Supplementary material for Dalton Transactions manuscript: Gas Phase Synthesis and Reactivity of Binuclear Gold Hydride Cations, $(R_3PAu)_2H^+$ (R=Me and Ph).

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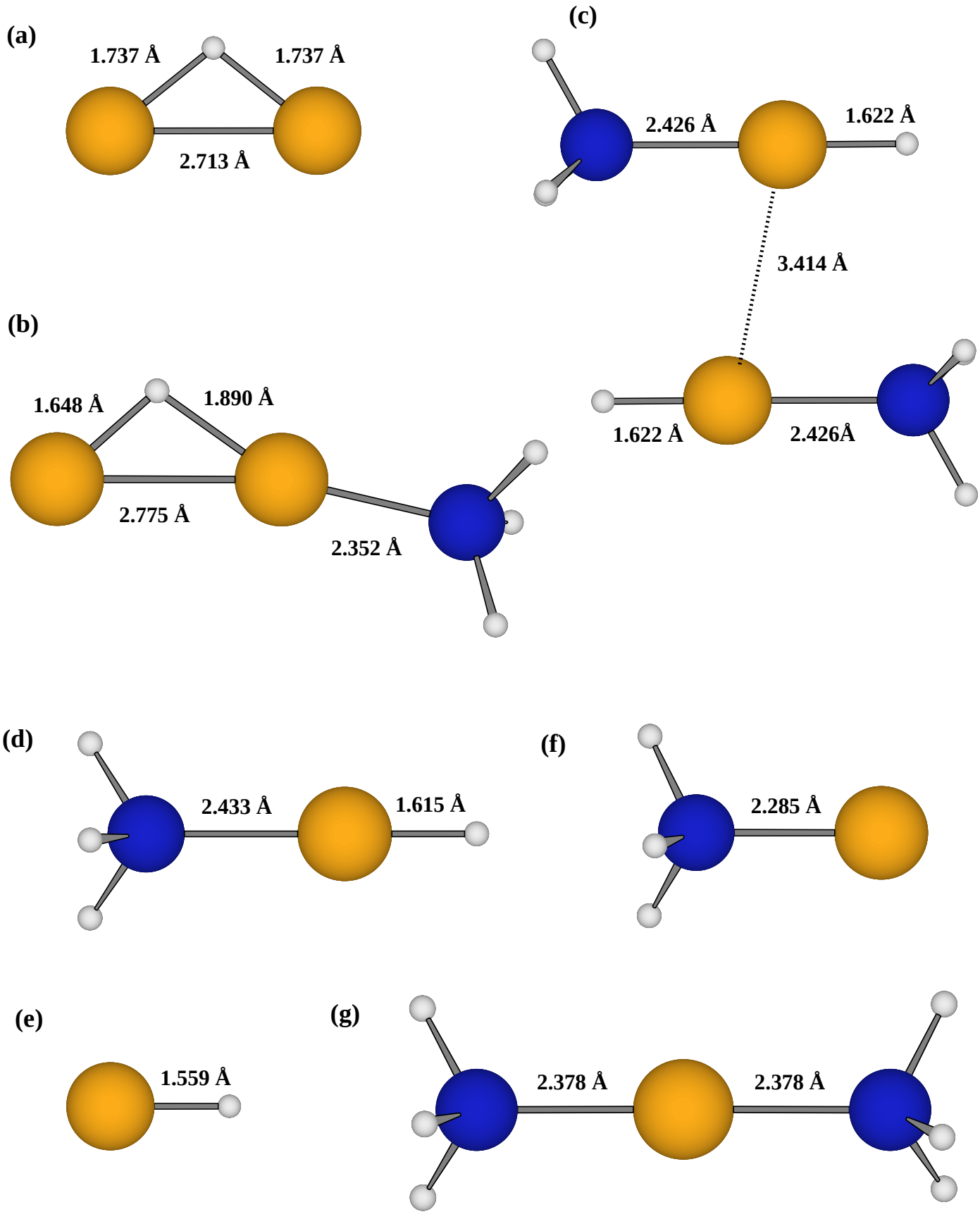
Table S1: Peak assignments for figs. 3, S1 and S3. Note that the *m/z* shown are for the strongest peak in the cluster if applicable.

