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REACTIONS INVOLVING TRANSITION METALS

XII *. SOME ATTEMPTS TO PREPARE ALKYLIDYNETRIRHODIUM CLUSTER COMPOUNDS

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Summary

Attempts to prepare alkylidyne-trirhodium cluster complexes $[RCRh_3(CO)_n(PPh_3)_{9-n}]$ by reaction of $Na[Rh(CO)_2(PPh_3)_2]$ with CX_4, CHX_3 ($X = Cl$ or Br) and CCl_3CF_3 have resulted only in the formation of $[RhX(CO)(PPh_3)_2]$. With $CHCl_3$ at —20°C the major product is $[Rh(CO)_2(PPh_3)_2]_2$, though to be formed by decomposition of $[RhH(CO)_2(PPh_3)_2]$. Reaction between $Na[Rh(CO)_2(PPh_3)_2]$ and perfluoroacyl chlorides has given the new compounds $[Rh(COR_F)(CO)_2(PPh_3)_2]$ ($R_F = CF_3$, C_2F_5 and C_3F_7), which do not decarbonylate even after 6—9 days at 120°C. Tetrafluoroethylene has been found to react with $[Rh(SnMe_3)(CO)_2(PPh_3)_2]$ under UV irradiation conditions to give $[Rh(CF{=}CF_2)(CO)_2(PPh_3)_2]$ in 33% yield. The latter does not react with $[RhH(CO)(PPh_3)_3]$ to form clusters, but surprisingly, its reaction with $Na[Co(CO)_4]$ resulted in a low yield of $CF_3CCo_3(CO)_9$; under similar conditions $Na[Rh(CO)_2(PPh_3)_2]$ caused only decomposition.

Introduction

The tricobaltcarbon cluster, Co_3C, in alkylidynetricobalt nonacarbonyl complexes, $RCCo_3(CO)_9$, is exceptionally stable [1—3], and there are many methods available for their preparation. Our study of some of these preparative routes [4—7], and reactions leading to the related alkylidyne-trinickel cluster compounds, $[RCNi_3(\eta\text{-}C_5H_5)_3]$ [8], has lead to a better understanding of the mechanisms by which these types of clusters can be formed. Other alkylidyne cluster complexes which have been isolated include the ruthenium and osmium deriva-

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* For Part XI see ref. 37.

tives $[CH_3CM_3H_3(CO)_9]$ which contain bridging hydride ligands [9], the mixed metal-alkylidyne clusters $[FePtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PEt_3)(\eta\text{-}C_5H_5)(\eta\text{-}C_9H_7)]$ and $[FeRhW(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu_2\text{-}CO)(CO)_5(\eta\text{-}C_5H_5)_3]$ [10], and the rhodium complexes $[Rh_3(\mu_3\text{-}CH)(\mu_3\text{-}CO)_2(\eta\text{-}C_5H_5)_3]$ [11]. The recent report [12] of the synthesis of the iridium complexes $[RCIr_3(CO)_9]$ (R = Me, Ph) by reaction of $NaIr(CO)_4$ with $RCCl_3$ prompts us to describe our attempts to prepare the analogous rhodium carbonyl complexes and some of the difficulties experienced.

Results and discussion

One method that has been frequently employed for the synthesis of alkylidyne trinonacarbonyl derivatives is the reaction of 1,1,1-trihalogenoalkanes with $NaCo(CO)_4$ [13] or $Co_2(CO)_8$ [14—18] in donor solvents, and this is the route employed for the successful preparation of the iridium analogue [12]. A difficulty in applying this route to the preparation of rhodium clusters is that $[Rh_2(CO)_8]$ is only stable under a very high pressure of carbon monoxide [19], and consequently there is no readily available route to the anion $[Rh(CO)_4]^-$. A report that moderately stable quaternary ammonium salts [20] containing this anion may be obtained by reduction of $[Rh(CO)_2Cl_2]$ with sodium in tetrahydrofuran has not proved to be reproducible in our hands. On the many occasions when this reaction has been attempted only once was a colourless solution obtained which had a simple IR spectrum having metal carbonyl absorptions at 2000w, 1900vs, and 1870s cm^{-1}. On other occasions a pale green solution was obtained which had IR bands at 1970w, 1940s, 1890vs, 1850sh, 1820w and 1760m cm^{-1}, which appears to consist of a mixture of anionic rhodium carbonyl cluster species. For this reason our efforts have been concentrated on the chemistry of the anion $[Rh(CO)_2(PPh_3)_2]^-$, which is readily available in quantitative yield by reduction of the dimer $[Rh(CO)_2(PPh_3)_2]_2$ [21].

