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The synthesis, properties, and crystal structure of $^{n}Bu_4N[Rh(CO)_2(OAc)_2]$, and the exchange of acetate, chloride, and iodide in $^{n}Bu_4N[Rh(CO)_2(X)_2]$ *

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Abstract

Reaction of $^{n}Bu_4N[Rh(CO)_2Cl_2]$, **1**, with silver acetate under CO gave the diacetate salt $^{n}Bu_4N[Rh(CO)_2(OAc)_2]$, **2**. The complex has been characterised spectroscopically [$\nu(CO_{term})$ 1986, 2066; $\nu(CO_2$-monodentate) 1615 cm^{-1}] and by a single-crystal X-ray determination. The anion is planar with monodentate acetates, Rh–O 2.074(6) and 2.053(7) Å. Complex **2** reacted immediately with MeI to give MeOAc and $[Rh(CO)_2I_2]^-$, **3**, which then oxidatively added more MeI normally. It also reacted with HCl to give HOAc and $[Rh(CO)_2Cl_2]^-$. Evidence was obtained for the formation of a labile mixed anion $[Rh(CO)_2I(OAc)]^-$ on reaction of $[Rh_2(CO)_4I_2]$ with $^{n}Bu_4N^+ OAc^-$. It is unlikely that the promotional effect of acetate in methyl acetate carbonylation is due to the participation of acetato-rhodium complexes. Since the lithium acetate reacts readily with iodomethane to give lithium iodide, the observed promotion probably arises from the formation of LiI. MeI reacted with $^{n}Bu_4N[Rh(CO)_2Cl_2]$, again via preliminary formation of $^{n}Bu_4N[Rh(CO)_2I_2]$, which then added MeI normally. IR spectra showed that the equilibrium, $\mathbf{1} + 2I^- \rightleftharpoons \mathbf{3} + 2Cl^-$, favoured the chloride **1** in CH_2Cl_2, and the iodide **3** in methanol.

Introduction

We have recently reported studies on the oxidative addition reaction of methyl iodide and diiodo(dicarbonyl)rhodate(I), $[Rh(CO)_2I_2]^-$, [1]. This is the key step which determines the overall rate of the catalytic cycle in which MeI reacts with CO to give MeCOI, and which underlies the important commercial processes by which methanol is converted into acetic acid [2] and methyl acetate into acetic anhydride [1–4].

One of the features of the latter process is the importance of promoters, a wide variety of which has been claimed. The best is iodide, often as LiI [3,4]. One suggestion to account for its effectiveness is that LiI reacts *in situ* with methyl acetate to give lithium acetate (eq. 1),

$$\text{LiI} + \text{MeOAc} = \text{LiOAc} + \text{MeI} \qquad (1)$$

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* Dedicated to the memory of Professor P. Pino.

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Workers at Celanese also noted the promotional effects of acetate (notably lithium acetate) on the carbonylation of methyl acetate. To explain these effects they proposed that anionic acetate liganded to rhodium giving a mixed iodide–acetate anion, $[Rh(CO)_2(I)(OAc)]^-$ (or, possibly, $[Rh(CO)_2(I)_2(OAc)]^{2-}$), which, it was suggested, reacted faster with methyl iodide than did $[Rh(CO)_2I_2]^-$ [4].

In our investigation of the effect of promoters on the oxidative addition step we have also investigated this possibility. We here present evidence (i) which shows that this process is unlikely to explain the promotion, and (ii) on some related reactions involving exchange of chloride and iodide.

Results and discussion

Synthesis and structure of $Bu_4N[Rh(CO)_2(OAc)_2]$

We investigated two routes to the mixed anion $[Rh(CO)_2(I)(OAc)]^-$, one from the diacetate **2**, the other from the neutral di-iodide dimer, $[Rh_2(CO)_4I_2]$.

