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Reactions of the Carboxylate A-frame Complexes, $[Rh(\mu\text{-}O_2CR)(CO)_2(\mu\text{-dppm})_2]ClO_4$ with Small Molecules. Heterolytic Activation of Dihydrogen by the Carbonyl Adducts $[Rh_2(\mu\text{-}CO)(\mu\text{-}O_2CR)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (R = CH_2Cl, $CHCl_2$, CCl_3, CF_3)

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Abstract

The reactivity of the carboxylate A-frame complexes $[Rh_2(\mu\text{-}O_2CR)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (R = H, CH_3, CH_2Cl, $CHCl_2$, CCl_3, CF_3) towards CO, H_2/CO mixtures and halogens has been investigated. Unlike the acetate and formate complexes, whose reactions with CO have been reported elsewhere, all four halocarboxylates reacted with CO to give labile, isolable adducts, $[Rh_2(\mu\text{-}CO)(\mu\text{-}O_2CR)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (R = CH_2Cl, $CHCl_2$, CCl_3, CF_3) at room temperature and pressure. In a most unusual reaction, the same halocarboxylate A-frame complexes promote the heterolytic activation of dihydrogen when reacted with an H_2/CO gas mixture. The carbonyl adducts have been shown to be intermediates in the formation of the product $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]ClO_4$. A rationale is proposed for this reaction in which only one metal centre is directly involved in the activation of H_2. The carboxylate A-frame complexes with R = H, CH_3 and CF_3 react with halogens to give the 1,2-transannular oxidative addition products $[Rh_2(\mu\text{-}O_2CR)X_2(CO)_2(\mu\text{-dppm})_2]ClO_4$ (X = Cl, Br, I). With R = H, CH_3 these are the sole products but with R = CF_3, several unidentified minor products, apparently containing Rh(III) centres, were also formed.

Introduction

In 1982, Mague and DeVries [1] reported the synthesis of the carboxylate bridged A-frame complexes $[Rh_2(\mu\text{-}O_2CR)(CO)_2(L_2)_2]PF_6$ (L_2 = dppm, R = CH_3; L_2 = dpam, R = CH_3, C_2H_5). All three complexes underwent rapid exchange of the terminal carbonyl groups at room temperature, but only for $[Rh_2(\mu\text{-}OAc)(CO)_2(\mu\text{-dppm})_2]PF_6$ could a bridging carbonyl adduct be detected, and then only at −70 °C; quite in contrast to other related A-frame complexes such as $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-dppm})_2]BPh_4$ [2]. Shortly thereafter, Eisenberg *et al.* [3] reported the synthesis of the formate $[Rh_2(\mu\text{-}O_2CH)(CO)_2(\mu\text{-dppm})_2]Y$ (Y^- = PF_6^- or BF_4^-) which reacted with CO in solution to give $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]Y$ via decarboxylation of the formate group. At the time these reports appeared, we had just developed a simple, general synthetic method for such carboxylate complexes consisting of the reaction of $[Rh_2(\mu\text{-}OC_2H_5)(CO)_2(\mu\text{-dppm})_2]ClO_4$ with the appropriate carboxylic acid [4]. We proceeded therefore to prepare the series $[Rh_2(\mu\text{-}O_2CR)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (R = H, CH_3, CH_2Cl, $CHCl_2$, CCl_3 and CF_3) in order to determine the influence, if any, of the nature of the carboxylate group on the reactivity of the complex towards carbon monoxide. At the same time we also investigated the reactivity of certain of these carboxylate complexes with halogens in an effort to see whether or not the tendency for these compounds to undergo transannular oxidative additions [5–9] could be influenced by the nature of the bridging carboxylate function. In addition to these results, we also wish to report on the reaction of the carboxylate complexes with H_2/CO mixtures to yield known $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]ClO_4$, which represents the first instance in which an isolable binuclear hydride complex has resulted from the addition of dihydrogen to a rhodium A-frame complex.

Results and Discussion

Reactions with Carbon Monoxide

In our hands, both the acetate and formate complexes $[Rh_2(\mu\text{-}O_2CR)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (R = CH_3, H) reacted with carbon monoxide with essentially the same results as reported previously [1, 3]. Thus the acetate failed to form a carbonyl adduct at room temperature and pressure whereas the formate complex decomposed to give $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]ClO_4$. Confirmation of the latter result was complicated, however, by substantial

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differences between our physical data for this complex and those reported by Eisenberg *et al.* [3]. Thus, $[Rh_2(\mu\text{-}O_2CH)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ reacted with CO in dichloromethane to give a wine-red solution from which could be isolated red-brown crystals upon the addition of diethyl ether. The red-brown complex exhibited infrared absorptions (Table I) at 2002(s), 1989(vs) and 1898(s) cm^{-1} in the solid state, whilst in dichloromethane solution the corresponding bands occurred at 2003(sh), 1992(vs) and 1902(m) cm^{-1}. By comparison, the solid state and solution values were reported for purple $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]PF_6$ as occurring at 1972(s), 1957(vs), 1870(s), and 1980(s), 1963(vs) and 1870(s) cm^{-1} respectively. In order to verify that the nature of the anion was not responsible for the observed discrepancies, we synthesized $[Rh_2(\mu\text{-}O_2CH)(CO)_2(\mu\text{-}dppm)_2]PF_6$ and reacted it with CO as described by Eisenberg. Once again, we obtained a wine-red solution from which a brown solid could be isolated. The infrared data on this compound were virtually identical to those of its perchlorate analogue except that in the solid state, two bridging carbonyl frequencies were observed at 1873 and 1898 cm^{-1}. In solution, however, only one band at 1902 cm^{-1} could be seen in this region. Needless to say, in all the products identified as containing the $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]^+$ cation, there was never any evidence for the presence of the formate group.

Although we generally obtained only brown or red-brown crystals of either salt of the above cation, it did prove possible to isolate purple crystals of the PF_6^- salt, in the form of a dichloromethane solvate, by recrystallization at –18 °C from dichloromethane and diethyl ether. In the solid state, infrared $\nu(CO)$ maxima for the purple form occurred at 1995(sh), 1984(s) and 1874(m) cm^{-1}, still at variance with the data reported by Eisenberg, while in CH_2Cl_2 solution the $\nu(CO)$ bands occurred in exactly the same positions as seen for the brown form. Thus, for the PF_6^- salt at least, there appears to be two different forms possible in the solid state. Despite the discrepancies in the infrared data, however, it

TABLE I. Infrared Data of Compounds Derived from the Carboxylates $[Rh_2(\mu\text{-}O_2CR)(CO)_2(\mu\text{-}dppm)_2]ClO_4$.

