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THE NATURE OF THE PRODUCT OF THE REACTION $[Rh(CO)_2Cl]_2$ WITH PPh_3 AT 1/1 MOLE RATIO OF PPh_3/Rh

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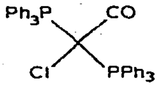
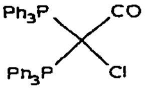
SUMMARY

Oxidation of the compounds* $RhAcac(CO)_2$ and $RhAcacPPh_3CO$ with halogens affords rhodium(III) carbonyl chloride, $[Rh(CO)_2Cl_3]_3$, and binuclear phosphine-containing complexes $(RhPPh_3COX_3)_2$ (X=Cl, Br). The nature of the reaction product of $[Rh(CO)_2Cl]_2$ with triphenylphosphine at a 1/1 mole ratio of PPh_3/Rh is discussed.

The reaction of μ,μ'-dichlorotetracarbonyldirhodium(I), $[Rh(CO)_2Cl]_2$, with an excess of triphenylphosphine results in the formation of the well-known complex (I), *trans*-$Rh(PPh_3)_2COCl$[1,2] with a carbonyl stretching frequency $\nu(CO)$ at ≈ 1965 cm^{-1}. There are indications in the literature that under some conditions another compound with $\nu(CO)$ at ≈ 1980 cm^{-1} is formed[3,4]. Furthermore, compounds containing both the above mentioned bands in their IR spectra have also been obtained[4,5]. The presence of an absorption maximum or shoulder at ≈ 1980 cm^{-1} has been ascribed to the *cis* isomer (II)[4].

Recently Uguagliati *et al.*[6] by reaction of PPh_3 with a benzene solution of $[Rh(CO)_2Cl]_2$ at a 1/1 mole ratio of PPh_3/Rh obtained a compound with $\nu(CO)$ 1980 cm^{-1} and ascribed to it formula (III) (X=Cl). Poilblanc and Gallay[7] reinvestigated this reaction and concluded that it led to the binuclear complex (IV) (X=Cl) via the formation of the non-isolable *cis*-dicarbonyl complex (V) with $\nu(CO)$ 2088, 2002 cm^{-1} as an intermediate.


(I)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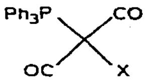
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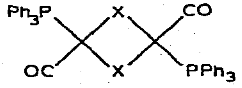
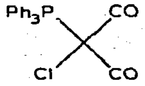

(IV)


(V)

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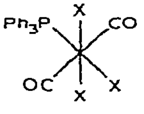
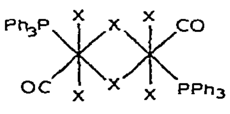
[*] Abbreviations used: Acac=acetylacetonate; Ph=phenyl.

Compounds of formula (IV) with X=Cl, Br and I, and with ν(CO) 1982, 1977 and 1972 cm^{-1} respectively, have been obtained by Faraone *et al.*[8] using other methods.

The rhodium complexes obtained[9] by oxidative addition of X_2 molecules (X=Cl, Br) to rhodium(I) complexes[6] have been characterized[9] in agreement with formula (III) as the *trans*-dicarbonyl derivatives (VI). If however the conclusions of Poilblanc and Gallay[7] are correct and the initial rhodium(I) complexes are of type (IV), formula (VII) must be ascribed to the corresponding rhodium(III) derivatives.



(VI)

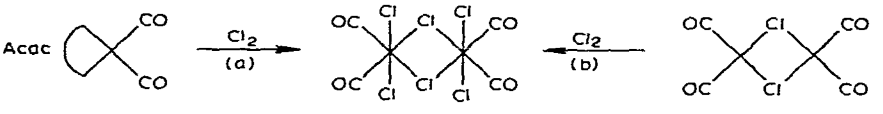


(VII)

Data obtained by us in connection with other studies and partly reported elsewhere[10] seem to have some bearing on this problem.

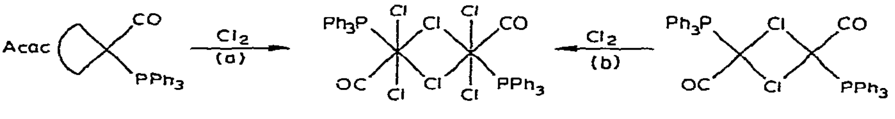
Treatment of RhAcac$(CO)_2$ with an excess of chlorine, and of RhAcacPPh$_3$CO with an excess of chlorine and bromine, result in products whose IR spectra do not exhibit bands characteristic of the ligand Acac. Cleavage of the metal–Acac bonds in chelate halogenation is not unexpected; thus, it is known[11] that Cu(Acac)$_2$ and Ni(Acac)$_2$ may be converted to Cu$(C_5H_6O_2X)_2$ (X=Cl, Br) and Ni$(C_5H_6O_2X)_2$ (X=Br) only under specific conditions. If these conditions are not met the reactions are accompanied by the elimination of acetylacetonate. Chlorination of RhAcac$(CO)_2$ yields a light brown product identical to the rhodium(III) carbonyl chloride obtained[10] on passing chlorine through a toluene solution of $[Rh(CO)_2Cl]_2$ [ν(CO) 2148, 2104(sh); ν(RhCl) 364, 345 cm^{-1}].

