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The synthesis of cationic trimetallic clusters with Au–W bonds. Crystal structure of $[\text{AuW}_2(\mu\text{-CR})_2(\text{CO})_4(\text{bipy})_2\text{Cl}_2] \cdot \text{PF}_6$ (R = C₆H₄Me-4)

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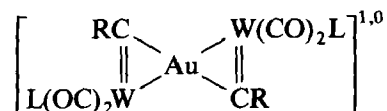
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Abstract

Reactions of the tungsten carbyne complexes $[\text{W}(\equiv\text{CR})(\text{CO})_2(\text{L} \wedge \text{L})\text{X}]$ (R = C₆H₄Me-4; L \wedge L = 2,2-bipyridine (bipy); X = Cl or Br), with $[\text{AuCl}(\text{tht})]$ (tht = tetrahydrothiophene) and TIPF_6 have given the cationic complexes of general formulae $[\text{AuW}_2(\mu\text{-CR})_2(\text{CO})_4(\text{L} \wedge \text{L})_2\text{XX}']\text{PF}_6$, where X or X' = Cl or Br. The compound with X = X' = Cl has been characterized by X-ray diffraction.

Introduction

The tungsten carbyne complexes $[\text{W}(\equiv\text{CR})(\text{CO})_2\text{L}]$ (L = $\eta^5\text{-C}_5\text{H}_5$, or $\text{HB}(\text{Pz})_3$; R = CH₃, or C₆H₄Me-4) and the anionic $[\text{W}(\equiv\text{CR})(\text{CO})_2(\eta\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]^-$, (R = C₆H₄Me-4), (R = C₆H₄Me-4), have been used [1] to prepare trimetallic clusters with a $[\text{W}_2\text{Au}]$ spine and two bridging carbyne ligands of the general type:



We describe here the results from a study in which the related neutral octahedral carbynes $[\text{W}(\equiv\text{CR})(\text{CO})_2(\text{L} \wedge \text{L})\text{X}]$ (L \wedge L = chelate ligand, X = Cl or Br) [2,3] were similarly employed.

Results and discussion

Reaction of the alkylidyne complex $[W(\equiv CR)(CO)_2(bipy)Cl]$ ($R = C_6H_4Me-4$) (Ia) (Fig. 1) with $[AuCl(tht)]$ (molar ratio 2/1) in the presence of $TlPF_6$ gave the orange salt $[AuW_2(\mu-CR)_2(CO)_4(bipy)_2Cl_2]PF_6$ (IIa), analogous to the known species $[AuW_2(\mu_2-CR)_2(CO)_4L_2]PF_6$ where L is an η^5 -anionic ligand [1].

The structure shown in Fig. 1b was consistent with the analytical and spectroscopic data * (see Experimental section) and was confirmed by X-ray crystallography (see below). The results of the X-ray diffraction study are given in Tables 1 and 2, and the structure of the cation of the salt IIa is shown in Fig. 2.

The cation contains a W–Au–W framework with the two Au–W bonds bridged by CC_6H_4Me-4 groups. The trimetallic linkage is not linear ($W(1)-Au-W(2)$ $152.1(1)^\circ$), and the dihedral angle between the planes defined by the two rings WCAu is 50.95° .

The Au–W separations (average value $2.781(1)$ Å) and the W– μC distances (average value $1.910(6)$ Å) are close to those in the bridging alkylidyne complexes $[AuW(\mu-CC_6H_4Me-4)(CO)_2(bipy)(C_6F_5)Br]$ [4] and $[AuW_2(\mu-CC_6H_4Me-4)_2(CO)_4(\eta^5-C_5H_5)_2]^+$ [1a]. These values suggest the presence of a Au–W interaction and a double bond $W=C$.

The Au– μC distances ($1.937(6)$ and $2.154(6)$ Å), which are in the range observed for the other cationic clusters of this type [1], and the nearly linear C–Au–C arrangement ($171.0(2)^\circ$) suggest that there are C–Au σ -bonds. There is, however, a ca. 0.2 Å difference between the two Au– μC distances that is not reflected in the Au–W and W– μC bond lengths. In the absence of a satisfactory explanation, this can be attributed to a crystal packing effect. However a similar feature although much less pronounced, has been observed for other compounds containing two sigma Au–C bonds [5].

