Synthesis of Cluster Complexes containing $Au_2(PPh_3)_2$ Moieties: Isolobal Models of the Interaction of H_2 with Metal Clusters. *X*-Ray Structure of $Au_2Fe_2Ir(\mu_4\text{-}C_2Ph)(CO)_7(PPh_3)_3$

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Reactions of several metal cluster complexes with $[O\{Au(PPh_3)\}_3][BF_4]$ in the presence of $[ppn]^+$ salts $[ppn = (Ph_3P)_2N]$ have given derivatives containing two $Au(PPh_3)$ moieties in which an Au–Au bond may or may not be present; in the title complex, an unusual Au–C interaction is present, which may model an intermediate stage in the addition of H_2 [isolobal with $Au_2(PPh_3)_2$] to the parent Fe_2Ir acetylide cluster, which reaction affords the hydrido-vinylidene complex $Fe_2Ir(\mu\text{-}H)(\mu_3\text{-}CCHPh)(CO)_8(PPh_3)$.

In 1981, Lauher and Wald[1] proposed the isolobal relationship $H^+ \leftarrow\!\circ\!\rightarrow [Au(PR_3)]^+$; this was originally considered in terms of the use of 1s(H) or 6s(Au) orbitals and later refined to use a 6sp(hy) or $(s-z)$hy orbital in the latter case (hy = hybrid).[2] In metal cluster complexes, the strict relationship fails in some cases, notably when two or more $Au(PR_3)$ groups are present, there being a marked tendency to form Au–Au bonds in such complexes.

There is an assumption that this analogy can be extended to H–H or Au–Au bonded systems, although the formation of the latter is also considered to represent a break-down of Lauher and Wald's original proposal.[3] We suggest that, to a first approximation, the isolobal analogies $H_2 \leftarrow\!\circ\!\rightarrow Au_2(PR_3)_2$ and $H_3^+ \leftarrow\!\circ\!\rightarrow [Au_3(PR_3)_3]^+$ may be useful. Thus, the complex $Au_2Fe(CO)_4(PPh_3)_2$ (**1**)[4] may be considered to be an analogue of the as yet unknown dihydrogen complex $Fe(\eta\text{-}H_2)(CO)_4$, while $Au_2Ru_3(\mu_3\text{-}S)(CO)_9(PPh_3)_2$ (**2**)[5] models the addition of H_2 to the parent cluster before cleavage of the H–H bond to give the known $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$.

In the trigold clusters, two arrangements of the $Au_3(PR_3)_3$ unit have been described, namely the open array found in $Au_3CoRu_3(CO)_{12}(PPh_3)_3$ (**3**),[6] and the closed form in $Au_3Ru_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ (**4**).[7] The energy difference between the acyclic and cyclic structures of H_3^+ attached to metals is calculated to be small,[8] and we suggest that a similar small energy difference exists between the two forms of $[Au_3(PR_3)_3]^+$. Which structure is adopted by any particular complex probably depends on the steric constraints and the number of types of interactions with other metal atoms.†

While earlier studies have shown the utility of the trigoldoxonium salt $[O\{Au(PPh_3)\}_3][BF_4]$ (**5**) as a reagent to introduce up to three[9] or more[10] $Au(PPh_3)$ groups into cluster complexes, the experimental realisation of further parallels between H_2 and $Au_2(PPh_3)_2$ derivatives has awaited the development of a generally applicable source of the latter group. Although the molecular structure of $Au_2(PPh_3)_2$ was reported in preliminary form ten years ago,[11] no applications of this reagent have been described since. Herein we describe a synthetic route to complexes containing $Au_2(PPh_3)_2$ groups, and the unusual structure of one of these.