Reaction between $Na[Rh(CO)_2(PPh_3)_2]$ and the halogenoalkanes CX_4, CHX_3 (X = Cl or Br) and CF_3CCl_3 in tetrahydrofuran at room temperature resulted in the formation of $[RhX(CO)(PPh_3)_2]$ with evolution of one molar equivalent of carbon monoxide (see Table 1). When the reaction with carbon tetrachloride was repeated in the presence of a carbene trapping agent, cyclohexene, a GLC analysis of the product mixture confirmed the presence of 7,7-dichloronorcarane. The dichlorocarbene formed in this reaction most probably arises by decomposition of a trichloromethylrhodium(I) intermediate formed by dis-

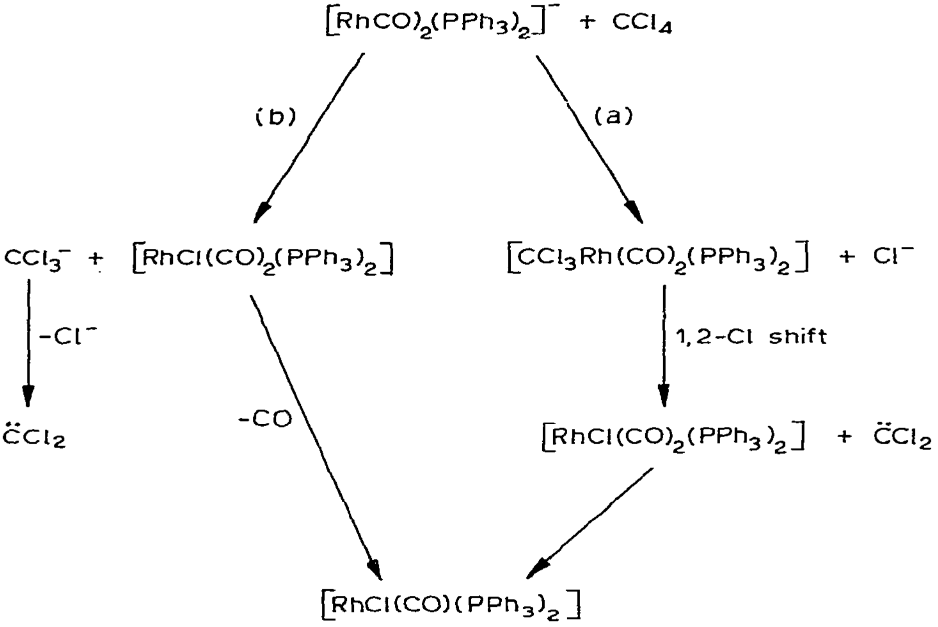
TABLE 1

REACTIONS OF $Na[Rh(CO)_2(PPh_3)_2]$ WITH HALOGENOALKANES

Reactant	Temp. (°C)	Time (h)	Product	Yield (%)
$CHCl_3$	20	16	$RhCl(CO)(PPh_3)_2$	34
$CHCl_3$	—20	2	$[Rh(CO)_2(PPh_3)_2]_2$	75
$CHBr_3$	20	15	$RhBr(CO)(PPh_3)_2$	63
CCl_4	20	14	$RhCl(CO)(PPh_3)_2$	58
CBr_4	20	16	$RhBr(CO)(PPh_3)_2$	53
CCl_3CF_3	20	15	$RhCl(CO)(PPh_3)_2$	47

