0.24739 (3)	59 (0.3)
O(1)	0.1016 (6)	0.1195 (2)	0.0713 (3)	72 (3)
O(2)	0.2649 (6)	0.0582 (2)	0.3011 (3)	73 (3)
O(3)	-0.0306 (5)	0.2170 (2)	0.2735 (3)	61 (3)
N	0.0530 (5)	0.1893 (2)	0.3782 (3)	50 (3)
C(1)	0.1832 (9)	0.0723 (3)	0.0410 (5)	69 (5)
C(2)	0.2823 (9)	0.0245 (3)	0.1098 (6)	75 (5)
C(3)	0.3145 (8)	0.0207 (3)	0.2335 (6)	65 (4)
C(4)	0.1655 (10)	0.0712 (4)	-0.0926 (6)	85 (6)
C(5)	0.4224 (9)	-0.0362 (3)	0.2982 (7)	77 (5)
C(6)	0.2040 (7)	0.2326 (3)	0.4513 (5)	59 (4)
C(7)	0.1225 (9)	0.2842 (3)	0.5158 (6)	81 (5)
C(8)	0.0048 (11)	0.2521 (5)	0.5897 (6)	99 (6)
C(9)	-0.1433 (9)	0.2116 (4)	0.5079 (6)	86 (6)
C(10)	-0.0747 (8)	0.1579 (3)	0.4417 (5)	64 (4)
C(11)	0.3406 (8)	0.1909 (3)	0.5376 (6)	78 (5)
C(12)	0.2954 (10)	0.2641 (4)	0.3668 (7)	88 (6)
C(13)	-0.2271 (10)	0.1286 (4)	0.3465 (7)	89 (6)
C(14)	0.0181 (11)	0.1035 (4)	0.5246 (7)	98 (7)
F(1)	0.2594 (10)	0.1134 (4)	-0.1236 (5)	191 (7)
F(2)	0.0060 (8)	0.0848 (4)	-0.1567 (4)	155 (6)
F(3)	0.1920 (12)	0.0159 (3)	-0.1345 (4)	183 (7)
F(4)	0.3532 (8)	-0.0630 (3)	0.3733 (6)	160 (6)
F(5)	0.4393 (9)	-0.0842 (2)	0.2276 (5)	150 (6)
F(6)	0.5800 (7)	-0.0191 (2)	0.3481 (6)	158 (6)

$$* U_{eq} = \frac{1}{3} \pi^2 \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

are attempting to define further the factors determining how the nitroxyl function interacts with transition-metal systems and to investigate the properties of the products obtained.

Bis(hexafluoroacetylacetonato)palladium(II) [ $\text{Pd}(\text{F}_6\text{acac})_2$ ] has been shown to have an extensive acid/base chemistry, forming a variety of different types of adducts (Siedle, Newmark & Pignolet, 1983). Consequently, we have investigated the interactions of this complex with several stable nitroxyl radicals. From  $\text{Pd}(\text{F}_6\text{acac})_2$  and 2,2,6,6-tetramethylpiperidyl-1-oxyl (tempo) in cyclohexane was obtained a small yield (<5%) of orange product. A crystal structure analysis was carried out in order to determine the nature of the metal-nitroxyl interaction in this material.

**Experimental.** Orange prisms obtained by vacuum sublimation at 351 K. Crystal dimensions  $0.17 \times 0.17 \times 0.30$  mm. Syntex  $P2_1$  diffractometer, graphite-monochromated  $\text{Mo K}\alpha$ . Lattice parameters from refinement of setting angles of 15 reflections with  $30^\circ \leq 2\theta \leq 35^\circ$ . Systematic absences  $h0l$ ,  $h+l \neq 2n$ ;  $0k0$ ,  $k \neq 2n$ . Nonstandard setting chosen to avoid highly obtuse  $\beta$  angle. Intensities measured for 4102 independent reflections ( $h, k, \pm l$ ) with  $2\theta \leq 55^\circ$ . Three standard reflections ( $23\bar{1}$ ,  $2\bar{1}0$ ,  $12\bar{1}$ ) measured after every 100 data; intensities corrected for 5% decline in standards. Scan rate  $2-12^\circ \text{ min}^{-1}$ ; scan range  $-1.1^\circ$  in  $2\theta$  from  $K\alpha_1$  to  $+1.2^\circ$  from  $K\alpha_2$ . Backgrounds evaluated from 96-step peak profile. No absorption correction. Total of 2498 observed reflections with  $I > 3\sigma(I)$ .  $R_{\text{int}}(F) = 0.0217$  for 95 nonzero  $0kl$ ,  $Ok\bar{l}$  pairs. Structure solved by Patterson and difference Fourier methods. Least-squares refinement on  $F$ ;

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

Distances and angles within the  $\text{CF}_3$  groups have been deposited.

