# The Preparation and Characterisation of Cationic Formyl Complexes of Ruthenium(II); Crystal and Molecular Structure † of the Complex *trans*-Bis[1,2-bis(diphenylphosphino(ethane-*PP'*]carbonyl(deuterioformyl)-ruthenium(II) Hexafluoroantimonate–Dichloromethane(1/1)

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Reactions of the complexes *trans*-$[Ru(CO)_2(dppe)_2][SbF_6]_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) or *cis*-$[Ru(CO)_2(dppm)_2][SbF_6]_2$ (dppm = $Ph_2PCH_2PPh_2$) with $[Na\{HB(OEt)_3\}]$ or $[K\{HB(OPr^i)_3\}]$ afford $[Ru(CHO)(CO)(P{-}P)_2][SbF_6]$ (P–P = dppe or dppm), without change of stereochemistry, in high yield. $[Li(HBEt_3)]$ gives $[Ru(CHO)(CO)(P{-}P)_2][BEt_4]$, the counter ion being introduced as an impurity in $[Li(HBEt_3)]$. $[Li(DBEt_3)]$ gives $[Ru(CDO)(CO)(P{-}P)_2][SbF_6]$ and a $^{13}C$ labelled analogue is prepared from *trans*-$[Ru(^{13}CO)_2(dppe)_2][SbF_6]_2$. The complexes are sufficiently stable in the solid state and in solution at −30 °C for full characterisation by spectroscopic means, one notable feature being the appearance of two peaks in the $\nu_{C-H}$ region of the i.r. spectrum of *cis*-$[Ru(CHO)(CO)(dppm)_2]Y$ (Y = $[SbF_6]$ or $[BEt_4]$) attributable to Fermi resonance between pure $\nu_{C-H}$ and $2\delta_{C-H}$. *trans*-$[Ru(CDO)(CO)(dppe)_2][SbF_6]{\cdot}CH_2Cl_2$ is orthorhombic, space group $Pn2_1a$ ($\equiv Pna2_1$, no. 33), with $a$ = 22.364(1), $b$ = 20.244(2), $c$ = 11.944(1) Å, and $Z$ = 4. The structure was obtained from 1 752 observed intensities measured on an automatic diffractometer and refined to an $R$ value of 0.084. The main features of interest are a long Ru–C (2.09 Å) bond and a Ru–C–O angle of 133°.

The transition-metal catalysed hydrogenation of carbon monoxide to produce organic products for the petrochemical industry has received much attention in recent years, as an alternative to the world's dwindling petroleum reserves. Although very high pressures and temperatures are required, carbon monoxide, over various catalysts, *e.g.* nickel, cobalt, iron, ruthenium, rhodium, and osmium, can be hydrogenated to form methane, higher hydrocarbons, alcohols and other oxygenated species.[1-3] Only for Rh,[4] Ru,[5-8] and possibly Co [9] has homogeneous catalytic activity been rigorously demonstrated.

To help elucidate the mechanism of these reactions, many compounds serving as models for postulated intermediates [10-15] have been studied, *e.g.* transition-metal bound formyl (–CHO), hydroxymethyl (–$CH_2OH$), methyl (–$CH_3$), and carbene (=$CH_2$) groups. The formation of a catalyst bound formyl group is generally regarded as one of the initial steps in the hydrogenation of carbon monoxide, although only two formyl species [16,17] have been made by direct CO insertion into a metal–hydride bond. Several others have been synthesised [14] *via* hydride reduction of co-ordinated CO and to a lesser extent *via* reaction of unsaturated metal species with acetic formic anhydride or formaldehyde.

In homogeneous medium, ruthenium complexes have been shown [5-8] to catalyse the hydrogenation of carbon monoxide, yet no fully characterised formyl complex of ruthenium has been isolated, although short-lived formyls formed by hydridic reduction of $[Ru_3(CO)_{12}]$,[18] $[Ru_3H(CO)_9(S)]^-$,[19] or $[Ru(\eta\text{-}C_5H_5)(CO)_3]^+$ [20] and the unstable $[RuH(CHO)(PPh_3)_3(S)]$ [21] (S = solvent) have been reported.

Furthermore, although many neutral and anionic formyl complexes are well known, $[IrH(CHO)(PMe_3)_4]^+$ [22] represented the single cationic metal formyl complex known, prior to the start of this work. In a preliminary communication,[23] we reported the facile synthesis of cationic formyl complexes of ruthenium(II) *via* the low-temperature hydridic reduction of $[Ru(CO)_2(P{-}P)_2][SbF_6]_2$ [P–P = $PPh_2(CH_2)_nPPh_2$; $n$ = 1, dppm; $n$ = 2, dppe].[24] We now report details of the synthesis and characterisation of these compounds, together with structural details of *trans*-$[Ru(CDO)(CO)(dppe)_2][SbF_6]{\cdot}CH_2Cl_2$.

## Results and Discussion

*Preparation of Formyl Cations.*—(*a*) 1,2-*Bis*(*diphenylphosphino*)*ethane* (*dppe*) *complexes.* The reaction of *trans*-$[Ru(CO)_2(dppe)_2][SbF_6]_2$ with $[Na\{HB(OEt)_3\}]$–thf (thf = tetrahydrofuran) (1 : 1.5 mol ratio) in $CH_2Cl_2$, under nitrogen at −30 °C for 2 h affords smooth conversion to *trans*-$[Ru(CHO)(CO)(dppe)_2][SbF_6]$ (1), sufficiently stable at low temperatures for crystallisation to give a pale yellow solid. Attempts to promote a second hydridic reduction of these monoformyl complexes by reduction of *trans*-$[Ru(CO)_2(dppe)_2][SbF_6]_2$ with excess $[Na\{HB(OEt)_3\}]$ or with the more nucleophilic $[K\{HB(OPr^i)_3\}]$–thf or $[Li(HBEt_3)]$–thf have so far proved unsuccessful. Reduction with $[K\{HB(OPr^i)_3\}]$ (H : Ru = 1.1, 2.5, or 5 : 1) forms a black solution, however the formyl species *trans*-$[Ru(CHO)(CO)(dppe)_2][SbF_6]$ (1) is the only product isolated.

