Mixed Rhenium–Gold Polyhydrides that contain ReAu and $ReAu_2$ Cores

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The reactions between $[ReH_5(PPh_3)_3]$ and $[Au(PR_3)]PF_6$ (R = Et or Ph) in acetone–CH_2Cl_2 give the complexes $[ReH_5(PPh_3)_3\{Au(PR_3)\}]PF_6$. Treatment of $[ReH_5(PPh_3)_3\{Au(PPh_3)\}]PF_6$ with NEt_3 affords the $ReAu_2$ cluster $[ReH_4(PPh_3)_3\{Au(PPh_3)\}_2]PF_6$. The complexes have been characterized by ^1H n.m.r., ^{31}P-$\{^1H\}$ n.m.r., and i.r. spectroscopies as well as by cyclic voltammetry.

Whereas the protonation of the dirhenium polyhydride complex $[Re_2(\mu\text{-}H)_4H_4(PPh_3)_4]$ with HBF_4 in CH_2Cl_2 affords the salt $[Re_2H_9(PPh_3)_4]BF_4$,[1] reactions with the isolobal[2–4] species $[Au(PR_3)]^+$ (R = Et or Ph) give the ReAu clusters $[Re_2H_8(PPh_3)_4\{Au(PR_3)\}]PF_6$, $[Re_2H_8(PPh_3)_4\{Au(PR_3)\}_2][PF_6]_2$, and related complexes derived therefrom by deprotonation and redox reactions.[1,5] In the case of the analogous dirhenium polyhydride complex $[Re_2(\mu\text{-}H)_4H_4(PMe_2Ph)_4]$, isomers of the neutral deprotonated Re_2Au_2 cluster $[Re_2H_6(PMe_2Ph)_4\{Au(PPh_3)\}_2]$ have been isolated and characterized.[6]

We have recently examined the related protonation of $[ReH_5(PPh_3)_3]$ to give $[ReH_6(PPh_3)_3]BF_4$[7] and herein describe the analogous reactions with $[Au(PR_3)]PF_6$ (R = Et or Ph) to give ReAu and $ReAu_2$ clusters, the smallest nuclearity clusters so far obtained from reactions between mononuclear rhenium polyhydride phosphine complexes and $[Au(PR_3)]^+$ species.

Results and Discussion

Reactions between equimolar amounts of $[ReH_5(PPh_3)_3]$ and $[Au(PR_3)]PF_6$ (R = Et or Ph) give the ReAu complexes $[ReH_5(PPh_3)_3\{Au(PR_3)\}]PF_6$ in high yield (*ca.* 80%). The compound $[ReH_5(PPh_3)_3\{Au(PPh_3)\}]PF_6$ behaves as a 1:1 electrolyte in acetone (*ca.* 1×10^{-3} mol dm^{-3}), $\Lambda_m = 124$ ohm^{-1} cm^2 mol^{-1}.[8] The Nujol mull i.r. spectra of these compounds also show the presence of PF_6^- with ν(P–F) at *ca.* 840 cm^{-1}. Bands that are assignable to ν(Re–H) were not observed.

The complex $[ReH_5(PPh_3)_3\{Au(PEt_3)\}]PF_6$ is more readily characterized by n.m.r. spectroscopy than its all PPh_3 analogue because of the presence of alkyl protons on the $Au(PEt_3)$ unit. In the ^1H n.m.r. spectrum (recorded in CD_2Cl_2 at room temperature), a single binomial pentet is observed at δ −3.11 p.p.m. [*J*(P–H) 18.8 Hz] assignable to the hydride ligands. This pattern indicates that hydride coupling to the Au bound P atom is equivalent to that of the three Re bound P nuclei. This may indicate a significant hydride interaction between the two metal centres. Elsewhere in the ^1H n.m.r. spectrum there is a multiplet due to the phenyl protons centred at δ *ca.* 7.2 p.p.m., a multiplet due to the methylene protons centred at δ *ca.* 1.7 p.p.m., and a multiplet due to the methyl protons centred at δ *ca.* 1.0 p.p.m. The aryl and alkyl protons integrate in a 3:1 ratio. In the ^{31}P-$\{^1H\}$ n.m.r. spectrum of $[ReH_5(PPh_3)_3\{Au(PEt_3)\}]PF_6$, two resonances, in a 3:1 ratio, at δ 31.9 (doublet) and 53.2 p.p.m. (quartet), respectively, along with a septet centred at δ −142.9 p.p.m. attributable to PF_6^-, are observed. The two downfield signals are coupled to one another with *J*(P–P) 8.6 Hz. Thus, while there is some fluxional process that renders the hydride ligands equivalent, there is no exchange of the phosphine ligands between metal centres at room temperature. ^1H N.m.r. spectral measurements over the temperature range 35 to −70 °C revealed little change in the hydride resonance.