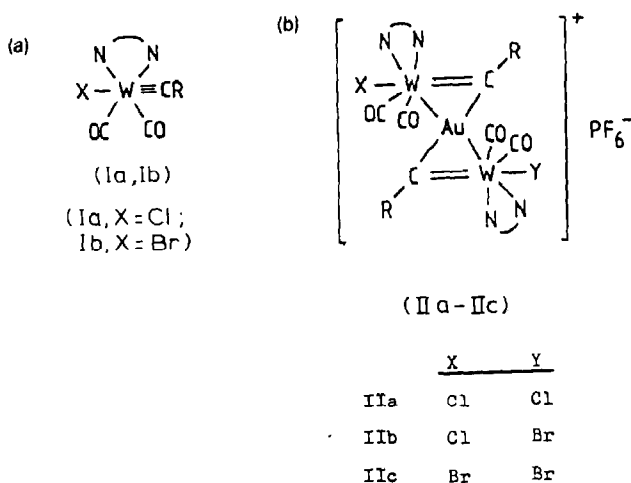


Fig. 1. $R = C_6H_4Me-4$; $N \wedge N = bipy$.

* The carbon of the bridging CR could not be observed in the weak ^{13}C NMR spectrum due to the insufficient solubility of the compound.

Table 1

Final atomic coordinates ($\times 10^5$ for Au and W; $\times 10^4$ otherwise) and equivalent isotropic thermal parameters for compound IIa

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Au	66127(2)	75031(2)	12487(2)	2.70(1)
W(1)	50411(2)	76327(2)	9731(2)	2.91(1)
W(2)	80688(2)	81922(2)	14655(2)	2.64(1)
Cl(1)	3714(1)	8065(1)	1341(1)	2.50(1)
Cl(2)	9254(1)	8957(1)	1044(1)	2.49(4)
P	909(1)	6201(1)	1283(1)	4.44(4)
F(1)	1104(3)	5349(3)	1802(3)	5.29(12)
F(2)	1509(3)	5939(4)	612(3)	7.91(17)
F(3)	1512(4)	6745(3)	1790(3)	7.99(18)
F(4)	273(3)	5681(3)	733(4)	7.67(16)
F(5)	273(4)	6421(3)	1944(5)	10.86(25)
F(6)	5733(2)	7978(3)	5756(4)	8.20(14)
C(1)	4428(3)	6831(4)	227(5)	4.65(16)
O(1)	4042(3)	6366(3)	-147(3)	6.95(15)
C(2)	4975(3)	8434(4)	-64(5)	4.53(15)
O(2)	4881(3)	8879(3)	-646(3)	6.66(13)
C(3)	7980(5)	9129(4)	2431(7)	8.65(26)
O(3)	7931(4)	9617(3)	2905(3)	7.60(16)
C(4)	8886(3)	7619(4)	2353(4)	3.49(13)
O(4)	9267(3)	7331(4)	2841(3)	7.30(16)
N(11)	5016(3)	6926(4)	2208(3)	4.73(13)
C(11)	4904(3)	6099(4)	2210(5)	4.28(15)
C(12)	4802(4)	5695(6)	2958(5)	6.99(22)
C(13)	4875(3)	6181(6)	3782(5)	6.67(22)
C(14)	5947(3)	7039(5)	3751(5)	5.28(18)
C(15)	5161(3)	7388(4)	2914(4)	4.28(15)
C(16)	5422(3)	8220(4)	2849(4)	3.60(13)
C(17)	5679(4)	8767(5)	3516(4)	6.01(20)
C(18)	5906(5)	9602(5)	3287(6)	8.17(27)
C(19)	5848(5)	9893(5)	2452(5)	6.48(21)
C(20)	5566(3)	9326(4)	1840(5)	4.65(16)
N(20)	5375(2)	8529(3)	1958(3)	3.73(11)
N(21)	8202(2)	7463(3)	279(3)	3.31(10)
C(21)	8674(3)	6657(4)	356(5)	5.92(18)
C(22)	8779(4)	6300(4)	-485(4)	4.62(15)
C(23)	8460(4)	6558(4)	-1227(4)	4.68(16)
C(24)	7994(3)	7318(4)	-1272(4)	3.89(14)
C(25)	7928(2)	7707(3)	-475(3)	2.24(10)
C(26)	7497(3)	8460(3)	-447(3)	2.74(11)
C(27)	7111(3)	8755(4)	-1100(4)	4.49(15)
C(28)	6672(3)	9520(4)	-1097(4)	5.10(16)
C(29)	6681(3)	9929(4)	-242(3)	3.33(12)
C(30)	7146(3)	9553(3)	424(4)	3.95(14)
N(30)	7491(2)	8836(2)	377(3)	3.66(11)
C(41)	5837(3)	7170(4)	365(4)	6.81(17)
C(42)	6070(3)	6577(3)	-354(3)	2.91(11)
C(43)	5853(3)	6753(4)	-1242(3)	4.16(14)
C(44)	6222(4)	6194(5)	-1936(5)	6.61(21)
C(45)	6660(3)	5558(4)	-1678(4)	4.36(15)
C(46)	6519(3)	5817(4)	-102(3)	3.41(12)
C(47)	6831(3)	5341(5)	-781(5)	5.81(18)
C(48)	7052(4)	5042(5)	-2319(4)	6.69(21)

