Supplementary Material (ESI) for Chemical Communications

Amalgamating at the Molecular Level. Study of the Strong Closed-Shell Au(I)···Hg(II) interaction.

José M. López-de-Luzuriaga,*[a] Miguel Monge,[a] M. Elena Olmos,[a] David Pascual[a] and Tania Lasanta[a]

[a] *Departamento de Química, Universidad de La Rioja, Grupo de Síntesis Química de La Rioja, UA-CSIC. Complejo Científico-Tecnológico, 26004-Logroño, SPAIN.*

ELECTRONIC SUPPLEMENTARY INFORMATION

Experimental Section.

General. All reactions were carried out under dry and deoxygenated argon atmosphere using Schlenk techniques. All solvents were distilled. $[Hg(C_6F_5)_2]$ was prepared according to literature methods.[1]

Instrumentation. Infrared spectra were recorded in the 4000-200 cm^{-1} range on a Perkin-Elmer FT-IR Spectrum 1000 spectrophotometer, using Nujol mulls between polyethylene sheets. ^1H, and ^{19}F and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Avance 400 in chloroform solutions. Chemical shifts are quoted relative to $SiMe_4$ (^1H external), $CFCl_3$ (^{19}F external) and H_3PO_4 85% (^{31}P external).

Synthesis of $[Au(C_6F_5)PMe_3]$ 1: To a dichloromethane solution (30 mL) of the $[Au(C_6F_5)(tht)]$ (0.4 g, 0.88 mmol) was added 1M THF solution of PMe_3 (0.88ml, 0.88 mmol). The reaction mixture was stirred for 30 min at room temperature. Evaporation of the solvent under vacuum and addition of *n*-hexane gave rise to complex **1** as a white solid in 54% yield. ^{19}F NMR (282 MHz, $CDCl_3$), δ -116.5 (m,2F, F_o), -158.6 (t, $^3J_{F-F}$=20 Hz, 1F, F_p), -162.5 (m, 2F, F_m). ^1H NMR (300 MHz, $CDCl_3$), δ 1.61 ppm (d). ^{31}P NMR (121.5 MHz, $CDCl_3$), δ 3.28 ppm (s). FT-IR (Nujol mulls): ν = 1502, 954.5, 786 cm^{-1} (Au-C_6F_5). Anal. Calcd for ($C_9H_9AuF_5P$): C, 24.56; H, 2.06%. Found: C, 24.16; H, 2.05%.

Synthesis of $[Au(C_6F_5)PMe_3]_2[Hg(C_6F_5)_2]$ 2: To a dichloromethane solution (30 mL) of $[Hg(C_6F_5)_2]$ (0.122 g, 0.227 mmol) was added $[Au(C_6F_5)_2PMe_3]$ (0.200 g, 0.454 mmol). The reaction mixture was stirred for 30 min at room temperature. Evaporation of the solvent under vacuum and addition of *n*-hexane gave rise to complex **2** as a white solid in 87% yield. ^{19}F NMR (282 MHz, $CDCl_3$), δ -119.7(m, $^3J_{F-Hg}$ = 414 Hz, 4F, F_o, Hg-C_6F_5), -150.6(m, 2F, F_p, Hg-C_6F_5), -159.0 (m, 4F, F_m, Hg-C_6F_5), -116.6 (m,4F, F_o, Au-

C_6F_5), -158.6(t, $^3J_{F\text{-}F}$=20 Hz, 2F, F_p, Au-C_6F_5), -162.5 ppm (m, 4F, F_m , Au-C_6F_5). ^{1}H NMR (300 MHz, $CDCl_3$), δ 1.6 ppm (d). ^{31}P NMR (121.5 MHz, $CDCl_3$), δ 3.3 ppm (s). FT-IR (Nujol mulls): ν = 1500, 960, 787 cm^{-1} (Au-C_6F_5), ν = 1637, 1371 and 805 cm^{-1} (Hg-C_6F_5). Anal. Calcd for ($C_{30}H_{18}Au_2F_{20}HgP_2$): C, 25.47; H, 1.28%. Found: C, 25.42; H, 1.28%.

