Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Synthesis and Applications of Fluorous Phosphines

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Dedicated to Prof. Barry Trost on the occasion of his 75th birthday.

	Formula	M. W.	F (wt%)	P[a]	P_M[r]	m. p. (°C)	b. p. (°C)	cone angle (°)	^{31}P NMR	Ref.
1a	$C_{18}H_{12}F_{27}P$	772	66.5	N/A	N/A	N/A	N/A	N/A	N/A	10a
1b	$C_{24}H_{12}F_{39}P$	1072	69.1	82.3	N/A	N/A	150[w]	103.2	-25.5	12a
1c	$C_{30}H_{12}F_{51}P$	1372	70.6	>332	N/A	47.5	175[x]	104.1	-25.4	13
1d	$C_{36}H_{12}F_{63}P$	1672	71.6	>332	N/A	100.8	N/A	N/A	-25.5	13
2a	$C_{21}H_{18}F_{27}P$	814	63	N/A	N/A	N/A	N/A	N/A	-34.5	22
2b	$C_{26}H_{18}F_{39}P$	1102	67.2	N/A	713[s]	N/A	N/A	N/A	-34.6	22
2c	$C_{33}H_{18}F_{51}P$	1414	68.5	82.3	832[s]	67.1	N/A	N/A	-34.8	22
2d	$C_{39}H_{18}F_{63}P$	1714	69.8	N/A	N/A	N/A	N/A	N/A	N/A	13
3	$C_{36}H_{24}F_{51}P$	1456	66.6	89.9	N/A	40.2	N/A	N/A	-32.8	22
4	$C_{39}H_{30}F_{51}P$	1498	64.7	89.9	N/A	N/A	N/A	N/A	N/A	16
5	$C_{25}H_{18}F_{35}P$	1014	65.6	N/A	N/A	N/A	N/A	N/A	-33.5	15
6	$C_{29}H_{14}F_{47}P$	1286	69.4	N/A	N/A	N/A	N/A	N/A	-27.8	15
7	$C_{31}H_{14}F_{51}P$	1386	69.9	N/A	N/A	59.5-60	N/A	N/A	-28.2	16
8	$C_{32}H_{16}F_{51}P$	1400	69.2	N/A	N/A	68.5-69	N/A	N/A	-31.3	16

	Formula	M. W.	F (wt%)	P[a]	P_M[r]	m. p. (°C)	b. p. (°C)	cone angle (°)	^{31}P NMR	Ref.
9	$C_{35}H_{22}F_{51}P$	1442	67.2	N/A	N/A	N/A	N/A	N/A	-34.7	16
10	$C_{35}H_{22}F_{51}P$	1442	67.2	N/A	N/A	49-49.5	N/A	N/A	-33.6	16
11	$C_{32}H_{20}F_{47}P$	1328	67.2	N/A	N/A	N/A	N/A	N/A	-34	22
12	$C_{30}H_{12}F_{51}P$	1372	70.6	>332	N/A	43.4-50	215[y]	N/A	-25.3	14a
13a	$C_{12}H_{14}F_{13}P$	436	56.7	N/A	N/A	N/A	N/A	N/A	N/A	18
13b	$C_{14}H_{18}F_{13}P$	464	53.2	N/A	N/A	N/A	N/A	N/A	5.16	17
13c	$C_{20}H_{26}F_{13}P$	544	45.4	N/A	N/A	N/A	N/A	N/A	-0.71	17
14	$C_{34}H_{20}F_{52}P_2$	1478	66.8	N/A	N/A	N/A	N/A	N/A	-24.1	18
15a	$C_{37}H_{26}F_{52}P_2$	1520	65	20.3	37.5[t]	N/A	N/A	N/A	-26.8	19
15b	$C_{45}H_{26}F_{68}P_2$	1920	67.3	82.3	141.9[t]	42	N/A	108.1	-26.7	19
15c	$C_{56}H_{26}F_{84}P_2$	2356	67.7	142	332.3[t]	73	N/A	N/A	-26.6	19
16a	$C_{40}H_{24}F_{42}P_2$	1555	63.5	N/A	N/A	N/A	N/A	105.5	-21.5	20
16b	$C_{48}H_{24}F_{68}P_2$	1954	66.1	N/A	N/A	63	N/A	105.7	-19.4	20
17a	$C_{26}H_{26}F_{26}P$	864	57.2	3.63	N/A	N/A	N/A	N/A	-24.1	21
17b	$C_{30}H_{26}F_{34}P$	1064	60.7	14.9	N/A	N/A	157-160[z]	N/A	-24	21
18	$C_{30}H_{48}F_{16}P_2$	774	39.3	N/A	N/A	52-54	N/A	N/A	-25.5	23
19a	$C_6F_{15}P$	388	73.5	N/A	N/A	N/A	N/A	N/A	13.7	24
19b	$C_9F_{21}P$	538	74.2	N/A	N/A	N/A	N/A	N/A	23.3	24
19c	$C_{12}F_{27}P$	688	74.6	N/A	N/A	N/A	N/A	N/A	23.7	24
19d	$C_{15}F_{33}P$	838	74.8	N/A	N/A	N/A	N/A	N/A	26.8	24
19e	$C_{18}F_{39}P$	988	75	N/A	N/A	N/A	N/A	N/A	25	24
19f	$C_8F_{19}P$	488	74	N/A	N/A	N/A	N/A	N/A	7.6	24
20a	$C_{18}H_{18}F_{21}P$	664	60.1	N/A	N/A	N/A	N/A	N/A	N/A	26
20b	$C_{14}H_{10}F_{21}P$	608	65.6	N/A	N/A	N/A	N/A	N/A	N/A	27