Table 1 (continued)

Atom	x	y	z	B_{eq}
C(51)	7438(3)	7691(4)	2330(4)	5.65(17)
C(52)	7271(3)	7210(3)	3100(3)	2.89(12)
C(53)	6902(3)	6423(3)	3096(4)	3.75(13)
C(54)	6778(3)	6086(3)	3850(4)	3.92(14)
C(55)	6887(3)	6472(4)	4659(5)	5.02(17)
C(56)	7284(4)	7329(3)	4672(3)	3.75(13)
C(57)	7457(3)	7693(4)	3866(3)	3.29(12)
C(58)	6652(4)	6109(4)	5525(4)	5.30(17)

The coordination around the W atoms can be considered pseudooctahedral and does not call for comment.

The IR spectrum of IIa in acetone solution showed, together with its two $\nu(\text{CO})$ bands, two additional bands corresponding to the free carbyne Ia. However, the ^1H NMR spectrum in this same solvent (which was similar to that of Ia but with all the signals shifted to lower frequencies) did not show any peaks corresponding to Ia. These observations suggest that the equilibrium shown in equation 1 exists in acetone solution and is rapid in the NMR time scale. We also observed that if the ^1H NMR spectrum of a mixture of Ia and IIa is taken in acetone the peaks of the two compounds can be observed well separated, though slightly broadened. This fact can be explained by assuming that the excess of Ia shifts the equilibrium of equation 1 to the left, and that there is no rapid direct exchange between the free molecules of Ia and those coordinated to the tungsten in IIa.



The reaction of the carbyne-bromo complex Ib with $[\text{AuCl}(\text{tht})]$ and TIPF_6 gave,

Table 2

Selected bond lengths (\AA) and angles ($^\circ$) in $[\text{Au}\{\text{W}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{bipy})\text{Cl}\}_2]\text{PF}_6$ (IIa)

W(1)-Au	2.773(1)	N(11)-W(1)	2.206(4)
W(2)-Au	2.789(1)	N(20)-W(1)	2.144(4)
C(41)-Au	1.937(6)	C(41)-W(1)	1.875(6)
C(51)-Au	2.154(6)	C(51)-W(2)	1.945(6)
Cl(1)-W(1)	2.523(3)	F(5)-P	1.586(8)
C(1)-W(1)	1.997(6)	O(1)-C(1)	1.143(8)
C(2)-W(1)	2.043(6)	C(52)-C(51)	1.453(8)
W(2)-Au-W(1)	152.1(1)	C(2)-W(1)-Au	100.2(2)
C(41)-Au-W(1)	42.5(2)	C(2)-W(1)-C(1)	88.0(2)
C(41)-Au-W(2)	142.8(2)	N(11)-W(1)-Cl(1)	83.7(2)
C(51)-Au-W(1)	136.4(2)	N(20)-W(1)-Au	73.4(1)
C(51)-Au-W(2)	44.1(2)	C(41)-W(1)-Cl(1)	160.6(2)
C(51)-Au-C(41)	171.0(2)	O(1)-C(1)-W(1)	174.7(6)
Cl(1)-W(1)-Au	155.3(1)	W(1)-C(41)-Au	93.3(2)
C(1)-W(1)-Au	122.4(2)	C(42)-C(41)-W(1)	147.3(4)
C(1)-W(1)-Cl(1)	80.5(2)	W(2)-C(51)-Au	85.6(2)