The diacetate salt, $Bu_4N[Rh(CO)_2(OAc)_2]$ **2**, was readily prepared by reaction of $Bu_4N[Rh(CO)_2Cl_2]$, **1**, with a large excess of silver acetate (20 equivalents, acetone, 25 °C) under an atmosphere of CO (eq. 2). The di-iodide anion, $Bu_4N[Rh(CO)_2I_2]$, **3**, could be used in place of **1**.

$$\underset{(\mathbf{1})}{Bu_4N[Rh(CO)_2Cl_2]} + 2\ AgOAc = \underset{(\mathbf{2})}{Bu_4N[Rh(CO)_2(OAc)_2]} + 2\ AgCl\downarrow \qquad (2)$$

Complex **2** was obtained as deep yellow crystals which were sensitive to air, moisture, and chlorinated solvents and were stored under CO at 0 °C. The complex was characterised spectroscopically: the IR spectrum in MeCN showed strong bands, $\nu(CO)$ 1985, 2065 (terminal CO), 1367 (CO_2, sym) and 1620 (CO_2, asymm), while that in CH_2Cl_2 was very similar [$\nu(CO)$ 1986, 2066 (terminal CO), 1371 (CO_2, sym) and 1615 (CO_2, asymm) cm^{-1}]. The presence of two terminal $\nu(CO)$ is consistent with a *cis*-dicarbonyl rhodium(I). The assignment of the two $\nu(CO_2)$ is consistent with a very asymmetric binding of the acetate, as would be expected if the acetate were monodentate. Thus for example, monodentate acetate in

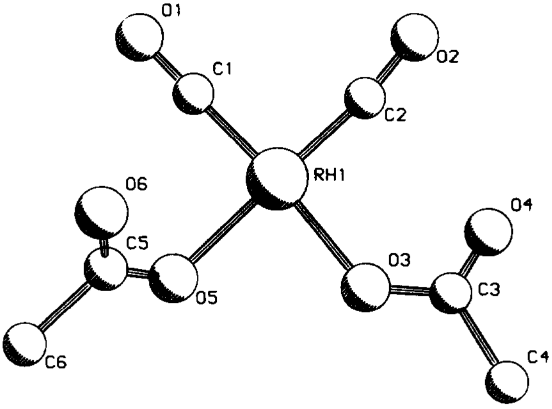


Fig. 1. Structure of complex **2** (hydrogens omitted).

[Rh(PPh$_3$)$_2$(OAc)(CO)] showed ν(CO$_2$) at 1377 and 1608 cm^{-1} [5], while ionic ^{n}Bu$_4$NOAc showed one ν(CO$_2$) at 1588 (MeCN) or 1579 (CH$_2$Cl$_2$) cm^{-1}.

The single crystal X-ray determination of complex **2** showed that the anion was essentially planar (rms deviation 0.045 Å), with the rhodium 0.010 Å from it. Both the terminal carbonyls and the acetates are *cis*. The acetates are bonded monodentate to the rhodium (Rh–O 2.074(6) and 2.053(7) Å), and are planar (rms deviations 0.006 and 0.007 Å) but are twisted in opposite directions from the mean plane of the anion by 21 and 67°, giving the anion very approximate C_2 symmetry. There are no significant short anion–cation interactions, and intramolecular non-bonded Rh–O distances are 3.17 and 3.24 Å.

Other square planar *cis*-dicarbonylrhodium(I) complexes which have been characterised by X-ray determinations and to which the structure of **2** may be compared include [Rh$_2$(CO)$_4$Cl$_2$] [6] Bu$_4$N[Rh(CO)$_2$Cl$_2$]$^-$ [7] [Rh(CO)$_2$(MeCOCHCOMe)] [8] and especially Me$_4$N[Rh(CO)$_2$(oxalate)] [9]. In the dichroic (blue-green) oxalate complex the Rh–O bonds are very similar [2.046(5), 2.044(4) Å] but the anions are stacked with appreciable Rh $\cdots$ Rh interactions [3.243(1)Å]. Presumably this is inhibited in anion **2** (intermolecular Rh $\cdots$ Rh distances, 8.297 Å) because the twist in the acetate–rhodium bonds makes close stacking more difficult.

