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SUPPORTING INFORMATION

New routes to organometallic molecular junctions via a simple thermal processing protocol

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*Crystallographically determined structures of **2***

Crystallographic data for the structure were collected at 150(2) K on an Oxford Diffraction Xcalibur diffractometer using Mo Kα radiation. Following analytical absorption corrections and solution by direct methods, the structure was refined against F^2 with full-matrix least-squares using the program SHELXL-2017.[1] The molecule is situated on a crystallographic inversion centre with the (4-(trimethylsilylethynyl)phenyl)ethynyl group disordered with the 3-thienylethynyl group plus a solvent molecule. The solvent molecule itself was modelled as being disordered over two sets of sites. The geometries of the disordered components were restrained to ideal values. All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atoms. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms. Crystallographic data have been deposited with the Cambridge Crsytallographic Data Centre (CCDC 1883917).

The molecular structure of complex **2**, the immediate precursor to heterobimetallic **3** is shown in Figure S1, with key bond lengths and angles summarised in Table S1. The structure features a crystallographic inversion centre and the structure was refined with a 50:50 population of each alkynyl ligand at each site. Disordered molecules of solvent of crystallisation ($CDCl_3$) were also present in the crystal. Attempts to obtain an ordered model in the non-centrosymmetric space group *P*1 were not successful. Disorder with respect to the position of the alkyne fragments has been noted previously for 'asymmetric' trans-bis(alkynyl) complexes, trans-[Ru(C≡CR)(C≡CR')$(dppe)_2$].[2] This disorder, combined with the fact that the aryl ring π-systems are not well aligned with the Ru(d) orbitals prevents meaningful correlations of the electronic character of the thiophene and phenylene moieties on the -C≡C-Ru-C≡C- backbone.[2]

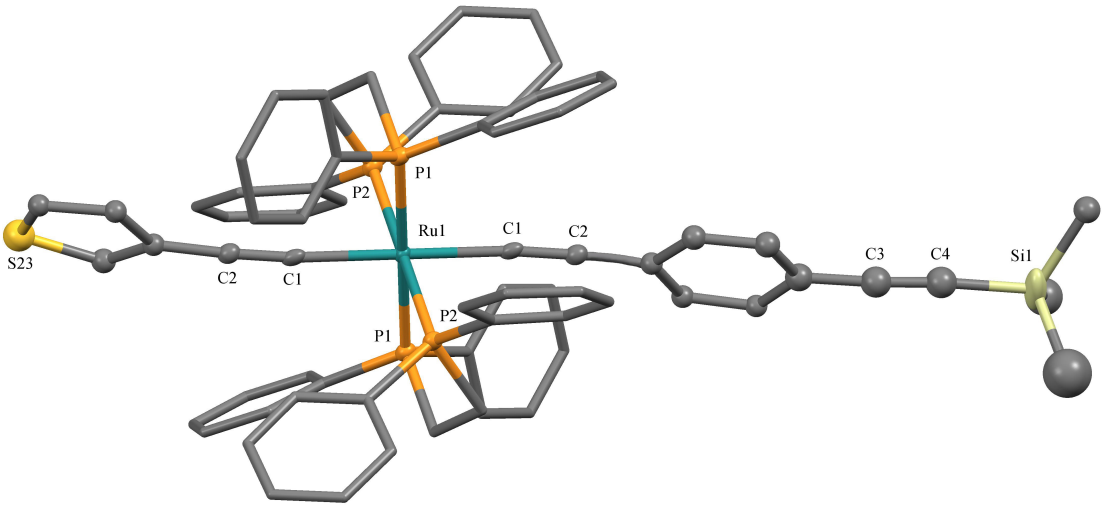

Figure S1. A plot of a molecule of **2** showing the atom labelling scheme. Solvent of crystallisation and hydrogen atoms have been omitted for clarity. Atomic displacement ellipsoids are plotted at 50% probability level.

Table S1. Crystal data and structure refinement for **2**.