Reaction of $[Li(HBEt_3)]$–thf with *trans*-$[Ru(CO)_2(dppe)_2][SbF_6]_2$ (3.5 : 1 mol ratio) at low temperature over 4 h affords a clear crimson solution yielding a pink solid at −30 °C. This turns pale brown on warming to room temperature but is otherwise unaltered. Although it does not contain $[SbF_6]^-$, this product has spectroscopic properties (see Table 1 and Experimental section) that show it to contain *trans*-$[Ru(CHO)(CO)(dppe)_2]^+$, and resonances in the $^1H$ and $^{11}B$ spectra indicate the presence of the symmetrical boron anion $[BEt_4]^-$ which has been previously reported.[25,26] The fact that the $[BEt_4]^-$ complex (2) is the only one isolated is surprising since it is more soluble in $CH_2Cl_2$ than the $[SbF_6]^-$

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† *Supplementary data available* (No. SUP 23706, 16 pp.): structure factors, thermal parameters, full bond lengths and angles. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Infrared data ($cm^{-1}$) for ruthenium formyl complexes

| Compound | $\nu_{C-H}$ | $\nu_{C\equiv O}$ | $\nu_{C=O}$ | $\delta_{C-H}$ |
|---|---|---|---|---|
| (1) *trans*-$[Ru(CHO)(CO)(dppe)_2][SbF_6]$ | 2 550 | 1 978 | 1 596 | 1 362 [a] |
| (2) *trans*-$[Ru(CHO)(CO)(dppe)_2][BEt_4]$ | 2 552 | 1 979 | 1 600 | |
| (3) *trans*-$[Ru(CDO)(CO)(dppe)_2][SbF_6]$ | 1 918 [b] | 1 984 | 1 595 | 1 040 [c] |
| (4) *trans*-$[Ru(^{13}CHO)(^{13}CO)(dppe)_2][BEt_4]$ | 2 502 | 1 928 | 1 558 | |
| (5) *cis*-$[Ru(CHO)(CO)(dppm)_2][SbF_6]$ | 2 720, 2 590 [d] | 1 970 | 1 600 | 1 350 |
| (6) *cis*-$[Ru(CHO)(CO)(dppm)_2][BEt_4]$ | 2 715, 2 578 [d] | 1 984 | 1 605 | 1 344 |
| (7) *cis*-$[Ru(CDO)(CO)(dppm)_2][SbF_6]$ | 1 962 [b] | 1 977 | 1 604 | 1 030 [c] |

[a] Calculated value assuming $\delta_{C-H}/\delta_{C-D} = 1.31$, not identified in spectrum. [b] $\nu_{C-D}$. [c] $\delta_{C-D}$. [d] Absorptions from Fermi resonance between $\nu_{C-H}$ and $2\delta_{C-H}$.

analogue. We suggest that this indicates tight ion-pair formation for the $[BEt_4]^-$ complex in solution, a suggestion supported by solid-state i.r. studies (see later).

Reaction of *trans*-$[Ru(CO)_2(dppe)_2][SbF_6]_2$ with $[Li(DBEt_3)]$ is much slower than the reaction with $[Li(HBEt_3)]$ (the reaction taking 16 h at −30 °C to go to completion) and yields the corresponding deuterioformyl complex *trans*-$[Ru(CDO)(CO)(dppe)_2][SbF_6]$ (3).

Although we have previously suggested [23] that $[BEt_4]^-$ is formed during the reaction by ethyl transfer between boron atoms and that there is a large isotope effect which slows down the exchange sufficiently for $[BEt_4]^-$ not to be formed in significant quantities from $[DBEt_3]^-$, it has recently been pointed out to us [27] that commercial $[Li(HBEt_3)]$ contains significant quantities of $[BEt_4]^-$. Indeed, $^{11}B$ n.m.r. studies on our batch of $[Li(HBEt_3)]$ show significant resonances at δ −16.54 [*] (30% of $^{11}B$ present) and −16.02 (25% of $^{11}B$ present attributable [26] to $[BEt_4]^-$), as well as much smaller resonances at δ 1.62 and 8.58. Proton coupled spectra show that the resonance at −16.54 is from $[BH_2Et_2]^-$ [28] [$J$(BH) = 69 Hz], whilst none of the other resonances shows coupling to a hydride. The fact that the major resonance (δ −3.88, 41%), which we assume arises from $[HBEt_3]^-$ shows no coupling to the hydridic hydrogen atom has previously been attributed [29] to exchange with $BEt_3$ present in solution. This also accounts [29] for the lower chemical shift than expected (δ −12.3) [30] for pure $[Li(HBEt_3)]$. We assume that $[BEt_4]^-$ and $[BH_2Et_2]^-$ are formed by a disproportionation of $[HBEt_3]^-$ similar to that reported [31] to occur for lithium alkoxyborohydrides.

After the reaction of *trans*-$[Ru(CO)_2(dppe)_2][SbF_6]_2$ with 3.5 mol equivalents of this $[Li(HBEt_3)]$ in $CH_2Cl_2$, the only boron-containing anion is $[BEt_4]^-$, but there are resonances at δ 86.5 $[BEt_3]$ and 53.5, the latter of which is also present if $[Li(HBEt_3)]$ is reacted with $CH_2Cl_2$ under similar conditions. However, the proportion of boron in the form of $[BEt_4]^-$ does not increase during the reaction. Very similar results are obtained using $[Li(DBEt_3)]$ except that $[BEt_4]^-$ only accounts for 7% of the boron present in solution.

On standing in $CH_2Cl_2$ for 2 weeks, the peaks from $[BEt_4]^-$ disappear, suggesting that the anion undergoes a slow reaction with the solvent.

Since high yields of $[Ru(CHO)(CO)(dppe)_2][BEt_4]$ (2) are only obtained if excess (*ca.* 3.5 mol) of $[Li(HBEt_3)]$ is employed, we now believe that the $[BEt_4]^-$ comes directly from the solution and isolation of the $[SbF_6]^-$ salt from the reaction of $[Ru(CO)_2(dppe)_2][SbF_6]_2$ with $[Li(DBEt_3)]$ can be attributed to the lower proportion of $[BEt_4]^-$ present in this solution. The longer time required for the reaction with $[Li(DBEt_3)]$ will also mean that more of the $[BEt_4]^-$ will be removed by the slow reaction with the solvent.