Table S2: The calculated B3LYP/6-31G(d) energies (in Hartrees) of the various structures used in the thermochemistry calculations in the text. The basis set used for Au is the LanL2DZ.

Table S3: Estimated thermochemistry for eqs. 11-13 using the DFT calculated energies from Table S2.

Figure S1: Structures with key bond lengths for gold species I – O.



B- List of the Cartesian coordinates of the structures presented in figures 3, 6 and S1 and discussed throughout the text:

Structure C: $Au_2H(PH_3)_2^+$ (Figure 3a)

Au	-1.453324	-0.167521	0.000208
H	-0.000055	-1.119668	0.000024
Au	1.453368	-0.167500	-0.000209
P	3.634510	0.728008	0.000519
P	-3.634686	0.728010	-0.000518
H	-4.625191	-0.085558	0.575904
H	-4.188894	1.017130	-1.259365
H	-3.818280	1.941320	0.685136
H	3.817798	1.941542	-0.684835
H	4.625081	-0.085259	-0.576209
H	4.188755	1.016878	1.259405

Structure F: $Au(PH_3)_2^+HAu$ (Figure 3b)

Au	1.465095	0.000205	-0.000057
P	1.646753	2.380674	0.000102
H	2.941916	2.927142	-0.002516
H	1.053310	3.033154	1.094276
H	1.048523	3.033927	-1.090996
P	1.649321	-2.379915	0.000117
H	1.055765	-3.033538	-1.093307
H	1.052898	-3.033557	1.091966
H	2.945172	-2.924734	0.001795
Au	-2.210668	-0.000429	0.000007
H	-0.638503	0.003930	-0.000528

Structure G: $Au(PH_3)_2^+AuH$ (Figure 3c)

Au	-1.218243	0.000603	-0.000057
P	-1.144622	-2.385468	0.000142
H	-2.393695	-3.031523	-0.001059
H	-0.490414	-2.959712	1.101562
H	-0.487948	-2.960038	-1.099637
P	-1.140490	2.386325	0.000136
H	-0.483033	2.959943	-1.099664
H	-0.485182	2.959280	1.101574
H	-2.388505	3.034438	-0.000855
Au	1.695921	-0.000737	-0.000055

H	3.268903	-0.004719	0.002733

Structure H: $Au(PH_3)_2^+HAu$ (Figure 3d)

Au	-1.334318	0.000058	-0.006428
P	-1.466091	-2.374686	0.005991
H	-2.751491	-2.940107	-0.061737
H	-0.926786	-3.005625	1.139944
H	-0.801475	-3.038681	-1.039440
P	-1.465537	2.374839	0.005937
H	-0.791988	3.039204	-1.033516
H	-0.935495	3.004976	1.144700
H	-2.750151	2.940725	-0.072129
Au	1.986250	-0.000106	-0.015148
H	1.429215	0.000971	1.447761

Transition state for isomerization of C to G (Figure 6)

Au	1.071959	0.137615	-0.000135
P	-0.638880	2.112009	0.000257
H	-0.195519	2.886647	-1.087327
H	-0.224418	2.874921	1.107220
H	-2.018181	2.412458	-0.017506
P	3.241719	-0.750263	0.000183
H	3.304162	-2.149488	-0.107767
H	4.006331	-0.491276	1.149794
H	4.082413	-0.319161	-1.039457
Au	-1.650044	-0.438420	-0.000061
H	-2.328676	-1.876710	0.003973

Structure I: Au_2H^+ (Figure S1a)