The ^1H and ^{31}P-$\{^1H\}$ n.m.r. spectra of $[ReH_5(PPh_3)_3\{Au(PPh_3)\}]PF_6$ are very similar to those of $[ReH_5(PPh_3)_3\{Au(PEt_3)\}]PF_6$. Pertinent data (in p.p.m.) are as follows: ^1H n.m.r., δ −3.08 [pentet, *J*(P–H) 19.8 Hz]; ^{31}P-$\{^1H\}$ n.m.r., δ 31.1 [intensity 3, doublet, *J*(P–P) 7.7 Hz], 52.1 [intensity 1, quartet, *J*(P–P) 7.7 Hz], and −142.9 (septet).

The electrochemical properties of these two compounds, as measured by cyclic voltammetry (c.v.) on solutions in 0.1 mol dm^{-3} NBu_4PF_6–CH_2Cl_2 at a platinum bead working electrode and referenced to an Ag–AgCl electrode,† are essentially identical. For $[ReH_5(PPh_3)_3\{Au(PPh_3)\}]PF_6$, a couple occurs at $E_{\frac{1}{2}} = ca.$ 1.15 V ($E_{p,a} = 1.21$, $E_{p,c} = 1.05$ V; $i_{p,a}/i_{p,c} > 1$) and is followed by an irreversible process at $E_{p,a} = ca.$ 1.55 V. The oxidation at 1.21 V is shifted to a much less accessible potential than for the starting material $[ReH_5(PPh_3)_3]$, which has $E_{\frac{1}{2}} = 0.37$ V *vs.* s.c.e.[9] The magnitude of this shift is consistent with those observed upon forming the $[Au(PR_3)]^+$ adducts of $[Re_2H_8(PPh_3)_4]$.[1] Similar behaviour is observed for $[ReH_5(PPh_3)_3\{Au(PEt_3)\}]PF_6$ with $E_{\frac{1}{2}} = 1.09$ V ($E_{p,a} = 1.16$, $E_{p,c} = 1.03$ V; $i_{p,a} \sim i_{p,c}$).

Although the reaction between $[ReH_5(PPh_3)_3]$ and $[Au(PPh_3)]PF_6$ in 1:2 stoicheiometric proportions gave the 1:1 complex $[ReH_5(PPh_3)_3\{Au(PPh_3)\}]PF_6$ rather than the expected $ReAu_2$ cluster, we were able to isolate such a species by a rather surprising means. We had previously shown that the $[Au(PR_3)]^+$ adducts of $[Re_2H_8(PPh_3)_4]$ are readily deprotonated upon treatment with NEt_3, *e.g.* $[Re_2H_8(PPh_3)_4\{Au(PPh_3)\}]PF_6$ is converted into $[Re_2H_7(PPh_3)_4\{Au(PPh_3)\}]$.[1] However, this is not the case when $[ReH_5(PPh_3)_3\{Au(PPh_3)\}]PF_6$ is treated with NEt_3 since deprotonation is accompanied by $[Au(PPh_3)]^+$ transfer to produce $[ReH_4(PPh_3)_3\{Au(PPh_3)\}_2]PF_6$; we have not yet been able to identify the other rhenium-containing species of this reaction although it does not appear to be $[ReH_5(PPh_3)_3]$. It is noteworthy that $[ReH_6(PPh_3)_3]^+$, $[ReH_5(PPh_3)_3\{Au(PPh_3)\}]^+$, and $[ReH_4(PPh_3)_3\{Au(PPh_3)\}_2]^+$ constitute an isoelectronic series.

The complex $[ReH_4(PPh_3)_3\{Au(PPh_3)\}_2]PF_6$ behaves as a 1:1 electrolyte in acetone (*ca.* 1×10^{-3} mol dm^{-3}), $\Lambda_m = 128$ ohm^{-1} cm^2 mol^{-1}, and its Nujol mull i.r. spectrum has ν(P–F) of PF_6^- at *ca.* 840 cm^{-1}. The ^1H n.m.r. spectrum of a solution of this complex in CD_2Cl_2 displays two resonances at room temperature: a multiplet due to the phenyl protons is centred at δ *ca.* 7.2 p.p.m. while the hydride ligands are characterized by a multiplet at δ −3.40 p.p.m. that can best be described as an overlapping quartet of triplets. Simulation of this spectrum (Figure) gave *J*(H–Re–P) *ca.* 25 and *J*(H–Au–P) *ca.* 20 Hz. The quite large value of *J*(H–Au–P) presumably reflects the presence of strong Re–H–Au interactions which may or may not also involve direct Re–Au bonding. The ^{31}P-$\{^1H\}$ n.m.r. spectrum displays a quartet at δ 51.3 p.p.m. [Au–P, *J*(P–P) 9.4

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† Under these same experimental conditions the ferrocenium–ferrocene couple has $E_{\frac{1}{2}} = 0.47$ V *vs.* Ag–AgCl.

