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THE REACTIONS OF $Cr(CO)_5PRH_2$ (R = Ph or cyclohexyl) COMPLEXES WITH MERCURY(II) AND SILVER(I) COMPOUNDS

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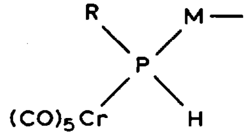
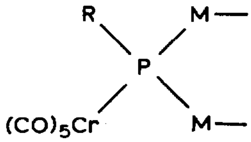
Summary

The μ_2-PRH and μ_3-PR bridged complexes $Cr(CO)_5[\mu_3\text{-}P(c\text{-}Hex)]\{Hg[\mu_2\text{-}P(c\text{-}Hex)_2]Cr(CO)_5\}_2$, $[Hg\{(\mu_2\text{-}PRH)Cr(CO)_5\}_3]^-$, (R = c-Hex, Ph) and $[Ag\{(\mu_2\text{-}PRH)Cr(CO)_5\}_n]^{1-n}$ (n = 1,2) have been prepared, and characterized by ^{31}P and ^{199}Hg NMR spectroscopy (c-Hex = cyclohexyl).

Introduction

We previously described the preparation of phosphido-bridged HgM and AgM (M = Cr, Mo, W) complexes derived from secondary phosphines [1–4]. We report here on the reactions of $Cr(CO)_5PRH_2$ with mercury(II) and silver(I) compounds. In these reactions, one or two metal atoms M (M = Hg or Ag) may become attached to the phosphorus atom as sketched below so leading to formulation of μ_2-PRH or μ_3-PR bridged complexes.





Results and discussion

Two mercury atoms are attached to phosphorus in the pentanuclear complex **1** which is formed according to eq. 1 (c-Hex denotes cyclohexyl):

Complex **1** was characterized by ^{31}P and ^{199}Hg NMR spectroscopy: the $^{31}P\{^1H\}$ NMR spectrum consists of a triplet along with a doublet due to coupling between

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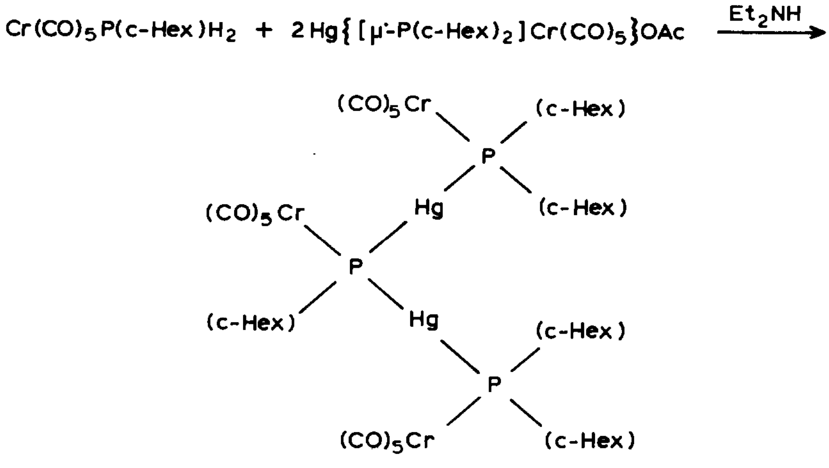


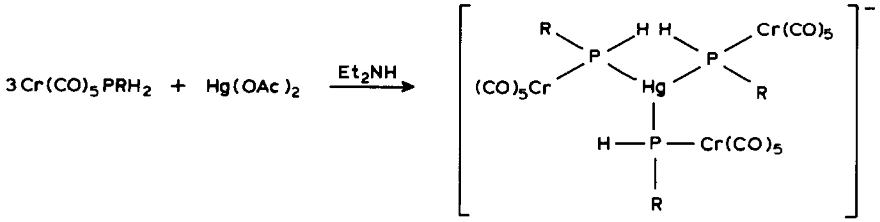
(1)

(1)

the μ_3 and the μ_2 phosphorus atoms. Particularly conclusive is the nearly doubled intensity of the ^{199}Hg satellite pattern of the μ_3 phosphorus, in accord with a statistical abundance of 28% for the isotopomer containing one ^{199}Hg atom. The ^{199}Hg{^{1}H} NMR spectrum of this isotopomer shows ddd multiplicity due to coupling of the ^{199}Hg atom to two phosphorus atoms via one bond and to one phosphorus atom via 3 bonds. The NMR data are given in the Experimental section.