	Compound	$\nu(CO)^a$, cm^{-1}	Others^b, cm^{-1}
	$[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]ClO_4$	2003 sh, 1992 vs, 1902 m (2002 s, 1989 vs, 1898 s)	–
	$[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]PF_6 \cdot CH_2Cl_2$ (purple crystals)	2003 sh, 1992 vs, 1902 m (1995 sh, 1984 vs, 1874 m)	–
	$[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]PF_6$ (brown crystals)	2003 sh, 1992 vs, 1902 m (2002 sh, 1988 vs, 1898 m, 1873 m)	–
1	$[Rh_2(\mu\text{-}CO)(\mu\text{-}O_2CCH_2Cl)(CO)_2(\mu\text{-}dppm)_2]ClO_4$	2001 sh, 1996 vs, 1836 m (1992 s, 1977 vs, 1821 m)	$\nu_a(CO_2)$, 1561 m $\nu_s(CO_2)$, 1376 m
2	$[Rh_2(\mu\text{-}CO)(\mu\text{-}O_2CCHCl_2)(CO)_2(\mu\text{-}dppm)_2]ClO_4$	1997 vs, 1839 m (1996 s, 1982 w, 1824 m)	$\nu_a(CO_2)$, 1595 m $\nu_s(CO_2)$, 1402 m
3	$[Rh_2(\mu\text{-}CO)(\mu\text{-}O_2CCCl_3)(CO)_2(\mu\text{-}dppm)_2]ClO_4$	1999 vs, 1840 m (1996 sh, 1988 vs, 1820 m)	$\nu_a(CO_2)$, 1614 m $\nu_s(CO_2)$, 1335 m
4	$[Rh_2(\mu\text{-}CO)(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-}dppm)_2]ClO_4 \cdot CH_2Cl_2$	2009 sh, 1997 vs, 1841 m (1997 s, 1988 vs, 1824 m)	$\nu_a(CO_2)$, 1623 s
5	$[Rh_2(\mu\text{-}O_2CH)Cl_2(CO)_2(\mu\text{-}dppm)_2]ClO_4 \cdot 0.5CH_2Cl_2 \cdot 0.5C_4H_{10}O$	2060 vs, 2032 m (2051 vs, 2022 m)	$\nu_a(CO_2)$, 1555 m $\delta(CH)$, 1353 m
6	$[Rh_2(\mu\text{-}O_2CH)Br_2(CO)_2(\mu\text{-}dppm)_2]ClO_4 \cdot 0.5CH_2Cl_2 \cdot 0.5C_4H_{10}O$	2057 vs, 2030 m (2048 vs, 2019 m)	$\nu_a(CO_2)$, 1555 s $\delta(CH)$, 1352 m
7	$[Rh_2(\mu\text{-}O_2CH)I_2(CO)_2(\mu\text{-}dppm)_2]ClO_4$	2048 vs, 2023 m (2040 vs, 2014 m)	$\nu_a(CO_2)$, 1560 m $\delta(CH)$, 1355 m
8	$[Rh_2(\mu\text{-}O_2CCH_3)Cl_2(CO)_2(\mu\text{-}dppm)_2]ClO_4 \cdot 0.5CH_2Cl_2 \cdot 0.5C_4H_{10}O$	2058 vs, 2031 m (2050 vs, 2021 m)	$\nu_a(CO_2)$, 1538 m
9	$[Rh_2(\mu\text{-}O_2CCH_3)Br_2(CO)_2(\mu\text{-}dppm)_2]ClO_4 \cdot 0.5CH_2Cl_2 \cdot 0.5C_4H_{10}O$	2056 vs, 2028 m (2047 vs, 2019 m)	$\nu_a(CO_2)$, 1537 m
10	$[Rh_2(\mu\text{-}O_2CCH_3)I_2(CO)_2(\mu\text{-}dppm)_2]ClO_4$	2047 vs, 2021 m (2046 vs, 2021 m)	$\nu_a(CO_2)$, 1539 m
11	$[Rh_2(\mu\text{-}O_2CCF_3)Cl_2(CO)_2(\mu\text{-}dppm)_2]ClO_4$	2063 s, 2033 sh (2064 s, 2035 m)	$\nu_a(CO_2)$, 1645 m
12	$[Rh_2(\mu\text{-}O_2CCF_3)Br_2(CO)_2(\mu\text{-}dppm)_2]ClO_4$	2060 s, 2030 sh (2062 s, 2030 m)	$\nu_a(CO_2)$, 1646 m
13	$[Rh_2(\mu\text{-}O_2CCF_3)I_2(CO)_2(\mu dppm)_2]ClO_4$	2051 s, 2023 m (2055 s, 2031 m)	$\nu_a(CO_2)$, 1647 m

[a] Recorded in dichloromethane solution. Solid state values in parentheses. [b] Solid state values.

does appear that the compounds isolated by ourselves and Eisenberg from the reaction of the formate A-frame complexes with CO are one and the same. This seems valid also when comparing ^1H and ^{31}P NMR data (Table II). At 360 MHz, $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]ClO_4$ exhibits multiplets at 7.56 (40 H, Ph), 4.18, 4.11 (2 H + 2 H, dppm-CH_2) and –9.76 (1 H, μ-H) ppm which are closely comparable to those reported previously, given the differences in conditions under which the spectra were obtained. Similarly, the ^{31}P chemical shift of 28.65 ppm obtained in CD_2Cl_2 is comparable to the 27.24 value reported. A closer comparison between the ^{31}P NMR data proved impossible since the value of 27.24 ppm was referenced to internal trimethylphosphate, the chemical shift of which ranges from –2.4 to +2.4 ppm relative to 85% H_3PO_4, depending upon conditions [10], and the fact that no further information concerning the symmetric AA′A″A‴XX′ multiplet was provided. We have successfully simulated[†] the ^{31}P NMR spectrum of $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (Fig. 1) using the following parameters (designation as shown in Fig. 1): $^{31}P = 28.65$ ppm; $^1J_{AX} = 109.7$, $^2J_{AA'} = 400$, $^2J_{AA''} = 78.1$, $^4J_{AA'''} = 40.7$, $^xJ_{AX'} = -0.7$, $^1J_{XX'} = 0.0$ Hz. As is typical for this spin system, the principal features of the spectrum are essentially invariant with respect to $^2J_{AA''}$ so that this parameter is poorly defined.

Unlike their acetate analogue, the halocarboxylate A-frame complexes $[Rh_2(\mu\text{-}O_2CR)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (R = CH_2Cl, $CHCl_2$, CCl_3 and CF_3) all react with CO to give isolable but labile adducts, $[Rh_2(\mu\text{-}O_2CR)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (**1**–**4**). The spectroscopic properties of these adducts are as anticipated. Thus, the infrared spectra of **1**–**4** all

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[†] All simulations were achieved using the LAME program.

TABLE II. ^1H and $^{31}P\{^1H\}$ NMR Data of Compounds Derived from the Carboxylates $[Rh_2(\mu\text{-}O_2CR)(CO)_2(\mu\text{-dppm})_2]ClO_4$.

