Synthesis of New Heterodinuclear Aminocarbyne Complexes: Crystal Structures of $[AuW\{\mu\text{-}CN(Et)Me\}(C_6F_5)(CO)_2(\eta\text{-}C_5H_5)]$ and $[\{CuW\{\mu\text{-}CN(Et)Me\}Cl(CO)_2(\eta\text{-}C_5H_5)\}_2]$†

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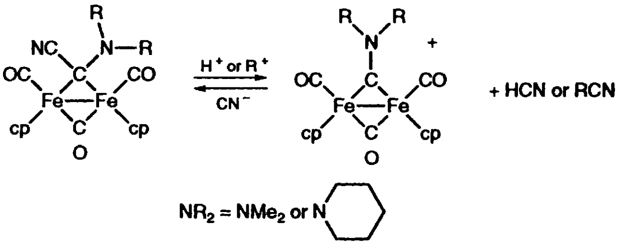
The aminocarbyne $[W\{\equiv CN(Et)Me\}(CO)_2(cp)]$ **1** (cp = η-C_5H_5) reacts with $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene) and CuCl to give the adducts $[AuW\{\mu\text{-}CN(Et)Me\}(C_6F_5)(CO)_2(cp)]$ **2** and $[\{CuW\{\mu\text{-}CN(Et)Me\}Cl(CO)_2(cp)\}_2]$ **3** respectively which have been structurally characterized by X-ray diffraction. Complex **2** crystallizes in space group $P\bar{1}$, a = 9.840(5), b = 11.577(6), c = 8.296(6) Å, α = 99.03(5), β = 91.01(6), γ = 81.92(4)°, Z = 2. Complex **3** crystallizes in space group $P2_1/a$, a = 7.788(2), b = 14.880(5), c = 11.712(5) Å, β = 95.35(3)°, Z = 2. Both adducts exhibit a molecule of **1** bonded to $Au(C_6F_5)$ or Cu_2Cl_2 fragments, respectively, through one of the W–C(carbyne) π bonds. A WCM ring is formed in which **1** preserves most of its identity and the coinage metals attain their preferred electron counts. The cationic Group 11 fragments $[M(PPh_3)^+]$ (M = Cu, Ag or Au) also react with complex **1** to form $[M\{W[\mu\text{-}CN(Et)Me](CO)_2(cp)\}_2]^+$ **5**; when M = Au NMR spectroscopy indicates that in addition to the trinuclear species **5**, the dimetallacyclopropene $[AuW\{\mu\text{-}CN(Et)Me\}(CO)_2(cp)(PPh_3)]^+$ **4** is also present. All these adducts have been spectroscopically characterised.

Homodinuclear complexes containing a bridging aminocarbyne CNR_2 have become a very well known class of organometallic compounds because of their simple preparation through electrophilic addition at the nitrogen atom of a bridging CNR ligand.[1] Other synthetic routes, although less general, have also been reported.[2–5] Significant examples include reactions of iron carbonyls with NR_2-containing molecules such as $R_2NC\equiv CNR_2$[2] or R_2NNO,[3] and insertion of isocyanide into the CoHCo bridge of the dinuclear complex $[Co_2(cp)_2(\mu\text{-}H)(\mu\text{-}PMe_2)_2]^+$ (cp = η-C_5H_5).[4] Moreover, we have recently demonstrated that μ-cyano(amino)carbenes can undergo CN abstraction by electrophiles to form the corresponding μ-carbynes (Scheme 1).[5] Reports describing heterodinuclear $[L_nM(\mu\text{-}CNR_2)M'L_n]$ compounds are still very scarce. To our knowledge only two iron–platinum complexes $[(OC)_3Fe\{\mu\text{-}CN(C_6H_3Me_2\text{-}2,6)R\}(\mu\text{-}dppm)Pt(PPh_3)]^+$ (R = H or Me, dppm = diphenylphosphinomethane) have so far been reported.[6] A possible method for obtaining this kind of complex is to extend the Stone[7] route to dimetallacyclopropene complexes by reacting a mononuclear aminoalkylidyne $L_nM\equiv CNR_2$ with suitable transition-metal fragments. The obvious candidate for such a reaction is the complex $[W\{\equiv CN(Et)Me\}(CO)_2(cp)]$ **1**, whose new, large scale, high-yield synthesis has been described by Filippou and Grünleitner.[8]

In the present paper we describe the reaction of complex **1** with various neutral and cationic Group 11 metal fragments $Au(C_6F_5)$, CuCl, $Au(PPh_3)^+$, $Ag(PPh_3)^+$ or $Cu(PPh_3)^+$, which provides new complexes possessing bridging aminocarbyne ligands. We report the molecular structure of two derivatives $[AuW\{\mu\text{-}CN(Et)Me\}(C_6F_5)(CO)_2(cp)]$ **2** and $[\{CuW\{\mu\text{-}CN(Et)Me\}Cl(CO)_2(cp)\}_2]$ **3**. Finally, the reaction of the new compound **2** with HSO_3CF_3 is presented and discussed.



Scheme 1

Results and Discussion

Reaction of the tungsten aminocarbyne complex $[W\{\equiv CN(Et)Me\}(CO)_2(cp)]$ **1** with $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene) in CH_2Cl_2 results in the displacement of the tht ligand to give complex $[AuW\{\mu\text{-}CN(Et)Me\}(C_6F_5)(CO)_2(cp)]$ **2** which has been isolated in *ca.* 70% yield as a red, moderately air-stable solid. The reaction closely resembles that occurring between $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(cp)]$ and $[Au(C_6F_5)(tht)]$ which yields $[AuW(\mu\text{-}CC_6H_4Me\text{-}4)(C_6F_5)(CO)_2(cp)]$.[9]

