Pyridyl-substituted Phospha-adamantane Ligands for the Methoxycarbonylation of Phenylacetylene

Timothy A. Shuttleworth, Alexandra M. Miles-Hobbs, Paul G. Pringle and Hazel A. Sparkes

School of Chemistry, University of Bristol, Cantock's Close, Bristol, United Kingdom, BS8 1TS.

Supporting Information

Crystal structures of $L_{3\text{-}7}$

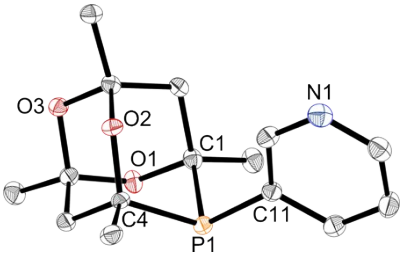

Fig. 1 Crystal structure of $\mathbf{L_3}$. Hydrogen atoms omitted for clarity. Thermal ellipsoids at 50% probability. Selected bond lengths (Å) and bond angles (°): P1-C1 1.8850(18), P1-C4 1.8757(16), P1-C11 1.8278(17); C1-P1-C4 92.73(7), C1-P1-C11 104.30(7), C4-P1-C11 106.49(8).

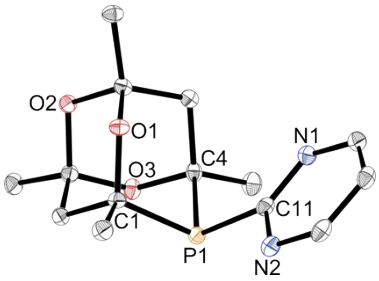

Fig. 2 Crystal structure of $\mathbf{L_4}$. Hydrogen atoms omitted for clarity. Thermal ellipsoids at 50% probability. Selected bond lengths (Å) and bond angles (°): P1-C1 1.8876(13), P1-C4 1.8718(14), P1-C11 1.8420(14); C1-P1-C4 93.02(6), C1-P1-C11 103.45(6), C4-P1-C11 105.98(6).

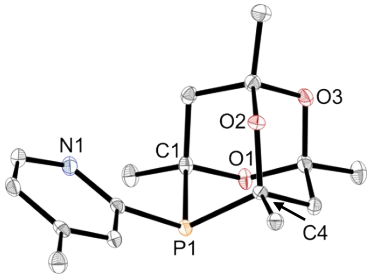

Fig. 3 Crystal structure of $\mathbf{L_{5a}}$. Hydrogen atoms omitted for clarity. Thermal ellipsoids at 50% probability. Selected bond lengths (Å) and bond angles (°): P1-C1 1.8826(14), P1-C4 1.8863(13), P1-C11 1.8416(14); C1-P1-C4 92.79(6), C1-P1-C11 106.66(6), C4-P1-C11 104.87(6).

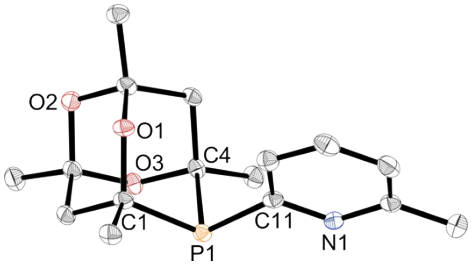

Fig. 4 Crystal structure of $\mathbf{L_{5b}}$. Hydrogen atoms omitted for clarity. Thermal ellipsoids at 50% probability. Selected bond lengths (Å) and bond angles (°): P1-C1 1.8805(15), P1-C4 1.8897(16), P1-C11 1.8429(17); C1-P1-C4 92.61(7), C1-P1-C11 105.06(7), C4-P1-C11 101.78(7).

