σ-Alkynyl Complexes of Manganese(I) as η^2-Bonding Ligands for Group 1B Metal–Ligand Fragments. *X*-Ray Crystal Structure of $[Mn_2Cu(\mu\text{-}CCBu^t)_2(CO)_6(dppe)_2]PF_6\cdot0.5CH_2Cl_2$†

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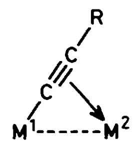
Several compounds of the types $[MnML(\mu\text{-}C{\equiv}CR)(CO)_3(dppe)]^{n+}$ {ML = CuCl (*n* = 0), $Au(C_6F_5)$ (*n* = 0), or $M[P(C_6H_4Me\text{-}2)_3]$ (*n* = 1; M = Cu, Ag, or Au); R = CH_2OMe, Bu^t, or Ph; dppe = $Ph_2PCH_2CH_2PPh_2$} and $[Mn_2M(\mu\text{-}C{\equiv}CR)_2(CO)_6(dppe)_2]^+$ have been prepared from the alkynyl complexes *fac*-$[Mn(CCR)(CO)_3(dppe)]$ and the appropriate reagents to generate the metal–ligand fragments ML. The salt $[Mn_2Cu(\mu\text{-}C{\equiv}CBu^t)_2(CO)_6(dppe)_2]PF_6\cdot0.5CH_2Cl_2$ has been characterized by *X*-ray diffraction. Several equilibria in solution involving the cationic species with free σ-alkynyl complex and $P(C_6H_4Me\text{-}2)_3$ have been observed and their reactions with Cl^- have been examined.

Owing to their similarity with acetylenes ($R^1C{\equiv}CR^2$), σ-alkynyl complexes of the type $[L_nM{-}C{\equiv}CR]$ can be expected to behave as π-bonding ligands by η^2-co-ordination and a number of compounds are known having C_2R groups bridging metal–ligand fragments in various ways.[1] In the case of the Group 1B transition metals, however, only a few monomeric species with $\mu\text{-}\eta^2$ bridges, either symmetrical or unsymmetrical (see below), have been reported and none of the known examples is cationic.

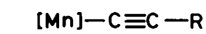


Therefore we considered it of interest to explore the ability of manganese acetylides of the type *fac*-$[Mn(CCR)(CO)_3(dppe)]$ [dppe = 1,2-bis(diphenylphosphino)ethane][2] to co-ordinate to different neutral or cationic Group 1B metal–ligand fragments that could be generated by displacement of a weakly co-ordinated ligand from a convenient precursor. A preliminary account of this work has been published.[3]

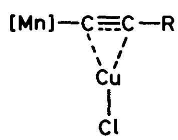
Results and Discussion

Reaction of the complexes *fac*-$[Mn(CCR)(CO)_3(dppe)]$ [R = CH_2OMe (**1a**), Bu^t (**1b**),[2] or Ph (**1c**)[2]] with a suspension of CuCl in CH_2Cl_2 afforded the compounds $[MnCuCl(\mu\text{-}CCR)(CO)_3(dppe)]$ (**2a**)—(**2c**) characterized by the data in Tables 1 and 2. The ν(CO) frequencies are higher than those of the starting σ-alkynyls and, more significantly, the ν(C≡C) frequency appears *ca.* 120 cm^{-1} lower, evidencing the side-on π-co-ordination of the C≡CR group.[1] This decrease is similar to that observed upon co-ordination of alk-1-ynes to copper (81—173 cm^{-1})[4] and also in the formation of many acetylene complexes.[5] An *X*-ray diffraction study, carried out on complex (**2c**),[6] revealed that, as found for $[RuCuCl(\mu\text{-}CCR)(C_5H_5)(PPh_3)_2]$[7] it is monomeric in the solid state and has a $\mu\text{-}\eta^2$-alkynyl bridge, with a symmetrical side-on π bond to copper and non-bonding Mn–Cu distances.

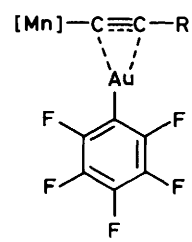
Attempts to prepare silver and gold analogues of (**2**) were unsuccessful. Thus, while no reaction occurred between (**1**) and AgCl in CH_2Cl_2, the σ-alkynyls reacted almost instantly with [AuCl(tht)] (tht = tetrahydrothiophene)[8] giving *fac*-[MnCl-



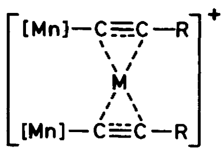
(**1a**) R = CH_2OMe
(**1b**) R = Bu^t
(**1c**) R = Ph



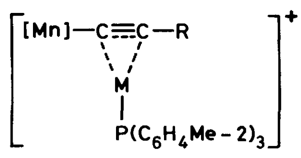
(**2a**) R = CH_2OMe
(**2b**) R = Bu^t
(**2c**) R = Ph



(**3a**) R = CH_2OMe
(**3b**) R = Bu^t



	M	R
(**4a**)	Cu	CH_2OMe
(**4b**)	Cu	Bu^t
(**5**)	Ag	Bu^t
(**6**)	Au	Bu^t



	M	R
(**7**)	Cu	Bu^t
(**8**)	Ag	Bu^t
(**9a**)	Au	Bu^t

[Mn] = $Mn(CO)_3(dppe)$

† 2,3-Bis[1′,2′-bis(diphenylphosphino)ethane]-2,2,2,3,3,3-hexacarbonyl-1,2; 1,3-di-μ-[η^2-t-butylethynyl-$C^{1'}$(Cu), $C^{1',2'}$(Mn)]-copperdimanganese hexafluorophosphate–dichloromethane (1/0.5).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