placement of chloride ion by the strong nucleophile [$\mathrm{Rh(CO)_2(PPh_3)_2}$]$^-$ [21—23] as shown in path (a) in Scheme 1. Similar 1,2-chlorine shifts have been proposed to explain the formation of dichlorocarbene in the reactions of $\mathrm{CCl_4}$ with $\mathrm{Co_2(CO)_8}$ [6] and $\mathrm{CCl_3HgPh}$ [7]. The alternative possibility that the dichlorocarbene is formed by loss of chloride ion from $\mathrm{CCl_3^-}$, path (b) in Scheme 1, is less plausible as the methide ion is a poorer leaving group than chloride ion. The formation of the ions $\mathrm{CX_3^-}$ by proton abstraction is, however, a distinct possibility in the reactions of chloroform and bromoform. When the reaction of chloroform with Na[$\mathrm{Rh(CO)_2(PPh_3)_2}$] was carried out at —20°C the major product was [$\mathrm{(Ph_3P)_2(CO)_2Rh}$]$_2$, a known decomposition product of [$\mathrm{RhH(CO)_2(PPh_3)_2}$] [24]. In a separate experiment it has been shown that [$\mathrm{(PPh_3)_2(CO)_2Rh}$]$_2$ reacts with chloroform at room temperature during 16 h to give [$\mathrm{RhCl(CO)(PPh_3)_2}$] in 63% yield. In an effort to establish the mechanism outlined in path (a) [Scheme 1] the synthesis of the proposed intermediate [$\mathrm{Rh(CCl_3)(CO)_2(PPh_3)_2}$] was attempted by a different route. The reaction between Na[$\mathrm{Rh(CO)_2(PPh_3)_2}$] and $\mathrm{CCl_3COCl}$ (1 : 1 molar ratio) in tetrahydrofuran at room temperature was carried out in the hope of preparing the complex [$\mathrm{Rh(COCCl_3)(CO)_2(PPh_3)_2}$]. This, by analogy with five-coordinate rhodium(III) [25—27] and iridium(III) [28,29] acyl complexes, might be expected to rearrange to the desired trichloromethylrhodium(I) complex. Instead, there was an immediate, vigorous reaction and [$\mathrm{RhCl(CO)(PPh_3)_2}$] was isolated in 64% yield. When this reaction was repeated using a molar ratio of anion to $\mathrm{CCl_3COCl}$ of 1 : 2 the product was [$\mathrm{RhCl_3(CO)(PPh_3)_2}$] formed in 71% yield. These results can be rationalised if the expected products [$\mathrm{Rh(COCCl_3)(CO)_2(PPh_3)_2}$] and [$\mathrm{Rh(CCl_3)(CO)_2(PPh_3)_2}$] are formed, but the latter decomposes by the pathway shown in Scheme 1. A similar decomposition of an intermediate [$\mathrm{RhCl_2(CCl_3)}$-

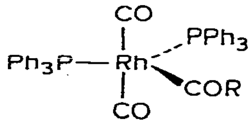
SCHEME 1.



$(CO)_2(PPh_3)_2]$ formed by decarbonylation of the oxidative-addition product $[RhCl_2(COCCl_3)(CO)(PPh_3)_2]$ could explain the formation of $[RhCl_3(CO)(PPh_3)_2]$ when an excess of trichloroacetyl chloride is used.

In all these reactions with halogenoalkanes the high thermodynamic stability of the complexes $[RhX(CO)(PPh_3)_2]$ (X = Br or Cl) appears to dictate the course of the reaction, and prevents cluster formation. Until a reliable method for the preparation of $[Rh(CO)_4]^-$ becomes available it seems unlikely that Rh_3C cluster complexes will be obtained by routes involving chlorinated or brominated organic compounds.

