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Preliminary communication

Distinct reaction pathways for some classical and nonclassical transition metal dihydrides

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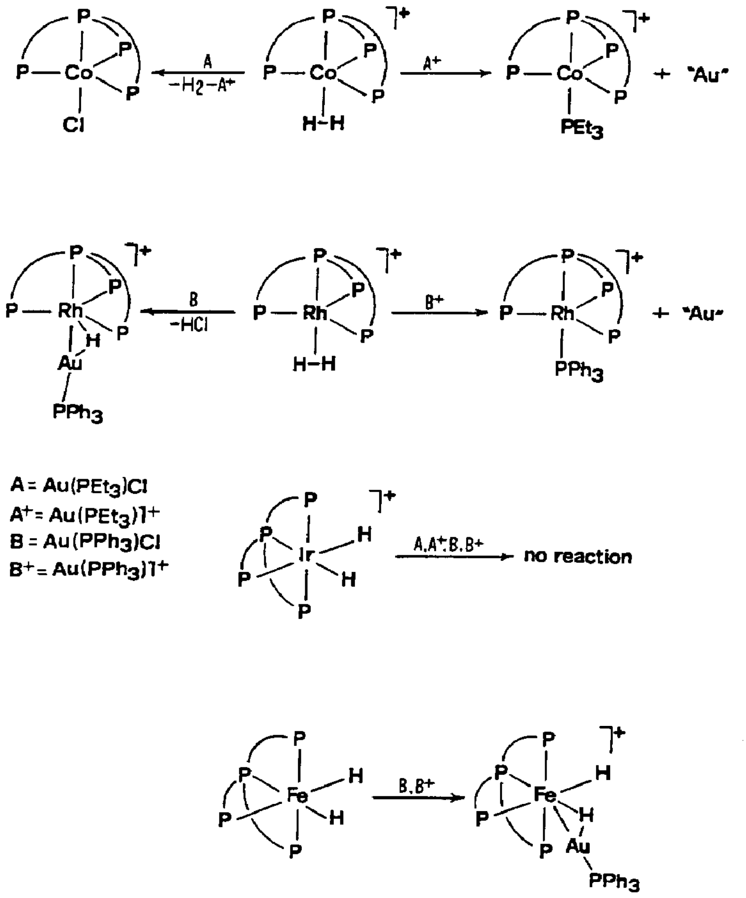
Abstract

Chlorophosphine gold(I) compounds [Au(PR_3)Cl] (R = Et, Ph) have been used as reagents for distinguishing classical from nonclassical structures in a family of dihydrides or dihydrogen complexes of iron, cobalt, rhodium and iridium stabilized by the tripodal polyphosphine PP_3 [$PP_3 = P(CH_2CH_2PPh_2)_3$]. Novel mixed transition-metal gold hydrides, including the first iron–gold species, are described.

The question of distinguishing classical $M(H)_2$ from nonclassical $M(H_2)$ structures in transition metal polyhydrides still attracts considerable attention [1]. We describe here some new reactions that could be used to decide whether a given polyhydrido complex contains only terminal M–H bonds or one or more H–H bonds. The method is based on the use of [Au(PR_3)Cl] (R = Et, Ph) complexes as diagnostic reagents, and exploits the ability of these gold(I) compounds to react differently with hydride or dihydrogen complexes. The complex, [Au(PR_3)Cl] readily generates the electrophilic fragment $[Au(PR_3)]^+$ which can react with terminal M–H bonds to form M–H–Au(PR_3) adducts [2]. Furthermore, these gold(I) complexes contain nucleophiles (Cl^- and PR_3) which can potentially either deprotonate [3] or displace [4] the dihydrogen ligand of η^2-H_2 complexes.