Reactions of Bu$_4$N[Rh(CO)$_2$(OAc)$_2$]

A sample of complex **2** was dissolved in CD$_3$I (20°C, N$_2$) and the solution was immediately analysed by ^{1}H NMR spectroscopy. The reaction was 92% complete in the time needed for dissolution and the products were, CH$_3$COOCD$_3$ (δ 1.94; 76%), CH$_3$COOOCCD$_3$ (δ 2.16; 8%), and a small amount (8%) of CH$_3$COOH (δ 2.01). The identities of the products and their relative amounts were confirmed by GC and IR. In addition, the IR spectrum showed that some ^{n}Bu$_4$N[Rh(CO)(COMe)I$_3$] (ν(CO) 1712, 1735, 2060 cm^{-1}), was also present, formed by the (much slower) oxidative addition of MeI to ^{n}Bu$_4$N[Rh(CO)$_2$I$_2$]. The acetic anhydride and acetic acid are clearly side-products, and the main reaction which occurs is summarised by eq. 3,

$$2\ \mathrm{CD_3I} + {}^n\mathrm{Bu_4N}\underset{(\mathbf{2})}{[\mathrm{Rh(CO)_2(OAc)_2}]} \rightarrow 2\ \mathrm{CD_3OAc} + {}^n\mathrm{Bu_4N}\underset{(\mathbf{3})}{[\mathrm{Rh(CO)_2I_2}]} \qquad (3)$$

and is related to that of ^{n}Bu$_4$NOAc with MeI which gives methyl acetate and ^{n}Bu$_4$NI [1].

It was found that the rate of the oxidative addition of MeI to the ^{n}Bu$_4$N[Rh(CO)$_2$I$_2$] formed in the above reaction was the same as had been measured earlier [1]. We conclude that the diacetate **2** does not directly oxidatively add MeI.

Surprisingly, complex **2** did not react with a 10 equivalent excess of ^{n}Bu$_4$NI (CO, 1 atm, 20°C, 48 h) in pure acetonitrile solution. Small changes indicative of the formation of some [Rh(CO)$_2$I$_2$]$^-$ were seen in the IR spectrum (small shoulder at 1594 cm^{-1}, indicative of the formation of some free acetate) at very large ratios of iodide ($\geqslant$ 50 equivalents). However, the spectrum of **2** changed entirely to that of [Rh(CO)$_2$I$_2$]$^-$ [ν(CO) 1986, 2059 cm^{-1}] and free acetate [ν(CO$_2$) 1588 cm^{-1}] on the addition of methanol (5%), in the presence of 10 equivalents of Bu$_4$NI per Rh.

Since the clean replacement of acetate in **2** by iodide to give the mixed salt ^{n}Bu$_4$N[Rh(CO)$_2$(I)(OAc)] was difficult, the reaction of [Rh$_2$(CO)$_4$I$_2$] with

^{n}Bu$_4$NOAc (1.1 equivalent per Rh, THF, CO, 1 atm, 20 ° C) was tried instead. That gave a pale yellow solution with an IR spectrum indicative of the presence of *cis*-dicarbonylrhodium anionic species [ν(CO) 1979, 2058 cm^{-1}]. On addition of diethyl ether, a yellow solid was formed, which was crystallised from acetone–diethyl ether to give deep yellow crystals. Unfortunately, these were not homogeneous; one was identified as ^{n}Bu$_4$N[Rh(CO)$_2$(OAc)$_2$], **2** [IR ν(CO$_2$, monodentate acetate) 1619 cm^{-1}; negative ion FAB mass-spectrum, *m/z* 277], others as ^{n}Bu$_4$N[Rh(CO)$_2$I$_2$], **3** [ν(CO) 1988, 2060 cm^{-1} in CH$_2$Cl$_2$]. Attempts to purify the material to obtain a homogeneous sample were unsuccessful; we conclude that the iodide and acetate ligands exchange rapidly (eq. 4) and that a mixture of the ^{n}Bu$_4$N$^+$ salts of the anions [Rh(CO)$_2$I$_2$]$^-$, [Rh(CO)$_2$(OAc)$_2$]$^-$, and probably [Rh(CO)$_2$I(OAc)]$^-$, is always present. The situation in both reactions seems quite analogous to that between [Rh(CO)$_2$I$_2$]$^-$ and [Rh(CO)$_2$Cl$_2$]$^-$, see below.