$(CO)_3(dppe)]$ {characterized by its ν(CO) absorptions in the i.r. spectrum} and probably the species $[\{Au(CCR)\}_n]$ (see refs. in part E of ref. 1) or [Au(CCR)(tht)] instead of the desired products. It is possible, however, that the latter reaction gives first the transient species $[MnAuCl(\mu\text{-}CCR)(CO)_3(dppe)]$ analogous to (**2**), then an intramolecular migration of the Cl from Au to the Mn atom gives the observed products. On the other hand the reaction of the σ-alkynyls (**1a**) and (**1b**) with $[Au(C_6F_5)(tht)]$[8] gave the stable compounds $[MnAu(C_6F_5)(\mu\text{-}CCR)(CO)_3(dppe)]$ (**3a**, R = CH_2OMe) and (**3b**, R = Bu^t) in which presumably the manganese alkynyl co-ordinates the $Au(C_6F_5)$ fragment in a side-on fashion. Thus, the ν(CO)

Table 1. Melting points, analytical, and i.r. data for the compounds

	Compound	M.p.[a] (°C)	Analysis[b] (%) C	H	I.r. (cm^{-1})[c] ν(C≡C)	ν(CO)[d]		
(**1a**)	$[Mn(CCCH_2OMe)(CO)_3(dppe)]$	124	65.4 (65.4)	4.90 (4.80)	2 109w	2 014	1 942	1 917
(**2a**)	$[MnCuCl(\mu\text{-}CCCH_2OMe)(CO)_3(dppe)]\cdot 0.5CH_2Cl_2$	135	54.0 (53.8)	4.20 (4.05)	1 980w	2 029	1 952	1 940
(**2b**)	$[MnCuCl(\mu\text{-}CCBu^t)(CO)_3(dppe)]$	185	58.0 (58.6)	4.85 (4.60)	1 983w	2 025	1 947	1 940
(**2c**)	$[MnCuCl(\mu\text{-}CCPh)(CO)_3(dppe)]$	182	60.3 (60.3)	3.90 (3.95)	1 989w	2 026	1 950	1 939
(**3a**)	$[MnAu(C_6F_5)(\mu\text{-}CCCH_2OMe)(CO)_3(dppe)]$[e]	142	48.9 (48.3)	3.15 (3.00)	*f*	2 026	1 955	1 940
(**3b**)	$[MnAu(C_6F_5)(\mu\text{-}CCBu^t)(CO)_3(dppe)]$[e]	93	49.9 (50.1)	3.65 (3.40)	*f*	2 023	1 952	1 935
(**4a**)	$[Mn_2Cu(\mu\text{-}CCCH_2OMe)_2(CO)_6(dppe)_2][PF_6]$[g]	185	55.0 (55.8)	4.20 (4.10)	1 992w	2 034	1 942br	
(**4b**)	$[Mn_2Cu(\mu\text{-}CCBu^t)_2(CO)_6(dppe)_2][PF_6]$	182	57.8 (58.2)	4.60 (4.60)	1 972w	2 029	1 947 (sh)	1 937
(**5**)	$[Mn_2Ag(\mu\text{-}CCBu^t)_2(CO)_6(dppe)_2][BF_4]$	165	57.9 (58.7)	4.75 (4.65)	1 996w	2 029	1 947 (sh)	1 935
(**6**)	$[Mn_2Au(\mu\text{-}CCBu^t)_2(CO)_6(dppe)_2][PF_6]$	184	52.7 (53.2)	4.40 (4.20)	*f*	2 024	1 952 (sh)	1 937
(**7**)	$[MnCu(\mu\text{-}CCBu^t)(CO)_3(dppe)\{P(C_6H_4Me\text{-}2)_3\}][PF_6]$[h]	157	58.5 (59.4)	4.90 (4.80)	2 000w	2 029	1 947	1 932
(**9a**)	$[MnAu(\mu\text{-}CCBu^t)(CO)_3(dppe)\{P(C_6H_4Me\text{-}2)_3\}][PF_6]$	150	54.0 (53.2)	4.30 (4.30)	*f*	2 026	1 942br	
(**9b**)	$[MnAu(\mu\text{-}CCPh)(CO)_3(dppe)(PPh_3)][PF_6]$	182	52.1 (53.2)	3.50 (3.55)	1 982w[i]	2 032	1 950br	

[a] Melts with decomposition. [b] Calculated values given in parentheses. [c] Measured in CH_2Cl_2 unless otherwise stated. Data for (**8**): 2 000m [ν(C≡C)], 2 029s, 1 940s br cm^{-1} [ν(CO)]. [d] All strong. [e] C_6F_5 absorptions (Nujol mull) at 1 500s, 1 060m, 954m, and 812m cm^{-1} (D. A. Long and D. Steele, *Spectrochim. Acta*, 1963, **19**, 1955; G. B. Deacon and J. H. S. Green, *ibid.*, 1968, **24**, 1125). [f] Obscured by the ν(CO) absorptions. [g] All the salts showed conductivities (5 × 10^{-4} mol dm^{-3} in acetone) in the range 110—140 Ω^{-1} cm^2 mol^{-1} as expected for 1:1 electrolytes (W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81). [h] Sample contaminated with some $[Cu\{P(C_6H_4Me\text{-}2)_3\}_x]PF_6$. [i] In Nujol mull.

Table 2. N.m.r. data for the compounds

Compound	$^{31}P\text{-}\{^1H\}$[a] dppe	$P(C_6H_4Me\text{-}2)_3$[c]	^1H N.m.r.[b] CH_3O–	–OCH_2–	Bu^t	–C_2H_4–	Ph, C_6H_4	C_6H_4Me-2[c]
(**1a**)	77.2		2.85	3.51		3.1	7.25	
(**1b**)[d]	78.1				0.71	2.84	7.32, 7.90	
(**2a**)[e]	75.3		2.82	3.22		*f*	7.42	
(**2b**)	75.8				0.59	3.06, 2.84	7.39, 7.79	
(**3a**)[g]	76.6		2.88	3.28		*f*	7.59	
(**3b**)[g]	77.7				0.67	2.96	7.35	
(**4a**)	74.0		2.60	3.00		*f*	7.29	
(**4b**)	73.8				0.43	3.04	7.36	
(**5**)	74.8				0.47	3.00, 3.20	7.84, 7.00	
(**6**)	76.0				0.45	2.95, 3.15	7.39	
(**7**)	72.3	−8.6			0.18	3.28, 3.06	7.41	2.49
(**8**)	73.0	−11.4[h]			0.29	3.24, 3.01	7.39	2.52
(**9a**)	74.3	21.2			0.28	2.96, 3.18	7.36	2.62
(**9b**)	78.5	37.0[i]						

