Supplementary Information

Fischer-type gold(I) carbene complexes stabilized by aurophilic interactions

Daniela I. Bezuidenhout[a*], Belinda van der Westhuizen[a], Amos J. Rosental[b], David C. Liles [a], Israel Fernández[c*]

[a] *Chemistry Department, University of Pretoria, Private Bag X20, Hatfield 0028, South Africa.*

E-mail: daniela.bezuidenhout@up.ac.za; Fax: +27-(0)12-420-4687; Tel: +27-(0)12-420-2626

[b]*Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich 8093, Switzerland.*

[c]*Departamento de QuímicaOrgánica I, Facultad de Química, Universidad Complutense, 28040 Madrid, Spain.*

E-mail: israel@quim.ucm.es; Tel: +34-913944310.

Contents

1. General information

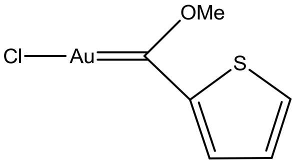
All operations were carried out under an inert atmosphere of nitrogen or argon gas using standard Schlenk techniques. Solvents were dried by refluxing on sodium metal (hexane, thf and diethylether) or over phosphorous pentoxide (CH_2Cl_2) and then distilled under nitrogen prior to use. Chemicals were used without further purification unless stated otherwise. Tetrahydrothiophenechloroaurate was synthesised according to literature procedures.[1] A Bruker AVANCE 500 spectrometer was used for NMR recordings. ^{1}H NMR spectra were recorded at 500.319 MHz and ^{13}C NMR spectra at 125.75 MHz. The signal of the solvent was used as reference: ^{1}H $CDCl_3$ at 7.26 ppm; CD_2Cl_2 at 5.32 ppm; ^{13}C $CDCl_3$ at 77.16 ppm; CD_2Cl_2 at 53.84 ppm. Mass spectrometry was done using a SYNAPT® G2 High Definition MS™ System from Waters. Crystal structure data collections for complexes **1**, **2**, **3**, **5** and **6** were performed using a Bruker diffractometer with a sealed tube Mo source, graphite monochromator and an APEX-II CCD detector and for complex **4** using a Bruker kappa geometry diffractometer with an IμS micro focus Mo source with focusing Montel optics and a Photon 100 CMOS detector. Data reduction was performed using Bruker SAINT and absorption corrections / scaling using Bruker SADABS (TWINABS for complex **1**). The structures were solved using Bruker SHELXTS and refined using SHELXTL (and Shelxl-2013 for complex **4**).

2. Synthesis of complexes

Precursor complexes for transmetallation were synthesized using the classical Fischer carbene route[2] and have previously been reported. [3,4,5]

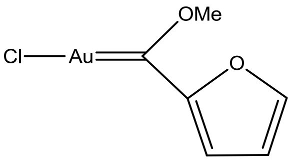
General method for preparation of gold(I) Fischer carbene complexes via transmetallation from their tungsten(0)carbene analogues[6]*:* 2 mmol of the corresponding Fischer carbene complex was dissolved in thf and cooled to -5°C after which 2 mmol of ClAu(tht) was added in one portion (4 mmol for biscarbene complexes). After one hour, the reaction mixture was filtered using canula filtration and the target complex crystallized from this solution using thf and hexane at 5°C.

[ClAu=C(OMe)Th] (1)



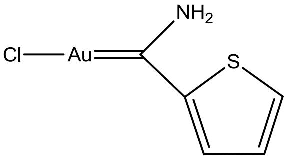
0.9g (2 mmol) of [$(CO)_5$W=C(OMe)Th] used as precursor complex. Yield: (84%, 0.6g), red crystals. ^{1}H NMR (CD_2Cl_2): δ 8.60 (br, 2H, H_α), 8.35 (d, J = 4.6 Hz, 2H, H_γ), 7.38 (dd, J = 4.8, 4.2 Hz, 2H, H_β), 4.78 (s, 3H, CH_3); ^{13}C NMR (CD_2Cl_2): 248.42(C_{carb}), 152.73 (C_α),n.o. (C_{ipso}), 145.56 (C_γ), 131.07 (C_β), 70.80 (CH_3). FAB-HRMS calcd for AuC_6H_6OSCl [M-Cl]$^+$: *m/z* 323.16; found, 322.98.

