Table 2. *Selected bond distances* (Å) *and angles* (°)

Nb—O(10)	1.878 (7)	O(10)—Nb—O(20)	107.3 (4)
Nb—O(20)	1.921 (8)	O(10)—Nb—O(30)	109.7 (4)
Nb—O(30)	1.890 (9)	O(10)—Nb—O(40)	110.0 (4)
Nb—O(40)	1.685 (9)	O(20)—Nb—O(30)	105.1 (4)
O(10)—C(11)	1.35 (1)	O(20)—Nb—O(40)	111.1 (4)
O(20)—C(21)	1.36 (1)	O(30)—Nb—O(40)	113.4 (4)
O(30)—C(31)	1.33 (1)	Nb—O(10)—C(11)	155.0 (9)
		Nb—O(20)—C(21)	146.0 (8)
		Nb—O(30)—C(31)	153.7 (9)

seen to adopt a tetrahedral geometry about the Nb atom using three aryl oxide O atoms and one terminal oxo ligand. Fractional coordinates and isotropic thermal parameters are collected in Table 1, while a listing of important bond distances and bond angles is given in Table 2.*

The Nb—O distance to the terminal oxo group, 1.685 (9) Å, compares well with the values reported for Nb monooxo complexes (Nugent & Mayer, 1987). The most common coordination number for Nb monooxo compounds is found to be six. A search in the Cambridge Structural Database for structural data for monomeric Nb monooxo fragments yielded 17 hits. Eleven entries show a distorted octahedral geometry of the central metal coordination sphere. It is, therefore, interesting to find that the complex [Nb($OC_6H_3Ph_2$-2,6)$_3$(O)] has only four-coordinate Nb atoms with a slightly distorted tetrahedral arrangement of ligands around the metal center. The Nb—O(aryl oxide) distances of 1.878 (7)–1.921 (8) Å and large Nb—O—Ar angles of 146.0 (8)–155.0 (7)° are common for niobium(V) and tantalum(V) aryl oxide compounds (Steffey, Fanwick & Rothwell, 1990).

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Structure of Bis(hexafluoroacetylacetonato)bis(triphenylphosphine oxide)nickel(II)

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Abstract. [Ni($C_5HF_6O_2$)$_2$($C_{18}H_{15}OP$)$_2$], $M_r = 1029.4$, triclinic, $P\bar{1}$, $a = 9.266$ (3), $b = 11.385$ (3), $c = 12.606$ (3) Å, $\alpha = 112.72$ (2), $\beta = 99.90$ (2), $\gamma = 103.24$ (2)°, $V = 1142.7$ (5) Å^3, $Z = 1$, $D_x = 1.496$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.587$ mm^{-1}, $F(000) = 522$, $T = 298$ K, $R = 0.0661$ and $wR = 0.0480$ for 268 variable parameters ($S = 1.24$) and 3000 reflections with $F > 0$. The Ni atom possesses an octahedral geometry and forms bonds to two equatorial F_6acac ligands [Ni—O(1) =

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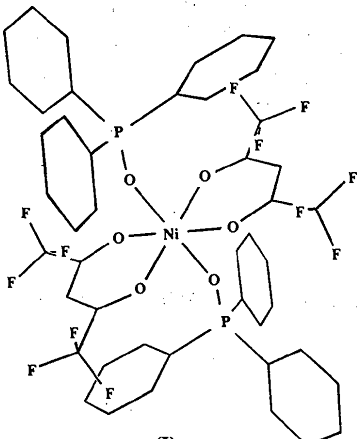
2.041 (3), Ni—O(2) = 2.048 (2) Å] and the O atoms of two symmetry-related axial triphenylphosphine oxide ligands [Ni—O(3) = 2.058 (3) Å]. Interaxial angles in the coordination sphere of the Ni atom range from 87.3 to 90.2°. The P atoms of the triphenylphosphine oxide groups possess tetrahedral geometries with a P—O bond that measures 1.486 (3) Å.

Introduction. During the course of our work with dichlorotris(triphenylphosphine)ruthenium(II), we found that $Ni(F_6acac)_2$ could be useful in controlling the number of vacant coordination sites at the Ru center by forming stable bis(triphenylphosphine) adducts of bis(F_6acac)Ni^{II} following phosphine dissociation from the Ru complex in non-polar solvents. Since phosphine dissociation is an important element in homogeneous catalytic reactions involving many of the transition-metal elements, this constituted an opportunity to modify the intrinsic reactivity of the complex, both with respect to catalytic reactions, as well as the coordination of a variety of ligands, particularly thiophenes and thiophene derivatives. During the course of these investigations we succeeded in obtaining excellent crystals of the title compound (I). Owing in part to our interest in the coordination chemistry of $Ni(F_6acac)_2$, we undertook a crystal structure determination of the Ni product formed in these reactions and now report the crystal structure of a new bis(hexafluoroacetylacetonato)nickel(II) complex containing *trans* triphenylphosphine oxide ligands.