The reaction of $Hg(OAc)_2$ and $Cr(CO)_5PRH_2$ (R = Ph, c-Hex) in the ratio of 1/3 in Et_2NH/toluene leads to the μ_2-PRH bridged tetranuclear complexes **2** and **3** (eq. 2):

The ^{199}Hg{^{1}H} NMR spectrum of **2** consists of two 1/3/3/1 quartets. The ^{31}P{^{1}H} NMR spectrum recorded at 145 MHz consists of an A_2B pattern (A,B = ^{31}P) together with the A_2B part of an A_2BX (X = ^{199}Hg) attributable to the isotopomer containing a ^{199}Hg atom and of an A_3 pattern with ^{199}Hg satellites (Fig. 1). The ^{31}P NMR spectrum of **2** (and **3**) shows that one hydrogen atom is attached to each phosphorus atom. The ^{199}Hg{^{1}H} NMR spectrum of **3** consists of a 1/3/3/1 quartet and of a second order pseudo-quartet. The ^{31}P{^{1}H} NMR spectrum of **3** consists of 2 AB_2 systems with ^{199}Hg satellites. The ^{199}Hg satellite



(2)

(**2**, R = c-Hex ;
3, R = Ph)

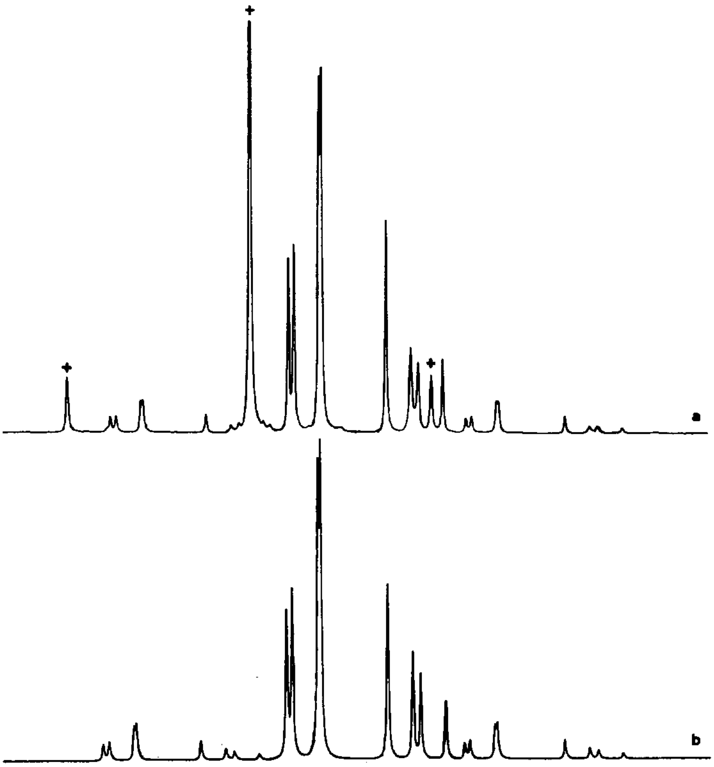


Fig. 1. Experimental (a) and computer-simulated (b) $^{31}P\{^1H\}$ spectra of 2. The A_3 and A_3X patterns designated by + in the experimental spectrum are not shown in the computer-simulated spectrum.

parts of the spectra of both **2** and **3** are resolved at ambient temperature. The NMR data are listed in the Experimental section.

The mercurates **2** and **3** contain 3 asymmetric phosphorus atoms and because of the molecular symmetry both species exist as 2 diastereomers. The appearance of the NMR spectra of the diastereomers depends on the molecular symmetry of **2** and **3**, on the rate of the internal rotation around the Hg–P bonds on the NMR time scale, and on the rate of inversion at the Hg center on the NMR time scale, as indicated below:

The *RRR/SSS* diastereomers should give A_3 spectra if there is rapid rotation on the NMR time scale around the Hg–P bonds or when a configuration with C_3 symmetry is stable on the NMR time scale. Otherwise there should be ABC type patterns. The *RRS/SSR* diastereomers should give rise to A_2B patterns when there is unhindered rotation around the Hg–P bonds and planar coordination of Hg by the phosphido groups in **2** and **3**. An A_2B type pattern is also expected when the mercury atoms adopt a pyramidal configuration and rapid rotation around the Hg–P bonds and there is rapid inversion of the Hg centers on the NMR time scale. Otherwise an ABC pattern should be observed. Possible degeneracy of the spectra because of isochronism must also be taken in account.