[ClAu=C(OMe)Fu] (2)



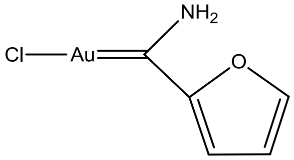
0.9g (2 mmol) of [$(CO)_5$W=C(OMe)Fu] employed as precursor complex. Yield: (77%, 0.53g), red crystals. ^{1}H NMR ($CDCl_3$): δ8.25 (d, J = 3.8 Hz, 2H, H_γ), 8.04 (br, 2H, H_α), 6.82 (dd, J = 3.9, 1.6 Hz, 2H, H_β), 4.79 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): 237.46 (C_{carb}), 158.43 (C_γ), 154.09 (C_α), 142.17 (C_β), 116.42 (C_{ipso}), 70.99 (CH_3). FAB-HRMS calcd for $AuC_6H_6O_2Cl$ [M-Cl]$^+$: *m/z* 307.09; found, 307.03.

[ClAu=C(NH_2)Th] (3)



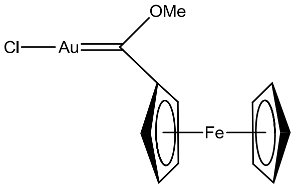
0.9g (2 mmol) of [$(CO)_5$W=C(NH_2)Th] used as starting material. Yield: (98%, 0.67g), light yellow crystals. ^{1}H NMR (CD_2Cl_2): δ9.12 (br, 1H, H_{syn}), 8.50 (br, 1H, H_{anti}), 8.09 (dd, J = 3.9, 1.2 Hz, 2H, H_α), 8.02 (dd, J = 5.0, 1.2 Hz, 2H, H_γ), 7.32 (dd, J = 5.0, 3.9 Hz, 2H, H_β); ^{13}C NMR (CD_2Cl_2): 197.93 (C_{carb}), 139.27 (C_α), 138.21 (C_γ), 130.15 (C_β). FAB-HRMS calcd for AuC_5H_5NSCl [M-Cl]$^+$: *m/z* 308.14; found, 307.98.

[ClAu=C(NH$_2$)Fu] (4)



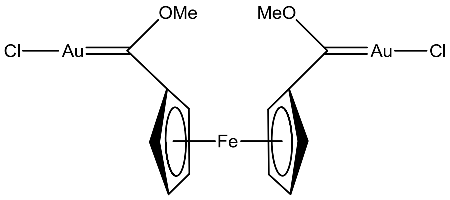
0.84g (2 mmol) of [(CO)$_5$W=C(NH$_2$)Fu] used as precursor complex. Yield: (92%, 0.60g), light yellow crystals. ^{1}H NMR (CD$_2$Cl$_2$): δ9.94 (br, 1H, H$_{syn}$), 9.19 (br, 1H, H$_{anti}$), 7.78 (br, 2H, H$_{ɣ}$), 7.59 (d, J = 3.6 Hz, 2H, H$_{\alpha}$), 6.64 (dd, J = 3.6, 1.7 Hz, 2H, H$_{ß}$); ^{13}C NMR (CD$_2$Cl$_2$): n.o. (C$_{carb}$), 155.38 (C$_{ipso}$), 149.48 (C$_{ɣ}$), 131.64 (C$_{\alpha}$), 114.58 (C$_{ß}$). FAB-HRMS calcd for AuC$_5$H$_5$NOCl [M-Cl]$^+$: *m/z*292.07; found, 292.00.

[ClAu=C(OMe)Fc] (5)



1.1g (2 mmol) of [(CO)$_5$W=C(OMe)Fc] employed as starting material. Yield: (64%, 0.59g), yellow crystals.^{1}H NMR (CD$_2$Cl$_2$): δ5.21 (br, 2H, H$_{\alpha}$), 5.07 (br, 2H, H$_{ß}$), 4.51 (s, 3H, CH$_3$), 4.50 (s, 5H, Cp); ^{13}C NMR (CD$_2$Cl$_2$): n.o. (C$_{carb}$), 87.02 (C$_{\alpha}$), 79.82 (C$_{ß}$), 72.10 (CH$_3$). FAB-HRMS calcd for AuFeC$_{12}$H$_{12}$OCl [M-Cl-CH$_3$+CH$_3$CN]$^+$: *m/z*451.06; found, 451.79.

