Crystal structure of [(1*R*)-(+)-3-benzoyl-camphoryl-*O*,*O*']cycloocta-1,5-diene)rhodium(I), $C_{25}H_{31}O_2Rh$

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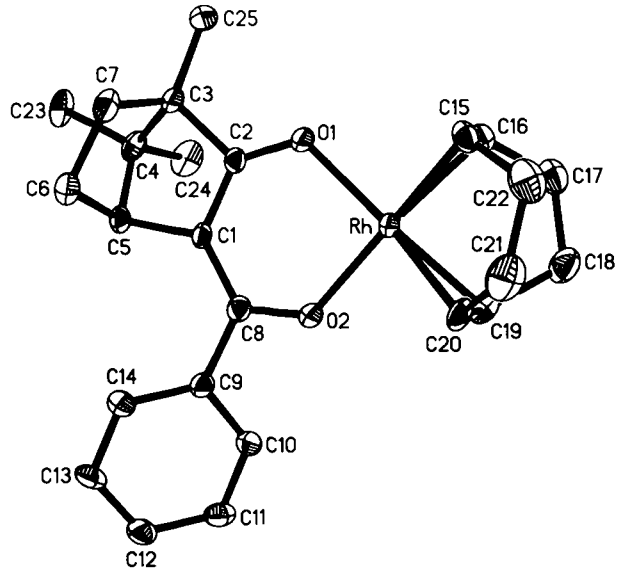

Abstract

$C_{25}H_{31}O_2Rh$, triclinic, $P\bar{1}$ (No. 1), $a = 6.406(1)$ Å, $b = 8.532(2)$ Å, $c = 10.226(2)$ Å, $\alpha = 72.38(3)°$, $\beta = 84.03(3)°$, $\gamma = 88.24(3)°$, $V = 529.8$ Å^3, $Z = 1$, $R_{gt}(F) = 0.033$, $wR_{obs}(F^2) = 0.101$, $T = 293$ K.

Source of material

$[Rh(COD)Cl]_2$ (0.75 mmol, 0.37 g) and (1*R*)-(+)-3-benzoylcamphor (1.65 mmol, 0.42 g) were mixed in 5 mL of diethylether and stirred for 15 min at room temperature. A solution of KOH (1g of KOH in 3 mL of H_2O) was then added and the stirring is continued for 30 min. When the reaction was achieved, 10 mL of diethylether was added and the precipitate was filtered. The organic phase was separated and the remaining aqueous phase was extracted with diethylether (5 × 5 mL). The combined extracts were dried over $MgSO_4$ and evaporated under reduced pressure. Pure yellow complex was crystallized from *n*-hexane (yield: 75%).

Discussion

Recently, several chiral, optically active rhodium complexes have been shown to be highly enantioselective catalysts in a variety of synthetic transformations [1-3]. In most cases, the catalyst is formed in situ from a suitable precursor and a chiral ligand. Often, and despite its successful application, reliable information about the very nature of the catalytically active species and its complexes with the substrate is not available.

As part of our study on natural complexes [4-6] and their application in the catalytic asymmetric reactions [7-8], we report here the preparation and crystal structure of the title compound. Its molecular structure shows there is an almost square-planar coordination geometry at the rhodium centre. The metal is coordinated by two oxygen atoms of the camphor-derived ligand and the double bonds of the cycloocta-1,5-diene.

Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.2 × 0.3 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.23 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 100 exposures, $\Delta\varphi = 2°$
$2\theta_{max}$:	48.62°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2854,2854
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 0\ \sigma(I_{obs})$, 2848
$N(param)_{refined}$:	257
Programs:	SHELXS-86 [9], SHELXL-93 [10]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(5)	2*i*	0.5337(9)	0.3525(8)	0.3850(6)	0.041
H(6A)	2*i*	0.872(1)	0.2900(9)	0.4716(7)	0.049
H(6B)	2*i*	0.780(1)	0.4227(9)	0.5416(7)	0.049
H(7A)	2*i*	0.7527(9)	0.2330(9)	0.7476(7)	0.051
H(7B)	2*i*	0.8556(9)	0.1029(9)	0.6789(7)	0.051
H(10)	2*i*	−0.017(1)	0.7073(8)	0.4381(6)	0.044
H(11)	2*i*	−0.010(1)	0.9166(8)	0.2324(7)	0.052
H(12)	2*i*	0.299(1)	0.9781(9)	0.0889(6)	0.054
H(13)	2*i*	0.606(2)	0.835(2)	0.152(1)	0.060
H(14)	2*i*	0.594(1)	0.6209(9)	0.3556(7)	0.049
H(17A)	2*i*	−0.384(1)	0.254(1)	1.1305(8)	0.064
H(17B)	2*i*	−0.405(1)	0.217(1)	0.9914(8)	0.064
H(18A)	2*i*	−0.400(1)	0.520(1)	1.0366(9)	0.072
H(18B)	2*i*	−0.514(1)	0.471(1)	0.9263(9)	0.072
H(21A)	2*i*	0.145(2)	0.682(1)	1.0133(9)	0.082
H(21B)	2*i*	−0.095(2)	0.699(1)	1.0550(9)	0.082
H(22A)	2*i*	−0.127(1)	0.446(1)	1.1822(8)	0.076
H(22B)	2*i*	0.114(1)	0.465(1)	1.1909(8)	0.076
H(23A)	2*i*	0.639(2)	−0.101(2)	0.510(1)	0.077
H(23B)	2*i*	0.808(2)	0.033(2)	0.499(1)	0.077
H(23C)	2*i*	0.675(2)	0.048(2)	0.376(1)	0.077
H(24A)	2*i*	0.270(1)	−0.053(1)	0.5448(8)	0.083
H(24B)	2*i*	0.268(1)	0.102(1)	0.4142(8)	0.083
H(24C)	2*i*	0.179(1)	0.114(1)	0.5594(8)	0.083
H(25A)	2*i*	0.599(1)	−0.1395(9)	0.7777(8)	0.082
H(25B)	2*i*	0.357(1)	−0.1047(9)	0.7972(8)	0.082
H(25C)	2*i*	0.511(1)	−0.0516(9)	0.8862(8)	0.082
H(16)	2*i*	−0.071(1)	0.1407(9)	1.0000(8)	0.01(1)
H(15)	2*i*	0.198(1)	0.2887(9)	1.0800(8)	0.01(1)
H(19)	2*i*	−0.255(1)	0.5605(9)	0.7604(8)	0.03(2)
H(20)	2*i*	0.039(1)	0.7190(9)	0.8000(8)	0.02(1)

