Can the solid state structures of the dihalogen adducts R_3EX_2 (E = P, As; R = alkyl, aryl; X = Br, I) with the molecular spoke geometry be considered good mimics of the gold(I) systems $[(R_3E)AuX]$ (E = As, P; R = alkyl, aryl; X = Cl, Br, I)?

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Supplementary material.

Compound characterising data:

Table 1 Physical and analytical data for **1, 1a, 2a – c**, **3a – d** and **4a – d**

Compound	Yield (%)	Colour	Analytical Data
1 $Ph_2(1-C_6H_4C_6H_5)P$	87	White	C 84.9 (85.2) H 5.6 (5.7) P 9.1 (9.2)
1a $Ph_2(1-C_6H_4C_6H_5)PI_2$	86	Yellow	C 48.1 (48.7) H 2.9 (3.2) I 43.0 (42.9)
2a [{$Ph_2(1-C_6H_4C_6H_5)P$}AuCl]	91	White	C 50.8 (50.5) H 3.3 (3.4) Cl 6.6 (6.2) P 5.4 (5.4)
2b [{$Ph_2(1-C_6H_4C_6H_5)P$}AuBr]	97	White	C 46.2 (46.9) H 3.0 (3.1) Br 12.7 (13.0) P 5.0 (5.0)
2c [{$Ph_2(1-C_6H_4C_6H_5)P$}AuI]	94	White	C 43.3 (43.5) H 2.7 (2.9) I 18.65 (19.1) P 4.6 (4.7)
3a [(2-MeO-C_6H_4)AuPPh_3]	93	White	C 52.9 (53.0) H 3.9 (3.9) P 5.4 (5.5)
3b [(2-MeO-C_6H_4)AuPCy_3]	75	White	C 51.4 (51.4) H 6.4 (6.7) P 5.1 (5.3)
3c [(2-MeO-C_6H_4)AuPPh_2-1-naphthyl]	79	White	C 56.6 (56.5) H 3.7 (3.5) P 5.0 (5.0)
3d [(2-MeO-C_6H_4)AuP$Ph_2C_6H_4$-2-OMe]	77	White	C52.6 (52.4) H 3.8 (4.1) P 5.1 (5.2)
4a [(2,5-$(MeO)_2$-C_6H_4)AuPPh_3]	89	White	C 51.9 (52.4) H 3.8 (4.1) P 5.2 (5.2)
4b [(2,5-$(MeO)_2$-C_6H_4)AuPCy_3]	59	White	C 50.1 (50.6) H 6.9 (6.9) P 5.5 (5.0)
4c [(2,5-$(MeO)_2$-C_6H_4)AuPPh_2-1-naphthyl]	75	White	C 56.2 (55.7) H 3.9 (4.1) P 4.6 (4.8)
4d[(2,5-$(MeO)_2$-C_6H_4)AuP$Ph_2C_6H_4$-2-OMe]	56	White	C 51.5 (51.8) H 4.0 (4.2) P 4.7 (4.9)

[a] Calculated in parenthesis.

Table 2 ^{31}P- and proton NMR data for **1, 1a, 2a – c**, **3a – d** and **4a – d**