	Compound	Chemical shifts (ppm)[a]
	$[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]ClO_4$	^{31}P: 28.65(m, dppm, $\lvert {}^1J_{Rh-P} + {}^xJ_{Rh-P}\rvert = 109.0$ Hz)[b] ^1H: 7.56(m, 40H, Phenyl); 4.18, 4.11(m, 4H, CH_2-dppm)[c] –9.76(m, 1H, H)
1	$[Rh_2(\mu\text{-}CO)(\mu\text{-}O_2CCH_2Cl)(CO)_2(\mu\text{-dppm})_2]ClO_4$	^{31}P: 33.80(m, dppm, $\lvert {}^1J_{Rh-P} + {}^xJ_{Rh-P}\rvert = 93.4$ Hz)[d]
2	$[Rh_2(\mu\text{-}CO)(\mu\text{-}O_2CCHCl_2)(CO)_2(\mu\text{-dppm})_2]ClO_4$	^{31}P: 32.78(m, dppm, $\lvert {}^1J_{Rh-P} + {}^xJ_{Rh-P}\rvert = 93.2$ Hz)[b, d]
3	$[Rh_2(\mu\text{-}CO)(\mu\text{-}O_2CCCl_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$	^{31}P: 32.70(m, dppm, $\lvert {}^1J_{Rh-P} + {}^xJ_{Rh-P}\rvert = 93.1$ Hz)[d]
4	$[Rh_2(\mu\text{-}CO)(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-dppm})_2]ClO_4 \cdot CH_2Cl_2$[e]	^{31}P: 32.62(m, dppm, $\lvert {}^1J_{Rh-P} + {}^xJ_{Rh-P}\rvert = 93.8$ Hz)[d]
5	$[Rh_2(\mu\text{-}O_2CH)Cl_2(CO)_2(\mu\text{-dppm})_2]ClO_4 \cdot 0.5CH_2Cl_2 \cdot 0.5C_4H_{10}O$[e]	^{31}P: 16.10(m, dppm, $\lvert {}^1J_{Rh-P} + {}^xJ_{Rh-P}\rvert = 80.8$ Hz)[b] ^1H: 7.57(m, 40H, Phenyl); 6.32(m, 1H, CH); 5.32(s, CH_2Cl_2); 4.15(m, 4H, CH_2-dppm); 3.40(q, 2H, OCH_2, $^3J_{H-H} = 7.0$ Hz); 1.15(t, 3H, CH_3, $^3J_{H-H} = 7.0$ Hz)
6	$[Rh_2(\mu\text{-}O_2CH)Br_2(CO)_2(\mu\text{-dppm})_2]ClO_4 \cdot 0.5CH_2Cl_2 \cdot 0.5C_4H_{10}O$[e]	^{31}P: 13.70(m, dppm, $\lvert {}^1J_{Rh-P} + {}^xJ_{Rh-P}\rvert = 81.2$ Hz) ^1H: 7.68(m, 40H, Phenyl); 6.36(m, 1H, CH); 5.32(s, CH_2Cl_2); 4.26(m, 4H, CH_2-dppm); 3.40(t, 3H, CH_3, $^3J_{H-H} = 7.0$ Hz); 1.15(t, 3H, CH_3, $^3J_{H-H} = 7.0$ Hz)
7	$[Rh_2(\mu\text{-}O_2CH)I_2(CO)_2(\mu\text{-dppm})_2]ClO_4$	^{31}P: 8.11(m, dppm, $\lvert {}^1J_{Rh-P} + {}^xJ_{Rh-P}\rvert = 82.7$ Hz) ^1H: 7.50(m, 40H, Phenyl); 6.52(m, 1H, CH); 4.84(m, 2H, CH_2-dppm); 4.35(m, 2H, CH_2-dppm)
8	$[Rh_2(\mu\text{-}O_2CCH_3)Cl_2(CO)_2(\mu\text{-dppm})_2]ClO_4 \cdot 0.5CH_2Cl_2 \cdot 0.5C_4H_{10}O$[e]	^{31}P: 15.90(m, dppm, $\lvert {}^1J_{Rh-P} + {}^xJ_{Rh-P}\rvert = 81.5$ Hz) ^1H: 7.52(m, 40H, dppm); 5.32(s, CH_2Cl_2); 3.99(m, 2H, CH_2-dppm)[c]; 4.25(m, 2H, CH_2-dppm)[c]; 3.40(q, 2H, OCH_2, $^3J_{H-H} = 7.0$ Hz); 1.15(t, 3H, CH_3, $^3J_{H-H} = 7.0$ Hz); 0.53(s, 3H, CH_3)
9	$[Rh_2(\mu\text{-}O_2CCH_3)Br_2(CO)_2(\mu\text{-dppm})_2]ClO_4 \cdot 0.5CH_2Cl_2 \cdot 0.5C_4H_{10}O$[e]	^{31}P: 13.68(m, dppm, $\lvert {}^1J_{Rh-P} + {}^xJ_{Rh-P}\rvert = 82.0$ Hz) ^1H: 7.69(m, 40H, Phenyl); 5.32(s, CH_2Cl_2); 4.09(m, 4H, CH_2-ddpm); 3.40(q, 2H, OCH_2, $^3J_{H-H} = 7.0$ Hz); 1.15(t, 3H, CH_3, $^3J_{H-H} = 7.0$ Hz); 0.55(s, 3H, CH_3)
10	$[Rh_2(\mu\text{-}O_2CCH_3)I_2(CO)_2(\mu\text{-dppm})_2]ClO_4$	^{31}P: 9.27(m, dppm, $\lvert {}^1J_{Rh-P} + {}^xJ_{Rh-P}\rvert = 83.4$ Hz) ^1H: 7.50(m, 40H, Phenyl); 4.98(m, 2H, CH_2-dppm); 4.31(m, 2H, CH_2-dppm); 0.60(s, 3H, CH_3)
11	$[Rh_2(\mu\text{-}O_2CCF_3)Cl_2(CO)_2(\mu\text{-dppm})_2]ClO_4$	^{31}P: 15.95(m, dppm, $\lvert {}^1J_{Rh-P} + {}^xJ_{Rh-P}\rvert = 74.5$ Hz)
12	$[Rh_2(\mu\text{-}O_2CCF_3)Br_2(CO)_2(\mu\text{-dppm})_2]ClO_4$	^{31}P: 13.91(m, dppm, $\lvert {}^1J_{Rh-P} + {}^xJ_{Rh-P}\rvert = 79.5$ Hz)
13	$[Rh_2(\mu\text{-}O_2CCF_3)I_2(CO)_2(\mu\text{-dppm})_2]ClO_4$	^{31}P: 9.93(m, dppm, $\lvert {}^1J_{Rh-P} + {}^xJ_{Rh-P}\rvert = 81.1$ Hz)

[a] Chemical shifts relative to Me_4Si (^1H) and 85% H_3PO_4 (^{31}P). All spectra run in CD_2Cl_2. [b] See text for derived coupling constants. [c] At 360 MHz. [d] Run at –35 °C under an atmosphere of CO. [e] The degree of dichloromethane solvation was determined by a separate recording of the ^1H NMR spectrum in acetone-d_6 [δ $^1H(CH_2Cl_2) = 5.60$ s].

