metal-organic papers

Dibromodicarbonylbis(triphenylphosphine)-ruthenium(II) dichloromethane solvate

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Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.008 Å
R factor = 0.038
wR factor = 0.090
Data-to-parameter ratio = 14.3

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

The title mononuclear ruthenium compound, [RuBr$_2$(CO)$_2$(PPh$_3$)$_2$]·CH$_2$Cl$_2$, has been prepared by a new synthetic route; it is the last complex of the series [RuX$_2$(CO)$_2$(PPh$_3$)$_2$] (X = F, Cl, Br, I) to be characterized by X-ray structure analysis. As expected, the cis–Br$_2$-cis-(CO)$_2$-$trans$-(PPh$_3$)$_2$ configuration is observed around the metal.

Comment

Ruthenium–carbonyl–halide compounds have been known for more than 75 years (Manchot & König, 1924). Their phosphine derivatives are directly accessible by reacting the desired ligand with [RuX$_2$(CO)$_2$] (X = F, Cl, Br and I) in methanol, affording the corresponding hexacoordinated complexes [RuX$_2$(CO)$_2$L$_2$] in good yield (Colton & Farthing, 1967). The triphenylphosphine series has been extensively studied by different groups, $e.g.$ [RuF$_2$(CO)$_2$(PPh$_3$)$_2$], (1) (Brewer $et\ al.$, 1995), [RuCl$_2$(CO)$_2$(PPh$_3$)$_2$], (2) (Batista $et\ al.$, 1994), the [RuBr$_2$(CO)$_2$(PPh$_3$)$_2$], (3), and [RuI$_2$(CO)$_2$(PPh$_3$)$_2$], (4) (Poza $et\ al.$, 1987). Their molecular structures have been determined by single-crystal X-ray analysis, except in the case of the bromo derivative, (3). Here, we report a new synthetic route and the X-ray structure analysis of [RuBr$_2$(CO)$_2$(PPh$_3$)$_2$], (3).
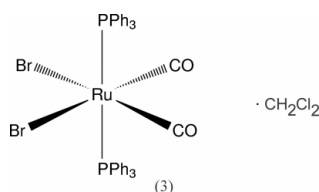
A mixture (1:1) of NiBr$_2$(PPh$_3$)$_2$ and Ru$_3$(CO)$_{12}$ in tetrahydrofuran at 358 K (closed reactor) affords compound (3) in reasonable yield. The molecular structure of (3) is presented in Fig. 1. The compound crystallizes with one molecule of CH$_2$Cl$_2$ per asymmetric unit.

As observed for analogs (1), (2) and (4), the cis (CO), cis (Br), $trans$ (PPh$_3$) isomer is formed. The bond lengths and angles are in accordance with the trend in covalent radius of the halide atoms. The Ru—Br distances 2.5927 (6) and 2.5940 (6) Å fall in between Ru—Cl and Ru—I [Ru—Cl 2.426 (1) and 2.453 (1) Å (Batista $et\ al.$, 1994), and Ru—I 2.767 (1) and 2.772 (1) Å (Poza $et\ al.$, 1987)], as expected. The influence of the halide $trans$ to the carbonyl is reflected in the ruthenium–carbonyl distances: the Ru—C distances (average) increase in the order of F < Cl < Br < I, with distances 1.841, 1.860, 1.875 and 1.885 Å, respectively. Otherwise, distances and angles are comparable with those of the analogs (1), (2) and (4). Selected bond lengths and angles are given in Table 1.
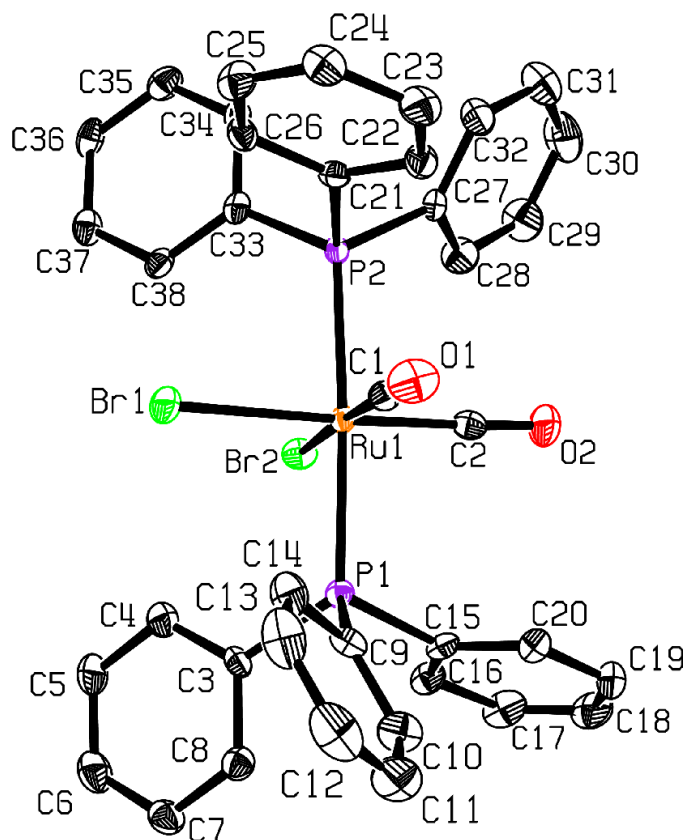
Figure 1
The molecular structure of (3); H atoms and the CH_2Cl_2 solvent molecule have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