In the light of the above considerations, The A_2B and the A_3 pattern observed for **2**, and the two AB_2 patterns observed for **3** are attributed to diastereomers. The appearance of two AB_2 patterns for **3** indicates restricted internal rotation around the Hg–P bonds.

The reaction of $Hg(OAc)_2$ with $Cr(CO)_5PRH_2$ in a 1/2 ratio does not give complexes of the type $[Hg\{(\mu\text{-}PRH)Cr(CO)_5\}_2]$. The ^{31}P NMR spectrum of the reaction solution shows the patterns for **2** or **3** and a broad peak. Consideration of the stoichiometry (eq. 3) suggests a composition $[HgPRCr(CO)_5]_n$ for this species,

$$2Hg(OAc)_2 + 4Cr(CO)_5PRH_2 \xrightarrow{Et_2NH} [Hg\{(\mu\text{-}PRH)Cr(CO)_5\}_3]^- + 1/n[HgPRCr(CO)_5]_n \qquad (3)$$

and this is consistent with the absence of a $^1J(P,H)$ coupling. This species has not yet been characterized.

Reaction of AgO_3SCF_3 with $Cr(CO)_5PRH_2$ in 1/1 ratio in Et_2NH/toluene at −30 °C proceeds according to eq. 4. Use of two equivalents of $Cr(CO)_5PRH_2$ leads

$$AgO_3SCF_3 + Cr(CO)_5PRH_2 \xrightarrow{Et_2NH} [Ag(\mu\text{-}PRH)Cr(CO)_5] \qquad (4)$$

$$(\mathbf{4}, R = c\text{-}Hex; \mathbf{5}, R = Ph)$$

to formation of **6** and **7**, according to eq. 5.

$$AgO_3SCF_3 + 2Cr(CO)_5PRH_2 \xrightarrow{Et_2NH} [Ag\{(\mu\text{-}PRH)Cr(CO)_5\}_2]^- \qquad (5)$$

$$(\mathbf{6}, R = c\text{-}Hex; \mathbf{7}, R = Ph)$$

The reaction of AgO_3SCF_3 with a mixture of $Cr(CO)_5PPh_2H$ and $Cr(CO)_5(c\text{-}Hex)H_2$ leads to the mixed phosphido argentate $[Ag\{(\mu\text{-}PPh_2Cr(CO)_5\}\{(\mu\text{-}P(c\text{-}Hex)H)\text{-}Cr(CO)_5\}]^-$ (**8**), together with the symmetric argentates, the three species being present in almost statistical ratio. All the Ag compounds decompose within 1 h at −30 °C, but were characterized by ^{31}P NMR spectroscopy. The data are summarized in the Experimental section.

The different outcomes of the reaction of Hg^{II} or Ag^{I} compounds with $Cr(CO)_5PRH_2$ in 1/2 are thought to be due to the higher affinity of Hg^{II} than of Ag^{I} for phosphorus. The reactions (3) and (5) are Lewis acid-base equilibria. The equilibrium position is governed by the affinities of P for H, P for M (M = Ag or Hg), N for M, and N for H when $Hg(OAc)_2$ and AgO_3SCF_3 are assumed to exist as NEt_2H solvates in NEt_2H/toluene. Whilst $[Ag\{(\mu\text{-}PRH)Cr(CO)_5\}_2]^-$ is stable, the higher affinity of Hg for P renders $[Hg\{(\mu\text{-}PRH)Cr(CO)_5\}_2]$ unstable. As outlined in eq. 3 another H is thus replaced by Hg. The stability of $[Hg\{(\mu\text{-}PRH)Cr(CO)_5\}_3]^-$ can be accounted for in terms of a reduced affinity of Hg for P, such affinity generally decreasing with n in complexes of the type HgL_n.

Experimental

The ^{31}P and ^{199}Hg NMR spectra were recorded on a Bruker WP-80 spectrometer or on a Bruker WM-360 spectrometer. The external references were 85% H_3PO_4 or aqueous $Hg(ClO_4)_2$ (2 mmol HgO/ml 60% $HClO_4$), chemical shifts are in ppm positive to high frequency, coupling constants are in Hz. Computer simulation and iteration of NMR spectra were performed with the program PANIC [5]. Chemical analyses were carried out with a Hereaus EA 415 apparatus.

Deoxygenated solvents and inert atmospheres were used in the preparation of all the complexes. $Cr(CO)_5PRH_2$ (R = Ph or c-Hex) were prepared by the general procedures previously described [6].