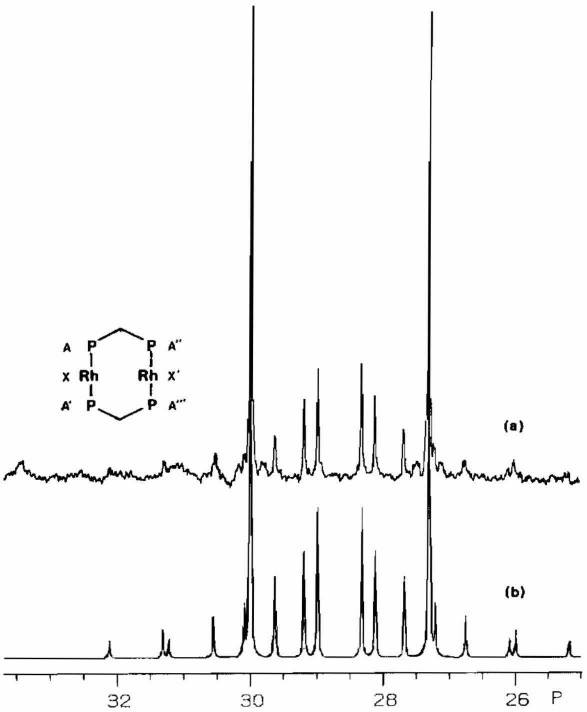

Fig. 1. Observed (a) and calculated (b) ^{31}P NMR spectra of $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]ClO_4$. Included is the labelling scheme used to designate the various derived coupling constants.

exhibit a medium intensity band at *ca.* 1840 cm^{-1} due to the bridging $\nu(CO)$. When $[Rh_2(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ was reacted with one equivalent of ^{13}CO in CH_2Cl_2 solution at –78 °C, the resulting adduct was $[Rh_2(\mu\text{-}O_2CCF_3)(\mu\text{-}CO)(CO)(^{13}CO)(\mu\text{-}dppm)_2]ClO_4$ ($\nu(CO)$ = 2006(vs), 1957(s), 1841(m) cm^{-1}) thereby establishing that the mode of adduct formation is the same as that observed for $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-}dppm)_2]^+$ [2]. The ^{31}P NMR spectra of **1**–**4** all show the downfield shift of *ca.* 10 ppm characteristic of A-frame carbonyl adducts and the minor features of the spectra reflect the characteristic changes in coupling constants. The spectra of **1**–**4** and their parent halocarboxylates are all closely comparable to those published previously for $[Rh_2(\mu\text{-}O_2CCH_3)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]^+$ [1] and its precursor. Thus, the spectra of **2** and its parent A-frame complex can be simulated successfully with the following derived constants: **2**; $^1J_{AX}$ = 91.9, $^2J_{AA'}$ = 350, $^2J_{AA''}$ = 77.8, $^4J_{AA'''}$ = 27.1, $^xJ_{AX'}$ = 1.2, $^1J_{XX'}$ = 0; $[Rh_2(\mu\text{-}O_2CCHCl_2)(CO)_2(\mu\text{-}dppm)_2]ClO_4$; $^1J_{AX}$ = 123.0, $^2J_{AA'}$ = 400, $^2J_{AA''}$ = 63.5, $^4J_{AA'''}$ = 9.0, $^xJ_{AX'}$ = 1.0, $^1J_{XX'}$ = 0.0. In the case of **2** the value of $^1J_{XX'}$ is only approximate since, even at –35 °C, exchange broadening of the spectrum was such that minor features resulting from a non-zero value of this parameter would not have been resolved. Regardless of this factor, the meaningful derived coupling constants for **2** and its parent differ by only a few Hz when compared to those of their acetate analogues.

The carbonyl adducts **1**–**4** were all stable to varying degrees with respect to CO loss in the solid state. On exposure to the atmosphere, samples of **1**–**4** all turned red within 48 hours. Loss of CO in this manner proved to be only a surface phenomenon, however, since infrared spectroscopy established that no significant CO loss had occurred. Nevertheless, under vacuum at 100 °C, loss of the bridging carbonyl was essentially complete within 30–45 min. In solution, **1**–**4** were only stable in the presence of a CO atmosphere. Our experience with handling these compounds suggested (only qualitatively of course) an increasing thermodynamic stability of the carbonyl adducts with the increasing electronegativity of the carboxylate substituent. Since this 'trend' obviously derives largely from changes in the enthalpy term, we had X-ray crystallographic studies of $[Rh_2(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ and $[Rh_2(\mu\text{-}O_2CCF_3)(\mu\text{-}CO)(CO)_2)(\mu\text{-}dppm)_2]ClO_4 \cdot CH_2Cl_2$ performed in the hope that some feature in either structure might be identified as being responsible for the observed differences in stability**. The structures of both compounds proved on the whole to be rather unremarkable. Thus, the cation $[Rh_2(\mu\text{-}O_2CCF_3)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]^+$ seems to be very similar overall to other A-frame carbonyl adducts [11], whereas the structure of the cation $[Rh_2(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-}dppm)_2]^+$ bears a strong resemblance to that of the face to face dimer *trans*-$Rh_2Cl_2(CO)_2(\mu\text{-}dppm)_2$ [12], once having taken into consideration the constraints associated with the limited bite size of the carboxylate ligand. Fig. 2 depicts in schematic form the coordination geometry around the rhodium atoms in each of the two cations in the plane perpendicular to the Rh_2P_4 plane. The largest difference between the two cations can be seen quite clearly in the dramatic lengthening of both Rh–O bond lengths by *ca.* 0.2 Å on forming the carbonyl adduct. Assuming that similar structural changes take place on forming the carbonyl adduct

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**Both X-ray diffraction studies were performed by Prof. T. S. Cameron of this department. Representative crystallographic data of the compounds investigated are: $[Rh_2(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-}dppm)_2]ClO_4$, Space Group $P2_1/b$ (monoclinic), a = 11.665(5) Å, b = 22.14(1) Å, c = 22.92(1) Å, β = 100.67(4)° (c axis unique), Z = 4. Total unique reflections measured = 3065 of which 2759 having $I > 3\sigma(I)$ were used in refinement. R = 0.079.