The spectroscopic properties of complex **2**, whose structure has been determined by X-ray diffraction (Fig. 1), are similar to those exhibited by $[AuW\{\mu\text{-}CC_6H_4Me\text{-}4\}(C_6F_5)(CO)_2(cp)]$. However some relevant differences, due to the presence of the electron-rich NR_2 substituent at the carbyne carbon atom, must be evidenced. The ^{13}C NMR spectrum (Table 2) shows one signal due to the μ-aminocarbyne carbon at δ 259.6, whereas the corresponding value for $[AuW\{\mu\text{-}CC_6H_4Me\text{-}4)(C_6F_5)(CO)_2(cp)]$ is *ca.* 28 ppm low-field shifted (δ 287.4). Moreover, the IR spectrum shows two ν(CO) absorptions at 1970 and 1893 cm^{-1} which occur at lower wavenumbers (*ca.* 50 cm^{-1}) compared with those of $[AuW(\mu\text{-}CC_6H_4Me\text{-}4)(C_6F_5)(CO)_2(cp)]$ (2019, 1955 cm^{-1}). These differences indicate a significantly higher electron density at the tungsten

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 IR data[a]

Complex	Colour	$\tilde{\nu}$(CO)/cm^{-1}	$\tilde{\nu}$(CN)/cm^{-1}
1 $[W\{\equiv CN(Et)Me\}(CO)_2(cp)]$	Yellow	1944, 1858	1576
2 $[AuW\{\mu\text{-}CN(Et)Me\}(C_6F_5)(CO)_2(cp)]$	Red	1970, 1893	1555[b]
3 $[\{CuW\{\mu\text{-}CN(Et)Me\}Cl(CO)_2(cp)\}_2]$	Red	1966, 1892	1555
5a $[Au\{W[\mu\text{-}CN(Et)Me](CO)_2(cp)\}_2]PF_6$	Red	1983, 1910	1567
5b $[Cu\{W[\mu\text{-}CN(Et)Me](CO)_2(cp)\}_2]PF_6$	Red	1966, 1895	1563[c]
5c $[Ag\{W[\mu\text{-}CN(Et)Me](CO)_2(cp)\}_2]NO_3$	Orange	1969, 1895	1564[d]
6 $[W\{\equiv CN(Et)(H)Me\}(CO)_2(cp)][SO_3CF_3]$	Red	1974, 1913[e]	

[a] In dichloromethane. [b] $\nu(C_6F_5)$ frequencies at 1498, 1452, 1048 and 953 cm^{-1} (KBr disc). [c] $\nu(PF_6)$ 836 cm^{-1}. [d] N–O stretch (asym) (ν_1) 1397 and 1296 cm^{-1}, (sym) (ν_3) 1020 cm^{-1}; out-of-plane deformation (ν_2) 818 cm^{-1}.[11] [e] The ν(CN) frequency cannot be assigned (see Results and Discussion section); $\nu(SO_3CF_3)$ frequencies at 1260, 1161 and 1031 cm^{-1} (KBr disc).

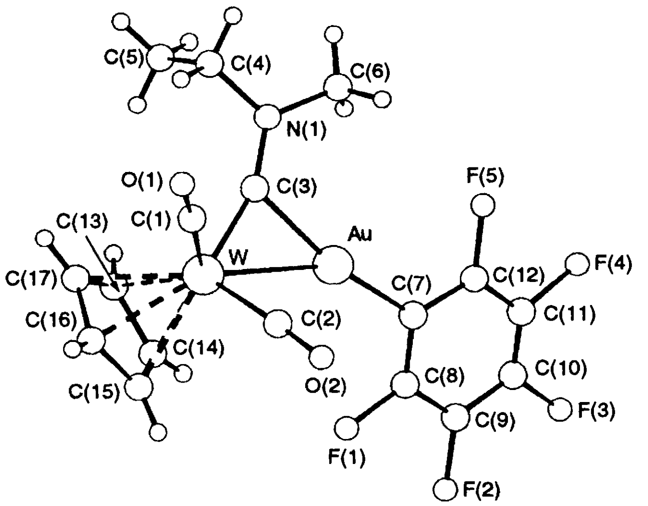


Fig. 1 The solid-state molecular structure of complex **2** showing the atom labelling scheme

atom in complex **2**, very likely as a consequence of the π donation from the nitrogen atom. There is strong evidence for the π-bond character in the μ-C–N interaction, both from the molecular structure (see later) and from the ν(C=N) IR absorption which occurs at 1555 cm^{-1}, within the range of the bridging aminocarbyne ligand $\mu\text{-}C{=}NR_2$ ($NR_2 = NMe_2$ or NC_5H_{10}) in homodinuclear complexes.[5] It is worth noting that the differences between complex **2** and $[AuW(\mu\text{-}CC_6H_4Me\text{-}4)(C_6F_5)(CO)_2(cp)]$ parallel well those between their corresponding mononuclear precursors $[W\{\equiv CN(Et)Me\}(CO)_2(cp)]$ **1** and $[W\{\equiv CC_6H_4Me\text{-}4\}(CO)_2(cp)]$, respectively.[8,10] In fact, complex **1** shows a higher field resonance for the carbyne carbon (δ 265.8 *vs.* δ 300.1) as well as lower ν(CO) absorptions (1944, 1858 cm^{-1} *vs.* 1990, 1919 cm^{-1}), *i.e.* the specific characteristics of the mononuclear aminocarbyne complexes are largely maintained in the corresponding dinuclear derivatives (see also section on molecular structure).

The great tendency of the aminocarbyne complex to add d^{10} metal fragments is confirmed from its reaction with CuCl. Treatment of a thf (tetrahydrofuran) solution of **1** with a slight excess of anhydrous CuCl readily affords the red, air-stable complex $[\{CuW\{\mu\text{-}CN(Et)Me\}Cl(CO)_2(cp)\}_2]$ **3** in about 70% yield. Its nature has been established by an X-ray diffraction study (Fig. 2). A comparison of the spectroscopic data characterising this species (Tables 1 and 2) with those found for the gold derivative **2** indicates a strict analogy between the two complexes. The effect of the different coinage metal may be observed in both the ^{1}H and ^{13}C NMR spectra which show a small but constant high-field shift of the signals for complex **3**, probably due to the lower deshielding character of the CuCl group.