When reactions between suitable substrates and (**5**) are carried out in the presence of one equivalent of [ppn][X] [ppn $= (Ph_3P)_2N$; X = Cl, OAc, $Co(CO)_4$, for example], good to high yields of related complexes containing two $Au(PPh_3)$

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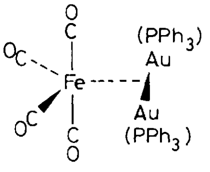
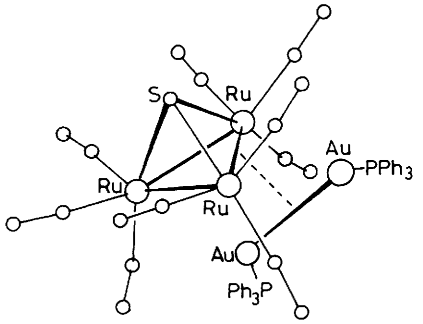
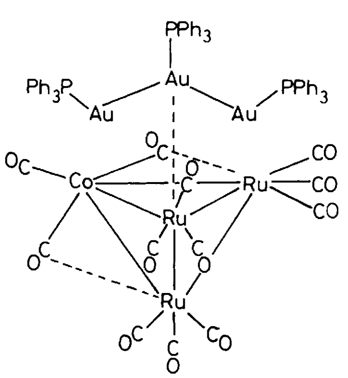
† A referee commented that 'pictures without Au–M bonds are essentially unreasonable.' Pictures (**1**)—(**4**) illustrate our general idea; the spatial arrangements of atoms have not been changed. We do not suggest that there are no Au–M bonds, but the formal interactions have been omitted for clarity. Many data are available which indicate that the Au–M interactions are very weak in these complexes.[19] These matters will be addressed further in the full paper.



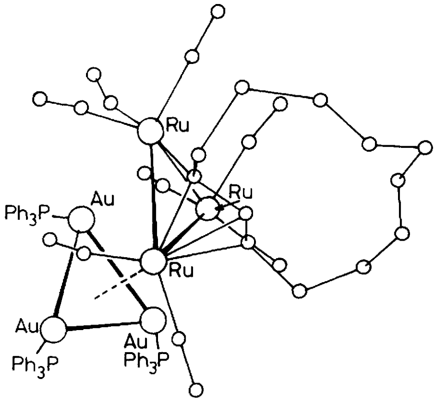
(**1**)



(**2**)



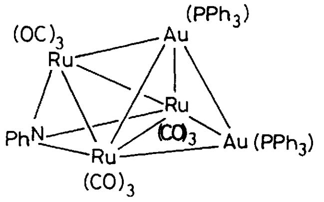
(**3**)



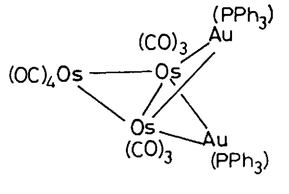
(**4**)

$[O\{Au(PPh_3)\}_3]BF_4$

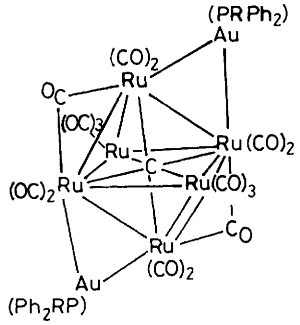
(**5**)



(**6**)



(**7**)



(**8**)

groups can be obtained. The $Au_2(PPh_3)_2$ ligand is a two-electron donor and often replaces a CO group; in the resulting complexes the Au–Au bond may or may not be preserved. The other products of the reactions are $AuX(PPh_3)$ and sparingly soluble [ppn][BF_4]. The reaction between (**5**) and [ppn][X] alone does not appear to give $Au_2(PPh_3)_2$, at least not in a form in which it can add to the substrate; possibly a trigold adduct is formed initially, which readily loses one $Au(PPh_3)$ moiety in the presence of [ppn][X].

Thus, the reaction between equimolar amounts of $Fe_2(CO)_9$, (**5**), and [ppn][$Co(CO)_4$] in tetrahydrofuran afforded (**1**), which contains an Au–Au bond.[4] The isolobal analogue is the unknown $Fe(\eta\text{-}H_2)(CO)_4$; the dihydride $FeH_2(CO)_4$ has been known since 1931.[12] In contrast, the reaction with $Co_2(CO)_8$ gave $AuCo(CO)_4(PPh_3)$, in a reaction which parallels exactly that of H_2 with the carbonyl.

