Direct Replacement of an Agostic Hydrogen Atom by an Isolobal Gold Ligand; *X*-Ray Crystal Structure of $[(\eta^5\text{-}C_5H_5)MoMn(\mu\text{-}PPh_2)\{\mu\text{-}\sigma:\eta^4\text{-}CH(Me)CHCHAu(PMe_2Ph)\}(CO)_4]$

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Treatment of the complex $[(\eta^5\text{-}C_5H_5)MoMn(\mu\text{-}PPh_2)\{\mu\text{-}\sigma:\eta^4\text{-}CH(Me)CHCH_2\}(CO)_4]$ (**1a**) with $[AuCl(PMe_2Ph)]$ in the presence of base gives $[(\eta^5\text{-}C_5H_5)MoMn(\mu\text{-}PPh_2)\{\mu\text{-}\sigma:\eta^4\text{-}CH(Me)CHCHAu(PMe_2Ph)\}(CO)_4]$ (**2**); *X*-ray structure analysis of (**2**) confirms that this reaction provides the first example of the direct replacement of an agostic hydrogen atom by a similarly bonded isolobal gold ligand.

We have previously described the synthesis of the complexes $[(\eta^5\text{-}C_5H_5)MoMn(\mu\text{-}PPh_2)(\mu\text{-}\sigma:\eta^4\text{-}CH(Me)CRCH_2)(CO)_4]$, (**1a**, R = H) and (**1b**, R = Me).[1] ^1H N.m.r. spectroscopy together with *X*-ray structure analysis of (**1b**) confirmed that both these complexes contain an allyl group which is η^3-bonded to the molybdenum atom and, in addition, is bonded to the manganese atom *via* an agostic[2] three-centre two-electron C–H–Mn interaction. Such an interaction is known to increase the acidity of the hydrogen atom concerned[3] and we now report that (**1a**) can be readily deprotonated (Scheme 1), forming an anion which reacts with $[AuCl(PMe_2Ph)]$ to give $[(\eta^5\text{-}C_5H_5)MoMn(\mu\text{-}PPh_2)\{\mu\text{-}\sigma:\eta^4\text{-}CH(Me)CHCHAu(PMe_2Ph)\}(CO)_4]$ (**2**).† An *X*-ray structure analysis of (**2**)‡ shows that it has a structure similar to that of (**1a**)[1] but with the agostic hydrogen atom replaced by an analogously bonded $Au(PMe_2Ph)$ group. The isolobal nature of H and AuL groups is well known[4] and there are many examples of Au–L bridged analogues of complexes containing H-bridged metal–metal bonds.[4,5] However, although complexes containing gold-bridged metal–carbon bonds have been characterised previously,[6,7] complex (**2**) provides the first example of an AuL-bridged analogue of a stable complex containing an agostic C–H–M interaction. The direct replacement of an agostic H-bridge by an AuL bridge has not been observed previously and is a striking demonstration of the application of the isolobal principle to this bonding situation.

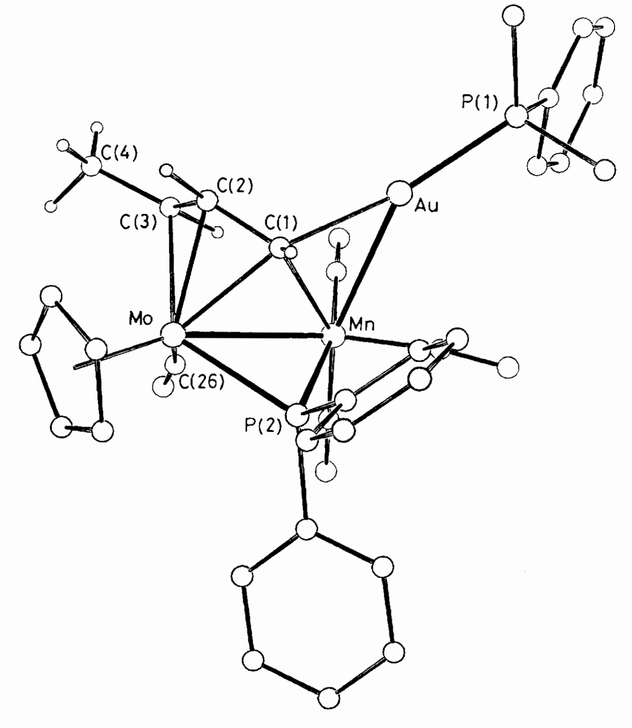

Figure 1. The molecular structure of $[(\eta^5\text{-}C_5H_5)MoMn(\mu\text{-}PPh_2)\{\mu\text{-}\sigma:\eta^4\text{-}CH(Me)CHCHAu(PMe_2Ph)\}(CO)_4]$ (**2**). Selected bond lengths and angles: Au–Mn 2.716(2), Au–P(1) 2.258(4), Au–C(1) 2.186(12), Mo–Mn 2.824(2), Mo–P(2) 2.430(3), Mo–C(1) 2.234(11), Mo–C(2) 2.233(11), Mo–C(3) 2.386(12), Mo–C(C_5H_5 av.) 2.341(11), Mn–P(2) 2.241(4), Mn–C(1) 2.263(10), Mn · · · C(26) 2.730(1), C(1)–C(2) 1.423(14), C(2)–C(3) 1.41(15), C(3)–C(4) 1.495(17) Å; Mn–Au–C(1) 53.7(3), Mo–Mn–Au 101.4(1), Mo–P(2)–Mn 74.3(1), Mo–C(1)–Mn 77.8(3)°.

