Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information for

Structural and conformational analysis of a biaryl phosphine integrating a calix[4]arene cavity. Can the phosphorus atom behave as an introverted donor ?

Christophe Gourlaouen,[a] Fethi Elaieb,[b] Eric Brenner,[b] Dominique Matt,*[b] Jack Harrowfield[c] and Louis Ricard [d]

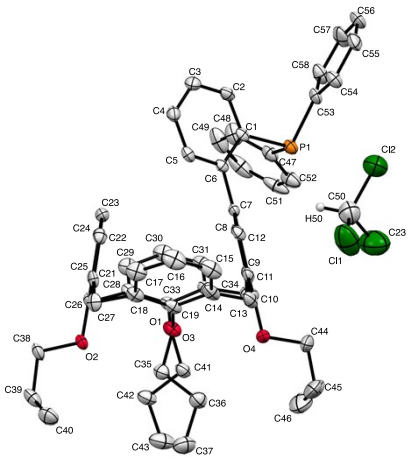

Table S1 Crystal and refinement data of L•$CHCl_3$

Formula	$C_{59}H_{62}Cl_3O_4P$	Z	8
Mr	972.40	D_{calcd} (mg.m^{-3})	1.239
Crystal size (mm^3)	0.30 x 0.30 x 0.15	μ(Mo$K\alpha$) (mm^{-1})	0.253
		F(000), e	4112
Crystal system	orthorhombic	Refl. measured	40548
Space group	*Pbca*	Refl. unique	9873
a (Å)	16.8473(19)	R_{int}	0.0616
b (Å)	16.4750(19)	Parameters ref.	628
c (Å)	37.556(4)	$R_1(F)/wR_2(F^2)$ (all refls.)	0.0967/0.2991
α (°)	90.0	GoF (F^2)	1.076
β (°)	90.0	$\Delta\rho_{fin}$(max/min) (eÅ^{-3})	1.106/-1.391
γ (°)	90.0		
V (Å^3)	10424(2)		

Table S2 Selected bond lengths (Å) and angles (°) for L•$CHCl_3$

lengths (Å)			
P1-C1	1.841(4)	H50-C7	2.860(5)
P1-C47	2.852(5)	H50-C12	2.795(5)
P1-C53	1.833(5)	C23…C7	4.241(5)
C10-O4	1.388(5)	C16…C30	10.122(6)
C33-O3	1.381(5)	C50-Cl1	1.722(8)
C26-O2	1.387(5)	C50-Cl2	1.744(8)
C19-O1	1.374(5)	C50-Cl3	1.768(8)
Selected angles (°)			
Bond angles		Torsion angles	
C1-P1-C53	102.2(2)	C1-C6-C7-C12	132.6(4)
C1-P1-C47	100.9(2)	P1-C1-C6-C7	- 8.3(6)
C53-P1-C47	101.1(2)	Interplane angles	
P1-C1-C6	120.1(3)	ring C27/ring C23	21.6
		ring C19/ring C33	68.6

Figure S1 The Hirshfeld surface for L.$CHCl_3$, as defined using CrystalExplorer and viewed, left to right, down a, down b and down c, where red regions define points of interaction exceeding dispersion.

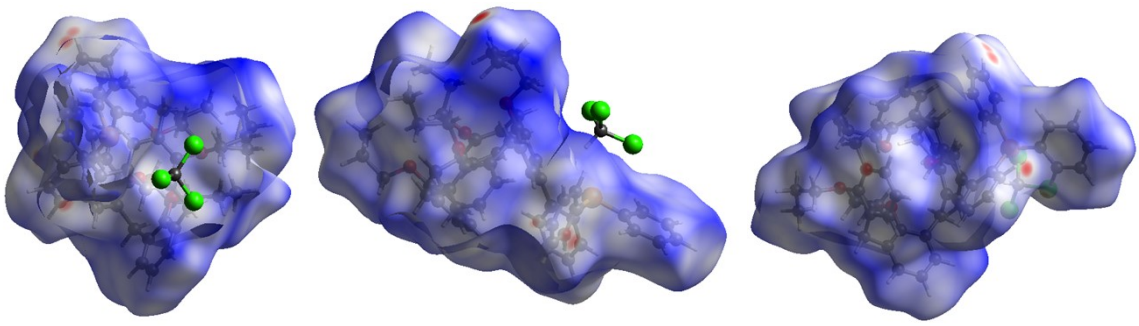

Figure S2 The Hirshfeld surface for [AuCl(L)], as defined using CrystalExplorer and viewed, left to right, down a, down b and down c, where red regions define points of interaction exceeding dispersion.