$$[\mathrm{Rh(CO)_2I_2}]^- + [\mathrm{Rh(CO)_2(OAc)_2}]^- \rightleftharpoons 2[\mathrm{Rh(CO)_2I(OAc)}]^- \qquad (4)$$

There was no evidence from this work that the mixed species, [Rh(CO)$_2$I(OAc)]$^-$, was present in large amount in these mixtures or that it reacted with methyl iodide, except via the preliminary formation of [Rh(CO)$_2$I$_2$]$^-$. Since carbonylation reactions are generally run with excess MeI, and under quite acid conditions, it is unlikely that significant amounts of acetato-liganded anions will be present. This makes it unlikely that the "acetate effect" noted in carbonylations, is due to the participation of acetato-rhodium complexes. We favour the explanation that, since the lithium acetate reacts readily with iodomethane to give lithium iodide (and methyl acetate; reverse of eq. 1), the observed effect arises from the formation of LiI, the true promoter.

We also noted that complex **2** did not react with hydrogen (2 atm, 20 ° C, in (CD$_3$)$_2$CO), but did react with traces of HCl present in normal bench CH$_2$Cl$_2$, to give [Rh(CO)$_2$Cl$_2$]$^-$.

Interconversions of [Rh(CO)$_2$Cl$_2$]$^-$ and [Rh(CO)$_2$I$_2$]$^-$ and related processes

To compare with the reaction found for ^{n}Bu$_4$N[Rh(CO)$_2$I$_2$] [1], we have examined the reaction of methyl iodide with ^{n}Bu$_4$N[Rh(CO)$_2$Cl$_2$]. The rate was measured in both THF and CH$_2$Cl$_2$ under pseudo first order conditions using a large excess of methyl iodide, as previously described [1]. The observed second order rate constants (3×10^{-5} M^{-1} s^{-1} in CH$_2$Cl$_2$; 3.2×10^{-5} M^{-1} s^{-1} in THF) were identical to those measured for the reaction of [Rh(CO)$_2$I$_2$]$^-$ and MeI in the same solvents. Close examination of the reaction showed a short induction period, during which the IR spectrum changed, consistent with the formation of [Rh(CO)$_2$I$_2$]$^-$. Thus the overall reaction again proceeded in two stages. In the first, fast step ($t_{1/2}$ ca. 40 s), halide exchange occured with the formation of [Rh(CO)$_2$I$_2$]$^-$ (shown by IR) and of methyl chloride (detected by GC), eq. 5,

$$[\mathrm{Rh(CO)_2Cl_2}]^- + 2\mathrm{MeI} = [\mathrm{Rh(CO)_2I_2}]^- + 2\ \mathrm{MeCl} \qquad (5)$$

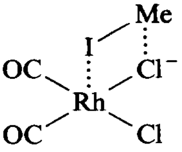
In confirmation of this, when the reaction was quenched after 10 min, the rhodium complex ^{n}Bu$_4$N[Rh(CO)$_2$I$_2$] (characterised by IR and microanalysis), was isolated in essentially quantitative yield. The second step is then the normal oxidative addition of MeI to [Rh(CO)$_2$I$_2$]$^-$, eq. 6, which proceeds at its normal rate ($t_{1/2}$ ca.

7000 s), slower than reaction 5. In methyl iodide as reactant and solvent (25 °C) reaction 5 was complete in ca. 10 min, while reaction 6 required ca. 600 min.

$$[Rh(CO)_2I_2]^- + MeI = [Rh(CO)(COMe)I_3]^- \qquad (6)$$

By contrast, in methanol the halide exchange was significantly slower ($t_{1/2}$ ca. 800 s) and comparable in rate to the oxidative addition ($t_{1/2}$ ca. 2200 s). The kinetics of the reaction in methanol are complex and it is possible that oxidative addition of MeI may be occurring to $[Rh(CO)_2Cl_2]^-$, $[Rh(CO)_2ICl]^-$ as well as to $[Rh(CO)_2I_2]^-$.