Preparation of **1**

0.2 mmol of $Cr(CO)_5P(c\text{-}Hex)H_2$ was added with stirring to a solution of 0.4 mmol of $Hg\{[\mu P(c\text{-}Hex)_2]Cr(CO)_5\}OAc$ in a mixture of 0.5 ml of Et_2NH and 1.5 ml of pyridine. The mixture turned yellow immediately. The solvent was removed at room temperature under reduced pressure, and the residual paste was triturated with methanol to give a solid product, which was filtered off, washed with small amounts of cold methanol, and recrystallized from CH_2Cl_2/methanol. The yield of yellow needles of **1**, mp 125–130 °C (dec.) is ca. 50%.

Anal. Found: C, 35.96; H, 3.63. $C_{45}H_{55}Cr_3Hg_2O_{15}P_3$ calc: C, 36.37; H, 3.73%. NMR (Et_2NH/pyridine (1/3), 303 K): δ(P) 38.0 (t, μ_3-P, ^1J(Hg,P) 1002, ^2J(P,P) 85), δ(P) 66.7 (d, μ_2-P, ^1J(Hg,P) 1302), δ(Hg) 1876 (ddd, ^3J(Hg, P) 20).

Preparation of **2**

0.9 mmol of $Cr(CO)_5P(c\text{-}Hex)H_2$ was added to a solution of 0.3 mmol of $Hg(OAc)_2$ in a mixture of 0.5 ml of Et_2NH and 1 ml of toluene at 0 °C. One equivalent of NaOMe was added, producing a precipitate of NaOAc. Centrifugation gave a clear red solution, which was stable for two weeks at 0 °C. Attempts to crystallize **2** as its $[Et_2NH]^+$ $[PNP]^+$, or $[PPh_4]^+$, salts were unsuccessful.

NMR (293 K): A_3: δ(P) −12.5 (J(Hg,P) 900); δ(Hg) 2657(q); A_2B: $\delta(P_A)$ −13.5($^1J(Hg,P_A)$ 882, $^2J(P_A,P_B)$ 72), $\delta(P_B)$ −15.3 ($^1J(Hg,P_B)$ 886), δ(Hg): 2626 (q).

Preparation of **3**

0.9 mmol of $Cr(CO)_5Ph_2H$ was added to a solution of 0.3 mmol of $Hg(OAc)_2$ in a mixture of 0.5 ml of Et_2NH and 1 ml of toluene at 0 °C. Two phases were formed and a few drops of MeOH were added to produce a homogenous reddish solution. The solution was stable for two weeks at 0 °C. Attempts to crystallize **3** as $[Et_2NH_2]^+$, $[PNP]^+$ or $[PPh_4]^+$ salts were unsuccessful.

NMR (293 K): AB_2: $\delta(P_A)$ −29.4 ($^1J(Hg,P_A)$ 849, $^2J(P_A,P_B)$ 76), $\delta(P_B)$ −29.7 ($^1J(Hg,P_B)$ 751), δ(Hg) 2415 (quartetoid); AB_2: $\delta(P_A)$ −30.3 ($^1J(Hg,P_A)$ 835), $\delta(P_B)$ −30.4 ($^1J(Hg,P_B)$ 805), δ(Hg) 2451 (q).

Preparation of **4–8**

Equivalent amounts of $Cr(CO)_5PRH_2$ (or half an equivalent of each of $Cr(CO)_5P(c\text{-}Hex)H_2$ and $Cr(CO)_5PPh_2H$ in the case of **8**) were added to a solution of 0.4 mmol of AgO_3SCF_3 in a mixture of 0.5 ml of Et_2NH and 1 ml toluene at −30 °C. The products decompose in solution at −30 °C within 1 h with formation of elemental silver.

NMR: **4**:δ(P) −75.7 ($^1J(^{107}Ag, P)$ 488), 233 K;
5:δ(P) −85.9 ($^1J(^{107}Ag, P)$ 488), 233 K;
6:δ(P) −77.9 ($^1J(^{107}Ag, P)$ 337), 213 K;
7:δ(P) −81.0 ($^1J(^{107}Ag, P)$ 307), 213 K;
8:δ(P) −72.9 (d, *P*(c-Hex)H, $^1J(^{107}Ag,P)$ 340, ^2J(P,P) 141),
δ(P) −2.0 (d, *P*Ph_2, $^1J(^{107}Ag,P)$ 348), 233 K.

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