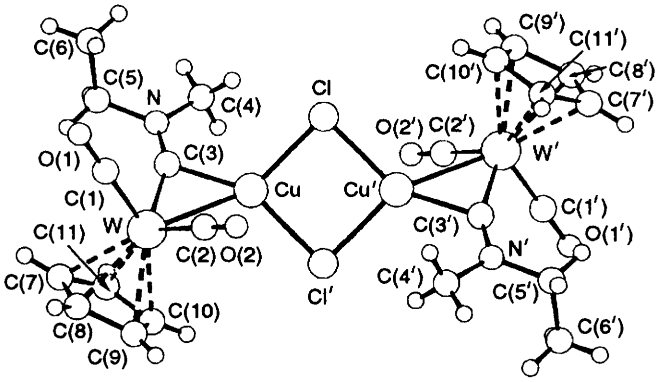


Fig. 2 The solid-state molecular structure of complex **3** showing the atom labelling scheme. Hydrogen atoms bear the same labelling as their corresponding carbon atoms

The cationic triphenylphosphine fragments $[M(PPh_3)]^+$ (M = Cu, Ag or Au), also react with complex **1**. In all three cases studied a simple adduct of the type $[MW\{\mu\text{-}CN(Et)Me\}(CO)_2(cp)(PPh_3)]^+$ **4** was not isolated in pure form. However, in the reaction with $[Au(PPh_3)]^+$, complex **4a** (M = Au) has been obtained in a mixture with other derivatives. The reactions investigated are described below.

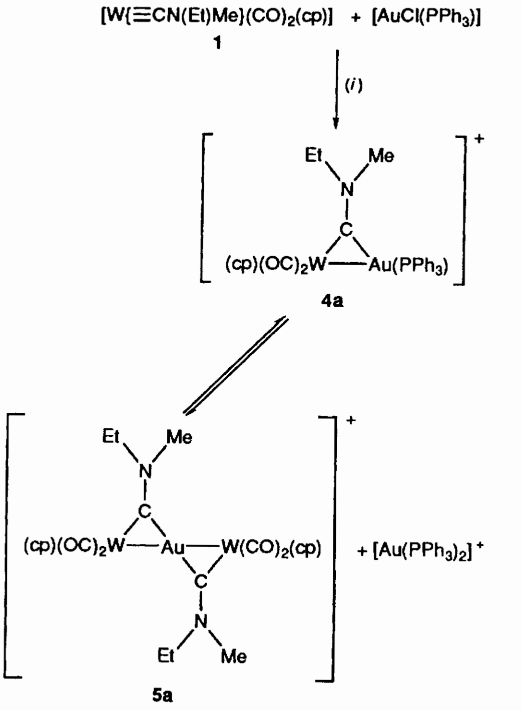
Treatment of a thf solution of $[Au(PPh_3)]^+$, obtained from $[AuCl(PPh_3)]$ and $AgSO_3CF_3$, with an equimolar amount of complex **1** affords a red solid which, upon spectroscopic investigation, reveals the presence of a mixture of products. Several dimetallacyclopropene complexes have shown the ability to add a carbene-like metal ligand to form trimetal derivatives; the tendency toward trinuclear carbyne-containing complexes is particularly evident in the case of $[AuW(CO)_2(cp)(PPh_3)(\mu\text{-}CC_6H_4Me\text{-}4)]^+$ which disproportionates in solution to give $[Au\{W(CO)_2(cp)(\mu\text{-}CC_6H_4Me\text{-}4)\}_2]^+$ and $[Au(PPh_3)_2]^+$.[12] Therefore, in view of similar chemical properties between the aminocarbyne and carbyne, the formation of both dinuclear, **4a**, and trinuclear, **5a**, derivatives as depicted in Scheme 2 could be predicted.

This assumption is in agreement with the NMR spectra of the red product, which consists of the signals due to $[AuW\{\mu\text{-}CN(Et)Me\}(CO)_2(cp)(PPh_3)]^+$ **4a**, $[Au\{W[\mu\text{-}CN(Et)Me](CO)_2(cp)\}_2]^+$ **5a** and $[Au(PPh_3)_2]^+$ species. The peak assignments reported in Table 2 have been made from comparison with the data for complex **5a** which was prepared by reacting 2 equivalents of complex **1** with [AuCl(tht)] in the presence of $TlPF_6$. Characteristic signals in the $^{13}C\text{-}\{^1H\}$ NMR spectrum of the mixture are a singlet at δ 266.9 (**5a**) and a doublet at δ 264.0 [*J*(PC) = 28.7 Hz] (**4a**) due to the bridging carbon atoms in the respective complexes which occur in the range expected. The presence of the equilibrium mixture described in Scheme 2 has been confirmed from the ^{1}H NMR

Table 2 Hydrogen-1 and carbon-13 NMR data[a]

