# Synthesis of Diphenylphosphido-bridged Manganese-Gold Complexes. Crystal Structures of $[N(PPh_3)_2][Au_2Mn(\mu\text{-}PPh_2)_2(CO)_4(C_6F_5)_2]$ and $[Au_2Mn_2(\mu\text{-}PPh_2)_4(CO)_8]$‡

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The complexes $[L_nMn(\mu\text{-}PPh_2)AuX]^z$ [$L_n$ = $(CO)_5$ or $(CO)_3$(bipy) (bipy = 2,2′-bipyridine); X = $P(C_6H_4Me\text{-}4)_3$, z = 1, perchlorate salt or X = $C_6F_5$, z = 0], $[(OC)_4Mn(\mu\text{-}PPh_2)_2(AuX)_2]^z$[X = $P(C_6H_4Me\text{-}4)_3$ or $PPh_3$, z = 1, perchlorate salt; X = $C_6F_5$, z = −1, $N(PPh_3)_2^+$ salt], $[L_nMn(\mu\text{-}PPh_2)Au(\mu\text{-}PPh_2)MnL_n]A$ [$L_n$ = $(CO)_5$, A = $ClO_4$; or $L_n$ = $(CO)_3$(bipy), A = $PF_6$], and $[Au_2Mn_2(\mu\text{-}PPh_2)_4(CO)_8]$ have been prepared from the corresponding salts $[Mn(PHPh_2)_yL_n]A$ (y = 1 or 2) by reaction with $[AuCl(PR_3)]$ (R = $C_6H_4Me$-4 or Ph), $[Au(C_6F_5)(tht)]$ or [AuCl(tht)] (tht = tetrahydrothiophene) in the presence of appropriate proportions of K(acac), Tl(acac), or $[N(PPh_3)_2]$[acac] (acac = acetylacetonate), or mixtures of these reagents. The compounds $[N(PPh_3)_2][Au_2Mn(\mu\text{-}PPh_2)_2(CO)_4(C_6F_5)_2]$ and $[Au_2Mn_2(\mu\text{-}PPh_2)_4(CO)_8]$ have been characterized by *X*-ray diffraction; both display short Au • • • Au interactions.

We have reported[1] the preparation of a series of octahedral manganese carbonyls of the type $[Mn(PHPh_2)_n(CO)_{6-n}]ClO_4$ (*n* = 1–4). Their cationic nature suggested the possibility of deprotonation of the co-ordinated $PHPh_2$ ligand, thus providing a synthetic route to new μ-$PPh_2$ species. As candidates to replace the $H^+$, we chose the gold(I) fragments $Au(PR_3)^+$, $Au(C_6F_5)$, and '$Au^+$,' accessible from $[AuCl(PR_3)]$ $[Au(C_6F_5)(tht)]$, or [AuCl(tht)] (tht = tetrahydrothiophene); this led to the preparation of several neutral, cationic, and anionic complexes containing Mn(μ-$PPh_2$)Au or Mn(μ-$PPh_2Au)_2$ groups. Some related $AgL^+$ derivatives of $[M(PHPh_2)_2(CO)_5]$ (M = Cr, Mo, or W) have recently been described.[2]

## Results and Discussion

The complex $[Mn(PHPh_2)(CO)_5]ClO_4$ (**1**) reacted rapidly at room temperature with $[Au(C_6F_5)(tht)]$ in the presence of K(acac) (acac = acetylacetonate) to give the neutral species $[AuMn(\mu\text{-}PPh_2)(CO)_5(C_6F_5)]$ (**2**). Similarly, the salt *fac*-$[Mn(PHPh_2)(CO)_3(bipy)]ClO_4$ (bipy = 2,2′-bipyridine) (**3a**) gave $[AuMn(\mu\text{-}PPh_2)(CO)_3(bipy)(C_6F_5)]$ (**4**). The analytical and spectroscopic data were consistent with this formulation (see Table 1 and the Experimental section). In particular, the low $^{31}P$ chemical shift of the μ-$PPh_2$ ligand implied the absence of a metal–metal bond.[3]

The complex (**3b**) (the $PF_6$ salt corresponding to **3a**) also reacted readily with $[AuCl(PR_3)]$ (R = $C_6H_4Me$-4) in the presence of Tl(acac) to give the cationic species $[AuMn(\mu\text{-}PPh_2)(CO)_3(bipy)(PR_3)]^+$ as its $PF_6$ salt (**5**). In contrast, however, the reaction between complex (**1**), $[AuCl(PR_3)]$, and Tl(acac) led to the 'symmetric' products $[AuMn_2(\mu\text{-}PPh_2)_2(CO)_{10}]ClO_4$ (**6**) and $[Au(PR_3)_2]ClO_4$; this was confirmed by preparing (**6**) directly from (**1**), [AuCl(tht)], K(acac), and Tl(acac) in a molar ratio 2:1:1:1. It is probable that the reaction of (**1**) with $[AuCl(PR_3)]$ and Tl(acac) initially gives the mixed product $[AuMn(\mu\text{-}PPh_2)(CO)_5(PR_3)]ClO_4$, analogous to (**5**), which is subsequently converted into (**6**) and $[Au(PR_3)_2]ClO_4$ by a symmetrization reaction of a type common in gold(I) chemistry.[4]

We found no evidence for the symmetrization of complex (**5**) in solution [the molar conductance of (**2**) and (**4**) in acetone showed that those neutral species also do not symmetrize], but the compound $[Au\{Mn(\mu\text{-}PPh_2)(CO)_3(bipy)\}_2]ClO_4$ (**7**) could be prepared from (**3a**) by the same method that gave (**6**) from (**1**).