[ClAu=C(OMe)Fc′(OMe)C=AuCl] (6)



1.5g (2 mmol) of [(CO)$_5$W=C(OMe)-Fc'-(OMe)C=W(CO)$_5$], used as precursor complex. Yield: (71%, 1.04g), light brown crystals. ^{1}H NMR (CD$_2$Cl$_2$): δ5.29 (br, 2H, H$_{\alpha}$), 5.10 (br, 2H, H$_{ß}$), 4.82 (s, 3H, CH$_3$); ^{13}C NMR (CD$_2$Cl$_2$): n.o. (C$_{carb}$), 97.79 (C$_{ipso}$),87.36 (C$_{\alpha}$), 80.68 (C$_{ß}$)76.37 (CH$_3$). FAB-HRMS calcd for Au$_2$FeC$_{14}$H$_{14}$O$_2$Cl$_2$ [M+H-2Cl]$^+$: *m/z* 665.08; found, 664.98.

3. Crystallographic data

Table 1a. Crystal data and structure refinement for complexes **1 - 3**.

		1	**2**	**3**
Empirical formula		$C_6H_6AuClOS$	$C_6H_6AuClO_2$	$C_5H_5AuClNS$
Formula weight		358.60	342.53	343.59
Temperature (K)		100(2)	100(2)	100(2)
Wavelength (Å)		0.71073	0.71073	0.71073
Crystal system		Monoclinic	Orthorhombic	Triclinic
Space group		$P2_1/c$	*Pbca*	$P\bar{1}$
Unit cell dimensions	*a*(Å)	9.4467(3)	11.6474(6)	10.054(3)
	b(Å)	9.4467(3)	6.5160(3)	10.469(3)
	c(Å)	6.5606(2)	19.9970(10)	13.322(4)
	α (°)	90	90	73.798(5)
	β (°)	68.2817(13)	90	73.987(5)
	γ (°)	90	90	61.977(5)
Volume ($Å^3$)		833.04(4)	1517.66(13)	1171.2(5)
Z		4	8	6
Density (calculated) (g/cm^3)		2.859	2.998	2.923
Absorption coefficient (mm^{-1})		18.158	19.670	19.360
F(000)		648	1232	924
Crystal size (mm^3)		0.47 x 0.13 x 0.03	0.25 x 0.05 x 0.02	0.26 x 0.02 x 0.02
Θ range for data collection (º)		2.16 – 34.72	2.04 – 30.52	1.62 – 30.50
Index ranges	*h*	-14 – 13	-16 – 16	-14 – 14
	k	0 – 21	-9 – 9	-14 – 14
	l	0 – 10	-28–27	-18 – 18
Reflections collected		3023	21813	18555
Independent reflections		3023	2255	6883
R(int)		0.0000	0.0356	0.0352
Θ(full) (º)		30.50	30.52	30.50
Completeness to Θ(full) (%)		98.7	97.3	96.4
Absorption correction		multi-scan	multi-scan	multi-scan
Max. & min. transmission		0.1149 & 0.0362	0.9525 & 0.5785	0.2740 & 0.1598

Refinement method		Full-matrix least-squares on F^2		
Data / restraints / parameters		3023 / 72 / 109	2255 / 0 / 92	6883 / 0 / 286
Goodness-of-fit on F^2		1.073	1.051	1.028
R indices [$I>2\sigma(I)$]	$R1$	0.0231	0.0169	0.0276
	$wR2$	0.0611	0.0262	0.0533
R indices (all data)	$R1$	0.0365	0.0249	0.0414
	$wR2$	0.0649	0.0278	0.0569
Largest diff. peak & hole (e.Å^{-3})		1.323 & -1.268	0.745 & -0.868	1.433 & -0.926

Table 1b. Crystal data and structure refinement for complexes **4** - **6**.