Au	0.006824	1.356490	0.000000
H	-1.078162	-0.001549	0.000000
Au	0.006824	-1.356470	0.000000

Structure J: $Au_2H(PH_3)^+$ (Figure S1b)

Au	0.999152	-0.112951	-0.000597
P	3.320537	0.265150	0.001393
H	3.935478	0.225917	1.263348
H	3.732182	1.505615	-0.513778
H	4.072521	-0.654330	-0.748072

Au	-1.770533	0.062976	0.000164
H	-0.609141	-1.106463	0.011771

Structure K: $(HAuPH_3)_2$ (Figure S1c)

Au	-1.633222	-0.496099	-0.000060
H	-1.511996	-2.113976	0.000716
P	-1.829922	1.922087	0.000155
H	-3.116674	2.508813	0.000090
H	-1.258880	2.634318	-1.071975
H	-1.259704	2.633021	1.073570
Au	1.633278	0.496095	-0.000022
H	1.512147	2.113888	-0.000728
P	1.829651	-1.922081	0.000223
H	1.259415	-2.632810	-1.073269
H	1.258834	-2.634493	1.072271
H	3.116516	-2.508513	0.000141

Structure L: $HAuPH_3$ (Figure S1d)

Au	0.451369	-0.000021	-0.000014
H	2.066457	0.000858	0.000565
P	-1.981558	0.000024	0.000030
H	-2.666809	-0.075487	1.231744
H	-2.667561	-1.029088	-0.681288
H	-2.666833	1.104981	-0.550350

Structure M: AuH (Figure S1e)

Au	0.000000	0.000000	0.019492
H	0.000000	0.000000	-1.539876

Structure N: $Au(PH_3)_2^+$ (Figure S1g)

Au	0.000024	0.001906	-0.004886
P	2.378450	-0.003781	0.009485
H	2.996868	-0.912622	-0.866205
H	2.975426	-0.317951	1.241981
H	2.998863	1.211998	-0.324781
P	-2.378445	-0.003749	0.009358
H	-3.001016	1.161379	-0.469809
H	-2.976564	-0.167405	1.270520
H	-2.995566	-1.013028	-0.748374

Structure O: $Au(PH_3)^+$ (Figure S1f)

Au	0.441238	0.000008	0.000000
P	-1.844141	-0.000002	0.000000
H	-2.398084	-0.663419	-1.104744
H	-2.399484	1.288526	-0.021758
H	-2.398098	-0.625713	1.126511

C- Supporting Tables:

Table S1: The peak assignments in Figures 1, 2, 4 and 5. Note that the *m/z* shown are for the strongest peak in the cluster if applicable.

m/z	**Assignment**	**Comments**
152	$[Ph_2\text{-}2H]^+$	Product of EED
183	$[PPh_2\text{-}2H]^+$	Product of EED of $[(Ph_3PAu)(PMe_3Au)H]^+$ and $[(Ph_3PAu)_2H]^+$
263	$[HPPh_3]^+$	Product of EED
459	$AuPPh_3^+$	
477	$AuPPh_3^+.H_2O$	Reaction with background
491	$AuPPh_3^+.MeOH$	Reaction with background
500	$AuPPh_3^+.CH_3CN$	Reaction with background
516	$(AuPPh_3)(Me_2NCH_2\text{-}H)^+$	
560	$(AuPPh_3)(DMG\text{-}2H)^+$	
644	$AuPPh_2^{\cdot +}$	Loss of $Ph^{\cdot}$
721	$Au(PPh_3)_2^+$	Most intense peak in MS of Ph_3PAuCl
919	$(AuPPh_3)_2H^+$	
953	$(AuPPh_3)_2Cl^+$	