The bis(diphenylphosphine) cationic complex $[Mn(PHPh_2)_2(CO)_4]ClO_4$ (**8**) reacted with 2 equivalents of $[Au(C_6F_5)(tht)]$ in the presence of a mixture of K(acac) and $[N(PPh_3)_2]$[acac] to give the stable anionic complex $[Au_2Mn(\mu\text{-}PPh_2)_2(CO)_4(C_6F_5)_2]^-$ as its $N(PPh_3)_2^+$ salt (**9**). The $^{31}P$ n.m.r. spectrum gave no indication of an Au • • • Au interaction, and the structure was therefore determined by *X*-ray diffraction (see Figure 1). In the solid state there is indeed a short Au • • • Au contact of 3.049 Å, a feature common in gold(I) complexes and regarded as a weakly stabilizing interaction.[5] The co-ordination geometry at gold is somewhat distorted from the ideally linear, with C–Au–P 173.4 and 173.7°. The Au–P bonds are long (2.313 and 2.322 Å), as expected for bridging phosphide ligands; however, no non-bridging phosphide–gold bond lengths are available for comparison. In the anion $[(AuBr)_2PPh_2]^-$ the Au–P bond length is much shorter at 2.243(3) Å, but the bromide ligands exert a much weaker *trans* influence.[6] The co-ordination axes at gold are not parallel and the molecule thus displays a 'twisted' conformation [*cf.* complex (**11**), see below]. The $C_6F_5$ rings display the usual narrow angles at the *ipso* carbons (114.8 and 114.2°).[7]

The cationic complexes $[Au_2Mn(\mu\text{-}PPh_2)_2(CO)_4(PR_3)_2]^+$ (as $ClO_4^-$ salts; **10a**, R = $C_6H_4Me$-4; **10b**, R = Ph) analogous

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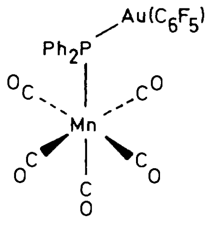
‡ Bis(triphenylphosphine)iminium 2,2,2,2-tetracarbonyl-1,2;2,3-bis(μ-diphenylphosphido)-1,3-bis(pentafluorophenyl)-1,3-digold-2-manganate and 2,2,2,2,4,4,4,4-octacarbonyl-1,2;1,4;2,3;3,4-tetrakis(μ-diphenylphosphido)-1,3-digold-2,4-dimanganese.

*Supplementary data available:* Complete bond lengths and angles, thermal parameters, structure factors, and H-atom co-ordinates can be obtained from the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany by quoting a full literature citation and the reference number CSD 53289.

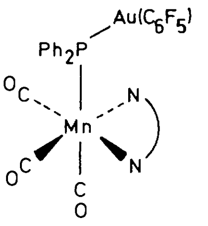
**Table 1.** Analytical and physical data for the AuMn complexes

| | Compound | M.p.[a] (°C) | Analysis (%)[b] C | H | N | $\nu_{max.}$(CO)[c]/cm$^{-1}$ |
|---|---|---|---|---|---|---|
| (**2**) | $[AuMn(\mu\text{-}PPh_2)(CO)_5(C_6F_5)]$ | 108 | 36.8(37.1) | 1.15(1.35) | | 2 130m, 2 038s[d] |
| (**4**) | $[AuMn(\mu\text{-}PPh_2)(CO)_3(bipy)(C_6F_5)]$ | 140 | 44.5(44.1) | 2.40(2.15) | 3.15(3.30) | 2 020s, 1 938s, 1 916s |
| (**5**) | $[AuMn(\mu\text{-}PPh_2)(CO)_3(bipy)\{P(C_6H_4Me\text{-}4)_3\}]PF_6$ | 101 | 50.0(49.0) | 3.85(3.45) | 2.40(2.50) | 2 030s, 1 948s, 1 922s |
| (**6**) | $[AuMn_2(\mu\text{-}PPh_2)_2(CO)_{10}]ClO_4$ | 140 | 38.9(38.6) | 2.00(1.90) | | 2 132m, 2 045s |
| (**7**) | $[AuMn_2(\mu\text{-}PPh_2)_2(CO)_6(bipy)_2]ClO_4$ | 120 | 47.5(47.8) | 2.95(2.85) | 4.30(4.45) | 2 028s, 1 945s, 1 921s |
| (**9**) | $[N(PPh_3)_2][Au_2Mn(\mu\text{-}PPh_2)_2(CO)_4(C_6F_5)_2]$ | 138 | 50.8(50.6) | 3.05(2.75) | 0.80(0.75) | 2 062m, 1 985s, 1 947m |
| (**10a**) | $[Au_2Mn(\mu\text{-}PPh_2)_2(CO)_4\{P(C_6H_4Me\text{-}4)_3\}_2]ClO_4$ | 135 | 51.3(51.3) | 3.80(3.80) | | 2 075s, 2 003s, 1 987vs, 1 974s |
| (**10b**) | $[Au_2Mn(\mu\text{-}PPh_2)_2(CO)_4(PPh_3)_2]ClO_4$ | 140 | 50.3(49.4) | 3.30(3.20) | | 2 082s, 2 003s, 1 987vs, 1 974s |
| (**11**) | $[Au_2Mn_2(\mu\text{-}PPh_2)_4(CO)_8]$ | 170 | 46.2(45.8) | 2.80(2.70) | | 2 065s, 1 998(sh), 1 982vs, 1 962s |

[a] With decomposition. [b] Calculated values are given in parentheses. [c] In $CH_2Cl_2$ solution. [d] In hexane: 2 125w, 2 040s, and 2 025vs cm$^{-1}$.



(**2**)



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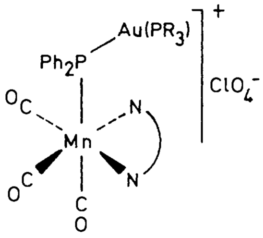

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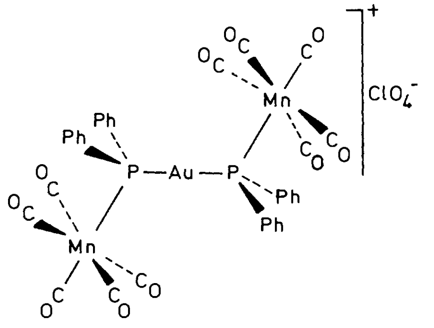

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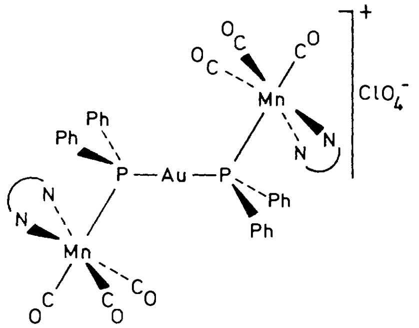