Computational details.

All calculations were performed using the Gaussian 09 suite of programs[2] using DFT/B3LYP,[3] Hartree-Fock and MP2[4] levels of theory

The interaction energy between ionic counterparts at Hartree-Fock (HF) and MP2 levels of theory was obtained according to equation:

$$\Delta E = E_{AB}^{(AB)} - E_{A}^{(AB)} - E_{B}^{(AB)} = V(R)$$

a counterpoise correction for the basis-set superposition error (BSSE)[5] on ΔE was thereby performed. We fitted the calculated points using a four-parameter equation, which had been previously used[6] to derive the Herschbach-Laurie relation:[7]

$$\Delta E = V(R) = Ae^{-BR} - CR^{-n}$$

Basis Sets. The 19-valence electron (VE) quasirelativistic (QR) pseudopotential (PP) of Andrae[8] was employed for gold together with two f-type polarization functions (exponents: 0.2, 1.19).[9] Similarly, the 20-valence valence electron (VE) quasirelativistic (QR) pseudopotential (PP) of Andrae[8] was employed for mercury together with two f-type polarization functions (exponents: 0.545, 1.58).[10]

The atoms F, P, and C were treated by Stuttgart pseudopotentials,[11] including only the valence electrons for each atom. For these atoms double-zeta basis sets of ref 10 were

used, augmented by d-type polarization functions.[12] For the H atom, a double-zeta, plus a p-type polarization function was used.[13]

Table S1. Main structural parameters for complex **1** and DFT optimized distances (Å) and angles (º) for model systems **A**, **B** and **C** at the MP2 equilibrium distances.

	M-M	Hg-C_{ipso}	Au-C	Au-P	Hg-C	C-Au-P	C-Hg-C
Complex **2**	3.186	3.288	2.085	2.288	2.091	176.81	179.96
Model **A**	3.098	3.176	2.063	2.356	2.119	177.39	177.85
Model **B**	3.011	3.469	2.058	2.346	2.112	180.0	180.0
Model **C**	3.009	-	2.058	2.346	-	180.0	-

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GEOMETRIES IN XYZ FORMAT FOR THE MODEL SYSTEMS AT THE MP2 EQUILIBRIUM DISTANCES

MODEL A

Hg	0.00000000	0.00000000	0.00000000
C	2.11886200	0.00000000	0.00000000
C	2.85041100	1.18003900	0.00000000
C	2.84797000	-1.17729400	-0.07983400
C	4.23966700	1.20647600	-0.06902200
C	4.23569500	-1.20475600	-0.15309100
C	4.93398200	0.00086400	-0.14489900
C	-2.11733400	-0.02496800	0.07525100
C	-2.83457500	-1.21125200	0.02711200
C	-2.86255400	1.14630500	0.09575000
C	-4.22361500	-1.25551500	0.00362200
C	-4.25359600	1.15592600	0.07623500
C	-4.93560501	-0.05822000	0.03097600
F	2.19724100	-2.36345300	-0.11203400
F	4.90020201	-2.35891701	-0.23677900
F	6.26139300	-0.00032900	-0.21438800
F	4.90840000	2.35700300	-0.07285900
F	2.20293600	2.35852400	0.03926000
F	-2.22829700	2.33258100	0.10629800
F	-4.93582300	2.29841500	0.09074600
F	-6.26454100	-0.07551200	0.00895400
F	-4.87679401	-2.41785100	-0.05065300
F	-2.17112400	-2.38965300	-0.02264100
H	1.09655390	-3.94938158	-2.06171432
P	-0.02148910	-3.37203957	-2.72752631
Au	-0.04321410	-1.02434657	-2.92343131
H	-0.05167610	-4.16495557	-3.91101931
H	-1.09006809	-3.96396456	-1.99642131
C	-0.05999110	1.03709043	-3.00136731
C	-1.24539610	1.76997743	-2.99093531
C	1.11410790	1.78751343	-3.03064831
C	-1.28029810	3.16088743	-3.00118231
F	-2.42971510	1.12991843	-2.94237331
C	1.12796590	3.17878843	-3.04179431
F	2.30874091	1.16507443	-3.02227431
C	-0.08147110	3.86922943	-3.02703631
F	-2.43936510	3.81892643	-2.97490031
F	2.27735090	3.85402843	-3.05471431
F	-0.09147810	5.19905443	-3.03357831