Complex	^1H	$^{13}C-\{^1H\}$
1[b]	1.13 [t, 3 H, NCH_2CH_3, J(HH) 7.2], 2.95 (s, 3 H, NCH_3), 3.14 [q, 2 H, NCH_2CH_3, J(HH) 7.2], 5.44 (s, 5 H, cp)	265.8 [μ-C, J(WC) 235], 226.0 [CO, J(WC) 189], 91.0 (cp), 47.6 (NCH_2CH_3), 37.7 (NCH_3), 13.7 (NCH_2CH_3)
2[b]	1.30 [t, 3 H, NCH_2CH_3, J(HH) 7.2], 3.36 (s, 3 H, NCH_3), 3.69 [q, 2 H, NCH_2CH_3, J(HH) 7.2], 5.76 (s, 5 H, cp)	259.6 [μ-C, J(WC) 174], 222.6 [CO, J(WC) 175], 136–152 (m, C_6F_5), 92.3 (cp), 53.1 (NCH_2CH_3), 39.8 (NCH_3), 14.0 (NCH_2CH_3)
3	1.13 [t, 3 H, NCH_2CH_3, J(HH) 7.2], 3.28 (s, 3 H, NCH_3), 3.55 [q, 2 H, NCH_2CH_3, J(HH) 7.2], 5.55 (s, 5 H, cp)	263.4 [μ-C, J(WC) 184], 222.6 [CO, J(WC) 181], 92.2 (cp), 41.5 (NCH_3), 13.8 (NCH_2CH_3)
4a	1.14 [t, 3 H, NCH_2CH_3, J(HH) 7.2], 3.22 (s, 3 H, NCH_3), 3.53 [q, 2 H, NCH_2CH_3, J(HH) 7.2], 5.77 (s, 5 H, cp), 6.8–7.4 (m, 15 H, PPh_3)	264.0 [d, μ-C, J(PC) 28.7], 220.8 [CO, J(WC) 175], 136–126 (C_6H_5), 92.8 (cp), 40.0 (NCH_3), 13.3 (NCH_2CH_3)
5a	1.22 [t, 3 H, NCH_2CH_3, J(HH) 7.2], 3.27 (s, 3 H, NCH_3), 3.58 [q, 2 H, NCH_2CH_3, J(HH) 7.2], 5.72 (s, 5 H, cp)	266.9 [μ-C, J(WC) 172], 221.8 [CO, J(WC) 168], 92.6 (cp), 41.0 (NCH_3), 13.3 (NCH_2CH_3)
5b[b,c]	1.21 [t, 3 H, NCH_2CH_3, J(HH) 7.2], 3.29 (s, 3 H, NCH_3), 3.56 [q, 2 H, NCH_2CH_3, J(HH) 7.2], 5.71 (s, 5 H, cp), 6.8–7.4 (m, 15 H, PPh_3)	268.1 (μ-C), 220.0 [(CO), J(WC) 177], 135–129 (C_6H_5), 93.0 (cp), 53.4 (NCH_2CH_3), 39.8 (NCH_3), 13.5 (NCH_2CH_3)
5c[b,c]	1.17 [t, 3 H, NCH_2CH_3, J(HH) 7.2], 3.28 (s, 3 H, NCH_3), 3.53 [q, 2 H, NCH_2CH_3, J(HH) 7.2], 5.61 (s, 5 H, cp), 6.9–7.6 (m, 15 H, PPh_3)	265.7 (μ-C), 220.0 (CO), 135–129 (C_6H_5), 91.5 (cp), 53.7 (NCH_2CH_3), 41.2 (NCH_3), 13.8 (NCH_2CH_3)
6[d]	1.31 [t, 3 H, NCH_2CH_3, J(HH) 7.2], 3.40 (s, 3 H, NCH_3), 3.72 (q, 2 H, NCH_2CH_3, J(HH) 7.2], 5.49 (s, br, 1 H, NH) 5.88 (s, 5 H, cp)	

[a] Chemical shifts in ppm with $SiMe_4$ as internal standard, coupling constants in Hz; room temperature. ^1H and ^{13}C NMR spectra measured in CD_2Cl_2 unless otherwise stated (with this solvent the signal of the NCH_2CH_3 carbon is not observed). [b] ^{13}C NMR spectrum measured in $CDCl_3$. [c] ^1H NMR spectrum measured in $CDCl_3$. [d] ^1H NMR spectrum measured in CD_3NO_2.



Scheme 2 (*i*) $AgSO_3CF_3$, $-AgCl$

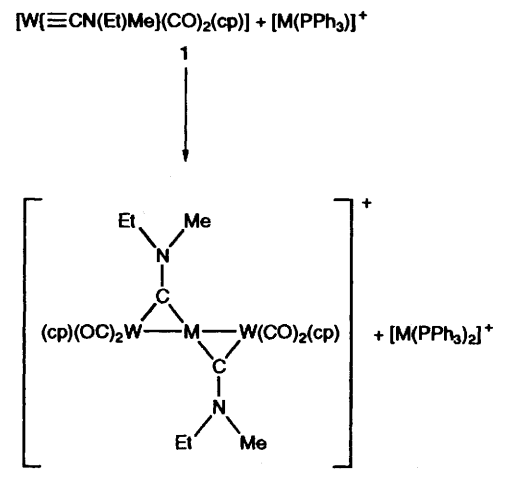
spectrum which does not vary with time and exhibits two singlets for the cyclopentadienyl ligand at δ 5.77 (**4a**) and δ 5.72 (**5a**) and two for the NCH_3 protons at δ 3.22 (**4a**) and 3.27 (**5a**). In addition, two sets of the signals expected for the $N(CH_2CH_3)$ protons are also observed. From the relative intensities, it has been estimated that at equilibrium **4a** and **5a** are present in a ratio of *ca.* 1 : 1. Finally, the ^{31}P NMR spectrum shows two peaks, one at δ 55.3 ascribed to the PPh_3 ligands of the dinuclear complex **4a** and the other at δ 45.5 for the $[Au(PPh_3)_2]^+$ cation.

The IR spectrum of the mixture in CH_2Cl_2 shows two strong, broad ν(CO) bands at 1983 and 1910 cm^{-1} and a broad band at 1567 cm^{-1} for ν(μ-CN). Since these absorptions are identical to those of complex **5a**, the IR analysis is not indicative of the nature or the composition of the mixture.

Complex **1** reacts readily with $[Cu(PPh_3)]PF_6$ {from $[CuI(PPh_3)]$ and $TlPF_6$} and also with $[Ag(NO_3)(PPh_3)]$ in dichloromethane to form the corresponding trinuclear derivatives $[M\{W[\mu\text{-}CN(Et)Me](CO)_2(cp)\}_2]^+$ (M = Cu **5b** or Ag **5c**) and $[M(PPh_3)_2]^+$ (Scheme 3). Unfortunately, all efforts to separate these complexes from $[M(PPh_3)_2]^+$ have failed.

