

## Di- $\mu$ -pivalamidato-bis[dicarbonyl(triphenyl-phosphine)ruthenium(II)](Ru—Ru)

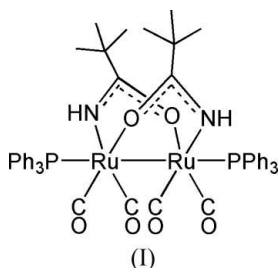
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The title dinuclear ruthenium complex,  $[\text{Ru}_2(\text{C}_5\text{H}_{19}\text{NO})_2(\text{C}_{18}\text{H}_{15}\text{P})_2(\text{CO})_4]$ , has been synthesized from  $\text{Ru}_3(\text{CO})_{12}$ , pivalamide and triphenylphosphine. The structure shows a  $\text{Ru}_2(\text{CO})_4$  sawhorse backbone with the two OCNH bridges being transoid with respect to each other.

### Comment

Sawhorse-type ruthenium complexes possessing carboxylate bridges have been known since 1969 (Crooks *et al.*, 1969). However, the corresponding carboxamide-bridged complexes were synthesized only 20 years later (Neumann *et al.*, 1989). We report here the synthesis of a new carbamide  $\text{Ru}_2(\text{CO})_4$  sawhorse-type complex,  $[\text{Ru}_2(\text{CO})_4(\text{HNOC}^t\text{Bu})_2(\text{PPh}_3)_2]$ , (I).



Dodecacarbonyltriruthenium reacts with pivalamide in refluxing tetrahydrofuran to give, in the presence of triphenylphosphine, the dinuclear complex (I) in good yield. The compound is air-stable and shows in the IR spectrum the typical CO bands [2013 (*s*), 1969 (*m*) and 1942  $\text{cm}^{-1}$  (*s*)] and carbamide bridge band [1567  $\text{cm}^{-1}$  (*s*)]. The  $^{31}\text{P}$  NMR shows a singlet at 19.8 p.p.m. corresponding to the two equivalent triphenylphosphine groups.

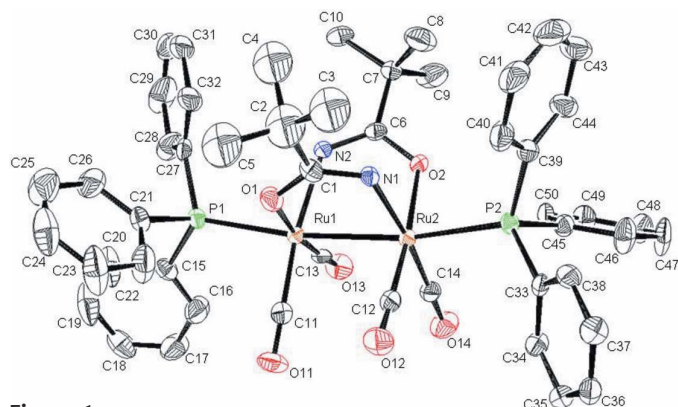


Figure 1

The molecular structure of  $[\text{Ru}_2(\text{CO})_4(\text{HNOC}^t\text{Bu})_2(\text{PPh}_3)_2]$ . Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

The single-crystal X-ray structure analysis of (I) reveals a typical  $\text{Ru}_2(\text{CO})_4$  sawhorse backbone with two *tert*-butylcarbamide bridges, the Ru—Ru distance [2.7330 (4) Å] being in the range of a Ru—Ru single bond, as observed in the analogous complexes  $[\text{Ru}_2(\text{CO})_4(\text{HNOCPh})_2(\text{MeCN})_2]$  (Neumann *et al.*, 1989) and  $[\text{Ru}_2(\text{CO})_4(\text{NC}_5\text{H}_4\text{O})_2(\text{PPh}_3)_2]$  (Sherlock *et al.*, 1989). The two phosphine ligands are in axial positions opposite the Ru—Ru bonds. Both Ru—P distances [2.4118 (9) and 2.4154 (9) Å] are slightly shorter than that observed in  $[\text{Ru}_2(\text{CO})_4(\text{NC}_5\text{H}_4\text{O})_2(\text{PPh}_3)_2]$  [2.440 (1) and 2.450 (1) Å; Sherlock *et al.*, 1989]. The *tert*-butylcarbamide ligands are in a head-to-tail arrangement, as observed in the analogous complex  $[\text{Ru}_2(\text{CO})_4(\text{HNOCPh})_2(\text{MeCN})_2]$  (Neumann *et al.*, 1989). The CO distances and remaining structural parameters appear to be normal for this type of complex (Neumann *et al.*, 1989; Sherlock *et al.*, 1989; Andreu *et al.*, 1991).

