Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

(Acetylacetonato)carbonyl[diallyl(*tert*-butyl)-phosphine]rhodium(I)

Edgar Ocando-Mavarez,[a]* Julián Ascanio,[a] Teresa González,[a] Reinaldo Atencio,[a] Merlín Rosales[b] and Ninoska Silva[a]

[a]Centro de Química, Instituto Venezolano de Investigaciones Científica (IVIC), Apartado 21827, Caracas 1020-A, Venezuela, and [b]La Universidad del Zulia, Facultad Experimental de Ciencias, Departamento de Química, Laboratorio de Química Inorgánica, Apartado 526, Maracaibo, Venezuela

Correspondence e-mail: eocando@ivic.ve

Received 7 July 2003
Accepted 16 July 2003
Online 24 July 2003

The crystal structure of the title compound, [Rh($C_5H_7O_2$)\-forcelb]($C_{10}H_{19}P$)(CO)], consists of discrete chiral molecules. The square-planar coordination geometry around Rh^I involves two O atoms of one acetylacetonate ligand, one carbonyl group and one P atom of a monodentate diallylphosphine. The double bonds of the allyl groups have a mutual π–π interaction.

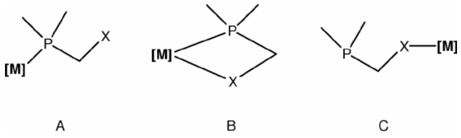
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.022
wR factor = 0.049
Data-to-parameter ratio = 14.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Transition metal complexes bearing functionalized phosphines are of interest because of their potential catalytic properties (Pruchnik *et al.*, 1998; Braunstein *et al.*, 2001; Appleby & Woollins, 2002; Jones *et al.*, 2002). In 1:1 complexes, β-functionalized phosphines can interact with the metal centre in three principal ways, as indicated in the *Scheme*.



In all these cases, the electronic and steric effects of the phosphine ligands may lead to transition metal complexes with useful new catalytic behaviour. As part of our work on the synthesis and reactivity of di-β-functionalized phosphines (Martín & Ocando-Mavarez, 1991; Ocando-Mavarez *et al.*, 1998), we have initiated studies on the use of diallyl-, dicyanomethyl- and dipropargylphosphines and their interactions with metal centres. Interestingly, a considerable group of 32 metal compounds containing monoallylphosphines have been structurally characterized, according to the Cambridge Structural Database (Version 5.24, with updates to April 2003; Allen, 2002). In contrast, only one crystal structure of a

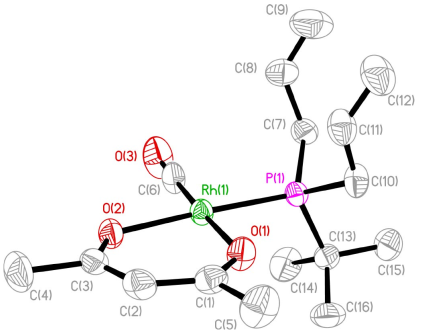
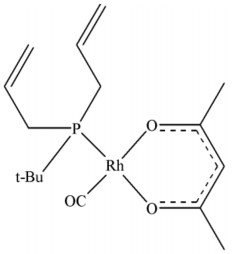


Figure 1
View of the title complex, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 35% probability level.

ruthenium complex (Jensen & Spicer, 2001) bearing a diallylphosphine is known so far. We report here the synthesis and crystal structure of the rhodium complex [(acac)Rh(CO)\-forcelb]{^{t}BuP(CH$_2$CH$=$CH$_2$)$_2$}] (acac is acetylacetonate), (I).



