Synthesis of New Heteronuclear Complexes with Bridging Carbyne Ligands Between Tungsten and Gold. *X*-Ray Crystal Structure of $[AuW(\mu-CC_6H_4Me-4)(CO)_2(bipy)(C_6F_5)Br]$†

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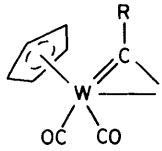
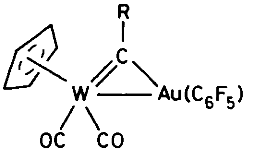
The compound $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ ($R = C_6H_4Me$-4) (**1**) reacts with $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene) to give the tungsten–gold complex $[AuW(\mu-CR)(CO)_2(C_6F_5)(\eta-C_5H_5)]$ (**2**), and the compound $[W(\equiv CR)(CO)_2(bipy)Br]$ (bipy = 2,2′-bipyridine) reacts similarly with $[Au(C_6F_5)(tht)]$ and $[AuCl(tht)]$ to give the analogous complexes $[AuW(\mu-CR)(CO)_2(bipy)X(Br)]$ (**4**; $X = C_6F_5$) and (**5**; X = Cl). In complex (**4**), which has been structurally characterized by *X*-ray diffraction, there is a Au–W bond asymmetrically bridged by a CR group; the W atom carries a chelating bipyridine, one bromide, and two terminal carbonyls, while the gold carries a C_6F_5 group. The heterometallic complex (**2**) reacts with the reagents $[Cu(thf)(\eta-C_5Me_5)]$ and $[Pt(PMe_3)_2(C_2H_4)]$ to give respectively the trimetallic compounds $[AuCuW(\mu_3-CR)(CO)_2(C_6F_5)(\eta-C_5H_5)(\eta-C_5Me_5)]$ (**6**) and $[AuPtW(\mu_3-CR)(CO)_2(PMe_3)_2(C_6F_5)(\eta-C_5H_5)]$ (**7**). The latter compound can also be prepared by treating $[Au(C_6F_5)(tht)]$ with $[PtW(\mu-CR)(CO)_2(PMe_3)_2(\eta-C_5H_5)]$.

It has been shown[1] that the alkylidyne complex $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ ($R = C_6H_4Me$-4) can behave as a ligand for a variety of transition metal–ligand fragments ML_n forming dimetallacyclopropenes of the type (**I**). On the other hand, we have recently observed[2] that the gold complex $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene) reacts with σ-alkynyl complexes of manganese to give species having the $Au(C_6F_5)$ fragment co-ordinated to a C≡C triple bond. Therefore it could be anticipated that substitution of the weakly co-ordinated ligand tht in the gold compounds $[Au(C_6F_5)(tht)]$ or $[AuCl(tht)]$, by tungsten carbynes, would lead to new alkylidyne-bridged bimetallic complexes with a gold–tungsten bond. Herein we report the preparation of new bi- and trimetallic complexes having W, Au, and Cu or Pt with bridging carbyne ligands.



(**I**) $R = C_6H_4Me-4$



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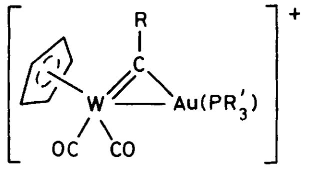

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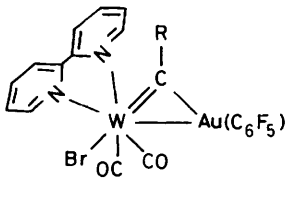
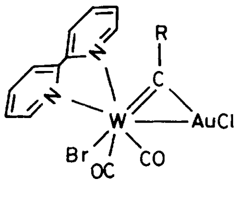


(**4**)



(**5**)

