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Chloro(1-{3-[2-(diphenylphosphanyl-κP)ethyl]-η^6-benzyl}-3,5-dimethyl-1*H*-pyrazole-κN^2)ruthenium(II) trifluoromethanesulfonate

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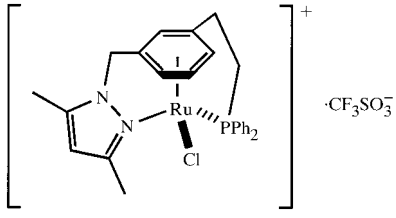
To address the question of the role of chirality at the metal in enantioselective catalysis, a pseudo-tetrahedral three-legged piano-stool complex has been prepared, *i.e.* $[RuCl(C_{26}H_{27}N_2P)](CF_3SO_3)$. Anchoring a phosphine and a pyrazole tether to an arene (PArN) yields, after η^6:η^1:η^1 coordination to ruthenium, $[\{\eta^6{:}\eta^1{:}\eta^1\text{-(PArN)}\}RuCl]^+$ as a 1:1 mixture of



(I)

enantiomers. Unfortunately, all attempts to resolve the enantiomers failed. The structure solution revealed the presence of racemic crystals.

Experimental

The synthesis of the ParN(CH_3) ligand, *i.e.* 1-{3-[2-(diphenylphosphanyl)ethyl]benzyl}-3,5-dimethyl-1*H*-pyrazole, is analogous to the synthesis of PArN(CF_3) (Therrien & Ward, 1999). Replacing the bis(trifluoromethyl)pyrazole by 3,5-dimethylpyrazole affords the corresponding ligand. Only its coordination to ruthenium is fully described. To a dichloromethane solution (25 ml) of $[RuCl_2(\eta^6\text{-}C_6H_5CO_2Et)]_2$ (0.129 g, 0.20 mmol), PArN(CH_3) (0.160 g, 0.40 mmol) was added. The mixture was stirred for 20 min. The volume was reduced to 10 ml and the product precipitated with hexane to afford quantitatively $[RuCl_2(\eta^6\text{-}C_6H_5CO_2Et)\{\eta^1\text{-ParN}(CH_3)\}]$. ^{1}H NMR ($CDCl_3$): 7.9–7.8 (*m*, 4H), 7.52 (*m*, 6H), 7.04 (*t*, 1H), 6.84 (*m*, 1H), 6.71 (*s*, 2H), 6.34 (*d*, 2H), 5.79 (*s*, 1H), 5.46 (*s*, 1H), 5.06 (*s*, 4H), 4.30 (*m*, 2H), 2.86 (*m*, 2H), 2.39 (*m*, 2H), 2.19 (*s*, 3H), 2.16 (*s*, 3H), 1.34 p.p.m. (*t*, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$): 23.2 p.p.m. Into a 25 ml pressure Schlenk flask was introduced $[RuCl_2(\eta^6\text{-}C_6H_5CO_2Et)\{\eta^1\text{-ParN}(CH_3)\}]$ (0.180 g, 0.25 mmol) in dichloromethane (10 ml). After three freeze–pump–thaw cycles, the solution was heated at 393 K for 48 h, cooled to room temperature and the product precipitated with hexane (200 ml). The yellow–orange solid was filtered off and washed with ether. Purification by flash chromatography with CH_2Cl_2–MeOH (20:1), yielded $[RuCl_2\{\eta^6{:}\eta^1\text{-ParN}(CH_3)\}]$ (0.038 g, 0.07 mmol, 27%). ^{1}H NMR ($CDCl_3$): 7.82 (*m*, 2H), 7.64 (*m*, 2H), 7.39 (*m*, 6H), 5.89 (*dd*, 1H), 5.85 (*s*, 1H), 5.71 (*d*, 1H), 5.36 (*d*, 1H), 5.16 (*d*, 1H), 5.03 (*d*, 1H), 4.68 (*s*, 1H), 3.49 (*m*, 2H), 2.53 (*m*, 2H), 1.64 (*s*, 3H), 1.27 p.p.m. (*s*, 3H). ^{31}P {^{1}H} NMR ($CDCl_3$): 46.2 p.p.m. To a $CHCl_3$ solution (5 ml) of $[RuCl_2\{\eta^6{:}\eta^1\text{-ParN}(CH_3)\}]$ (300 mg, 0.51 mmol), $AgOSO_2CF_3$ (180 mg, 0.51 mmol) was added. The mixture was stirred at room temperature for 24 h. After filtration through Celite, the solution was evaporated to dryness to afford quantitatively $[RuCl\{\eta^6{:}\eta^1{:}\eta^1\text{-ParN}(CH_3)\}](OSO_2CF_3)$. After a week at room temperature in $CHCl_3$, crystals suitable for X-ray analysis were obtained. ^{1}H NMR ($CDCl_3$): 8.03 (*m*, 2H), 7.7–7.1 (*m*, 8H), 6.79 (*s*, 1H), 6.33 (*br*, 1H), 6.21 (*d*, 1H), 5.66 (*s*, 1H), 5.53 (*d*, 1H), 5.18 (*d*, 1H), 4.69 (*d*, 1H), 3.81 (*m*, 1H), 3.48 (*m*, 1H), 3.18 (*m*, 1H), 2.91 (*m*, 1H), 1.44 (*s*, 3H), 1.26 p.p.m (*s*, 3 H). ^{31}P {^{1}H} NMR ($CDCl_3$): 47.4 p.p.m.

Crystal data

$[RuCl(C_{26}H_{27}N_2P)](CF_3O_3S)$	$Z = 2$
$M_r = 684.06$	$D_x = 1.637$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 9.3674$ (3) Å	Cell parameters from 3988 reflections
$b = 11.0111$ (3) Å	$\theta = 1.50$–$26.39°$
$c = 13.6724$ (4) Å	$\mu = 0.847$ mm^{-1}
$\alpha = 94.198$ (1)°	$T = 293$ (2) K
$\beta = 92.139$ (1)°	Plate, orange
$\gamma = 98.968$ (1)°	0.42 × 0.11 × 0.08 mm
$V = 1387.57$ (7) Å^3	

Data collection

Siemens SMART CCD diffractometer	4074 reflections with $I > 2\sigma(I)$
ω scans, 1271 frames, 0.30°, 20 s, detector distance 5.5 cm, detector angle 23.0°	$R_{int} = 0.039$
	$\theta_{max} = 26.39°$
	$h = -11 \rightarrow 11$
	$k = -13 \rightarrow 7$
6978 measured reflections	$l = -16 \rightarrow 15$
5008 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0109P)^2 + 4.6884P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.051$	
$wR(F^2) = 0.120$	
$S = 1.183$	$(\Delta/\sigma)_{max} < 0.001$
5008 reflections	$\Delta\rho_{max} = 0.54$ e Å^{-3}
356 parameters	$\Delta\rho_{min} = -0.84$ e Å^{-3}
H-atom parameters constrained	

Data collection: *SMART* (Siemens 1994–1996); cell refinement: *SAINT* (Siemens 1994–1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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