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Synthesis, structure, and reactions of a bimetallacyclic carbene complex of ruthenium, $\overline{RuBr_2(CO)[=C(C_6H_4PPh_2)_2]}$

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Abstract

Reaction of $Ru(CF_3)Br(CO)_2(PPh_3)_2$ with an excess of BBr_3 produces a red salt identified as $[\overline{RuBr(CO)_2\{=C(C_6H_4PPh_2)_2\}}]BBr_4$. Upon standing this solid loses CO and BBr_3, to form $\overline{RuBr_2(CO)[=C(C_6H_4PPh_2)_2]}$, A, the structure of which has been determined by X-ray diffraction. The geometry about ruthenium is approximately octahedral, with the two phosphorus atoms of the tridentate bisphosphinocarbene ligand mutually *trans*, and one bromide *trans* to the carbene carbon. The other bromide and the carbonyl ligand are statistically interchanged about a crystallographic diad axis which passes through the carbene carbon, the ruthenium, and the *trans* bromide. The Ru–P distance is 2.353(2) Å, the Ru–Br distances are 2.638(2) Å (*trans* to carbene) and 2.537(2) Å (*trans* to CO), and the Ru=C(carbene) distance is 1.941(12) Å. Bromide is removed from compound A by treatment with $AgSbF_6$ in MeCN to give $[\overline{RuBr(CO)(CH_3CN)\{=C(C_6H_4PPh_2)_2\}}]SbF_6$, and this when treated with CO gives $[\overline{RuBr(CO)_2\{=C(C_6H_4PPh_2)_2\}}]SbF_6$. The dicarbonyl cation reacts with $NaBH_4$ to give $\overline{RuBr(CO)_2[CH(C_6H_4PPh_2)_2]}$, and with $HNEt_2$ to give $\overline{RuBr(CO)_2[C(NEt_2)(C_6H_4PPh_2)_2]}$.

Introduction

In a number of cases, reaction between boron trihalides and transition metal complexes containing a metal-bound trifluoromethyl ligand results in exchange of fluorine to give a new trihalomethyl complex [1,2]. This exchange is specific for fluorines on the carbon α to the metal, e.g.:

$$Mn(CF_3)(CO)_5 \xrightarrow{BCl_3} Mn(CCl_3)(CO)_5$$

$$Re(CF_2CF_3)(CO)_5 \xrightarrow{BCl_3} Re(CCl_2CF_3)(CO)_5$$

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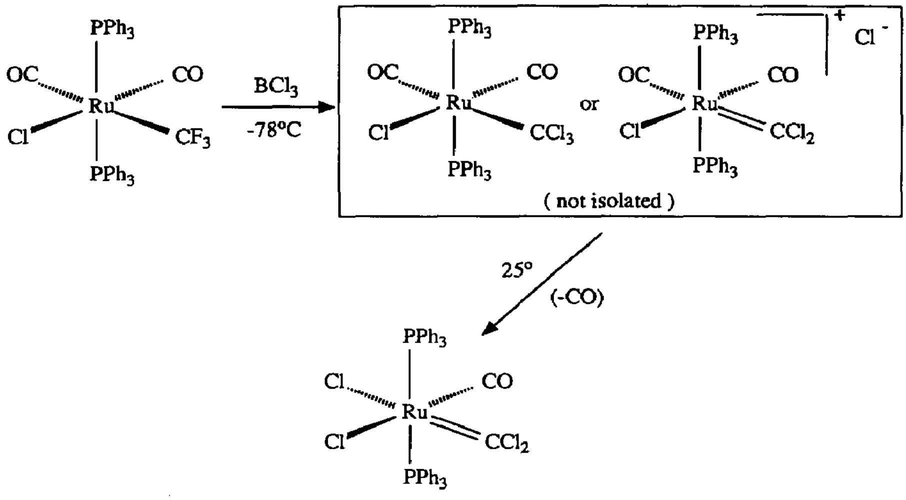


The mechanism of this halide exchange is not known with certainty, but a stepwise process involving a cationic intermediate, $[L_nM{=}CX_2]^+$, with a BX_4^- counterion is likely, viz.:

$$L_nM{-}CF_3 + BCl_3 \rightarrow [L_nM{=}CF_2]^+[BCl_3F]^- \rightarrow L_nM{-}CF_2Cl + BCl_2F$$