Results and Discussion

The reaction of the tungsten carbyne complex $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ (**1**; $R = C_6H_4Me$-4) with $[Au(C_6F_5)(tht)]$ in CH_2Cl_2 resulted in the displacement of the tetrahydrothiophene ligand giving the orange crystalline compound $[AuW(\mu-CR)(CO)_2(C_6F_5)(\eta-C_5H_5)]$ (**2**), data for which are given in Tables 1 and 2. The ^{13}C n.m.r. spectrum of (**2**) showed a weak signal at 287.4 p.p.m., which is near to the value corresponding to the μ-CR carbon in the related species $[AuW(\mu-CR)(CO)_2(PPh_3)(\eta-C_5H_5)]^+$ (**3**) (292.6 p.p.m.)[3a] and $[AuW(\mu-CR)(CO)_2(PPh_3)(\eta^5-C_2B_9H_9Me_2)]$ (292.9 p.p.m.),[3b] therefore the structure proposed for (**2**) is analogous to that of (**3**). The 12-electron fragments $Au(C_6F_5)$ and $Au(PR'_3)^+$ are isolobal[4] with H^+ (or CH_3^+)[5] suggesting that, similarly to what has been pointed out[3b] for $[AuW(\mu-CR)(CO)_2(PPh_3)(\eta^5-C_2B_9H_9Me_2)]$, the bonding in (**2**) could also be described by one of the situations (**IIa**)—(**IIc**). Structure (**IIa**) can be compared with a terminal alkylidene complex having a WCAu interaction analogous to that described for agostic hydrogen[6] and could be related to the 16-electron species $[W(CHR)(CO)_2(\eta-C_5H_5)]^+$ proposed as an intermediate[7] in the protonation of (**1**). The semibridging alkylidyne structure (**IIb**) is akin to a cationic carbyne hydride complex similar to that of $[Mo(\equiv CCH_2Bu^t)H\{P(OMe)_3\}_2(\eta-C_5H_5)]^+$ which is the thermodynamic product of protonation of the parent neutral molybdenum neopentylidyne complex.[8] In both structures (**IIa**) and (**IIb**) the tungsten atom would carry a higher positive charge than in the starting carbyne (**1**) which is in consonance with the higher ν(CO) frequencies observed for (**2**). Another view of compound

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† 2-(2,2′-Bipyridine)-2-bromo-2,2-dicarbonyl-1-pentafluorophenyl-μ-*p*-tolylmethylidyne-goldtungsten (*Au–W*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Analytical[a] and physical data for the gold–tungsten complexes

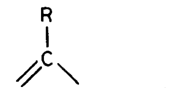
Complex	M.p.(θ_c/°C)	Colour	$\nu(CO)^b$/cm^{-1}	Analysis (%)		
(**2**) $[AuW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(C_6F_5)(\eta\text{-}C_5H_5)]$	129	Orange	2 019, 1 955[c]	32.95 (32.65)	1.55 (1.55)	
(**4**) $[AuW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(bipy)(C_6F_5)Br]$	157[d]	Red	2 013, 1 938[c]	33.40 (33.10)	1.70 (1.60)	2.95 (2.95)
(**5**) $[AuW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(bipy)ClBr]$	124[d]	Orange	2 012, 1 937	29.75 (29.60)	1.90 (1.85)	3.40 (3.45)
(**6**) $[AuCuW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(C_6F_5)(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$	106[d]	Violet	1 983, 1 901[c]	37.80 (38.35)	2.85 (2.80)	
(**7**) $[AuPtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(C_6F_5)(\eta\text{-}C_5H_5)]$	149	Red-brown	1 932, 1 809[c]	29.95 (28.95)	2.90 (2.70)	

[a] Calculated values are given in parentheses. [b] In dichloromethane. [c] All the C_6F_5 compounds have $\nu(C_6F_5)$ frequencies at 1 497, 1 050, and 952 cm^{-1} in Nujol mull. [d] With decomposition.

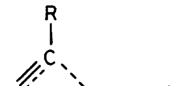
Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the gold–tungsten complexes

Complex	$^1H(\delta)$	$^{13}C(\delta)^b$
(**2**)[c–e]	2.47 (s, 3 H, Me-4), 5.90 (s, 5 H, C_5H_5), 7.00—7.74 (m, 4 H, C_6H_4)	287.4 (μ-C), 214.0 [CO, *J*(WC) 169.8], 149.9 (C^1, C_6H_4), 149.7—136.0 (m, C_6F_5), 142.4 (C^4, C_6H_4), 130.1 (C^2, C_6H_4), 129.5 (C^3, C_6H_4), 93.1 (C_5H_5), 22.0 (Me-4)
(**4**)[c–e]	2.36 (s, 3 H, Me-4), 7.14—9.2 (m, 12 H, C_6H_4 and bipy)	264.3 (μ-C), 213.7 [CO, *J*(WC) 159.6], 154.0, 140.9, 126.9, 124.9 (bipy), 148—134 (C_6F_5), 146.5 (C^1, C_6H_4), 139.6 (C^4, C_6H_4), 128.5 (C^2, C_6H_4), 128.1 (C^3, C_6H_4), 20.5 (Me-4)
(**5**)[d,e]	2.31 (s, 3 H, Me-4), 6.93—8.95 (m, 12 H, bipy and C_6H_4)	261.3 (μ-C), 216.0 [CO, *J*(WC) 184.3], 155.1, 154.3, 141.1, 127.4, 124.0 (bipy), 147.3 (C^1, C_6H_4), 141.1 (C^4, C_6H_4), 130.0 (C^2, C_6H_4), 129.2 (C^3, C_6H_4), 21.5 (Me-4)
(**6**)[c,f,g]	1.90 (s, 30 H, C_5Me_5), 2.10 (s, 3 H, Me-4), 4.77 (s, 5 H, C_5H_5), 6.87—7.52 (m, 4 H, C_6H_4)	261.9 [μ-C, *J*(WC) 132.7], 212.5 [CO, *J*(WC) 176.1], 208.9 [CO, *J*(WC) 159.4], 157.0 (C^1, C_6H_4), 149.1—139.9 (C_6F_5), 137.3 (C^4, C_6H_4), 125.1 ($C^{2,3}$, C_6H_4), 109.2 (C_5Me_5), 92.3 (C_5H_5), 21.3 (Me-4), 9.4 (C_5Me_5)
(**7**)[c,d,g,h]	1.23 [d, 9 H, PMe, *J*(PH) 9, *J*(PtH) 38], 1.68 [d, 9 H, PMe, *J*(PH) 7.8, *J*(PtH) 22], 2.35 (s, 3 H, Me-4), 5.39 (s, 5 H, C_5H_5), 6.87—7.15 (m, 4 H, C_6H_4)	270.4 [d, μ-C, *J*(PC) 12.2], 219.6, 217.6 (CO), 158.3—127.8 ($C^{1,4}$ of C_6H_4 and C_6F_5), 127.5 (C^2, C_6H_4), 127.4 (C^3, C_6H_4), 92.4 (C_5H_5), 21.0 (Me-4), 19.1—18.3 (m, PMe_3)