(I)

Experimental. Greenish yellow well formed crystals of the title compound were obtained in good yield following the reaction of dichlorotris(triphenylphosphine)ruthenium(II) with anhydrous bis(F_6acac)Ni^{II} in toluene. The Ni fraction was extracted into diethyl ether and then allowed to crystallize by slow evaporation. A regularly shaped crystal displaying a prismatic habit with approximate dimensions 0.15 × 0.15 × 0.20 mm was mounted on the end of a glass fiber in an arbitrary orientation. Triclinic symmetry was suggested on the basis of interaxial angles and confirmed by a Delaunay reduction procedure. Refined cell parameters were determined from the setting angles of 25 reflections with $15 < 2\theta < 30°$. Data collection was carried out at ambient temperature using a Nicolet *R3m/V* diffractometer utilizing the ω-scan technique in bisecting geometry and graphite-monochromated Mo $K\alpha$ radiation; scan rate variable 3–15° min^{-1}; scan range 1.5° in ω. Three standards ($2\overline{1}\overline{4}$, $23\overline{3}$, $\overline{1}4\overline{2}$) measured every 100 data showed no significant variation over the period of data collection. A total of 3225 reflections $(+h, +k, +l;$ $h_{max} = 9$, $k_{max} = 12$, $l_{max} = 13)$ with $3.5 < 2\theta < 45°$ $[(\sin\theta/\lambda)_{max} = 0.538\ Å^{-1}]$ were obtained and corrected for Lorentz and polarization effects. This led to 3000 unique reflections ($R_{int} = 7.44\%$) that were

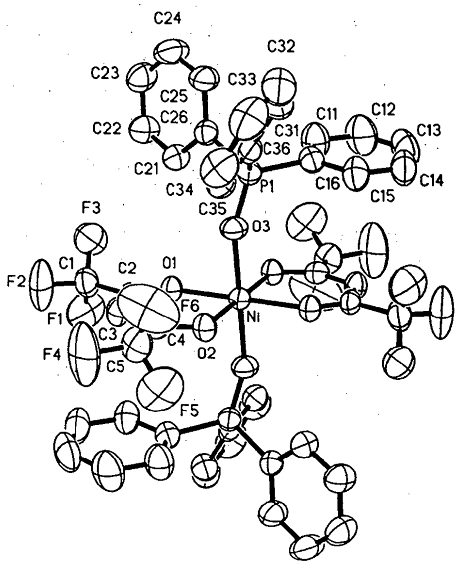


Fig. 1. A perspective view of the structure illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level and H atoms have been omitted for clarity.

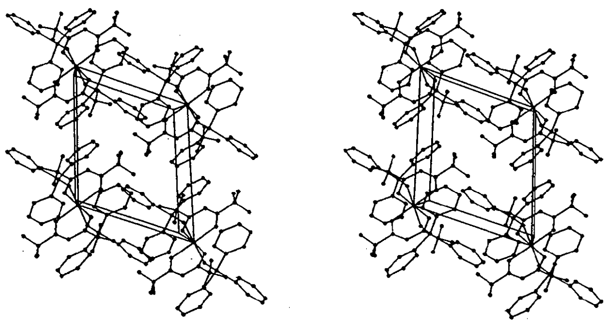


Fig. 2. A stereoview packing diagram projected down the crystallographic *a* axis.

corrected for absorption effects empirically on the basis of azimuthal scans of seven strong reflections spanning a range of 2θ values (minimum and maximum transmission factors were 0.898 and 0.962, respectively). Structure solution was carried out using the *SHELXTL-PC* collection of crystallographic software (Sheldrick, 1990). Intensity statistics favored a centrosymmetric cell which was assigned to the $P\bar{1}$ space group. The location of the Ni atom was determined from a sharpened Patterson map and used as an initial phasing model. All remaining non-H were atoms located on difference Fourier maps and refined anisotropically using scattering factors, including terms for anomalous dispersion, taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Phenyl rings were refined as rigid idealized polygons (C—C = 1.395 Å) with H atoms placed in idealized positions with fixed isotropic $U = 0.08$ Å^2. Refinement was based on F using weights of the form $w^{-1} = [\sigma^2(F) + 0.0003(F^2)]$. Convergence to conventional R values of $R = 0.0661$ and $wR = 0.0480$ with a goodness-of-fit of 1.24 was obtained using 268 variable parameters and 3000 reflections with $F > 0$. No reflections had intensities beyond the range for valid coincidence correction. For the final cycle, maximum shift/σ = 0.000 with minimum and maximum residual electron densities of -0.31 and 0.36 e Å^{-3}. A view of the structure illustrating that atomic numbering scheme is presented in Fig. 1; in Fig. 2. is shown a stereoview packing diagram of the complex. Atomic positional parameters and equivalent isotropic thermal parameters for all non-H atoms are presented in Table 1.* Pertinent bond distances and angles are given in Table 2.