	Formula	M. W.	F (wt%)	P[a]	P_M[r]	m. p. (°C)	b. p. (°C)	cone angle (°)	^{31}P NMR	Ref.
20c	$C_{22}H_{22}F_{21}P$	716	55.7	N/A	N/A	N/A	N/A	N/A	N/A	27
21	$C_{10}F_{24}P_2$	638	71.5	N/A	N/A	N/A	N/A	N/A	4.7	24
22	$C_{20}H_{14}F_{13}P$	532	46.4	N/A	N/A	42-44	N/A	N/A	N/A	12a
23	$C_{22}H_{13}F_{26}P$	802	61.6	N/A	N/A	35-37	N/A	N/A	N/A	12a
24a	$C_{15}H_{10}F_7P$	354	37.6	N/A	N/A	N/A	N/A	N/A	N/A	26
24b	$C_{16}H_{10}F_9P$	404	42.3	N/A	N/A	N/A	N/A	N/A	N/A	26
24c	$C_{18}H_{11}F_{12}P$	486	46.9	N/A	N/A	N/A	N/A	N/A	N/A	10a
24d	$C_{18}H_{10}F_{13}P$	504	49	N/A	N/A	N/A	N/A	N/A	1.07-2.25	25, 26
24e	$C_{18}H_{10}F_{11}P$	466	44.8	N/A	N/A	N/A	N/A	N/A	N/A	26
24f	$C_{20}H_{10}F_{17}P$	604	53.5	N/A	N/A	N/A	N/A	N/A	1.29-2.39	26
24g	$C_{22}H_{11}F_{21}P$	705	56.6	1.17[b], 0.28[c] 0.16[d], 0.27[e], 0.4[f]	N/A	52-52.9	N/A	N/A	1.15-2.41	26
24h	$C_{24}H_{11}F_{25}P$	805	59	N/A	N/A	80.2-81.8	N/A	N/A	1.45-2.55	26
25a	$C_{30}H_{26}F_{21}P$	817	48.8	N/A	N/A	76-77	N/A	N/A	-0.8	27
25b	$C_{24}H_{14}F_{21}O_2P$	764	52.2	N/A	N/A	176-177	N/A	N/A	-0.91	27
25c	$C_{24}H_{14}F_{21}O_2P$	764	52.2	N/A	N/A	N/A	N/A	N/A	3.65	27
25d	$C_{22}H_8F_{23}P$	740	59.1	N/A	N/A	63-64	N/A	N/A	-0.38	27
26	$C_{50}H_{20}F_{52}P_2$	1703	58	N/A	N/A	88-90	N/A	N/A	N/A	12a
27	$C_{64}H_{40}F_{52}P_2$	1834	53.9	N/A	N/A	80-82	N/A	N/A	-11.5	45
28a	$C_{66}H_{60}F_{52}Si_4P_2$	2014	49.1	0.4[g]	1.6[u]	N/A	N/A	N/A	-11.3	46a
28b	$C_{74}H_{60}F_{68}Si_4P_2$	1938	66.7	N/A	3.7[u]	N/A	N/A	N/A	-11.3	46a
29	$C_{94}H_{64}F_{104}Si_4P_2$	3342	59.1	12[g]	8[u]	N/A	N/A	N/A	-11.4	46a
30	$C_{122}H_{68}F_{156}Si_4P_2$	4670	63.5	>50[g]	23[u]	N/A	N/A	N/A	-11.4	46a
31a	$C_{42}H_{40}F_{16}P_2$	910	33.4	N/A	N/A	60-63	N/A	N/A	-18.9	23