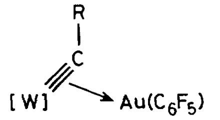
[a] Chemical shifts in p.p.m., coupling constants in Hz; room temperature. [b] Hydrogen-1 decoupled to high frequency of $SiMe_4$. [c] The ^{19}F n.m.r. spectrum in $CDCl_3$ with reference to external $CFCl_3$ showed three complex multiplets at −116 (2 F), −159 (1 F), and −162 (2 F) p.p.m. [d] Proton n.m.r. spectrum measured in $CDCl_3$. [e] $^{13}C\text{-}\{^1H\}$ N.m.r. spectrum measured in CD_2Cl_2. [f] Proton n.m.r. spectra measured in C_6D_6. [g] $^{13}C\text{-}\{^1H\}$ N.m.r. spectrum measured in C_6D_6. [h] $^{31}P\text{-}\{^1H\}$ N.m.r. spectrum in $CDCl_3$ in p.p.m. with reference to external 85% H_3PO_4: −20.4 [d, *J*(PPt) 4 572, *J*(PP) < 5] and −23.9 p.p.m. [d, *J*(PPt) 2 825, *J*(PP) < 5 Hz].



(**IIa**)



(**IIb**)



(**IIc**)

(**2**) is to consider it as an η^2-acetylene complex with a small degree of π retrodonation from the gold fragment to the W≡C triple bond, (**IIc**), as proposed in the case of the derivative $[Au(C_6F_5)\{\eta^2\text{-}PhCCMn(CO)_3(Ph_2PCH_2CH_2PPh_2)\}]$,[2] although the chemistry of the AuC_6F_5 group is dominated by the σ-bonded species.[9] On the other hand, the spectroscopic properties of (**2**) in $CDCl_3$ indicated that this compound does not disproportionate in solution to give $[Au\{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ and $[Au(C_6F_5)_2]^-$, in contrast with the behaviour of (**3**) and other gold(I) complexes.[2,9,10] Consistently, the molar conductivity in 1,2-dichloroethane (0.2 Ω^{-1} cm^2 mol^{-1}) was far from the value expected for a 1:1 electrolyte (18—20 Ω^{-1} cm^2 mol^{-1}).[11] In acetone solution the complex dissociated with formation of (**1**) and $[Au(C_6F_5)(Me_2CO)]$ as revealed by the i.r. spectrum.

Similarly to the reaction of (**1**) with $[Au(C_6F_5)(tht)]$ to give (**2**), the alkylidyne complex $[W(\equiv CR)(CO)_2(bipy)Br]$ (R = C_6H_4Me-4, bipy = 2,2′-bipyridine) reacted readily with $[Au(C_6F_5)(tht)]$ and also with $[AuCl(tht)]$ * to give respectively $[AuW(\mu\text{-}CR)(CO)_2(bipy)(C_6F_5)Br]$ (**4**) and $[AuW(\mu\text{-}CR)(CO)_2(bipy)ClBr]$ (**5**). The signal at *ca.* 260 p.p.m. in the ^{13}C n.m.r. spectra is near to that expected for the free carbyne complex[12,13] and therefore the structures shown can be proposed. Similar complexes having AgCl or AuCl bonded to osmium carbynes have been reported.[14] In the case of compound (**4**) the structure has been established by *X*-ray diffraction. The results are summarized in Tables 3 and 4 and in the Figure.