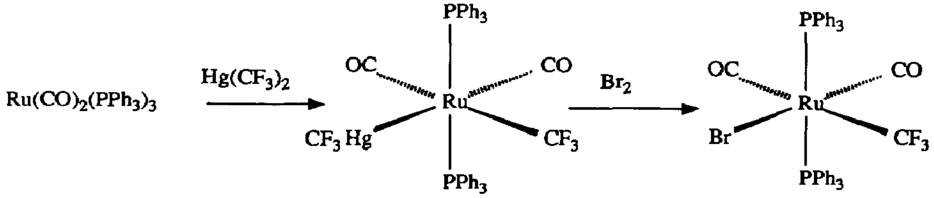
$$\xrightarrow{\text{etc.}} \xrightarrow{\text{etc.}} L_nM\text{-}CCl_3$$

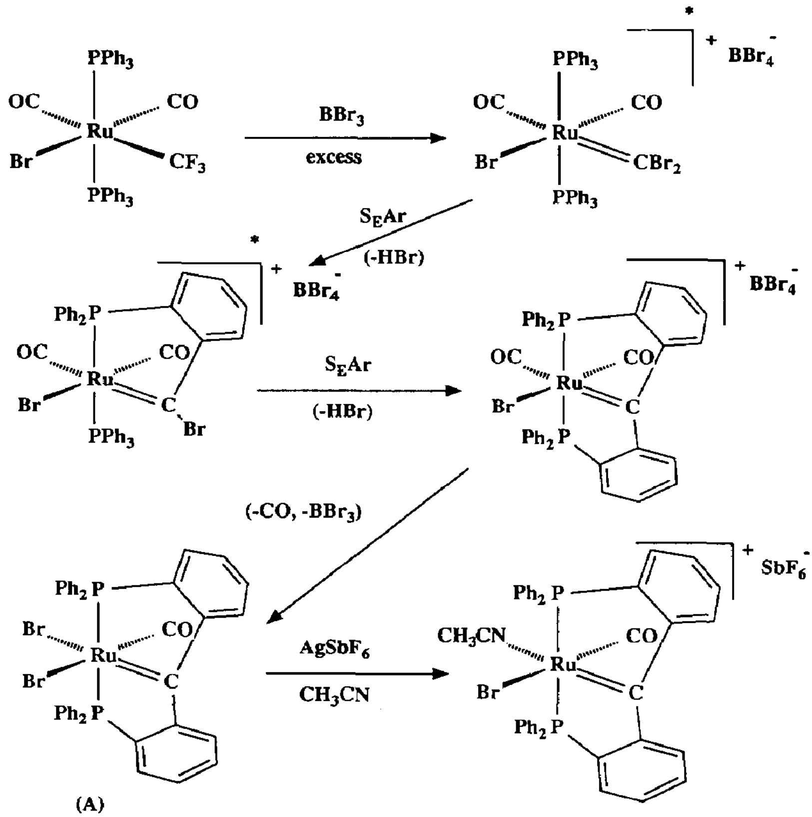
An example of this process is the reaction of $Ru(CF_3)Cl(CO)_2(PPh_3)_2$ [3], with BCl_3, which leads in high yield [4] to the known dichlorocarbene complex $RuCl_2(=CCl_2)(CO)(PPh_3)_2$ [5].

In an endeavour to use this approach for the synthesis of previously unknown dibromocarbene complexes of ruthenium the reaction between a trifluoromethyl complex of ruthenium and boron tribromide was examined, and the results are reported below. Some of these results have been mentioned briefly in a review [6].

Results and discussion

To avoid complications resulting from mixtures of different halide ligands the compound $Ru(CF_3)Br(CO)_2(PPh_3)_2$ was chosen for reactions with BBr_3. This compound was prepared from $Ru(CF_3)(HgCF_3)(CO)_2(PPh_3)_2$ [3] through reaction with Br_2.