## (a) Metal coordination sphere

Pd-O(1)	2.078 (4)	Pd-O(3)	2.009 (4)
Pd-O(2)	2.058 (4)	Pd-N	1.985 (4)
O(1)-Pd-O(2)	90.0 (2)	O(2)-Pd-O(3)	154.4 (2)
O(1)-Pd-O(3)	115.6 (2)	O(2)-Pd-N	115.0 (2)
O(1)-Pd-N	155.0 (2)	O(3)-Pd-N	39.4 (1.4)

(b)  $\text{F}_6\text{acac}$  ligand

O(1)-C(1)	1.264 (7)	C(1)-C(4)	1.526 (8)
O(2)-C(3)	1.237 (7)	C(2)-C(3)	1.397 (9)
C(1)-C(2)	1.369 (9)	C(3)-C(5)	1.519 (9)

Pd-O(1)-C(1)	122.9 (4)	C(1)-C(2)-C(3)	124.1 (6)
Pd-O(2)-C(3)	124.9 (4)	O(2)-C(3)-C(2)	128.4 (6)
O(1)-C(1)-C(2)	129.6 (6)	O(2)-C(3)-C(5)	113.1 (6)
O(1)-C(1)-C(4)	112.5 (6)	C(2)-C(3)-C(5)	118.5 (6)
C(2)-C(1)-C(4)	117.9 (6)		

(c) tempo<sup>-</sup> ligand

O(3)-N	1.346 (5)	C(7)-C(8)	1.570 (11)
N-C(6)	1.543 (7)	C(8)-C(9)	1.536 (11)
N-C(10)	1.541 (7)	C(9)-C(10)	1.525 (9)
C(6)-C(7)	1.536 (8)	C(10)-C(13)	1.521 (9)
C(6)-C(11)	1.522 (8)	C(10)-C(14)	1.527 (9)
C(6)-C(12)	1.513 (9)		

Pd-O(3)-N	69.4 (2)	C(7)-C(6)-C(12)	111.1 (6)
Pd-N-O(3)	71.2 (2)	C(11)-C(6)-C(12)	107.1 (5)
Pd-N-C(6)	115.4 (3)	C(6)-C(7)-C(8)	111.5 (6)
Pd-N-C(10)	117.2 (3)	C(7)-C(8)-C(9)	110.4 (5)
O(3)-N-C(6)	111.9 (4)	C(8)-C(9)-C(10)	113.0 (5)
O(3)-N-C(10)	112.9 (4)	N-C(10)-C(9)	107.9 (5)
C(6)-N-C(10)	118.7 (4)	N-C(10)-C(13)	107.7 (5)
N-C(6)-C(7)	107.8 (4)	N-C(10)-C(14)	110.3 (5)
N-C(6)-C(11)	110.1 (5)	C(9)-C(10)-C(13)	109.7 (6)
N-C(6)-C(12)	108.5 (4)	C(9)-C(10)-C(14)	112.5 (6)
C(7)-C(6)-C(11)	112.2 (5)	C(13)-C(10)-C(14)	108.8 (6)

weights as defined by Corfield, Doedens & Ibers (1967) with  $p = 0.05$ . Atomic scattering factors, including anomalous-dispersion corrections, from *International Tables for X-ray Crystallography* (1974). H atoms included in fixed idealized positions; orientations of methyl groups obtained from difference Fourier map. Final refinement included 226 variable parameters; in final cycle largest  $\Delta/\sigma = 0.25$ . Final  $R = 0.042$ ,  $wR = 0.056$ ,  $S = 1.51$ . For all measured reflections  $R = 0.096$ . Maximum peak height on final difference Fourier map  $1.3 \text{ e \AA}^{-3}$  in vicinity of  $\text{CF}_3$  group. All computations carried out with local version of the *UCLA Crystallographic Program Package* (Strouse, 1981).

**Discussion.** Final atomic parameters for nonhydrogen atoms are in Table 1.\* Intramolecular distances and angles are listed in Table 2.

\* Lists of structure factors, anisotropic thermal parameters, H-atom positions, distances and angles in  $\text{CF}_3$  groups, and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39964 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The crystal structure consists of discrete molecular units in which the Pd atom is bound to a chelating F<sub>6</sub>acac ring and to a reduced nitroxyl ligand. The latter group is bound in an  $\eta^2$  fashion *via* its N and O atoms. Its characterization as a reduced nitroxyl radical is based upon the stoichiometry of the complex and upon details of the ligand structure (see below). The coordination geometry about the Pd atom is essentially planar. The maximum deviation from the least-squares plane defined by N, O(1), O(2), and O(3) is 0.026 Å and the Pd atom is within 0.002 Å of this plane. A view of the molecular structure is shown in Fig. 1. The six-membered chelate ring is planar within experimental error. The Pd—O distances of 2.078 (4) and 2.058 (4) Å are substantially longer than those in Pd(F<sub>6</sub>acac)<sub>2</sub> and in most square-planar mixed-ligand Pd(F<sub>6</sub>acac) derivatives (Siedle, Newmark & Pignolet, 1983, and references therein). The only comparable long distance is that of 2.059 (5) Å *trans* to a C-bound F<sub>6</sub>acac ligand (Siedle & Pignolet, 1981).

