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Organometallic Chemistry

Synthesis of the gold-dirhenium ferrocenylacetylide cluster. The crystal structure of $Re_2(\mu\text{-}C{\equiv}CFc)\{Au(PPh_3)\}(CO)_8$

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The thermal reaction of $Re_2(CO)_8(NCMe)_2$ with $Au(C{\equiv}CFc)PPh_3$ afforded the cluster $Re_2(\mu\text{-}C{\equiv}CFc)\{Au(PPh_3)\}(CO)_8$, which was characterized by X-ray diffraction analysis.

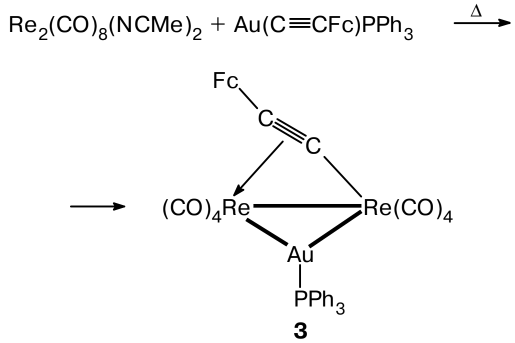
Key words: acetylide complexes of gold and rhenium, gold-dirhenium cluster, X-ray diffraction analysis, ferrocenylacetylenes.

One of the widely accepted procedures for the synthesis of acetylide derivatives of transition metal clusters[1] is based on reactions of mononuclear acetylide complexes with metal carbonyl clusters. This procedure was used also for the preparation of mixed gold-triosmium clusters. Thus the reactions of gold acetylides $Au(C{\equiv}CPh)L$ ($L = PPh_3$ or PMe_2Ph) and $Au(C{\equiv}CFc)PPh_3$ with $Os_3(CO)_{10}(NCMe)_2$ afforded products of the oxidative addition of the gold acetylide compounds to the Os_3 clusters, *viz.*, $Os_3(\mu\text{-}C{\equiv}CPh)(AuL)(CO)_{10}$ ($L = PPh_3$ (**1a**) or PMe_2Ph (**1b**))[2] and $Os_3(\mu_3\text{-}C{\equiv}CFc)\{Au(PPh_3)\}(CO)_9$ (**2**),[3] respectively. In the present study, we synthesized a gold-dirhenium ferrocenylacetylide cluster according to an analogous reaction.

Results and Discussion

The reaction of $Re_2(CO)_8(NCMe)_2$ with $Au(C{\equiv}CFc)PPh_3$ in boiling toluene gave rise to orange crystals of the complex $Re_2(\mu\text{-}C{\equiv}CFc)\{Au(PPh_3)\}(CO)_8$ (**3**) in 77% yield (Scheme 1) and a small amount of unidentified red compound **4**. It should be noted that a phenylacetylide analog of **3**, *viz.*, the complex $Re_2(\mu\text{-}C{\equiv}CPh)\{Au(PPh_3)\}(CO)_8$ (**5**), has been prepared recently[4] in 7% yield by the reaction of $Re_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)(CO)_8$ with $Na[Co(CO)_4]$ and then

Scheme 1



$$Re_2(CO)_8(NCMe)_2 + Au(C{\equiv}CFc)PPh_3 \xrightarrow{\Delta}$$

3

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with AuCl(PPh$_3$). The ^{1}H NMR spectrum (in CDCl$_3$) of product **3** provides evidence for the presence of the ferrocenyl group (δ 4.23 (5 H), 4.28 (2 H), and 4.58 (2 H)) and the phenyl groups of the triphenylphosphine ligand. The ^{31}P NMR spectrum of complex **3** has a singlet signal at δ 82.01. For comparison, the ^{31}P NMR spectra of the complexes Au(C≡CFc)PPh$_3$ and **2** have signals at δ 43.18 and 72.86, respectively.[3]

The structure of complex **3** was established by single-crystal X-ray diffraction analysis. The molecular structure of complex **3** is shown in Fig. 1. The selected geometric parameters are given in Table 1. The molecule contains the triangular AuRe$_2$ core. The ferrocenylacetylide ligand is σ,π-coordinated to two Re atoms. The Re(1)—Re(2) bond (3.1863(4) Å) in complex **3** is somewhat elongated as compared to the analogous bond in Re$_2$(CO)$_{10}$ (3.041(1) Å).[5] On the whole, the structural parameters of complex **3** are close to those found[4] for phenylacetylide analog **5**. The Re—Re distances in complexes **3** and **5** (3.1863(4) and 3.179(2) Å, respectively) are somewhat larger than that (3.089(1) Å) found[6] in the hydridoacetylide complex Re$_2$(μ-H)(μ-C≡CPh)(CO)$_8$ (**6**). The Re(1)—Au(1) and Re(2)—Au(1) distances are nonequivalent (2.7326(4) and 2.8693(3) Å, respectively). In tetranuclear gold-triosmium cluster **1b** [2] containing the analogously σ,π-coordinated phenylacetylide ligand, two Os—Au distances differ to a smaller extent (2.770(1) and 2.794(1) Å), whereas the corresponding Os—Au distances in cluster **2** [3] containing the σ,2π-coordinated ligand are 2.780(1) and 2.783(1) Å. In