(I)

The crystal structure of (I) has one molecule in the asymmetric unit (Fig. 1). The complex has no molecular or crystallographic symmetry, and the chiral molecule crystallizes in space group $P2_12_12_1$. The square-planar coordination environment around the metal centre consists of two O atoms of one acetylacetonate ligand, one carbonyl group and one P atom of a monodentate diallylphosphine. All non-H atoms of the acac ligand, together with atoms Rh, P and C6, lie in a plane, with a mean deviation of only 0.0247 Å. The Rh1—P1 distance [2.2387 (8) Å] is shorter than that observed in the ruthenium complex (2.326 Å) reported previously (Jensen & Spicer, 2001). A slightly asymmetric coordination of the acac ligand is observed, in which the Rh1—O2 distance [2.082 (2) Å] is longer than that for Rh1—O1 [2.032 (2) Å]. This asymmetry may be attributed to a *trans*-influence of the phosphine ligand, as has previously been invoked by Jensen & Spicer (2001). The conformation adopted by both allyl groups places the double bonds far away from the metal centre, precluding any intramolecular interaction between these bonds and Rh$^{\rm I}$. It is noted, however, that the two allyl groups are approximately parallel to each other, with a centroid-to-centroid distance of only 3.569 Å, indicative of a π–π interaction.

Experimental

The synthesis of the diallylphosphine was carried out according to the procedure of Martín *et al.* (1992). Under vacuum (Burford *et al.*, 1994), 155 mg (0.911 mmol) of ^{t}BuP(CH$_2$CH$=$CH$_2$)$_2$ was distilled over a suspension of [(acac)Rh(CO)$_2$] (230 mg, 0.893 mmol) in CH$_2$Cl$_2$ (15 ml) and maintained under agitation at 195 K for 10 min. The cold bath was removed and the reaction mixture was stirred at room temperature for 30 min. The solvent was removed under vacuum and the solid residue was washed with pentane (5 ml) at 243 K, affording 310 mg [yield 87%; m.p. 351–353 K (with decomposition)] of a dark yellow solid. ^{1}H NMR (CDCl$_3$): 1.27 (*d*, $^3J_{\rm HP}$ = 14.19 Hz, 9H, ^{t}Bu), 1.86 (*s*, 3H, CH$_3$—acac), 2.04 (*s*, 3H, CH$_3$—acac), 2.67 (*m*, 2H, P—CH$_2$), 2.83 (*m*, 2H, P—CH$_2$), 5.14 (*m*, 4H, C$=$CH$_2$), 5.43 (*s*, H—acac), 6.01 (*m*, 2H, CH$=$C); ^{13}C NMR (CDCl$_3$): 27.13 (*s*, CH$_3$—acac), 27.64 (*bs*, CH$_3$—^{t}Bu), 27.92 (*d*, $^1J_{\rm CP}$ = 24.55 Hz, PCH$_2$), 32.99 (*d*, $^1J_{\rm CP}$ = 26.42 Hz, C—^{t}Bu), 100.53 (*s*, CH—acac), 118.52 (*s*, $=$CH$_2$), 132.20 (*s*, CH$=$), 184.88 (*s*, C—O—acac), 187.90 (*s*, C—O—acac), 189.80 (*dd*, $^1J_{\rm CRh}$ = 75.96 Hz, $^2J_{\rm CP}$ = 24.27 Hz, CO); ^{31}P NMR CDCl$_3$): 55.68 (*d*, $^1J_{\rm PRh}$ = 170.00 Hz); IR (cm^{-1}): 1962, 1579, 1520, 1378.

Crystal data

[Rh(C$_5$H$_7$O$_2$)(C$_{10}$H$_{19}$P)(CO)]
M_r = 400.25
Orthorhombic, $P2_12_12_1$
a = 11.970 (2) Å
b = 12.270 (3) Å
c = 12.758 (3) Å
V = 1873.7 (7) Å^3
Z = 4
D_x = 1.419 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 26.4–31.7°
μ = 1.00 mm^{-1}
T = 293 (2) K
Prism, yellow
0.36 × 0.30 × 0.15 mm

Data collection

Rigaku AFC-7*S* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min}$ = 0.766, $T_{\rm max}$ = 0.860
3098 measured reflections
2795 independent reflections
2580 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.013
$\theta_{\rm max}$ = 25.0°
$h = -10 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = -1 \rightarrow 15$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.049
S = 1.05
2795 reflections
190 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0248P)^2 + 0.2043P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.25 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.21 e Å^{-3}
Absolute structure: Flack (1983), 956 Friedel pairs
Flack parameter = −0.05 (3)

Table 1
Selected geometric parameters (Å, °).

