Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Synthesis, structural and photophysical properties of dimethylphosphino(perfluoro)phenylene-based gold(I) dimers

Felix Müller,[a] Lucas Wickemeyer,[a] Jan Schwabedissen,[a] Martin Ertl,[b] Beate Neumann,[a] Hans-Georg Stammler,[a] Uwe Monkowius[b] and Norbert W. Mitzel[a]

[a]Lehrstuhl für Anorganische Chemie und Strukturchemie; Centrum für Molekulare Materialien CM2, Fakultät für Chemie, Universität Bielefeld, Universitätsstraße 25, D-33615 Bielefeld, Germany.

[b]School of Education, Chemistry, Johannes Kepler University Linz, Altenbergerstr. 69, A-4040 Linz, Austria.

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NMR spectroscopic data

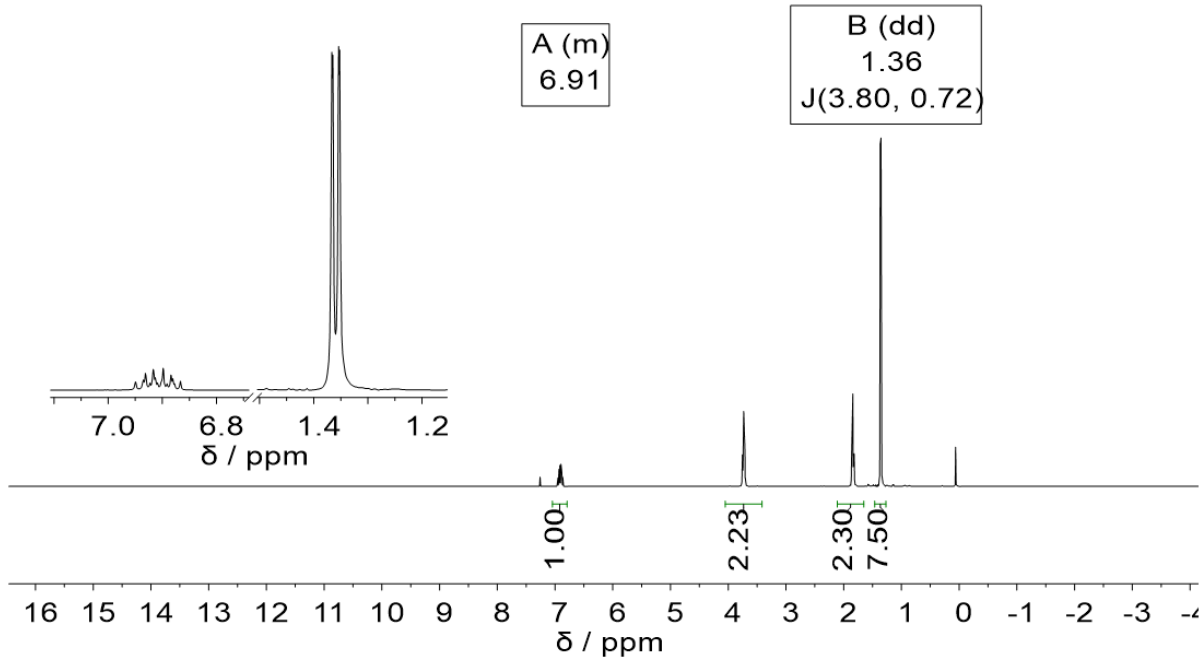


Figure S5. ^{1}H NMR spectrum of a solution of the mixture of tetrahydrofuran and dimethyl(2,3,4,5-tetrafluorophenyl)phosphane (**2**) in $CDCl_3$ (293 K, 300 MHz).

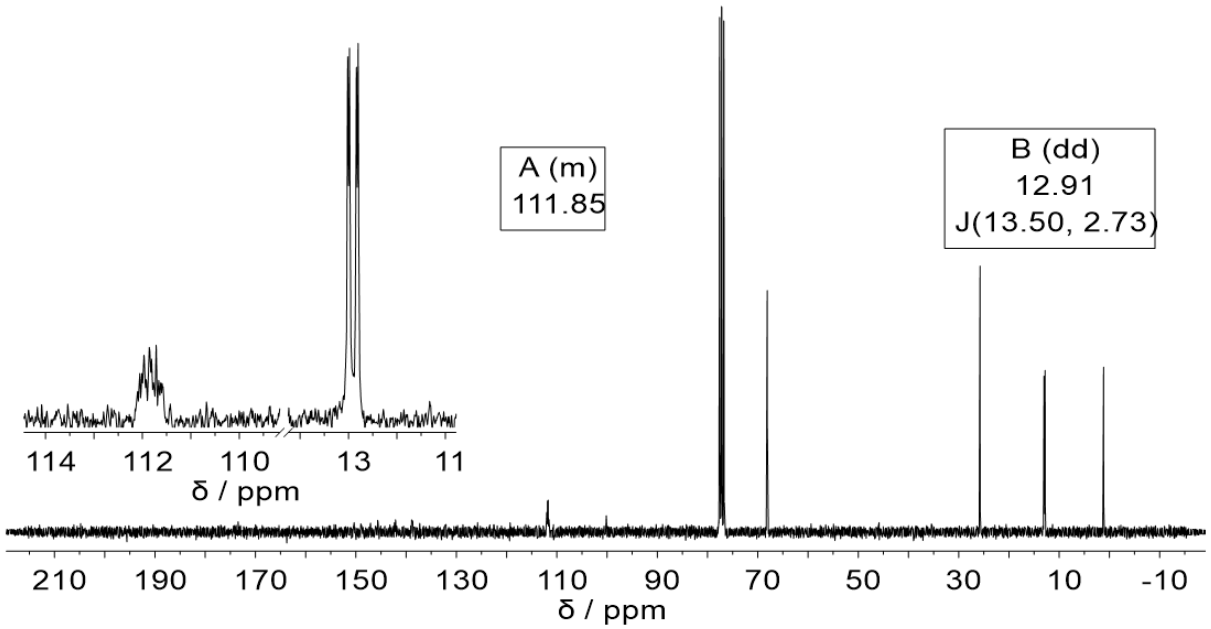


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of a solution of the mixture of tetrahydrofuran and dimethyl(2,3,4,5-tetrafluorophenyl)phosphane (**2**) in $CDCl_3$ (293 K, 75 MHz).

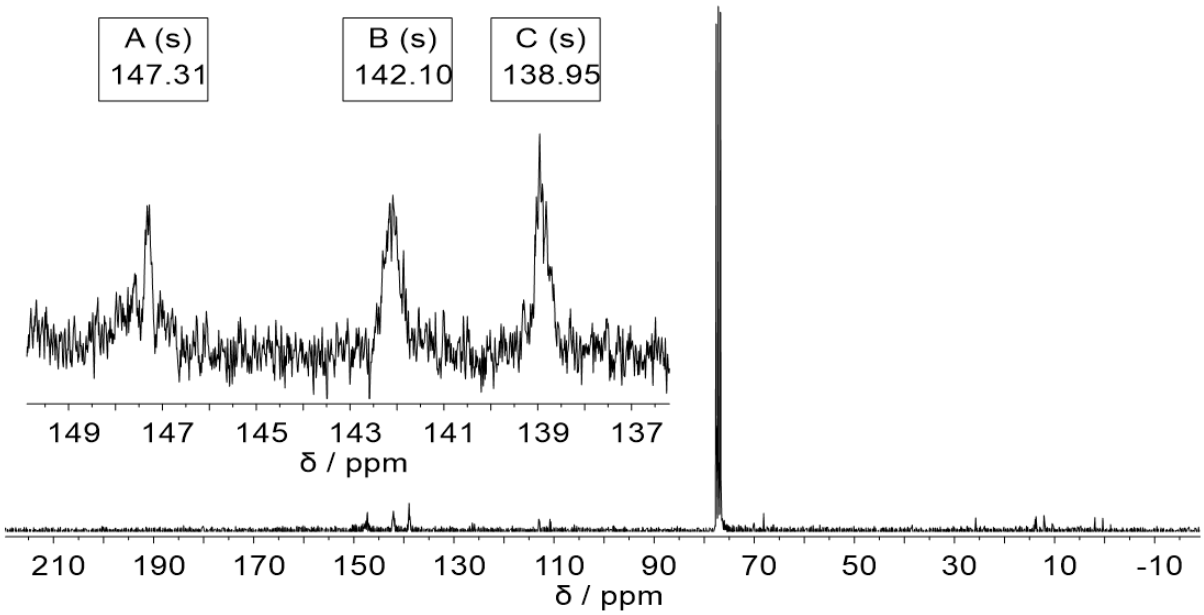


Figure S7. $^{13}C\{^{19}F\}$ NMR spectrum of a solution of the mixture of tetrahydrofuran and dimethyl(2,3,4,5-tetrafluorophenyl)phosphane (**2**) in $CDCl_3$ (293 K, 75 MHz).

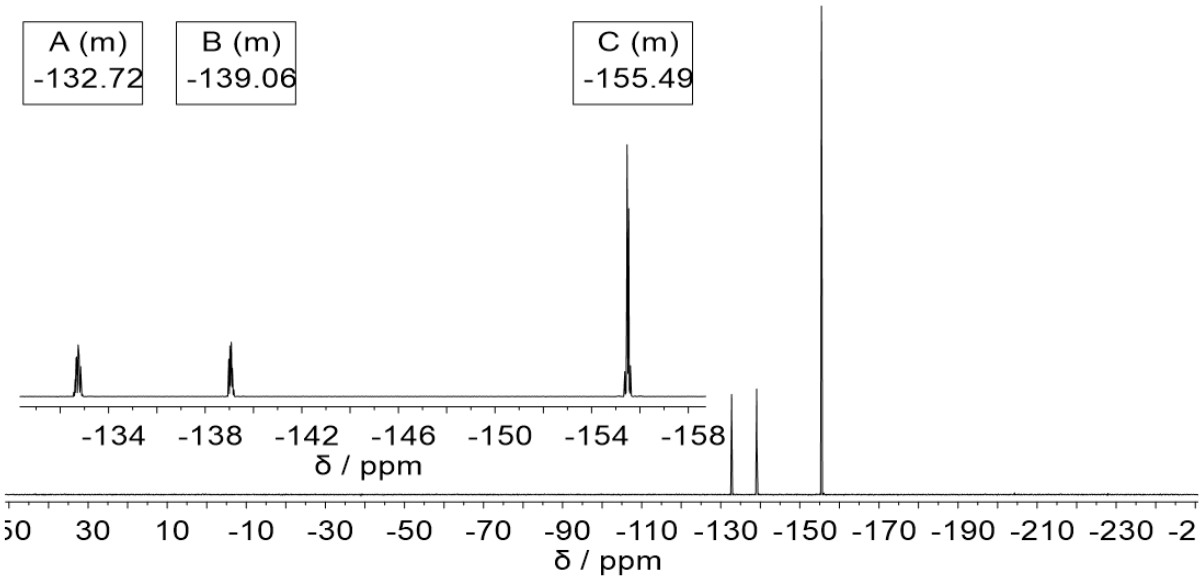


Figure S8. ^{19}F NMR spectrum of a solution of the mixture of tetrahydrofuran and dimethyl(2,3,4,5-tetrafluorophenyl)phosphane (**2**) in $CDCl_3$ (293 K, 282 MHz).