The dimensions of the W–C(1)–Au ring are very similar to these corresponding to $[Au\{W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)\}_2]PF_6$[15] and comparison with the data[3b,16] for the dimetallacyclopro-

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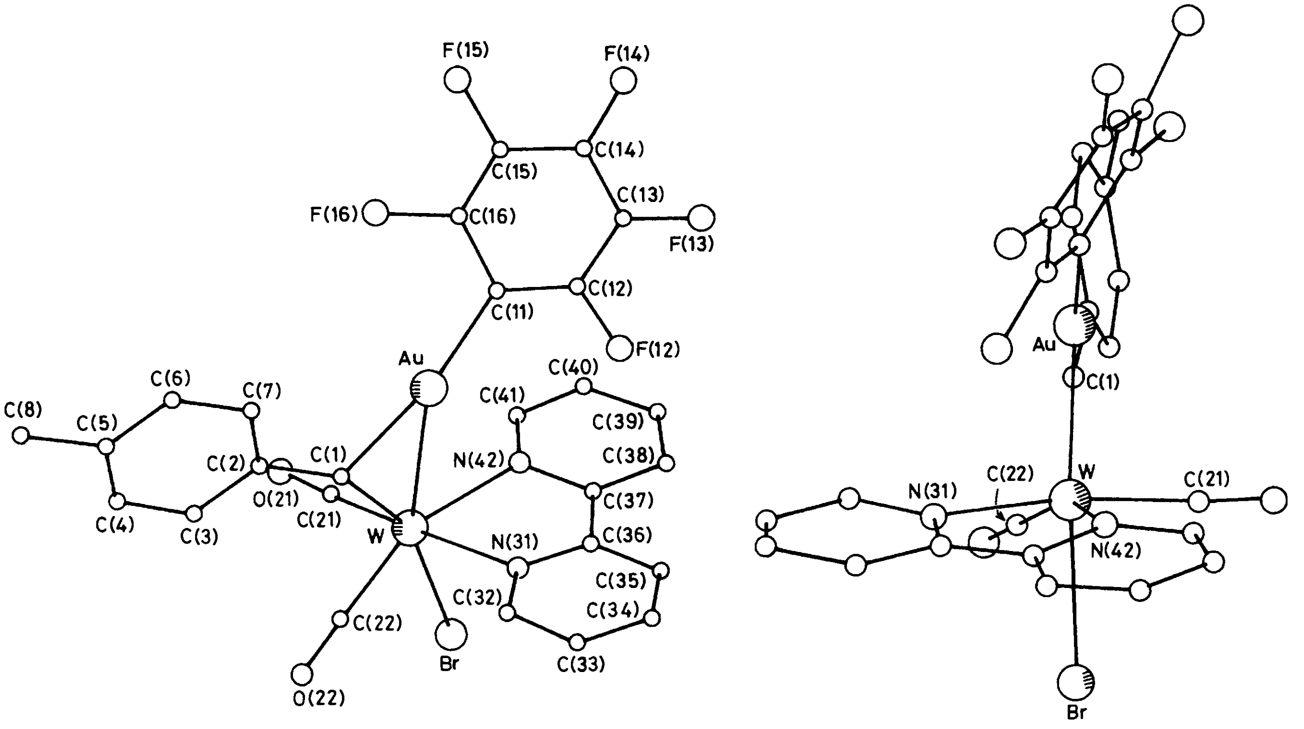
* This complex did not react with (**1**) to give analogous products.



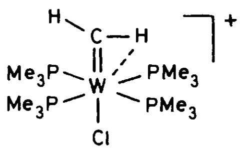
(*a*) (*b*)

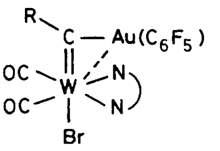
Figure. View of $[AuW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(bipy)(C_6F_5)Br]$ (**4**) showing (*a*) the atom numbering and (*b*) the approximate octahedral co-ordination around the W atom