Discussion. The ability of many Ru complexes to catalyze the oxidation of phosphines to phosphine oxides is well established; in this case exposure to air during the process of separating the two components was sufficient to effect the conversion of triphenylphosphine to triphenylphosphine oxide. In the Ni complex that was isolated, both triphenylphosphine oxide ligands are coordinated axially and the two F_6acac ligands occupy equatorial sites. The entire molecule resides at the cell origin and the asymmetric unit consists of one half of a centrosymmetric Ni^{II} molecule.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* (Å$^2 \times 10^3$)

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ni	0	0	0	34 (1)
P(1)	−1644 (1)	1362 (1)	−1714 (1)	40 (1)
F(1)	−2049 (4)	1040 (3)	3362 (3)	106 (2)
F(2)	−1290 (4)	3120 (3)	3866 (3)	120 (2)
F(3)	−3114 (3)	1805 (3)	2297 (3)	102 (2)
F(4)	3579 (4)	4678 (3)	3651 (3)	140 (2)
F(5)	4654 (3)	3461 (3)	2616 (3)	115 (2)
F(6)	3485 (4)	4455 (3)	1908 (3)	145 (2)
O(1)	−1135 (3)	602 (2)	1261 (2)	43 (1)
O(2)	1906 (3)	1657 (2)	1077 (2)	44 (1)
O(3)	−743 (3)	1157 (2)	−743 (2)	48 (1)
C(1)	−1774 (6)	1912 (5)	2928 (4)	61 (3)
C(2)	−631 (5)	1700 (5)	2183 (3)	42 (2)
C(3)	792 (5)	2705 (4)	2602 (3)	50 (2)
C(4)	1923 (4)	2603 (4)	2020 (3)	42 (2)
C(5)	3410 (6)	3805 (4)	2556 (4)	66 (3)
C(11)	−3792 (3)	−959 (3)	−3601 (3)	74 (3)
C(12)	−4242	−2126	−4680	94 (3)
C(13)	−3181	−2403	−5325	88 (3)
C(14)	−1669	−1513	−4890	76 (3)
C(15)	−1219	−345	−3810	63 (2)
C(16)	−2281	−68	−3166	46 (2)
C(21)	−3816 (3)	1409 (3)	−502 (2)	50 (2)
C(22)	−5153	1630	−224	61 (2)
C(23)	−6018	2157	−828	70 (3)
C(24)	−5546	2463	−1711	80 (3)
C(25)	−4209	2241	−1989	66 (3)
C(26)	−3344	1714	−1385	43 (2)
C(31)	−809 (3)	2936 (3)	−2903 (2)	58 (2)
C(32)	155	4024	−2974	76 (3)
C(33)	1449	4930	−2008	82 (3)
C(34)	1780	4748	−972	76 (3)
C(35)	816	3660	−901	55 (2)
C(36)	−478	2754	−1866	42 (2)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Ni—O(1)	2.041 (3)	Ni—O(2)	2.048 (2)
Ni—O(3)	2.058 (3)	P(1)—O(3)	1.486 (3)
P(1)—C(16)	1.799 (3)	P(1)—C(26)	1.789 (3)
P(1)—C(36)	1.799 (3)	O(1)—C(2)	1.247 (4)
O(2)—C(4)	1.253 (4)	C(1)—C(2)	1.531 (7)
C(2)—C(3)	1.389 (5)	C(3)—C(4)	1.380 (6)
C(4)—C(5)	1.526 (5)		

O(1)—Ni—O(2)	89.8 (1)	O(1)—Ni—O(3)	89.7 (1)
O(2)—Ni—O(3)	87.3 (1)	O(1)—Ni—O(1*A*)	180.0 (1)
O(2)—Ni—O(1*A*)	90.2 (1)	O(3)—Ni—O(1*A*)	90.3 (1)
O(2)—Ni—O(2*A*)	180.0 (1)	O(3)—Ni—O(2*A*)	92.7 (1)
O(3)—Ni—O(3*A*)	180.0 (1)	O(3)—P(1)—C(16)	113.8 (2)
O(3)—P(1)—C(26)	110.8 (2)	C(16)—P(1)—C(26)	106.7 (1)
O(3)—P(1)—C(36)	110.0 (1)	C(16)—P(1)—C(36)	106.7 (2)
C(26)—P(1)—C(36)	108.6 (2)	Ni—O(1)—C(2)	124.7 (3)
Ni—O(2)—C(4)	124.0 (2)	Ni—O(3)—P(1)	153.9 (1)
O(1)—C(2)—C(1)	113.1 (3)	O(1)—C(2)—C(3)	128.8 (4)
C(1)—C(2)—C(3)	118.0 (3)	C(2)—C(3)—C(4)	122.9 (3)
O(2)—C(4)—C(3)	129.2 (3)	O(2)—C(4)—C(5)	113.4 (4)
C(3)—C(4)—C(5)	117.3 (3)	P(1)—C(16)—C(11)	120.2 (1)
P(1)—C(16)—C(15)	119.5 (1)	P(1)—C(26)—C(21)	117.2 (1)
P(1)—C(26)—C(25)	122.8 (1)	P(1)—C(36)—C(31)	122.7 (1)
P(1)—C(36)—C(35)	117.3 (1)		