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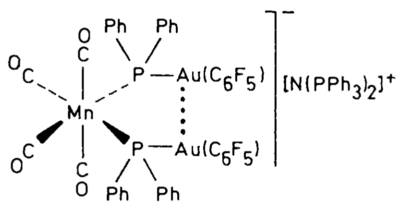

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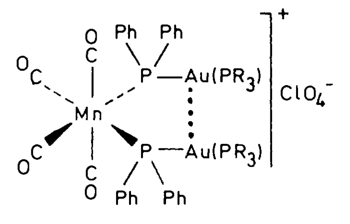

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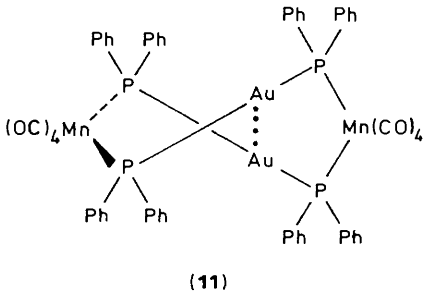

(**11**)

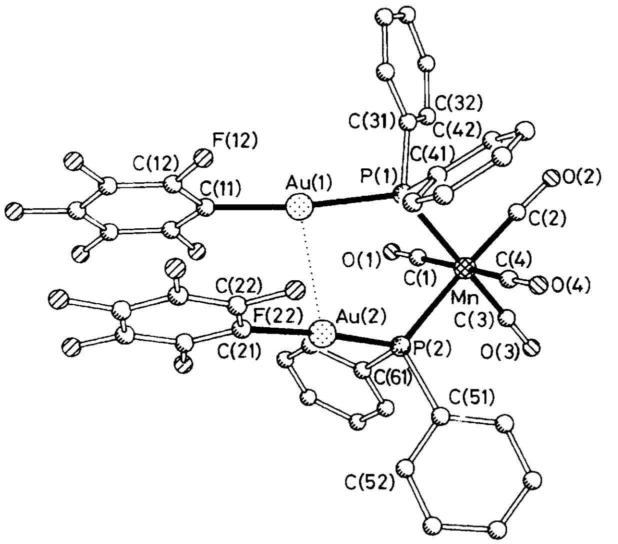

**Figure 1.** The cation of (**9**), showing the atom numbering scheme; H atoms omitted, radii arbitrary. Selected bond lengths (Å) and angles (°): Au(1)–P(1) 2.313(2), Au(1)–C(11) 2.063(6), Au(2)–P(2) 2.322(1), Au(2)–C(21) 2.073(5), Mn–P(1) 2.406(1), Mn–P(2) 2.404(1), Mn–C(1) 1.844(5), Mn–C(2) 1.809(8), Mn–C(3) 1.813(5), and Mn–C(4) 1.849(4); P(1)–Au(1)–C(11) 173.4(2), P(2)–Au(2)–C(21) 173.7(1), Au(1)–P(1)–Mn 121.9(1), and Au(2)–P(2)–Mn 122.1(1). Non-bonded contact: Au(1) ••• Au(2) 3.049(1)

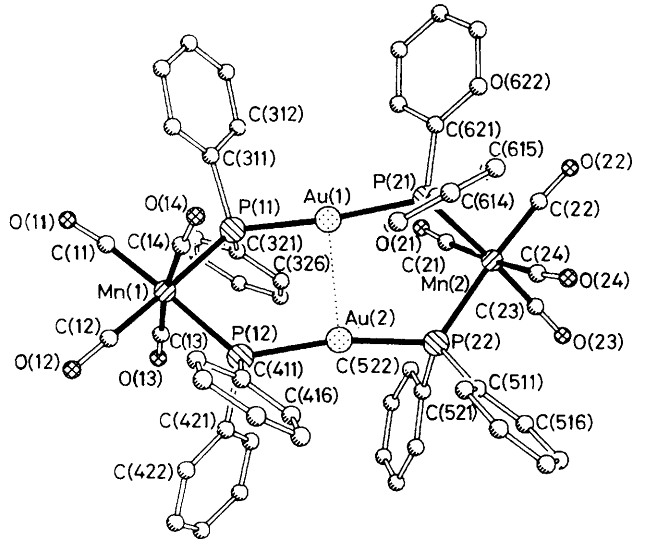

**Figure 2.** The molecule of (**11**) in the crystal, showing the atom numbering scheme; radii arbitrary, H atoms omitted. Selected bond lengths (Å) and angles (°): Au(1)–P(21) 2.341(3), Au(1)–P(11) 2.335(3), Au(2)–P(22) 2.338(3), Au(2)–P(12) 2.332(3), Mn(1)–P(11) 2.392(3), Mn(1)–P(12) 2.393(3), Mn(2)–P(21) 2.419(4), Mn(2)–P(22) 2.410(3), Mn(1)–C(11) 1.826(12), Mn(1)–C(12) 1.817(14), Mn(1)–C(13) 1.834(12), Mn(1)–C(14) 1.842(13), Mn(2)–C(21) 1.859(15), Mn(2)–C(22) 1.834(18), Mn(2)–C(23) 1.820(17), and Mn(2)–C(24) 1.864(13); P(11)–Au(1)–P(21) 173.8(1), P(21)–Au(2)–P(22) 168.3(1), Au(1)–P(11)–Mn(1) 120.9(1), Au(1)–P(21)–Mn(2) 113.8(2), Au(2)–P(12)–Mn(1) 121.3(1), and Au(2)–P(22)–Mn(2) 124.1(1). Non-bonded contact: Au(1) ••• Au(2) 2.855(1)