Perfluoroalkyltetracarbonylcobalt(I) derivatives $[RCF_2Co(CO)_4]$ (R = F, CF_3, CHF_2, and C_2F_5) have been found to react with $Na[Co(CO)_4]$ to give the corresponding cluster complexes, $RCCo_3(CO)_9$, under mild conditions. In order to explore whether a similar route could be applied to the synthesis of Rh_3C clusters it was necessary to prepare some perfluoroalkylrhodium(I) complexes. Wilkinson et al. [30] have prepared the complex $[Rh(CF_2CF_2H)(CO)(PPh_3)_2]$ by an insertion reaction between C_2F_4 and $[RhH(CO)(PPh_3)_3]$, and in this Department the complex $[Rh(CF_3C{=}CHCF_3)(CO)(PPh_3)_2]$ has been prepared by a similar insertion reaction with hexafluorobut-2-yne [31], but as far as we are aware there are no examples of saturated perfluoroalkylrhodium(I) complexes reported. For reasons outlined above our attempts to prepare the complexes $[RCF_2Rh(CO)_4]$ (R = F or C_2F_5) by the reaction of $(CF_3CO)_2O$ or n-C_3F_7COCl with the product of reduction of $[Rh(CO)_2Cl]_2$ met with no success, and an alternative route to perfluoroalkylrhodium(I) complexes by decarbonylation of perfluoroacylrhodium(I) complexes was explored. The anhydrides $(RCO)_2O$ (R = CF_3, C_2F_5, and n-C_3F_7) have been found to react readily with $Na[Rh(CO)_2(PPh_3)_2]$ in tetrahydrofuran at room temperature to give the new fluoroacyl complexes $[Rh(COR)(CO)_2(PPh_3)_2]$ [Table 2] as air-stable, yellow crystalline solids. Their IR spectra [Table 2] showed a band in the region of 1680—1695 cm^{-1} for the acyl carbonyl group and strong bands in the region of 900—1200 cm^{-1} due to C—F stretching vibrations. Each compound showed only one sharp band in the metal carbonyl region indicative of *trans* axial carbonyl ligands and overall C_{2v} symmetry as shown below. A similar stereochemistry has been found for perfluoroaromatic derivatives of the type $[Rh(Ar_F)(CO)_2(PPh_3)_2]$ [21,22]. All efforts to decarbonylate these complexes have



failed, and even after heating at 120°C in vacuo over 6—9 days they were recovered unchanged with only slight decomposition; at higher temperatures substantial decomposition occurred. This contrasts with the behaviour of acylrhodium(III) complexes of the type $[Rh(COR)Cl_2(PPh_3)_2]$ which decarbonylate spontaneously at room temperature [25—27], and the perfluoroacyliridium(III) complexes $[IrCl(COCF_3)(O_2CCF_3)(CO)(PPh_3)_2]$ and $[IrCl_2(COCF_3)(PPh_3)_2]$ which decarbonylate on warming at 75°C during 25 h. The resistance of the complexes $[Rh(COR_F)(CO)_2(PPh_3)_2]$ to decarbonylation is presumably related to the fact that being eighteen-electron species dissociation of a carbonyl ligand

TABLE 2

IR DATA (cm^{-1}) [a] AND ^{19}F NMR CHEMICAL SHIFTS [b]

Compound	$\nu(C{\equiv}O)$ [c]	$\nu(C{=}O)$	
$Rh(COCF_3)(CO)_2(PPh_3)_2$	1980	1692	+3.5s
$Rh(COCF_2^1CF_3^2)(CO)_2(PPh_3)_2$	1983	1686	—4.9(F^2, t, 3, $J(F^1—F^2)$ = 1.4 Hz); —41.2(F^1, q, 2)
$Rh(COCF_2^1CF_2^2CF_3^3)(CO)_2(PPh_3)_2$	1983	1687	—2.8(F^3, t, 3, $J(F^2—F^3)$ = 9.6 Hz); —38.3(F^2, m, 2); —49.0(F^3, m, 2)

[a] Solutions in CH_2Cl_2. [b] Saturated solutions in CH_2Cl_2. All values quoted in ppm with reference to external trifluoroacetic acid, and positive values to high frequency (low field). [c] Recorded using a X10 expansion.

must take place prior to migration of the fluoroalkyl group to the vacated coordination site [32]. When the rhodium atom is in a low oxidation state and is coordinated to two good donor ligands, such as PPh_3, the bond to the carbonyl ligands is so strong that the necessary dissociation does not occur at moderate temperatures. This same trend is found with acylcobalt(I) complexes where $[Co(COCF_3)(CO)_4]$ decarbonylates at 55°C, while $[Co(COCF_3)(CO)_3(PPh_3)]$ does not decarbonylate below 130°C [33].