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*	0.3825(8)	0.3600(7)	0.5793(6)	0.023(3)	0.031(3)	0.030(3)	0.003(2)	0.004(2)	–0.012(3)
C(2)	2*i*	0.3723(8)	0.2350(7)	0.7060(6)	0.021(3)	0.031(3)	0.034(3)	–0.001(2)	0.000(2)	–0.010(3)
C(3)	2*i*	0.5255(9)	0.1017(8)	0.6882(6)	0.028(3)	0.035(4)	0.031(3)	0.009(2)	0.002(2)	–0.009(3)
C(4)	2*i*	0.5045(9)	0.1138(8)	0.5347(7)	0.030(3)	0.043(4)	0.047(3)	0.006(3)	–0.007(3)	–0.028(3)
C(5)	2*i*	0.5431(9)	0.3004(8)	0.4838(6)	0.031(3)	0.043(4)	0.027(3)	0.005(3)	0.004(2)	–0.011(3)
C(6)	2*i*	0.759(1)	0.3141(9)	0.5335(7)	0.033(3)	0.046(4)	0.046(3)	–0.001(3)	0.003(3)	–0.018(3)
C(7)	2*i*	0.7440(9)	0.1832(9)	0.6747(7)	0.031(3)	0.060(5)	0.042(3)	0.009(3)	–0.006(2)	–0.022(3)
C(8)	2*i*	0.2697(9)	0.5087(8)	0.5532(6)	0.027(3)	0.037(4)	0.032(3)	0.003(2)	–0.005(2)	–0.010(3)
C(9)	2*i*	0.2845(9)	0.6379(8)	0.4182(6)	0.034(3)	0.032(4)	0.028(3)	0.006(2)	–0.002(2)	–0.010(3)
C(10)	2*i*	0.108(1)	0.7304(8)	0.3801(6)	0.042(3)	0.030(4)	0.035(3)	0.000(3)	0.001(2)	–0.007(3)
C(11)	2*i*	0.112(1)	0.8569(8)	0.2573(7)	0.056(4)	0.033(4)	0.038(3)	0.008(3)	–0.010(3)	–0.006(3)
C(12)	2*i*	0.297(1)	0.8941(9)	0.1720(6)	0.062(4)	0.040(4)	0.027(3)	0.006(3)	0.002(3)	–0.003(3)
C(13)	2*i*	0.480(2)	0.808(2)	0.209(1)	0.050(6)	0.040(7)	0.041(6)	–0.001(5)	–0.001(4)	0.013(5)
C(14)	2*i*	0.472(1)	0.6802(9)	0.3306(7)	0.046(4)	0.040(4)	0.032(3)	0.003(3)	0.000(3)	–0.003(3)
C(15)	2*i*	0.058(1)	0.323(1)	1.0644(8)	0.027(4)	0.056(6)	0.031(3)	–0.005(3)	0.001(3)	–0.005(4)
C(16)	2*i*	–0.101(1)	0.243(1)	1.0228(8)	0.033(4)	0.040(4)	0.032(3)	–0.002(3)	0.004(3)	–0.006(3)
C(17)	2*i*	–0.331(1)	0.284(1)	1.0337(8)	0.045(4)	0.065(5)	0.046(4)	–0.006(3)	0.002(3)	–0.013(4)
C(18)	2*i*	–0.382(1)	0.464(1)	0.9662(9)	0.037(4)	0.053(5)	0.085(6)	0.004(3)	0.006(4)	–0.019(5)
C(19)	2*i*	–0.208(1)	0.556(1)	0.851(1)	0.037(5)	0.039(5)	0.052(5)	0.015(4)	–0.005(3)	–0.019(4)
C(20)	2*i*	–0.040(1)	0.628(1)	0.8822(9)	0.048(5)	0.032(4)	0.060(5)	0.007(4)	0.013(4)	–0.026(4)
C(21)	2*i*	0.008(2)	0.631(1)	1.0223(9)	0.074(6)	0.067(6)	0.081(6)	0.000(4)	–0.005(4)	–0.049(6)
C(22)	2*i*	0.009(1)	0.465(1)	1.1285(8)	0.068(5)	0.080(7)	0.046(4)	–0.008(4)	–0.006(4)	–0.025(5)
C(23)	2*i*	0.672(2)	0.014(2)	0.474(1)	0.052(6)	0.061(8)	0.055(7)	0.011(6)	0.013(5)	–0.046(7)
C(24)	2*i*	0.285(1)	0.065(1)	0.5110(8)	0.047(4)	0.063(5)	0.070(5)	–0.001(3)	–0.013(3)	–0.040(4)
O(1)	2*i*	0.2689(9)	0.2248(7)	0.8207(5)	0.034(4)	0.039(4)	0.027(3)	0.013(3)	0.001(3)	–0.007(2)
O(2)	2*i*	0.1380(9)	0.5430(7)	0.6443(5)	0.039(4)	0.032(3)	0.032(3)	0.010(3)	0.004(3)	–0.007(2)
Rh	2*i*	0.0635[a]	0.4085[a]	0.8459[a]	0.0270(2)	0.0298(2)	0.0252(2)	0.0050(1)	0.0022(1)	–0.0089(2)
C(25)	2*i*	0.495(1)	–0.0637(9)	0.7973(8)	0.057(4)	0.035(4)	0.055(4)	0.016(3)	0.013(3)	0.003(4)

a: arbitrarily fixed for definition of origin.

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