(* intermediates not isolated)

Scheme 1

Reaction between $Ru(CF_3)Br(CO)_2(PPh_3)_2$ and 1 equivalent of BBr_3

When $Ru(CF_3)Br(CO)_2(PPh_3)_2$ was treated with approximately one equivalent of BBr_3 a bright orange product was isolated, but could not be purified. However, from the similarity of the IR spectrum to that of $RuCl_2(=CCl_2)(CO)(PPh_3)_2$ [5], and from further reactions, it was clearly a mixture of $RuBr_2(CO)_2(PPh_3)_2$, $RuBr_2(=CFBr)(CO)(PPh_3)_2$ (mostly), and possibly smaller amounts of other dihalocarbene complexes. Reaction with water produced exclusively $RuBr_2(CO)_2$-$(PPh_3)_2$, and reaction with Me_2NH gave substantial amounts of $RuBr_2(=CFNMe_2)$-$(CO)(PPh_3)_2$. A related compound, $RuCl_2(=CFNMe_2)(CO)(PPh_3)_2$, has previously been prepared by reaction between $RuCl_2(=CF_2)(CO)(PPh_3)_2$ and Me_2NH [3].

Reaction between $Ru(CF_3)Br(CO)_2(PPh_3)_2$ and excess BBr_3

Increasing the amount of BBr_3 used in the reaction with $Ru(CF_3)Br(CO)_2(PPh_3)_2$ afforded a dark orange solid, which fumed in moist air and had an IR spectrum compatible with a salt-like material (ν(CO) at 2080, 2020 cm^{-1}, appropriate for a cation; and ν(B–Br) at 605 cm^{-1} for BBr_4^-). Upon standing this solid lost CO and

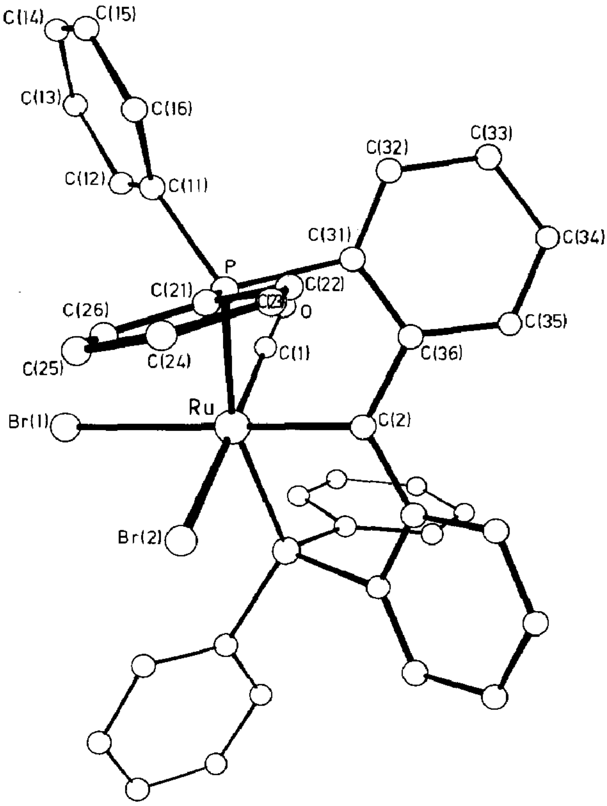


Fig. 1. The molecular geometry and atomic numbering scheme for $\overline{RuBr_2(CO)[=C(C_6H_4PPh_2)_2]}$. Only one of the alternative positions for Br(2), C(1) and O is depicted.

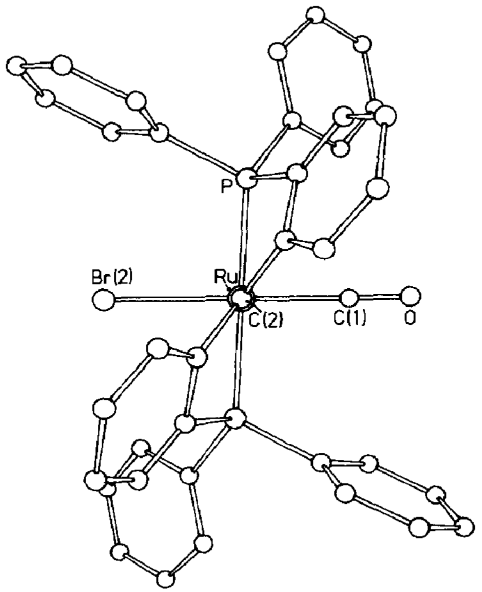


Fig. 2. View of the molecule looking down the C(2)–Ru–Br(1) direction. Br(1) is obscured. Only one of the alternative positions for Br(2), C(1) and O is depicted.