Rh1—C6	1.797 (4)	C1—C5	1.490 (5)
Rh1—O1	2.036 (2)	C2—C3	1.395 (5)
Rh1—O2	2.082 (2)	C3—C4	1.500 (5)
Rh1—P1	2.2387 (8)	C7—C8	1.493 (5)
P1—C10	1.826 (3)	C8—C9	1.267 (7)
P1—C7	1.834 (3)	C10—C11	1.487 (5)
P1—C13	1.869 (3)	C11—C12	1.270 (6)
O1—C1	1.272 (4)	C13—C16	1.528 (5)
O2—C3	1.264 (4)	C13—C15	1.529 (5)
O3—C6	1.141 (4)	C13—C14	1.536 (5)
C1—C2	1.377 (5)		
C6—Rh1—O1	177.45 (14)	C7—P1—C13	103.08 (17)
C6—Rh1—O2	94.38 (13)	C10—P1—Rh1	111.84 (13)
O1—Rh1—O2	88.03 (10)	C7—P1—Rh1	117.82 (11)
C6—Rh1—P1	89.44 (12)	O3—C6—Rh1	178.8 (3)
O1—Rh1—P1	88.15 (7)	C8—C7—P1	115.5 (3)
O2—Rh1—P1	176.15 (7)	C9—C8—C7	125.3 (5)
C10—P1—C7	104.8 (2)	C11—C10—P1	115.2 (2)
C10—P1—C13	104.03 (16)	C12—C11—C10	126.0 (4)

All H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.96 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXTL-NT* (Bruker, 1998); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *SHELXTL-NT*; software used to prepare material for publication: *SHELXTL-NT*.

The authors thank FONACIT-MCT, Venezuela, for financial support (project Nos. S1-97001379 and LAB-9700821).

m634 Edgar Ocando-Mavarez *et al.* • [Rh(C$_5$H$_7$O$_2$)(C$_{10}$H$_{19}$P)(CO)] *Acta Cryst.* (2003). E**59**, m633–m635

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Appleby, T. & Woollins, J. D. (2002). *Coord. Chem. Rev.* **235**, 121–140.

Braunstein, P., Naud, F., Dedieu, A., Rohmer, M.-M., DeCian, A. & Rettig, S. (2001). *Organometallics*, **20**, 2966–2981.

Bruker (1998). *SHELXTL-NT*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Burford, N., Muller, J. & Parks, T. M. (1994). *J. Chem. Educ.* **71**, 807–809.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Jensen, S. B. & Spicer, M. D. (2001). *Acta Cryst.* E**57**, o978–o979.

Jones, N. G., Green, M. L. H., Vei, I., Cowley, A., Morize, X. & Braunstein, P. (2002). *J. Chem. Soc. Dalton Trans.* pp. 1487–1493.

Martín, G. & Ocando-Mavarez, E. (1991). *Heteroatom. Chem.* **2**, 651–654.

Martín, G., Ocando-Mavarez, E., Osorio, A., Laya, M. & Canestrari, M. (1992). *Heteroatom Chem.* **3**, 395–401.

Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1999). *TEXSAN.* Version 1.10. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Ocando-Mavarez, E., Rosales, M. & Silva, N. (1998). *Heteroatom. Chem.* **9**, 253–259.

Pruchnik, F. P., Smoleński, P. & Wajda-Hermanowicz, K. (1998). *J. Organomet. Chem.* **570**, 63–69.

Acta Cryst. (2003). E**59**, m633–m635 Edgar Ocando-Mavarez *et al.* • [Rh($C_5H_7O_2$)($C_{10}H_{19}P$)(CO)] **m635**