[a] Measured in $CDCl_3$; values in p.p.m. relative to external 85% H_3PO_4. The PF_6 salts exhibit a heptet centred at −143 p.p.m. with $^1J(PF)$ = 711 Hz. [b] Measured in $CDCl_3$; values in p.p.m. relative to $SiMe_4$. [c] For the free $P(C_6H_4Me\text{-}2)_3$ ligand: $\delta(^1H)$ 2.43, $\delta(^{31}P)$ −29.9 p.p.m. [d] Data from ref. 2. [e] CH_2Cl_2 signal at 5.22 p.p.m. [f] Broad absorption overlapped with the CH_2OMe signals. [g] ^{19}F N.m.r. (in $CDCl_3$, relative to external $CFCl_3$): three complex multiplets centred at −116 (2 F), −160 (1 F), and −163.8 p.p.m. (2 F). [h] Doublet doublet, $^1J(^{107}Ag-^{31}P)$ = 583, $^1J(^{109}Ag-^{31}P)$ = 673.7 Hz. [i] For PPh_3.

Table 3. Selected bond lengths (Å) and angles (°) for compound **(4b)***

C(101)–Cu	2.078(13)	C(102)–C(101)	1.244(18)	Mn(1)–C(101)	2.032(12)	C(12)–Mn(1)	1.808(11)
C(102)–Cu	2.078(12)	C(202)–C(201)	1.230(16)	Mn(2)–C(201)	2.026(11)	C(13)–Mn(1)	1.830(14)
C(201)–Cu	2.086(11)	C(103)–C(102)	1.502(19)	P(11)–Mn(1)	2.332(4)	O(11)–C(11)	1.184(19)
C(202)–Cu	2.080(14)	C(203)–C(202)	1.497(17)	P(12)–Mn(1)	2.335(3)	O(12)–C(12)	1.150(14)
				C(11)–Mn(1)	1.765(15)	O(13)–C(13)	1.145(17)
C(102)–Cu–C(101)	34.8(5)	C(101)–C(102)–Cu	72.6(7)	C(11)–Mn(1)–P(11)	88.1(4)	C(12)–Mn(1)–C(11)	89.6(6)
C(201)–Cu–C(101)	158.4(5)	C(103)–C(102)–C(101)	164.0(14)	C(11)–Mn(1)–P(12)	92.4(4)	C(13)–Mn(1)–C(101)	90.1(5)
C(202)–Cu–C(102)	145.6(5)	P(11)–Mn(1)–C(101)	92.5(3)	C(12)–Mn(1)–C(101)	95.5(5)	C(13)–Mn(1)–P(11)	177.2(5)
C(202)–Cu–C(201)	34.3(5)	P(12)–Mn(1)–C(101)	82.7(3)	C(12)–Mn(1)–P(11)	83.9(4)	C(13)–Mn(1)–P(12)	97.1(4)
C(102)–C(101)–Cu	72.6(8)	P(12)–Mn(1)–P(11)	84.2(1)	C(12)–Mn(1)–P(12)	167.9(4)	C(13)–Mn(1)–C(11)	89.4(6)
Mn(1)–C(101)–C(102)	170.5(10)	C(11)–Mn(1)–C(101)	174.9(4)				

* The bond lengths and angles around Mn(2) are equal, within experimental error, to those around Mn(1).

frequencies in the i.r. spectra of complexes **(3)** are very similar to those of the CuCl species **(2)** and, although no bands assignable to the ν(C≡C) vibrations could be observed, these bands could be obscured by the ν(CO) absorptions at lower frequencies. This may be expected because the formation of a π complex (side-on) between the alkynyl and the gold fragment would result in a decrease of 100—180 cm^{-1} in the ν(C≡C) frequency[9] which would bring this weak band near the region of the broad ν(CO) absorptions.

Compounds **(2)** reacted with $TlPF_6$ in the presence of the corresponding alkynyl **(1)** in CH_2Cl_2 to give the cationic species $[Mn_2Cu(\mu\text{-CCR})_2(CO)_6(dppe)_2]PF_6$ [R = CH_2OMe **(4a)** or Bu^t **(4b)**]. Only small changes were observed in the ν(CO) and ν(C≡C) frequencies in going from **(2)** to **(4)** (Table 1), but the shieldings of the protons of the CCR groups and the phosphorus of the dppe ligand relative to the free alkynyls **(1)** (Table 2) are more pronounced.

In order to study the co-ordination of the two alkynyls to the copper atom, an *X*-ray structure determination was carried out on compound **(4b)**. The results are summarized in Tables 3 and 4 and the structure of the cation is shown in the Figure.

The co-ordination around the copper is pseudotetrahedral with four almost identical Cu–C bonds [average 2.081(1) Å], very similar to those observed in other complexes of copper with acetylides.[6,10] Therefore, each manganese atom is linked to the copper by one μ-η^2-$CCBu^t$ bridge with a symmetrical side-on bond to the copper with non-bonding Mn–Cu distances [average 3.472(2) Å].