*trans*-$[Ru(^{13}CO)_2(dppe)_2]^{2+}$, formed from $[RuCl_2(dppe)_2]$, $Ag[SbF_6]$, and $^{13}CO$, similarly reacts with excess $[Li(HBEt_3)]$ to give *trans*-$[Ru(^{13}CHO)(^{13}CO)(dppe)_2][BEt_4]$ (4).

(*b*) *Bis(diphenylphosphino)methane* (*dppm*) *complexes*. Reductions of *cis*-$[Ru(CO)_2(dppm)_2][SbF_6]_2$ with $[Na\{HB(OEt)_3\}]$, $[Li(HBEt_3)]$, or $[Li(DBEt_3)]$ in nitromethane or methylene chloride at −30 °C yield the formyls *cis*-$[Ru(CHO)(CO)(dppm)_2][SbF_6]$ (5), *cis*-$[Ru(CHO)(CO)(dppm)_2][BEt_4]$ (6), and *cis*-$[Ru(CDO)(CO)(dppm)_2][SbF_6]$ (7) respectively, the complexes readily precipitating out during the reaction. Unfortunately the complexes (particularly the $[SbF_6]^-$ salts) are virtually insoluble in all common organic solvents at low temperature, and too unstable at ambient temperatures for complete characterisation. However, the presence of a formyl group has been confirmed by i.r. studies (Table 1), and semi-characterised low-temperature $^1H$ and $^{31}P$ spectra of the more soluble *cis*-$[Ru(CHO)(CO)dppm)_2][BEt_4]$ (6) have been obtained in $CD_2Cl_2$.

Mixtures of *cis*- and *trans*-$[Ru(CO)_2(dppm)_2][SbF_6]_2$ also give *cis*-$[Ru(CHO)(CO)(dppm)_2][SbF_5]$ (5) as the only nitromethane-insoluble product on reaction with $[Na\{HB(OEt)_3\}]$, but $^{31}P$ n.m.r. studies on crude reaction solutions show a singlet at δ −10.67 which we tentatively assign to *trans*-$[Ru(CHO)(CO)(dppm)_2]^+$.

Although the isolated products from $CH_3NO_2$ and $CH_2Cl_2$ are the same, $^{31}P$ n.m.r. studies suggest that small amounts of other compounds, presumably derived from *e.g.* $[CH_2NO_2]^-$ are formed in $CH_3NO_2$. This is more noticeable for the dppm complexes, but the amount of these products is still only small, and therefore has made it impossible to isolate these products. On one occasion *cis*-$[Ru(CHO)(CO)(dppm)_2][SbF_6]$ (5) failed to precipitate from $CH_3NO_2$ and the major species isolated contained nitrogen. Although not fully characterised we tentatively assign it as *trans*-$[Ru(CO)(CH_2NO_2)(dppm)_2][SbF_6]$.

*Spectroscopic Details.*—(*a*) *Infrared spectra.* The relevant infrared details of the formyl complexes are given in Table 1. A variation in the values of $\nu_{C-H}$,[†] $\nu_{C\equiv O}$, and $\nu_{C=O}$ is noted on changing the anion from $[SbF_6]^-$ to $[BEt_4]^-$, which is more noticeable for the dppm complexes (*N.B. cis* isomer). We interpret this as arising from tight ion-pair formation when $[BEt_4]^-$ is the counter anion since no interaction is observed between the cation and $[SbF_6]^-$ in the solid-state structure of *trans*-$[Ru(CDO)(CO)(dppe)_2][SbF_6]$ (3) (see later). This might also account for the precipitation of the more soluble $[BEt_4]^-$ complex (see above). In anionic formyls, similar effects have been attributed [19,32] to ion pairing, the cation interacting with the oxygen atom of the formyl group.

The i.r. spectra of the dppm formyl complexes show *two*

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[*] Boron shifts are in p.p.m. to high frequency of external $BF_3{\cdot}OEt_2$.

[†] Throughout this section $\nu_{C-H}$, $\nu_{C-D}$, $\delta_{C-H}$, and $\delta_{C-D}$ refer to the formyl C–H or C–D bond.

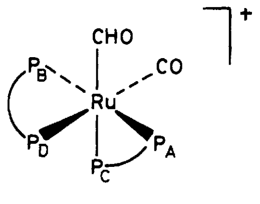

**Figure 1.** Proposed structure and phosphorus atom assignments for *cis*-$[Ru(CHO)(CO)(dppm)_2]^+$; $P\frown P$ = dppm

bands in the $\nu_{C-H}$ region, although there is only one aldehydic C–H bond present.* This doublet can be attributed to the result of Fermi resonance between the aldehydic C–H stretching vibration and the first overtone band of the aldehydic C–H bending vibration ($\delta_{C-H}$), a known [34,35] phenomenon for aldehydes. Hence for *cis*-$[Ru(CHO)(CO)(dppm)_2]^+$ the frequencies of the doublet arising from Fermi resonance of $\nu_{C-H}$ with $2\delta_{C-H}$ are 2 720 and 2 590 $cm^{-1}$. The values for the $\delta_{C-H}$ and $\delta_{C-D}$ bands are 1 350 and 1 030 $cm^{-1}$ respectively ($\delta_{C-H}/\delta_{C-D} = 1.31$) so that pure $2\delta_{C-H} = 2\,700$ $cm^{-1}$. If the total energy of the system is unaffected by resonance, pure $\nu_{C-H} = 2\,610$ $cm^{-1}$. The absorption at 1 962 $cm^{-1}$ in the i.r. spectrum of *cis*-$[Ru(CDO)(CO)(dppm)_2]^+$ can then be attributed to $\nu_{C-D}$ ($\nu_{C-H}/\nu_{C-D} = 1.33$).