### Experimental

All manipulations were carried out under a nitrogen atmosphere. Organic solvents were degassed and saturated with nitrogen prior to use. Pivalamide was purchased from Aldrich and used as received. Dodecacarbonyltriruthenium (Kaes, 1989) was prepared according to published methods. A solution of  $\text{Ru}_3(\text{CO})_{12}$  (100 mg, 0.16 mmol) and pivalamide (50 mg, 0.49 mmol) in dry tetrahydrofuran (25 ml) was heated at 393 K in a pressure Schlenk tube for 4 h. The solvent was then evaporated to give a yellow-brown residue which was dissolved in tetrahydrofuran and triphenylphosphine (123 mg, 0.47 mmol) was added. The solution was stirred at room temperature for 2 h, evaporated and the product isolated from the residue by crystallization from a tetrahydrofuran/hexane mixture. In order to improve the purity, the raw product was subjected to chromatography on silica gel using dichloromethane as eluent, giving a yellow-brown powder (138 mg). Crystals were obtained by slow diffusion of hexane into a chloroform solution containing (I).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.68–7.52 (*m*, 12H,  $\text{H}_{\text{ar}}$ ), 7.48–7.37 (*m*, 18H,  $\text{H}_{\text{ar}}$ ), 4.83 (*br*, 2H, NH), 0.65 (*s*, 18H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  206.28 (2C, CONH), 188.98 (4C, CO), 133.76 (6C,  $\text{C}_{\text{ar}}$ ), 129.53 (12C,  $\text{C}_{\text{ar}}$ ), 128.42 (18C,  $\text{C}_{\text{ar}}$ ), 39.41 [2C,  $\text{C}(\text{CH}_3)_3$ ], 28.19 [6C,  $\text{C}(\text{CH}_3)_3$ ].  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.82. IR (CaF<sub>2</sub>, THF): 2013 (*s*, CO), 1969 (*m*), 1942 (*s*), 1567 (*s*, OCNH)  $\text{cm}^{-1}$ .

### Crystal data

$[\text{Ru}_2(\text{C}_5\text{H}_{19}\text{NO})_2(\text{C}_{18}\text{H}_{15}\text{P})_2(\text{CO})_4]$   
 $M_r = 1039.05$   
 Monoclinic,  $P2_1/c$   
 $a = 15.5453$  (12) Å  
 $b = 17.5491$  (14) Å  
 $c = 18.1924$  (12) Å  
 $\beta = 108.262$  (8)°  
 $V = 4713.0$  (6) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.464$  Mg  $\text{m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 7998 reflections  
 $\theta = 2.4$ – $25.9^\circ$   
 $\mu = 0.76$   $\text{mm}^{-1}$   
 $T = 173$  (2) K  
 Rod, yellow  
 $0.45 \times 0.24 \times 0.12$  mm

### Data collection

Stoe IPDS diffractometer	8729 independent reflections
$\varphi$ scans	5326 reflections with $I > 2\sigma(I)$
Absorption correction: refined from $\Delta F$ (DIFABS; Walker & Stuart, 1983)	$R_{\text{int}} = 0.067$
$T_{\text{min}} = 0.620$ , $T_{\text{max}} = 0.887$	$\theta_{\text{max}} = 25.9^\circ$
36846 measured reflections	$h = -19 \rightarrow 18$
	$k = -21 \rightarrow 21$
	$l = -20 \rightarrow 20$

### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.034$	$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2]$
$wR(F^2) = 0.068$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.83$	$(\Delta/\sigma)_{\text{max}} = 0.009$
8729 reflections	$\Delta\rho_{\text{max}} = 0.78 \text{ e } \text{\AA}^{-3}$
565 parameters	$\Delta\rho_{\text{min}} = -0.70 \text{ e } \text{\AA}^{-3}$

H atoms were included in calculated positions (N–H = 0.88, C–H = 0.95 or 0.98 Å) and refined as riding atoms, with  $U_{\text{iso}}(\text{H}) = 1.2$  or 1.5 times  $U_{\text{eq}}(\text{C}, \text{N})$ . In the structure, one *tert*-butyl group (C2–C5) displays elongated ellipsoids, suggesting the presence of disorder. However, an attempt to treat a disordered *tert*-butyl group over two sites did not give satisfactory results and no reliable models could be produced. The anisotropic displacement parameters for the three C atoms were then refined using some rigid bond restraints. The large elongated displacement ellipsoids certainly reflect a partial free rotation of the three C atoms around the C–C axis.

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 2000); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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