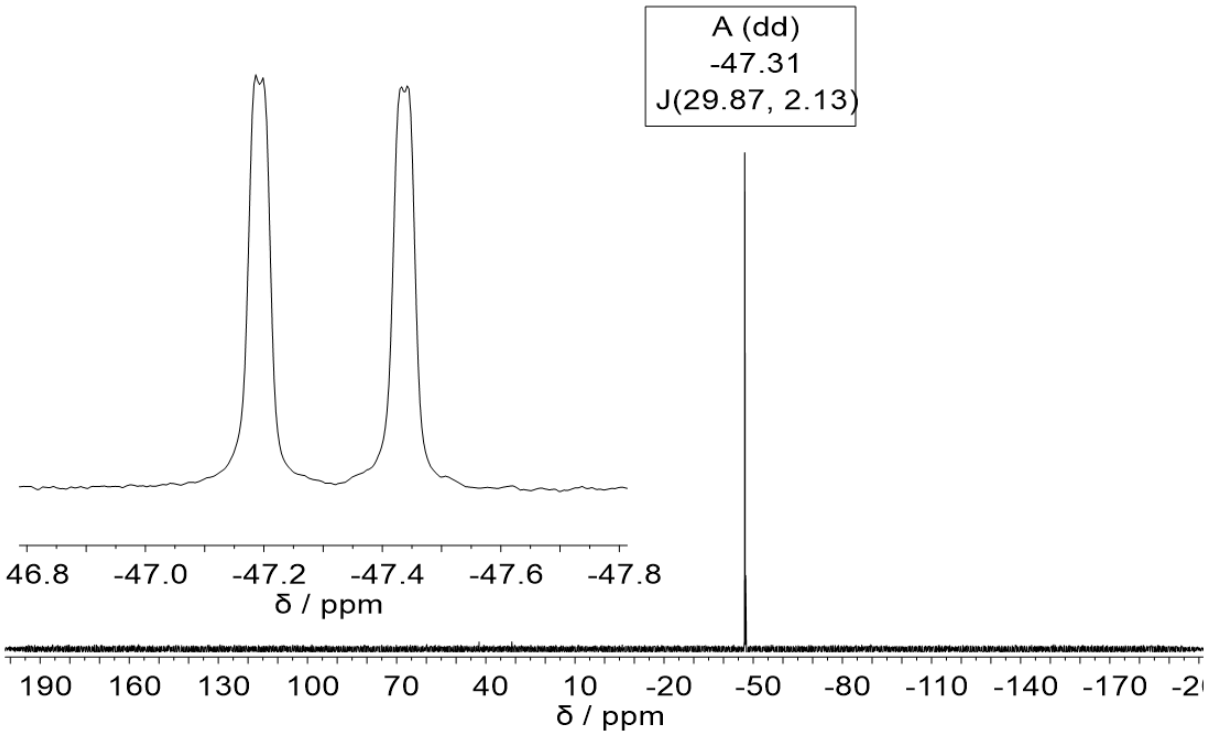


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of a solution of the mixture of tetrahydrofuran and dimethyl(2,3,4,5-tetrafluorophenyl)phosphane (**2**) in $CDCl_3$ (293 K, 121 MHz).

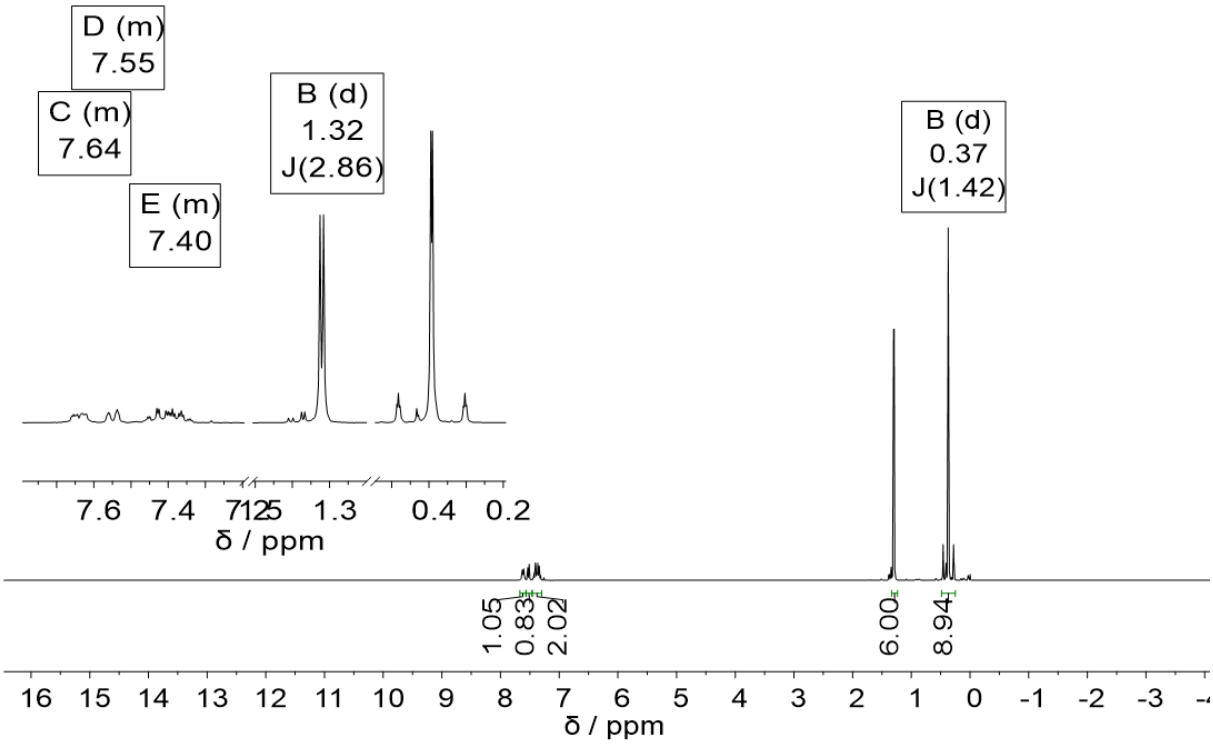


Figure S10. ^{1}H NMR spectrum of a solution of dimethyl(2-(trimethylstannyl)phenyl)phosphane (**3**) in $CDCl_3$ (293 K, 500 MHz).

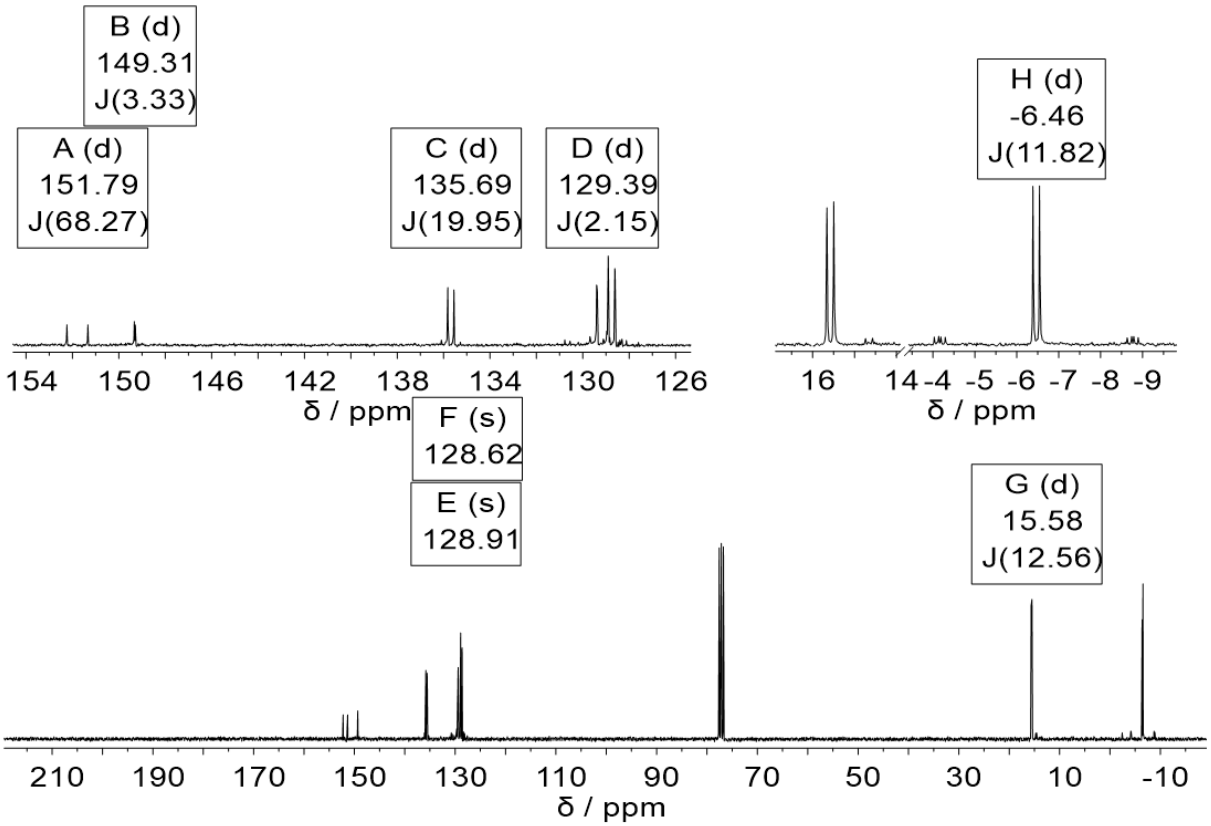


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of a solution of dimethyl(2-(trimethylstannyl)phenyl)phosphane (**3**) in $CDCl_3$ (293 K, 75 MHz).

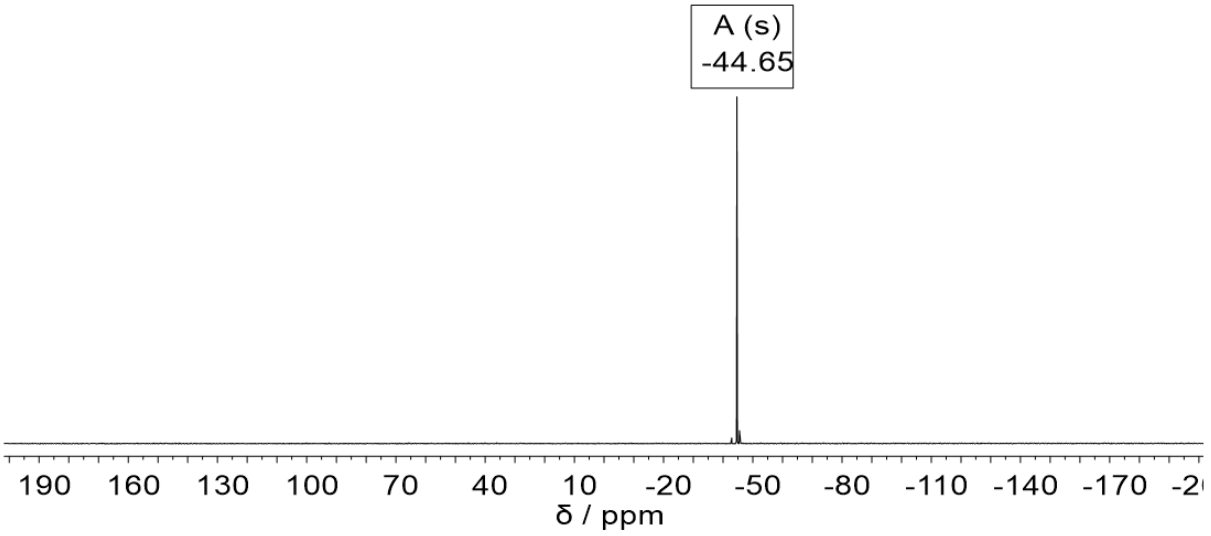


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of a solution of dimethyl(2-(trimethylstannyl)phenyl)phosphane (**3**) in $CDCl_3$ (293 K, 202 MHz).

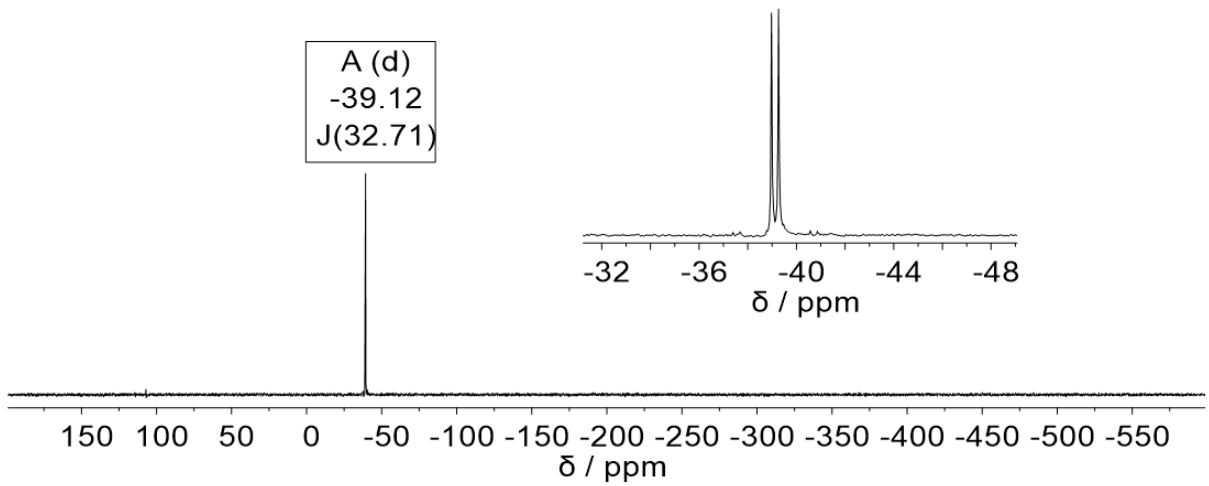


Figure S13. $^{119}Sn\{^{1}H\}$ NMR spectrum of a solution of dimethyl(2-(trimethylstannyl)phenyl)phosphane (**3**) in $CDCl_3$ (293 K, 186 MHz).