The nature of the aminocarbyne derivatives has been assigned on the basis of spectroscopic data which are similar to those of **5a** [*i.e.* μ-C at δ 268.1 (**5b**) and δ 265.7 (**5c**)]. Contrary to the case for gold, there is no evidence for the presence of complexes of type **4** among the reaction products and the ^{31}P NMR spectra exhibit only one peak at δ 12.5 and two peaks at δ 2.0 and δ −143.5 for **5c** and **5b** respectively. The latter is a heptet [J(PF) 702 Hz] that can be assigned to the PF_6^- anion. These chemical shift values fit those reported in the literature for the $[Ag(PPh_3)_2]^+$ and $[Cu(PPh_3)_2]^+$ complexes.[13]

The results discussed strongly indicate that the chemistry of $[W\{\equiv CN(Et)Me\}(CO)_2(cp)]$ is similar to that of analogous alkylidyne complexes. These similarities are also found for the dinuclear complexes. For example, the treatment of $[AuW\{\mu\text{-}CN(Et)Me\}(C_6F_5)(CO)_2(cp)]$ **2** with nucleophiles such as $PMePh_2$, $NEtH_2$, CN^- or H^- results in metal–metal bond cleavage with concomitant formation of the free aminocarbyne **1**. However, since it has been reported[11] that the protonation reactions of dinuclear alkylidyne complexes vary greatly depending on the nature of the μ-carbon substituent, we



M
5b Cu
5c Ag

Scheme 3

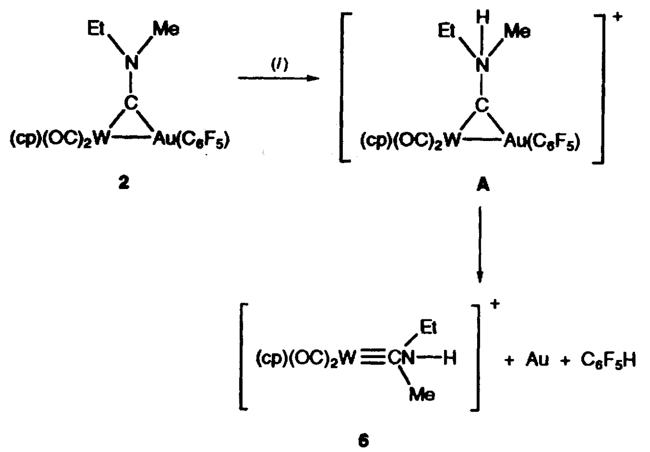
have extended these reactions to [AuW{μ-CN(Et)Me}(C_6F_5)$(CO)_2$(cp)].

The reaction of complex **2** with a small excess of HSO_3CF_3 in CH_2Cl_2 at −50 °C affords a red, slightly soluble oil that, on standing at room temperature, becomes more and more soluble with concomitant deposition of metallic gold. The IR spectrum of the same solution shows, in the carbonyl region, four bands at 1997, 1974, 1942 and 1913 cm^{-1} whose relative intensities change on standing. The two bands at 1974 and 1913 cm^{-1} increase while the bands at 1997 and 1942 cm^{-1} decrease and disappear after about 3 h. Moreover, the ^1H NMR spectrum in CD_3NO_2, recorded immediately after the addition of HSO_3CF_3, appears rather complicated since the signals are all duplicated, suggesting the presence of a mixture of products. In addition, a broad resonance at δ 5.49 assigned to a NH proton and a multiplet at δ 7.10 due to the C_6F_5H molecule are present in the spectrum. However, as observed for the IR spectra, the relative intensities of the signals change with time and the final spectrum recorded for the red, crude product obtained after washing with diethyl ether is that reported in Table 2 for compound **6**.

It is reasonable to propose, on the basis of spectroscopic evidence, that the reaction of complex **2** with HSO_3CF_3 affords an unstable bimetallic intermediate, **A**, which in turn decomposes to give [W{≡CN(H)(Et)Me}$(CO)_2$(cp)]$^+$ **6**, metallic gold and C_6F_5H (Scheme 4). The ammonium-like salt **6** decomposes in solution precluding further NMR characterization.

It is noteworthy that the protonation of [W{≡CN(Et)Me}-$(CO)_2$(cp)] with HX (X = Br, I or SO_3CF_3) leads exclusively to the formation of an aminocarbene complex [W{=C(H)N(Et)Me}X$(CO)_2$(cp)].[14]

Molecular Structure of the Gold(I) *and Copper*(I) *Adducts of* [W{CN(Me)Et}$(CO)_2$(cp)].—The structure of the gold derivative [AuW{μ-CN(Et)Me}(C_6F_5)$(CO)_2$(cp)] **2** is shown in Fig. 1 and relevant bond lengths and angles in Table 3. The overall molecular configuration is asymmetric and the bonding of the Au(C_6F_5) fragment to the electron-precise aminocarbyne complex **1** leads to the formation of the AuWC triangle. The difference between complex **2** and its carbyne analogues[9] is the presence of the aminocarbyne ligand, which gives rise to significant differences in electronic structure. Unlike the normal carbynes, in which the carbyne atom is exclusively triply bonded to the metal atom [R–C≡W], the aminocarbynes possess a localized C–W and a delocalized N•••C•••W π bond.[15] These differences are scarcely relevant to the bonds in the AuWC triangle. The nitrogen atom is planar hybridized and can be described as an iminium cation involved in multiple bonding to the carbyne carbon [N–C(3) 1.29(2) Å]. The carbyne carbon exhibits substantially linear hybridization with some distortion [N–C(3)–W 160(1)°] and formally donates two electrons to the tungsten atom, assuming that the electron taken from the iminium atom is localized on the metal (N^+=C=W^-). While the N–C(3) distance supports the heteroallene formulation, the C(3)–W value indicates the role of the $N\overset{\cdots}{-}C\overset{\cdots}{-}W$ structure. The W–C(3) interaction, in spite of the involvement in the bond to the gold atom, is quite short [1.90(1) Å] and equal to the value found in the uncomplexed aminocarbyne cation [W(CNEt$_2$)$(CO)_5$]$^+$ [1.90(3) Å].[16] It is of interest that a longer bond has been reported for the complexed carbene derivative [AuW{μ-C(H)C_6H_4Me}$(CO)_2$(cp)-(PPh_3)] [2.27(1) Å].[11] These observations suggest that the short W–C(3) distance results from a significant contribution of the delocalized N•••C•••W π bond. In conclusion, the tungsten atom attains its closed electronic configuration with a mechanism which is somewhere inbetween the resonance structures N–C≡W and N^+=C=W^-.