$[Rh_2(\mu\text{-}O_2CCF_3)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]ClO_4 \cdot CH_2Cl_2$. Space group $P2_1/n$ (monoclinic), a = 13.972(5) Å, b = 19.197(7) Å, c = 21.111(6) Å, γ = 101.00(3)° (c axis unique), Z = 4. Total unique reflections measured = 3776 of which 2833 having $I > 3\sigma(I)$ were used in refinement. R = 0.054.

Further information concerning the data set, its collection, solution and refinement may be obtained by writing to Prof. Cameron.

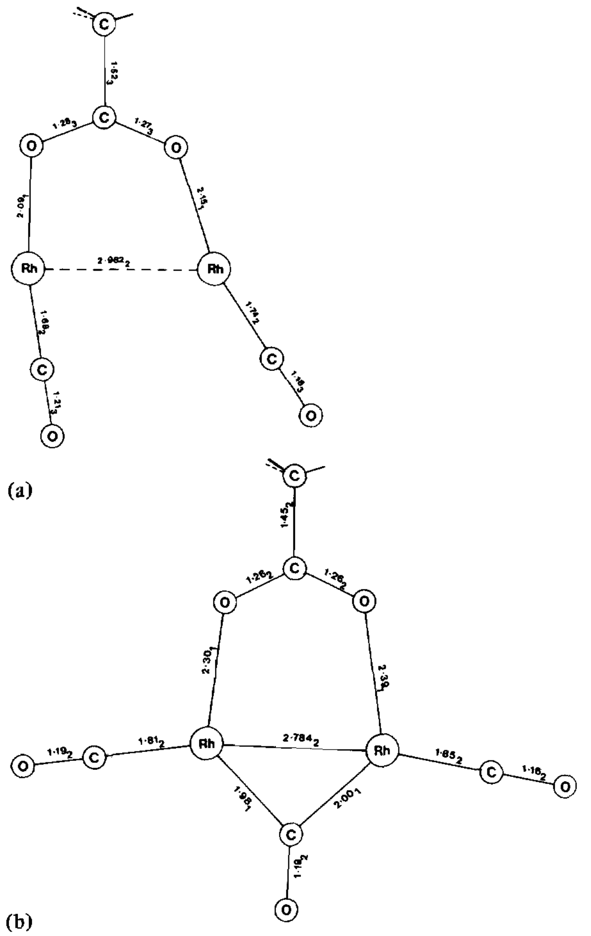


Fig. 2. Schematic representations of the cations $[Rh_2(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-dppm})_2]^+$ (a) and $[Rh_2(\mu\text{-}CO)(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-dppm})_2]^+$ (b) in the equatorial plane (perpendicular to the Rh_2P_4 framework).

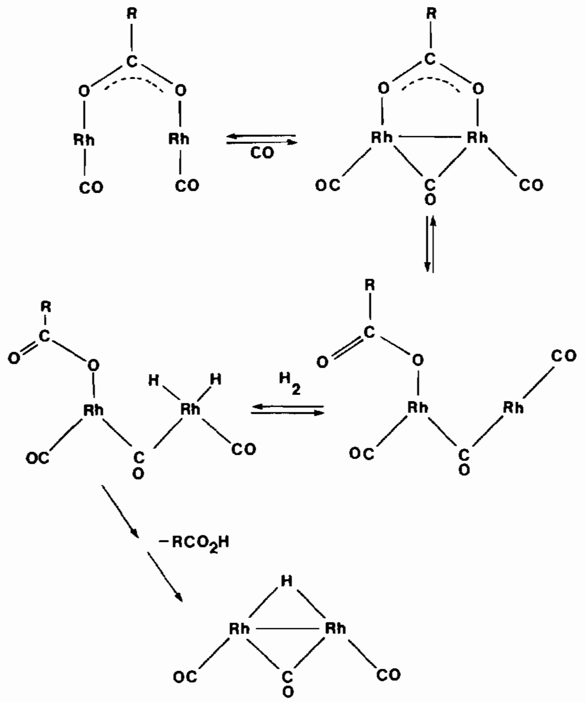
of the acetate $[Rh_2(\mu\text{-}O_2CCH_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$, these changes could well be responsible for the observed stability trend. Because of its 'softer' character, acetate functions as a better ligand towards Rh(I) than does the considerably 'harder' trifluoroacetate ligand. Thus, a substantial lengthening of the Rh–O distances should have a proportionately greater destabilizing influence for $[Rh_2(\mu\text{-}O_2CCH_3)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]ClO_4$ than for its trifluoroacetate analogue. All other things being equal, therefore, one might expect the acetate carbonyl adduct to be the less stable of the two. Regardless of the veracity or otherwise of this argument, the weakening of the Rh–O bonds on forming the CO adducts appears to be a very real phenomenon and can be used to account for the unexpected reactivity of the carboxylate complexes towards H_2/CO mixtures (*vide infra*).

Reactions with Carbon Monoxide and Dihydrogen

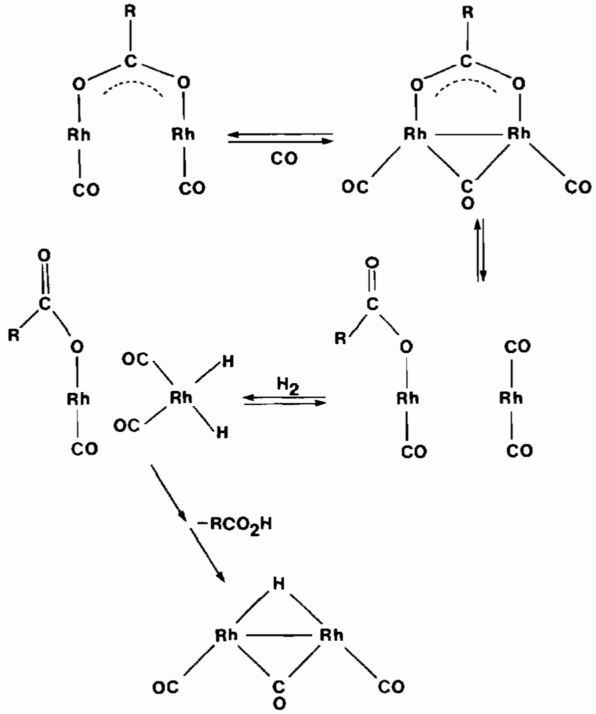
None of the carboxylate complexes used in this study were found to react with dihydrogen alone. With dihydrogen/carbon monoxide mixtures, however, (normally 1:1 v/v), all four halocarboxylates react smoothly to give $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]ClO_4$, identified by comparison with an authentic sample. No such reaction was observed for the acetate complex. Formation of the product in these reactions was fairly slow, thereby indicating that the rapidly formed carbonyl adducts occur as intermediates. This was verified in the case of the trifluoroacetate complex. Bubbling a mixture of carbon monoxide and dihydrogen slowly through a solution of $[Rh_2(\mu\text{-}O_2CCF_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ resulted in complete conversion to the carbonyl adduct within the first 30 seconds (ν(CO) = 2009(sh), 1997(vs), 1841(m)). With time, a band at 1902 cm^{-1} gradually grew at the expense of the 1841 cm^{-1} maximum. Once the 1841 cm^{-1} band had disappeared, no further changes occurred with the continued passage of the gas mixture. Corresponding changes occurred in the terminal ν(CO) region but were, of course, less well defined because of the overlap between starting material and product maxima. At no time during the course of the reaction could bands attributable to other intermediates be discerned.