		4	**5**	**6**
Empirical formula		$C_{10}H_{10}Au_2Cl_2N_2O_2$	$C_{12}H_{12}AuClFeO$	$C_{14}H_{14}Au_2Cl_2FeO_2$
Formula weight		655.03	460.49	734.94
Temperature (K)		150(2)	100(2)	100(2)
Wavelength (Å)		0.71073	0.71073	0.71073
Crystal system		Triclinic	Orthorhombic	Triclinic
Space group		$P\bar{1}$	*Pbcn*	$P\bar{1}$
Unit cell dimensions	a(Å)	8.7646(3)	18.3338(3)	6.867(3)
	b(Å)	9.3480(3)	9.7882(2)	9.991(4)
	c(Å)	9.5155(3)	13.3550(2)	12.498(5)
	α (°)	82.3723(14)	90	101.711(5)
	β (°)	68.2817(13)	90	91.574(5)
	γ (°)	85.2985(15)	90	108.988(5)
Volume (Å^3)		717.41(4)	2396.62(7)	789.9(5)
Z		2	8	2
Density (calculated) (g/cm^3)		3.032	2.552	3.090
Absorption coefficient (mm^{-1})		20.792	13.635	19.770
F(000)		584	1712	664
Crystal size (mm^3)		0.325 x 0.156 x 0.068	0.15 x 0.09 x 0.06	0.08 x 0.07 x 0.03
Θ range for data collection (°)		2.199 – 33.139	2.22 – 36.40	1.67 – 28.42
Index ranges	h	-13 – 13	-26 – 30	-9 – 9
	k	-14 – 14	-16 – 16	-13 – 13
	l	-14 – 14	-22 – 19	-16 – 16
Reflections collected		39322	43609	9970

Independent reflections		5472	5477	3926
R(int)		0.0506	0.0481	0.0273
Θ(full) (°)		33.139	30.499	28.42
Completeness to Θ(full) (%)		100.0	99.9	98.7
Absorption correction		multi-scan	multi-scan	multi-scan
Max. & min. transmission		0.7484 & 0.2550	0.3065 & 0.1987	0.2627 & 0.1660
Refinement method		Full-matrix least-squares on F^2		
Data / restraints / parameters		5472 / 0 / 175	5477 / 0 / 146	3926 / 0 / 192
Goodness-of-fit on F^2		1.087	1.007	1.105
R indices [$I>2\sigma(I)$]	*R*1	0.0246	0.0265	0.0260
	*wR*2	0.0622	0.0384	0.0542
R indices (all data)	*R*1	0.0279	0.0520	0.0391
	*wR*2	0.0637	0.0425	0.0575
Largest diff. peak & hole (e.Å^{-3})		3.377 & -1.602	0.933 & -1.141	2.226 & -1.138

The structure of complexes **1-6** were determined by single crystal x-ray diffraction analysis. The thiophene moieties in **1** and **3** were found to be disordered by a rotation of approximately 180° about the C_{ring}–$C_{carbene}$ bonds with ratios of the orientation with S approximately trans to X to that approximately cis to X about C_{ring}–$C_{carbene}$ bond of 0.909 : 0.091 for **1** (X = O) and 0.745 : 0.255 for **3** (X = N). In the asymmetric unit cell of the crystal structure of 3 there are 3 molecules of the complex of which just two have an aurophilic interaction.

4. Computational data

Computational Details

All the calculations reported in this paper were obtained with the GAUSSIAN 09 suite of programs.[7] The geometries of complexes **2** and **6** were optimized at the metahydrid M06 functional[8] using the triple-ξ valence plus polarization basis set def2-TZVP[9] for all atoms. This protocol is denoted M06/def2-TZVP. Both complexes were characterized by frequency calculations,[10] and have a positive defined Hessian matrix indicating that they are minima on the potential energy surface.

Donor-acceptor interactions have been computed using the natural bond orbital (NBO) method.[11] The energies associated with these two-electron interactions have been computed according to the following equation:

$$\Delta E^{(2)}_{\phi\phi*} = -n_{\phi} \frac{\langle \phi^{*} | \hat{F} | \phi \rangle^{2}}{\varepsilon_{\phi*} - \varepsilon_{\phi}}$$

where $\hat{F}$ is the DFT equivalent of the Fock operator and ϕ and ϕ□ are two filled and unfilled Natural Bond Orbitals having ε_{ϕ} and $\varepsilon_{\phi^{*}}$ energies, respectively; n_{ϕ}□ stands for the occupation number of the filled orbital.