Table 1

Selected bond distances (Å) and angles (°) for $RuBr_2(CO)[=C(C_6H_4PPh_2)_2]$

Ru–Br(1)	2.638(2)	P–C(11)	1.826(9)
Ru–Br(2)	2.537(2)	P–C(21)	1.816(9)
Ru–P	2.353(2)	P–C(31)	1.831(9)
Ru–C(1)	2.00	C(1)–O	1.15
Ru–C(2)	1.941(12)	C(2)–C(36)	1.471(10)
Br(1)–Ru–Br(2)	89.8(1)	C(11)–P–C(21)	103.2(4)
Br(1)–Ru–P	99.0(1)	C(11)–P–C(31)	106.9(4)
Br(1)–Ru–C(1)	89.4	C(21)–P–C(31)	103.3(4)
Br(1)–Ru–C(2)	180.0	Ru–C(2)–C(36)	119.7(5)
Br(2)–Ru–P	94.3(1)	P–C(11)–C(12)	118.6(7)
Br(2)–Ru–C(1)	179.6	P–C(11)–C(16)	119.6(7)
Br(2)–Ru–C(2)	90.2(1)	C(12)–C(11)–C(16)	121.7(9)
P–Ru–P′	162.0(1)	P–C(21)–C(22)	121.9(7)
P–Ru–C(1)	94.1	P–C(21)–C(26)	118.0(7)
P–Ru–C(2)	81.0(1)	C(22)–C(21)–C(26)	120.0(9)
C(1)–Ru–C(2)	90.6	P–C(31)–C(32)	126.0(7)
Ru–P–C(11)	127.8(3)	P–C(31)–C(36)	112.3(6)
Ru–P–C(21)	115.3(3)	C(32)–C(31)–C(36)	121.7(8)
Ru–P–C(31)	97.4(3)		

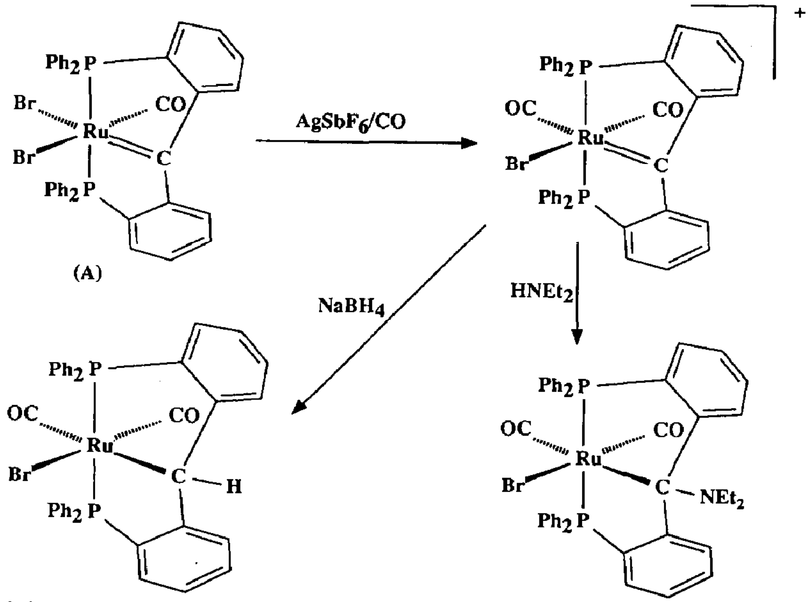
BBr_3 to form a purple compound, which was shown by an X-ray crystal structure determination to be the bicyclic complex $RuBr_2(CO)[=C(C_6H_4PPh_2)_2]$ (**A**). A possible sequence of steps involved in the formation of **A**, based upon precedents for electrophilic dihalocarbene ligands participating in metallacycle formation [7], is depicted in Scheme 1.