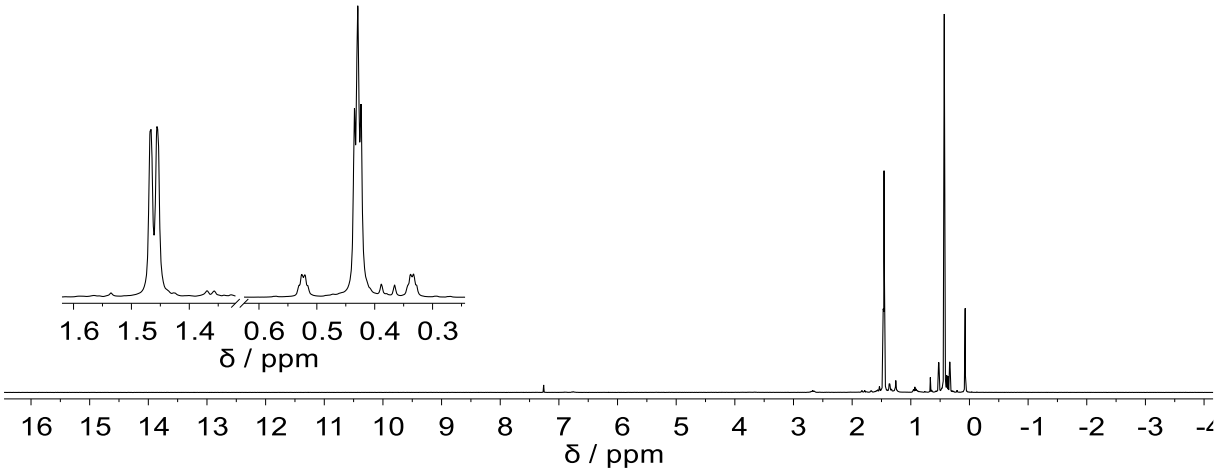


Figure S14. ^{1}H NMR spectrum of a solution of dimethyl[2,3,4,5-tetrafluoro-6-(trimethyl-stannyl)phenyl]phosphane (**4**) in $CDCl_3$ (293 K, 300 MHz).

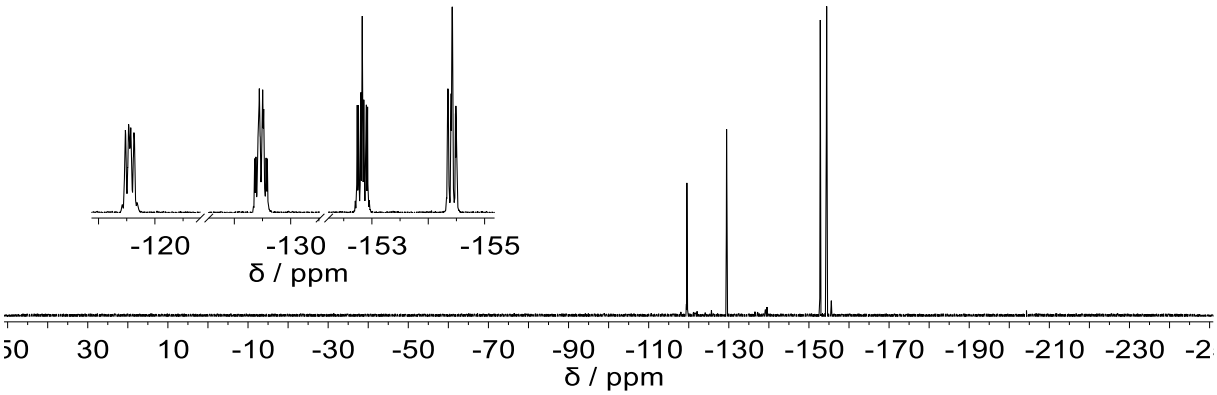


Figure S15. ^{19}F NMR spectrum of a solution of dimethyl[2,3,4,5-tetrafluoro-6-(trimethyl-stannyl)phenyl]phosphane (**4**) in $CDCl_3$ (293 K, 282 MHz).

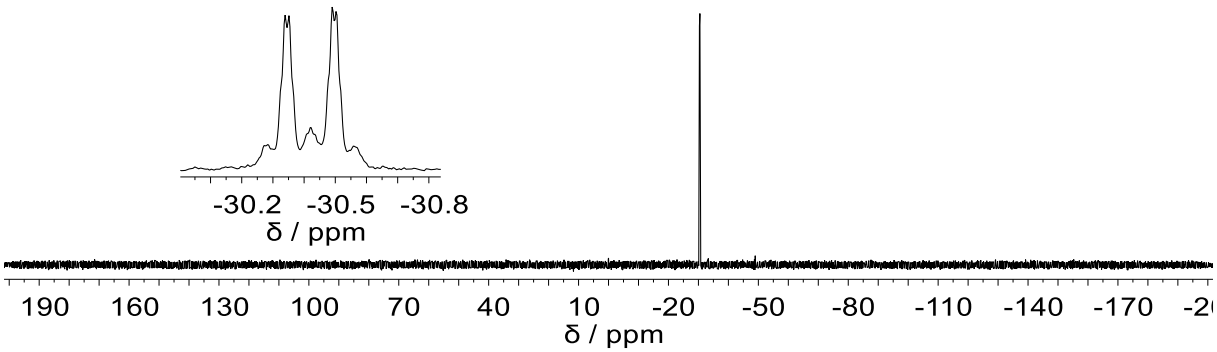


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of a solution of dimethyl[2,3,4,5-tetrafluoro-6-(trimethyl-stannyl)phenyl]phosphane (**4**) in $CDCl_3$ (293 K, 121 MHz).

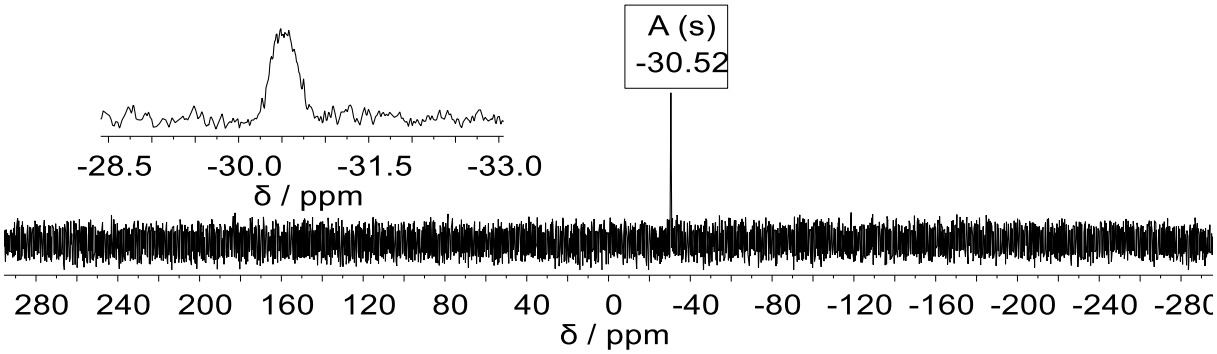


Figure S17. $^{119}Sn\{^{1}H\}$ NMR spectrum of a solution of dimethyl[2,3,4,5-tetrafluoro-6-(trimethyl-stannyl)phenyl]phosphane (**4**) in $CDCl_3$ (293 K, 187 MHz).

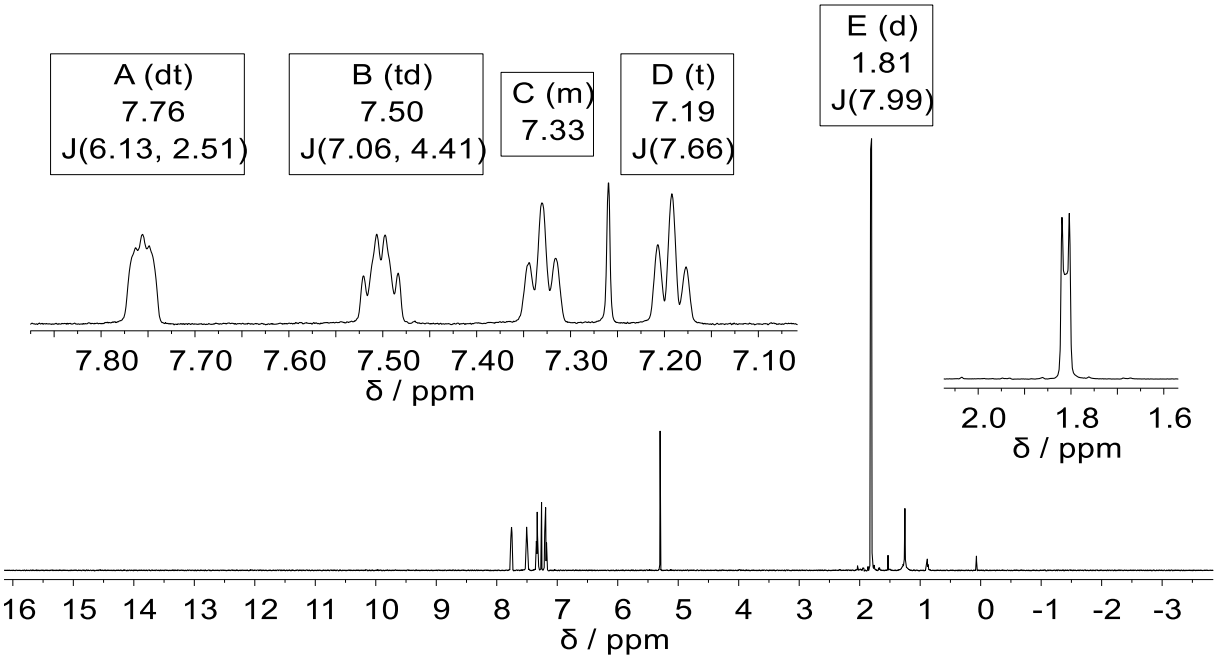


Figure S18. ^{1}H NMR spectrum of a solution of bis[(2-dimethylphosphino)phenyl]di-gold(I) (**5**) in $CDCl_3$ (293 K, 500 MHz).

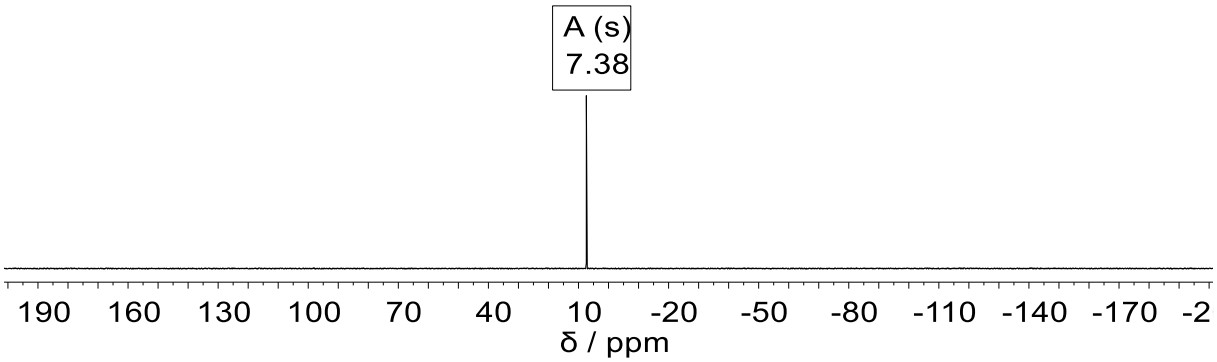


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of a solution of bis[(2-dimethylphosphino)phenyl]di-gold(I) (**5**) in $CDCl_3$ (293 K, 202 MHz).