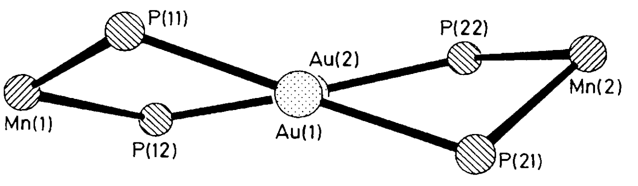

**Figure 3.** The eight-membered central ring of complex (**11**), viewed approximately along the Au ••• Au vector and showing the 'twist' conformation

to (**9**) could also be prepared from (**8**) and [AuCl(PR$_3$)] (2 equivalents) in the presence of Tl(acac) (2 equivalents). Our attempts to obtain crystals suitable for *X*-ray structure determination were unsuccessful; nevertheless, the $^{31}$P n.m.r. spectra indicated a possible Au ••• Au interaction, because the pattern of the multiplets was consistent with an AA′BB′ spin system with a finite coupling between the PPh$_3$ groups. The attempted crystallizations occasionally yielded crystals of [Au(PR$_3$)$_2$]ClO$_4$, but we found no clear evidence for symmetrization processes in solution; the gold phosphine complexes might have arisen during the syntheses. However, the reaction of (**8**) with [AuCl(tht)] (2 equivalents) in the presence of K(acac) (2 equivalents) gave a solution of the anionic tetracarbonyl complex [Mn(CO)$_4$(PPh$_2$AuCl)$_2$]$^-$, analogous to (**9**) [i.r. in CH$_2$Cl$_2$: 2 055s, 1 998(sh), 1 979vs, and 1 953s cm$^{-1}$], which was not isolated but was treated with 1 equivalent of (**8**) and two of Tl(acac) to give the very stable neutral complex [Au$_2$Mn$_2$(μ-PPh$_2$)$_4$(CO)$_8$] (**11**).

The crystal structure analysis of (**11**) (Figure 2) confirms the presence of the eight-membered ring. This feature generally promotes short Au ••• Au contacts,[5] and a particularly short contact of 2.855 Å is observed here. The Au–P bonds are slightly longer than in (**9**) (2.332—2.341 Å) and the deviation from linearity at Au(2) is marked [P–Au–P 168.3 and 173.8° for Au(2) and Au(1) respectively]. The ring displays a twisted conformation (Figure 3).

The above preparations could also be performed by deprotonating the PHPh$_2$ ligands with LiBu (at low temperature),[8] but the use of the acac derivatives was very convenient; the desired products could be obtained in one-pot reactions by using suitable proportions of the reagents. Thallium acetylacetonate had the additional advantage of eliminating Cl$^-$ ions.

## Experimental

All reactions were carried out under dry nitrogen, using Schlenk techniques and purified solvents. The i.r. spectra were recorded with a Perkin-Elmer 298 spectrophotometer. N.m.r. spectra were recorded on Varian FT-80A and Bruker AC-300 instruments: $^1$H in CDCl$_3$ relative to SiMe$_4$, proton-decoupled $^{31}$P in CH$_2$Cl$_2$ relative to external 85% H$_3$PO$_4$, and $^{19}$F in CH$_2$Cl$_2$ relative to external CFCl$_3$. The molar conductivities ($\Lambda$) were measured in 5 × $10^{-4}$ mol dm$^{-3}$ solution in acetone (not under N$_2$) and are quoted in $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

The starting materials [Mn(PHPh$_2$)(CO)$_5$]ClO$_4$,[1] *fac*-[Mn(PHPh$_2$)(CO)$_3$(bipy)]ClO$_4$ (or PF$_6$),[1] [Mn(PHPh$_2$)$_2$(CO)$_4$]ClO$_4$,[1] [AuCl(tht)],[9] and [Au(C$_6$F$_5$)(tht)][9] were prepared as described elsewhere. The salts M(acac) (M = K or Tl) were prepared from KOH or Tl$_2$CO$_3$.[10] The salt [N(PPh$_3$)$_2$][acac] was used directly as prepared by stirring a 1 : 1 molar mixture of Tl(acac) and [N(PPh$_3$)$_2$]Cl in CH$_2$Cl$_2$ overnight, filtering, and drying *in vacuo*.

[AuMn(μ-PPh$_2$)(CO)$_5$(C$_6$F$_5$)] (**2**).—To a vigorously stirred suspension of K(acac) (0.046 g, 0.333 mmol) in CH$_2$Cl$_2$ (15 cm$^3$) were added [Au(C$_6$F$_5$)(tht)] (0.15 g, 0.333 mmol) and [Mn(PHPh$_2$)(CO)$_5$]ClO$_4$ (0.16 g, 0.333 mmol). After 5 min, the volatiles were removed and the residue extracted with diethyl ether–hexane (1 : 1 4 × 20 cm$^3$). The extracts were filtered, concentrated *in vacuo* to *ca.* 6 cm$^3$, and cooled to give yellow microcrystalline (**2**) (0.13 g, 53%). I.r. (Nujol): 1 490s, 1 050w, and 952vs cm$^{-1}$ ($C_6F_5$). N.m.r.: $^{31}P$, 11.0 (vbr, μ-$PPh_2$); $^{19}F$, − 130.3 (m, 2 F), − 173.5 (m, 1F), and − 176.9 p.p.m. (m, 2 F) ($C_6F_5$). Λ = 5.7.

[AuMn(μ-$PPh_2$)(CO)$_3$(bipy)($C_6F_5$)] (**4**).—To a vigorously stirred suspension of K(acac) (0.057 g, 0.415 mmol) in $CH_2Cl_2$ (15 cm$^3$) were added [Au($C_6F_5$)(tht)] (0.188 g, 0.415 mmol) and *fac*-[Mn($PHPh_2$)(CO)$_3$(bipy)]$ClO_4$ (0.241 g, 0.415 mmol). After 60 min the volatiles were removed *in vacuo*. The residue was extracted (4 × 20 cm$^3$) with diethyl ether–hexane (1 : 1) and the extracts filtered and concentrated to *ca.* 5 cm$^3$ to give complex (**4**) as a solid that was recrystallized from hexane–diethyl ether as brown-yellow microcrystals (0.18 g, 51.3%). I.r. (Nujol): 1 490s, 1 050w, and 952w cm$^{-1}$ ($C_6F_5$). N.m.r.: $^{31}P$, 59.5 (μ-$PPh_2$); $^{19}F$, − 115 (m, 2F), − 161 (m, 1F), and − 163 p.p.m. (m, 2F) ($C_6F_5$). Λ = 9.6.