A mixture of $Ru_3(CO)_{12}$ (64 mg, 0.1 mmol) and $NiBr_2(PPh_3)_2$ (70 mg, 0.1 mmol) was dissolved in tetrahydrofuran (40 ml) under an N_2 atmosphere using a high-pressure Schlenk tube. The solution was heated to 358 K for 16 h, until it became red–brown, and the characteristic $Ru_3(CO)_{12}$ absorption at $\nu_{CO} = 2061$ cm^{-1} was no longer observed in the IR spectrum. Then the solution was cooled, concentrated to 1 ml and chromatographed on silica thin-layer chromatography plates (4:1 cyclohexane/dichloromethane). The third yellow–orange band was collected, to afford (3) in 46% yield. ^{1}H NMR (200 MHz, CDCl$_3$): 7.8–7.2 (m, 30H). ^{31}P NMR (81 MHz, CDCl$_3$): 36.2 (s). IR (KBr, cm^{-1}, ν_{CO}): 2058 (s), 1984 (s).

Crystal data

[RuBr$_2$(CO)$_2$(PPh$_3$)$_2$]·CH$_2$Cl$_2$	$D_x = 1.622$ Mg m^{-3}
$M_r = 926.38$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 8000
$a = 10.2056 (6)$ Å	reflections
$b = 40.436 (3)$ Å	$\theta = 2.0$–$25.9°$
$c = 10.3584 (6)$ Å	$\mu = 2.78$ mm^{-1}
$\beta = 117.423 (6)°$	$T = 153 (2)$ K
$V = 3794.3 (4)$ Å^3	Block, yellow
$Z = 4$	$0.45 \times 0.25 \times 0.25$ mm

Data collection

Stoe IPDS diffractometer	4461 reflections with $I > 2\sigma(I)$
φ scans	$R_{int} = 0.050$
Absorption correction: multi-scan	$\theta_{max} = 25.9°$
(Blessing, 1995)	$h = -12 \rightarrow 11$
$T_{min} = 0.339$, $T_{max} = 0.407$	$k = -49 \rightarrow 49$
15317 measured reflections	$l = -12 \rightarrow 12$
6181 independent reflections	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.038$	$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2]$
$wR(F^2) = 0.090$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.93$	$(\Delta/\sigma)_{max} = 0.001$
6181 reflections	$\Delta\rho_{max} = 1.12$ e Å^{-3}
433 parameters	$\Delta\rho_{min} = -0.87$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—O1	1.140 (6)	P1—Ru1	2.4215 (12)
C1—Ru1	1.880 (5)	P2—Ru1	2.4255 (12)
C2—O2	1.131 (6)	Br1—Ru1	2.5940 (6)
C2—Ru1	1.871 (5)	Br2—Ru1	2.5927 (6)
O1—C1—Ru1	179.0 (5)	P1—Ru1—P2	175.94 (4)
O2—C2—Ru1	178.0 (4)	Br2—Ru1—Br1	98.48 (2)
C2—Ru1—C1	91.2 (2)		

The H atoms were included in calculated positions and treated as riding atoms. Residual electron densities greater than 1 e Å^{-3} are observed around the Ru atom at a distance of 0.93 Å.

Data collection: *EXPOSE* in *IPDS* (Stoe & Cie, 2000); cell refinement: *CELL* in *IPDS*; data reduction: *INTEGRATE* in *IPDS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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