The atoms C(101),C(102),Mn(1),Cu and C(201),C(202), Mn(2),Cu form two planes [largest deviations from the mean plane are 0.02(2) Å for C(101) and C(201)]; the dihedral angle between these is 71(1)°. This arrangement of the CuC_4 group can be compared to that observed in the complex $[Pt(PhCCPh)_2]$ (dihedral angle 82°)[11] or in the cationic cluster $[AuW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]PF_6$ (dihedral angle 62°),[12] which can be related to **(4b)** by the isolobal analogy between the groups $CMn(CO)_3$(dppe), CPh, and $W(CO)_2(C_5H_5)$.[13]

The angle C(201)–Cu–C(101) [158.4(5)°] is larger than C(202)–Cu–C(102) [145.6(5)°]. This could be due to the effect of the fragment *fac*-$Mn(CO)_3$(dppe) being bulkier than the Bu^t group. The angles Mn(1)–C(101)–C(102) [170.5(10)°] and C(103)–C(102)–C(101) [164.0(14)°] deviate from linearity within the range encountered in many acetylene complexes.[5,14] Although steric factors could be significant, these values suggest some π back-bonding from the copper to the alkynyl group. The C(102)–C(101) and C(202)–C(201) distances (average 1.237 Å) are, however, very similar to that found in the alkynyl **(1b)** (1.212 Å). The co-ordination around the manganese atoms in **(4b)** is

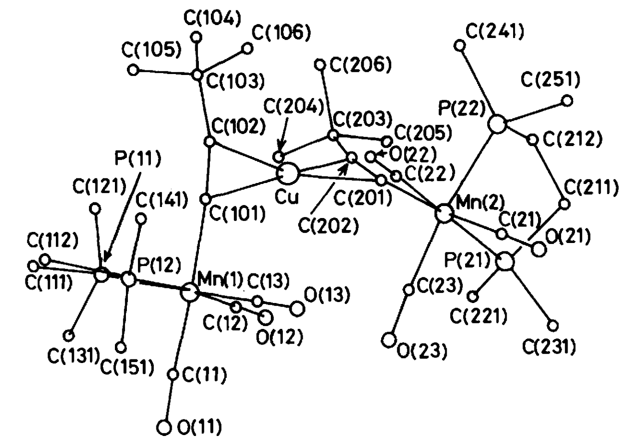


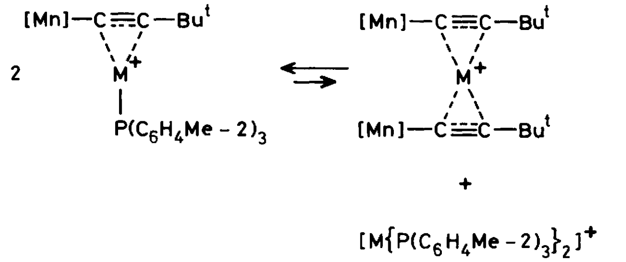
Figure. Molecular structure of the cation $[Mn_2Cu(\mu\text{-}CCBu^t)_2(CO)_6(dppe)_2]^+$ with the atom numbering. The phenyl rings have been omitted for clarity

almost identical, within experimental error, to that of **(1b)**[15] and will not be discussed here.

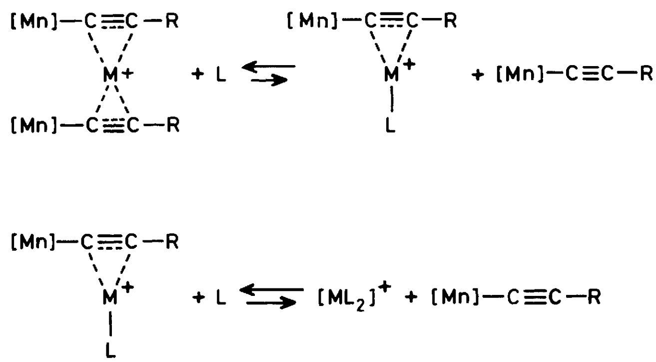
The silver and gold complexes **(5)** and **(6)** analogous to the copper species **(4b)** were prepared by reacting $[Ag(NCMe)_4]BF_4$ (or simply $AgBF_4$), or [AuCl(tht)] and $TlPF_6$ respectively, in CH_2Cl_2 with a two-fold excess of **(1b)**.* On the basis of the spectroscopic properties the structure of these complexes is assumed to be analogous to that of **(4b)**. Although in the Au complex ν(C≡C) is probably masked by the ν(CO) absorptions [as for **(3)**], the i.r. spectrum of the Ag compound **(5)** showed a medium intensity band at 1 996 cm^{-1} which can be assigned to the ν(C≡C) vibration, 113 cm^{-1} lower than for **(1b)**. As for copper, this decrease is similar to that observed for other alkynyl groups upon co-ordination to Ag^+ cations.[16]

Similar to the formation of **(4b)**, the chloro complex **(2b)** reacted with $TlPF_6$ in the presence of the phosphine $P(C_6H_4Me\text{-}2)_3$ giving mainly the cationic species $[MnCu(\mu\text{-}CCBu^t)(CO)_3(dppe)\{P(C_6H_4Me\text{-}2)_3\}]PF_6$ **(7)**, but always mixed with either **(4b)** or uncharacterized copper–phosphine complexes $[Cu\{P(C_6H_4Me\text{-}2)_3\}_x]PF_6$ (probably x = 2 in solution[17]), or

* As mentioned above, **(1b)** reacts quickly with [AuCl(tht)] giving *fac*-$[MnCl(CO)_3(dppe)]$. It was not possible to establish unambiguously if this happens also in the presence of $TlPF_6$ (i.r. monitoring) but this does not affect the formation of **(6)**. Thus, we found that reacting first **(1b)** and [AuCl(tht)] (2:1), to form a (1:1) mixture of *fac*-$[MnCl(CO)_3(dppe)]$ and **(1b)**, followed by stirring with $TlPF_6$ for 30 h, also produced **(6)** in good yield.



Scheme 1.



Scheme 2. For M = Cu or Ag; in the case of M = Au both reactions are totally shifted to the right and the reverse reactions were not observed [L = $P(C_6H_4Me\text{-}2)_3$]

both, depending on the work-up. The analogous species, $[MnM(\mu\text{-}CCBu^t)(CO)_3(dppe)\{P(C_6H_4Me\text{-}2)_3\}]A$ [M = Ag, A = BF_4 (**8**); M = Au, A = PF_6 (**9a**)]* could be formed directly from the σ-alkynyl complex (**1b**) or from the bis(alkynyl) complexes (**5**) and (**6**).