Reactions between (**5**), [ppn]$^+$ salts, and cluster complexes have given derivatives which contain two $Au(PPh_3)$ groups: (a) retaining an Au–Au bond, as found [2.955(1) Å] in $Au_2Ru_3(\mu_3\text{-}NPh)(CO)_9(PPh_3)_2$ (**6**),‡ obtained from $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}CO)(CO)_9$; (b) sited close together, but with an Au · · · Au separation too long for there to be appreciable Au–Au bonding, as in $Au_2Os_3(CO)_{10}(PPh_3)_2$ [(**7**), X = $Au(PPh_3)$, in Scheme 1]‡ obtained from $Os_3(CO)_{11}(NCMe)$;

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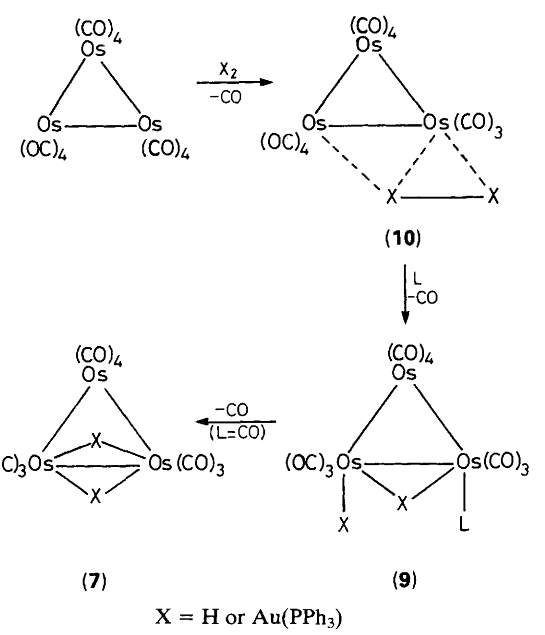
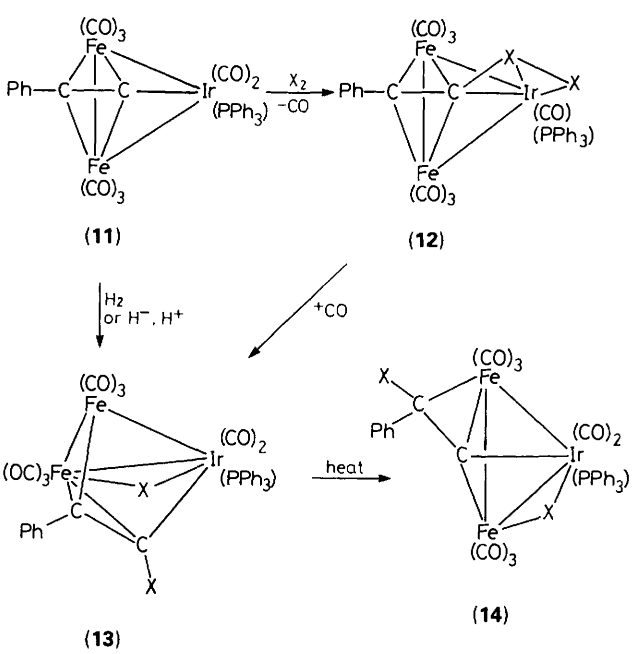
‡ *Selected spectroscopic data* for (**6**): ν(CO) (cyclohexane) 2055sh, 2024vs, 1963s, br., cm^{-1}; FAB MS (*m/z*) 1566 (M^+), 1538—1314 ($M-n$CO)$^+$ (n = 1—9), 1237 (M − 9CO − Ph)$^+$, 721 [$Au(PPh_3)_2$]$^+$, 459 [$Au(PPh_3)$]$^+$. (**8**) (R = Ph): ν(CO) (CH_2Cl_2) 2067w, 2049s, 2017vs, 1965w, 1822w, br., cm^{-1}; FAB MS (*m/z*) 1988 (M^+), 1960 (M − CO)$^+$, 1530 [M − $Au(PPh_3)$]$^+$, 721 [$Au(PPh_3)_2$]$^+$; 459 [$Au(PPh_3)$]$^+$. $Au_2Fe_2Ir(\mu_4\text{-}C_2Ph)(CO)_7(PPh_3)_3$ (**12**): ν(CO) (CH_2Cl_2) 2018m, 1978m, 1962m, 1885w, 1876sh cm^{-1}; FAB MS (*m/z*) 1784 (M + H)$^+$, 1699—1587 (M − nCO)$^+$ (n = 3—7), 1324 [M − $Au(PPh_3)$]$^+$, 919 [$Au_2(PPh_3)_2$ + H]$^+$, 721 [$Au(PPh_3)_2$]$^+$, 459 [$Au(PPh_3)$]$^+$. $Fe_2Ir(\mu\text{-}H)(\mu_3\text{-}HC_2Ph)(CO)_8(PPh_3)$ (**13**): ν(CO) (cyclohexane) 2076w, 2047s, 2023m, 2009vs, 1986m, 1970m, 1955w cm^{-1}; ^{1}H NMR ($CDCl_3$) δ − 23.48 [d, J(PH) 12 Hz, 1H, FeH], 7.1—7.5 (m, 20H, Ph), 7.81 [d, J(PH) 5 Hz, 1H, CH]; FAB MS (*m/z*) 894 (M)$^+$, 838—670 [M − nCO]$^+$ (n = 2—8). $Fe_2Ir(\mu\text{-}H)(\mu_3\text{-}CCHPh)(CO)_8(PPh_3)$ (**14**): ν(CO) (cyclohexane) 2072m, 2045vs, 2022s, 2009vs, 1986s, 1971m, 1961w, 1954w cm^{-1}; ^{1}H NMR ($CDCl_3$) δ − 17.96 [d, J(PH) 13 Hz, Fe$_2$*H*], 6.93 (s, 1H, CC*H*Ph), 7.35 (m, 20H, Ph); FAB MS (*m/z*) 894 (M^+), 866—670 (M − nCO)$^+$ (n = 1—8).