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

W–Au	2.782 9(1)	C(2)–C(1)	1.469(4)
C(1)–Au	2.080(3)	F(12)–C(12)	1.306(4)
C(11)–Au	2.056(3)	F(13)–C(13)	1.322(4)
Br–W	2.617 1(4)	F(14)–C(14)	1.360(4)
C(1)–W	1.890(3)	F(15)–C(15)	1.415(4)
C(21)–W	2.014(4)	F(16)–C(16)	1.373(4)
C(22)–W	1.967(3)	O(21)–C(21)	1.165(4)
N(31)–W	2.248(2)	O(22)–C(22)	1.145(3)
N(42)–W	2.228(2)		
C(1)–Au–W	42.8(1)	N(31)–W–C(1)	106.9(1)
C(11)–Au–W	149.8(1)	N(31)–W–C(21)	170.7(1)
C(11)–Au–C(1)	167.3(1)	N(31)–W–C(22)	95.1(1)
Br–W–Au	155.86(4)	N(42)–W–Au	73.9(1)
C(1)–W–Au	48.4(1)	N(42)–W–Br	82.1(1)
C(1)–W–Br	155.1(1)	N(42)–W–C(1)	120.7(1)
C(21)–W–Au	100.3(1)	N(42)–W–C(21)	98.8(1)
C(21)–W–Br	85.1(1)	N(42)–W–C(22)	158.1(1)
C(21)–W–C(1)	81.6(1)	N(42)–W–N(31)	73.7(1)
C(22)–W–Au	124.3(1)	W–C(1)–Au	88.9(1)
C(22)–W–Br	78.8(1)	C(2)–C(1)–Au	118.9(2)
C(22)–W–C(1)	80.2(1)	C(2)–C(1)–W	151.3(2)
C(22)–W–C(21)	90.0(1)	O(21)–C(21)–W	177.2(3)
N(31)–W–Au	83.2(1)	O(22)–C(22)–W	177.6(3)
N(31)–W–Br	88.3(1)		

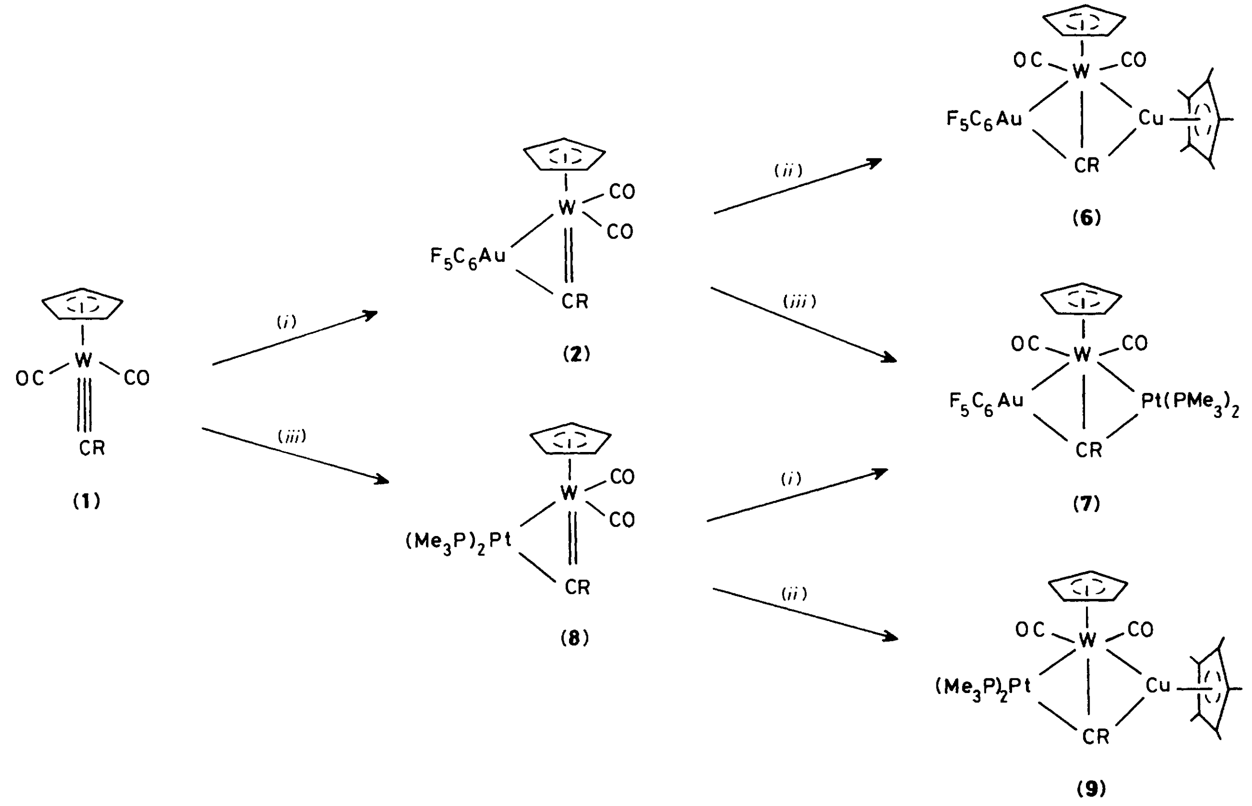
penes of general formula (**I**) revealed that the W–C(1) bond length [1.890(3) Å] lies at the shorter end of the range (1.91—2.03 Å) and is intermediate between that corresponding to a W=C bond (around 2.15 Å) and a W≡C bond (1.77—1.90 Å),[17] while the C(2)–C(1)–W angle [151.3(2)°] is larger than in the other cases (131—146°). On the other hand the