Scheme 4 (*i*) HSO_3CF_3 in CH_2Cl_2 at −50 °C

Another structural feature to be considered is the planarity of the molecule if the ancillary CO, cp and Me groups are ignored. With respect to this molecular plane the two non-equivalent W–C (carbyne) π bonds can be defined as in-plane localized and orthogonal delocalized, respectively. The Au(C_6F_5) fragment attains the preferred two-co-ordinate 14-electron configuration by accepting an electron pair from the in-plane localized W–C (carbyne) π orbital, resembling the co-ordination of an olefin ligand. This interaction perturbs, but does not disrupt, the electronic structure of the donor. In relation to these differences between carbynes and aminocarbynes, the Au–W and Au–C(3) distances [2.727(1) and 2.13(2) Å, respectively] can be compared with the corresponding values in compounds such as [AuWBr(bipy)(C_6F_5)$(CO)_2$(μ-CC_6H_4Me-4)] (bipy = 2,2′-bipyridine) [2.783(1) and 2.080(3) Å][9] and [Au{W$(CO)_2$(cp)-(μ-CC_6H_4Me-4)}$_2$]$^+$ [2.752(1) and 1.83(2) Å].[17]

The molecular structure of the copper adduct [{CuW-{μ-CN(Et)Me}(μ-Cl)$(CO)_2$(cp)}$_2$] is reported in Fig. 2; it is dimeric and contains a quasi regular Cu_2Cl_2 square placed around an inversion centre in the crystal [Cu–Cl 2.32_{av} Å, Cl′–Cu–Cl 91.4(2)°]. The copper(I) ions attain a 16-electron configuration by co-ordination of the in-plane W–C π bond, in much the same way as in the gold(I) derivative. The dihedral angle between the Cu_2Cl_2 square and the CuWCN fragment is 36.7° and a flatter geometry seems hindered by the Cl•••Me contacts [Cl•••H(4C) 2.70(1) Å, sum of their van der Waals radii *ca.* 2.95 Å], see Fig. 2. This geometric feature shows further that the W=C group binds to acidic fragments with a mechanism

Table 3 Selected bond lengths (Å) and angles (°) for [AuW{μ-CN(Et)Me}(C_6F_5)$(CO)_2$(cp)] **2**

Au–C(7)	2.07(2)	W–C(15)	2.37(1)
Au–C(3)	2.13(2)	W–C(14)	2.37(1)
Au–W	2.727(1)	W–C(13)	2.32(1)
W–C(3)	1.90(1)	N(1)–C(3)	1.29(2)
W–C(1)	1.95(1)	N(1)–C(4)	1.47(1)
W–C(2)	1.96(1)	N(1)–C(6)	1.47(1)
W–C(17)	2.29(1)	O(1)–C(1)	1.13(1)
W–C(16)	2.32(1)	O(2)–C(2)	1.14(1)
		C(4)–C(5)	1.54(1)
C–C(phenyl)$_{av}$	1.36(1),1.35(1),1.35(1)*		
C(7)–Au–C(3)	162.9(6)	C–F$_{av}$	1.34(2)
C(7)–Au–W	150.3(4)	C(3)–N(1)–C(4)	118(1)
N(1)–C(3)–W	160(1)	N(1)–C(4)–C(5)	108(2)
N(1)–C(3)–Au	115(1)	C(3)–N(1)–C(6)	126(2)
W–C(3)–Au	84.8(6)	C(4)–N(1)–C(6)	115(2)
C(1)–W–C(2)	81.2(7)	C(8)–C(7)–Au	120(1)
		C(12)–C(7)–Au	122(1)

* *Ortho*, *meta* and *para*, respectively.

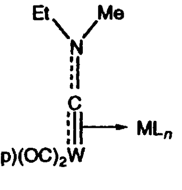
Table 4 Selected bond lengths (Å) and angles (°) for [{CuW{μ-CN(Et)Me}Cl$(CO)_2$(cp)}$_2$] **3**

W–C(3)	1.89(1)	Cu–Cl′	2.307(4)
W–C(1)	1.94(1)	Cu–Cl	2.324(4)
W–C(2)	1.96(1)	Cu ··· Cu′	3.233(3)
W–C(11)	2.31(1)	N–C(3)	1.30(1)
W–C(10)	2.33(1)	N–C(5)	1.44(2)
W–C(7)	2.33(1)	N–C(4)	1.45(2)
W–C(9)	2.37(1)	O(1)–C(1)	1.16(1)
W–C(8)	2.37(1)	O(2)–C(2)	1.16(1)
W–Cu	2.610(1)	C(5)–C(6)	1.53(2)
Cu–C(3)	2.01(1)		
C(1)–W–C(2)	83.0(6)	C(5)–N–C(4)	114(1)
C(3)–Cu–Cl	116.7(4)	N–C(3)–W	154.6(9)
Cl′–Cu–Cl	91.4(2)	N–C(3)–Cu	120.6(8)
Cl′–Cu–W	112.6(1)	W–C(3)–Cu	84.0(5)
C(3)–N–C(5)	123(1)	N–C(5)–C(6)	110(1)
C(3)–N–C(4)	123(1)		

Symmetry transformations used to generate equivalent atoms: $-x, -y+1, -z+1$.

similar to that of the unsaturated hydrocarbons; in fact, all the known three-co-ordinate d^{10} complexes containing olefins or acetylenes have planar configurations. The co-ordinated molecule W{CN(Me)Et}$(CO)_2$(cp) has a geometry strictly comparable to that in the gold derivative [N–C(3) 1.30(1), C(3)–W 1.89(1) Å, N–C(3)–W 154.6(9)°].