For *trans*-$[Ru(CHO)(CO)(dppe)_2]^+$, $\nu_{C-H} = 2\,550$ and $\nu_{C-D} = 1\,918$ $cm^{-1}$ ($\nu_{C-H}/\nu_{C-D} = 1.33$), *i.e.* no resonance occurs. This probably arises because of the greater difference between $\nu_{C-H}$ and $2\delta_{C-H}$ (174 $cm^{-1}$), assuming that $\delta_{C-H}/\delta_{C-D} = 1.31$; {*cf.* 90 $cm^{-1}$ for *cis*-$[Ru(CHO)(CO)(dppm]_2{}^+$}, so any Fermi-resonance interaction will be weak and intensity stealing from $\nu_{C-H}$ by $2\delta_{C-H}$ will be negligible. It is interesting to note that unlike aldehydes, pure $\nu_{C-H}$ in these formyls is $<2\delta_{C-H}$.

(*b*) *N.m.r. spectra* (*see Experimental section*). The $^1H$ n.m.r. spectra ($CD_3NO_2$) of $[Ru(CHO)(CO)(dppe)_2]^+$ confirm the *trans* stereochemistry and the presence of the formyl group [δ 13.6, quin, *J*(PH) = 8 Hz]. The *trans* stereochemistry is further confirmed by the observation of a single resonance in the $^{31}P$ n.m.r. spectrum at δ 47.1† (45.9 at −30 °C) which rapidly disappears at room temperature.

In addition, the $[BEt_4]^-$ complexes show the expected [25] resonances at δ 0.73 [t of 1 : 1 : 1 : 1 q, *J*($CH_3B$) = 3 Hz] and −0.03 [q of 1 : 1 : 1 : 1 q, *J*($CH_2B$) = 4.5 Hz] in the $^1H$ n.m.r. spectra, and a singlet [26] at δ −16.11 p.p.m. (relative to $BF_3 \cdot OEt_2$) in the $^{11}B$ spectra.

The low-temperature $^{13}C$ n.m.r. spectrum of $[Ru(^{13}CHO)(^{13}CO)(dppe)_2]^+$ shows two low-field resonances, one at δ 261.9 p.p.m. [d of quin, *J*(PC) = 9.5, *J*(CC) = 22.12 Hz] characteristic [14] of a formyl carbon atom, and the other from the carbonyl at δ 198.7 [d of quin, *J*(PC) = 9.5 Hz]. These assignments are confirmed since only the lower field resonance splits into a further doublet on off-resonance decoupling.

For $[Ru(CHO)(CO)(dppm)_2]^+$, the assignment of *cis* stereochemistry is less certain since $^{31}P$ spectra of the $[BEt_4]^-$ complex dissolved and run at −30 °C in $CH_2Cl_2$ show considerable decomposition to $[RuH(CO)_2(dppm)_2]^+$ which has a very complex $^{31}P$ n.m.r. spectrum.[36] Nevertheless, three of the four resonances from the formyl complex (Figure 1) are visible (see Experimental section) and indicate *cis* stereochemistry; the fourth is probably buried under the resonances [36] from $[RuH(CO)_2(dppm)_2]^+$ at δ 2.0. In addition, *cis* stereochemistry is suggested by the observation of a broad formyl resonance at δ 13.1 p.p.m. in the $^1H$ n.m.r. spectrum with an obvious unique coupling to a *trans* phosphorus atom, *J*(PH) = 42 Hz, *cf.* 8 Hz for the *cis* couplings in *trans*-$[Ru(CHO)(CO)(dppe)_2]^+$.

**Table 2.** Selected bond lengths (Å) for $[Ru(CDO)(CO)(dppe)_2][SbF_6] \cdot CH_2Cl_2$ (3)

| | | | |
|---|---|---|---|
| Ru–P(11) | 2.393(14) | Ru–P(12) | 2.397(13) |
| Ru–P(21) | 2.412(14) | Ru–P(22) | 2.420(14) |
| Ru–C(1) | 2.09(4) | Ru–C(2) | 1.83(3) |
| C(1)–O(1) | 1.19(1) | C(2)–O(2) | 1.20(1) |
| C(11)–C(12) | 1.48(6) | C(21)–C(22) | 1.44(9) |
| P–C(Ph) | 1.78(3)—1.90(3), mean 1.83 | | |
| P–C($CH_2$) | 1.82(5)—1.90(7), mean 1.87 | | |
| Sb–F | 1.59(7)—1.77(6) | | |

**Table 3.** Selected bond angles (°) for $[Ru(CDO)(CO)(dppe)_2][SbF_6] \cdot CH_2Cl_2$ (3)

| | | | |
|---|---|---|---|
| P(11)–Ru–P(12) | 83.2(5) | P(21)–Ru–P(22) | 81.1(5) |
| P(11)–Ru–C(1) | 87(1) | P(11)–Ru–C(2) | 89(2) |
| P(21)–Ru–C(1) | 91(1) | P(21)–Ru–C(2) | 96(2) |
| P(12)–Ru–C(1) | 85(1) | P(12)–Ru–C(2) | 88(2) |
| P(22)–Ru–C(1) | 92(1) | P(22)–Ru–C(2) | 92(2) |
| C(1)–Ru–C(2) | 173(2) | | |
| Ru–C(1)–O(1) | 133(3) | | |
| Ru–C(2)–O(2) | 180(4) | | |

*Stability of the Ruthenium Formyl Complexes*.—All of the formyl complexes described above are sufficiently stable in the solid state for isolation and handling at room temperature and are stable in solution below −30 °C. At higher temperatures, however, they all decompose.

For example, *cis*-$[Ru(CHO)(CO)(dppm)_2]^+$ decomposes almost instantaneously on dissolution in $CH_2Cl_2$, whilst *trans*-$[Ru(CHO)(CO)(dppe)_2]^+$ decomposes with a half-life of 9 min in $CH_2Cl_2$ at 35 °C (i.r. evidence). *trans*-$[Ru(CDO)(CO)(dppe)_2]^+$ is somewhat more stable than its protio-analogue having a half-life of *ca.* 16 min at 35 °C. The products of these decomposition reactions and their mechanisms will be the subject of a future publication.[36]

*X-Ray Structure of trans*-$[Ru(CDO)(CO)(dppe)_2][SbF_6] \cdot CH_2Cl_2$.—The slightly enhanced stability of *trans*-$[Ru(CDO)(CO)(dppe)_2][SbF_6]$ compared with its non-deuteriated analogue meant that crystals could be grown at low temperature. These crystals were very small and this, together with the fact that there is disorder in the orientation of the $[SbF_6]^-$ ions and $CH_2Cl_2$ molecules has limited the precision of the structure determination (see Experimental section). Thus hydrogen atoms were not located and standard deviations for bond lengths (Table 2) and angles (Table 3) are large.