Compound	^{31}P (δ)	^{1}H (δ)
1	– 13.4	7.50 – 7.00 (bm, Ph-H)
1a	– 22.3	Not recorded
2a	26.2	7.54 – 6.98 (bm Ph-H)
2b	28.5	7.55 – 6.96 (bm Ph-H)
2c	32.9	7.54 – 6.95 (bm Ph-H)
3a	43.7	7.54(m, 1H, H6); 7.14(m, 1H, H3); 6.98(m, 1H, H4); 6.92(m, 1H, H5); 3.78(s, OCH_3); ligand: 7.64(bm, 5H, Ph-H); 7.44(bm, 10H, Ph-H).
3b	57.7	7.45(m, 1H, H6); 7.08(m, 1H, H3); 6.94(m, 1H, H4); 6.86(m, 1H, H5); 3.79(s, 3H, OCH_3); ligand: 2.06, 1.84, 1.72, 1.55, 1.29(m, 33H, Cy-H)
3c*	39.3	7.11(m, 1H, H3); 6.95(m, 1H, H4); 6.87(m, 1H, H5); 3.77(s, 3H, OCH_3); ligand: 8.76(d, 1H, J_{HH} 5, nap-H); 7.97(d, 1H, J_{HH} 8, nap-H); 7.90(d, 1H, J_{HH} 8, nap-H); 7.70(m,2H, nap-H); 7.46 (m, 11H, Ph-H); 7.40(t, 1H, J_{HH} 7.75, nap-H); 7.04(dd, 1H, J_{PH}12.5, J_{HH} 7, nap-H)
3d*	38.4	7.52(m, 1H, H2); 7.12(m, 1H, H5); 6.90(m, 1H, H3); 3.77(s, 3H, OCH_3); ligand: 7.67(m, 4H, Ph-H); 7.45(m, 7H, Ph-H); 6.95 (m 4H, Ph-H); 3.83(s, 3H, OCH_3); 3.77(s, 3H, OCH_3).
4a	43.5	7.16(m, 1H, H6); 6.87(m, 1H, H3); 6.65(m, 1H, H4); 3.82(s, 3H, OCH_3); 3.78(s, 3H, OCH_3); ligand: 7.62(m, 5H, Ph-H); 7.46(m, 10H, Ph-H)
4b	57.5	7.08(bs, 1H, H6); 6.84(m, 1H, H3); 6.58(m, 1H, H4); 3.77(s, 3H, OCH_3); 3.76(s, 3H, OCH_3); ligand: 2.05, 1.85, 1.73, 1.54. 1.29(m, 33H, PCy-H)
4c	39.0	7.12(m, 1H, H6); 6.84(m, 1H, H3); 6.63(m, 1H, H4); 3.76(s, 3H, OCH_3); 3.75(s, 3H, OCH_3); ligand: 8.75(d, 10, 1H, nap-H); 7.98(d, 8, 1H, nap-H); 7.90(d, 8, 1H, nap-H); 7.70(m, 2H, nap-H); 7.45(m, 10H, Ph-H); 7.40(m, 1H, nap-H); 7.03(m, 1H, nap-H);
4d	38.1	7.14(m, 1H, H6); 6.83(m, 1H, H5); 6.62(m, 1H, H4); 3.77(s, 3H, OCH_3); 3.76(s, 3H, OCH_3); ligand: 7.66(m, 4H, Ph-H); 7.45(m, 7H, Ph-H); 6.96(m, 3H, Ph-H); 3.80(s, 3H, OCH_3).

[a]Spectra recorded at 295 K in $CDCl_3$ and referenced to either H_3PO_4 (^{31}P) and $CHCl_3$ (^{1}H); *metallated ring resonance obscured by ligand resonance.