[AuMn(μ-$PPh_2$)(CO)$_3$(bipy){P($C_6H_4$Me-4)$_3$}]$PF_6$ (**5**).—To a solution of [Mn($PHPh_2$)(CO)$_3$(bipy)]$PF_6$ (0.222 g, 0.350 mmol) in acetone (20 cm$^3$) were added [AuCl{P($C_6H_4$Me-4)$_3$}] (0.190 g, 0.35 mmol) and Tl(acac) (0.108 g, 0.35 mmol). After 10 min the solution was filtered and concentrated *in vacuo* to *ca.* 4 cm$^3$. Addition of an excess of hexane gave brown-yellow microcrystals of complex (**5**) (0.33 g, 83%). I.r. (Nujol): 837s cm$^{-1}$ ($PF_6$). N.m.r.: $^1H$, 8.61, 8.22, 7.75, 7.19 (vbr, $C_6H_5$, $C_6H_4$, bipy), and 2.40 (s, Me-4). $^{31}P$ (− 60 °C), 53.8 p.p.m. [$AB_q$, $\delta_A$ = 42.6 (μ-$PPh_2$), $\delta_B$ = 65.1 ($PR_3$), $J_{AB}$ = 249]; some samples

**Table 2.** Atomic co-ordinates ( × 10$^4$) for compound (**9**)

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Au(1) | 2 556.7(1) | 2 013.9(1) | 2 828.2(1) |
| Au(2) | 3 835.5(1) | 3 101.4(1) | 1 746.2(1) |
| C(11) | 2 459(3) | 2 620(3) | 3 673(3) |
| C(12) | 1 728(4) | 3 453(4) | 3 614(3) |
| C(13) | 1 663(4) | 3 904(4) | 4 148(4) |
| C(14) | 2 328(5) | 3 515(5) | 4 771(3) |
| C(15) | 3 063(4) | 2 681(5) | 4 863(3) |
| C(16) | 3 115(3) | 2 257(4) | 4 314(3) |
| F(12) | 1 040(2) | 3 879(2) | 3 000(2) |
| F(13) | 927(3) | 4 718(3) | 4 061(2) |
| F(14) | 2 251(3) | 3 945(3) | 5 303(2) |
| F(15) | 3 726(3) | 2 292(3) | 5 485(2) |
| F(16) | 3 863(2) | 1 437(3) | 4 439(2) |
| C(21) | 3 240(3) | 4 294(3) | 2 062(3) |
| C(22) | 2 434(3) | 5 058(4) | 1 701(3) |
| C(23) | 1 999(4) | 5 767(4) | 1 984(4) |
| C(24) | 2 382(5) | 5 743(4) | 2 657(4) |
| C(25) | 3 193(5) | 5 008(5) | 3 050(3) |
| C(26) | 3 603(3) | 4 304(4) | 2 742(3) |
| F(22) | 2 021(2) | 5 133(2) | 1 014(2) |
| F(23) | 1 194(3) | 6 494(3) | 1 600(3) |
| F(24) | 1 954(3) | 6 431(3) | 2 958(3) |
| F(25) | 3 559(3) | 4 962(3) | 3 728(2) |
| F(26) | 4 394(2) | 3 582(2) | 3 163(2) |
| P(1) | 2 497(1) | 1 315(1) | 1 920(1) |
| P(2) | 4 654(1) | 1 735(1) | 1 471(1) |
| C(31) | 1 815(3) | 458(3) | 2 431(3) |
| C(32) | 2 185(4) | − 564(3) | 2 716(3) |
| C(33) | 1 624(5) | − 1 151(4) | 3 125(4) |
| C(34) | 720(5) | − 753(5) | 3 255(4) |
| C(35) | 358(4) | 263(5) | 3 004(4) |
| C(36) | 905(4) | 861(4) | 2 589(3) |
| C(41) | 1 651(3) | 2 241(3) | 1 070(3) |
| C(42) | 1 153(3) | 1 974(4) | 618(3) |
| C(43) | 603(4) | 2 670(5) | − 71(3) |
| C(44) | 535(4) | 3 643(5) | − 321(3) |
| C(45) | 1 027(3) | 3 931(4) | 118(3) |
| C(46) | 1 578(3) | 3 230(3) | 813(3) |
| C(51) | 5 349(3) | 2 193(3) | 622(3) |
| C(52) | 5 893(3) | 2 758(4) | 681(3) |
| C(53) | 6 446(4) | 3 132(5) | 75(4) |
| C(54) | 6 439(5) | 2 948(6) | − 613(4) |
| C(55) | 5 921(4) | 2 410(4) | − 693(3) |
| C(56) | 5 385(4) | 2 022(4) | − 80(3) |
| C(61) | 5 601(3) | 1 023(3) | 2 283(3) |
| C(62) | 5 398(4) | 937(4) | 3 065(3) |
| C(63) | 6 078(6) | 372(5) | 3 692(4) |
| C(64) | 6 964(7) | − 98(6) | 3 565(5) |
| C(65) | 7 182(5) | − 40(5) | 2 812(5) |
| C(66) | 6 488(4) | 523(4) | 2 162(4) |
| Mn | 3 892.8(5) | 621.7(5) | 1 359.6(4) |
| C(1) | 4 324(4) | − 236(4) | 2 409(3) |
| O(1) | 4 606(3) | − 782(3) | 3 047(2) |
| C(2) | 3 274(4) | − 124(4) | 1 175(4) |
| O(2) | 2 883(4) | − 563(4) | 1 011(3) |
| C(3) | 4 971(4) | − 7(4) | 1 031(3) |
| O(3) | 5 650(3) | − 452(3) | 860(2) |
| C(4) | 3 410(3) | 1 583(4) | 349(3) |
| O(4) | 3 105(3) | 2 152(3) | − 274(2) |
| P(3) | 8 049(1) | 3 125(1) | 3 860(1) |
| P(4) | 6 905(1) | 5 236(1) | 3 010(1) |
| N | 7 379(3) | 4 198(3) | 3 713(2) |
| C(71) | 9 107(3) | 2 856(3) | 4 463(3) |
| C(72) | 9 939(3) | 2 142(4) | 4 475(3) |
| C(73) | 10 701(4) | 1 916(5) | 4 992(3) |
| C(74) | 10 640(4) | 2 386(5) | 5 494(3) |
| C(75) | 9 838(5) | 3 107(4) | 5 476(3) |
| C(76) | 9 056(4) | 3 339(4) | 4 963(3) |
| C(81) | 7 479(3) | 2 229(3) | 4 430(3) |
| C(82) | 7 991(4) | 1 263(4) | 4 900(3) |
| C(83) | 7 523(6) | 589(5) | 5 341(3) |
| C(84) | 6 570(6) | 871(6) | 5 315(4) |
| C(85) | 6 050(5) | 1 832(6) | 4 838(5) |
| C(86) | 6 505(4) | 2 498(4) | 4 410(3) |
| C(91) | 8 386(3) | 2 944(3) | 2 954(3) |
| C(92) | 7 912(4) | 2 503(4) | 2 644(3) |
| C(93) | 8 075(5) | 2 481(6) | 1 897(4) |
| C(94) | 8 708(5) | 2 903(6) | 1 447(4) |
| C(95) | 9 185(4) | 3 343(5) | 1 731(3) |
| C(96) | 9 034(3) | 3 372(4) | 2 493(3) |
| C(101) | 6 595(3) | 5 194(3) | 2 083(3) |
| C(102) | 7 015(3) | 5 574(3) | 1 382(3) |
| C(103) | 6 718(4) | 5 566(4) | 672(3) |
| C(104) | 6 012(4) | 5 183(4) | 655(3) |
| C(105) | 5 597(4) | 4 782(4) | 1 349(3) |
| C(106) | 5 896(3) | 4 781(4) | 2 066(3) |
| C(111) | 5 830(3) | 5 834(3) | 3 344(3) |
| C(112) | 5 802(4) | 5 715(4) | 4 132(3) |
| C(113) | 4 987(4) | 6 218(5) | 4 391(3) |
| C(114) | 4 228(4) | 6 839(4) | 3 858(4) |
| C(115) | 4 253(4) | 6 950(4) | 3 074(4) |
| C(116) | 5 046(4) | 6 462(4) | 2 804(3) |
| C(121) | 7 624(3) | 6 039(4) | 2 781(3) |
| C(122) | 8 588(4) | 5 667(5) | 2 972(3) |
| C(123) | 9 137(5) | 6 295(6) | 2 749(4) |
| C(124) | 8 718(6) | 7 285(6) | 2 358(5) |
| C(125) | 7 779(6) | 7 663(5) | 2 174(5) |
| C(126) | 7 224(5) | 7 042(4) | 2 384(4) |
| O(200) | 318(16) | 9(19) | 9 805(14) |
| C(201) | 628(16) | − 170(17) | 9 066(13) |
| C(202) | − 196(16) | 806(17) | 8 691(14) |
| C(203) | 1 510(16) | − 83(16) | 9 415(14) |
| C(204) | 1 212(20) | − 1 142(18) | 9 732(16) |