Mixing $AgBF_4$ with $P(C_6H_4Me\text{-}2)_3$ and (**1b**) in 1:1:1 molar ratio in CH_2Cl_2 gave a mixture of $[Ag\{P(C_6H_4Me\text{-}2)_3\}_2]BF_4$, (**5**),† and the expected (**8**), the latter being the most abundant (^1H and ^{31}P-{^1H} n.m.r., Table 2). Significantly, the phosphorus of the $P(C_6H_4Me\text{-}2)_3$ ligand showed coupling with the Ag isotopes. It was also observed that mixing (**5**) and $[Ag\{P(C_6H_4Me\text{-}2)_3\}_2]BF_4$ in 1:1 molar ratio resulted in the very fast formation of a mixture of (**8**), (**5**), and $[Ag\{P(C_6H_4Me\text{-}2)_3\}]BF_4$ in approximate 5:1:1 molar ratio. All these results strongly suggest that in solution the equilibrium shown in Scheme 1 (M = Ag) is rapidly established.

In the case of gold, compound (**9a**) could be obtained pure by reacting (**1b**) with $[AuCl\{P(C_6H_4Me\text{-}2)_3\}]$ and $TlPF_6$. In the same way, the analogous compound (**9b**) was prepared from *fac*-$[Mn(CCPh)(CO)_3(dppe)]$ and $[AuCl(PPh_3)]$. In similar experiment[20] the alkynyl $[Au(CCPh)(PPh_3)]$ was treated with $[Au(BF_4)(PPh_3)]$ to give $[Au_2(\mu\text{-}CCPh)(PPh_3)_2]BF_4$; on the basis of the small decrease in the ν(C≡C) frequency, it was assumed that the $AuPPh_3$ fragment was not co-ordinated to the C≡C bond, forming a symmetrical σ-alkynyl bridge.

The species (**9a**) is the kinetic product of the reaction between (**1b**) and $[AuCl\{P(C_6H_4Me\text{-}2)_3\}]$ with $TlPF_6$ because, after one month in solution, a mixture of (**9a**), (**6**), and $[Au\{P(C_6H_4Me\text{-}2)_3\}_2]PF_6$ (*ca.* 3:1:1)‡ is formed. Therefore, the equilibrium observed for Ag^+ shown in Scheme 1 also occurs for M = Au but the reactions involved are much slower. A similar equilibrium is obtained by dissolving $[AuW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]PF_6$ in CH_2Cl_2.[21] It is also known that mixed phosphine complexes $[AuLL']^+$ are unstable with regard to $[AuL_2]^+$ and $[AuL'_2]^+$.[22] Although, as suggested by the results below, the mechanism for the reactions of Scheme 1 may involve dissociation of the phosphine complexes (as proposed for the carbyne species[21]), it is possible that, in the case of M = Au, a four-centre (either bimolecular or assisted) mechanism[23] is operative.

The formation of mixtures in the preparation of (**7**)—(**9a**) suggested that, depending on the metal and reaction conditions, the alkynyls co-ordinated to Cu, Ag, or Au could be displaced by the phosphine or *vice versa*; several experiments were carried out to study this. The results can be represented by the equilibria in Scheme 2,§ which indicates that the Cu^+ and Ag^+ cations behave similarly while the Au^+ systems are very different. Apparently, for Cu^+ and Ag^+ the alkynyl has more co-ordinating ability than the phosphine, while the opposite is true for Au^+. Steric factors may be significant here; it is known, for example, that for Cu[17,25] and Ag,[26] steric as well as electronic factors are important in their co-ordination chemistry with phosphorus ligands.

The reaction of (**6**) with excess $P(C_6H_4Me\text{-}2)_3$ to give (**1b**) and $[Au\{P(C_6H_4Me\text{-}2)_3\}_2]^+$, although slow, is analogous to the rapid reaction between $[AuW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(C_5H_5)_2]PF_6$ and PPh_3 to give $[Au(PPh_3)_2]PF_6$ and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(C_5H_5)]$.[12]

Finally we observed that the cationic bis(alkynyl) complexes (**4b**), (**5**), and (**6**) reacted with $[NMe_3(CH_2Ph)]Cl$ in CH_2Cl_2, giving different results depending on the metal M. Thus, the copper species (**4b**) gave a mixture of (**1b**) and (**2b**), and a large excess of Cl^- was necessary to convert the latter into free (**1b**) and, presumably, $CuCl_2^-$. The silver compound (**5**) reacted instantly, giving AgCl and free (**1b**), while the gold analogue (**6**) reacted less quickly giving a 1:1 molar mixture of (**1b**) and *fac*-$[MnCl(CO)_3(dppe)]$. The last result suggests that the chloride ion displaces one σ-alkynyl from (**6**), giving (**1b**) and the transient unstable species $[MnAuCl(\mu\text{-}CCBu^t)(CO)_3(dppe)]$ in which an intramolecular migration of Cl from Au to Mn led to the *fac*-chlorotricarbonyl complex as mentioned above. Compounds (**7**)—(**9a**) also reacted quickly with Cl^-, giving free (**1b**) and presumably $[MCl\{P(C_6H_4Me\text{-}2)_3\}]$, but in the case of the copper species (**7**), a quantity of (**2b**) was also formed as evidenced by the i.r. spectra.

Experimental

All reactions were carried out under dry argon. The i.r. spectra were measured with a Perkin-Elmer 298 spectrometer and calibrated against the 1 602 cm^{-1} band of polystyrene. The n.m.r. spectra were recorded with a Varian F.T. 80-A instrument. The complexes (**1**) were prepared as previously reported[2] and the same procedure was used to obtain the

* The structure proposed for compounds (**7**)—(**9a**) probably corresponds to the alkynyl–phosphine species present in solution; in the case of gold it is likely that the same structure is maintained in the solid, but we could not establish this. Electronic differences have been shown to exist between the Cu and Au compounds[18] which could result in different structures.

