[Ni(saden)]ClO_4 (Podlahová, Knížek, Loub & Hašek, 1988), [Ni(saden)]NCS (Loub, Podlahová, Kopf & Weiss, 1989), [Pd(saden)]ClO_4 (Kratochvíl, Nováková, Haber, Ondráček & Hájek, 1989), [Cu(saden)H_2O]PF_6 (Cusmano Priolo, Rotondo, Rizzardi, Bruno & Bombieri, 1983) and [Cd(saden)C_2H_5OH]ClO_4 (Loub, Podlahová, Haber, Kopf & Weiss, 1990).

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Structure of Carbonyl(2-quinolinecarboxylato-*κN*,*κO*)-(triphenylphosphite-*κP*)rhodium(I)

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Abstract. $[Rh(C_{10}H_6NO_2)(CO)\{P(C_6H_5O)_3\}]$, $M_r = 613{\cdot}4$, monoclinic, $P2_1/c$, $a = 11{\cdot}727\,(6)$, $b = 11{\cdot}380\,(5)$, $c = 19{\cdot}866\,(3)$ Å, $\beta = 102{\cdot}08\,(2)^\circ$, $V = 2592{\cdot}5$ Å^3, $Z = 4$, $D_m = 1{\cdot}53$, $D_x = 1{\cdot}57$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 7{\cdot}70$ cm^{-1}, $F(000) = 1240$, final $R = 0{\cdot}042$ for 2796 observed reflections. The structure indicates that the complex has square-planar geometry about the Rh atom and that the carbonyl group *trans* to the N atom of the 2-carboxyquinolinato ligand was substituted by the triphenylphosphite ligand. The N atom of the chelate ring therefore has a larger thermodynamic *trans* influence than the O atom. The π-acceptor properties of triphenylphosphite resulted in a relatively strong bond between Rh and P [bond distance 2·172 (2) Å] as compared to the Rh—P bond [bond distance 2·258 (2) Å] in the corresponding phosphine complex.

Experimental. An equivalent amount of triphenylphosphite (0·23 g dissolved in 1 cm^3 acetone) was added dropwise to a suspension of 0·25 g [Rh(quin)-$(CO)_2$] in 2 cm^3 acetone, where quin is the 2-quinolinecarboxylato ligand (Graham, Lamprecht, Potgieter, Roodt & Leipoldt, 1990). The resulting yellow precipitate was recrystallized from acetone to yield well formed crystals of the title compound, suitable for X-ray analysis. The density was determined by flotation in sodium iodide solution. A crystal of dimensions 0·20 × 0·15 × 0·35 mm was used for data collection on an Enraf–Nonius CAD-4F diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The $\omega/2\theta$-scan technique, with variable scan width $\Delta\omega = (0{\cdot}53 + 0{\cdot}34\tan\theta)^\circ$, scan speed 3·30° min^{-1} in ω and a maximum scan time of 50 s per reflection, was used. The unit-cell parameters were determined from least-squares refinement of 25 reflections with $7 < \theta < 16^\circ$, with total measuring range $3 < \theta < 25^\circ$. Empirical absorption corrections (North, Phillips & Matthews, 1968) with a minimum correction factor 0·90 and maximum 0·99 were used. The mean intensity of three standard reflections was measured over 3600 s of X-ray exposure time, and varied from the initial value by −2·0%. All possible reflections with $(\sin\theta)/\lambda < 0{\cdot}71$ Å^{-1} in the index range $0 < h < 13$, $0 < k < 13$, $-23 < l < 23$, gave 3947 unique with 2796 considered as observed [$I > 3{\cdot}0\sigma(I)$]. The structure was solved by the heavy-atom method using *SHELXS86* (Sheldrick, 1990) and was subjected to anisotropic full-matrix least-squares refinement on F using *SHELX76* (Sheldrick, 1976). The H-atom positions were calculated riding on the adjacent C atoms assuming C—H = 1·08 Å, and were refined with an overall temperature factor. Neutral-atom scattering factors (Cromer & Mann, 1968) and