The Cu–W and Cu–C(3) interactions [2.610(1) and 2.01(1) Å, respectively] are both 0.12 Å shorter than the corresponding values in the gold analogue and give an indication of the difference in atomic size between the two coinage metals in the same oxidation state but with inequivalent co-ordination geometries. Table 4 reports the relevant bond lengths and angles. The rationalisation of the anchoring mode of the acidic fragment, ML$_n$ to the molecular complex **1** is depicted below. This bonding model is the simplest among those put forward for analogous complexes containing the dimetallacyclopropene ring and combines observation of the valence rules for the metal centres with structural and spectroscopic evidence.[9]



Experimental

All reactions were carried out under dry argon using standard Schlenk techniques. Solvents were purified according to standard procedures and distilled prior to use. The IR spectra were recorded on a Perkin-Elmer 983-G spectrometer, ^{1}H and ^{13}C NMR spectra on a Varian Gemini 200 spectrometer and ^{31}P NMR spectra on a Varian Gemini 300 spectrometer (85% H_3PO_4 external standard). Elemental analyses were determined by Pascher Microanalytical Laboratorium (Remagen, Germany). Melting points are uncorrected. The compounds [AuCl(tht)], [Au(C_6F_5)(tht)],[18] CuCl,[19] [CuI(PPh_3)][20] and [Ag(NO_3)(PPh_3)][21] were prepared or purified by literature methods. The aminocarbyne [W{≡CN(Et)Me}$(CO)_2$(cp)] was synthesized by methods analogous to those previously reported.[8]

Syntheses.—[AuW{μ-CN(Et)Me}(C_6F_5)$(CO)_2$(cp)] **2**. A solution of **1** (109 mg, 0.29 mmol) in thf (30 cm^3) was treated with [Au(C_6F_5)(tht)] (157 mg, 0.35 mmol). After 30 min at room temperature the solution was filtered through a Celite pad (*ca.* 2 × 3 cm) and the solvent evaporated to dryness. The resulting red residue was crystallized from CH_2Cl_2–light petroleum (b.p. 30–40 °C) at −20 °C to give red crystals (146 mg, 68%) (Found: C, 27.80; H, 1.80; N, 1.90. Calc. for $C_{17}H_{13}AuF_5NO_2W$: C, 27.65; H, 1.75; N, 1.90%). M.p. 95 °C (decomp.).

[{CuW{μ-CN(Et)Me}Cl$(CO)_2$(cp)}$_2$] **3**. To a solution of **1** (29 mg, 0.077 mmol) in thf (25 cm^3) was added solid CuCl (11 mg, 0.11 mmol). After stirring at room temperature for 30 min the solution was filtered through a Celite pad (*ca.* 2 × 3 cm) and concentrated *in vacuo*. The compound was crystallized from thf–light petroleum at −20 °C to give red crystals (26 mg, 71%) (Found: C, 27.45; H, 2.70; N, 3.00. Calc. for $C_{11}H_{13}ClCuNO_2W$: C, 27.85; H, 2.75; N, 2.95%). M.p. 165 °C (decomp.).

[Au{W[μ-CN(Et)Me](CO)$_2$(cp)}$_2$]PF_6 **5a**. A mixture of [AuCl(tht)] (22 mg, 0.070 mmol) and $TlPF_6$ (69 mg, 0.21 mmol) in thf (10 cm^3) was stirred for 15 min. After this time solid aminocarbyne [W{≡CN(Et)Me}$(CO)_2$(cp)] (50 mg, 0.14 mmol) was added and stirring was continued for 20 min. The mixture was then filtered through Celite and after removal of the solvent *in vacuo* a red powder (55 mg, 82%) was obtained (Found: C, 23.10; H, 2.35; N, 2.65. Calc. for $C_{22}H_{26}AuF_6N_2O_4PW_2$: C, 24.20; H, 2.40; N, 2.55%).

Reactions of [W{≡CN(Et)Me}$(CO)_2$(cp)] **1**.—*With* [AuCl(PPh_3)]. A solution of [AuCl(PPh_3)] (201 mg, 0.40 mmol) in thf (50 cm^3) was treated with $AgSO_3CF_3$ (102 mg, 0.40 mmol). After filtration to remove AgCl, complex **1** (149 mg, 0.40 mmol) was added. The mixture was stirred for 30 min and then filtered through a Celite pad (*ca.* 2 × 3 cm). The solvent was removed *in vacuo* and the oily residue washed twice with diethyl ether (2 × 15 cm^3). A red powder (254 mg) containing [AuW{μ-CN(Et)Me}$(CO)_2$(cp)(PPh_3)][SO_3CF_3] **4a**, [Au{W[μ-CN(Et)Me](CO)$_2$(cp)}$_2$][SO_3CF_3] **5a** and [Au(PPh_3)$_2$][SO_3CF_3] was obtained.

With [CuI(PPh_3)]. A mixture of complex **1** (50 mg, 0.13 mmol) and $TlPF_6$ (70 mg, 0.2 mmol) in CH_2Cl_2 (30 cm^3) was treated with [CuI(PPh_3)] (61 mg, 0.13 mmol). After stirring for 1 h, during which time the suspension turned red, IR spectra and TLC showed that all the starting aminocarbyne was consumed. The suspension was filtered through a Celite pad (*ca.* 2 × 3 cm) and removal of the solvent *in vacuo* afforded a red powder (90 mg) containing [Cu{W[μ-CN(Et)Me](CO)$_2$(cp)}$_2$]PF_6 **5b** and [Cu(PPh_3)$_2$]PF_6.