† The ^1H n.m.r. spectrum of a solution of $AgBF_4$ and $P(C_6H_4Me\text{-}2)_3$ in 1:2 molar ratio, which should generate the cation $[Ag\{P(C_6H_4Me\text{-}2)_3\}_2]^+$ *in situ*,[19] showed a peak at 2.35 p.p.m., identical to that of the product formed in the reaction of $AgBF_4$ with $P(C_6H_4Me\text{-}2)_3$ and (**1b**).

‡ This was confirmed by independently preparing it by reacting [AuCl(tht)] and $P(C_6H_4Me\text{-}2)_3$ (1:2) in the presence of $TlPF_6$.

§ The ^1H and ^{31}P-{^1H} n.m.r. spectra of some of the products showed broad signals indicating fast interchange between free and co-ordinated (**1b**) and $P(C_6H_4Me\text{-}2)_3$ in the species $[MMn(\mu\text{-}CCR)(CO)_3(dppe)\{P(C_6H_4Me\text{-}2)_3\}]^+$ and $[M\{P(C_6H_4Me\text{-}2)_3\}_2]^+$. This has been observed for some silver phosphine[19] and alkyne[24] complexes and copper phosphine[17] complexes.

Table 4. Final atomic co-ordinates ($\times 10^5$ for Cu and Mn, $\times 10^4$ for other atoms) for compound (**4b**)*

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Cu	83 293(6)	9 490(9)	56 932(6)	C(211)	8 195(11)	3 881(11)	3 663(11)
C(101)	8 085(4)	202(7)	6 367(6)	C(212)	7 978(10)	3 203(15)	3 249(9)
C(102)	8 180(5)	−338(7)	5 971(6)	P(22)	7 662(1)	2 216(2)	3 503(2)
C(103)	8 221(7)	−1 170(9)	5 587(7)	C(221)	7 577(5)	4 955(7)	4 336(6)
C(104)	8 837(10)	−1 429(14)	5 780(16)	C(222)	7 327(6)	5 401(10)	3 702(7)
C(105)	7 963(10)	−1 956(10)	5 825(9)	C(223)	7 001(7)	6 140(11)	3 678(10)
C(106)	7 849(13)	−1 036(13)	4 787(8)	C(224)	6 897(6)	6 464(11)	4 240(12)
Mn(1)	79 297(7)	9 009(11)	71 088(8)	C(225)	7 160(8)	6 000(10)	4 871(9)
P(11)	7 217(1)	−105(2)	7 082(1)	C(226)	7 492(7)	5 255(8)	4 921(7)
C(111)	7 558(5)	−1 041(7)	7 712(5)	C(231)	8 696(6)	4 308(9)	5 128(11)
C(112)	8 144(5)	−1 221(7)	7 689(6)	C(232)	8 871(7)	3 941(13)	5 804(10)
P(12)	8 560(1)	−158(2)	7 857(2)	C(233)	9 414(8)	4 361(14)	6 333(11)
C(121)	6 740(5)	−677(8)	6 279(6)	C(234)	9 705(10)	4 978(17)	6 116(21)
C(122)	6 376(6)	−1 330(9)	6 327(7)	C(235)	9 539(15)	5 247(23)	5 457(21)
C(123)	5 988(7)	−1 733(10)	5 714(9)	C(236)	8 989(8)	4 947(14)	4 953(17)
C(124)	5 971(8)	−1 497(11)	5 072(9)	C(241)	7 018(6)	2 042(8)	2 703(6)
C(125)	6 334(6)	−763(11)	5 032(7)	C(242)	6 516(7)	1 756(10)	2 727(8)
C(126)	6 716(5)	−414(9)	5 625(6)	C(243)	6 007(7)	1 514(12)	2 104(11)
C(131)	6 696(5)	376(8)	7 367(6)	C(244)	6 103(11)	1 670(15)	1 494(10)
C(132)	6 167(6)	703(9)	6 844(8)	C(245)	6 581(12)	1 942(18)	1 420(11)
C(133)	5 763(7)	1 141(10)	7 084(11)	C(246)	7 062(7)	2 131(11)	2 067(7)
C(134)	5 889(8)	1 244(11)	7 804(10)	C(251)	8 058(5)	1 213(12)	3 465(6)
C(135)	6 391(8)	907(10)	8 283(9)	C(252)	7 808(7)	364(11)	3 431(7)
C(136)	6 810(6)	465(8)	8 078(7)	C(253)	8 030(10)	−439(17)	3 366(9)
C(141)	9 248(5)	−476(11)	7 794(6)	C(254)	8 499(18)	−446(26)	3 296(14)
C(142)	9 571(6)	233(13)	7 723(9)	C(255)	8 841(9)	315(27)	3 335(11)
C(143)	10 146(7)	−26(17)	7 737(9)	C(256)	8 602(7)	1 300(18)	3 415(8)
C(144)	10 312(7)	−908(18)	7 820(9)	C(21)	7 184(5)	1 575(9)	4 534(6)
C(145)	9 982(8)	−1 567(14)	7 916(11)	O(21)	6 926(4)	939(6)	4 538(5)
C(146)	9 441(7)	−1 351(11)	7 885(10)	C(22)	6 893(5)	3 148(9)	4 033(6)
C(151)	8 810(5)	−17(9)	8 791(6)	O(22)	6 452(4)	3 507(7)	3 739(5)
C(152)	8 760(6)	−634(12)	9 218(7)	C(23)	7 565(5)	3 009(8)	5 352(7)
C(153)	9 011(9)	−491(19)	9 975(11)	O(23)	7 553(4)	3 305(6)	5 848(5)
C(154)	9 289(10)	264(17)	10 254(10)	P	8 927(2)	3 802(2)	2 113(2)
C(155)	9 358(10)	891(13)	9 811(11)	F(1)	8 991(9)	4 100(14)	2 868(11)
C(156)	9 088(8)	764(14)	9 062(7)	F(2)	8 895(9)	3 276(14)	1 426(11)
C(11)	7 848(5)	1 458(8)	7 809(7)	F(3)	8 561(10)	2 996(15)	2 134(11)
O(11)	7 797(4)	1 840(6)	8 278(5)	F(4)	9 529(9)	3 383(15)	2 654(11)
C(12)	7 330(6)	1 535(8)	6 495(7)	F(5)	8 592(7)	4 542(11)	1 574(8)
O(12)	6 932(4)	1 929(6)	6 130(5)	F(6)	9 530(9)	4 275(15)	2 328(11)
C(13)	8 473(6)	1 731(9)	7 148(6)	F(1′)	9 038(10)	2 862(13)	2 523(10)
O(13)	8 771(4)	2 324(7)	7 181(5)	F(2′)	8 260(9)	3 558(15)	1 822(11)
C(201)	8 341(5)	2 014(6)	5 048(5)	F(3′)	9 176(8)	3 333(12)	1 600(9)
C(202)	8 837(5)	1 734(7)	5 345(6)	F(4′)	9 133(10)	4 702(15)	1 960(11)
C(203)	9 475(5)	1 633(8)	5 599(7)	F(5′)	8 759(7)	4 345(10)	2 642(8)
C(204)	9 774(6)	1 831(11)	6 381(6)	Cl	187(8)	2 929(13)	8 374(9)
C(205)	9 684(6)	2 304(11)	5 185(8)	Cl	−7(10)	3 340(16)	8 241(11)
C(206)	9 607(6)	633(9)	5 426(9)	Cl′	698(7)	3 228(12)	9 692(8)
Mn(2)	75 637(7)	26 021(10)	45 305(8)	Cl′	582(11)	3 645(19)	9 772(13)
P(21)	8 018(1)	3 929(2)	4 448(2)	C	376(14)	3 859(22)	8 921(16)