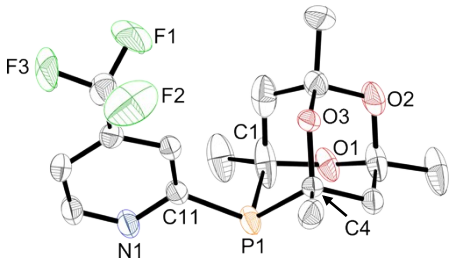

Fig. 5 Crystal structure of $\mathbf{L_{6a}}$. Disorder in CF_3 group and in CgP moiety not shown. Hydrogen atoms omitted for clarity. Thermal ellipsoids at 50% probability. Selected bond lengths (Å) and bond angles (°): P1-C1 1.883(3), P1-C4 1.8655(18), P1-C11 1.8372(18); C1-P1-C4 92.65(9), C1-P1-C11 102.74(10), C4-P1-C11 105.57(8).

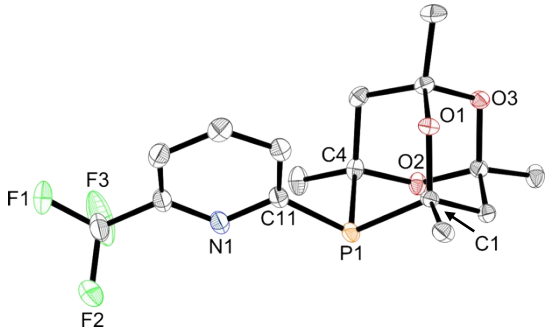

Fig. 6 Crystal structure of $\mathbf{L_{6b}}$. Hydrogen atoms omitted for clarity. Thermal ellipsoids at 50% probability. Selected bond lengths (Å) and bond angles (°): P1-C1 1.8730(12), P1-C4 1.8927(13), P1-C11 1.8451(13); C1-P1-C4 92.76(5), C1-P1-C11 106.38(5), C4-P1-C11 99.79(5).

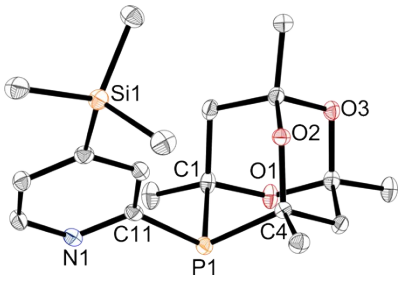

Fig. 7 Crystal structure of $\mathbf{L_{7a}}$. Hydrogen atoms omitted for clarity. Thermal ellipsoids at 50% probability. Selected bond lengths (Å) and bond angles (°): P1-C1 1.8915(14), P1-C4 1.8774(13), P1-C11 1.8468(13); C1-P1-C4 92.43(6), C1-P1-C11 102.52(6), C4-P1-C11 104.90(6).

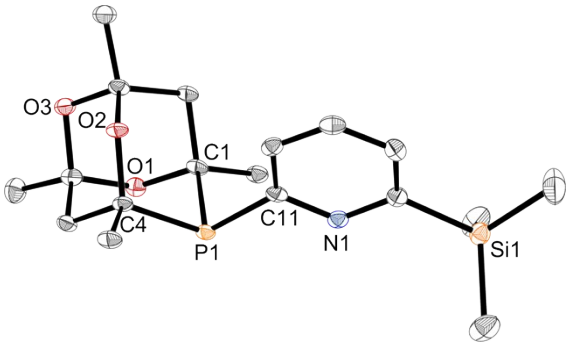

Fig. 8 Crystal structure of $\mathbf{L_{7b}}$. Hydrogen atoms omitted for clarity. Thermal ellipsoids at 50% probability. Selected bond lengths (Å) and bond angles (°): P1-C1 1.888(3), P1-C4 1.866(3), P1-C11 1.843(3); C1-P1-C4 92.88(12), C1-P1-C11 101.27(12), C4-P1-C11 107.10(13).