Nevertheless, the presence of the formyl ligand can be inferred from the marked bending of the Ru–C(1)–O(1) vector at C(1) (Figure 2, Table 3). The angle at C(1) and the C(1)–O(1) bond lengths are similar to those observed for the only other formyl compounds for which crystallographic data are available [37–39] (Table 4).

The only other feature of note is the Ru–C(1) bond length (2.09 Å) which is similar to those found for Ru–C single bonds [40] and considerably longer than that found [41] in $[\{Ru_3Cl_3(COEt)_2(OH)(CO)_6\}_2] \cdot C_6H_6$ where the bridging propionyl ligand is perhaps better considered as an ethylruthenoxycarbene

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* Two and even three bands in this region have been reported [33] for mononuclear monoformyl species.

† $^{31}P$ Chemical shifts are to high frequency of external 85% $H_3PO_4$.

**Table 4.** Crystallographic data for known formyl complexes of transition elements

| Compound | C=O/Å | M–C–O/° | Ref. |
|---|---|---|---|
| *trans*-$[Ru(CDO)(CO)(dppe)_2][SbF_6]$ | 1.19 | 133 | This work |
| $[Rh(CHO)(oep)]$ * | 1.175 | 130 | 39 |
| $[Re(CHO)(\eta\text{-}C_5H_5)(NO)(PPh_3)]$ | 1.220 | 128 | 37 |
| $[NEt_4][Fe(CHO)(CO)_3\{P(OC_6H_3Me_2\text{-}3,5)_3\}]$ | 1.195 | 134 | 38 |

* oep = 2,3,7,8,12,13,17,18-Octaethylporphyrinate(2–).

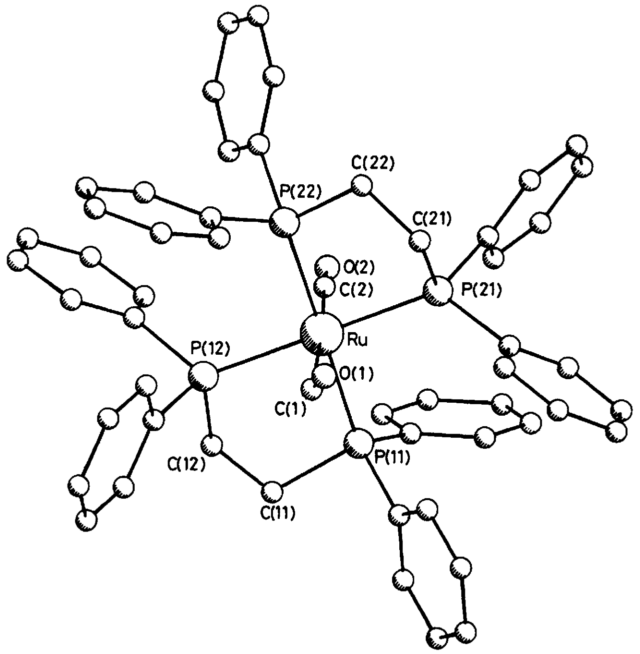

**Figure 2.** Solid-state structure and atomic-numbering scheme for the cation of *trans*-$[Ru(CDO)(CO)(dppe)_2][SbF_6]\cdot CH_2Cl_2$

with Ru=C double bonds (1.944, 1.996 Å) and C–O single bonds (1.276, 1.246 Å).

Metal formyls normally have rather shorter M–C bonds than those observed in alkyl complexes and this is attributable to a significant contribution from (II) (Figure 3). The length of the Ru–C bond in this case is indicative of a lesser contribution from (II), as would be expected since the metal already bears a positive charge.

Unfortunately, no crystal structures of ruthenium acyl complexes are available for comparison with the formyl derivatives since $[Ru\{C(R)O\}I(CO)(PPh_3)_2]$ (R = Me or *p*-tolyl) both contain [42] $\eta^2$-acyl ligands. Here again, Ru–C bond lengths are short whilst C–O bond lengths are long.

Very recently, the crystal structure of $[Ru_2(CO)_3(dppm)(COC_6H_4)]$, which contains an acyl group bridging the two rutheniums *via* the acyl carbon atom and an *ortho*-carbon atom of the phenyl ring, has been determined.[43] In this compound, Ru–C (2.124 Å), C=O (1.217 Å), and Ru–C–O (124.3°) are very similar to those observed for $[Ru(CDO)(CO)(dppe)_2][SbF_6]$.

## Experimental

Microanalyses were by Elemental Microanalysis Ltd. Infrared spectra were recorded on Nujol mulls between CsI plates on a Perkin-Elmer 577 grating spectrometer and $^1H$ n.m.r. spectra on a Varian Associates R34 220-MHz spectrometer. Phosphorus-31, $^{13}C$, $^{11}B$, $^1H$, and $^2H$ n.m.r. spectra were recorded on $CH_2Cl_2$ solutions at ambient temperature on a JEOL FX90Q spectrometer (City of London Polytechnic, ICI Wilton and ICI Runcorn) or a Bruker WM250 multinuclear spectrometer (University of Liverpool) operating in the Fourier-transform mode with proton-noise decoupling ($^{31}P$, $^{13}C$, and $^{11}B$). All solvents were dried before use by (*a*) distillation from sodium diphenylketyl [diethyl ether, tetrahydrofuran, and light petroleum (b.p. 40—60 °C)], (*b*) distillation from calcium hydride (dichloromethane), or (*c*) from molecular sieves (nitromethane). All solvents were thoroughly degassed before use and manipulations were carried out under nitrogen using standard Schlenk-line and catheter-tubing techniques. All preparations and purifications of formyl complexes were performed at $-35$ °C ($\pm 5$ °C) in a methanol–$CO_2$ bath.