The mechanism of the halide exchange is not yet clear. One possibility would be a concerted reaction, via a 4-centre transition state, in which iodomethane initially coordinates to the rhodium. Complexes of iodomethane are now known, for example, $[Ir(H_2)(IMe)_2(PPh_3)_2]SbF_6$. There the Ir–I–$CH_3$ angles are 106 and 108°, close to tetrahedral [10]. Such a coordination in **A** would bring the methyl into close proximity to the chloride, as shown.



(A)

We have also investigated the halide preferences in reaction 7

$$[Rh(CO)_2Cl_2]^- + 2\,I^- \xrightleftharpoons{K_{eq}} [Rh(CO)_2I_2]^- + 2\,Cl^- \qquad (7)$$

Since ν(CO) for the chloride **1** (1993, 2070 in CH_2Cl_2; 2001, 2075 in methanol) were different to those from the iodide **3** (1988, 2060 in CH_2Cl_2; 1990, 2060 cm^{-1} in methanol) the reactions were monitored by IR spectroscopy. On addition of even a small excess of chloride to **3** in CH_2Cl_2 the spectrum changed to that of **1**. By contrast, in the presence of only 10% methanol in CH_2Cl_2, addition of iodide to a solution of the chloride **1**, iodide was the preferred ligand and the spectrum changed to that of **3**. In each case the changes were instantaneous on mixing, and no further changes occurred on standing. We estimate K_{eq} to be about 0.02 in CH_2Cl_2 and 50 in 10% methanol in CH_2Cl_2; similar data were obtained by Forster, using UV-visible spectroscopy, who found K_{eq} to be ca. 0.01 in $C_2H_4Cl_2$, 0.005 in MeCN, and 30 in MeCN–water (10%) [11].

When equimolar solutions of $Ph_4As[Rh(CO)_2Cl_2]$ and $Ph_4As[Rh(CO)_2I_2]$ were mixed in CH_2Cl_2 and the resultant IR spectrum was electronically subtracted from that of the sum of the IR spectra of the components, a clean difference spectrum was obtained, with ν(CO) 1989, 2063 cm^{-1}. This is almost certainly the ν(CO) of the mixed salt, $Ph_4As[Rh(CO)_2ClI]$.

The far IR spectra of $Ph_4As[Rh(CO)_2Cl_2]$ and $Ph_4As[Rh(CO)_2I_2]$ show ν(Rh–Cl) bands at 291, 320 cm^{-1} and ν(Rh–I) bands at 176, 195 cm^{-1} respectively. When the IR spectrum of the residue (which remains after the solvent had been removed from an equimolar mixture of the two anions) was examined, a band at 302 cm^{-1}, ν(Rh–Cl), and one at 188 cm^{-1}, ν(Rh–I), were found, in addition to those characteristic of each of the parent anions. These bands are also probably due to the mixed species, $Ph_4As[Rh(CO)_2ClI]$.

The FAB anion mass-spectrum of $Ph_4As[Rh(CO)_2Cl_2]$, shows peaks for M^- at m/z 229, $(M-CO)^-$ at 201, and $(M-2CO)^-$ at 173. The analogous peaks are found in a sample of $Ph_4As[Rh(CO)_2I_2]$, M^- 413, $(M-CO)^-$ 385, and $(M-2CO)^-$ 357. An equimolar mixture of $Ph_4As[Rh(CO)_2Cl_2]$ and $Ph_4As[Rh(CO)_2I_2]$ showed the above peaks and also those expected for $[Rh(CO)_2ClI]^-$: M^- 321, $(M-CO)^-$ 293, and $(M-2CO)$ 265.