It would appear, therefore, that the formation of the carbonyl adducts 1–4 is essential to the activation of dihydrogen by these A-frame complexes. This, in turn, would appear to be a direct consequence of the fact that the carboxylate group is much less firmly bound in the carbonyl adducts than it is in the parent A-frame complexes (*vide supra*), allowing for facile one-ended dissociation of the carboxylate group. Dissociation in such a manner would create a 16-electron Rh(I) site suitable for the oxidative addition of dihydrogen (Scheme 1). Subsequent elimination of H^+ and RCO_2^- would then generate the product. Significantly, there is no need to propose, nor is there any evidence to support, the binuclear 1,2-addition of dihydrogen. The failure of the acetate A-frame complex to react with H_2/CO mixtures can be rationalized by noting that the first equilibrium in Scheme 1 lies well to the left for this complex at room temperature and pressure. It should be noted here that we have no concrete evidence for the maintenance of the carbonyl bridge during the reaction sequence depicted in Scheme 1. A similar scheme can be proposed in which the carbonyl bridge is lost upon dissociation of the carboxylate function (Scheme 2). The only advantage to maintaining the bridge is that the depicted *cis* addition of H_2 to the Rh(I) centre would not necessitate invoking a topological change at the Rh(III) centre so generated before forming the ultimate product.

If the carbonyl bridge is lost to give a face to face dimer, such an isomerization would be necessary after *cis* dihydrogen addition. Furthermore, there would be a sizeable steric barrier associated with such an addition.



Scheme 1



Scheme 2

It is intersting to note at this point that Sanger [13] has correlated the ability of certain A-frame complexes to form bridging carbonyl adducts with their ability to function as homogeneous hydrogenation catalysts. In these cases, it seems to us quite possible that the catalytic species is in fact the carbonyl adduct. We have encountered at least one example of an A-frame complex being contaminated by persistent traces of its carbonyl adduct, despite being synthesized in the complete absence of carbon monoxide [14]. We have also encountered other examples where the early stages of decomposition of certain A-frames (*e.g.* $[Rh_2(\mu\text{-I})(CO)_2(\mu\text{-dppm})_2]^+$) [4] are accompanied by substantial amounts of the carbonyl adduct††. Furthermore, in the case of $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-dppm})_2]^+$, a significant lengthening of the Rh–Cl bond lengths was also observed upon the formation of the carbonyl adduct [12, 15], making this possibly a general phenomenon. We feel, therefore, that it is likely that the catalysis proceeds at rhodium(I) sites generated by the breaking of the bridge in the carbonyl adducts. If our view is correct, then the so-called 'active site' in A-frames is indeed an important factor in their ability to function as homogeneous catalysts but more for its role in labilizing the bridging ligand than for substrate activation.

Reaction with Halogens

From the foregoing, it is clear that the various modes of behaviour exhibited by the carboxylate A-frame complexes $[Rh_2(\mu\text{-}O_2CR)(CO)_2(\mu\text{-dppm})_2]$-$ClO_4$ are typified by those examples with R = H, CH_3 and CF_3. Consequently, only these examples were chosen for this study. As it turned out, both the formate and acetate behaved similarly but the trifluoroacetate complex behaved differently by yielding a number of products on the addition of halogens.

The addition of one equivalent of halogen X_2 to $[Rh_2(\mu\text{-}O_2CR)(CO)_2(\mu\text{-dppm})_2]ClO_4$ yielded solely the transannular oxidative addition products $[Rh_2(\mu\text{-}O_2CR)X_2(CO)_2(\mu\text{-dppm})_2]ClO_4$ (X = Cl, Br, I; R = H, **5**–**7**; R = CH_3, **8**–**10**). The crystallization procedure employed yielded **5**, **6**, **8** and **9** as dichloromethane/diethyl ether hemisolvates. The solvent of crystallization could not be removed even by heating to 100 °C under vacuum for 24 h. All complexes exhibited electrical conductivities characteristic of 1:1 electrolytes in acetone solution. The stoichiometry of the oxidation reactions was established by following the titration of $[Rh_2(\mu\text{-}O_2CCH_3)(CO)_2(\mu\text{-dppm})_2]ClO_4$ with bromine and $[Rh_2(\mu\text{-}O_2CH)(CO)_2(\mu\text{-dppm})_2]ClO_4$ with iodine by infrared spectroscopy. The addition of one equivalent

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[††] It is interesting to note in this regard that Sanger reports the existence of an induction period for certain catalysts.

of bromine in aliquots (0.25 equiv. of bromine at a time) to a dichloromethane solution of [$Rh_2(\mu$-$O_2CCH_3)(CO)_2(\mu$-dppm$)_2$]ClO_4 (0.05 g) resulted in a decrease in the intensity of the carbonyl frequencies of [$Rh_2(\mu$-$O_2CCH_3)(CO)_2(\mu$-dppm$)_2$]ClO_4 (ν(CO) = 2001(s) and 1985(vs) cm^{-1}) and the appearance of new bands at 2056 and 2028 cm^{-1}. This continued until the mole ratio reached one, at which stage the ν(CO) bands of [$Rh_2(\mu$-$O_2CCH_3)(CO)_2(\mu$-dppm$)_2$]ClO_4 had completely disappeared. No further changes were observed in the region studied with further addition of bromine. This clearly established the stoichiometry of the oxidation to be 1:1. Similar behaviour was observed for the iodine/[$Rh_2(\mu$-$O_2CH)(CO)_2(\mu$-dppm$)_2$]ClO_4 titration.

The IR spectra of **5**–**10** all showed an increase in the carbonyl stretching frequencies by about 40–60 cm^{-1} relative to the appropriate A-frame starting material. This supports the formation of a rhodium(II) dimer since similar shifts were observed in the oxidation of $Rh_2Br_2(CO)_2(\mu$-dppm$)_2$ with iodine and bromine to give the corresponding rhodium(II) dimers [7]. Not surprisingly, the frequency shift of 40–60 cm^{-1} observed for these transannular rhodium(I) to rhodium(II) oxidations is significantly less than the approximately 100 cm^{-1} increase observed in the oxidation of the monomeric rhodium(I) complex, $RhCl(CO)(PPh_3)_2$ with iodine to give the rhodium(III) complex, $RhI_2Cl(CO)(PPh_3)_2$ [16].