All AIM results described in this work correspond to calculations performed at the M06/6-31G(d)/WTBS(for Au) level on the optimized geometries obtained at the M06/def2-TZVP level. The WTBS (well-tempered basis sets)[12] have been recommended for AIM calculations involving transition metals.[13] The topology of the ED was conducted using the AIMAll program package.[14]

Cartesian coordinates (in Å) and total energies (in a. u., non corrected zero-point vibrational energies included) of all the stationary points discussed in the text. All calculations have been performed at the M06/def2-TZVP + ΔZPVE level of theory.

2: E= -1956.921904

Cl	2.474597000	0.832710000	-2.376430000
O	0.039296000	2.200837000	2.034530000
C	1.404238000	2.112500000	2.476445000
H	1.699299000	1.061039000	2.529097000
H	1.428395000	2.569677000	3.462203000
H	2.047303000	2.653129000	1.781655000
O	-2.524378000	2.380258000	1.496808000
C	-2.291877000	1.948551000	-0.680940000
H	-1.823734000	1.712005000	-1.624851000
C	-3.722010000	2.452960000	0.918446000
C	-3.650045000	2.197994000	-0.417155000
H	-4.470745000	2.197473000	-1.115175000
Au	1.050951000	1.404200000	-0.652640000
C	-1.628645000	2.070525000	0.512162000
C	-0.238681000	1.950174000	0.800496000
H	-4.550217000	2.697795000	1.565670000
Cl	2.064525000	-1.432712000	2.415479000
C	0.778175000	-2.358419000	-2.476313000
H	1.266447000	-3.030042000	-1.769858000
H	0.695243000	-2.820553000	-3.456673000
H	1.322444000	-1.412531000	-2.538103000
C	-2.800955000	-1.331635000	0.653562000
H	-2.302449000	-1.235526000	1.606633000
C	-4.290659000	-1.453717000	-0.966221000
C	-4.176586000	-1.248800000	0.375018000
H	-4.982123000	-1.068908000	1.067480000

H	-5.145441000	-1.482493000	-1.624477000
Au	0.574125000	-1.605591000	0.662221000
C	-0.790493000	-1.803473000	-0.811239000
C	-2.171192000	-1.585564000	-0.536921000
O	-3.103038000	-1.656251000	-1.534364000
O	-0.569144000	-2.104565000	-2.045516000

6: E= -1969.885921

C	-0.426321000	1.499019000	-1.137117000
Au	1.110858000	-1.626058000	-0.159064000
Au	1.110660000	1.626157000	0.159059000
Fe	-2.854235000	-0.000074000	0.000066000
Cl	2.764642000	-1.791355000	-1.758722000
C	-3.585824000	1.785544000	0.741686000
H	-4.182768000	1.878252000	1.636154000
Cl	2.764373000	1.791499000	1.758785000
O	-0.351306000	-1.292862000	2.408929000
O	-0.351419000	1.292783000	-2.408957000
C	-2.181653000	1.811441000	0.681316000
H	-1.493181000	1.944490000	1.504267000
C	-1.793877000	1.605020000	-0.684253000
C	-2.992227000	-1.438297000	1.451100000
H	-3.034203000	-1.233669000	2.509646000
C	-0.426164000	-1.499048000	1.137077000
C	-1.793707000	-1.605158000	0.684200000
C	-4.086038000	-1.553463000	0.569466000
H	-5.126855000	-1.444924000	0.835888000
C	-2.992375000	1.437930000	-1.451140000
H	-3.034325000	1.233133000	-2.509655000
C	-2.181442000	-1.811451000	-0.681381000
H	-1.492949000	-1.944307000	-1.504346000
C	-3.585607000	-1.785711000	-0.741761000
H	-4.182526000	-1.878355000	-1.636253000
C	-4.086225000	1.553059000	-0.569538000
H	-5.127024000	1.444343000	-0.835959000
C	0.942645000	1.147531000	-3.021391000
H	1.595479000	1.953601000	-2.686282000
H	0.774105000	1.204721000	-4.093659000
H	1.374823000	0.181902000	-2.745844000
C	0.942736000	-1.147538000	3.021399000
H	1.595591000	-1.953634000	2.686395000
H	0.774142000	-1.204648000	4.093662000
H	1.374914000	-0.181922000	2.745811000

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