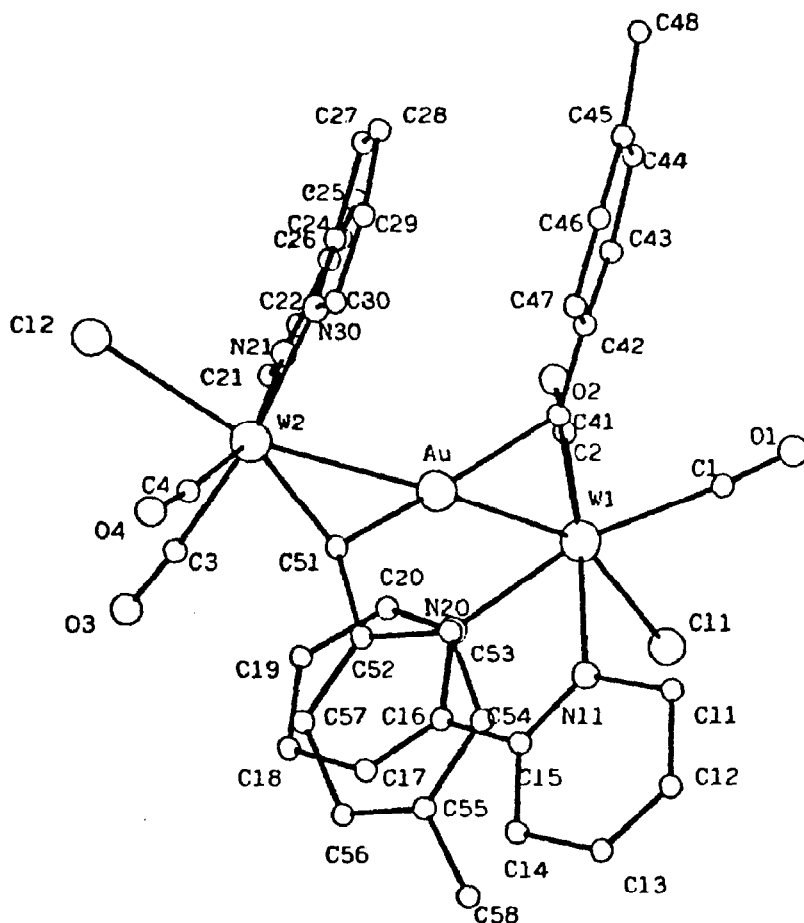


Fig. 2. The molecular structure of $[\text{AuW}_2(\mu_2\text{-CR})_2(\text{CO})_4(\text{bipy})_2\text{Cl}_2]^+$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$).

instead of the expected single product **Ic***, a mixture of products which contained the compounds **Ia**, **Ib** and **Ic** (Fig. 1b) having Cl or Br coordinated to the tungsten atom. This was evident from the complexity of the ^1H NMR spectrum of the product mixture, which, however, also showed clearly that **Ia** was present. Furthermore like the C_5H_5 analogue [1a], the product reacted with PPh_3 with displacement of the carbene molecules coordinated to the Au atom to give the carbynes **Ia** and **Ib** instead of only **Ib**.

Crystals were obtained by slow diffusion of diethyl ether into a acetone solution of the mixture of **Ia**–**Ic**, and when one of those crystals was selected and studied crystallographically it was found that it corresponded to the dichloro derivative **Ia** (see above).

The formation of **Ia** along with **Ib** and **Ic** in the reaction of **Ib** and $[\text{AuCl}(\text{tht})]$ with TIPF_6 is not surprising, because, as shown elsewhere [3], in the reaction of **Ib** with $[\text{AuCl}(\text{tht})]$ a fast interchange of Br and Cl between the W and Au centers

* If the reaction of **Ib** (or **Ia**) with $[\text{AuCl}(\text{tht})]$ is carried out in the presence of a large excess of TIPF_6 further complications arise because the carbynes can react, although slowly, with TIPF_6 with elimination of the halide ligand.

takes place and the derivative having the chloride ligand bonded to the tungsten is favoured.