showed a weak peak at 42.0 p.p.m. due to $[Au\{P(C_6H_4Me\text{-}4)_3\}_2]PF_6$. Λ = 132.5.

$[AuMn_2(\mu\text{-}PPh_2)_2(CO)_{10}]ClO_4$ (**6**).—To a mixture of $[Mn(PHPh_2)(CO)_5]ClO_4$ (0.299 g, 0.622 mmol) and [AuCl(tht)] (0.099 g, 0.308 mmol) in acetone (15 $cm^3$) was added with stirring Tl(acac) (0.189 g, 0.622 mmol). After 5 min the mixture was filtered and the filtrate was concentrated *in vacuo* to *ca.* 4 $cm^3$. Addition of an excess of diethyl ether gave complex (**6**) as a white precipitate that was washed with ether and dried *in vacuo* (0.162 g, 49.3%). I.r. (Nujol): 1 100s, br $cm^{-1}$ ($ClO_4$). $^{31}P$ N.m.r. (−40 °C): 20.9 p.p.m. (s, $\mu$-$PPh_2$). Λ = 139.7.

$[AuMn_2(\mu\text{-}PPh_2)_2(CO)_6(bipy)_2]ClO_4$ (**7**).—To a mixture of *fac*-$[Mn(PHPh_2)(CO)_3(bipy)]ClO_4$ (0.182 g, 0.313 mmol) and [AuCl(tht)] (0.050 g, 0.155 mmol) in acetone (15 $cm^3$) was added Tl(acac) (0.095 g, 0.313 mmol). After 40 min (although the reaction was completed almost instantly), the mixture was filtered, concentrated to *ca.* 4 $cm^3$, and mixed with an excess of diethyl ether to give complex (**7**) as a orange-brown solid (0.15 g, 76%). I.r. (Nujol): 1 100 $cm^{-1}$ ($ClO_4$). $^{31}P$ N.m.r.: 58.9 p.p.m. ($\mu$-$PPh_2$). Λ = 143.

$[N(PPh_3)_2][Au_2Mn(\mu\text{-}PPh_2)_2(CO)_4(C_6F_5)_2]$ (**9**).—To a solid mixture of $[Au(C_6F_5)(tht)]$(0.15 g, 0.33 mmol), K(acac) (0.023 g, 0.166 mmol), and $[N(PPh_3)_2][acac]$ (0.11 g, 0.17 mmol), were added $CH_2Cl_2$ (20 $cm^3$) and $[Mn(PHPh_2)_2(CO)_4]ClO_4$ (0.105 g, 0.164 mmol) with stirring. After 15 min, the mixture was filtered and concentrated to *ca.* 4 $cm^3$. Addition of an excess of hexane gave complex (**9**) as a precipitate that was recrystallized from $CH_2Cl_2$–hexane as yellow microcrystals (0.153 g, 52%). I.r. (Nujol): 1 490m, 1 050m, and 952s $cm^{-1}$ ($C_6F_5$). N.m.r.: $^{31}P$ (−60 °C), 32.6 (br, $\mu$-$PPh_2$) and 21.8 [s, $N(PPh_3)_2{}^+$]; $^{19}F$, −115.7 (m, 2F), −163.7 (m, 1F), and −164.9 p.p.m. (m, 2F) ($C_6F_5$). Λ = 91.