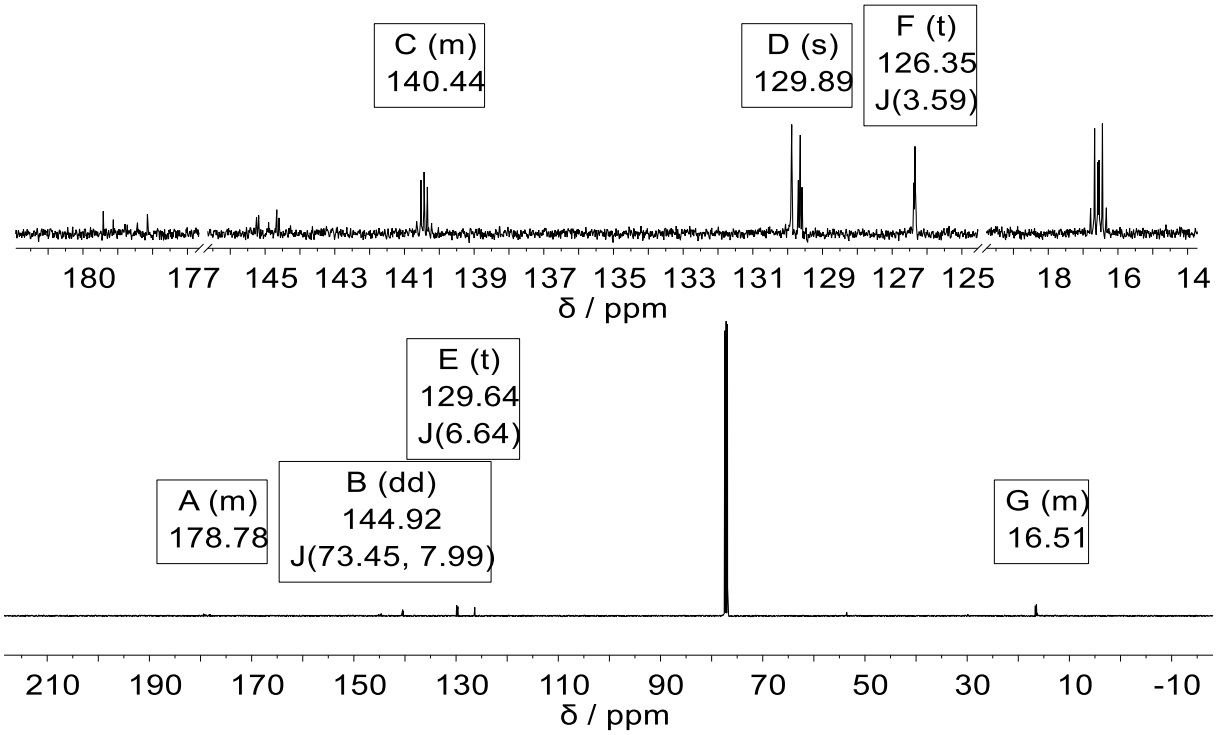


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of a solution of bis[(2-dimethylphosphino)phenyl]di-gold(I) (**5**) in $CDCl_3$ (293 K, 75 MHz).

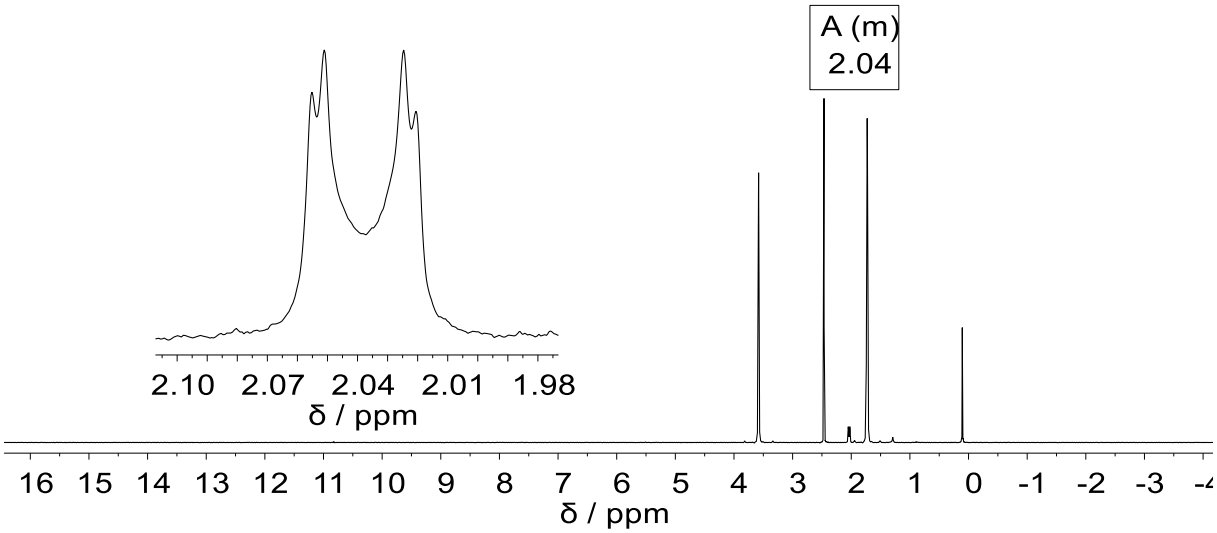


Figure S21. ^{1}H NMR spectrum of a solution of bis[(2-dimethylphosphino)-3,4,5,6-tetrafluorophenyl]di-gold(I) (**6**) in [D_8]THF (293 K, 300 MHz).

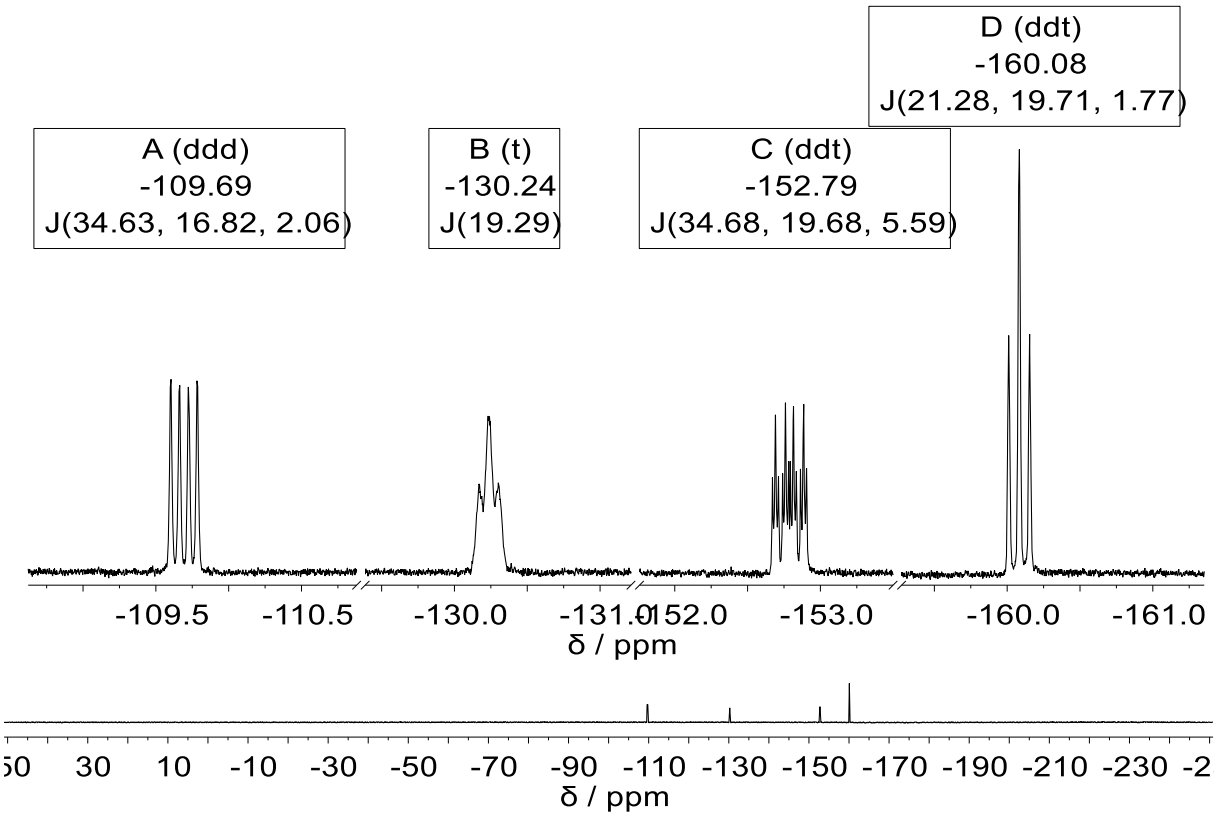


Figure S22. ^{19}F NMR spectrum of a solution of bis[(2-dimethylphosphino)-3,4,5,6-tetrafluorophenyl]di-gold(I) (**6**) in [D_8]THF (293 K, 282 MHz).

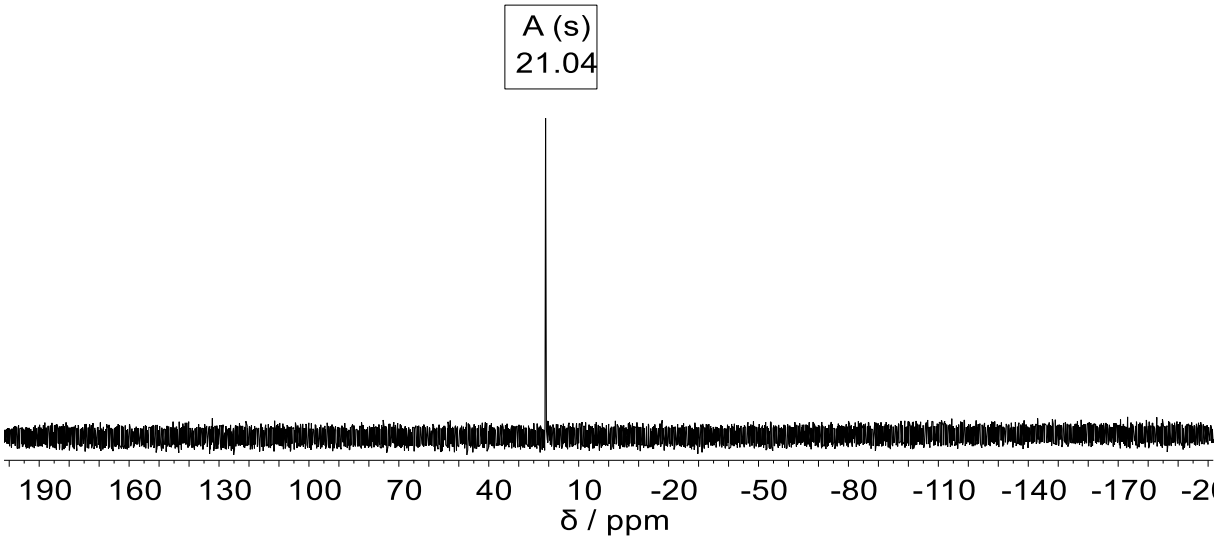


Figure S23. $^{31}P\{^{1}H\}$ NMR spectrum of a solution of bis[(2-dimethylphosphino)-3,4,5,6-tetrafluorophenyl]di-gold(I) (**6**) in $[D_8]$THF (293 K, 121 MHz).