The configuration of the reduced nitroxyl is quite similar to that which has been observed in PdCl(PPh<sub>3</sub>)(tempo<sup>-</sup>), the only other complex of this ligand for which crystal structure data are available (Dickman & Doedens, 1982). The specific structural features which identify this ligand as a reduced species rather than a neutral radical are the N—O distance of 1.346 (5) Å and the pyramidal configuration of the N atom, which is displaced by 0.35 Å from the plane defined by C(6), C(10), and O(3). Nitroxyl radicals, both free and complexed, are characterized by shorter N—O distances (*ca* 1.27 Å) and smaller out-of-plane displacements, typically about 0.15 Å when the N atom is part of a six-membered ring (Dickman & Doedens, 1981; Berliner, 1970; Capiomont & Lajzerowicz-Bonneteau, 1974). The binding of the tempo<sup>-</sup> ligand to Pd is more

symmetrical in the F<sub>6</sub>acac complex than in the chloro-triphenylphosphine derivative, primarily because of a significantly shorter Pd—N distance.

Other complexes containing coordinated tempo<sup>-</sup> have been obtained from reactions of tempo with PdCl<sub>2</sub>, PdBr<sub>2</sub>, and PdCl<sub>2</sub><sup>-</sup> (Beck & Schmidtner, 1967; Okunaka, Matsubayashi & Tanaka, 1977). Once formed, the Pd( $\eta^2$ -tempo<sup>-</sup>) grouping is rather stable, tending to be retained under conditions which lead to substitution of other ligands (Okunaka, Matsubayashi & Tanaka, 1975). This point was not specifically investigated in the present case because of the small amount of Pd(F<sub>6</sub>acac)(tempo<sup>-</sup>) available. The nature of the process by which the tempo is reduced is not clear. Because the product is formed in low yield, a variety of possibilities must be considered. These include, among others, disproportionation of the nitroxyl radical (perhaps metal-assisted) and reduction by an adventitious reducing agent. In the present case no other products which might shed light on the reduction pathway were isolated; however, in another system where reduction occurred, substantial amounts of nitroxyl cation were also produced (Okunaka, Matsubayashi & Tanaka, 1977). This could be indicative of a disproportionation pathway.

#### References

- BECK, W. & SCHMIDTNER, K. (1967). *Chem. Ber.* **100**, 3363–3367.  
 BERLINER, L. J. (1970). *Acta Cryst.* **B26**, 1198–1202.  
 CAPIOMONT, A. & LAJZEROWICZ-BONNETEAU, J. (1974). *Acta Cryst.* **B30**, 2160–2166.  
 CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197–204.  
 DICKMAN, M. H. & DOEDENS, R. J. (1981). *Inorg. Chem.* **20**, 2677–2681.  
 DICKMAN, M. H. & DOEDENS, R. J. (1982). *Inorg. Chem.* **21**, 682–684.  
 DICKMAN, M. H. & DOEDENS, R. J. (1983). *Inorg. Chem.* **22**, 1591–1594.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)  
 OKUNAKA, M., MATSUBAYASHI, G. & TANAKA, T. (1975). *Bull. Chem. Soc. Jpn.* **48**, 1826–1829.  
 OKUNAKA, M., MATSUBAYASHI, G. & TANAKA, T. (1977). *Bull. Chem. Soc. Jpn.* **50**, 907–909.  
 PORTER, L. C., DICKMAN, M. H. & DOEDENS, R. J. (1983). *Inorg. Chem.* **22**, 1962–1964.  
 PORTER, L. C. & DOEDENS, R. J. (1984). *Acta Cryst.* **C40**, 1814–1817.  
 PORTER, L. C. & DOEDENS, R. J. (1985). *Inorg. Chem.* **24**. In the press.  
 SIEDLE, A. R., NEWMARK, R. A. & PIGNOLET, L. H. (1983). *Inorg. Chem.* **22**, 2281–2286.  
 SIEDLE, A. R. & PIGNOLET, L. H. (1981). *Inorg. Chem.* **20**, 1849–1853.  
 STROUSE, C. E. (1981). Personal communication.

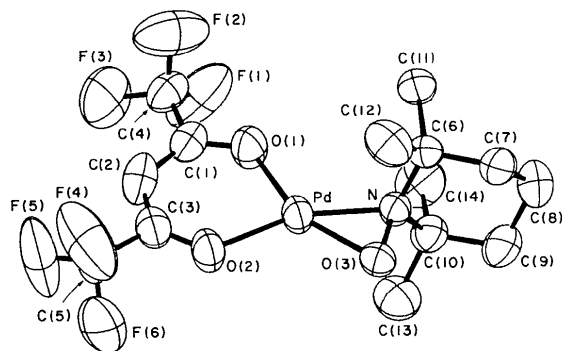


Fig. 1. A view of the molecular structure of Pd(F<sub>6</sub>acac)(tempo<sup>-</sup>). Thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.