With [Ag(NO_3)(PPh_3)]. Complex **1** (41 mg, 0.11 mmol) was treated with [Ag(NO_3)(PPh_3)] (47 mg, 0.11 mmol) in CH_2Cl_2

Table 5 Crystal data and experimental details for complexes **2** and **3**

	2	**3**
Formula	$C_{17}H_{13}AuF_5NO_2W$	$C_{22}H_{26}Cl_2Cu_2N_2O_4W_2$
M	739.1	948.1
T/K	293	293
System	Triclinic	Monoclinic
Space group	$P\bar{1}$(no. 2)	$P2_1/a$ (no. 14)
a/Å	9.840(5)	7.788(2)
b/Å	11.577(6)	14.880(5)
c/Å	8.296(6)	11.712(5)
α/°	99.03(5)	90
β/°	91.01(6)	95.35(3)
γ/°	81.92(4)	90
U/Å^3	924.1(1)	1351.3(1)
Z	2	2
F(000)	672	888
Crystal size/mm	0.15 × 0.23 × 0.35	0.12 × 0.25 × 0.28
λ(Mo-Kα)/Å	0.710 69	0.710 69
μ(Mo-Kα)/mm^{-1}	14.2	9.93
θ range/°	2.5–25	2.5–25
ω scan width/°	0.9	0.9
Octants explored	$\pm h, k, \pm l$	$\pm h, k, l$
Measured reflections	3428	4860
Unique reflections used in the refinement	3250	2362
No. of refined parameters	229	146
Goodness of fit on F^2	1.01	0.98
Final R indices [$I > 2\sigma(I)$] R_1 (on F), wR_2 (on F^2)*	0.047, 0.098	0.044, 0.091

* $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

Table 6 Atomic coordinates (× 10^4) for complex **2**

Atom	x	y	z
Au	22 541(6)	24 458(5)	3 804(7)
W	25 955(5)	7 059(5)	22 779(7)
N(1)	4 652(14)	2 577(13)	2 510(18)
O(1)	5 340(11)	−890(13)	2 530(19)
O(2)	2 659(14)	−745(12)	−1 191(13)
F(1)	−833(15)	2 459(13)	−715(19)
F(2)	−2 440(20)	3 787(19)	−2 523(26)
F(3)	−1 521(27)	5 498(16)	−3 742(18)
F(4)	1 141(26)	5 906(14)	−3 200(18)
F(5)	2 795(19)	4 535(14)	−1 511(21)
C(1)	4 338(11)	−300(11)	2 416(22)
C(2)	2 666(15)	−182(12)	60(11)
C(3)	3 695(14)	1 918(13)	2 168(19)
C(4)	5 494(19)	2 441(18)	3 966(21)
C(5)	4 753(33)	3 247(28)	5 429(34)
C(6)	4 971(28)	3 499(23)	1 591(36)
C(7)	1 037(17)	3 440(12)	−1 105(19)
C(8)	−296(17)	3 300(16)	−1 328(21)
C(9)	−1 147(24)	3 950(19)	−2 243(24)
C(10)	−686(24)	4 821(20)	−2 893(22)
C(11)	636(23)	4 980(18)	−2 654(22)
C(12)	1 499(8)	4 326(7)	−1 756(9)
C(13)	1 226(8)	1 659(7)	4 473(9)
C(14)	303(8)	1 362(7)	3 189(9)
C(15)	454(8)	112(7)	2 800(9)
C(16)	1 470(8)	−364(7)	3 843(9)
C(17)	1 947(8)	593(7)	4 878(9)

Table 7 Atomic coordinates (× 10^4) for complex **3**

Atom	x	y	z
W	21 939(5)	46 639(3)	19 563(4)
Cu	1 245(2)	5 067(1)	3 974(1)
Cl	181(6)	6 097(3)	5 221(4)
N	4 313(14)	6 042(8)	3 502(9)
O(1)	1 878(14)	6 328(9)	347(9)
O(2)	−1 802(12)	4 883(10)	1 903(8)
C(1)	1 970(16)	5 701(8)	945(9)
C(2)	−317(10)	4 804(12)	1 941(10)
C(3)	3 141(15)	5 496(8)	3 056(9)
C(4)	4 492(21)	6 289(14)	4 703(17)
C(5)	5 622(17)	6 422(11)	2 859(14)
C(6)	5 183(21)	7 396(15)	2 537(18)
C(7)	4 319(12)	3 966(6)	998(8)
C(8)	2 717(13)	3 644(7)	478(6)
C(9)	1 897(10)	3 158(7)	1 318(8)
C(10)	2 992(14)	3 180(7)	2 358(6)
C(11)	4 489(11)	3 680(7)	2 160(8)

(20 cm^3). The yellow solution immediately turned orange and after 1 h of stirring at room temperature the mixture was worked-up as described above giving an orange powder (82 mg) containing $[Ag\{W[\mu\text{-}CN(Et)Me](CO)_2(cp)\}_2]NO_3$ **5c** and $[Ag(PPh_3)_2]NO_3$.

Structure Determinations of Complexes **2** *and* **3**.—Crystal data and details of measurements are reported in Table 5.

Diffraction intensities for both species were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature. Both structures were solved by direct methods and refined by full-matrix least squares (based on F^2) using the SHELXS 86 and SHELXL 93 suit of programs.[22] Absorption corrections were applied by azimuthal scans of some reflections.[23] All non-hydrogen atoms were allowed to vibrate anisotropically; a 'rigid body' model was applied to the cyclopentadienyl rings (C–C 1.42, C–H 0.93 Å), while the phenyl C–C distances in **2** were constrained to a C_{2v} symmetry. The H atoms were added in calculated positions (C–H 0.97 and 0.96 Å for methylene and methyl hydrogens, respectively) with their thermal parameters fixed to 1.2 times the equivalent isotropic thermal parameter of their parent C atoms. The final ΔF maps contained peaks not exceeding 0.8 e Å^{-3} in the proximity of the Au atom for **2** and 1.1 e Å^{-3} in the proximity of the W atom for **3**.

Fractional atomic coordinates for **2** and **3** are listed in Tables 6 and 7, respectively.

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

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