X-Ray crystal structure

The molecular geometry of $RuBr_2(CO)[=C(C_6H_4PPh_2)_2]$ (**A**) is shown in Figs. 1 and 2. Important bond distances and angles are presented in Table 1. The ruthenium is in a distorted octahedral arrangement of two bromides, a carbonyl, and a tridentate bis(phosphino)-carbene moiety. The Ru–Br(1) bond for the bromide *trans* to the carbene is 2.638(2) Å, significantly longer (by 50 σ) than the Ru–Br(2) bond *trans* to CO of 2.537(2) Å. Such a lengthening is consistent with the known strong structural *trans*-influence of other carbene ligands and with the ease of bromide removal from the complex with Ag^+, which is described below. The Ru–Br(1) and Ru–C(2) bonds are required to be strictly colinear. The bis(phosphino)-carbene ligand shows evidence of considerable strain, as would be expected. The bond lengths (Table 2) are normal (Ru–P 2.353(2), P–C 1.82-1.83, Ru–C(2) 1.94(1) Å) but many of the bond angles are far from ideal values. In particular we note: (i) the values of the angles P–Ru–P′ 162.0°, Ru–P–C(11) 127.8(3)°, Ru–P–C(21) 115.3(3)°, and Ru–P–C(31) 97.4(3)°; and (ii) the asymmetry of the angles at C(31) and C(36).

Further reactions of $RuBr_2(CO)[=C(C_6H_4PPh_2)_2]$

Reaction between compound **A** and $AgSbF_6$ in acetonitrile leads to a precipitate of AgBr, and from the solution orange crystals of $\{RuBr(CO)(CH_3CN)\{=C(C_6H_4PPh_2)_2\}\}SbF_6$ can be isolated (Scheme 1). A similar reaction carried out in CH_2Cl_2



Scheme 2

and with introduction of CO, leads to the dicarbonyl compound $[RuBr(CO)_2\{=C(C_6H_4PPh_2)_2\}]SbF_6$. The carbene centre in these cations has enhanced reactivity towards nucleophiles, and the dicarbonyl cation when treated with $NaBH_4$ gives $RuBr(CO)_2[CH(C_6H_4PPh_2)_2]$ and with diethylamine forms $RuBr(CO)_2[C(NEt_2)(C_6H_4PPh_2)_2]$. These reactions are depicted in Scheme 2. IR data for all the new compounds are reported in Table 2.

Experimental

The general experimental techniques have been described previously [8]. Reactions involving BBr_3 were performed by use of standard Schlenk procedures. $Hg(CF_3)_2$ [9] and $Ru(CO)_3(PPh_3)_2$ [10] were prepared by published methods.

Table 2

IR data (cm^{-1}) for ruthenium complexes [a]

Compound	ν(CO)	Other bands
$Ru(CF_3)(HgCF_3)(CO)_2(PPh_3)_2$	2018,1963	1102,1051,1012,960, ν(CF)
$Ru(CF_3)Br(CO)_2(PPh_3)_2$	2064,2002	1074,1007,995,983,975,968, ν(CF)
$[RuBr(CO)_2\{=C(C_6H_4PPh_2)_2\}]BBr_4$	2080,2020	1565,1320,1300; 605, ν(BBr)
$RuBr_2(CO)[=C(C_6H_4PPh_2)_2]$	1985	1568,1300,1280,1270
$[RuBr(CO)L\{=C(C_6H_4PPh_2)_2\}]SbF_6$	2020	1569,1310,1290; 660, ν(SbF)
$RuBr(CO)_2[CH(C_6H_4PPh_2)_2]$	2025,1965	1580
$RuBr(CO)_2[C(NEt_2)(C_6H_4PPh_2)_2]$	2030,1970	1575,1320,1210

[a] Measured as Nujol mulls. All bands strong. L = CH_3CN.

$Ru(CF_3)(HgCF_3)(CO)_2(PPh_3)_2$

A solution of $Ru(CO)_3(PPh_3)_2$ (3.0 g) and $Hg(CF_3)_2$ (1.6 g) in degassed toluene (180 ml) was heated under reflux for 45 min. The solution was then cooled and the solvent removed on a rotary evaporator. The residual solid was dissolved in a minimum of CH_2Cl_2 and MeOH (30 ml) was added. Removal of CH_2Cl_2 under reduced pressure gave a white solid, which was recrystallised from CH_2Cl_2/MeOH to yield white crystals (3.1 g, 72%). M.p. 199–201 °C. Anal. Found: C, 47.62; H, 3.38. $C_{40}H_{30}F_6HgO_2P_2Ru$ calcd.: C, 47.08; H, 2.96%. This compound has been further characterised by an X-ray crystal structure analysis [3].