Attempts to isolate the iodo-chloride anion were unsuccessful. However, the three sets of data taken together provide reasonable evidence for the presence of the mixed anion, $[Rh(CO)_2ClI]^-$ in an equimolar mixture of Ph_4As $[Rh(CO)_2Cl_2]$ and $Ph_4As[Rh(CO)_2I_2]$. We may make the *qualitative* estimate that roughly equal amounts of the three anions are present. Thus it appears that the equilibrium (8) does indeed occur under suitable conditions,

$$[Rh(CO)_2Cl_2]^- + [Rh(CO)_2I_2]^- \rightleftharpoons 2[Rh(CO)_2ClI]^- \qquad (8)$$

Similar conclusions were reached by Palyi et al. concerning the intermediacy of $[Rh_2(CO)_4ClI]$ in hexane solutions containing $[Rh(CO)_4Cl_2]$ and $[Rh_2(CO)_4I_2]$ [12].

Conclusion

In summary then we have shown that while rhodium(I) *cis*-dicarbonyls form reasonably stable anions of the type $[Rh(CO)_2X_2]^-$ with a variety of X, including acetate, mixed anions $[Rh(CO)_2XY]^-$ are not favoured, are not isolable by conventional means, and exist only in mixtures with $[Rh(CO)_2X_2]^-$ and $[Rh(CO)_2Y_2]^-$, probably as minor components. We have found no compelling reason to invoke them as particularly reactive intermediates in oxidative addition reactions.

Experimental

All operations were carried out under dry nitrogen. Solvents were purified as described [1], and then distilled under nitrogen immediately prior to use. Microanalyses were performed by the University of Sheffield microanalysis service. GC analyses were carried out on a Perkin–Elmer 8700 chromatograph (FID detector/H_2 carrier gas; DB1 wide bore capillary column (15 m) for liquid analyses; Porapak QS column (2.5 m) for gas analyses). IR spectra were measured on a Perkin–Elmer 1710 or a 1600 FT spectrometer using CaF_2 solution cells (0.1 mm spacing) with electronic subtraction of solvent. Measurements were at 20 °C using a 2 cm^{-1} resolution. ^1H NMR spectra were measured on a Bruker AM 250, and mass-spectra of complexes on a Kratos MS 80 [FAB] spectrometer operating in the negative ion mode and using *p*-nitrobenzyl alcohol (halide complexes) or sulpholane (acetate complex) as matrix. All the rhodium complexes were stored under nitrogen or carbon monoxide in the refrigerator at ca 0 °C. The anionic rhodium(I) chlorides, iodides and acetates had useful shelf lives of ca 1–2 months under these conditions.

$^nBu_4N[Rh(CO)_2Cl_2]$, 1

This was prepared by a modification of the method of Vallarino [13] from $[Rh_2(CO)_4Cl_2]$ [14] (0.16 g, 0.8 mmol) in methanol (20 cm^3) and $^nBu_4NCl$ (0.96

mmol) in methanol (5 cm^3) under nitrogen. After filtration and the removal of part of the solvent it was crystallised at 0 °C. (Analysis. Found: C, 45.6; H, 7.7; N, 2.6; Cl, 15.0. $C_{18}H_{36}Cl_2NO_2Rh$ calc.: C, 45.7; H, 7.6; N, 3.0; Cl, 15.0%. FAB mass-spectrum *m/z* 229, M^-; ν(CO) 1993, 2070 cm^{-1}.)

$^nBu_4N[Rh(CO)_2(OAc)_2]$, 2

A pale yellow solution of $^nBu_4N[Rh(CO)_2Cl_2]$ (**1**) (1.43 g, 3 mmol) in acetone (6 cm^3) under CO (1 atm) was added to an excess of AgOAc (4 g) in a foil-wrapped flask. The mixture was stirred (5 cm^3) and filtered to yield a deep yellow/orange solution. The volume of the solution was reduced under CO, until solid began to separate; the solid was redissolved on warming, and ether (1 cm^3) was added dropwise. Acetone (0.05 cm^3) was added and the solution was left to crystallise under CO at 0 °C to give yellow crystals of **2**; yield 0.47 g, 30%. (Analysis. Found: C, 50.7; H, 8.15; N, 2.7. $C_{22}H_{42}NO_6Rh$ calc.: C, 50.9; H, 8.2; N, 2.7.) ^{1}H NMR (250 MHz, $(CD_3)_2CO$) δ 3.46 (8H, t, N–CH_2), 1.84 (8H, q, N–CH$_2$–CH_2), 1.76 (6H, s, RhO$_2$CCH_3), 1.44 (8H, sxt, N–(CH$_2$)$_2$–CH_2), 0.99 (12H, t, N–(CH$_2$)$_3$–CH_3),