	Formula	M. W.	F (wt%)	P[a]	P_M[r]	m. p. (°C)	b. p. (°C)	cone angle (°)	^{31}P NMR	Ref.
31b	$C_{42}H_{40}F_{16}P_2$	910	33.4	N/A	N/A	94-96	N/A	N/A	-39.3	23
32	$C_{28}H_{20}F_8P_2$	570	26.7	N/A	N/A	N/A	N/A	N/A	N/A	26, 27
33	$C_{30}H_{20}F_{12}P_2$	670	34	N/A	N/A	N/A	N/A	N/A	N/A	26, 27
34	$C_{42}F_{63}P$	1732	69.1	N/A	N/A	117	N/A	N/A	N/A	47
35a	$C_{24}H_{14}F_{13}P$	580	42.6	N/A	N/A	N/A	120-124*	103.4	-6.7	12a
35b	$C_{24}H_{14}F_{13}P$	580	42.6	N/A	N/A	76-78	N/A	N/A	N/A	12a
36a	$C_{30}H_{13}F_{26}P$	898	55	1.56[h]	N/A	54-56	N/A	N/A	-4	48a
36b	$C_{34}H_{13}F_{34}P$	1098	58.8	3.17[h]	N/A	53-55	N/A	N/A	-4.4	48a
37	$C_{26}H_{18}F_{13}P$	608	40.6	0.12[b], 0.02[i], 0.05[j]	N/A	N/A	N/A	N/A	-5.11	49
38	$C_{25}H_{16}F_{13}P$	594	41.6	0.09[b], 0.01[i], 0.12[j]	N/A	N/A	N/A	N/A	-5.39	49
39	$C_{30}H_{13}F_{26}P$	898	55	N/A	N/A	N/A	N/A	N/A	N/A	12a
40a	$C_{41}H_{11}F_{52}P$	1534	64.4	9[h]	N/A	56-58	N/A	N/A	-5.3	48a
40b	$C_{50}H_{11}F_{68}P$	1934	66.8	N/A	N/A	N/A	N/A	N/A	N/A	48a
41	$C_{34}H_{21}F_{26}P$	954	51.8	1.86[b], 0.05[i], 0.05[j]	N/A	N/A	N/A	N/A	-5.91	49
42	$C_{32}H_{17}F_{26}P$	926	53.3	3.34[b], 1.05[i], 0.18[j]	N/A	N/A	N/A	N/A	-6.29	49
43	$C_{36}H_{12}F_{39}P$	1216	60.9	2.2[i], 4.4[j]	N/A	65-67	N/A	105.8	N/A	12a
44a	$C_{41}H_{11}F_{52}P$	1534	64.4	99[h]	N/A	N/A	N/A	N/A	-6.3	48a
44b	$C_{56}H_{10}F_{81}P$	2252	68.3	N/A	N/A	N/A	N/A	N/A	N/A	48a
45a	$C_{42}H_{24}F_{39}P$	1300	57	30.03[b], 0.08[i], 0.75[j]	N/A	N/A	N/A	N/A	-6.65	49
45b	$C_{48}H_{24}F_{51}P$	1600	60.6	N/A	>999[v]	N/A	N/A	N/A	N/A	49, 63
46	$C_{39}H_{18}F_{39}P$	1258	58.9	18.48[b], 0.51[i], 6.84[j]	N/A	N/A	N/A	N/A	-7.12	49
47a	$C_{45}H_{30}F_{39}P$	1342	55.2	0.242	N/A	91.5-92.7	N/A	N/A	-7.3	50
47b	$C_{51}H_{30}F_{51}P$	1642	59	1.99	>999[v]	120-121	N/A	N/A	-7.4	50, 63
47c	$C_{57}H_{30}F_{63}P$	1882	63.6	N/A	N/A	139.7-140.5	N/A	N/A	-7.1	50