Hirshfeld Analysis

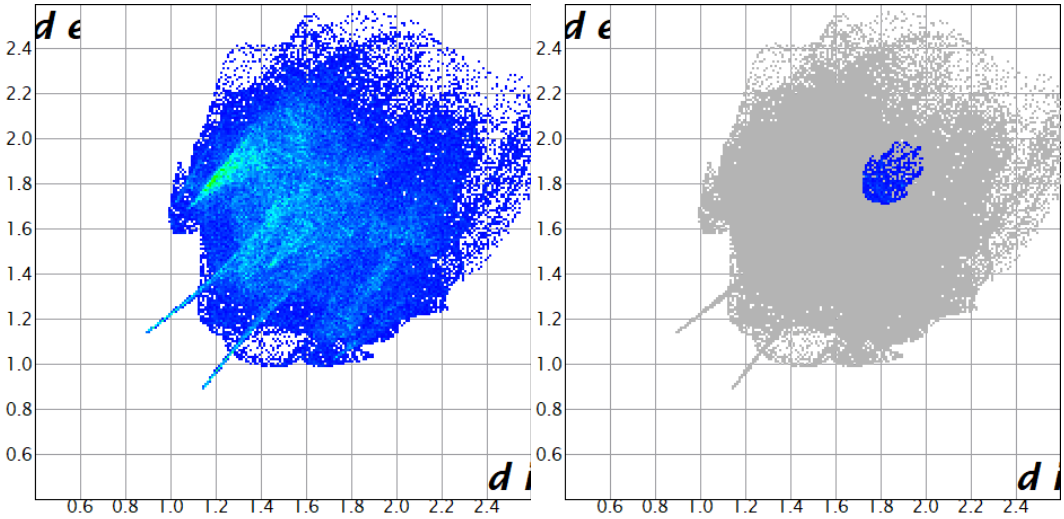


Figure S24. Fingerprint plot for **5**. C···C contacts are highlighted in the plot on the right which account for 0.8% of the surface area; d_i, d_e in Å.

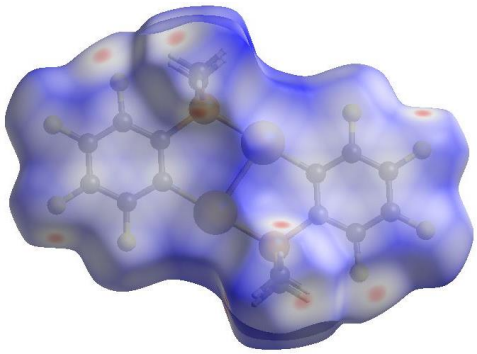


Figure S25. Hirshfeld surface for **6** mapped with d_{norm}. The overlapped surfaces are marked in red, touching areas in white and separated areas in blue.

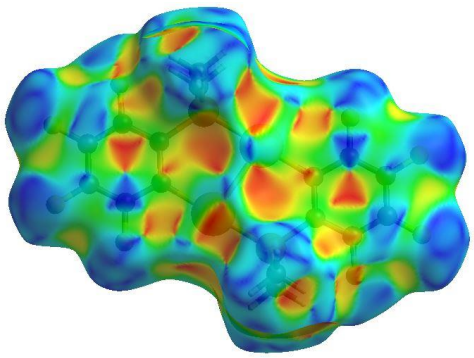


Figure S26. Hirshfeld surface for **6** mapped with shape index.

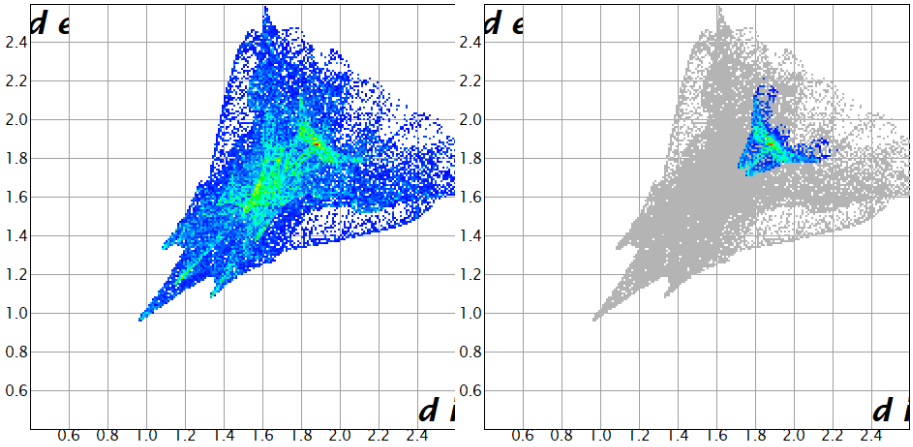


Figure S27. Fingerprint plot for **6**. C···C contacts are highlighted on the right which account for 10.6% of the surface area; d_i, d_e in Å.

Table S1. Distribution of contacts based on their contributions to the Hirshfeld surface area for **5** in %.

inside ↓, outside →	all	Au	P	C	H	Cl
all	100	9.0	0.0	12.8	67.5	10.6
Au	12.4	2.3	0.0	3.7	6.4	0.0
P	0.1	0.0	0.0	0.0	0.1	0.0
C	18.3	3.5	0.0	0.8	12.9	1.2
H	69.2	3.3	0.0	8.4	48.1	9.4

Table S2. Distribution of contacts based on their contributions to the Hirshfeld surface area for **6** in %.

inside ↓, outside →	all	Au	P	F	C	H
all	100	3.7	0.0	37.3	14.7	44.3
Au	5.2	0.0	0.0	4.3	0.6	0.3
P	0.0	0.0	0.0	0.0	0.0	0.0
F	38.0	2.9	0.0	5.7	3.5	25.9
C	14.8	0.6	0.0	3.6	10.6	0.0
H	42.0	0.2	0.0	23.7	0.0	18.1

Crystallographic data

Table S3. Crystallographic data for compounds **3**, **4**, **5** and **6**.

	3[a]	**4**[b]	**5**	**6**[c]
Empirical formula	$C_{11}H_{19}PSn$	$C_{11}H_{15}F_4PSn$	$C_{17}H_{22}Au_2Cl_2P_2$	$C_{16}H_{12}Au_2F_8P_2$
M_r	300.92	372.89	753.12	812.13
λ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	100.0(1)	100.0(1)	100.01(10)	200.0(1)
F(000)	600	1456	692	736
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$C2/m$
a [Å]	7.78125(10)	12.1460(1)	9.1778(3)	15.16837(19)
b [Å]	10.56152(12)	7.1602(1)	11.0554(3)	6.99146(10)
c [Å]	16.2469(2)	32.5086(3)	11.4165(3)	8.76220(11)
α [°]	90	90	87.267(2)	90
β [°]	99.6724(12)	100.118(1)	67.328(3)	97.2703(12)
γ [°]	90	90	68.529(3)	90
V [Å^3]	1316.22(3)	2783.23(5)	988.78(5)	921.75(2)
Z	4	8	2	2
$\rho_{calcd.}$ [g cm^{-3}]	1.519	1.780	2.530	2.926
μ [mm^{-1}]	2.023	1.972	15.248	16.148
Θ_{max} [°]	110.342	69.942	64.624	74.184
Index ranges h	$-17 \le h \le 17$	$-19 \le h \le 19$	$-13 \le h \le 13$	$-25 \le h \le 25$
Index ranges k	$-24 \le k \le 22$	$-11 \le k \le 11$	$-16 \le k \le 16$	$-11 \le k \le 11$
Index ranges l	$-37 \le l \le 37$	$-52 \le l \le 52$	$-16 \le l \le 17$	$-14 \le l \le 14$
Reflexes collected	156309	141539	60949	25772
Independent reflexes	16781	12229	6669	2449
R_{int}	0.0525	0.0570	0.0559	0.0354
Observed refl. [$I>2\sigma(I)$]	13305	11463	6448	2327
Parameters	202	317	213	84
R_1 [$I>2\sigma(I)$]	0.0252	0.0580	0.0255	0.0148
wR_2 [$I>2\sigma(I)$]	0.0515	0.0927	0.0624	0.0336
R_1 (all data)	0.0390	0.0615	0.0266	0.0179
wR_2 (all data)	0.0560	0.0938	0.0629	0.0343
GoF	1.063	1.373	1.171	1.111
ρ_{max}/ρ_{min} [e Å^{-3}]	0.69/−1.63	2.16/−3.23	2.17/−1.65	1.17/−0.99
CCDC number	2114608	2114609	2114610	2114611

[a]*In situ* grown crystal. Ultrasonic at 200 K, at 240 K polycrystalline material, at 289.0 K all melted except one seed crystal, cooled with 1K/h to 127 K, 5 K/h to 240 K and 360 K/h to 100K. The hydrogen atoms of one methyl group are disordered with ratio 60:40. The C-H distances of disordered hydrogen atoms were restrained to be same and their thermal parameters were constrained to be equal. [b]Hydrogen atoms were considered using a riding model. The crystal undergoes a phase transition between 150 K and 125 K resulting in polycrystalline material.

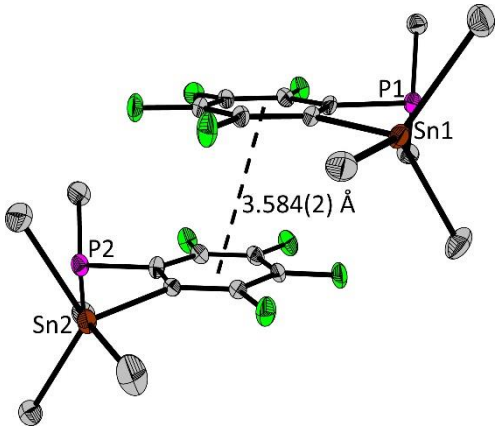


Figure S28. Side view onto the $C_6F_4(PMe_2)(SnMe_3)$ dimer **4** which illustrates the displaced layered arrangement of two molecules by short intermolecular aryl-aryl interactions (centroid···centroid distance: 3.584(2) Å) by dotted lines.

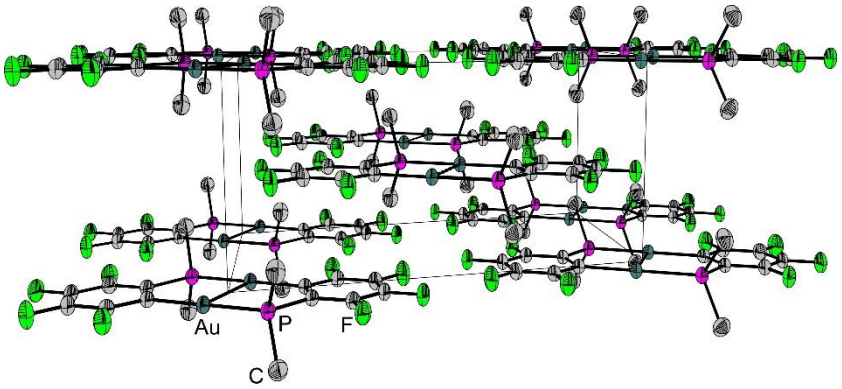


Figure S29. One filled unit cell of the fluorinated dimer **6** with completed fragments of broken off molecules.

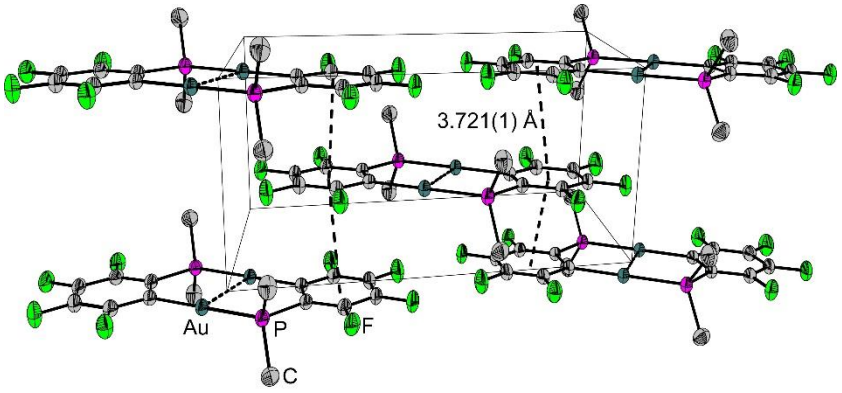


Figure S30. Front column of the unit cell of the fluorinated dimer **6** with completed fragments of broken off molecules. Illustration of the intermolecular aryl-aryl interactions (centroid···centroid distance: 3.721(1) Å) by dotted lines.