977	$(AuPPh_3)_2CH_3COO^+$	
1011	$Na(AuPPh_3Cl)_2^+$	
1119	$(AuPPh_3Cl)(AuPPh_3CH_3COO)Ag^+$	
1020	$(AuPPh_3)_2[DMG\text{-}H]^+$	
1095	$Ag(AuPPh_3Cl)_2^+$	
1377	$(AuPPh_3)_3^+$	
197	Au^+	Seen in the $P(Me)_3$ case only
243	$AuPCH_3^+$	Product of EED
273	$AuPMe_3^+$	
330	$(AuPMe_3)(Me_2NCH_2\text{-}H)^+$	
333	$[Au(PMe_3)_2\text{-}CH_4]^+$	Loss of CH_4
349	$Au(PMe_3)_2^+$	
374	$(AuPMe_3)(DMG\text{-}2H)^+$	
723	$(AuPMe_3Cl)_2Ag^+$	
547	$(AuPMe_3)_2H^+$	
581	$(AuPMe_3)_2Cl^+$	
605	$(AuPMe_3)_2(CH_3COO)^+$	
648	$(AuPMe_3)_2(DMG\text{-}H)^+$	
471	$AuHAuPMe_3^+$	
535	$AuPPh_3PMe_3^+$	

731	$(AuPPh_3)(AuPMe_3)(-H)^+$	
733	$(AuPPh_3)(AuPMe_3)H^+$	
767	$(AuPPh_3)(AuPMe_3)Cl^+$	
791	$(AuPPh_3)(AuPMe_3)(CH_3COO)^+$	
834	$(AuPPh_3)(AuPMe_3)(DMG\text{-}H)^+$	
911	$(AuPPh_3)(AuPMe_3)Cl.AgCl^+$	

DMG = N,N-Dimethyl glycine; PMe_3= trimethyl phosphine; PPh_3= triphenyl phosphine

Table S2: The calculated B3LYP/6-31G(d) energies (in Hartrees) of the various structures used in the thermochemistry calculations in the text. The basis set used for Au is the LanL2DZ.

species	E(B3LYP)	ZPE[-]	ZPE(Scaled)	E(B3LYP Scaled)	Relative isomer stability (kJ/mol)
$Au_2H(PH_3)_2^+$ (**C**)	-957.66847	0.062880	0.061660	-957.60681	0
isomer **F**	-957.62871	0.062160	0.060954	-957.56775	102.5
isomer **G**[*]	-957.62330	0.062000	0.060800	-957.56251	116.3
Isomer **H**	-957.62699	0.061567	0.060373	-957.56661	105.5
TS (**C** → **G**)	-957.61368	0.061679	0.060482	-957.55320	140.8
Au_2H^+ (**I**)	-271.22467	0.005411	0.005306	-271.21936	
$Au_2H(PH_3)^+$ (**J**)	-614.45202	0.034144	0.033482	-614.41854	
$(H_3PAuH)_2$ (**K**)	-958.45986	0.069101	0.067760	-958.39210	
H_3PAuH (**L**)	-479.22393	0.033706	0.033052	-479.19088	
AuH (**M**)	-136.04665	0.004785	0.0046922	-136.041958	
$Au(PH_3)_2^+$ (**N**)	-821.57147	0.055732	0.054651	-821.51682	
$Au(PH_3)^+$ (**O**)	-478.35010	0.027950	0.027408	-478.32270	
PH_3	-343.13781	0.024242	0.023772	-343.11404	

* This structure is the minimum energy structure from the output of the IRC calculation in the forward direction.

[-] Zero point energy from the frequency calculation.

Table S3: Estimated thermochemistry for eqs. 11-13 using the DFT calculated energies from Table S2.

Eq.#	**Reactions in text**	**ΔH (kJ mol^{-1})**
11	$Au_2H(PH_3)_2^+ \rightarrow PH_3 + Au_2H(PH_3)^+$	194.9
12	$Au_2H(PH_3)_2^+ \rightarrow Au(PH_3)^+ + AuH(PH_3)$	244.8
13	$Au_2H(PH_3)_2^+ \rightarrow AuH + Au(PH_3)_2^+$	126.1