	Formula	M. W.	F (wt%)	P[a]	P_M[r]	m. p. (°C)	b. p. (°C)	cone angle (°)	^{31}P NMR	Ref.
48	$C_{84}H_{45}F_{102}P$	3022	64.1	N/A	N/A	N/A	N/A	N/A	N/A	51
49a	$C_{48}H_{42}F_{39}Si_3P$	1474	50.3	0.26[a], 1.1[k], 1.5[l]	293[g,s], 76[s]	89	N/A	N/A	-4.66	52a
49b	$C_{54}H_{42}F_{51}Si_3P$	1774	54.6	2.2[a], 4.6[k], 2.2[l]	887[g,s]	101	N/A	N/A	-4.67	52a
50a	$C_{69}H_{45}F_{78}Si_3P$	2470	60	7.8[a], 17[k], 5.7[l]	N/A	67	N/A	N/A	-4.62	52a
50b	$C_{81}H_{45}F_{102}Si_3P$	3070	63.1	7.8[a], 28[k], 9.2[l]	N/A	72	N/A	N/A	-4.7	52a
51a	$C_{90}H_{48}F_{117}Si_3P$	3466	64.1	4.3[a], 9.4[k], 15[l]	N/A	50-55	N/A	N/A	-4.49	52a
51b	$C_{108}H_{48}F_{153}Si_3P$	4894	59.4	2.1[a], 12[k], 20[l]	N/A	124	N/A	N/A	-4.49	52a
52a	$C_{76}H_{28}F_{68}P_2$	2294	56.3	N/A	N/A	N/A	N/A	N/A	-15.4	54a
52b	$C_{92}H_{26}F_{102}P_2$	3130	61.9	N/A	N/A	N/A	N/A	N/A	-15.85	54a
52c	$C_{60}H_{30}F_{34}P_2$	1459	44.3	N/A	N/A	N/A	N/A	N/A	-14.2	54a
52d	$C_{56}H_{30}F_{26}P_2$	1259	39.2	N/A	N/A	N/A	N/A	N/A	-13.5	54c
52e	$C_{60}H_{38}F_{26}P_2$	1315	37.6	N/A	N/A	N/A	N/A	N/A	-15.4	54c
53	$C_{76}H_{36}F_{60}O_4P_2$	2215	51.5	N/A	N/A	49-50	N/A	N/A	-17.3	56c
54	$C_{92}H_{54}F_{78}Si_2P_2$	2759	53.7	3.8[m], 49[n], 49[o]	N/A	N/A	N/A	N/A	-14.1	55
55	$C_{56}H_{26}F_{45}O_3P$	1633	52.4	N/A	N/A	49	N/A	N/A	-15.5	56a
56	$C_{56}H_{22}F_{49}OP$	1672	55.7	N/A	N/A	39-41	N/A	N/A	-11.2	56d
57	$C_{81}H_{47}F_{78}OSi_2P$	2605	56.9	N/A	N/A	N/A	N/A	N/A	-12.2	56d
58	$C_{42}H_{18}F_{45}O_3P$	1457	58.7	24.6[p], 10.4[q]	N/A	N/A	N/A	N/A	-9.5	58c

Footnotes:

a. Partition Coefficient in Perfluoro(methyl)cyclohexane (PFMCH)/Toluene bi-phase at ambient condition, unless stated otherwise.
b. FC-72/MeOH.
c. FC-72/Acetone

d. FC-72/EtOAc
e. FC-72/$CHCl_3$
f. FC-72/Benzene
g. Measured at 0^{o}C.
h. 1,3-dimethylperfluorocyclohexane/Toluene.
i. FC-72/THF
j. FC-72/Toluene
k. PFMCH/Octane
l. PFMCH/Pentane
m. C_6F_{14}/Benzene
n. C_6F_{14}/MeCN
o. C_6F_{14}/DMF
p. Galden D-100/Methanol
q. Galden D-100/Toluene
r. Partition Coefficient of the metal complex at ambient temperature (PFMCH: Toluene).
s. Measured as the RhP_3Cl complex.
t. Measured as the (P^P)PdO_2CCF_3 complex.
u. Measured as the (P^P)$NiCl_2$ complex.
v. Measured as the nickel salicylaldiminato phosphine complex.
w. 0.05 mmHg
x. 5 x 10^{-5} mmHg
y. 0.009 Torr
z. 0.02 mmHg
* 0.04 mmHg

The reference numbers listed here are the same as in the main text of the paper:

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