Both reactions can be represented by the scheme:



(1)

For triphenylphosphine derivatives the following scheme seems probable:



(2)

(VII) (IV)

On chlorinating RhAcacPPh$_3$CO an orange-yellow compound with ν(CO) 2114; ν(RhCl) 355, 338 cm^{-1} was isolated. Bromination of RhAcacPPh$_3$CO with excess bromine led to the formation of an orange compound with ν(CO) 2104 cm^{-1}. The preparative method employed and analytical and spectral evidence suggest[10] formula (VII) for these products. Thus halogenation of RhAcacPPh$_3$CO apparently proceeds according to path (a) in eqn. (2) in a similar manner to that occurring in path (a) in eqn. (1). On the other hand, one cannot overlook the similarities between the spectroscopic characteristics of complexes (VII) obtained via path (a) in equation 2 and those of the rhodium(III) complexes described elsewhere[9], *i.e.* ν(CO) 2111; ν(RhCl) 354, 339 cm^{-1} (chloride complex); and ν(CO) 2100 cm^{-1} (bromide complex). These similarities may be explained if it is assumed (*i*) that the rhodium(I) complexes described[6] as having formula (III) do in fact possess structure (IV), and (*ii*) if account is taken of the fact that complexes of type (VII) are the most probable products of the oxidative addition of halogen to compounds of type (IV) as depicted in path (b) of eqn. (2). These assumptions are in agreement with the concepts of Poilblanc and Galley. Thus it appears that the complexes (VII) which we mistakenly claimed as having first synthesized[10] were actually initially obtained by Deganello *et al.*[9] who suggested that they possessed formula (VI).

EXPERIMENTAL

$[Rh(CO)_2Cl_3]_2$

Method (*a*). Dry chlorine was passed through a solution of $RhAcac(CO)_2$ (0.5 g) in toluene (30 ml) for 1 h. The solution and the precipitate which began to separate almost immediately once the passage of chlorine had commenced were allowed to stand overnight in a closed reaction vessel. The light brown precipitate (0.35 g) was filtered (in a dry argon flow), washed with toluene and dried *in vacuo*. The product was soluble in ethanol, acetone and dimethylformamide (the solutions were unstable). When stored in air, the colour of the product darkens. (Found: Rh, 38.80; Cl, 39.85. $[Rh(CO)_2Cl_3]_2$ calcd.: Rh, 38.80; Cl, 40.27%.)

Method (*b*). Dry chlorine was passed through a solution of $[Rh(CO)_2Cl]_2$ (0.5 g) in toluene (20 ml) for 4 h. Formation of a precipitate was observed during the first few seconds of this treatment. The reaction mixture was allowed to stand overnight, then the resulting light brown product (0.48 g) was filtered, washed with toluene and dried *in vacuo*. (Found: Rh, 38.60; Cl, 39.95%.)

$(RhPPh_3COCl_3)_2$

Chlorine was passed through a solution of $RhAcacPPh_3CO$ (0.5 g) in carbon tetrachloride (30 ml) for 15 min. The colour of the solution rapidly changed from yellow to red and an orange-yellow crystalline precipitate was formed. After 30 min the passage of chlorine was discontinued and the product (0.45 g) was separated, washed with hexane and dried. The product was soluble in dimethylformamide. (Found: Rh, 20.40; Cl, 21.00. $(RhPPh_3COCl_3)_2$ calcd.: Rh, 20.62; Cl, 21.32%.)

$(RhPPh_3COBr_3)_2$

A solution of bromine (0.82 ml) in CCl_4 (10 ml) was added to a solution of $RhAcacPPh_3CO$ (0.5 g) in CCl_4 (50 ml). An orange precipitate was immediately formed. After 30 min the product (0.61 g) was separated, washed with hexane and dried. The product was soluble in dimethylformamide. (Found: Rh, 16.50; Br, 37.70. $RhPPh_3COBr_3$ calcd.: Rh, 16.28; Br, 37.88%.)

IR spectra (in Nujol mulls) were recorded using a IKS-14A model spectrophotometer with LiF and NaCl prisms (4000–700 cm^{-1}) and a IKS-21 model with a CsI prism (400–250 cm^{-1}). The starting materials were synthesized according to the procedures described previously[12,13].

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Note added in proof. Recently J. Gallay, D. de Montauzon and R. Poilblanc (*J. Organometal. Chem.*, 38 (1972) 179) obtained (VII) via path (b) of eqn. (2).