* Primes indicate alternative atomic positions for the disordered PF_6^- and CH_2Cl_2 molecules.

analogous compound with R = CH_2OMe. The compounds [AuCl(tht)] and [Au(C_6F_5)(tht)] were prepared as described elsewhere.[8]

Preparation of [MnCuCl(μ-CCR)$(CO)_3$(dppe)], (**2a**)—(**2c**).—Solid CuCl (0.10 g, 1.0 mmol) was added to a solution of (**1b**) (0.16 g, 0.26 mmol) in CH_2Cl_2 (30 cm^3) and the mixture stirred for 30 min. The precipitate was filtered off and the resulting solution evaporated to dryness. The residue was extracted with CH_2Cl_2 (20 cm^3), ethanol (5 cm^3) was added and the mixture was concentrated at reduced pressure to give pale green microcrystals of (**2b**) which were washed with ethanol (3 cm^3) and diethyl ether (2 × 3 cm^3). Yield 0.13 g, 70%. Compounds (**2a**) and (**2c**) were similarly prepared (reaction time, yield): (**2a**) (1 h, 75%); (**2c**) (30 min, 70%).

Preparation of [MnAu(C_6F_5)(μ-CCR)$(CO)_3$(dppe)], (**3a**) *and* (**3b**).—To a solution of (**1b**) (0.033 g, 0.053 mmol) in CH_2Cl_2 (5 cm^3) was added [Au(C_6F_5)(tht)] (0.020 g, 0.046 mmol) and the mixture stirred for 5 min. The resulting solution was evaporated to dryness and the residue washed once with hexane (3 cm^3), dissolved in diethyl ether (15 cm^3) and filtered through Celite. Hexane (15 cm^3) was added and the solution concentrated *in vacuo* to *ca.* 2 cm^3 to give a white microcrystalline precipitate of (**3a**) (0.03 g, 58%). Compound (**3b**) was similarly prepared in 56% yield.

Preparation of [Mn_2Cu(μ-CCR)$_2(CO)_6$(dppe)$_2$]PF_6 (**4a**) *and* (**4b**).—To a solution of (**2b**) (0.2 g, 0.27 mmol) in CH_2Cl_2 (20 cm^3) were added (**1b**) (0.173 g, 0.28 mmol) and $TlPF_6$ (0.15 g, 0.42 mmol) and, after stirring for 28 h, the mixture was filtered through Celite. The filtrate was concentrated to *ca.* 5 cm^3 and diethyl ether (40 cm^3) added. The resulting oily residue was stirred with diethyl ether overnight to give (**4b**) as a solid which was recrystallized from CH_2Cl_2–diethyl ether (0.25 g, 65%). Compound (**4a**) was similarly prepared in 50% yield.

Preparation of $[Mn_2Ag(\mu\text{-}CCBu^t)_2(CO)_6(dppe)_2]BF_4$ (**5**).—To a solution of (**1b**) (0.022 g, 0.36 mmol) in CH_2Cl_2 (10 cm^3), the salt $AgBF_4$ (0.033 g, 0.15 mmol) was added and the mixture stirred in the absence of light for 60 min. The resulting solution was filtered through Celite and concentrated *in vacuo* to *ca.* 3 cm^3. Slow addition of diethyl ether (60 cm^3) caused precipitation of pale yellow microcrystalline (**5**) (0.15 g, 70%).

Preparation of $[Mn_2Au(\mu\text{-}CCBu^t)_2(CO)_6(dppe)_2]PF_6$ (**6**).—To a vigorously stirred mixture of (**1b**) (0.25 g, 0.404 mmol) and solid $TlPF_6$ (0.20 g, 0.56 mmol) in CH_2Cl_2 (15 cm^3), solid [AuCl(tht)] (0.065 g, 0.202 mmol) was added and stirring was continued for 30 h. The resulting mixture was filtered through Celite; the filtrate was concentrated *in vacuo* to *ca.* 3 cm^3 and diethyl ether (60 cm^3) was added slowly with stirring to give a precipitate which was washed with diethyl ether (3 × 20 cm^3). The crude product was recrystallized from CH_2Cl_2–diethyl ether as a white powder (0.23 g, 72%).