$[Au_2Mn(\mu\text{-}PPh_2)_2(CO)_4\{P(C_6H_4Me\text{-}4)_3\}_2]ClO_4$ (**10a**).—To a solution of $[Mn(PHPh_2)_2(CO)_4]ClO_4$ (0.20 g, 0.31 mmol) in acetone (15 $cm^3$) was added $[AuCl\{P(C_6H_4Me\text{-}4)_3\}]$ (0.33 g, 0.61 mmol) and Tl(acac) (0.19 g, 0.62 mmol). After 15 min the solution was filtered and concentrated to *ca.* 4 $cm^3$. Addition of an excess of hexane gave (**10a**) as pale yellow microcrystals (0.40 g, 78%). I.r. (Nujol): 820 $\{P(C_6H_4Me\text{-}4)_3\}$ and 1 100 $cm^{-1}$ ($ClO_4$). N.m.r.: $^1H$ 7.65, 6.99(br) ($C_6H_4$, $C_6H_5$), and 2.36 (s, Me-4); $^{31}P$ (−90 °C) AA′BB′ m (the part B was very broad and unresolved), $\delta_A$ 40 ($PR_3$), $\delta_B$ = 56 p.p.m. ($\mu$-$PPh_2$), $J_{AB}$ 260, $J_{AA'}$ 5, $J_{BB'}$ 85, and $J_{AB'}$ 0 Hz (linewidth *ca.* 15 Hz). Λ = 143.

The pale yellow compound (**10b**) was similarly prepared in 45% yield. I.r. (Nujol): 1 100 $cm^{-1}$ ($ClO_4$). $^{31}P$ N.m.r. (−80 °C): AA′BB′ m (the part B was very broad and unresolved), $\delta_A$ 42 ($PR_3$), $\delta_B$ 57 p.p.m. ($\mu$-$PPh_2$), $J_{AB}$ 255, $J_{AA'}$ 5, $J_{BB'}$ 70, and $J_{AB'}$ 0 (linewidth *ca.* 15 Hz). Λ = 124.

$[Au_2Mn_2(\mu\text{-}PPh_2)_4(CO)_8]$ (**11**).—A mixture of $[Mn(PHPh_2)_2(CO)_4]ClO_4$ (0.087 g, 0.136 mmol), [AuCl(tht)] (0.087 g, 0.272 mmol), and K(acac) (0.038 g, 0.272 mmol) in $CH_2Cl_2$ (15 $cm^3$) was vigorously stirred for 10 min. More $[Mn(PHPh_2)_2(CO)_4]ClO_4$ (0.087 g, 0.136 mmol) and Tl(acac)

**Table 3.** Atomic co-ordinates ( × $10^4$) for compound (**11**)

| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| Au(1) | 2 173.3(2) | 1 393.4(4) | 974.8(1) | C(516) | 2 021(8) | 5 361(12) | 2 741(5) |
| Au(2) | 2 968.2(2) | 3 373.0(4) | 1 501.7(1) | C(521) | 1 905(7) | 5 571(11) | 1 527(4) |
| Mn(1) | 4 133(1) | 1 906(2) | 485.0(6) | C(522) | 1 449(8) | 5 748(13) | 1 061(5) |
| Mn(2) | 813(1) | 2 966(2) | 1 769.7(6) | C(523) | 1 509(9) | 6 806(15) | 785(6) |
| P(11) | 2 834(2) | 1 523(3) | 319(1) | C(524) | 2 020(8) | 7 675(15) | 975(5) |
| C(311) | 2 539(6) | 99(9) | −29(3) | C(525) | 2 456(9) | 7 578(17) | 1 444(6) |
| C(312) | 1 801(7) | 26(12) | −267(4) | C(526) | 2 385(8) | 6 469(13) | 1 709(5) |
| C(313) | 1 529(8) | −1 048(13) | −507(5) | P(12) | 4 079(2) | 3 071(3) | 1 225(1) |
| C(314) | 1 992(7) | −2 037(13) | −495(4) | C(411) | 4 729(6) | 2 606(10) | 1 799(3) |
| C(315) | 2 701(7) | −1 992(12) | −261(4) | C(412) | 5 261(7) | 1 702(11) | 1 817(4) |
| C(316) | 2 983(7) | −910(11) | −27(4) | C(413) | 5 701(8) | 1 433(13) | 2 276(5) |
| C(321) | 2 362(6) | 2 666(11) | −125(4) | C(414) | 5 602(8) | 1 999(14) | 2 707(5) |
| C(322) | 2 408(7) | 2 610(13) | −628(4) | C(415) | 5 103(8) | 2 904(14) | 2 700(5) |
| C(323) | 2 098(9) | 3 510(14) | −963(6) | C(416) | 4 665(7) | 3 181(12) | 2 243(4) |
| C(324) | 1 729(9) | 4 436(16) | −793(6) | C(421) | 4 416(6) | 4 629(10) | 1 143(3) |
| C(325) | 1 677(10) | 4 508(17) | −291(6) | C(422) | 5 162(7) | 4 897(12) | 1 233(4) |
| C(326) | 1 989(7) | 3 631(12) | 47(5) | C(423) | 5 409(9) | 6 084(13) | 1 160(5) |
| P(21) | 1 421(2) | 1 126(3) | 1 576(1) | C(424) | 4 915(8) | 6 941(14) | 976(5) |
| C(611) | 1 975(7) | 385(12) | 2 126(4) | C(425) | 4 168(8) | 6 718(13) | 886(5) |
| C(612) | 2 734(8) | 408(14) | 2 185(5) | C(426) | 3 925(7) | 5 530(11) | 960(4) |
| C(613) | 3 170(11) | −200(17) | 2 586(6) | C(11) | 4 211(6) | 1 056(11) | −83(4) |
| C(614) | 2 854(11) | −779(17) | 2 935(6) | O(11) | 4 307(5) | 601(8) | −442(3) |
| C(615) | 2 129(11) | −764(17) | 2 895(6) | C(12) | 5 121(7) | 2 180(12) | 595(4) |
| C(616) | 1 665(11) | −173(16) | 2 494(6) | O(12) | 5 748(5) | 2 365(10) | 659(4) |
| C(621) | 734(7) | −16(11) | 1 300(4) | C(13) | 3 990(7) | 3 339(11) | 134(4) |
| C(622) | 358(14) | −771(24) | 1 574(9) | O(13) | 3 891(6) | 4 202(8) | −94(3) |
| C(623) | −140(15) | −1 644(24) | 1 299(10) | C(14) | 4 171(7) | 545(12) | 886(4) |
| C(624) | −255(10) | −1 781(17) | 815(7) | O(14) | 4 158(6) | −256(8) | 1 143(3) |
| C(625) | 127(10) | −1 092(16) | 557(7) | C(21) | 559(8) | 3 114(14) | 1 074(6) |
| C(626) | 604(8) | −204(13) | 805(5) | O(21) | 374(6) | 3 131(10) | 655(3) |
| P(22) | 1 957(2) | 4 065(3) | 1 831(1) | C(22) | −61(10) | 2 175(16) | 1 772(6) |
| C(511) | 2 322(6) | 4 416(10) | 2 497(4) | O(22) | −615(7) | 1 742(17) | 1 788(5) |
| C(512) | 2 871(7) | 3 751(11) | 2 769(4) | C(23) | 378(9) | 4 402(15) | 1 878(5) |
| C(513) | 3 148(7) | 4 024(12) | 3 277(5) | O(23) | 128(7) | 5 305(13) | 1 969(5) |
| C(514) | 2 863(8) | 4 933(12) | 3 508(5) | C(24) | 1 104(8) | 2 635(13) | 2 454(5) |
| C(515) | 2 295(8) | 5 579(14) | 3 251(5) | O(24) | 1 239(6) | 2 388(11) | 2 865(3) |