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$) *for* [Rh(quin)(CO){P(OPh)$_3$}] *with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Rh	2084·4 (4)	2696·6 (4)	4259·7 (3)	43·3 (1)
P	2989·9 (15)	1021·6 (14)	4359·9 (9)	44·6 (4)
O(1)	4260 (4)	966 (4)	4200 (2)	53 (1)
O(5)	3259 (4)	3233 (4)	5089 (3)	67 (1)
O(2)	2282 (4)	−12 (4)	3923 (2)	52 (1)
O(3)	3409 (4)	524 (4)	5117 (2)	55 (1)
C(11)	4559 (5)	1540 (6)	3636 (3)	46 (2)
C(12)	5042 (6)	2628 (6)	3734 (3)	58 (2)
O(4)	623 (6)	1802 (6)	2971 (3)	101 (2)
C(1)	1167 (6)	2162 (6)	3474 (4)	57 (2)
C(16)	4446 (6)	959 (6)	3027 (4)	61 (2)
C(15)	4849 (7)	1487 (7)	2491 (4)	65 (2)
N	1422 (4)	4417 (4)	4400 (3)	44 (1)
O(6)	3887 (5)	4777 (5)	5745 (3)	80 (1)
C(410)	416 (6)	4989 (6)	4076 (3)	46 (2)
C(47)	−1629 (7)	6127 (7)	3440 (4)	67 (2)
C(42)	2116 (6)	4961 (5)	4927 (3)	47 (2)
C(32)	3153 (7)	909 (8)	6246 (4)	71 (2)
C(41)	3184 (6)	4303 (6)	5288 (4)	55 (2)
C(31)	2713 (6)	450 (6)	5611 (4)	56 (2)
C(46)	−904 (7)	6654 (7)	3963 (4)	64 (2)
C(48)	−1347 (7)	5018 (7)	3215 (4)	70 (2)
C(34)	1509 (11)	197 (10)	6645 (6)	102 (4)
C(33)	2540 (10)	772 (9)	6759 (5)	90 (3)
C(36)	1645 (9)	−113 (9)	5472 (5)	101 (3)
C(44)	904 (6)	6638 (6)	4845 (4)	55 (2)
C(22)	3605 (6)	−1693 (6)	4213 (3)	50 (2)
C(14)	5345 (7)	2572 (7)	2577 (4)	66 (2)
C(26)	1777 (6)	−1837 (6)	3406 (3)	50 (2)
C(21)	2586 (6)	−1198 (5)	3857 (3)	46 (2)
C(45)	142 (6)	6109 (6)	4301 (4)	50 (2)
C(43)	1895 (6)	6088 (6)	5157 (3)	53 (2)
C(23)	3821 (6)	−2860 (6)	4098 (4)	55 (2)
C(24)	3016 (7)	−3506 (6)	3638 (4)	60 (2)
C(25)	2012 (7)	−3003 (6)	3290 (4)	60 (2)
C(49)	−359 (6)	4456 (7)	3528 (4)	63 (2)
C(13)	5446 (7)	3143 (7)	3195 (4)	70 (2)
C(35)	1060 (10)	−208 (11)	6002 (6)	124 (4)

anomalous-dispersion corrections for rhodium were taken from *International Tables for X-ray Crystallography* (1962, Vol. III, p. 216). The final R was 0·042 and $wR = 0·043$ with unit weights, $(\Delta\rho)_{max} = 0·80$, $(\Delta\rho)_{min} = -0·36$ e $Å^{-3}$ and $(\Delta/\sigma)_{max} = 0·118$. S was not calculated.

The final atomic coordinates are given in Table 1, with selected geometrical parameters in Table 2.* Fig. 1 shows a perspective view of the molecule (Johnson, 1976) with atomic labels. The packing in the unit cell is shown in the stereoview in Fig. 2.