The following dihydrogen and dihydride complexes were investigated: $[(PP_3)Co(H_2)]PF_6$ (1) [5], $[(PP_3)Rh(H_2)]BF_4$ (2) [6], $[(PP_3)Ir(H)_2]BPh_4$ (3) [7] and $[(PP_3)Fe(H)_2]$ (4) [8] [$PP_3 = P(CH_2CH_2PPh_2)_3$]. In a typical procedure, the metal hydride was stirred in tetrahydrofuran (THF) at room temperature with one equivalent of either [Au(PR_3)Cl] or $[Au(PR_3)]^+$ prepared *in situ* by using $TlPF_6$ as chloride scavenger. The results obtained are summarized in Scheme 1.

Treatment of the η^2-H_2 complex **1** with $[Au(PEt_3)]^+$ results in the quantitative formation of $[(PP_3)Co(PEt_3)]PF_6$ (5) [9]. The reaction is accompanied by reduction of Au(I) to Au. By contrast, when the compound is treated with [Au(PEt_3)Cl], the



Scheme 1

chloride [(PP$_3$)CoCl] (**6**) is obtained [10]; dihydrogen is evolved and the [Au(PEt$_3$)]$^+$ fragment remains intact. After **6** is filtered off, [Au(PEt$_3$)Cl] is recovered by addition of PPNCl in ethanol. In keeping with occurrence of a simple ligand displacement reaction, compound **6** maintains the trigonal bipyramidal geometry of the starting complex **1** and the formal oxidation state of the metal.

Like complex **1**, the rhodium analog **2** reacts with [Au(PPh$_3$)]$^+$ to give a trigonal bipyramidal phosphine adduct, [(PP$_3$)Rh(PPh$_3$)]PF$_6$ (**9**) [11]. Interestingly, the cobalt and rhodium complexes differ from each other in the reaction with intact [Au(PPh$_3$)Cl]. Thus, instead of losing H$_2$, compound **2** loses HCl and forms the novel binuclear system [(PP$_3$)Rh(μ-H)Au(PPh$_3$)]PF$_6$ (**7**) [12*]. In addition to the detailed spectroscopic characterization reported in ref. 12*, the structural formula of **7** as given in Scheme 1 has been confirmed by a preliminary X-ray diffraction study [13]. The reaction leading to **7** may be viewed as involving heterolytic splitting of the dihydrogen ligand [3a] promoted by [Au(PPh$_3$)Cl] through its electrophilic [Au(PPh$_3$)]$^+$ and nucleophilic Cl$^-$ components. Compound **7** can, indeed, be obtained simply by reacting the monohydride [(PP$_3$)RhH] (**8**) [11] in THF with

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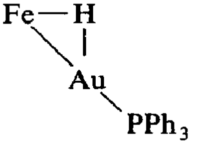
* Reference number with asterisk indicates a note in the list of references.

$[Au(PPh_3)]^+$ generated *in situ*. The different reactions of the H_2-complexes **1** and **2** with $[Au(PR_3)Cl]$ are consistent with the presence of a more activated dihydrogen ligand in the rhodium complex [5]. Accordingly, the reactions of η^2-H_2 complexes with chlorophosphine gold(I) compounds might also provide information about the nature of the H–H bonding interaction.

No reaction is observed between the classical dihydride iridium(III) complex **3** and either $[Au(PR_3)Cl]$ or $[Au(PR_3)]^+$ ($R = Et, Ph$). While the stability of **3** towards $[Au(PR_3)Cl]$ can be ascribed to the absence of protic species, the charge, rather than steric factors connected with the octahedral geometry of the complex, is probably responsible for its stability in the presence of $[Au(PPh_3)]^+$. It is noteworthy that the neutral, isoelectronic dihydride complex $[(PP_3)Fe(H)_2]$ (**4**) reacts with either $[Au(PPh_3)Cl]$ or $[Au(PPh_3)]^+$ to give the novel complex $[(PP_3)Fe(H)(\mu\text{-}H)Au(PPh_3)]^+$, which can be isolated as its Cl^- (**10a**) or PF_6^- (**10b**) salt [14*]. It is also noteworthy that no gold iron hydride has been so far reported [2a]. In the absence of an X-ray, study, the spectroscopic data for **10a–b** do not permit us to discriminate between a linear (**A**) or bent (**B**) array of the FeHAuPPh$_3$ moiety, but the $J(H_bP_{Au})$ coupling constant of 80 Hz appears to be more consistent with structure **B** [a value for $J(H_bP_{Au})$ of 84.3 Hz was found for **7**] [1].