Beveridge and Clarke [34] have demonstrated that low yields of the complex $[CF_3CCo_3(CO)_9]$ may be obtained by the reaction between C_2F_4 and $[Co(SnR_3)(CO)_4]$ (R = Me or Ph) under either thermal or photochemical conditions. It is envisaged that these reactions involve the intermediate formation of the vinyl complex $[Co(CF{=}CF_2)(CO)_4]$ which undergoes further reaction with either the tin derivative or $[Co(CO)_4]^-$ derived from it. When a solution of $[Rh(SnMe_3)(CO)_2(PPh_3)_2]$ in benzene under a pressure of tetrafluoroethylene was irradiated with UV light for 16 h, chromatography of the product mixture gave the known compound $[Rh(CF{=}CF_2)(CO)_2(PPh_3)_2]$ [23] in 33% yield. The same product was obtained in a much lower yield (6%) on leaving the reactants to stand at room temperature for 16 h without irradiation. This indicates that insertion of tetrafluoroethylene into the tin—rhodium bond does occur followed by loss of Me_3SnF, and provides some support for the mechanism proposed by Beveridge and Clarke for the reaction with $[Co(SnR_3)(CO)_4]$. Unfortunately, the perfluorovinylrhodium complex is so stable that it does not react further to form a cluster. Attempted reaction of the vinyl complex with $[RhH(CO)(PPh_3)_2]$ during 7 h at 50°C in tetrahydrofuran gave only recovered starting materials. Surprisingly, however, reaction between $[Rh(CF{=}CF_2)(CO)_2(PPh_3)_2]$ and $Co_2(CO)_8$ in tetrahydrofuran after 15 h at 50°C gave a 7% yield of $CF_3CCo_3(CO)_9$ illustrating the great stability of the Co_3C cluster. The reaction of $Na[Rh(CO)_2(PPh_3)_2]$ with the vinyl complex at the reflux temperature of tetrahydrofuran during 6 h resulted in almost complete decomposition of the vinyl complex to a brown amorphous solid.

Experimental

IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer. ^{19}F NMR spectra were determined on saturated solutions in CH_2Cl_2 with trifluoroacetic acid as external reference. All solvents were thoroughly dried by standard procedures and distilled before use. Except where stated reactions were carried out under an atmosphere of dry carbon monoxide. The compounds $[Rh(CO)_2(PPh_3)_2]_2$ [35], $Na[Rh(CO)_2(PPh_3)_2]$ [21], $[Rh(SnMe_3)(CO)_2(PPh_3)_2]$ [36], $[RhH(CO)(PPh_3)_3]$ [24] and $[Rh(CF_2CF_2H)(CO)(PPh_3)_2]$ [30] were prepared by previously reported procedures.

Reactions of $Na[Rh(CO)_2(PPh_3)_2]$ with halogenoalkanes

In a typical experiment the halogenoalkane (2.96 mmol) was added to a solution of the sodium salt (2.64 mmol) in tetrahydrofuran (75—100 cm^3) at room temperature. The mixture was stirred at room temperature for 14—16 h, and was then chromatographed (alumina, grade III, benzene eluent) to give the corresponding halogenocarbonyl-bis(triphenylphosphine)rhodium(I) complex, which was recrystallised from a mixture of chloroform and ethanol. The results of individual experiments are given in Table 1.

Reaction of $Na[Rh(CO)_2(PPh_3)_2]$ with trichloroacetyl chloride

Addition of trichloroacetyl chloride (0.24 g, 1.32 mmol) to a solution of the sodium salt (1.32 mmol) in tetrahydrofuran (40 cm^3) at room temperature caused an immediate, vigorous reaction. The solution was stirred for a further 3 h before chromatography to give chlorocarbonyl-bis(triphenylphosphine)-rhodium(I) (0.59 g, 0.85 mmol, 65%).

When this reaction was repeated using trichloroacetyl chloride (0.55 g, 3.03 mmol) and $Na[Rh(CO)_2(PPh_3)_2]$ (1.32 mmol) in tetrahydrofuran (40 cm^3) during 1 h a yellow precipitate of trichlorocarbonyl-bis(triphenylphosphine)-rhodium(III) (0.71 g, 0.93 mmol, 71%) was obtained.