(0.0826 g, 0.272 mmol) were added and stirring was continued for 90 min. The mixture was filtered and concentrated to *ca.* 4 $cm^3$. Addition of an excess of hexane gave yellow microcrystals of complex (**11**) (0.102 g, 51.0%). $^{31}P$ N.m.r. (−50 °C): 28.2 p.p.m. (μ-$PPh_2$). Λ = 4.8.

X-*Ray Structure Determination of Complex* (**9**).—Pale yellow prisms were obtained by diffusion of di-isopropyl ether into a dichloromethane solution. The crystals cracked on exposure to air and were therefore sealed in glass capillaries for *X*-ray investigations. They proved to contain half an ether molecule per asymmetric unit.

*Crystal data.* $C_{36}H_{30}NP_2^+$ $C_{40}H_{20}Au_2F_{10}MnO_4P_2^-\cdot 0.5C_6H_{14}O$, $M$ = 1 855, triclinic, space group $P\bar{1}$, $a$ = 14.900(4), $b$ = 15.462(4), $c$ = 18.110(5) Å, $\alpha$ = 66.87(2), $\beta$ = 87.18(2), $\gamma$ = 72.23(2)°, $U$ = 3 641.6 $Å^3$, $Z$ = 2, $D_c$ = 1.69 Mg $m^{-3}$, $F(000)$ = 1 814, $\lambda(Mo\text{-}K_\alpha)$ = 0.710 69 Å, $\mu$ = 4.3 $mm^{-1}$, crystal size 0.8 × 0.3 × 0.15 mm.

*Data collection and processing.* Stoe-Siemens four-circle diffractometer in profile-fitting mode[11] with monochromated Mo-$K_\alpha$ radiation. 13 710 Intensities registered to $2\theta_{max.}$ 50°, 12 799 unique ($R_{int}$ 0.023), 10 566 with $F > 4\sigma(F)$ used for all calculations (program system SHELX, locally modified by its author Professor G. M. Sheldrick). Absorption corrections based on ψ scans, with transmission factors 0.58—0.96. Cell constants refined from 2θ values of 40 reflections in the range 20—22°.

*Structure solution and refinement.* Heavy-atom method, followed by blocked full-matrix refinement on $F$ to $R$ 0.032, $R'$ 0.031. All non-H atoms anisotropic except for disordered solvent; H atoms included using a riding model. Weighting scheme $w^{-1} = \sigma^2(F) + 0.0002F^2$. 904 Parameters; $S$ 1.4; maximum $\Delta/\sigma$ 0.17 for solvent, otherwise 0.07; maximum $\Delta\rho$ 1 e $Å^{-3}$ in solvent region, 0.6 e $Å^{-3}$ near Au.

Final atomic co-ordinates are presented in Table 2, with selected bond lengths and angles in Figure 1.

X-*Ray Structure Determination of Complex* (**11**).—Yellow plates were obtained by diffusion of hexane into a dichloromethane solution.

*Crystal data.* $C_{56}H_{40}Au_2Mn_2O_8P$, $M$ = 1 469, monoclinic, space group $P2_1/c$, $a$ = 18.448(4), $b$ = 11.004(2), $c$ = 27.024(5) Å, $\beta$ = 100.67(2)°, $U$ = 5 391 $Å^3$, $Z$ = 4, $D_c$ = 1.81 Mg $m^{-3}$, $F(000)$ = 2 832, $\mu$ = 6.0 $mm^{-1}$, crystal size 0.6 × 0.25 × 0.1 mm, plate face 201.

*Data collection and processing.* As for complex (**9**) but with the following differences: 10 141 reflections measured, 9 416 unique ($R_{int}$ 0.044), 7 199 with $F > 4\sigma(F)$ used for calculations. Transmission factors 0.39—0.99. Cell constants from 64 reflections in the range 20—25°.

*Structure solution and refinement.* Heavy-atom method, followed by full-matrix refinement on $F$ to $R$ 0.059, $R'$ 0.055. Atoms Au, Mn, O, and P anisotropic, C isotropic, H included using a riding model. Weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,35F^2$; 369 parameters; $S$ 1.8; maximum $\Delta/\sigma$ 0.002; maximum $\Delta\rho$ 1.5 e $Å^{-3}$ near Au.

Final atomic co-ordinates are presented in Table 3, with selected bond lengths and angles in Figure 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

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