X = H or Au(PPh3)

Scheme 1



X = H or Au(PPh3)

Scheme 2

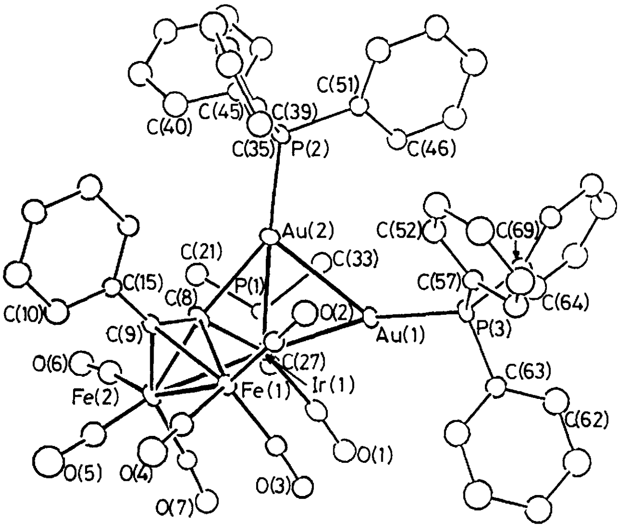


Figure 1. Molecular structure and crystallographic numbering scheme for (**12**), $Au_2Fe_2Ir(\mu_4\text{-}C_2Ph)(CO)_7(PPh_3)_3$. Selected parameters: Au(1)–Au(2) 2.847(1), Au(1)–Ir 2.633(1), Au(2)–Ir 2.726(1), Ir–Fe(1) 2.709(3), Ir–Fe(2) 2.744(4), Fe(1)–Fe(2) 2.501(5), Au(2)–C(8) 2.39(2), Ir–C(8) 1.96(2), Fe(1)–C(8) 2.07(2), Fe(2)–C(8) 2.08(2), C(8)–C(9) 1.34(3), Fe(1)–C(9) 2.14(2), Fe(2)–C(9) 2.06(2) Å. The diagram was drawn with ORTEP (15% probability ellipsoids) with only *ipso* carbon atoms of $P(1)Ph_3$ shown for clarity.

or (c) sited as far apart as possible, as in $Au_2Ru_6C(CO)_{16}(PRPh_2)_2$ (**8**) (R = Ph),‡ obtained from $Ru_6C(CO)_{17}$. The *X*-ray structures of (**7**) [X = $Au(PEt_3)$]¹³ and (**4**) (R = Me)¹⁴ have been determined previously; we have determined those of (**6**) and (**8**) (R = Ph), which are not exceptional, and these will be described elsewhere. It is of interest to recall that (**8**) (R = Me) is fluxional in solution, being in equilibrium with the isomer containing an $Au_2(PMePh_2)_2$ moiety capping an Ru_3 face.[14]