Empirical formula	$C_{72}H_{65}Cl_3P_4RuSSi$
Formula weight	1321.69
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 9.4433(5) Å
	b = 13.3386(6) Å
	c = 13.8508(6) Å
	α= 77.282(4)°
	β= 74.659(4)°
	γ = 72.451(4)°
Volume	1585.38(13) Å^3
Z	1
Density (calculated)	1.384 Mg/m^3
μ	0.569 mm^{-1}
Crystal size	0.31 x 0.06 x 0.045 mm^3
θ range for data collection	3.04 to 27.48°.
Index ranges	-12<=h<=12, -16<=k<=18, -15<=l<=18
Reflections collected	11994
Independent reflections	7035 [R(int) = 0.0436]
Completeness to θ = 26.50°	99.8 %
Absorption correction	Analytical
Max. and min. transmission	0.978 and 0.902
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7035 / 131 / 457
Goodness-of-fit on F^2	1.087
Final R indices [I>2σ(I)]	R1 = 0.0706, wR2 = 0.1518
R indices (all data)	R1 = 0.0906, wR2 = 0.1610
Largest diff. peak and hole	2.236 and -1.479 e.Å^{-3}
CCDC No.	1883917

Table S2 Crystallographically determined bond lengths (Å) and angles (°) for compound **2**.

Ru1—C1	2.050 (4)	C222—H222	0.95
Ru1—C1^{i}	2.050 (4)	C223—C224	1.384 (7)
Ru1—P1	2.3485 (11)	C223—H223	0.95
Ru1—P1^{i}	2.3485 (11)	C224—C225	1.390 (7)
Ru1—P2^{i}	2.3559 (12)	C224—H224	0.95
Ru1—P2	2.3559 (12)	C225—C226	1.374 (7)
P1—C121	1.829 (5)	C225—H225	0.95
P1—C111	1.838 (5)	C226—H226	0.95
P1—C10	1.861 (5)	C1—C2	1.220 (6)
C111—C112	1.390 (7)	C2—C31	1.421 (6)
C111—C116	1.403 (6)	C2—C21	1.421 (6)
C112—C113	1.398 (6)	C21—C22	1.394 (12)
C112—H112	0.95	C21—C25	1.453 (13)
C113—C114	1.371 (7)	C22—S23	1.685 (13)
C113—H113	0.95	C22—H22	0.95
C114—C115	1.381 (7)	S23—C24	1.651 (16)
C114—H114	0.95	C24—C25	1.434 (13)
C115—C116	1.394 (7)	C24—H24	0.95
C115—H115	0.95	C25—H25	0.95
C116—H116	0.95	C31—C36	1.398 (9)
C121—C122	1.385 (7)	C31—C32	1.400 (9)
C121—C126	1.395 (7)	C32—C33	1.383 (9)
C122—C123	1.390 (7)	C32—H32	0.95
C122—H122	0.95	C33—C34	1.422 (9)
C123—C124	1.376 (8)	C33—H33	0.95
C123—H123	0.95	C34—C35	1.385 (10)

C124—C125	1.367 (8)	C34—C3	1.440 (16)
C124—H124	0.95	C35—C36	1.395 (9)
C125—C126	1.390 (7)	C35—H35	0.95
C125—H125	0.95	C36—H36	0.95
C126—H126	0.95	C3—C4	1.234 (16)
C10—C20	1.525 (6)	C4—Si1	1.807 (12)
C10—H10J	0.99	Si1—C102	1.828 (19)
C10—H10K	0.99	Si1—C103	1.992 (16)
C20—P2	1.844 (5)	Si1—C101	2.07 (3)
C20—H20A	0.99	C101—H10A	0.98
C20—H20B	0.99	C101—H10B	0.98
P2—C211	1.833 (5)	C101—H10C	0.98
P2—C221	1.846 (5)	C102—H10D	0.98
C211—C212	1.399 (7)	C102—H10E	0.98
C211—C216	1.409 (7)	C102—H10F	0.98
C212—C213	1.383 (7)	C103—H10G	0.98
C212—H212	0.95	C103—H10H	0.98
C213—C214	1.372 (8)	C103—H10I	0.98
C213—H213	0.95	C01—Cl3	1.666 (17)
C214—C215	1.391 (8)	C01—Cl1	1.672 (17)
C214—H214	0.95	C01—Cl2	1.734 (18)
C215—C216	1.379 (7)	C01—H01	1
C215—H215	0.95	C02—Cl5	1.69 (2)
C216—H216	0.95	C02—Cl6	1.72 (2)
C221—C222	1.389 (6)	C02—Cl4	1.824 (19)
C221—C226	1.414 (6)	C02—H02	1
C222—C223	1.389 (6)		
C1—Ru1—C1^{i}	180	C211—C216—H216	119.5
C1—Ru1—P1	92.65 (12)	C222—C221—C226	118.6 (4)