MODEL B

Hg	0.00000000	0.00000000	0.00000000
C	2.11186100	0.00000000	0.00000000
C	2.84219400	1.18278500	0.00000000
C	2.84219400	-1.18278500	0.00000000
C	4.23311799	1.20711900	0.00000000
C	4.23311799	-1.20711900	0.00000000
C	4.92933200	-0.00000000	0.00000000
C	-2.11186100	0.00000000	-0.00000000

C	-2.84219400	-1.18278499	-0.00000000
C	-2.84219400	1.18278500	-0.00000000
C	-4.23311800	-1.20711899	0.00000000
C	-4.23311800	1.20711900	-0.00000000
C	-4.92933200	-0.00000000	-0.00000000
F	2.19530800	-2.36169100	0.00000000
F	4.90276699	-2.35835999	0.00000000
F	6.25759400	-0.00000000	0.00000000
F	4.90276699	2.35835999	-0.00000000
F	2.19530800	2.36169100	0.00000000
F	-2.19530800	2.36169100	-0.00000000
F	-4.90276700	2.35836000	-0.00000000
F	-6.25759400	-0.00000000	-0.00000000
F	-4.90276700	-2.35835999	-0.00000000
F	-2.19530800	-2.36169100	0.00000000
H	1.09220600	-3.34269084	-2.36485772
P	0.00000000	-2.66658884	-2.98413872
Au	-0.00000000	-0.32028685	-2.99391672
H	-0.01471200	-3.34830185	-4.23632572
H	-1.08228000	-3.33536384	-2.34063772
C	0.00000000	1.73753716	-3.00249272
C	-1.17863700	2.47787116	-2.99456872
C	1.17905200	2.47714716	-3.01707772
C	-1.21431900	3.88779315	-2.99839472
F	-2.37057400	1.84906316	-2.98009072
C	1.20351500	3.86869116	-3.02397672
F	2.37068000	1.84759616	-3.02537272
C	0.00000000	4.56880215	-3.01429172
F	-2.35867000	4.57905415	-2.98798372
F	2.35992300	4.53951916	-3.03824572
F	0.00002700	5.90239716	-3.01997672

MODEL C

Au	0.00000000	0.00000000	0.00000000
C	2.05784100	0.00000000	0.00000000
C	2.84072600	1.15084100	0.00000000
C	2.75379400	-1.20527700	0.01892100
C	4.23215100	1.12375200	0.01721300
C	4.14342300	-1.28052600	0.03650100
C	4.88699300	-0.10411300	0.03557300
P	-2.34632200	-0.00000000	0.00000000
F	2.25596100	2.36495500	-0.01734000
F	4.94545700	2.25454100	0.01635300
F	6.21959400	-0.15317800	0.05220000
F	4.77147501	-2.46066700	0.05415100
F	2.08113000	-2.37313900	0.02069200
H	-3.02281199	0.55890400	1.12379400
H	-3.02500000	0.69120700	-1.04650200
H	-3.01777400	-1.25535000	-0.07702300
P	-0.38307727	-2.69392098	2.74910113
Au	-0.36605127	-0.35528998	2.95631113
H	0.73144173	-3.23453798	2.09673613
H	-0.42841027	-3.38799998	3.96409013
H	-1.47183427	-3.20465298	2.03232913
C	-0.35837727	1.70382202	3.14089613
C	0.81881173	2.44584302	3.14988513
C	-1.53150627	2.44191502	3.26577513

C	0.84827373	3.83189202	3.27389413
F	2.01072274	1.82293802	3.03459913
C	-1.55341427	3.82780902	3.39244013
F	-2.72690928	1.81489602	3.26840713
C	-0.35064026	4.52747802	3.39628213
F	2.00620771	4.50335306	3.27744766
F	-2.70766227	4.49528402	3.51022913
F	-0.34702326	5.85716702	3.51662713