$$Fe—H—Au—PPh_3$$

(A)



(B)

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12 Compound 7. IR (Nujol mulls): ν(RhHAu) not detected. Λ_M (1×10^{-3} M $C_2H_5NO_2$ solution) = 87 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 121.42 MHz, 294 K, AM_3QX spin system in which A

and M denote the apical and the terminal atoms of the PP_3 ligand, whereas Q and X indicate the phosphorus atom bonded to gold and the ^{103}Rh nucleus, respectively): δ_A, 161.06 ppm, ddq; δ_M, 67.55 ppm, ddd; δ_Q, 47.60, ddq. $J_{AM} = 20.7$ Hz, $J_{AQ} = 46.7$ Hz, $J_{AX} = 104.6$ Hz, $J_{MQ} = 14.2$ Hz, $J_{MX} = 136.3$ Hz, $J_{QX} = 46.4$ Hz. ^{1}H NMR (CD_3COCD_3, 300 MHz, 294 K): δ_{RhHAu}, -3.74 ppm, dddq. $J_{HA} = 50.9$ Hz, $J_{HM} = 3.9$ Hz, $J_{HQ} = 84.3$ Hz, $J_{HRh} = 17.8$ Hz. Anal., calcd (found): $C_{60}H_{58}AuF_6P_6Rh$; C, 52.27 (52.06); H, 4.24 (4.31); Rh, 7.46 (7.29).

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14 Compounds **10a** and **10b**. After taking account of the presence of different counter anions, the two compounds exhibit the same spectroscopic properties. IR (Nujol mulls): 1890 cm^{-1} (br w), $\nu(FeH_t)$. $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 121.42 MHz, 294 K, AM_3Q spin system in which A and M denote the apical and the terminal atoms of the PP_3 ligand, respectively, whereas Q indicates the phosphorus atom bonded to gold): δ_A, 177.49 ppm, qd; δ_M, 94.28 ppm, br; δ_Q, 48.56, dq. $J_{AM} = 32.1$ Hz, $J_{AQ} = 19.1$ Hz, $J_{MQ} = 2.7$ Hz. (193 K, AM_2QV spin system in which A, M and V denote the apical and the terminal atoms of the PP_3 ligand, respectively, whereas Q indicates the PPh_3 phosphorus atom): δ_A, 177.81 ppm, dtd; δ_M, 90.32 ppm, ddd; δ_Q, 47.72, ddt; δ_V, 104.83 ppm, ddt. $J_{AM} = 32.2$ Hz, $J_{AQ} = 18.1$ Hz, $J_{AV} = 32.3$ Hz, $J_{MQ} = 13.8$ Hz, $J_{MV} = 16.0$ Hz, $J_{QV} = 16.6$ Hz. ^{1}H NMR (CD_2Cl_2, 300 MHz, 294 K) δ_{FeH2Au}, -8.58 ppm, br, $w_{1/2} = 60$ Hz. (CD_2Cl_2, 193 K): δ_{Hb} -6.65 ppm, br d; $J_{HPAu} = 80$ Hz. δ_{Ht} -10.24 ppm, br q; $J_{HP} = 47$ Hz. Compound **10a**: anal., calcd (found): $C_{60}H_{59}AuClFeP_5$; C, 58.91 (58.55); H, 4.86 (5.00); Cl, 2.90 (2.80); Fe, 4.57 (4.43). Λ_M (1×10^{-3} *M* $C_2H_5NO_2$ solution) = 69 Ω^{-1} cm^2 mol^{-1}. Compound **10b**: anal., calcd (found): $C_{60}H_{59}AuF_6FeP_6$; C, 54.07 (53.86); H, 4.46 (4.49); Fe, 4.19 (4.18). Λ_M (1×10^{-3} *M* $C_2H_5NO_2$ solution) = 83 Ω^{-1} cm^2 mol^{-1}.