C1^{i}—Ru1—P1	87.36 (12)	C222—C221—P2	121.9 (4)
C1—Ru1—P1^{i}	87.35 (12)	C226—C221—P2	119.5 (3)
C1^{i}—Ru1—P1^{i}	92.64 (12)	C221—C222—C223	120.6 (4)
P1—Ru1—P1^{i}	180.00 (3)	C221—C222—H222	119.7
C1—Ru1—P2^{i}	80.31 (12)	C223—C222—H222	119.7
C1^{i}—Ru1—P2^{i}	99.69 (12)	C224—C223—C222	120.6 (5)
P1—Ru1—P2^{i}	97.06 (4)	C224—C223—H223	119.7
P1^{i}—Ru1—P2^{i}	82.94 (4)	C222—C223—H223	119.7
C1—Ru1—P2	99.69 (12)	C223—C224—C225	119.1 (5)
C1^{i}—Ru1—P2	80.31 (12)	C223—C224—H224	120.5
P1—Ru1—P2	82.94 (4)	C225—C224—H224	120.5
P1^{i}—Ru1—P2	97.06 (4)	C226—C225—C224	121.0 (5)
P2^{i}—Ru1—P2	180	C226—C225—H225	119.5
C121—P1—C111	102.0 (2)	C224—C225—H225	119.5
C121—P1—C10	102.0 (2)	C225—C226—C221	120.1 (4)
C111—P1—C10	102.4 (2)	C225—C226—H226	119.9
C121—P1—Ru1	120.00 (15)	C221—C226—H226	119.9
C111—P1—Ru1	119.46 (16)	C2—C1—Ru1	174.8 (4)
C10—P1—Ru1	108.45 (15)	C1—C2—C31	176.6 (5)
C112—C111—C116	118.6 (4)	C1—C2—C21	176.6 (5)
C112—C111—P1	120.4 (3)	C22—C21—C2	128.8 (7)
C116—C111—P1	121.0 (4)	C22—C21—C25	105.5 (14)
C111—C112—C113	120.2 (4)	C2—C21—C25	125.6 (13)
C111—C112—H112	119.9	C21—C22—S23	114.0 (10)
C113—C112—H112	119.9	C21—C22—H22	123
C114—C113—C112	120.7 (5)	S23—C22—H22	123
C114—C113—H113	119.7	C24—S23—C22	96.4 (12)
C112—C113—H113	119.7	C25—C24—S23	106 (2)
C113—C114—C115	120.0 (4)	C25—C24—H24	126.8