C(1)–Au distance [2.080(3) Å] is shorter and comparable to the C–Au(C_6F_5) bond length observed in the complex $[(C_6F_5)Au\{Ph_2CHPPh_2Me\}Au(C_6F_5)]$ [2.090(10) Å][18] and in $[AuMe(PPh_3)]$ [2.124(28) Å][19] and therefore may indicate a single C–Au bond. These considerations and the W–Au separation [2.782 9(1) Å] seem to suggest that, in spite of the short C–W bond, the bonding in compound (**4**) may approach the situation depicted in (**IIa**). In this case, an interesting comparison can be made between (**4**) [as in (**IIa**)] and the complex $[W(=CH_2)(PMe_3)_4Cl]^+$ which, at low temperature, has a grossly distorted (approximately T-shaped) methylidene ligand.[20] Although in complex (**4**) the W atom displays seven-co-ordination, because of the small angle C(1)–W–Au [48.4(1)°] the structure could be roughly described as a very distorted octahedron with one site occupied by a bulky group ($RCAuC_6F_5$) which is responsible for the deformations of the $WBr(CO)_2(bipy)$ fragment [see Figure (*b*)]. In particular the angle N(42)–W–C(22) [158.1(1)°] deviates significantly from 180° due to the orientation of the bonds. This orientation can be measured by the dihedral angles C(22)–W–Au–C(1) (−28.20), C(21)–W–Au–C(1) (68.96), N(31)–W–C(1)–Au (64.25), and N(42)–W–C(1)–Au (−16.48°). The other important deviation from the octahedral geometry is the angle N(42)–W–N(31) [73.7(1)°] due to the characteristics of the chelating bipyridine.

As for compound (**2**) the spectroscopic properties and the conductivity in 1,2-dichloroethane of (**4**) and (**5**) indicated no



Scheme. (*i*) $[Au(C_6F_5)(tht)]$ in CH_2Cl_2; (*ii*) $[Cu(thf)(\eta-C_5Me_5)]$ in thf; (*iii*) $[Pt(PMe_3)_2(C_2H_4)]$ in hexane

symmetrization in solution and in polar solvents like acetone the free carbyne $[W(\equiv CR)(CO)_2(bipy)Br]$ is generated.

The gold–tungsten complex (**2**) has an unsaturated CW bond, analogous to that in the platinum–tungsten species (**8**) (see Scheme). Accordingly, complex (**2**) reacted with $[Cu(thf)(\eta-C_5Me_5)]$[21] in tetrahydrofuran (thf) to give the trimetallic species $[AuCuW(\mu_3-CR)(CO)_2(C_6F_5)(\eta-C_5H_5)(\eta-C_5Me_5)]$ (**6**). The formulation proposed for (**6**) is in accord with the ^{13}C n.m.r. spectrum which showed a weak signal at 261.9 p.p.m. close to that found for the cluster $[CuPtW(\mu_3-CR)(CO)_2(PMe_3)_2(\eta-C_5H_5)(\eta-C_5Me_5)]$ (**9**) (266.5 p.p.m.).[21] Similarly, the reaction of (**2**) with $[Pt(PMe_3)_2(C_2H_4)]$ gave the compound $[AuPtW(\mu_3-CR)(CO)_2(PMe_3)_2(C_6F_5)(\eta-C_5H_5)]$ (**7**) (Scheme). Because of the instability of this compound, the ^{13}C n.m.r. spectrum showed, together with the expected peaks (Table 2), other signals that corresponded to (**2**) and (**8**) and a doublet at 14.3 p.p.m. [*J*(PC) 35.1 Hz] that could not be assigned[22] to free PMe_3 and that may correspond to $[Au(C_6F_5)(PMe_3)]$. Compound (**7**) could also be obtained from (**8**) and $[Au(C_6F_5)(tht)]$ in CH_2Cl_2, and is analogous to $[AuPtW(\mu_3-CC_6H_4Me-4)(CO)(PMe_3)_3(\eta-C_5H_5)]PF_6$[3a] which contains the fragment $Au(PMe_3)^+$ instead of $Au(C_6F_5)$.