Verification of the dimeric nature of **5**–**10** was afforded by ^{31}P NMR spectroscopy. Spectra of all six complexes were closely comparable and representative of the AA′A″A‴XX′ spin system. Fig. 3 shows the observed and calculated ^{31}P NMR spectra for **5**. The derived coupling constants are: $^1J_{AX}$ = 82.9, $^2J_{AA'}$ = 350, $^2J_{AA''}$ = 56.7, $^4J_{AA'''}$ = 29.5, $^xJ_{AX'}$ = −2.1 and $^1J_{XX'}$ = 9.2 Hz. ^1H NMR spectra of **5**–**10** were also consistent with the proposed structural assignments. At 80 MHz, the dppm methylene signals in compounds **5**, **6**, **8** and **9** overlapped somewhat, as seen in other A-frame complexes bridged by unsaturated ligands [4, 17, 18]. Accordingly, when run at 360 MHz, the individual methylene multiplets in **8**, for example, were well resolved.

Unlike its formate and acetate analogues, [$Rh_2(\mu$-$O_2CCF_3)(CO)_2(\mu$-dppm$)_2$]ClO_4 reacted with halogens to give complex mixtures of products, the largest components of which were the transannular oxidative addition products [$Rh_2(\mu$-$O_2CCF_3)X_2(CO)_2(\mu$-dppm$)_2$]ClO_4 (X = Cl, Br, I; **11**–**13**) easily identifiable by their characteristic ^{31}P NMR spectra and dominant infrared absorptions. Little definitive information on the nature of the by-products could be obtained. There were, however, at least two, possibly three differing minor products depending on the halogen involved. Infrared spectra of the mixtures produced showed minor peaks which could be attributed to terminal carbonyls attached to Rh(III) and ketonic-type carbonyls [19, 20], indicating that oxidation has occurred to give doubly bridged Rh(III) centres rather than single bridged Rh(II) centres joined by a Rh–Rh bond. Without further knowledge of the nature of these by-products, however, it is impossible to speculate on the role played by the trifluoroacetate group in the formation of these mixtures.

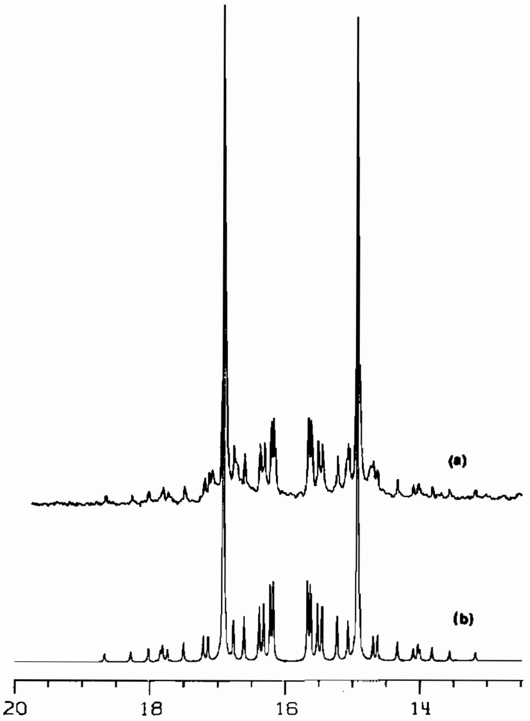

Fig. 3. Observed (a) and calculated (b) ^{31}P NMR spectra of [$Rh_2(\mu$-$O_2CH)Cl_2(CO)_2(\mu$-dppm$)_2$]ClO_4 (**5**).

Experimental

Details of the techniques used for all physical measurements have been described elsewhere, as have the more general preparative details [4, 18].

Reactions with Carbon Monoxide

[$Rh_2(\mu$-$O_2CH)(CO)_2(\mu$-dppm$)_2$]ClO_4. Preparation of [$Rh_2(\mu$-$H)(\mu$-$CO)(CO)_2(\mu$-dppm$)_2$]ClO_4

[$Rh_2(\mu$-$O_2CH)(CO)_2(\mu$-dppm$)_2$]ClO_4 (0.10 g, 0.085 mmol) was dissolved in 5 ml of dichloromethane in a 10 ml flask sealed with a rubber septum. Carbon monoxide (2 ml, 1 equiv.) was injected into this reaction flask using a gas syringe. The red solution was stirred for 1 h during which time it turned burgundy red. The addition of diethyl ether precipitated a red-brown crystalline product.

Recrystallization was from dichloromethane-diethyl ether in an atmosphere of carbon monoxide (0.085 g, 86%).

An analogous procedure was used to prepare $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]PF_6$ for purposes of comparison. The colour changes observed were similar and a brown crystalline product was obtained (71%).

$[Rh_2(\mu\text{-}O_2CR)(CO)_2(\mu\text{-}dppm)_2]ClO_4$. *Synthesis of* $[Rh_2(\mu\text{-}O_2CR)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]ClO_4$: **1**, *R = CH_2Cl*; **2**, *R = $CHCl_2$*; **3**, *R = CCl_3*; **4**, *R = CF_3*

In a typical experiment, carbon monoxide was bubbled through a solution of $[Rh_2(\mu\text{-}O_2CR)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ (0.10 g) (R = CH_2Cl, $CHCl_2$, CCl_3, CF_3) for 10 min. The addition of diethyl ether while the carbon monoxide flow was maintained precipitated the product, which was filtered off, washed with diethyl ether and dried in air. Recrystallization was achieved from dichloromethane-diethyl ether in the presence of an atmosphere of carbon monoxide.

1, yellow-orange crystals (0.089 g, 87%). **2**, bright yellow crystals (0.090 g, 88%). **3**, yellow crystals, rapidly turning yellow-orange in air (0.082 g, 80%). **4**, bright yellow crystals, obtained as a dichloromethane solvate (0.090 g, 83%). *Anal.* Calcd. for $C_{55}H_{46}F_3P_4O_9Cl_3Rh_2$: C, 49.60; H, 3.42; F, 4.20; P, 9.13%. Found: C, 49.86; H, 3.38; F, 2.95; P, 9.52%. **1**–**4** all decomposed with loss of CO upon heating, hence no melting points are available.