C113—C114—H114	120	S23—C24—H24	126.8
C115—C114—H114	120	C24—C25—C21	117 (2)
C114—C115—C116	120.1 (5)	C24—C25—H25	121.3
C114—C115—H115	119.9	C21—C25—H25	121.3
C116—C115—H115	119.9	C36—C31—C32	122.1 (15)
C115—C116—C111	120.4 (5)	C36—C31—C2	120.2 (14)
C115—C116—H116	119.8	C32—C31—C2	117.8 (6)
C111—C116—H116	119.8	C33—C32—C31	119.6 (11)
C122—C121—C126	118.2 (5)	C33—C32—H32	120.2
C122—C121—P1	122.4 (4)	C31—C32—H32	120.2
C126—C121—P1	119.4 (4)	C32—C33—C34	119.8 (12)
C121—C122—C123	120.9 (5)	C32—C33—H33	120.1
C121—C122—H122	119.6	C34—C33—H33	120.1
C123—C122—H122	119.6	C35—C34—C33	118.4 (17)
C124—C123—C122	119.8 (5)	C35—C34—C3	121.2 (17)
C124—C123—H123	120.1	C33—C34—C3	120.2 (11)
C122—C123—H123	120.1	C34—C35—C36	123 (3)
C125—C124—C123	120.6 (5)	C34—C35—H35	118.6
C125—C124—H124	119.7	C36—C35—H35	118.6
C123—C124—H124	119.7	C35—C36—C31	117 (3)
C124—C125—C126	119.7 (5)	C35—C36—H36	121.6
C124—C125—H125	120.2	C31—C36—H36	121.6
C126—C125—H125	120.2	C4—C3—C34	173.9 (13)
C125—C126—C121	120.9 (5)	C3—C4—Si1	176.5 (13)
C125—C126—H126	119.6	C4—Si1—C102	107.7 (7)
C121—C126—H126	119.6	C4—Si1—C103	110.9 (7)
C20—C10—P1	110.1 (3)	C102—Si1—C103	110.3 (8)
C20—C10—H10J	109.6	C4—Si1—C101	105.0 (9)
P1—C10—H10J	109.6	C102—Si1—C101	109.5 (11)

C20—C10—H10K	109.6	C103—Si1—C101	113.3 (9)
P1—C10—H10K	109.6	Si1—C101—H10A	109.5
H10J—C10—H10K	108.2	Si1—C101—H10B	109.5
C10—C20—P2	106.8 (3)	H10A—C101—H10B	109.5
C10—C20—H20A	110.4	Si1—C101—H10C	109.5
P2—C20—H20A	110.4	H10A—C101—H10C	109.5
C10—C20—H20B	110.4	H10B—C101—H10C	109.5
P2—C20—H20B	110.4	Si1—C102—H10D	109.5
H20A—C20—H20B	108.6	Si1—C102—H10E	109.5
C211—P2—C20	104.2 (2)	H10D—C102—H10E	109.5
C211—P2—C221	100.0 (2)	Si1—C102—H10F	109.5
C20—P2—C221	98.6 (2)	H10D—C102—H10F	109.5
C211—P2—Ru1	121.19 (15)	H10E—C102—H10F	109.5
C20—P2—Ru1	104.92 (15)	Si1—C103—H10G	109.5
C221—P2—Ru1	124.16 (15)	Si1—C103—H10H	109.5
C212—C211—C216	117.9 (4)	H10G—C103—H10H	109.5
C212—C211—P2	121.6 (4)	Si1—C103—H10I	109.5
C216—C211—P2	120.5 (4)	H10G—C103—H10I	109.5
C213—C212—C211	120.6 (5)	H10H—C103—H10I	109.5
C213—C212—H212	119.7	Cl3—C01—Cl1	107.3 (14)
C211—C212—H212	119.7	Cl3—C01—Cl2	104.6 (13)
C214—C213—C212	120.6 (5)	Cl1—C01—Cl2	102.7 (15)
C214—C213—H213	119.7	Cl3—C01—H01	113.7
C212—C213—H213	119.7	Cl1—C01—H01	113.7
C213—C214—C215	120.0 (5)	Cl2—C01—H01	113.7
C213—C214—H214	120	Cl5—C02—Cl6	99.2 (16)
C215—C214—H214	120	Cl5—C02—Cl4	106.5 (14)
C216—C215—C214	119.8 (5)	Cl6—C02—Cl4	93.3 (15)
C216—C215—H215	120.1	Cl5—C02—H02	117.9

C214—C215—H215	120.1	Cl6—C02—H02	117.9
C215—C216—C211	120.9 (5)	Cl4—C02—H02	117.9
C215—C216—H216	119.5		
Symmetry code: (i) −*x*, −*y*, −*z*.			

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

References

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