The well known reaction between H_2 and $Os_3(CO)_{12}$ (Scheme 1) affords $Os_3(\mu\text{-}H)_2(CO)_{10}$ (**7**) (X = H),[15] whose structure is analogous to that of (**7**) [X = $Au(PEt_3)$], mentioned above. Addition of ligands, L, gave $Os_3H(\mu\text{-}H)(CO)_{10}(L)$ (**9**) (X = H).[16] Further study of the reaction of '$Au_2(PPh_3)_2$' with $Os_3(CO)_{11}(NCMe)$ showed that (**7**) [X = $Au(PPh_3)$] was formed from an intermediate $Os_3\{Au_2(PPh_3)_2\}(CO)_{11}$, previously shown to have structure (**10**) [X = $Au(PPh_3)$][17] in which an Au–Au bond is present. Scheme 1 depicts a possible course of the interaction of X_2 [X = H or $Au(PR_3)$] with $Os_3(CO)_{12}$, from which it can be seen that (**10**) [X = $Au(PPh_3)$] represents an early stage in the reaction.

In a separate study, we have been investigating the chemistry of $Fe_2Ir(\mu_3\text{-}C_2Ph)(CO)_8(PPh_3)$ (**11**). Addition of equimolar amounts of (**5**) and [ppn][$Co(CO)_4$] to (**11**) immediately gave the Au_2Fe_2Ir cluster (**12**), whose unusual structure was revealed by a single crystal *X*-ray structure determination,§ Figure 1. The $Au_2(PPh_3)_2$ unit is seen to interact with the Ir and C(8) atoms, the Au(1)–Au(2) separation [2.847(1) Å] being consistent with the presence of a bonding interaction between these atoms. The Au_2Fe_2Ir metal core is a dimetallated triangle, with the C_2Ph ligand bridging four of the metal atoms.

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§ *Crystal data* for (**12**): $C_{69}H_{50}Au_2Fe_2IrO_7P_3\cdot EtOH$, M = 1827.9, monoclinic, space group Cc, a = 12.956(1), b = 26.604(4), c = 19.190(2) Å, β = 97.14(1)°, U = 6563.1 Å³, D_c = 1.850 Mg m⁻³, Z = 4. Monochromatized Mo-K_α radiation, λ = 0.7107 Å, μ = 69.87 cm⁻¹, T = 293 K, analytical absorption correction (max./min. transmission factors: 0.340, 0.241, respectively). Total of 4614 reflections measured ($1.0 \leq \theta \leq 22.5°$) on CAD4 diffractometer, 4508 unique and 3473 satisfied $I \geq 2.5\sigma(I)$. Structure solved by direct methods (SHELXS) and refined by full-matrix least-squares techniques (SHELX). Anisotropic thermal parameters for Au, Fe, Ir, P, C(8), and C(9). Phenyl rings refined as hexagonal rigid groups and hydrogen atoms included in their calculated positions. Refinement converged (for preferred chirality) with R = 0.048, R_w = 0.047 for weighting scheme $w = [\sigma^2(F) + 0.006\,|F|^2]^{-1}$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

However, an alternative view is that the structure is intermediate between the initial approach of the $Au_2(PPh_3)_2$ unit to the cluster, which might be expected to result in an Au_2M_2 system such as that found in (**6**), and the fully developed alkyne or vinylidene structures (**13**) and (**14**) (Scheme 2). The hydrogen analogues (X = H)‡ have been obtained from (**11**) by sequential addition of H^- and H^+, or from the reaction with H_2 (80 °C, 30 atm, 7 h; cyclohexane), respectively.

Scheme 2 depicts the reaction between (**11**) and X_2. After cleavage of the H–H bond in precursor (**12**) (X = H), modelled by (**12**) [X = Au(PPh$_3$)], formation of the μ-hydrido-alkyne cluster (**13**) (X = H) is followed by the well known isomerisation to (**14**) (X = H), as found for several related complexes.[18]

In conclusion, we have developed a new route to complexes containing either two Au(PPh$_3$) groups or the $Au_2(PPh_3)_2$ ligand. Some of these complexes have isolobal analogues in the corresponding hydrido complexes, while an attractive view of the structures of (**7**) and (**12**) is that they model steps in the addition of H_2 to the cluster complexes $Os_3(CO)_{12}$ and (**11**), respectively (Schemes 1 and 2). A more detailed discussion of the extension of these isolobal analogies and a comparison of the bonding between H_2 and $Au_2(PR_3)_n$ (n = 2,3) will be given in a full paper.

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