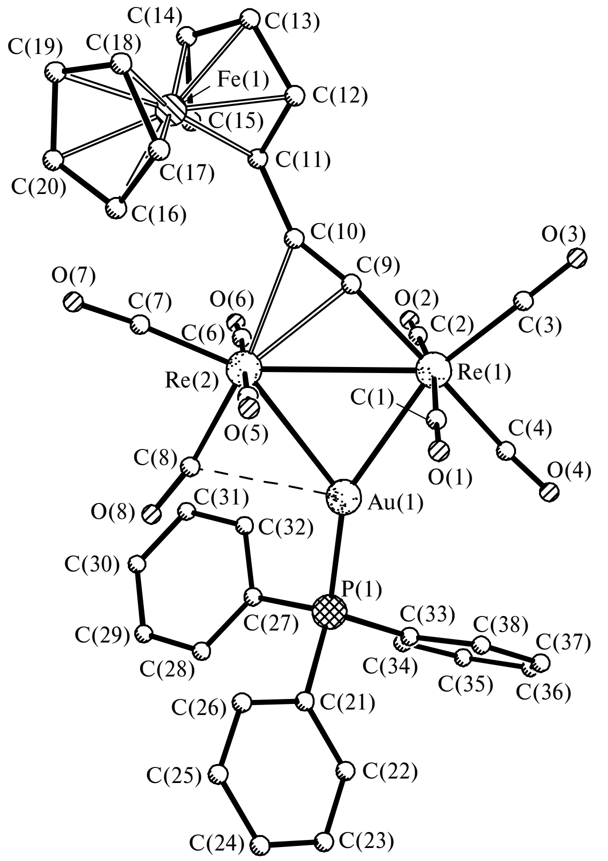

Fig. 1. Molecular structure of cluster **3**.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in complex **3**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Re(1)—Re(2)	3.1863(4)	P(1)—Au(1)—C(8)	97.96(11)	Au(1)—Re(1)—Re(2)	57.382(6)	C(9)—Re(2)—Re(1)	40.12(11)
Re(1)—C(1)	1.990(5)	P(1)—Au(1)—Re(1)	151.15(3)	C(7)—Re(2)—C(8)	86.1(2)	C(10)—Re(2)—Re(1)	70.18(13)
Re(1)—C(2)	2.010(5)	C(8)—Au(1)—Re(1)	109.98(11)	C(7)—Re(2)—C(6)	89.8(2)	Au(1)—Re(2)—Re(1)	53.336(9)
Re(1)—C(3)	1.925(5)	P(1)—Au(1)—Re(2)	137.72(3)	C(8)—Re(2)—C(6)	89.9(2)	C(33)—P(1)—C(27)	106.1(2)
Re(1)—C(4)	1.978(4)	C(8)—Au(1)—Re(2)	40.78(11)	C(7)—Re(2)—C(5)	89.32(19)	C(33)—P(1)—C(21)	104.5(2)
Re(1)—C(9)	2.056(4)	Re(1)—Au(1)—Re(2)	69.282(9)	C(8)—Re(2)—C(5)	93.1(2)	C(27)—P(1)—C(21)	104.9(2)
Re(2)—C(5)	2.014(5)	C(3)—Re(1)—C(4)	89.7(2)	C(6)—Re(2)—C(5)	176.8(2)	C(33)—P(1)—Au(1)	114.92(15)
Re(2)—C(6)	2.006(5)	C(3)—Re(1)—C(1)	92.7(2)	C(7)—Re(2)—C(9)	115.92(18)	C(27)—P(1)—Au(1)	107.21(17)
Re(2)—C(7)	1.903(5)	C(4)—Re(1)—C(1)	91.9(2)	C(8)—Re(2)—C(9)	157.86(18)	C(21)—P(1)—Au(1)	118.23(16)
Re(2)—C(8)	1.944(5)	C(3)—Re(1)—C(2)	95.9(2)	C(6)—Re(2)—C(9)	92.52(19)	O(1)—C(1)—Re(1)	178.3(4)
Re(2)—C(9)	2.319(4)	C(4)—Re(1)—C(2)	87.8(2)	C(5)—Re(2)—C(9)	85.07(18)	O(2)—C(2)—Re(1)	177.6(5)
Re(2)—C(10)	2.390(5)	C(1)—Re(1)—C(2)	171.44(19)	C(7)—Re(2)—C(10)	85.88(19)	O(3)—C(3)—Re(1)	177.7(5)
Au(1)—Re(1)	2.7326(4)	C(3)—Re(1)—C(9)	92.85(19)	C(8)—Re(2)—C(10)	171.93(19)	O(4)—C(4)—Re(1)	176.1(5)
Au(1)—Re(2)	2.8693(3)	C(4)—Re(1)—C(9)	175.01(19)	C(6)—Re(2)—C(10)	90.55(19)	O(5)—C(5)—Re(2)	176.0(4)
Au(1)—P(1)	2.3306(12)	C(1)—Re(1)—C(9)	92.31(19)	C(5)—Re(2)—C(10)	86.30(17)	O(6)—C(6)—Re(2)	175.7(5)
Au(1)—C(8)	2.689(5)	C(2)—Re(1)—C(9)	87.63(19)	C(9)—Re(2)—C(10)	30.12(17)	O(7)—C(7)—Re(2)	175.3(4)
P(1)—C(33)	1.815(5)	C(3)—Re(1)—Au(1)	163.09(14)	C(7)—Re(2)—Au(1)	150.62(14)	O(8)—C(8)—Re(2)	169.9(5)
P(1)—C(27)	1.816(5)	C(4)—Re(1)—Au(1)	73.66(14)	C(8)—Re(2)—Au(1)	64.63(14)	O(8)—C(8)—Au(1)	114.2(4)