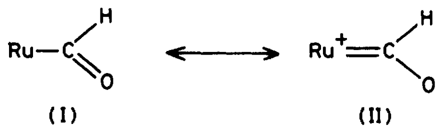

**Figure 3.** Possible resonance forms for a ruthenium bound formyl

The solution of $[Na\{BH(OEt)_3\}]$-thf was prepared by the standard literature method [31] and its molarity determined by decomposition with excess hydrochloric acid and back titration with sodium hydroxide.

The compounds $[Li(HBEt_3)]$, $[Li(DBEt_3)]$, and $[K\{HB(OPr^i)_3\}]$ were purchased from Aldrich Chemicals as 1 mol dm$^{-3}$ solutions in thf. All hydrides were stored under nitrogen prior to use.

The preparation of *trans*-$[RuCl_2(dppe)_2]$,[44] *trans*-$[Ru(CO)_2(dppe)_2][SbF_6]_2$, and *cis*-$[Ru(CO)_2(dppm)_2][SbF_6]_2$ [24] were by standard routes.

(*a*) trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*di*[$^{13}$C]*carbonylruthenium*(II) *Hexafluoroantimonate*.—To *trans*-$[RuCl_2(dppe)_2]$ (0.6 g, 0.62 mmol) dissolved in $CH_2Cl_2$ (40 cm$^3$) in a glass pressure bottle (100 cm$^3$ volume) was added $Ag[SbF_6]$ (0.4665 g, 1.36 mmol) and the vessel quickly sealed. This was then connected to a mercury diffusion pump vacuum line, and cooled in a liquid-nitrogen bath. When the solvent had solidified the vessel was evacuated to $10^{-4}$ Torr (Torr = 101 325/760 Pa) and then sealed. The vessel was then allowed to warm up to room temperature, and the process repeated three times so as to remove any gases from the vessel. Whilst cooled at $-196$ °C, four samples [21 cm$^3$ at 0.5 atm (*ca.* $5 \times 10^4$ Pa)] of $^{13}CO$ (96% enriched) were introduced into the vessel. After sealing, the vessel was allowed to warm up to room temperature and then heated at 80 °C overnight. After cooling and the release of pressure, the grey solution was filtered to remove silver chloride, and diethyl ether was added to the brown solution until precipitation of the product occurred. Recrystallisation of the pale brown product from $CH_2Cl_2$–diethyl ether at $-30$ °C yielded the complex as white crystals, yield 0.39 g, 44%. I.r.: $\nu_{CO}$ = 1 994 cm$^{-1}$ {*cf.* for *trans*-$[Ru(CO)_2(dppe)_2][SbF_6]_2$, $\nu_{CO}$ = 2 040 cm$^{-1}$}. $^{31}P$ N.m.r.:

**Table 5.** Fractional atomic co-ordinates

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Ru | 1 674(1) | 2 500 | 2 433(3) |
| P(11) | 1 245(5) | 1 867(6) | 944(9) |
| P(12) | 943(5) | 3 300(5) | 1 872(9) |
| C(11) | 623(20) | 2 386(25) | 321(39) |
| C(12) | 705(21) | 3 109(22) | 405(38) |
| C(111) | 822(13) | 1 128(11) | 1 129(25) |
| C(112) | 822(13) | 760(11) | 2 116(25) |
| C(113) | 502(13) | 169(11) | 2 173(25) |
| C(114) | 184(13) | −54(11) | 1 242(25) |
| C(115) | 185(13) | 314(11) | 255(25) |
| C(116) | 504(13) | 905(11) | 199(25) |
| C(121) | 1 754(12) | 1 704(16) | −185(23) |
| C(122) | 1 920(12) | 2 181(16) | −970(23) |
| C(123) | 2 365(12) | 2 041(16) | −1 752(23) |
| C(124) | 2 645(12) | 1 426(16) | −1 750(23) |
| C(125) | 2 480(12) | 949(16) | −965(23) |
| C(126) | 2 034(12) | 1 088(16) | −183(23) |
| C(131) | 250(9) | 3 332(12) | 2 645(22) |
| C(132) | −303(9) | 3 301(12) | 2 110(22) |
| C(133) | −829(9) | 3 321(12) | 2 738(22) |
| C(134) | −801(9) | 3 372(12) | 3 902(22) |
| C(135) | −247(9) | 3 403(12) | 4 437(22) |
| C(136) | 278(9) | 3 383(12) | 3 809(22) |
| C(141) | 1 140(14) | 4 204(11) | 1 671(27) |
| C(142) | 899(14) | 4 682(11) | 2 381(27) |
| C(143) | 1 020(14) | 5 349(11) | 2 194(27) |
| C(144) | 1 382(14) | 5 538(11) | 1 297(27) |
| C(145) | 1 622(14) | 5 059(11) | 587(27) |
| C(146) | 1 501(14) | 4 392(11) | 774(27) |
| P(21) | 2 370(5) | 1 687(6) | 3 124(10) |
| P(22) | 2 105(5) | 3 130(6) | 3 954(9) |
| C(21) | 2 418(32) | 1 906(40) | 4 669(57) |
| C(22) | 2 600(20) | 2 586(29) | 4 745(36) |
| C(211) | 1 873(14) | 569(17) | 4 151(24) |
| C(212) | 1 747(14) | −103(17) | 4 250(24) |
| C(213) | 1 973(14) | −549(17) | 3 465(24) |
| C(214) | 2 325(14) | −322(17) | 2 581(24) |
| C(215) | 2 451(14) | 351(17) | 2 481(24) |
| C(216) | 2 225(14) | 796(17) | 3 266(24) |
| C(221) | 3 112(13) | 1 683(17) | 2 548(33) |
| C(222) | 3 187(13) | 1 749(17) | 1 394(33) |
| C(223) | 3 751(13) | 1 660(17) | 917(33) |
| C(224) | 4 240(13) | 1 505(17) | 1 595(33) |
| C(225) | 4 164(13) | 1 439(17) | 2 749(33) |
| C(226) | 3 601(13) | 1 528(17) | 3 225(33) |
| C(231) | 1 645(13) | 3 566(16) | 5 005(24) |
| C(232) | 1 570(13) | 4 245(16) | 4 872(24) |
| C(233) | 1 224(13) | 4 600(16) | 5 636(24) |
| C(234) | 955(13) | 4 275(16) | 6 534(24) |
| C(235) | 1 031(13) | 3 596(16) | 6 668(24) |
| C(236) | 1 376(13) | 3 241(16) | 5 903(24) |
| C(241) | 2 646(12) | 3 802(14) | 3 714(26) |
| C(242) | 3 092(12) | 3 905(14) | 4 512(26) |
| C(243) | 3 533(12) | 4 380(14) | 4 326(26) |
| C(244) | 3 528(12) | 4 752(14) | 3 343(26) |
| C(245) | 3 082(12) | 4 649(14) | 2 545(26) |
| C(246) | 2 641(12) | 4 174(14) | 2 731(26) |
| Sb | −805(2) | 2 678(2) | 8 029(3) |
| F(1) | −64(19) | 2 473(26) | 7 963(33) |
| F(2) | −913(19) | 2 231(21) | 6 787(34) |
| F(3) | −692(27) | 3 055(31) | 9 336(48) |
| F(4) | −1 515(17) | 3 001(20) | 8 091(31) |
| F(5) | −686(23) | 3 400(26) | 7 228(45) |
| F(6) | −1 008(27) | 2 016(32) | 8 632(52) |
| C(1) | 998(17) | 2 125(18) | 3 460(28) |
| O(1) | 997(16) | 1 919(19) | 4 393(27) |
| C(2) | 2 188(18) | 2 870(23) | 1 422(34) |
| O(2) | 2 525(14) | 3 116(16) | 767(25) |
| C(3) | 365(28) | 1 304(33) | 6 449(51) |
| Cl(1) | 1 047(8) | 1 340(9) | 7 008(14) |
| Cl(2) | 286(9) | 439(12) | 5 795(17) |