Key structural features of this complex arc similar to those observed in other bis adducts of $Ni(F_6acac)_2$ (Porter, Dickman & Doedens, 1988; Cervantes-Lee & Porter, 1991*a*). The six O atoms of the ligands provide the Ni atom with a coordination geometry that deviates only slightly from that expected for a complex possessing ideal ocatahedral geometry, with interaxial O—*M*—O bond angles that range from 87.3 (1) to 92.7 (1)° for O(2)—Ni—O(3) and O(3)—Ni—O(2*A*), respectively. Bonds to the O atoms of the axial ligands are longer, on average, by 0.014 Å compared with those to the O atoms of the equator-

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* Lists of structure factors, H-atom coordinates, anisotropic thermal parameters, and CF_3 bond angles and distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55176 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0620]

ial F_6acac groups, the latter showing some variation but being well in the range typically observed in *trans* octahedral Ni^{II} complexes containing equatorial F_6acac ligands [Ni—O(1) = 2.041 (3), Ni—O(2) = 2.048 (2) Å] (Porter, Dickman & Doedens, 1988; Cervantes-Lee & Porter, 1991*a*,*b*; Romero, Cervantes-Lee & Porter, 1992). The two F_6acac ligands are essentially coplanar and the Ni atom is displaced by less than 0.20 Å from the least-squares plane defined by the five-atom rings formed by the O—C—C—C—O atoms of these groups. Other structural features of these ligands will not be discussed further, except to note that we found no evidence for significant disorder in the F-atom positions associated with any of the trifluoromethyl groups.

Structural details associated with the triphenylphosphine oxide ligands show many of the structural features typically observed in other transition-metal complexes containing these ligands. The P atoms possess a tetrahedral geometry with interaxial bond angles ranging from 106.7 (1) to 110.8 (2)°. The P—O bond measures 1.486 (3) Å and is longer than the 1.46 Å bond length observed in the crystal structure of free triphenylphosphine oxide (Bandoli, Bortolozzo, Clemente, Croatto & Panattoni, 1970). The triphenylphosphine oxide ligands coordinate in a bent manner with the Ni—O(3)—P(1) atoms defining an angle of 153.9 (1)°. This bond angle is considerably more obtuse than the 140.4 (3)° *M*—O—P angle observed in the structure of *trans* (dinitrato-*O*,*O*′)bis(triphenylphosphine oxide)copper(II), the only other monomeric *trans* triphenylphosphine oxide complex for which structural data are available (Ferrari, Gasparri, Pelizzi & Tarasconi, 1986).

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Structure of μ-Dioxane-bis[(ethanol)bis(hexafluoroacetylacetonato)nickel(II)]

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Abstract. $[Ni_2(C_5HF_6O_2)_4(C_2H_6O)_2(C_4H_8O_2)]$, M_r = 1125.9, triclinic, $P\bar{1}$, a = 9.890 (4), b = 10.942 (4), c = 11.114 (4) Å, α = 100.48 (3), β = 105.45 (3), γ = 108.87 (3)°, V = 1048.5 (7) Å^3, Z = 1, D_x = 1.783 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 1.057 mm^{-1}, $F(000)$ = 560, T = 298 K, R = 0.0747 and wR = 0.0638, for 298 variable parameters (S = 1.40) and 2759 reflections with $F > 0\sigma(F)$. A centrosymmetric complex containing a bridging molecule of dioxane is formed by two $Ni(F_6acac)_2$ complexes, each of which contains a molecule of ethanol coordinating axially [Ni(1)—O(5) = 2.032 (4) Å]. The Ni centers possess an octahedral coordination geometry and each forms bonds to two equatorial F_6acac ligands. The bridging dioxane ligand is located on a crystallographic center of inversion, possesses a chair conformation, and forms bonds to the two Ni atoms that measure 2.136 (4) Å.

Introduction. Examples of transition-metal complexes containing dioxane ligands are rare. In those instances where stable adducts containing a covalently bound dioxane molecule have been prepared, polymeric structures have frequently been obtained

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