Reactions of $Na[Rh(CO)_2(PPh_3)_2]$ with perfluorocarboxylic anhydrides

(a) Trifluoroacetic anhydride. Trifluoroacetic anhydride (0.56 g, 2.65 mmol) in tetrahydrofuran (25 cm^3) was added dropwise to a solution of the sodium salt (2.64 mmol) in the same solvent (100 cm^3) at 0°C. The solution was then stirred at room temperature for 16 h before chromatography (a 70/30 mixture of Et_2O/CH_2Cl_2 as eluent) to give $[Rh(COCF_3)(CO)_2(PPh_3)_2]$ (0.40 g, 0.57 mmol, 22%) as a yellow solid, which was recrystallised from a diethyl ether/hexane mixture. Anal. Found: C, 61.2; H, 4.0; F, 6.9. $C_{40}H_{30}F_3P_2O_3Rh$ calcd.: C, 61.5; H, 3.9; F, 7.3%.

(b) Pentafluoropropionic anhydride. Using a similar procedure to that described above a solution of pentafluoropropionic anhydride (0.82 g, 2.64 mmol) added dropwise to the anion (2.64 mmol) in tetrahydrofuran (100 cm^3) gave $[Rh(COC_2F_5)(CO)_2(PPh_3)_2]$ (0.86 g, 1.04 mmol, 39%) as yellow crystals, which were recrystallised from a diethyl ether/hexane mixture. Anal. Found: C, 59.0; H, 3.6; F, 10.9. $C_{41}H_{30}F_5P_2O_3Rh$ calcd.: C, 59.3; H, 3.6; F, 11.4%.

(c) Heptafluorobutyric anhydride. The anhydride (1.67 g, 3.96 mmol) and sodium salt (3.96 mmol) in tetrahydrofuran (100 cm^3) after 16 h at room temperature gave, after chromatography, yellow crystals of $[Rh(COC_3F_7)(CO)_2(PPh_3)_2]$ (1.46 g, 1.65 mmol, 42%). Anal. Found: C, 57.2; H, 3.5; F, 14.0. $C_{42}H_{30}F_7P_2O_3Rh$ calcd.: C, 57.3; H, 3.4; F, 14.0%.

Reaction of $[Rh(SnMe_3)(CO)_2(PPh_3)_2]$ with tetrafluoroethylene

Benzene (15 cm^3) and tetrafluoroethylene (0.36 g, 3.40 mmol) were condensed onto $[Rh(SnMe_3)(CO)_2(PPh_3)_2]$ (0.50 g, 0.59 mmol) contained in a silica tube (40 cm^3 capacity) cooled at —196°C. The tube was irradiated with UV light for 16 h, and the product mixture was chromatographed (benzene eluent) to give $[Rh(CF{=}CF_2)(CO)_2(PPh_3)_2]$ (0.15 g, 0.20 mmol, 33%) as yellow crystals, which were recrystallised from a mixture of benzene and methanol.

A repeat of this reaction using benzene (15 cm^3), tetrafluoroethylene (0.56 g, 5.60 mmol), and $[Rh(SnMe_3)(CO)_2(PPh_3)_2]$ (0.51 g, 0.61 mmol) in a Pyrex reaction tube after 16 h gave $[Rh(CF{=}CF_2)(CO)_2(PPh_3)_2]$ (25 mg, 0.03 mmol, 6%).

Reaction of octacarbonyldicobalt with $[Rh(CF{=}CF_2)(CO)_2(PPh_3)_2]$

A solution of $[Rh(CF{=}CF_2)(CO)_2(PPh_3)_2]$ (0.38 g, 0.50 mmol) in tetrahydrofuran (30 cm^3) was added dropwise to a solution of octacarbonyldicobalt (0.51 g, 1.50 mmol) in tetrahydrofuran (50 cm^3) that had been previously stirred for 1 h at 45°C to cause disproportionation into $[Co(THF)_6]^{2+}$-2 $[Co(CO)_4]^-$. The mixture was then stirred for 15 h at 50°C, and a brown decomposition product (0.19 g) was filtered off. The filtrate was chromatographed (hexane eluent) to give deep violet crystals of $CF_3CCo_3(CO)_9$ (35 mg, 0.07 mmol, 7%) identified by IR, ^1H NMR spectroscopy and mass spectrometry.

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