Experimental

All reactions were carried out under dry argon. Solvents were purified according to standard procedures[23] and distilled prior to use. Light petroleum refers to that fraction of b.p. 60—65 °C. I.r. spectra were recorded on a Perkin-Elmer 298 spectrophotometer and calibrated against the absorption of polystyrene at 1 601.4 cm^{-1}. N.m.r. spectra were recorded on Varian FT-80A, JEOL FX 90Q, and JEOL FX 200 instruments. The compounds $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ ($R = C_6H_4Me-4$),[24] $[PtW(\mu-CC_6H_4Me-4)(CO)_2(PMe_3)_2(\eta-C_5H_5)]$,[25] $[AuCl(tht]$ and $[Au(C_6F_5)(tht)]$[26] were prepared by literature methods. The carbyne $[W(\equiv CR)(CO)_2(bipy)Br]$ was synthesized by a method analogous to the previously reported procedure for similar compounds.[13]

Synthesis of the Complexes.—$[AuW(\mu-CC_6H_4Me-4)(CO)_2(C_6F_5)(\eta-C_5H_5)]$ (**2**). A solution of $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ (90 mg, 0.22 mmol) in CH_2Cl_2 (7 cm^3) was treated with $[Au(C_6F_5)(tht)]$ (0.1 g, 0.22 mmol). After 10 min the solution was filtered through a Celite pad and concentrated *in vacuo*. Addition of light petroleum gave orange microcrystals (washed with light petroleum) of $[AuW(\mu-CC_6H_4Me-4)(CO)_2(C_6F_5)(\eta-C_5H_5)]$ (0.1 g, 58.9%).

$[AuW(\mu-CC_6H_4Me-4)(CO)_2(bipy)(C_6F_5)Br]$ (**4**). To a stirred solution of $[W(\equiv CC_6H_4Me-4)(CO)_2(bipy)Br]$ (50 mg, 0.087 mmol) in CH_2Cl_2 (10 cm^3) was added solid $[Au(C_6F_5)(tht)]$ (38 mg, 0.087 mmol). After 10 min the mixture was filtered through Celite and concentrated *in vacuo*. Addition of light petroleum gave red microcrystals of $[AuW(\mu-CC_6H_4Me-4)(CO)_2(bipy)(C_6F_5)Br]$ (48 mg, 60%).

$[AuW(\mu-CC_6H_4Me-4)(CO)_2(bipy)ClBr]$ (**5**). To a stirred solution of $[W(\equiv CC_6H_4Me-4)(CO)_2(bipy)Br]$ (50 mg, 0.087 mmol) in CH_2Cl_2 (8 cm^3) was added solid $[AuCl(tht)]$ (26 mg, 0.087 mmol) and stirring was continued for 10 min. After filtration of the orange solution, concentration *in vacuo*, followed by addition of light petroleum, afforded orange microcrystals (washed with light petroleum) of $[AuW(\mu-CC_6H_4Me-4)(CO)_2(bipy)ClBr]$ (50 mg, 70.8%).

$[AuCuW(\mu_3-CC_6H_4Me-4)(CO)_2(C_6F_5)(\eta-C_5H_5)(\eta-C_5Me_5)]$ (**6**). A mixture of C_5Me_5H (54 mg, 0.396 mmol) and $LiBu^n$ (0.396 mmol in light petroleum) in thf (10 cm^3) was cooled to −78 °C. Solid CuCl (36 mg, 0.38 mmol) was added, and after 1 h the compound $[AuW(\mu-CC_6H_4Me-4)(CO)_2(C_6F_5)(\eta-C_5H_5)]$ (0.12 g, 0.168 mmol) was added. The mixture

Table 4. Final atomic co-ordinates ($\times 10^5$) for complex (**4**)

Atom	*X/a*	*Y/b*	*Z/c*
Au	86 355(1)	76 297(1)	−2 010(1)
W	73 406(1)	65 039(1)	9 088(1)
Br	69 777(3)	53 893(4)	27 077(4)
C(1)	7 020(2)	7 011(2)	−811(3)
C(2)	6 337(2)	7 015(2)	−2 229(3)
C(3)	5 383(3)	6 356(3)	−2 747(3)
C(4)	4 731(3)	6 425(3)	−4 123(4)
C(5)	4 970(3)	7 129(3)	−4 922(3)
C(6)	5 913(3)	7 798(4)	−4 390(3)
C(7)	6 584(3)	7 753(3)	−3 018(3)
C(8)	4 245(3)	7 143(4)	−6 391(3)
C(11)	10 150(3)	8 298(2)	−39(3)
C(12)	10 853(3)	8 742(3)	1 126(3)
F(12)	10 534(2)	8 900(2)	2 251(2)
C(13)	11 881(3)	9 176(3)	1 239(4)
F(13)	12 505(2)	9 687(2)	2 384(3)
C(14)	12 323(3)	9 023(3)	109(5)
F(14)	13 312(2)	9 455(2)	142(3)
C(15)	11 639(3)	8 505(4)	−1 100(4)
F(15)	12 013(3)	8 457(3)	−2 283(3)
C(16)	10 626(3)	8 169(3)	−1 171(4)
F(16)	9 989(2)	7 707(2)	−2 408(2)
C(21)	7 459(3)	4 864(3)	−187(3)
O(21)	7 541(2)	3 937(2)	−859(3)
C(22)	5 599(3)	6 675(3)	374(3)
O(22)	4 585(2)	6 795(3)	106(3)
N(31)	7 397(2)	8 177(2)	2 414(3)
C(32)	6 485(3)	9 109(3)	2 283(4)
C(33)	6 538(4)	10 062(3)	3 349(4)
C(34)	7 502(4)	10 143(3)	4 387(4)
C(35)	8 459(4)	9 116(3)	4 509(4)
C(36)	8 378(3)	8 155(3)	3 444(3)
C(37)	9 328(3)	7 118(3)	3 424(3)
C(38)	10 394(4)	7 018(5)	4 467(4)
C(39)	11 214(3)	5 963(6)	4 267(5)
C(40)	11 052(4)	5 138(4)	3 124(4)
C(41)	9 998(3)	5 317(4)	2 168(4)
N(42)	9 173(2)	6 316(3)	2 266(2)