Related literature. The present structure can be compared with the carbonyltriphenylphosphine complex (Graham, Lamprecht, Potgieter, Roodt & Leipoldt, 1990) and the bistriphenylphosphite complex (Lamprecht, Beetge, Leipoldt & De Waal, 1986) of the same 2-carboxyquinolinato ligand. The Rh—P bond distances of 2·172 (2) (present structure), 2·153 (1) and 2·147 (2) (bisphosphite

Table 2. *Selected interatomic bond distances* (Å) *and angles* (°) *in* [Rh(quin)(CO){P(OPh)$_3$}] *with e.s.d.'s in parentheses*

Rh—P	2·171 (2)	Rh—O(5)	2·009 (5)
Rh—C(1)	1·806 (7)	Rh—N	2·145 (5)
P—O(1)	1·588 (4)	P—O(2)	1·589 (4)
P—O(3)	1·586 (5)	O(1)—C(11)	1·404 (7)
O(5)—C(41)	1·288 (8)	O(2)—C(21)	1·409 (7)
O(3)—C(31)	1·403 (8)	O(4)—C(1)	1·143 (8)
N—C(410)	1·383 (7)	N—C(42)	1·337 (8)
O(6)—C(41)	1·218 (8)	C(410)—C(45)	1·409 (9)
C(42)—C(41)	1·506 (9)	C(42)—C(43)	1·403 (9)

P—Rh—O(5)	87·3 (1)	P—Rh—C(1)	88·6 (2)
O(5)—Rh—C(1)	173·5 (3)	P—Rh—N	166·6 (1)
O(5)—Rh—N	79·7 (2)	C(1)—Rh—N	104·7 (2)
Rh—P—O(1)	118·6 (2)	Rh—P—O(2)	114·2 (2)
O(1)—P—O(2)	105·4 (3)	Rh—P—O(3)	116·7 (2)
O(1)—P—O(3)	93·3 (2)	O(2)—P—O(3)	106·1 (2)
P—O(1)—C(11)	122·8 (4)	Rh—O(5)—C(41)	117·4 (4)
P—O(2)—C(21)	130·2 (4)	P—O(3)—C(31)	125·1 (4)
Rh—C(1)—O(4)	177·3 (7)	Rh—N—C(410)	131·8 (4)
Rh—N—C(42)	110·3 (4)	C(410)—N—C(42)	117·8 (5)
N—C(410)—C(45)	120·5 (6)	N—C(42)—C(41)	116·8 (6)
N—C(42)—C(43)	123·7 (6)	C(41)—C(42)—C(43)	119·5 (6)
O(5)—C(41)—O(6)	124·7 (7)	O(5)—C(41)—C(42)	115·3 (6)
O(6)—C(41)—C(42)	120·0 (6)		

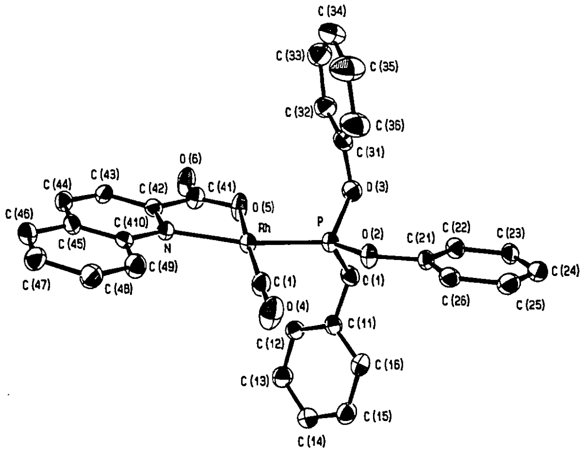

Fig. 1. Perspective view and atomic labelling of the molecule (H atoms omitted for clarity).