$Ru(CF_3)Br(CO)_2(PPh_3)_2$

$Ru(CF_3)(HgCF_3)(CO)_2(PPh_3)_2$ (2.0 g) was dissolved in 100 ml of CH_2Cl_2 and a CH_2Cl_2 solution of Br_2 (2 g in 10 ml) was added until the colour of Br_2 just persisted. EtOH (300 ml) was added and the CH_2Cl_2 removed under reduced pressure. The resulting white solid was filtered off and recrystallised from CH_2Cl_2/EtOH as a partial CH_2Cl_2 solvate (1.34 g, 82%) M.p. 233–237 °C. Anal. Found: C, 54.54; H, 4.09. $C_{39}H_{30}BrF_3O_2P_2Ru.(CH_2Cl_2)_{0.25}$ calcd.: C, 55.34; H, 3.61%.

$[RuBr(CO)_2\{=C(C_6H_4PPh_2)_2\}]BBr_4$

A solution of $Ru(CF_3)Br(CO)_2(PPh_3)_2$ (1.0 g) in CH_2Cl_2 (50 ml) was cooled to -78 °C, 10 ml of a solution of BBr_3 in CH_2Cl_2 (0.96 mol l^{-1}) were added, and the solution was allowed to warm to room temperature, turning a deep-orange colour. The solution was stirred for a further 20 min, and the volume then reduced to 10 ml under reduced pressure. Hexane (40 ml) was added to precipitate the orange solid (1.19 g, 89%). The instability of this compound prevented satisfactory determination of analytical data, but the formulation was clear from the IR spectrum and from the following reaction.

$RuBr_2(CO)[=C(C_6H_4PPh_2)_2]$

A solid sample of $[RuBr(CO)_2\{=C(C_6H_4PPh_2)_2\}]BBr_4$ (500 mg) was kept in a desiccator for 5 days during which the solid changed from orange to purple. The product was purified by chromatography on a silica-gel column (25 × 3 cm) with CH_2Cl_2 as the initial eluant to remove $RuBr_2(CO)_2(PPh_3)_2$ and an unidentified orange impurity. The product was then eluted with CH_2Cl_2 : THF (9 : 1) and recrystallised from CH_2Cl_2/cyclohexane to yield purple crystals (260 mg, 70%). M.p. 254–256 °C. Anal. Found: C, 55.22; H, 3.83; Br, 20.30. $C_{38}H_{28}Br_2OP_2Ru$ calcd.: C, 55.43; H, 3.43; Br, 19.41%.

$[RuBr(CO)(CH_3CN)\{=C(C_6H_4PPh_2)_2\}]SbF_6$

$RuBr_2(CO)[=C(C_6H_4PPh_2)_2]$ (200 mg) and $AgSbF_6$ (90 mg) were dissolved in acetonitrile (30 ml) and the mixture was stirred for 20 min. The bright orange solution was then filtered through Celite to remove AgBr. Isopropanol (30 ml) was added and the volume reduced under reduced pressure to yield a solid product which was recrystallised from CH_2Cl_2/isopropanol to give orange crystals (170 mg, 69%). Anal. Found: C, 46.05; H, 3.46; Br, 7.57. $C_{40}H_{31}BrF_6NOP_2RuSb.(CH_2Cl_2)_{0.25}$ (solvent apparent in ^1H NMR) calcd.: C, 46.43; H, 3.05; Br, 7.67%.

[RuBr(CO)$_2${=C(C_6H_4PPh$_2$)$_2$}]SbF$_6$

$RuBr_2(CO)[{=}C(C_6H_4PPh_2)_2]$ (200 mg) and $AgSbF_6$ (90 mg) were added to frozen CH_2Cl_2 (40 ml) in a Fisher–Porter pressure bottle (500 ml capacity) under a CO pressure of 28 psi. The mixture was warmed to room temperature, stirred for 10 min, and filtered through Celite to remove AgBr. The solvent was removed under vacuum to yield an orange oil (190 mg, 78%), which resisted all attempts at crystallisation. This oil was used in the preparations below.