δ 41.9* [t, *J*(PC) = 12 Hz]. $^{13}$C N.m.r.: δ 195.8 [quin, *J*(PC) = 12.2 Hz].

(*b*) trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*carbonyl*(*formyl*)*ruthenium*(II) *Hexafluoroantimonate–Dichloromethane* (1/1) (1).—To a solution of *trans*-[Ru(CO)$_2$(dppe)$_2$][SbF$_6$]$_2$ (0.54 g, 0.38 mmol) in CH$_2$Cl$_2$ (30 cm$^3$) at --35 °C was added [Na{BH(OEt)$_3$}]-thf (2.3 cm$^3$, 0.33 mol dm$^{-3}$, 0.76 mmol) and the solution stirred under nitrogen for 4 h. The yellow-brown solution was then filtered into diethyl ether (200 cm$^3$, −35 °C) and left overnight at −30 °C. The resultant pale brown precipitate was collected and dried *in vacuo* to yield the crude formyl (0.32 g, 66%). Analytically pure samples of the complex were obtained by dissolving the crude material in CH$_2$Cl$_2$ (20 cm$^3$) at −35 °C, filtering, adding diethyl ether (cooled to −35 °C) to the filtrate until incipient precipitation, and standing at −35 °C for several days. Yield of the pale yellow-brown, air stable, analytically pure complex was 0.21 g, 43% (Found: C, 51.6; H, 4.1; P, 10.4. $C_{55}H_{51}Cl_2F_6O_2P_4RuSb$ requires C, 51.8; H, 4.0; P, 9.7%). $^1$H N.m.r.: † δ 5.32 (s, CH$_2$Cl$_2$), 13.6 [quin, *J*(PH) = 8 Hz, CHO]. $^{31}$P N.m.r.: δ 47.1 (s) (45.9 at −30 °C).

(*c*) trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*carbonyl*(*deuterioformyl*)*ruthenium*(II) *Hexafluoroantimonate–Dichloromethane* (1/1) (3).—The complex *trans*-[Ru(CO)$_2$(dppe)$_2$][SbF$_6$]$_2$ (0.54 g, 0.38 mmol) was stirred with [Li(DBEt$_3$)] (0.8 cm$^3$, 1.0 mol dm$^{-3}$, 0.76 mmol) for 16 h at −35 °C. The resulting black solution was worked up as described in (*b*) above to give the pale yellow crystalline complex. Yield 0.21 g, 43% (Found: C, 51.4; H, 4.0; F, 9.7; P, 9.6. $C_{55}H_{50}Cl_2DF_6O_2P_4RuSb$ requires C, 51.8; H, 4.0; F, 8.9; P, 9.7%). $^1$H N.m.r.: δ 5.32 (s, CH$_2$Cl$_2$).

(*d*) trans-*Bis*[*bis*(1,2-*diphenylphosphino*)*ethane*]*carbonyl*(*formyl*)*ruthenium*(II) *Tetraethylborate–Dichloromethane* (1/1) (2).—This complex was prepared as in (*b*) from *trans*-[Ru(CO)$_2$(dppe)$_2$][SbF$_6$]$_2$ (0.6 g, 0.42 mmol) and [Li(HBEt$_3$)]-thf (1.5 cm$^3$, 1.0 mol dm$^{-3}$, 1.5 mmol). Filtration into diethyl ether (50 cm$^3$, −35 °C) gave a clear pink solution from which the complex separated as analytically pure pink crystals (yield 0.34 g, 69%). These turned red-brown on collection and warming to room temperature *in vacuo* (Found: C, 64.4; H, 6.5; B, 0.9; P, 10.4. $C_{63}H_{71}BCl_2O_2P_4Ru$ requires C, 64.8; H, 6.1; B, 1.0; P, 10.6%). $^1$H N.m.r. (at room temperature after decomposition): δ 5.32 (s, CH$_2$Cl$_2$), 0.73 [t of 1 : 1 : 1 : 1 q, *J*(HB) = 3, *J*(HH) = 7 Hz, C*H*$_3$CH$_2$B], −0.03 [q of 1 : 1 : 1 : 1 q, *J*(HB) = 4.5 Hz, CH$_3$C*H*$_2$B]. $^{11}$B N.m.r.: δ −16.11 (s).

(*e*) trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*][$^{13}$C]*carbonyl*-

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* In a previous publication,[24] the $^{31}$P chemical shift for *trans*-[Ru(CO)$_2$(dppe)$_2$][SbF$_6$] was incorrectly quoted as −41.1 p.p.m., it should have read +41.1.

† Methylene and phenyl resonances of dppe and dppm were not analysed.