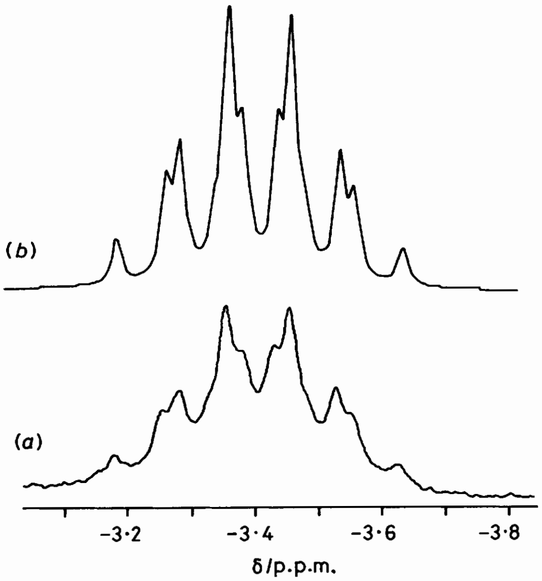

Figure. Proton n.m.r. spectrum (recorded in CD_2Cl_2) of the Re–H resonance of $[ReH_4(PPh_3)_3\{Au(PPh_3)\}_2]PF_6$: (*a*) experimental data, (*b*) simulated spectrum

Hz] and a triplet at δ 30.1 p.p.m. [Re–P, *J*(P–P) 9.4 Hz], in an intensity ratio of 2:3, together with a septet at δ −143.0 p.p.m. atrributable to PF_6^-.

The c.v. of a solution of the $ReAu_2$ cluster in 0.1 mol dm^{-3} NBu_4PF_6–CH_2Cl_2 shows a couple at $E_{\frac{1}{2}}$ = 0.68 V *vs.* Ag–AgCl (this corresponds to a bulk oxidation of the complex) and an irreversible reduction process at $E_{p,c}$ = *ca.* −1.2 V. Interestingly, the shift in the potential for the $1+ \longrightarrow 2+$ oxidation in 0.1 mol dm^{-3} NBu_4PF_6–CH_2Cl_2 for the set of complexes $[ReH_6(PPh_3)_3]^+$, $[ReH_5(PPh_3)_3\{Au(PPh_3)\}]^+$, and $[ReH_4(PPh_3)_3\{Au(PPh_3)\}_2]^+$, *viz.* $E_{p,a}$ = *ca.* 1.6,* 1.2, and 0.75 V, respectively, mirrors fairly closely the shifts between $[Re_2H_9(PPh_3)_4]^+$, $[Re_2H_8(PPh_3)_4\{Au(PPh_3)\}]^+$, and $[Re_2H_7(PPh_3)_4\{Au(PPh_3)\}_2]^+$, *viz.* $E_{p,a}$ = *ca.* 1.05, 0.5, and 0.2 V, respectively.[1] Thus as H^+ is replaced by $[Au(PPh_3)]^+$ the metal centre(s) becomes more electron rich.

Conclusions

The present work is an extension of our interest in small Re–Au clusters. The isolation of ReAu and $ReAu_2$ clusters provides examples of well defined molecular polyhydride complexes which complement recent studies on the synthesis and characterization of Re_2Au and Re_2Au_2 clusters that have been designed around the starting materials $[Re_2H_8(PR_3)_4]$ (PR_3 = PPh_3 or PMe_2Ph).[1,5,6] Previously, the reactions between $[ReH_5(PMe_2Ph)_3]$ and $[Au(PPh_3)(OR)]$ (R = Bu^t or $C_6H_2Bu^t_3$-2,4,6),[10] and between $[ReH_7(PPh_3)_2]$ (or $[ReH_7\{P(C_6H_4Me\text{-}p)_3\}_2]$) and $[Au(PPh_3)]NO_3$[5,11] have been examined, but in these instances the larger $ReAu_3$,[10] and $ReAu_5$[5,11] or $ReAu_4$[5] clusters were obtained. Clearly, by varying the nature of the mononuclear rhenium hydride starting material a wide variety of cluster sizes (so far from ReAu up to $ReAu_5$) can be isolated. Such a methodology is also adaptable to related Re–Cu[12,13] and Re–Ag[13] cluster chemistry.