RuBr(CO)$_2$[CH(C_6H_4PPh$_2$)$_2$]

To a solution of freshly prepared $[RuBr(CO)_2\{{=}C(C_6H_4PPh_2)_2\}]SbF_6$ (250 mg) in CH_2Cl_2 (30 ml) was added dropwise a solution of $NaBH_4$ (15 mg) in EtOH (15 ml). n-Hexane (40 ml) was then added, whereupon a yellow oil containing $NaSbF_6$ and $RuBr(CO)_2[C(OEt)(C_6H_4PPh_2)_2]$ formed. This was removed by filtration through Celite and the volume of the colourless filtrate was reduced to ca. 1 ml, when white crystals of the product formed (69 mg, 37%). M.p. 226–228 °C. ^1H NMR ($CDCl_3$): δ, 5.51, s, 1H, C–*H*; δ, 7.10–8.05, m, 28H, aromatic Hs. Anal. Found: C, 62.52; H, 4.46. $C_{39}H_{29}BrO_2P_2Ru \cdot C_6H_{14}$ (solvent evident in ^1H NMR) calcd.: C, 62.94; H, 4.99%.

RuBr(CO)$_2$[C(NEt$_2$)(C_6H_4PPh$_2$)$_2$]

Diethylamine was added dropwise to a solution of $[RuBr(CO)_2\{{=}C(C_6H_4\text{-}PPh_2)_2\}]SbF_6$ (20 mg) in CH_2Cl_2 until the orange colour of the solution was discharged. The solution was then reduced in volume to ca. 5 ml and transferred to a 10 × 3 cm silica-gel chromatography column. Elution with CH_2Cl_2 gave a yellow band, the solid from which was recrystallized from CH_2Cl_2/cyclohexane to give pale-yellow crystals (127 mg, 76%). M.p. > 250 °C. ^1H NMR ($CDCl_3$): δ, 1.20, t, N–CH_2–CH_3; δ, 3.52, q, N–CH_2–CH_3, J(HH) 6 Hz; δ, 7.20–7.85, m, 28H, aromatic Hs. Anal. Found: C, 61.33; H, 5.23. $C_{43}H_{38}BrNO_2Ru$ calcd.: C, 61.21; H, 4.54%.

X-Ray crystallography

Dark orange-red crystals of $RuBr_2(CO)[{=}C(C_6H_4PPh_2)_2]$ were obtained from THF/EtOH as small tablets, and that selected for the diffractometer measured 0.175 × 0.10 × 0.06 mm. Systematic absences from the monoclinic diffraction pattern (hkl when $h + k = 2n + 1$, and $h0l$ when $l = 2n + 1$) were consistent with space groups Cc or $C2/c$. The structure was satisfactorily solved and refined in space-group $C2/c$. Unit cell dimensions were derived from least-squares fits to the observed setting angles of twenty-five reflections in the theta range 11.9–16.9° using graphite monochromated Mo-K_α radiation with a Nonius CAD-4 diffractometer.

Crystal data. $C_{38}H_{28}Br_2OP_2Ru$, M 823.48, monoclinic, a 18.985(4), b 9.937(1), c 21.171(2) Å, β 123.80(1)°, V 3319.2 Å^3, D_c 1.648 g cm^{-3}, Z 4, $F(000)$ 1631.98, Mo-K_α λ 0.7107 Å, graphite monochromator, μ 31.40 cm^{-1}.

Intensity data collection employed the $2\theta/\omega$ scan technique with a total background/peak count time ratio of 1/2. The omega scan angle was 0.80 + 0.35 tan θ. Reflections were counted for either 60 s or else until $\sigma(I)/I$ was 0.020.($\sigma(I) = 20.1166/NPI\sqrt{C + 4B}$, where the constant term is the maximum possible scan rate, NPI is the ratio of the maximum possible scan rate for the measurement, C is total counts, B is total background). Crystal alignment and possible decomposition were monitored throughout the data collection by remeasuring three selected standard reflections after every 100 measurements, but no non-statistical variations were observed. Data were collected to the practical diffraction limit of $\theta = 26°$. The data were corrected for Lorentz, polarisation and absorption effects (max. and min. transmission coefficient 0.9638 and 0.8968, respectively) to yield 1974 unique observed reflections ($I > 2.5\sigma(I)$). Computing was carried out using the SDP suite of programs on a PDP-11 for initial data processing, and SHELX-76 on an IBM 4341 computer for structure solution and refinement.