Table 1

Bond lengths (Å) and bond angles (°) for $^nBu_4N[Rh(CO)_2(O_2CCH_3)_2]$, **2**

Rh(1)–O(3)	2.053(7)	Rh(1)–O(5)	2.074(6)
Rh(1)–C(1)	1.826(11)	Rh(1)–C(2)	1.817(12)
N(1)–C(7)	1.515(10)	N(1)–C(11)	1.530(9)
N(1)–C(15)	1.517(11)	N(1)–C(19)	1.522(9)
O(1)–C(1)	1.150(14)	O(2)–C(2)	1.165(14)
O(3)–C(3)	1.274(15)	O(4)–C(3)	1.201(16)
O(5)–C(5)	1.282(11)	O(6)–C(5)	1.216(10)
C(3)–C(4)	1.522(18)	C(5)–C(6)	1.530(13)
C(7)–C(8)	1.521(13)	C(8)–C(9)	1.525(13)
C(9)–C(10)	1.520(18)	C(11)–C(12)	1.534(11)
C(12)–C(13)	1.512(12)	C(13)–C(14)	1.518(14)
C(15)–C(16)	1.507(13)	C(16)–C(17)	1.537(16)
C(17)–C(18)	1.521(19)	C(19)–C(20)	1.550(10)
C(20)–C(21)	1.530(12)	C(21)–C(22)	1.519(13)
O(3)–Rh(1)–O(5)	83.7(3)	O(3)–Rh(1)–C(1)	174.7(4)
O(5)–Rh(1)–C(1)	91.5(4)	O(3)–Rh(1)–C(2)	96.3(4)
O(5)–Rh(1)–C(2)	176.8(4)	C(1)–Rh(1)–C(2)	88.6(5)
C(7)–N(1)–C(11)	111.2(6)	C(7)–N(1)–C(15)	106.2(6)
C(11)–N(1)–C(15)	111.2(6)	C(7)–N(1)–C(19)	112.0(6)
C(11)–N(1)–C(19)	104.6(5)	C(15)–N(1)–C(19)	111.6(6)
Rh(1)–O(3)–C(3)	124.9(7)	Rh(1)–O(5)–C(5)	120.5(5)
Rh(1)–C(1)–O(1)	177.5(9)	Rh(1)–C(2)–O(2)	172.7(10)
O(3)–C(3)–O(4)	126.3(11)	O(3)–C(3)–C(4)	115.0(11)
O(4)–C(3)–C(4)	118.7(12)	O(5)–C(5)–O(6)	126.6(9)
O(5)–C(5)–C(6)	113.0(7)	O(6)–C(5)–C(6)	120.3(9)
N(1)–C(7)–C(8)	116.1(7)	C(7)–C(8)–C(9)	111.2(8)
C(8)–C(9)–C(10)	112.3(9)	N(1)–C(11)–C(12)	115.9(6)
C(11)–C(12)–C(13)	108.9(7)	C(12)–C(13)–C(14)	112.0(8)
N(1)–C(15)–C(16)	117.1(7)	C(15)–C(16)–C(17)	110.1(9)
C(16)–C(17)–C(18)	112.1(11)	N(1)–C(19)–C(20)	115.8(6)
C(19)–C(20)–C(21)	109.8(6)	C(20)–C(21)–C(22)	112.8(7)

[2.91 (s, br, H_2O)]. FAB mass-spectroscopy, m/z 277 (M^-, 249 ($M-$CO), 218 ($M-$OAc). IR spectrum, ν(CO) 2066, 1986 (terminal carbonyls, *cis*), ν(CO_2-asymm) 1615br, ν(CO_2-symm) 1371 cm^{-1} (CH_2Cl_2) and ν(CO) 2065, 1985, ν(CO_2) 1620br cm^{-1} (MeCN).