P(1)—C(21)	1.820(5)	C(1)—Re(1)—Au(1)	85.07(14)	C(6)—Re(2)—Au(1)	88.30(15)	Re(2)—C(8)—Au(1)	74.59(16)
C(9)—C(10)	1.225(7)	C(2)—Re(1)—Au(1)	86.64(14)	C(5)—Re(2)—Au(1)	93.98(13)	C(10)—C(9)—Re(1)	170.5(4)
C(10)—C(11)	1.456(6)	C(9)—Re(1)—Au(1)	103.98(12)	C(9)—Re(2)—Au(1)	93.45(11)	C(10)—C(9)—Re(2)	78.1(3)
		C(3)—Re(1)—Re(2)	139.39(14)	C(10)—Re(2)—Au(1)	123.44(13)	Re(1)—C(9)—Re(2)	93.28(17)
		C(4)—Re(1)—Re(2)	130.91(14)	C(7)—Re(2)—Re(1)	156.04(14)	C(9)—C(10)—C(11)	152.6(5)
		C(1)—Re(1)—Re(2)	87.75(13)	C(8)—Re(2)—Re(1)	117.86(14)	C(9)—C(10)—Re(2)	71.7(3)
		C(2)—Re(1)—Re(2)	85.99(14)	C(6)—Re(2)—Re(1)	91.39(14)	C(11)—C(10)—Re(2)	135.6(4)
		C(9)—Re(1)—Re(2)	46.61(12)	C(5)—Re(2)—Re(1)	88.15(13)		

cluster **3**, each Re atom is coordinated by four CO groups. One of these groups, *viz*., C(8)O(8), is nonlinear (the Re(2)—C(8)—O(8) angle is 169.9(5)°) and is semibridging in character due to a weak interaction with the Au atom (the C(8)—Au(1) distance is 2.689(5) Å).

The bridging ferrocenylacetylide ligand in complex **3** forms a σ-bond with the Re(1) atom (Re(1)—C(9), 2.056(4) Å) and a π-bond with the Re(2) atom (Re(2)—C(9), 2.319(4) Å; Re(2)—C(10), 2.390(5) Å). For comparison, the corresponding distances in the σ,π-phenylacetylide ligand in dirhenium complexes **5** and Re_2(μ-C≡CPh)(μ-CH=CH_2)$(CO)_5$(μ-$Ph_2PCH_2PPh_2$)[7] are 2.11(2), 2.29(2), 2.40(2) Å and 2.09(2), 2.34(1), 2.48(2) Å, respectively. In cluster **3**, the C(10)—C(9)—Re(1)—Au(1)—Re(2) fragment is planar to within 0.03 Å. The C(9)—C(10) distance in complex **3** (1.225(7) Å) is somewhat larger than the C≡C distance (1.200(9) Å) in the σ-acetylide ligand in the complex Re_2(μ-H)(σ-C≡CPh)$(CO)_7$(μ-$Me_2PCH_2PMe_2$)[7] due, probably, to π-coordination. The corresponding C≡C distances in complexes **5** and **6** are 1.18(3) and 1.23(1) Å, respectively.[4,6] However, it should be noted that virtually no elongation of the C≡C bond in the σ,π-acetylide ligand (1.201(8) Å) was observed in the cluster Os_3(μ-H)(μ-C≡CPh)$(CO)_9$(PMe_2Ph).[8]