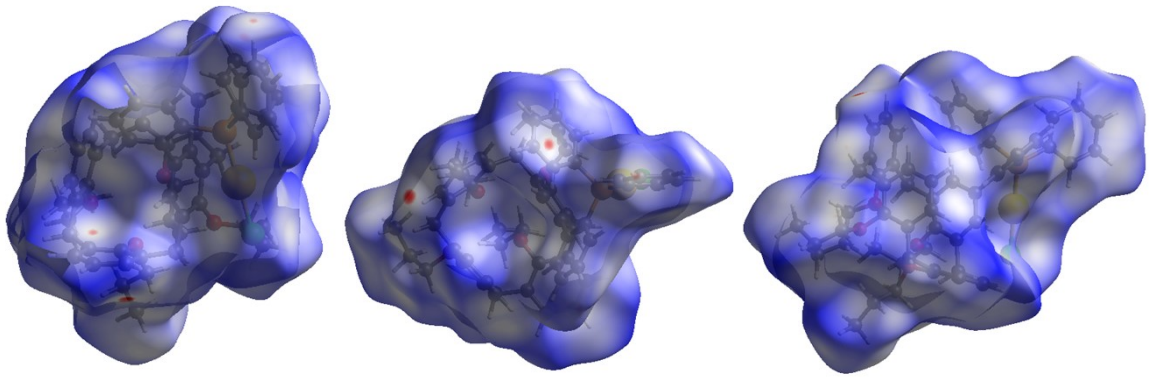

Figure S3 Part of one of the chains of L molecules in the crystal of L·$CHCl_3$ running parallel to b, with the C···C interactions exceeding dispersion shown as dashed lines.

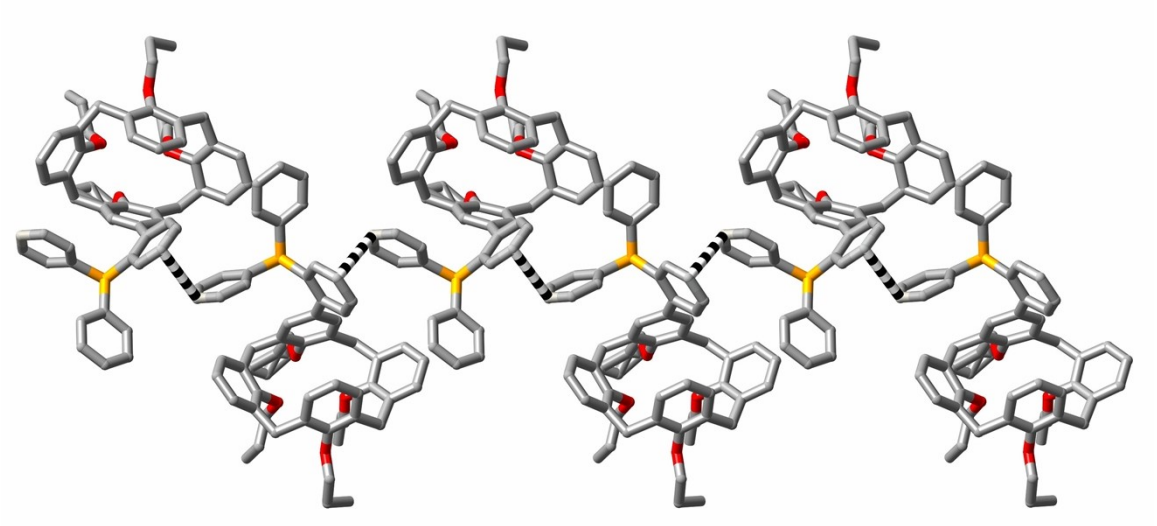

Figure S4 Non-covalent interactions (NCI) in conformer **D** (optimised structure) with (attractive) electrostatic interactions in blue, attractive dispersion forces in green, and steric repulsions in red.

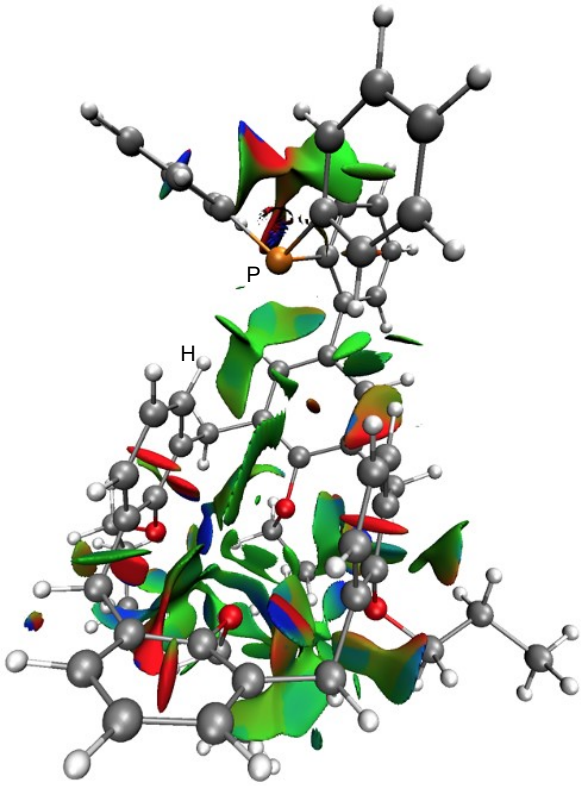

Fig. S5 Non-covalent interactions in $[Au(CO)L]^+$ (optimised structure; introverted L), with (attractive) electrostatic interactions in blue, attractive dispersion forces in green, and steric repulsions in red.