Crystal structure of tetra-n-butylammonium cis*-di(acetato-*O*)-dicarbonylrhodate(I), 2*

Tetra-n-butylammonium *cis*-di(acetato-*O*)dicarbonylrhodate(I) $C_{22}H_{42}NO_6Rh$, $M = 519.48$, was crystallised from acetone/ether as yellow blocks. Crystal dimensions 0.55 × 0.35 × 0.30 mm, monoclinic, $a = 9.948(8)$, $b = 13.871(13)$, $c = 20.476(18)$ Å, $\beta = 101.35(7)°$, $U = 2770(4)$ Å^3; $D_c = 1.246$ g cm^{-3}, $Z = 4$, space group $P2_1/n$ (a non-standard setting of $P2_1/c$, C_{2h}^5, no. 14), Mo-K_α radiation ($\lambda = 0.71069$ Å), μ(Mo-K_α) = 6.35 cm^{-1}, F(000) = 1095.87.

The selected crystal was coated with Araldite. Three-dimensional, room-temperature X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 4-circle diffractometer by the omega scan method. The 2942 independent reflections for

Table 2

Atom coordinates (×10^4) and temperature factors (Å^2 ×10^3) for ^{n}Bu$_4$N[Rh(CO)$_2$(O$_2$CCH$_3$)$_2$], 2

Atom	x	y	z	U_{eq} [a]
Rh(1)	840(1)	2250(1)	3123(1)	61(1)
N(1)	5278(6)	3457(4)	1215(3)	43(2)
O(1)	1213(10)	3587(7)	4281(5)	126(5)
O(2)	3752(7)	2669(7)	3071(4)	112(4)
O(3)	412(7)	1287(5)	2349(3)	86(3)
O(4)	2078(10)	1674(7)	1827(5)	133(5)
O(5)	−1202(6)	2041(4)	3172(3)	64(2)
O(6)	−755(7)	1296(5)	4157(3)	71(3)
C(1)	1090(11)	3056(8)	3841(5)	81(5)
C(2)	2600(12)	2488(8)	3048(5)	86(5)
C(3)	1087(12)	1211(8)	1883(6)	89(5)
C(4)	578(15)	433(10)	1370(6)	136(8)
C(5)	−1529(9)	1669(6)	3692(4)	54(3)
C(6)	−3071(9)	1708(8)	3681(5)	77(4)
C(7)	4104(8)	4173(6)	1120(4)	50(3)
C(8)	3116(8)	4078(7)	1596(5)	61(4)
C(9)	1881(10)	4741(8)	1395(6)	87(5)
C(10)	882(11)	4668(10)	1867(7)	117(7)
C(11)	6126(8)	3504(5)	1924(4)	46(3)
C(12)	6783(9)	4482(6)	2142(4)	51(3)
C(13)	7561(11)	4403(7)	2853(4)	71(4)
C(14)	8236(11)	5348(7)	3106(5)	81(4)
C(15)	6138(8)	3718(6)	706(4)	50(3)
C(16)	7396(10)	3115(8)	700(5)	74(4)
C(17)	8202(11)	3528(10)	196(5)	100(6)
C(18)	9397(13)	2884(12)	115(7)	142(8)
C(19)	4773(8)	2420(5)	1134(4)	43(3)
C(20)	3780(9)	2185(6)	470(4)	57(3)
C(21)	3593(10)	1092(6)	397(4)	66(4)
C(22)	2533(12)	809(8)	−213(5)	95(5)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor. Atoms N(1), C(7)–C(22) consitute the tetra-n-butylammonium cation.

which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 8 azimuthal scans. The structure was solved by Patterson and Fourier techniques and refined by blocked cascade least-squares methods. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Refinement converged at a final R 0.0665 (unit weights), with allowance for the thermal anisotropy of all non-hydrogen atoms. Complex scattering factors were taken from ref. 15 and from the program package SHELXTL as implemented on the Data General Nova 3 computer [16]. Bond lengths and angles are given in Table 1, atomic coordinates and temperature factors in Table 2. Hydrogen atom coordinates and structure factors are available from the author.

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