Experimental

All reactions were carried out under dry nitrogen by Schlenk techniques. IR spectra were recorded with a Perkin Elmer 298 spectrophotometer and calibrated against the 1901.4 cm^{-1} polystyrene absorption. NMR spectra were recorded with a Bruker AC-300 instrument. The ^1H and ^{13}C NMR are given in ppm relative to internal TMS. The carbynes $[\text{W}(\equiv\text{CR})(\text{CO})_2(\text{L} \wedge \text{L})\text{X}]$ [2,3] and the compound $[\text{AuCl}(\text{tht})]$ [6] were prepared as described previously.

Preparation of $[\text{AuW}_2(\mu_2\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_4(\text{bipy})_2\text{Cl}_2]\text{PF}_6$

To a vigorously stirred solution of $[\text{W}(\equiv\text{CR})(\text{CO})_2(\text{bipy})\text{Cl}]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$) (0.05 g, 0.09 mmol) in CH_2Cl_2 (10 ml) was added $[\text{AuCl}(\text{tht})]$ (0.015 g, 0.047 mmol), followed by TIPF_6 (0.025 g, 0.071 mmol). After 1 h the orange solution was filtered through Celite and concentrated to ca. 2 ml. Addition of diethyl ether (10 ml) gave orange microcrystals of crude IIa (0.037 g, 56%). Pure samples were obtained by recrystallization from acetone/diethyl ether. Analysis, found: C, 33.8; H, 2.1; N, 4.1. $\text{AuCl}_2\text{F}_6\text{N}_4\text{PW}_2\text{C}_{40}\text{H}_{30}\text{O}_4$ calcd: C, 34.0; H, 2.1; N, 4.0%. IR (cm^{-1} , in CH_2Cl_2): $\nu_{\text{max}}(\text{CO})$ 2024s, 1955s. IR (Nujol): 840s, br (PF_6). ^1H NMR (CDCl_3): 9.05 (d, 4H, 2,2'-bipy), 8.48 (d, 4H, 5,5'-bipy), 8.40 (t, 4H, 4,4'-bipy), 7.81 (t, 4H, 3,3'-bipy), 7.00 and 6.95 (AB q, J 8 Hz, 4H, C_6H_4), 2.57 (s, 6H, Me-4).

Similarly the carbyne $[\text{W}(\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{bipy})\text{Br}]$ gave 0.031 g (51%) of a mixture of the products IIa, IIb, and IIc in a ratio that depended on the reaction time. Crystallization of the product from acetone/diethyl ether gave crystals of IIa.

Crystal structure determination of IIa

Crystal data. $\text{C}_{40}\text{H}_{30}\text{N}_4\text{O}_4\text{Cl}_2\text{W}_2\text{Au} \cdot \text{PF}_6$, M 1411.1, monoclinic, a 17.538(3), b 16.158(3), c 15.260(2) Å, β 93.22(2)°, V 4318(1) Å³, $P2_1/n$, D_x 2.170 g cm⁻³, Z = 4, $F(000)$ 2640, $\lambda(\text{Mo-K}\alpha)$ 0.71069 Å, $\mu(\text{Mo-K}\alpha)$ 93.50 cm⁻¹, at 288 K.

A prismatic crystal (0.07 × 0.07 × 0.1 mm) was selected and mounted on a Philips PW-1100 four circle diffractometer. The unit-cell parameters were determined from 25 reflections ($4 \leq \theta \leq 12^\circ$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo- K_α radiation, using the ω -scan technique, with scan width 0.8° and scan speed 0.03° s^{-1} . 4432 reflections were measured in the range $2 \leq \theta \leq 25^\circ$, 4148 of which were assumed as observed applying the condition $I \geq 2.5\sigma(I)$. Three reflections were measured every two hours as orientation and intensity control and no significant intensity decay was observed. Lorentz-polarization and absorption corrections were made. The structure was solved by Patterson methods, and refined by full-matrix least-squares, using the SHELX76 program [7]. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma(F_o)^{-2}$. f , f' and f'' were taken from ref. [8]. The final R was 0.029 ($R_w = 0.030$) for all observed reflections. Max. peak in final difference synthesis was $0.4\text{ e} \text{ \AA}^{-3}$, Max. shift/e.s.d. was 0.3 in U_{23} of C(52) atom.

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