Structure determination and refinement

The structure was solved by using conventional heavy-atom Patterson and electron density maps. The molecule is positioned about a crystallographic diad axis which passes through one bromine, the ruthenium, and the carbene carbon. The second bromine is statistically interchanged across the diad axis with the carbonyl ligand. The model refined has one half of a bromine and one half of a carbonyl on each side of the axis. The carbonyl atoms could not be individually resolved because of the overlap in difference Fourier maps with the bromine, and hence they were constrained into likely positions and assigned fixed isotropic temperature factors. The bromine position and isotropic temperature factor were refined however. The

Table 3

Atomic coordinates and temperature factors for $RuBr_2(CO)[=C(C_6H_4PPh_2)_2]$

Atom	x	y	z	U
Ru	0.0000 [a]	0.2255(1)	0.2500 [a]	0.023*
Br(1)	0.0000 [a]	0.4910(1)	0.2500 [a]	0.052*
Br(2)	0.1603(1)	0.2266(2)	0.3393(1)	0.041(1)
P	0.0005(1)	0.1885(2)	0.1405(1)	0.027(1)
O	0.1991 [b]	0.2288 [b]	0.3605 [b]	0.050 [b]
C(1)	0.1264 [b]	0.2276 [b]	0.3201 [b]	0.050 [b]
C(2)	0.0000 [a]	0.0302(13)	0.2500 [a]	0.029(3)
C(11)	−0.0503(6)	0.2899(9)	0.0540(5)	0.033(2)
C(12)	−0.1137(7)	0.3824(10)	0.0403(6)	0.045(3)
C(13)	−0.1563(7)	0.4530(13)	−0.0283(7)	0.059(3)
C(14)	−0.1364(8)	0.4350(13)	−0.0796(7)	0.060(3)
C(15)	−0.0726(8)	0.3442(12)	−0.0653(7)	0.058(3)
C(16)	−0.0285(7)	0.2701(11)	0.0016(6)	0.046(3)
C(21)	0.1034(6)	0.1500(9)	0.1579(5)	0.031(2)
C(22)	0.1253(6)	0.0202(10)	0.1502(6)	0.040(2)
C(23)	0.2077(7)	−0.0034(11)	0.1659(6)	0.051(3)
C(24)	0.2652(7)	0.0990(11)	0.1892(7)	0.053(3)
C(25)	0.2436(7)	0.2281(12)	0.1980(7)	0.057(3)
C(26)	0.1628(7)	0.2535(11)	0.1834(6)	0.049(3)
C(31)	−0.0533(5)	0.0253(9)	0.1143(5)	0.027(2)
C(32)	−0.0992(6)	−0.0293(10)	0.0424(5)	0.037(2)
C(33)	−0.1363(7)	−0.1577(10)	0.0311(6)	0.045(3)
C(34)	−0.1264(7)	−0.2269(11)	0.0948(6)	0.046(3)
C(35)	−0.0798(6)	−0.1713(9)	0.1671(5)	0.035(2)
C(36)	−0.0432(5)	−0.0431(9)	0.1774(5)	0.028(2)

[a] Fixed by crystallographic symmetry. * $U_{equiv.} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$. [b] Parameter not refined.

ruthenium and the bromine on the diad axis were assigned anisotropic thermal parameters, and all carbon atoms were assigned individual isotropic temperature factors. No attempts were made to locate hydrogen atoms.

Refinement was by full-matrix least-squares procedures minimising the function $\Sigma w(|F_o| - |F_c|)^2$. Atomic scattering factors and dispersion corrections were for neutral atoms. At convergence, R and R_w $(\{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2})$ were 0.060 and 0.063, respectively. Reflection weights in the final cycle were $w = 2.047/(\sigma^2(F) + 6.76 \times 10^{-4}F^2)$.

Final atomic coordinates are listed in Table 3. The molecular geometry and atomic numbering scheme are shown in Fig. 1. A complete list of bond lengths and angles, and tables of observed and calculated structure factor amplitudes are available on request from the authors (G.R.C).

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