The neutral gold complex (**2**) is most conveniently obtained in one step from (**1a**) by deprotonation with the nitrogen base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in CH_2Cl_2 solution in the presence of $[AuCl(PMe_2Ph)]$. The colour of the

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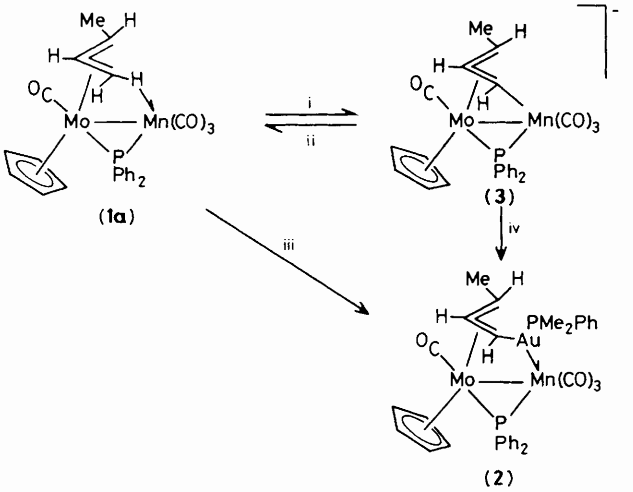
† *Spectroscopic data:* (**2**) ν_{CO} (CH_2Cl_2) 1968s, 1887m, 1863m, and 1809w cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 7.8—7.2 (m, 15H, Ph), 5.0 (obscured, H^3), 4.98 [d, ^3J(PH) 1.3, 5H, C_5H_5], 2.06 [dq, J_{13} 9.5, J_{12} 6.3 Hz, 1H, H^1], 1.90 [d, ^2J(PH) 9.8 Hz, 3H, P*Me*^{a}Me^{b}Ph], 1.89 [d, ^2J(PH) 9.7 Hz, 3H, PMe^a*Me*^{b}Ph], 1.59 (d, 3H, Me^2), and 1.28 [ddd, ^3J(PH) 21.8, 7.0, J_{34} 7.0 Hz, 1H, H^4].

‡ *Crystal data* for (**2**): $C_{33}H_{32}AuMnMoO_4P_2$, $M = 902.40$, monoclinic, space group $P2_1/c$, $a = 13.195(2)$, $b = 13.943(2)$, $c = 17.981(3)$ Å, $\beta = 103.60°$, $U = 3215.35$ Å^3, $Z = 4$, $F(000) = 1752$, $D_c = 1.876$ g cm^{-3}, μ(Mo-K_α) 52.14 cm^{-1}, $R = 0.0551$, $R_w = 0.0575$ for 4154 diffractometer data, with $I/\sigma(I) \geqslant 3.0$. 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.



Scheme 1. *Reagents and conditions:* i, $LiBu^n$, thf, room temperature; ii, CF_3CO_2H, thf, room temperature; iii, DBU, $[AuCl(PMe_2Ph)]$, CH_2Cl_2, room temperature; iv, $[AuCl(PMe_2Ph)]$, CH_2Cl_2, room temperature.

solution changes from orange to bright red in 30 s and, after column chromatography, (**2**) was isolated in *ca.* 80% yield.

The structure of (**2**), shown in Figure 1, is remarkably similar to that of (**1b**) despite the replacement of the agostic C–H–Mn bond in (**1a**) by a C–Au–Mn bond in (**2**), although the Mo–Mn distance of 2.824(2) Å in (**2**) is greater than that in (**1b**) [2.806(1) Å] for which a partial multiple metal–metal bond has been postulated.[1] The Au–Mn bond length of 2.716(2) Å in (**2**) is longer than the corresponding distance in complexes such as $[(Ph_3P)AuMn(CO)_4P(OC_6H_5)_3]$ [2.57(1) Å][8] containing two-centre two-electron bonds and is closer to those of 2.696(6) and 2.681(6) Å found in $[Mn_2(\mu\text{-}PPh_2)\{\mu\text{-}Au(PMe_2Ph)\}(CO)_8]$[9] in which a three-centre two-electron bond is also involved.

Deprotonation of complex (**1a**) with $LiBu^n$ in tetrahydrofuran (thf) followed by addition of excess of CD_3CO_2D to the solution gave complex $[^2H_1]$-(**1a**) with a parent molecular ion at *m/z* 569. The ^1H n.m.r. spectrum of $[^2H_1]$-(**1a**) reveals that the deuterium is located exclusively at the agostic site and does not migrate to other sites over long periods in solution. This evidence strongly indicates that the anion from which (**2**) is derived should be formulated as $[(\eta^5\text{-}C_5H_5)MoMn(\mu\text{-}PPh_2)\{\mu\text{-}\sigma:\eta^4\text{-}CH(Me)CHCH\}(CO)_4]^-$ (**3**) as shown in Scheme 1. In addition to reacting with $[AuCl(PMe_2Ph)]$ the anion (**3**) reacts with a variety of electrophiles to give stable products.

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