Table 3. $^{13}C\{^{1}\}$-NMR data for **1, 2a – c**, **3a – d** and **4a – d**

Compound	δ ppm
1	148.2 (d, J_{CP}28.3, q); 141.7 (d, J_{CP} 5.9, q); 137. (d, J_{CP} 11.2); 135.8 (d, J_{CP} 14.1, q); 134.1; 133.8 (d, J_{CP} 4.2,); 130.5 (d, J_{CP} 5.3); 128.6; 128.4; 128.3; 127.6; 127.2 (d, J_{CP} 7.4).
2a	147.9 (d, J_{CP} 14.7, q); 139.8 d, J_{CP} 6.6, q); 134.3 (d, J_{CP} 5.9); 133.6 (d, J_{CP} 6.6); 131.9 (d, J_{CP} 8.1); 131.7 (d, J_{CP} 2.2); 131.4 (d, J_{CP} 2.2); 129.6 (d, J_{CP} 62.4, q); 129.6; 129.1 (d, J_{CP} 12.5); 128.3; 128.3; 127.5 (d, J_{CP} 8.8); 127.3 (d, J_{CP} 60.9).
2b	148.0 (d, J_{CP} 15.4, q); 139.9 (d, J_{CP} 7.3, q); 134 (d, J_{CP} 13.2); 133.7 (d, J_{CP} 6.6); 132.2 (d, J_{CP} 8.1); 131.7 (d, J_{CP} 2.2); 131.3 (d, J_{CP} 2.2); 129.8 (d, J_{CP} 60.9, q); 129.7; 129.1 (d, J_{CP} 11.7); 128.5; 127.6 (d, J_{CP} 60.2, q); 127.5 (d, J_{CP} 8.1).
2c	147.9 (d, J_{CP} 15.4, q); 139.9 (d, J_{CP} 7.3, q); 134.3 (d, J_{CP} 14.7); 133.8 (d, J_{CP} 5.9); 131.9 (d, J_{CP} 8.8); 131.6 (d, J_{CP} 2.9); 130.2 (d, J_{CP} 58.7, q); 129.7; 129.1 (d, J_{CP} 11.7); 128.6; 128.5; 128.0 (d, J_{CP} 57.2, q); 127.5 (d, J_{CP} 8.1).
3a	165.3 (C2); 159.1(d, J_{PC} 113, C1); 139.8(C6); 126.7 (C4); 120.8(d, J_{PC} 5, C5); 110.1(d, J_{PC} 3.8, C3); 55.6 (OCH_3); ligand 134.5(d, J_{PC} 12.5); 131.2(d, J_{PC} 48.8); 131.0 (d, J_{PC} 1.5); 128.9(d, J_{PC} 10); 55.6 (OCH_3).
3b	165.6 (C2); 163.0(d, J_{PC} 105, C1); 139.5(C6); 126.1 (C4); 120.8(d, J_{PC} 5, C5); 110.6(d, J_{PC} 3.8, C3); 55.8 (OCH_3); ligand 33.3, 33.1, 30.7, 27.3, 27.1, 20.0.
3c	165.3 (C2); 158.5(d, J_{PC} 112, C1); 139.8(C6); 126.6 (C4); 120.7(d, J_{PC} 5.4, C5); 110.1(d, J_{PC} 4.2, C3); 55.6 (OCH_3); ligand: 135.0(d, J_{PC} 14.5); 133.8(d, J_{PC} 7.2); 133.6; 133.5; 133.3(d, J_{PC} 5.3); 132.1(d, J_{PC} 1.5); 131.2(d, J_{PC} 1.8); 130.5(d, J_{PC} 51.2); 129.0(d, J_{PC} 10.9); 128.8; 127.3(d, J_{PC} 47.2); 127.1; 126.5(d, J_{PC} 10.4); 124.9(d, J_{PC} 11.2).
3d	165.4 (C2); 158.7 (d, J_{PC} 114, C1); 139.9(C6); 126.5 (C4); 120.7(d, J_{PC} 6.3, C5); 110.1(d, J_{PC} 4.5, C3); 55.6 (OCH_3); ligand: 161.3, 134.8(d, J_{PC} 6.4); 134.5(d, J_{PC} 14.5); 133.0(d, J_{PC} 1.5); 131.2(d, J_{PC} 51.4); 130.7; 128.7(d, J_{PC} 10.9); 121.1(d, J_{PC} 9); 119.2(d, J_{PC} 50.6); 111.7(d, J_{PC} 3.6); 56.1(s).
4a	160.5(d, J_{PC} 110, C1); 160.0 (C2); 154.0(d, J_{PC} 7.5, C5); 125.0 (C6); 111.5(C4); 111.3(d, J_{PC} 5.5, C3); 56.8 (OCH_3); 55.7 (OCH_3); ligand 134.5(d, J_{PC} 13.6); 131.1(d, J_{PC} 49.6); 131.0 (d, J_{PC} 1.8); 128.9(d, J_{PC} 10.9).
4b	164.8(d, J_{PC} 104, C1); 160.33(C2); 154.3(d, J_{PC} 7.1, C5); 126.1 (C6); 112.2(d, J_{PC} 3.7, C3), 110.9(C4); 57.3 (OCH_3); 55.7 (s, OCH_3); ligand 33.3, 33.1, 30.6, 27.3, 27.1, 20.0.
4c	160.0(d, J_{PC} 109.3, C1); 160.0 (C2); 154.0(d, J_{PC} 6.3, C5); 125.2(C6); 114.6(C4); 111.4(d, J_{PC} 3.7, C3); ligand: 135.0(d, J_{PC} 14.5); 133.8(d, J_{PC} 7.2); 133.6; 133.5; 133.3(d, J_{PC} 5.3); 132.1(d, J_{PC} 1.5); 131.2(d, J_{PC} 1.8); 130.4(d, J_{PC} 51.4); 129.1(d, J_{PC} 11); 128.9; 127.1(d, J_{PC} 47.2); 127.2; 125.9(d, J_{PC} 10.4); 124.9(d, J_{PC} 11.2); 55.9 (s, OCH_3).
4d	160.2 (d, J_{PC} 107, C1); 160.2 (C2); 154.0(d, J_{PC} 6.3, C5); 125.5 (C6); 111.6(d, J_{PC} 5.5, C3); 111.2(C4); 56.9 (OCH_3); 55.7 (OCH_3); ligand: 161.3, 134.8(d, J_{PC} 6.4); 134.5(d, J_{PC} 14.5); 133.0(d, J_{PC} 1.8); 131.0(d, J_{PC} 50.5); 130.7(s); 128.7(d, J_{PC} 10.9); 121.0(d, J_{PC} 9); 119.1(d, J_{PC} 50.5); 111.6(d, J_{PC} 5.3); 56.1(s).

[a]Spectra recorded in $CDCl_3$, resonances singlets unless otherwise stated, coupling constants in Hz, q = quaternary resonances confirmed by DEPT 135.