Quantum-Chemical and Topological Analysis

Topological parameters of the electron density were derived from the wave function files of the respective optimized PBE0(D3BJ)/def2-TZVPP structures of **5** and **6** using the AIMALL-Program.

Within this program the scheme of interacting quantum atoms (IQA) can be applied to calculate the energy of two atoms even if they are not involved in a bonding interaction with each other. Subsequent partitioning of the total energy between two atoms (E_{IQA}) into a Coulomb term (E_{C_IQA}) and an exchange-correlation term (E_{XC_IQA}) can be performed.

The following tables list the sum of the electronic and thermal Energies (E_A) and the sum of electronic and thermal free energies (E_B) from the optimized PBE0/def2-TZVPP geometries, dispersion is included in the right columns (D3BJ). Both values are reported in Hartrees.

Table S4. Energies (a.u.) of the optimized geometries for **5** and the artificially generated dimers **5'** and energy difference between the C_i and C_2 conformers (E_{Ci}–E_{C2} in kJ/mol)

	PBE0/def2-TZVPP		PBE0(D3BJ)/def2-TZVPP	
	E_A	E_B	E_A	E_B
5 C_{2h}	–1574.942796	–1575.022020	–1575.004381	–1575.084218
5' C_i	–1577.267992	–1577.356659	–1577.330340	–1577.415106
5' C_2	–1577.268956	–1577.361300	–1577.331901	–1577.419018
5' ΔE	2.5	12.2	4.1	10.3

Table S5. Energies (a.u.) of the optimized geometries for **6** and the artificially generated dimers **6'** and energy difference between the C_i and C_2 conformers (E_{Ci}–E_{C2} in kJ/mol)

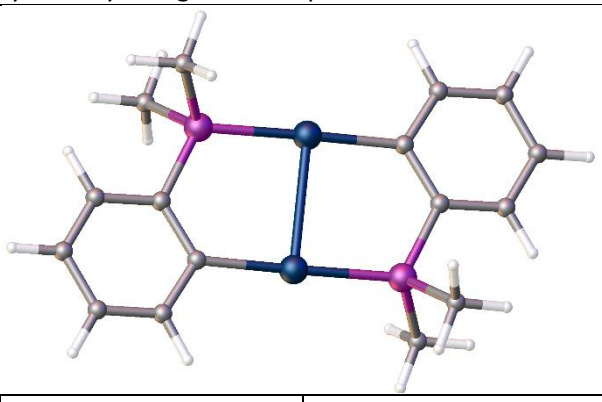
	PBE0/def2-TZVPP		PBE0(D3BJ)/def2-TZVPP	
	E_A	E_B	E_A	E_B
6 C_{2h}	–2368.516012	–2368.609055	–2368.579502	–2368.672582
6' C_i	–2370.845744	–2370.958402	–2370.911327	–2371.011706
6' C_2	–2370.847160	–2370.953358	–2370.911534	–2371.015286
6' ΔE	3.7	–13.2	0.5	9.4

Table S6. Intermetallic Au-Au distances in Å from the optimized geometries of the different fully- (**5**, **6**) and unsupported (**5'**, **6'**) derivatives. Basis set for all calculations was def2-TZVPP.

	XRD	PBE0	PBE0(D3BJ)
5, C_{2h}	2.888(1)	2.8898	2.8831
5', C_i		3.6758	3.2950
5', C_2		3.3185	3.1006
6, C_{2h}	2.851(1)	2.8669	2.8596
6', C_i		4.3242	3.3283
6', C_2		3.3816	3.1384

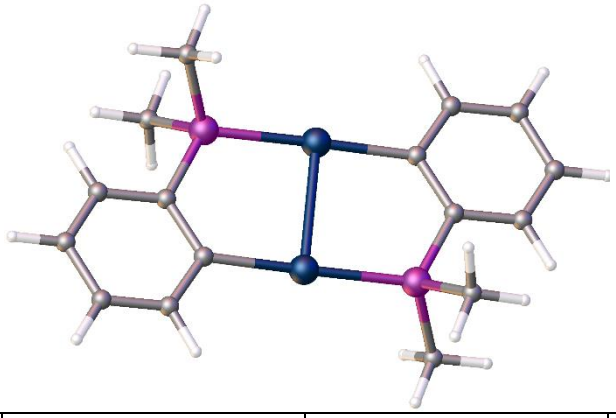
The following the Cartesian coordinates in Å of the optimized structures at the PBE0(D3BJ)/def2-TZVPP level of theory are given.

Table S7. Cartesian coordinates of the optimized geometry without dispersion-correction for the fully-supported dimer **5** in C_{2h} symmetry along with a depiction of the structure.



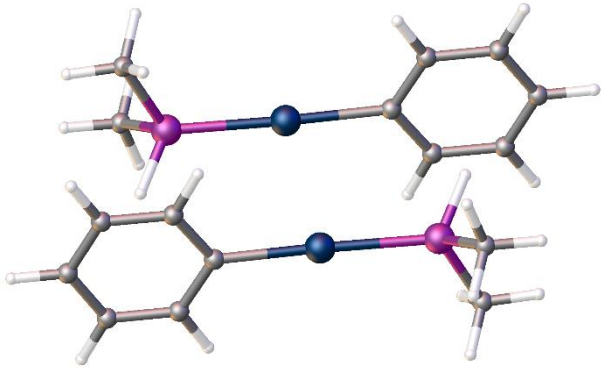
Au	-0.105205	1.441445	0.000000
Au	0.105205	-1.441445	0.000000
P	2.204728	1.358999	0.000000
P	-2.204728	-1.358999	0.000000
C	-2.163586	1.466649	0.000000
C	2.163586	-1.466649	0.000000
C	2.954639	-0.301571	0.000000
C	-2.954639	0.301571	0.000000
C	2.858357	-2.686222	0.000000
C	4.241942	-2.757958	0.000000
C	4.998792	-1.594431	0.000000
C	4.350919	-0.373497	0.000000
C	-2.858357	2.686222	0.000000
C	-4.241942	2.757958	0.000000
C	-4.998792	1.594431	0.000000
C	-4.350919	0.373497	0.000000
H	2.294325	-3.612876	0.000000
H	4.734365	-3.725082	0.000000
H	6.082136	-1.638158	0.000000
H	4.947869	0.533938	0.000000
H	-2.294325	3.612876	0.000000
H	-4.734365	3.725082	0.000000
H	-6.082136	1.638158	0.000000
H	-4.947869	-0.533938	0.000000
C	2.954639	2.213860	1.425511
C	2.954639	2.213860	-1.425511
C	-2.954639	-2.213860	1.425511
C	-2.954639	-2.213860	-1.425511
H	4.045292	2.186121	1.385924
H	2.618644	3.252397	1.436039
H	2.618930	1.731336	2.344072
H	4.045292	2.186121	-1.385924
H	2.618930	1.731336	-2.344072
H	2.618644	3.252397	-1.436039
H	-4.045292	-2.186121	1.385924
H	-2.618644	-3.252397	1.436039
H	-2.618930	-1.731336	2.344072
H	-4.045292	-2.186121	-1.385924
H	-2.618930	-1.731336	-2.344072
H	-2.618644	-3.252397	-1.436039

Table S8. Cartesian coordinates of the optimized geometry with dispersion-correction for the fully-supported dimer **5** in C_{2h} symmetry along with a depiction of the structure.



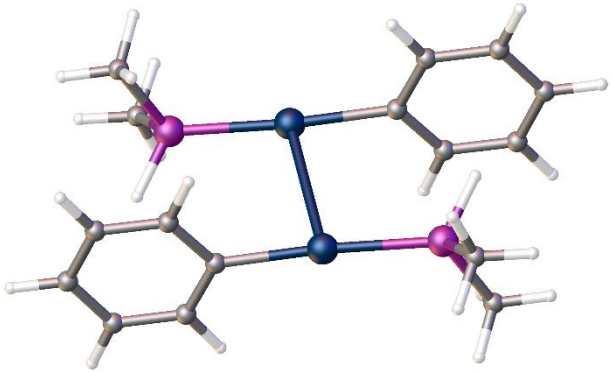
Au	-0.104057	1.438121	0.000000
Au	0.104057	-1.438121	0.000000
P	2.199170	1.350395	0.000000
P	-2.199170	-1.350395	0.000000
C	-2.159035	1.470357	0.000000
C	2.159035	-1.470357	0.000000
C	2.949281	-0.306004	0.000000
C	-2.949281	0.306004	0.000000
C	2.852753	-2.689762	0.000000
C	4.236106	-2.760486	0.000000
C	4.992664	-1.596653	0.000000
C	4.345086	-0.376037	0.000000
C	-2.852753	2.689762	0.000000
C	-4.236106	2.760486	0.000000
C	-4.992664	1.596653	0.000000
C	-4.345086	0.376037	0.000000
H	2.288229	-3.615883	0.000000
H	4.729142	-3.727065	0.000000
H	6.075800	-1.640445	0.000000
H	4.940395	0.532177	0.000000
H	-2.288229	3.615883	0.000000
H	-4.729142	3.727065	0.000000
H	-6.075800	1.640445	0.000000
H	-4.940395	-0.532177	0.000000
C	2.949281	2.199768	1.425519
C	2.949281	2.199768	-1.425519
C	-2.949281	-2.199768	1.425519
C	-2.949281	-2.199768	-1.425519
H	4.039637	2.170969	1.384222
H	2.612728	3.237803	1.440828
H	2.613519	1.711307	2.340742
H	4.039637	2.170969	-1.384222
H	2.613519	1.711307	-2.340742
H	2.612728	3.237803	-1.440828
H	-4.039637	-2.170969	1.384222
H	-2.612728	-3.237803	1.440828
H	-2.613519	-1.711307	2.340742
H	-4.039637	-2.170969	-1.384222
H	-2.613519	-1.711307	-2.340742
H	-2.612728	-3.237803	-1.440828

Table S9. Cartesian coordinates of the optimized geometry without dispersion-correction for the unsupported dimer **5'** in C_i symmetry along with a depiction of the structure.



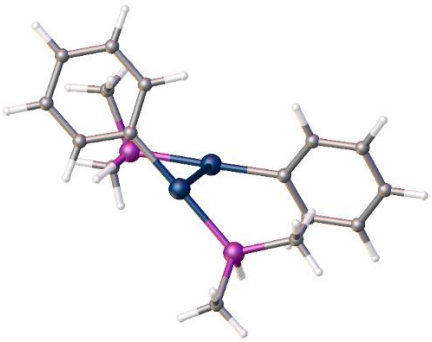
Au	-0.586612	1.675165	-0.477063
Au	0.586612	-1.675165	0.477063
P	1.506753	2.631780	-0.502517
P	-1.506753	-2.631780	0.502517
C	-2.476371	0.885139	-0.445734
C	2.476371	-0.885139	0.445734
C	3.026528	-0.230846	1.556210
C	-3.026528	0.230846	-1.556210
C	3.281135	-0.948075	-0.700409
C	4.549610	-0.382402	-0.743185
C	5.062134	0.269164	0.370480
C	4.294776	0.337911	1.524480
C	-3.281135	0.948075	0.700409
C	-4.549610	0.382402	0.743185
C	-5.062134	-0.269164	-0.370480
C	-4.294776	-0.337911	-1.524480
H	2.910177	-1.448047	-1.589772
H	5.142589	-0.453328	-1.649839
H	6.053271	0.709004	0.342156
H	4.687975	0.832371	2.407687
H	-2.910177	1.448047	1.589772
H	-5.142589	0.453328	1.649839
H	-6.053271	-0.709004	-0.342156
H	-4.687975	-0.832371	-2.407687
C	2.016592	3.446168	1.042939
C	1.776206	3.900572	-1.783118
C	-1.776206	-3.900572	1.783118
C	-2.016592	-3.446168	-1.042939
H	3.016519	3.873591	0.952796
H	1.301797	4.232992	1.289200
H	2.014339	2.706943	1.844031
H	2.786788	4.309688	-1.731566
H	1.616244	3.457252	-2.766822
H	1.051286	4.705376	-1.651767
H	-2.786788	-4.309688	1.731566
H	-1.051286	-4.705376	1.651767
H	-1.616244	-3.457252	2.766822
H	-3.016519	-3.873591	-0.952796
H	-2.014339	-2.706943	-1.844031
H	-1.301797	-4.232992	-1.289200
H	2.453718	-0.162934	2.476446
H	-2.453718	0.162934	-2.476446
H	2.582160	1.753480	-0.736201
H	-2.582160	-1.753480	0.736201

Table S10. Cartesian coordinates of the optimized geometry with dispersion-correction for the unsupported dimer **5'** in C_i symmetry along with a depiction of the structure.