Experimental

Starting Materials.—The complex $[ReH_5(PPh_3)_3]$ was prepared by the standard literature method.[14] All other reagents and solvents were obtained from commercial sources. Solvents were thoroughly deoxygenated prior to use. All reactions were carried out under an atmosphere of nitrogen.

Preparations.—(*a*) $[ReH_5(PPh_3)_3\{Au(PPh_3)\}]PF_6$. A solution of $[Au(PPh_3)]PF_6$ in acetone (5 cm^3) was prepared by reacting $[AuCl(PPh_3)]$ (0.050 g, 0.100 mmol) with $AgPF_6$ (0.025 g, 0.099 mmol). This mixture was filtered into CH_2Cl_2 (5 cm^3) that contained $[ReH_5(PPh_3)_3]$ (0.100 g, 0.102 mmol). The solution was stirred for 10 min, then mixed with diethyl ether (25 cm^3) and filtered into n-pentane (50 cm^3). The white precipitate of $[ReH_5(PPh_3)_3\{Au(PPh_3)\}]PF_6$ was filtered off and recrystallized from dichloromethane–diethyl ether–n-pentane; yield 0.125 g (77%) (Found: C, 54.0; H, 4.4. $C_{72}H_{65}AuF_6P_5Re$ requires C, 54.65; H, 4.1%).

(*b*) $[ReH_5(PPh_3)_3\{Au(PEt_3)\}]PF_6$. This compound was prepared in the same manner as (*a*), starting from $[AuCl(PEt_3)]$ (0.036 g, 0.102 mmol), $TlPF_6$ (0.036 g, 0.102 mmol), and $[ReH_5(PPh_3)_3]$ (0.080 g, 0.082 mmol); yield 0.092 g (78%) (Found: C, 50.0; H, 4.9. $C_{60}H_{65}AuF_6P_5Re$ requires C, 50.1; H, 4.6%).

(*c*) $[ReH_4(PPh_3)_3\{Au(PPh_3)\}_2]PF_6$. A solution of $[ReH_5(PPh_3)_3\{Au(PPh_3)\}]PF_6$ (0.118 g, 0.082 mmol) in acetonitrile (5 cm^3) was treated with NEt_3 (1 cm^3) and refluxed for 20 min. The mixture was filtered into diethyl ether (50 cm^3) and n-pentane (50 cm^3) added to the filtrate to induce precipitation of the yellow product; yield 0.047 (62% based on Au) (Found: C, 52.2; H, 4.0. $C_{90}H_{79}Au_2F_6P_6Re$ requires C, 53.0; H, 3.9%).

Physical Measurements.—Infrared spectra (4 800—400 cm^{-1}) were recorded as Nujol mulls on an IBM IR/32 spectrometer. Proton n.m.r. spectra were recorded at 90 MHz using a Perkin-Elmer R-32 spectrometer or at 200 MHz with a Varian XL-200 spectrometer. Resonances were referenced internally to residual protons in CD_2Cl_2 (δ 5.35 p.p.m.). The ^{31}P n.m.r. spectra were recorded on a Varian XL-200 spectrometer operating at 80.98 MHz with an internal deuterium lock and aqueous 85% H_3PO_4 as external standard. Positive chemical shifts are downfield from H_3PO_4. Conductivities were measured on an Industrial Instruments Inc. model RC 16B2 conductivity bridge. Cyclic voltammetry experiments were performed on CH_2Cl_2 solutions containing 0.1 mol dm^{-3} NBu_4PF_6 as the supporting electrolyte. The $E_{\frac{1}{2}}$ [taken as $(E_{p,a} + E_{p,c})/2$] and $E_{p,a}$ values were referenced to the Ag–AgCl reference electrode at room temperature and are uncorrected for junction potentials. Voltammetric measurements were obtained with a Bioanalytical Systems Inc. model CV-1A instrument in conjunction with a Hewlett-Packard model 7035B *x–y* recorder.

Microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

Acknowledgements

We thank the National Science Foundation for research support and the National Institute of Health (through the Division of Sponsored Resources) for funds for the purchase of the Varian XL-200 spectrometer.

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* Data for this complex have not been reported previously ($E_{p,a}$ = 1.61 V *vs.* Ag–AgCl).

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Received 24*th July* 1987; *Paper* 7/1347