Reactions with Carbon Monoxide and Dihydrogen Mixture

$[Rh_2(\mu\text{-}O_2CR)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ (R = CF_3: 0.10 g; R = CH_2Cl, $CHCl_2$, CCl_3: 0.05 g) was dissolved in 10 ml of dichloromethane in a two necked flask. A mixture of carbon monoxide/dihydrogen (1:1) was bubbled through this solution for a period of 5 min. The flask was then capped under an atmosphere of the reactant gas mixture and stirred for a period of time (R = CH_2Cl, 3 h; R = $CHCl_2$ and CCl_3, 0.75 h; R = CF_3, 0.5 h) after which the solution was burgundy red in colour. The addition of diethyl ether in an atmosphere of carbon monoxide/dihydrogen precipitated a red-brown solid. This was filtered and recrystallized from dichloromethane-diethyl ether in the presence of carbon monoxide/dihydrogen to give the red-brown crystalline product. (R = CH_2Cl: 0.037 g, 78%; R = $CHCl_2$: 0.039 g, 85%; R = CCl_3: 0.032 g, 71%; R = CF_3: 0.082 g, 88%). In all cases characterization was by comparison with an authentic sample.

Reactions with Halogens

$[Rh_2(\mu\text{-}O_2CH)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ *with Chlorine: Synthesis of* $[Rh_2(\mu\text{-}O_2CH)Cl_2(CO)_2(\mu\text{-}dppm)_2]ClO_4\cdot(CH_2Cl_2)_{0.5}\cdot(C_4H_{10}O)_{0.5}$ *(5)*

$[Rh_2(\mu\text{-}O_2CH)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ (0.10 g, 0.085 mmol) was dissolved in 5 ml of dichloromethane and to it was added dropwise with stirring a dichloromethane solution saturated with chlorine gas until no further colour change was apparent. The addition of diethyl ether to the orange solution precipitated a yellow orange solid. The product was filtered off, washed with diethyl ether and recrystallized from dichloromethane-diethyl ether to give yellow-orange crystals (0.091 g, 81%). M.P. 192–196 °C. *Anal.* Calcd. for $C_{55.5}H_{51}Cl_4O_{8.5}P_4Rh_2$: C, 50.25; H, 3.87; Cl, 10.69%. Found: C, 50.35; H, 3.77; Cl, 10.68%. Λ_M = 130 $cm^2\ \Omega^{-1}\ mol^{-1}$ (acetone).

With Bromine: Synthesis of $[Rh_2(\mu\text{-}O_2CH)Br_2(CO)_2(\mu\text{-}dppm)_2]ClO_4\cdot(CH_2Cl_2)_{0.5}(C_4H_{10}O)_{0.5}$ *(6)*

To a solution of $[Rh_2(\mu\text{-}O_2CH)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ (0.10 g, 0.092 mmol) in 5 ml of dichloromethane was added one equivalent of bromine (0.014 g) with stirring. The red solution immediately turned orange-brown. The addition of diethyl ether precipitated an orange solid which was recrystallized from dichloromethane-diethyl ether to give orange crystals (0.085 g, 71%). M.P. 191–196 °C (dec). *Anal.* Calcd. for $C_{55.5}H_{51}O_{8.5}P_4Cl_2Br_2Rh_2$: C, 47.09; H, 3.63%. Found: C, 47.88; H, 3.52%. Λ_M = 126 $cm^2\ \Omega^{-1}\ mol^{-1}$ (acetone).

With Iodine: Synthesis of $[Rh_2(\mu\text{-}O_2CH)I_2(CO)_2(\mu\text{-}dppm)_2]ClO_4$ *(7)*

To a solution of $[Rh_2(\mu\text{-}O_2CH)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ (0.10 g, 0.085 mmol) in 5 ml of dichloromethane was added one mol of iodine (0.022 g) with stirring. The red solution immediately turned red-brown and deposited a black crystalline solid upon the addition of diethyl ether. The product was filtered and recrystallized from dichloromethane-diethyl ether to give black crystals with a green lustre (0.098 g, 81%). M.P. 230–238 °C (dec). *Anal.* Calcd. for $C_{53}H_{45}O_8P_4ClI_2Rh_2$: C, 44.55; H, 3.18; I, 17.77%. Found: C, 43.88; H, 3.08%; I, 15.43%. Λ_M = 129 $cm^2\ \Omega^{-1}\ mol^{-1}$ (acetone).

$[Rh_2(\mu\text{-}O_2CCH_3)(CO)_2(\mu\text{-}dppm)_2]ClO_4$. *Synthesis of* $[Rh_2(\mu\text{-}O_2CCH_3)X_2(CO)_2(\mu\text{-}dppm)_2]ClO_4\cdot(CH_2Cl_2)_{0.5}\cdot(C_4H_{10}O)_{0.5}$ *(***8***, X = Cl;* **9***, X = Br) and* $[Rh_2(\mu\text{-}O_2CCH_3)I_2(CO)_2(\mu\text{-}dppm)_2]ClO_4$ *(***10***)*

Procedures analogous to those described above for the formate complexes yielded:

8: yellow-orange crystals (0.081 g, 71%). M.P. > 300 °C. *Anal.* Calcd. for $C_{56.5}H_{53}O_{8.5}P_4Cl_4Rh_2$:

C, 50.62; H, 3.98%. Found: C, 50.39; H, 3.89%. $\Lambda_M = 131$ cm^2 Ω^{-1} mol^{-1} (acetone).

9: orange crystals (0.090 g, 75%). M.P. 260–265 °C (dec). *Anal.* Calcd. for $C_{56.5}H_{53}Br_2O_{8.5}P_4Cl_2Rh_2$: C, 47.46; H, 3.71; Br, 11.20%. Found: C, 47.41; H, 3.57; Br, 11.54%. $\Lambda_M = 125$ cm^2 Ω^{-1} mol^{-1} (acetone).

10: brown solid (0.091 g, 75%). *Anal.* Calcd. for $C_{54}H_{47}O_8P_4ClI_2Rh_2$: C, 44.95; H, 3.74%. Found: C, 44.40; H, 3.06%. $\Lambda_M = 123$ cm^2 Ω^{-1} mol^{-1} (acetone).

Reaction of [$Rh_2(\mu$-$O_2CCF_3)(CO)_2(\mu$-dppm$)_2$]-ClO_4 with Chlorine

The reaction procedure was similar to those described above and the yield of the orange crude material was 0.062 g. Spectroscopic data indicated the presence of a mixture of compounds (see text).

Reaction of [$Rh_2(\mu$-$O_2CCF_3)(CO)_2(\mu$-dppm$)_2$]-ClO_4 with Bromine

The reaction procedure was similar to those described above. A brown solid was isolated by the addition of diethyl ether (0.080 g). Spectroscopic data indicated the presence of a mixture of products (see text).

Reaction of [$Rh_2(\mu$-$O_2CCF_3)(CO)_2(\mu$-dppm$)_2$]-ClO_4 with Iodine

The procedure was similar to those described above. A brown crystalline solid was obtained by the addition of diethyl ether (0.084 g). Spectroscopic data indicated the formation of a mixture of products (see text). *Anal.* Calcd. for $C_{54}H_{44}O_8F_3P_4ClI_2Rh_2$: C, 43.33; H, 2.96%. Found: C, 43.14; H, 2.75%.

Acknowledgements

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