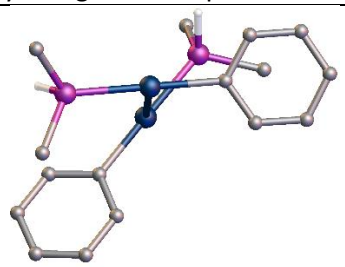
Au	-0.374678	1.550933	-0.410432
Au	0.374678	-1.550933	0.410432
P	1.693260	2.553510	-0.443560
P	-1.693260	-2.553510	0.443560
C	-2.282832	0.812972	-0.395920
C	2.282832	-0.812972	0.395920
C	2.830966	-0.149004	1.500712
C	-2.830966	0.149004	-1.500712
C	3.104056	-0.927075	-0.733666
C	4.387908	-0.398235	-0.766609
C	4.899749	0.264833	0.341145
C	4.115308	0.381442	1.479680
C	-3.104056	0.927075	0.733666
C	-4.387908	0.398235	0.766609
C	-4.899749	-0.264833	-0.341145
C	-4.115308	-0.381442	-1.479680
H	2.731560	-1.434204	-1.617883
H	4.993307	-0.503651	-1.661300
H	5.901782	0.678797	0.319104
H	4.506239	0.887973	2.356761
H	-2.731560	1.434204	1.617883
H	-4.993307	0.503651	1.661300
H	-5.901782	-0.678797	-0.319104
H	-4.506239	-0.887973	-2.356761
C	2.151597	3.434041	1.080096
C	1.905860	3.808932	-1.746908
C	-1.905860	-3.808932	1.746908
C	-2.151597	-3.434041	-1.080096
H	3.148775	3.869102	0.997359
H	1.421586	4.222237	1.271122
H	2.134732	2.730398	1.911519
H	2.895957	4.266308	-1.701728
H	1.769492	3.338455	-2.721399
H	1.142931	4.580251	-1.632224
H	-2.895957	-4.266308	1.701728
H	-1.142931	-4.580251	1.632224
H	-1.769492	-3.338455	2.721399
H	-3.148775	-3.869102	-0.997359
H	-2.134732	-2.730398	-1.911519
H	-1.421586	-4.222237	-1.271122
H	2.240647	-0.040219	2.405571
H	-2.240647	0.040219	-2.405571
H	2.812022	1.730093	-0.660689
H	-2.812022	-1.730093	0.660689

Table S11. Cartesian coordinates of the optimized geometry without dispersion-correction for the unsupported dimer **5'** in C_2 symmetry along with a depiction of the structure.



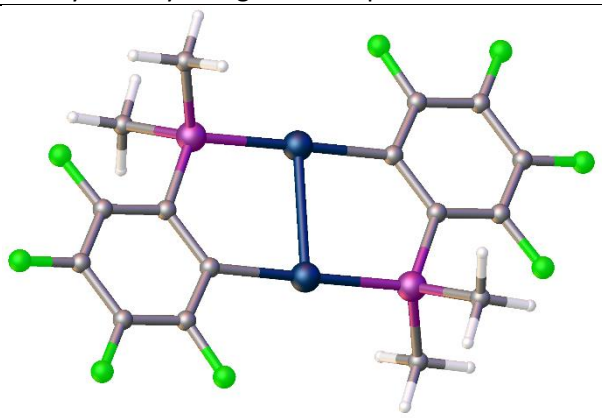
Au	-1.049491	1.285201	0.539322
Au	1.049491	-1.285201	0.539322
P	0.638616	2.618021	1.361959
P	-0.638616	-2.618021	1.361959
C	-2.624655	0.196552	-0.193822
C	2.624655	-0.196552	-0.193822
C	2.696633	0.175622	-1.543550
C	-2.696633	-0.175622	-1.543550
C	3.689634	0.210562	0.621564
C	4.758085	0.948620	0.126108
C	4.799268	1.303139	-1.214690
C	3.762739	0.909592	-2.049647
C	-3.689634	-0.210562	0.621564
C	-4.758085	-0.948620	0.126108
C	-4.799268	-1.303139	-1.214690
C	-3.762739	-0.909592	-2.049647
H	3.694159	-0.058637	1.673723
H	5.565814	1.242397	0.789387
H	5.632938	1.875820	-1.606349
H	3.783709	1.175391	-3.101920
H	-3.694159	0.058637	1.673723
H	-5.565814	-1.242397	0.789387
H	-5.632938	-1.875820	-1.606349
H	-3.783709	-1.175391	-3.101920
C	0.087411	3.967534	2.457946
C	1.712266	3.433434	0.145750
C	-0.087411	-3.967534	2.457946
C	-1.712266	-3.433434	0.145750
H	0.930996	4.553581	2.827098
H	-0.591049	4.619772	1.905650
H	-0.460204	3.547861	3.302792
H	2.457534	4.060388	0.637540
H	2.216030	2.670079	-0.449457
H	1.097789	4.046932	-0.515220
H	-0.930996	-4.553581	2.827098
H	0.591049	-4.619772	1.905650
H	0.460204	-3.547861	3.302792
H	-2.457534	-4.060388	0.637540
H	-2.216030	-2.670079	-0.449457
H	-1.097789	-4.046932	-0.515220
H	1.900991	-0.112901	-2.223278
H	-1.900991	0.112901	-2.223278
H	1.579448	1.964038	2.181968
H	-1.579448	-1.964038	2.181968

Table S12. Cartesian coordinates of the optimized geometry with dispersion-correction for the unsupported dimer **5'** in C_2 symmetry along with a depiction of the structure.



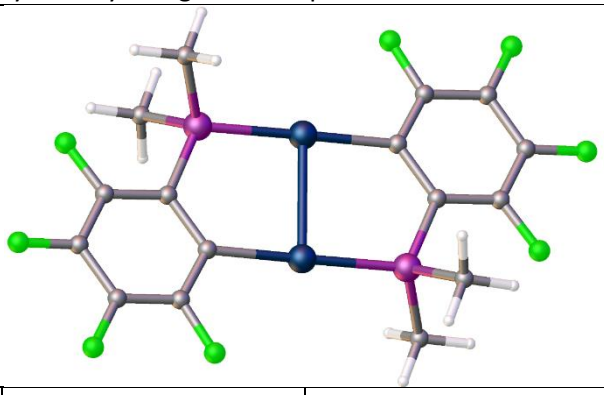
Au	-0.930042	1.240322	0.569516
Au	0.930042	-1.240322	0.569516
P	0.716990	2.571946	1.458415
P	-0.716990	-2.571946	1.458415
C	-2.434943	0.116446	-0.246334
C	2.434943	-0.116446	-0.246334
C	2.370650	0.321092	-1.576126
C	-2.370650	-0.321092	-1.576126
C	3.564468	0.272875	0.484677
C	4.570509	1.051993	-0.073572
C	4.480845	1.465581	-1.394919
C	3.374369	1.093800	-2.146130
C	-3.564468	-0.272875	0.484677
C	-4.570509	-1.051993	-0.073572
C	-4.480845	-1.465581	-1.394919
C	-3.374369	-1.093800	-2.146130
H	3.669799	-0.042683	1.518246
H	5.431733	1.332477	0.524550
H	5.265288	2.070911	-1.835437
H	3.290288	1.410642	-3.180686
H	-3.669799	0.042683	1.518246
H	-5.431733	-1.332477	0.524550
H	-5.265288	-2.070911	-1.835437
H	-3.290288	-1.410642	-3.180686
C	0.151421	3.854179	2.622902
C	1.755323	3.464498	0.270194
C	-0.151421	-3.854179	2.622902
C	-1.755323	-3.464498	0.270194
H	0.986146	4.439855	3.011905
H	-0.545753	4.516317	2.107091
H	-0.379384	3.382595	3.450786
H	2.510994	4.064356	0.779233
H	2.243746	2.742159	-0.384969
H	1.119142	4.112890	-0.334449
H	-0.986146	-4.439855	3.011905
H	0.545753	-4.516317	2.107091
H	0.379384	-3.382595	3.450786
H	-2.510994	-4.064356	0.779233
H	-2.243746	-2.742159	-0.384969
H	-1.119142	-4.112890	-0.334449
H	1.513432	0.054898	-2.186339
H	-1.513432	-0.054898	-2.186339
H	1.677567	1.894776	2.234318
H	-1.677567	-1.894776	2.234318

Table S13. Cartesian coordinates of the optimized geometry without dispersion-correction for the fully-supported dimer **6** in C_{2h} symmetry along with a depiction of the structure.



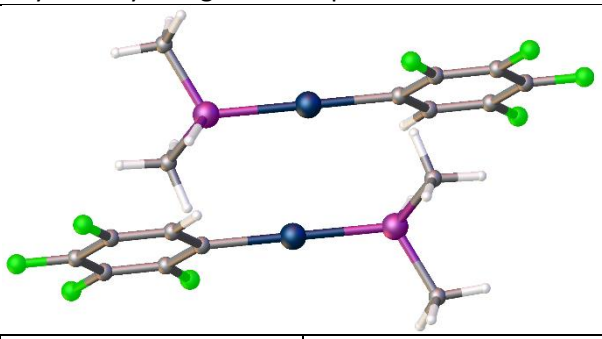
Au	-0.068065	1.430907	0.000000
Au	0.068065	-1.430907	0.000000
P	2.233754	1.359786	0.000000
P	-2.233754	-1.359786	0.000000
C	-2.134299	1.467126	0.000000
C	2.134299	-1.467126	0.000000
C	2.951889	-0.317604	0.000000
C	-2.951889	0.317604	0.000000
C	2.775464	-2.693009	0.000000
C	4.153154	-2.832068	0.000000
C	4.945763	-1.697571	0.000000
C	4.336122	-0.458024	0.000000
C	-2.775464	2.693009	0.000000
C	-4.153154	2.832068	0.000000
C	-4.945763	1.697571	0.000000
C	-4.336122	0.458024	0.000000
F	2.069474	-3.830782	0.000000
F	4.725485	-4.026297	0.000000
F	6.267591	-1.804689	0.000000
F	5.145800	0.611207	0.000000
F	-2.069474	3.830782	0.000000
F	-4.725485	4.026297	0.000000
F	-6.267591	1.804689	0.000000
F	-5.145800	-0.611207	0.000000
C	2.951889	2.215607	1.437629
C	2.951889	2.215607	-1.437629
C	-2.951889	-2.215607	1.437629
C	-2.951889	-2.215607	-1.437629
H	4.040680	2.233894	1.400577
H	2.566916	3.236997	1.452723
H	2.623995	1.712297	2.347969
H	4.040680	2.233894	-1.400577
H	2.623995	1.712297	-2.347969
H	2.566916	3.236997	-1.452723
H	-4.040680	-2.233894	1.400577
H	-2.566916	-3.236997	1.452723
H	-2.623995	-1.712297	2.347969
H	-4.040680	-2.233894	-1.400577
H	-2.623995	-1.712297	-2.347969
H	-2.566916	-3.236997	-1.452723

Table S14. Cartesian coordinates of the optimized geometry with dispersion-correction for the fully-supported dimer **6** in C_{2h} symmetry along with a depiction of the structure.