The results of the present study provide additional evidence that σ,π-coordination of the acetylide ligand in bi- and polynuclear metal complexes can cause only insignificant elongation of the C≡C bond, unlike the σ,π,π-coordination, which may lead to substantial elongation of this bond. For example, the C≡C bond length in complex **2** is 1.32(2) Å.[3]

Experimental

The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.13 and 161.98 MHz, respectively; 25 °C). The IR spectra were measured on a Bruker IFS-113v instrument. The reactions were carried out in an atmosphere of argon. The chromatographic separation was performed in air. Silica gel L200/280 μm (Chemapol) and Sorbfil chromatographic plates were used for the preparative chromatographic separation of the reaction products. The $Re_2(CO)_8(NCMe)_2$ complex was synthesized from $Re_2(CO)_{10}$ according to a procedure described previously.[9]

Reaction of $Re_2(CO)_8(NCMe)_2$ with Au(C≡CFc)PPh_3. A mixture of $Re_2(CO)_8(NCMe)_2$ (90 mg, 0.133 mmol) and Au(C≡CFc)PPh_3 (90 mg, 0.133 mmol) in toluene (40 mL) was refluxed for 20 min. The solvent was evaporated and two major fractions (orange and red-brown) were isolated from the residue by chromatography. The orange fraction was additionally purified by preparative TLC. Orange crystals of the complex Re_2(μ-C≡CFc){Au(PPh_3)}$(CO)_8$ (**3**) were obtained by crystallization from a hexane—CH_2Cl_2 mixture; the yield was 130 mg (77%). IR (CH_2Cl_2), ν(CO)/cm^{-1}: 2091 v.w, 2062 m, 2001 v.s, 1966 s, 1938 s. ^{1}H NMR ($CDCl_3$), δ: 4.23 (s, 5 H, C_5H_5); 4.28 (t, 2 H, C_5H_4, J = 2.0 Hz); 4.58 (t, 2 H, C_5H_4, J = 2.0 Hz); 7.40—7.60 (m, 15 H, C_6H_5). ^{31}P NMR ($CDCl_3$), δ: 82.01 (s).

Table 2. Crystallographic parameters and details of X-ray diffraction study of compound **3**

Parameter	Characteristic
Molecular formula	$C_{38}H_{24}O_8PAuFeRe_2$
Molecular weight	1264.76
Space group	$P\bar{1}$
Temperature/K	110
a/Å	10.915(1)
b/Å	12.962(1)
c/Å	13.679(2)
α/deg	109.436(2)
β/deg	103.165(2)
γ/deg	92.157(2)
V/Å^3	1763.5(3)
Z	2
d_{calc}/g cm^{-3}	2.382
Diffractometer	Bruker SMART 1000 CCD
Radiation	Mo-Kα (λ = 0.71073 Å)
μ/cm^{-1}	153.13
$2\theta_{max}$/deg	60
Number of independent reflections (R_{int})	10190 (0.0313)
R_1 (based on F for reflections with $I > 2\sigma(I)$)	0.0354 (8824 reflections)
wR_2 (based on F^2 for all reflections)	0.0902
Number of parameters in the refinement	460

The red-brown fraction was additionally purified by chromatography. Red crystals of complex **4** (10 mg) were obtained by crystallization. IR (CH_2Cl_2), ν(CO)/cm^{-1}: 2010 v.s, 1997 v.s, 1992 v.s, 1933 s, 1916 m. ^{1}H NMR ($CDCl_3$), δ: 4.16 (s, 5 H, C_5H_5); 4.55 (t, 2 H, C_5H_4, J = 2.0 Hz); 4.98 (t, 2 H, C_5H_4, J = 2.0 Hz); 7.40—7.60 (m, 15 H, C_6H_5). ^{31}P NMR ($CDCl_3$), δ: 90.41 (s).

X-ray diffraction study of cluster 3. A single crystal of complex **3** suitable for X-ray diffraction study was obtained by crystallization from a hexane—CH_2Cl_2 mixture. The atomic coordinates were deposited with the Cambridge Structural Database. The principal crystallographic characteristics are given in Table 2. The X-ray data were processed using the SAINT program.[10] The empirical absorption correction was applied based on repeated measurements of the intensities of equivalent reflections (the SADABS program[11]). The structure was solved by the direct method and refined by the full-matrix least-squares method based on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. The H atoms were placed in geometrically calculated positions and refined using the riding model. All calculations were carried out with the use of the SHELXTL-97 program package.[12]

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