was warmed to 0 °C. Removal of volatile material *in vacuo*, extraction with light petroleum (3 × 30 cm^3), concentration, and cooling the extracts to −30 °C afforded dark violet crystals of [AuCuW(μ_3-CC$_6$H$_4$Me-4)(CO)$_2$(C$_6$F$_5$)(η-C$_5$H$_5$)(η-C$_5$Me$_5$)] (95 mg, 58.24%).

[AuPtW(μ_3-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)$_2$(C$_6$F$_5$)(η-C$_5$H$_5$)] (**7**). (*a*) The complex [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)] (63 mg, 0.083 mmol) in CH$_2$Cl$_2$ (10 cm^3) was treated with [Au(C$_6$F$_5$)(tht)] (36 mg, 0.083 mmol). The red-brown solution was filtered through a Celite pad and the solvent removed *in vacuo*. The red-brown solid was washed with light petroleum–ether (1:1). The extracts were concentrated and cooled (−70 °C), affording red-brown microcrystals of [AuPtW(μ_3-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)$_2$(C$_6$F$_5$)(η-C$_5$H$_5$)] (62 mg, 66%).

(*b*) The complex [Pt(cod)$_2$] (53 mg, 0.13 mmol) was added portionwise to rapidly stirred light petroleum (10 cm^3) at 0 °C under an atmosphere of ethylene. The resultant pale yellow solution was treated under ethylene with PMe$_3$ (0.26 mmol) in light petroleum (5 cm^3). After stirring for 5 min, the ethylene atmosphere was replaced by one of nitrogen and [AuW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(C$_6$F$_5$)(η-C$_5$H$_5$)] (0.1 g, 0.13 mmol) was added. A red-brown precipitate formed within minutes. The solution was concentrated *in vacuo*, cooled to −50 °C, decanted, and the residue was washed with cold (−50 °C) light petroleum and extracted with light petroleum–ether (1:1). The extracts were concentrated and cooled to −70 °C, affording red-brown microcrystals of [AuPtW(μ_3-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)$_2$(C$_6$F$_5$)(η-C$_5$H$_5$)] (72 mg, 49.46%).

Structure Determination of Compound (**4**).—*Crystal data.* C$_{26}$H$_{15}$AuBrF$_5$N$_2$O$_2$W, *M* 943.1, triclinic, a = 11.926(2), b = 11.408(2), c = 10.422(1) Å, α = 100.07(1), β = 106.62(1), γ = 77.92(1)°, U = 1 318.6(6) Å^3, space group $P\bar{1}$, Z = 2, D_c = 2.375 g cm^{-3}, F(000) = 868, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 120.07 cm^{-1}, 288 K.

An equidimensional crystal (radii 0.1 mm) was selected and mounted on a Philips PW-1100 four-circle diffractometer. Unit-cell parameters were determined from 25 reflections ($4 \leqslant \theta \leqslant 12°$) and refined by least squares. Intensities were collected with graphite-monochromatized Mo-K_α radiation, using the ω-scan technique, scan width 0.8°, and scan speed 0.03° s^{-1}. 3 196 Reflections were measured in the range $2 \leqslant \theta \leqslant 25°$, 3 084 of which were assumed observed [$I \geqslant 2.5\sigma(I)$]. Three reflections were measured every 2 h as orientation and intensity control, but significant intensity decay was not observed. Lorentz-polarization and absorption corrections were made.

The Au, W, and Br atoms were located from MULTAN 84 [27] and the remaining non-hydrogen atoms using the DIRDIF system of computer programs. The structure was refined by the least-squares method using the SHELX 76 computer program.[28] The function minimized was $\Sigma w\|F_o| - |F_c\|^2$, where $w = [\sigma^2(F_o) + 0.0005|F_o|^2]^{-1}$. The final R was 0.020 (R' = 0.022) for all observed reflections.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, and remaining bond lengths and angles.

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