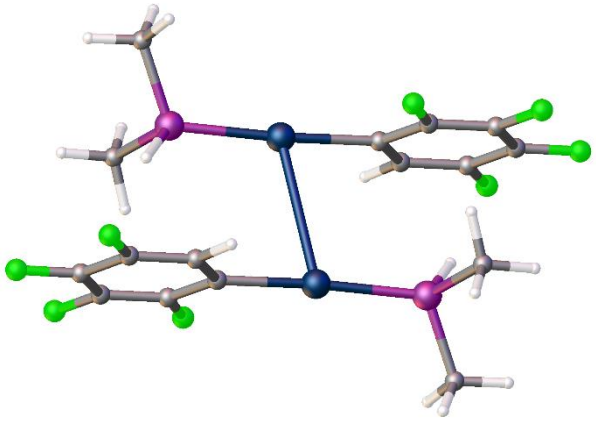
Au	-0.067778	1.427869	0.000000
Au	0.067778	-1.427869	0.000000
P	2.227411	1.352778	0.000000
P	-2.227411	-1.352778	0.000000
C	-2.130668	1.469804	0.000000
C	2.130668	-1.469804	0.000000
C	2.947126	-0.320685	0.000000
C	-2.947126	0.320685	0.000000
C	2.771030	-2.695498	0.000000
C	4.148714	-2.832991	0.000000
C	4.940843	-1.697854	0.000000
C	4.331375	-0.458618	0.000000
C	-2.771030	2.695498	0.000000
C	-4.148714	2.832991	0.000000
C	-4.940843	1.697854	0.000000
C	-4.331375	0.458618	0.000000
F	2.064520	-3.832549	0.000000
F	4.722449	-4.026456	0.000000
F	6.262593	-1.804982	0.000000
F	5.140456	0.611005	0.000000
F	-2.064520	3.832549	0.000000
F	-4.722449	4.026456	0.000000
F	-6.262593	1.804982	0.000000
F	-5.140456	-0.611005	0.000000
C	2.947126	2.200581	1.438007
C	2.947126	2.200581	-1.438007
C	-2.947126	-2.200581	1.438007
C	-2.947126	-2.200581	-1.438007
H	4.035629	2.213039	1.398826
H	2.565775	3.222967	1.458900
H	2.617117	1.691771	2.344348
H	4.035629	2.213039	-1.398826
H	2.617117	1.691771	-2.344348
H	2.565775	3.222967	-1.458900
H	-4.035629	-2.213039	1.398826
H	-2.565775	-3.222967	1.458900
H	-2.617117	-1.691771	2.344348
H	-4.035629	-2.213039	-1.398826
H	-2.617117	-1.691771	-2.344348
H	-2.565775	-3.222967	-1.458900

Table S15. Cartesian coordinates of the optimized geometry without dispersion-correction for the unsupported dimer **6'** in C_i symmetry along with a depiction of the structure.



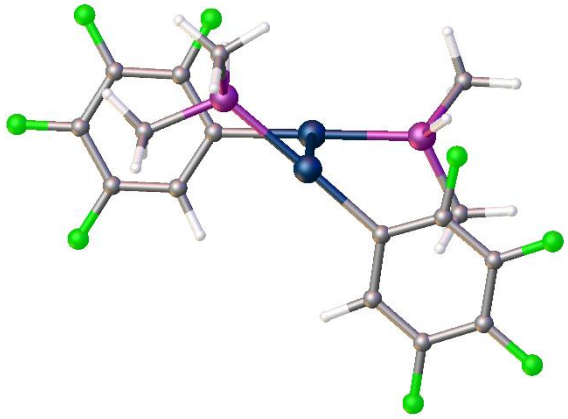
Au	-1.168693	1.786501	-0.309241
Au	1.168693	-1.786501	0.309241
P	0.974812	2.591531	-0.225884
P	-0.974812	-2.591531	0.225884
C	-3.094339	1.076004	-0.390782
C	3.094339	-1.076004	0.390782
C	3.909734	-1.221834	1.520143
C	-3.909734	1.221834	-1.520143
C	3.657973	-0.417085	-0.686182
C	4.949441	0.086787	-0.675372
C	5.734118	-0.071857	0.453947
C	5.199323	-0.732252	1.548214
C	-3.657973	0.417085	0.686182
C	-4.949441	-0.086787	0.675372
C	-5.734118	0.071857	-0.453947
C	-5.199323	0.732252	-1.548214
F	2.953131	-0.221553	-1.817656
F	5.444001	0.726236	-1.732817
F	6.972784	0.405977	0.478146
F	5.963408	-0.880300	2.633639
F	-2.953131	0.221553	1.817656
F	-5.444001	-0.726236	1.732817
F	-6.972784	-0.405977	-0.478146
F	-5.963408	0.880300	-2.633639
C	1.214069	4.093674	0.772334
C	1.772595	2.950372	-1.818139
C	-1.772595	-2.950372	1.818139
C	-1.214069	-4.093674	-0.772334
H	2.264484	4.387959	0.796662
H	0.619591	4.904999	0.349658
H	0.865445	3.908927	1.789084
H	2.793807	3.307067	-1.675188
H	1.794181	2.039710	-2.416737
H	1.192606	3.707243	-2.348230
H	-2.793807	-3.307067	1.675188
H	-1.192606	-3.707243	2.348230
H	-1.794181	-2.039710	2.416737
H	-2.264484	-4.387959	-0.796662
H	-0.865445	-3.908927	-1.789084
H	-0.619591	-4.904999	-0.349658
H	3.550750	-1.727183	2.408798
H	-3.550750	1.727183	-2.408798
H	1.886384	1.696585	0.367882
H	-1.886384	-1.696585	-0.367882

Table S16. Cartesian coordinates of the optimized geometry with dispersion-correction for the unsupported dimer **6'** in C_i symmetry along with a depiction of the structure.



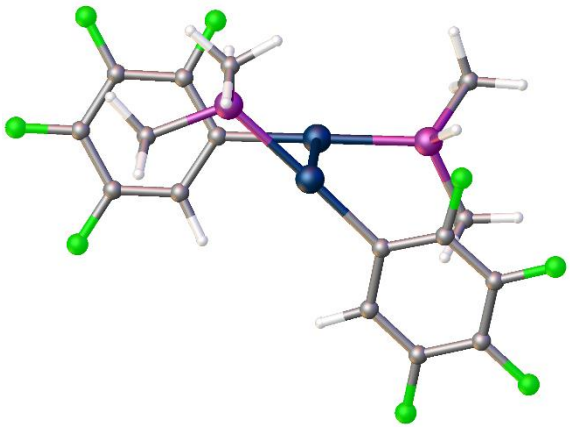
Au	-0.409647	1.612571	-0.033331
Au	0.409647	-1.612571	0.033331
P	1.631005	2.643990	0.032036
P	-1.631005	-2.643990	-0.032036
C	-2.307957	0.842557	-0.145197
C	2.307957	-0.842557	0.145197
C	2.993507	-0.713061	1.359019
C	-2.993507	0.713061	-1.359019
C	2.975722	-0.410691	-0.985227
C	4.250816	0.133060	-0.946532
C	4.904904	0.257927	0.267287
C	4.262314	-0.174288	1.417148
C	-2.975722	0.410691	0.985227
C	-4.250816	-0.133060	0.946532
C	-4.904904	-0.257927	-0.267287
C	-4.262314	0.174288	-1.417148
F	2.395181	-0.477102	-2.195532
F	4.849961	0.554372	-2.057559
F	6.123569	0.783446	0.317616
F	4.902898	-0.052721	2.582554
F	-2.395181	0.477102	2.195532
F	-4.849961	-0.554372	2.057559
F	-6.123569	-0.783446	-0.317616
F	-4.902898	0.052721	-2.582554
C	1.660889	4.229377	0.922457
C	2.365043	3.025012	-1.585171
C	-2.365043	-3.025012	1.585171
C	-1.660889	-4.229377	-0.922457
H	2.658951	4.670487	0.907392
H	0.952318	4.915932	0.457200
H	1.351157	4.066956	1.955392
H	3.361943	3.453629	-1.473345
H	2.424709	2.117989	-2.186133
H	1.718863	3.737210	-2.101032
H	-3.361943	-3.453629	1.473345
H	-1.718863	-3.737210	2.101032
H	-2.424709	-2.117989	2.186133
H	-2.658951	-4.670487	-0.907392
H	-1.351157	-4.066956	-1.955392
H	-0.952318	-4.915932	-0.457200
H	2.541633	-1.026851	2.292261
H	-2.541633	1.026851	-2.292261
H	2.657660	1.935249	0.681659
H	-2.657660	-1.935249	-0.681659

Table S17. Cartesian coordinates of the optimized geometry without dispersion-correction for the unsupported dimer **6'** in C_2 symmetry along with a depiction of the structure.



Au	1.527292	-0.725426	-0.301511
Au	-1.527292	0.725426	-0.301511
P	2.359316	1.261723	-1.086948
P	-2.359316	-1.261723	-1.086948
C	0.897609	-2.544153	0.422595
C	-0.897609	2.544153	0.422595
C	-0.705508	2.787845	1.788992
C	0.705508	-2.787845	1.788992
C	-0.662937	3.610535	-0.426351
C	-0.259627	4.859997	0.021082
C	-0.078438	5.073968	1.376998
C	-0.306814	4.024848	2.253299
C	0.662937	-3.610535	-0.426351
C	0.259627	-4.859997	0.021082
C	0.078438	-5.073968	1.376998
C	0.306814	-4.024848	2.253299
F	-0.808932	3.474651	-1.756754
F	-0.040164	5.855460	-0.832693
F	0.306814	6.265255	1.818587
F	-0.131007	4.241456	3.559361
F	0.808932	-3.474651	-1.756754
F	0.040164	-5.855460	-0.832693
F	-0.306814	-6.265255	1.818587
F	0.131007	-4.241456	3.559361
C	3.779012	1.116723	-2.216062
C	2.885012	2.457497	0.174930
C	-3.779012	-1.116723	-2.216062
C	-2.885012	-2.457497	0.174930
H	4.109433	2.096690	-2.564263
H	4.600272	0.619924	-1.697380
H	3.497082	0.503410	-3.072737
H	3.239947	3.382740	-0.281356
H	2.039617	2.674458	0.829093
H	3.684156	2.016482	0.772804
H	-4.109433	-2.096690	-2.564263
H	-4.600272	-0.619924	-1.697380
H	-3.497082	-0.503410	-3.072737
H	-3.239947	-3.382740	-0.281356
H	-2.039617	-2.674458	0.829093
H	-3.684156	-2.016482	0.772804
H	-0.869230	2.009610	2.525054
H	0.869230	-2.009610	2.525054
H	1.453560	2.016059	-1.857069
H	-1.453560	-2.016059	-1.857069

Table S18. Cartesian coordinates of the optimized geometry with dispersion-correction for the unsupported dimer **6'** in C_2 symmetry along with a depiction of the structure.



Au	1.496693	-0.471408	-0.325781
Au	-1.496693	0.471408	-0.325781
P	2.182579	1.551999	-1.146168
P	-2.182579	-1.551999	-1.146168
C	0.980385	-2.305908	0.439673
C	-0.980385	2.305908	0.439673
C	-0.700175	2.502463	1.797649
C	0.700175	-2.502463	1.797649
C	-0.882602	3.419497	-0.373631
C	-0.526112	4.672740	0.100819
C	-0.257108	4.841199	1.448460
C	-0.349989	3.743185	2.289391
C	0.882602	-3.419497	-0.373631
C	0.526112	-4.672740	0.100819
C	0.257108	-4.841199	1.448460
C	0.349989	-3.743185	2.289391
F	-1.119063	3.328653	-1.694367
F	-0.430968	5.714544	-0.719495
F	0.086710	6.035236	1.915487
F	-0.086710	3.916379	3.586820
F	1.119063	-3.328653	-1.694367
F	0.430968	-5.714544	-0.719495
F	-0.086710	-6.035236	1.915487
F	0.086710	-3.916379	3.586820
C	3.588427	1.495712	-2.298009
C	2.651023	2.782103	0.101410
C	-3.588427	-1.495712	-2.298009
C	-2.651023	-2.782103	0.101410
H	3.848781	2.493351	-2.655168
H	4.447671	1.055690	-1.789927
H	3.332797	0.860649	-3.146896
H	2.903511	3.737680	-0.359817
H	1.819230	2.917073	0.792854
H	3.510174	2.407255	0.659630
H	-3.848781	-2.493351	-2.655168
H	-4.447671	-1.055690	-1.789927
H	-3.332797	-0.860649	-3.146896
H	-2.903511	-3.737680	-0.359817
H	-1.819230	-2.917073	0.792854
H	-3.510174	-2.407255	0.659630
H	-0.750625	1.681861	2.503186
H	0.750625	-1.681861	2.503186
H	1.215233	2.235809	-1.905210
H	-1.215233	-2.235809	-1.905210