Preparation of $[MnCu(\mu\text{-}CCBu^t)(CO)_3(dppe)\{P(C_6H_4Me\text{-}2)_3\}]PF_6$ (**7**).—*Method* (*a*). To a solution of (**2b**) (0.15 g, 0.21 mmol) and $P(C_6H_4Me\text{-}2)_3$ (0.064 g, 0.21 mmol) in CH_2Cl_2 (15 cm^3), solid $TlPF_6$ (0.10 g, 0.28 mmol) was added and the mixture stirred overnight and filtered. To the filtrate enough diethyl ether was added slowly to produce a first precipitate which was filtered off. Addition of more diethyl ether until no more precipitate was formed gave 0.060 g of (**7**) including *ca.* 20% (w/w) of (**4b**). Concentration of the mother-liquor to *ca.* 3 cm^3 and addition diethyl ether caused precipitation of more (**7**) (0.030 g) with *ca.* 10% of (**4b**).

Method (*b*). To a solution of (**2b**) (0.070 g, 0.10 mmol) and $P(C_6H_4Me\text{-}2)_3$ (0.050 g, 0.16 mmol) in CH_2Cl_2 (10 cm^3), solid $TlPF_6$ (0.10 g, 0.28 mmol) was added and the mixture stirred for 5 h and filtered. The filtrate was concentrated to *ca.* 1 cm^3 and diethyl ether (70 cm^3) was added to give a solid (0.070 g), which comprised (**7**) and unidentified copper–phosphine complexes. This product was dissolved in CH_2Cl_2 (5 cm^3) and enough diethyl ether was added to produce a first precipitate which was filtered off. The resulting liquid was concentrated to 1 cm^3 and addition of diethyl ether (60 cm^3) gave pale yellow (**7**) (0.035 g) with some $[Cu\{P(C_6H_4Me\text{-}2)_3\}_x]PF_6$.

Preparation of $[MnAu(\mu\text{-}CCBu^t)(CO)_3(dppe)\{P(C_6H_4Me\text{-}2)_3\}]PF_6$ (**9a**).—To a vigorously stirred mixture of (**1b**) (0.20 g, 0.32 mmol) and $TlPF_6$ (0.2 g, 0.56 mmol) in CH_2Cl_2 (5 cm^3), was added solid $[AuCl\{P(C_6H_4Me\text{-}2)_3\}]$ (0.135 g, 0.25 mmol) and stirring was continued for 1 h. After addition of more CH_2Cl_2 (15 cm^3), the mixture was filtered through Celite and the filtrate was concentrated *in vacuo* to *ca.* 0.5 cm^3. Addition of diethyl ether (60 cm^3) gave a solid (0.23 g) which was redissolved in CH_2Cl_2 (8 cm^3) and mixed slowly with diethyl ether (*ca.* 14 cm^3) to give a first precipitate which was filtered off. The filtrate was concentrated *in vacuo* to 1 cm^3 and more diethyl ether (60 cm^3) was added to give pale yellow microcrystalline (**9a**) (0.17 g, 54%).

Preparation of $[MnAu(\mu\text{-}CCPh)(CO)_3(dppe)(PPh_3)]PF_6$ (**9b**).—To a solution of (**1b**) (0.15 g, 0.235 mmol) in CH_2Cl_2 (20 cm^3), $TlPF_6$ (0.085 g, 0.235 mmol) and $[AuCl(PPh_3)]$ (0.116 g, 0.235 mmol) were added and the mixture was stirred for 2 h. The precipitate was filtered off and the filtrate concentrated to 5 cm^3. Addition of diethyl ether gave a creamy precipitate which was recrystallized from CH_2Cl_2–ethanol (2:1) as white microcrystals (0.21 g, 72%).

Crystal Structure Determination of Compound (**4b**).—*Crystal data.* $C_{70}H_{66}CuMn_2F_6O_6P_5 \cdot 0.5CH_2Cl_2$, M = 1 488.04, monoclinic, a = 25.411(4), b = 14.862(3), c = 20.892(4) Å, β = 114.00(3)°, U = 7 216(4) $Å^3$, space group $P2_1/n$, D_c = 1.370 g cm^{-3}, Z = 4, $F(000)$ = 3 052, $\lambda(Mo\text{-}K_\alpha)$ = 0.710 69 Å, $\mu(Mo\text{-}K_\alpha)$ = 8.61 cm^{-1}.

A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a Philips PW-1100 four-circle diffractometer. The unit-cell parameters were determined at room temperature from 25 reflections ($4 \leqslant \theta \leqslant 9°$) and refined by least-squares methods. Intensities were collected with graphite-monochromatized Mo-K_α radiation, using the ω-scan technique, scan width 1°, and scan speed 0.03° s^{-1}. Three reflections were measured each 2 h as orientation and intensity control; significant variations were not observed. 5 200 Independent reflections were measured in the range $2 \leqslant \theta \leqslant 25.5°$, 5 088 of which were taken as observed, applying the condition $I \geqslant 2.5\sigma(I)$. Lorentz and polarization corrections, but no absorption, were made.

The structure was determined by direct methods, using the MULTAN system of computer programs.[27] An E-map gave the positions of the Cu, Mn, and P atoms. The remaining non-hydrogen atoms were located by DIRDIF-matrix least-squares method,[28] using the SHELX 76 computer program.[29] The function minimized was $w||F_o| - |F_c||^2$, where $w = (\sigma^2 + 0.0134|F_o|^2)^{-1}$; values of ($f$, f', and f'' were taken from International Tables of X-Ray Crystallography.[30] After three cycles of isotropic refinement, disorder of the F atoms of the PF_6^- ion was observed, and a difference synthesis revealed three peaks that were assigned to half a molecule of CH_2Cl_2. No attempt to locate the H atoms was made due to computer problems. The final R was 0.074 (R' = 0.081) for all observed reflections.

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