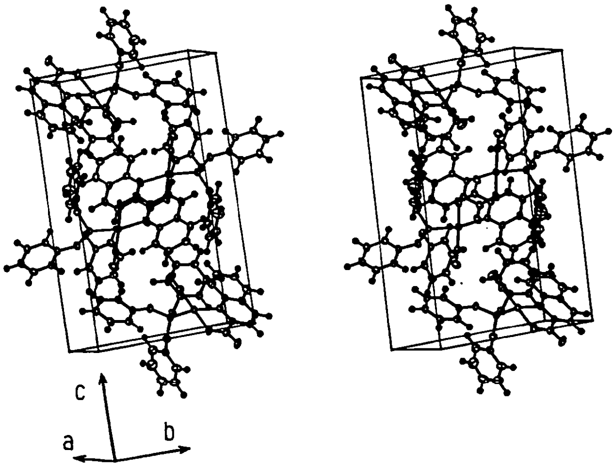

Fig. 2. Stereoview showing the packing in the unit cell.

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* Lists of least-squares planes and deviations, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54115 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

complex) and 2·258 (2) Å (phosphine complex) show that although triphenylphosphite is a weaker σ-electron donor it is a much better π-electron acceptor than triphenylphosphine, resulting in a relatively strong Rh—P bond. The greater thermodynamic *trans* influence of the N atom, relative to that of the O atom of the chelate ring, is proved by the substitution of the carbonyl group *trans* to the N atom and is consistent with the summarized *trans* influence of different donor atoms (Graham, Lamprecht, Potgieter, Roodt & Leipoldt, 1990).

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Tris(dimethyldithiophosphinato)chromium(III) – Orthorhombic Form

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Abstract. $C_6H_{18}CrP_3S_6$, $M_r = 427·51$, orthorhombic, $P2_12_12_1$, $a = 9·107\,(1)$, $b = 9·632\,(2)$, $c = 21·530\,(2)$ Å, $V = 1888\,(1)$ Å^3, $Z = 4$, $D_x = 1·50$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 14·6 cm^{-1}, $F(000) = 876$, T = 294 (1) K, $R = 0·030$ for 3040 unique observed reflections of 4184 total data. The complex has trigonally distorted octahedral geometry [average trigonal twist 12·1 (3)°] similar to that observed for the monoclinic form. Cr—S 2·432 (4), P—S 2·010 (2) Å.

Experimental. The title compound was prepared by the method of Cavell, Byers & Day (1971) and crystallized from ethanol/CH_2Cl_2 to give two crystal forms – the known monoclinic modification (Buranda & Pinkerton, 1990) and a new orthorhombic form as dark blue rods.

Blue rod, 0·40 × 0·10 × 0·05 mm, mounted on a glass fiber, Enraf–Nonius CAD-4 diffractometer, graphite monochromator, θ–2θ scan technique, backgrounds obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974), unit-cell constants from the setting angles of 25 reflections in the range $10 < \theta < 14°$. Empirical absorption correction (from 0·858 to 0·999 on I), $2\theta_{\max} = 52·0°$, $0 < h < 11$, $0 < k < 11$, $-26 < l < 26$; anisotropic decay (from 0·949 to 1·080 on I); reflection averaging $R_{\rm int} = 2·3\%$, 4184 total reflections measured, 3717 non-symmetry equivalent reflections, 3040 reflections with $F_o^2 > 3·0\sigma(F_o^2)$. Solution by direct methods (*MULTAN*; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), refinement by full-matrix least squares, function minimized was $\sum w(|F_o| - |F_c|)^2$, weight w is defined as $4F_o^2/\sigma^2(F_o^2)$, H atoms refined as riding atoms. 145 refined parameters, $R = 0·030$, $wR = 0·038$, $S = 1·09$, largest shift $= 0·03\sigma$, high peak in final difference map 0·37 (11) e Å^{-3}, low peak $-0·24$ (11) e Å^{-3}, enantiomorph confirmed by R factor test ($R = 0·035$ for enantiomorph, bulk sample is racemic mixture of enantiomorphic crystals). Scattering factors for neutral atoms and the values for f' and f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV); computer programs *MolEN* (Fair, 1990).

Final atomic coordinates are reported in Table 1, bond lengths and angles in Table 2.* Fig. 1 prepared using *ORTEP* (Johnson, 1976).

Related literature. The structures of a number of tris(dithiophosphinato)chromium(III) complexes

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* Lists of structure factors, anisotropic thermal parameters, torsion angles, least-squares-planes data and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54199 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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