([$^{13}$C]*formyl*)*ruthenium*(II) *Tetraethylborate* (4).—This was prepared as in (*d*). The isolated solid was dissolved in degassed $CD_2Cl_2$, sealed in an n.m.r. tube and stored at −196 °C until its low-temperature (−30 °C) $^{13}$C n.m.r. spectrum could be recorded. $^{13}$C N.m.r.: δ 261.9 [d of quin, $J$(PC) = 9.5, $J$(CC) = 22.12 Hz (splits into further doublet on off-resonance decoupling), CHO], 198.7 [d of quin, $J$(PC) = 9.5 Hz, CO].

(*f*) cis-*Bis*[*bis*(*diphenylphosphino*)*methane*]*carbonyl*(*formyl*)-*ruthenium*(II) *Hexafluoroantimonate* (5).—$[Na\{HB(OEt_3)_3\}]$-thf (2.4 cm$^3$, 0.33 mol dm$^{-3}$, 0.78 mmol) was added to a solution of *cis*-$[Ru(CO)_2(dppm)_2][SbF_6]_2$ (0.55 g, 0.39 mmol) in nitromethane (7 cm$^3$) at −35 °C. The immediately formed bright yellow solution faded over a period of 0.5 h, during which time the complex precipitated as white microcrystals. After 4 h, the white solid was collected, washed with cold degassed $CH_3NO_2$ (2 × 10 cm$^3$, −35 °C), and dried *in vacuo*. After drying and warming to ambient temperature, the product was washed with light petroleum and again dried *in vacuo*. Yield 0.39 g, 86%. Analytical figures were variable and inaccurate suggesting contamination with $Li[SbF_6]$ and/or boron-containing residues.

On one occasion, the product failed to precipitate during the reaction. The yellow solution was filtered into diethyl ether (200 cm$^3$), and the resulting precipitate collected and recrystallised from $CH_2Cl_2$–diethyl ether {Found: C, 50.9; H, 3.9; N, 1.2. *trans*-$[Ru(CO)(CH_2NO_2)(dppm)_2][SbF_6]$ requires C, 52.1; H, 3.8; N, 1.2%}. I.r.: 1 965vs ($\nu_{CO}$), 1 620w br, 1 568m, 1 245m, 1 050m, 918s cm$^{-1}$.* $^{31}$P N.m.r.: δ 13.3 (s).

(*g*) cis-*Bis*[*bis*(*diphenylphosphino*)*methane*]*carbonyl*(*formyl*)-*ruthenium*(II) *Tetraethylborate* (6).—This was prepared as in (*f*), but using $[Li(HBEt_3)]$ (1.6 cm$^3$, 1.0 mol dm$^{-3}$, 1.6 mmol) as the hydride source. The solution effervesced initially, on addition of the hydride (due to reaction with the solvent, $CH_3NO_2 + H^- \longrightarrow CH_2NO_2^- + H_2\uparrow$), however the formyl started to precipitate after *ca.* 30 min. Similar treatment as in (*f*) gave the complex as pale grey microcrystals. Yield 0.32 g, 80%. $^1$H N.m.r. (−35 °C): δ 0.73 [t of 1 : 1 : 1 : 1 q, $J$(HB) = 3, $J$(HH) = 7 Hz, $CH_3CH_2B$], −0.03 [q of 1 : 1 : 1 : 1 q, $J$(HB) = 4.5 Hz, $CH_3CH_2B$], 13.1 [d of m, $J(HP_C)$ = 42 Hz]. $^{31}$P N.m.r. (−35 °C): δ $P_A$ −22.1 (d of t), $P_B$ −5.9 (ddd), $P_C$ −17.9 (q), $P_D$ not observed (obscured by resonance of decomposition product); $J(P_AP_C) = J(P_AP_D) = J(P_BP_C) = J(P_CP_D)$ = 20, $J(P_AP_B)$ = 210, $J(P_BP_D)$ = 48 Hz. For assignments see Figure 1. $^{11}$B N.m.r.: δ −16.11 (s).

(*h*) cis-*Bis*[*bis*(*diphenylphosphino*)*methane*]*carbonyl*(*deuterioformyl*)*ruthenium*(II) *Hexafluoroantimonate* (7).—As in (*g*), but using $[Li(DBEt_3)]$-thf (0.8 cm$^3$, 1.0 mol dm$^{-3}$, 0.8 mmol). Yield 0.37 g, 82%.

*Crystal Structure Determination.*—*Crystal data.* $[Ru(CDO)(CO)(Ph_2PCH_2CH_2PPh_2)_2][SbF_6]\cdot CH_2Cl_2$, $M$ = 1 276.5, Orthorhombic, $a$ = 22.364(1), $b$ = 20.244(2), $c$ = 11.944(1) Å, $U$ = 5 407 (1) Å$^3$, space group $Pn2_1a$(≡ $Pna2_1$, no. 33), $Z$ = 4, $D_c$ = 1.566 g cm$^{-3}$, μ(Cu-$K_\alpha$) = 32.7 cm$^{-1}$, λ = 1.541 8 Å, $F$(000) = 2 560.

*Data collection.* CAD4 Diffractometer, Ni-filtered Cu-$K_\alpha$ radiation, ω/2θ scan mode, ω width = 0.85 + 0.15 tanθ°, scan speed = 1.27—6.77 ° min$^{-1}$, $3.0 \leqslant \theta \leqslant 60°$. 4 685 Reflections measured, 4 157 unique, 1 752 observed [$F_o > 3\sigma(F_o)$], corrected for absorption empirically.

*Structure solution and refinement.* A standard heavy-atom method was used. Refinement was difficult due to disorder in the orientation of the $[SbF_6]^-$ ions and $CH_2Cl_2$ solvent molecules. Only Ru and Sb atoms were refined anistropically, all others were isotropic; phenyl rings were treated as regular hexagons and refined as rigid groups, with no hydrogen atoms included. Unit weights were used; final $R$ value = 0.084 (198 parameters). Final atomic co-ordinates are given in Table 5. Programs and computers used, and sources of scattering factor data are as given in ref. 45.

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* Peaks quoted are those not present in the i.r. spectrum of *trans*-$[RuCl(CO)(dppm)_2][SbF_6]$.[36]

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