Table 1 Crystal data and structure refinement for $\mathbf{L_2}$, *meso*-**1c**, *meso*-**1d**, *meso*-**1e**, *meso*-**1g** and **5.**

Compound	**L2**	*meso*-**1c**	*meso*-**1d**	*meso*-**1e**	*meso*-**1g**	**5**
Empirical formula	$C_{15}H_{20}NO_3P$	$C_{32}H_{44}Cl_2N_2O_6P_2Pt$	$C_{32}H_{44}Cl_2N_2O_6P_2Pt$	$C_{32}H_{38}Cl_2F_6N_2O_6P_2Pt$	$C_{36}H_{56}Cl_2N_2O_6P_2PtSi_2$	$C_{31}H_{42}BCl_3F_4N_2O_6P_2Pd$
Formula weight	293.29	880.62	880.62	988.57	996.93	900.16
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	orthorhombic	triclinic	triclinic	triclinic	triclinic	orthorhombic
Space group	*Pbca*	*P*-1	*P*-1	*P*-1	*P*-1	$Pca2_1$
a/Å	8.0100(2)	8.2419(2)	8.7414(2)	8.2583(2)	8.8531(2)	29.1906(14)
b/Å	11.3652(3)	10.5796(3)	10.2111(3)	10.6521(3)	10.6257(3)	9.8378(5)
c/Å	32.3906(8)	11.4154(3)	11.1847(3)	11.5490(3)	11.9101(3)	13.0430(6)
α/°	90	117.5507(14)	64.6586(13)	116.7870(10)	79.9244(15)	90
β/°	90	91.9459(15)	88.5905(15)	93.6870(10)	83.9717(15)	90
γ/°	90	100.8508(15)	77.9537(15)	98.8740(10)	88.2507(15)	90
Volume/Å^3	2948.69(13)	858.31(4)	880.03(4)	885.69(4)	1096.92(5)	3745.6(3)
Z	8	1	1	1	1	4
ρ_{calc}g/cm^3	1.321	1.704	1.662	1.853	1.509	1.596
μ/mm^{-1}	0.193	4.381	4.273	4.280	3.490	0.859
F(000)	1248.0	440.0	440.0	488.0	504.0	1832.0
Crystal size/mm^3	0.55 × 0.33 × 0.21	0.23 × 0.18 × 0.12	0.41 × 0.37 × 0.13	0.26 × 0.21 × 0.15	0.44 × 0.27 × 0.26	0.44 × 0.27 × 0.15
Radiation	MoKα λ = 0.71073	MoKα λ = 0.71073	MoKα λ = 0.71073	MoKα λ = 0.71073	MoKα λ = 0.71073	MoKα λ = 0.71073
2Θ range for data collection/°	2.514 to 53.56	4.064 to 55.848	4.04 to 56.11	3.996 to 55.908	3.894 to 55.94	4.14 to 55.818
Index ranges	-10 ≤ h ≤ 9, -14 ≤ k ≤ 14, -38 ≤ l ≤ 41	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -14 ≤ l ≤ 15	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15	-11 ≤ h ≤ 11, -14 ≤ k ≤ 13, -15 ≤ l ≤ 15	-38 ≤ h ≤ 38, -12 ≤ k ≤ 12, -17 ≤ l ≤ 8
Reflections collected	21667	15546	15951	16102	19978	32854
R_{int}	0.0258	0.0425	0.0252	0.0296	0.0201	0.0501
Data/restraints/parameters	3146/0/185	4100/0/210	4268/0/210	4241/0/236	5264/56/251	6803/86/514
Goodness-of-fit on F^2	1.032	1.052	1.070	1.074	1.078	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0294, wR_2 = 0.0736	R_1 = 0.0265, wR_2 = 0.0466	R_1 = 0.0225, wR_2 = 0.0565	R_1 = 0.0185, wR_2 = 0.0445	R_1 = 0.0176, wR_2 = 0.0447	R_1 = 0.0270, wR_2 = 0.0558
Final R indexes [all data]	R_1 = 0.0337, wR_2 = 0.0764	R_1 = 0.0273, wR_2 = 0.0469	R_1 = 0.0227, wR_2 = 0.0566	R_1 = 0.0185, wR_2 = 0.0446	R_1 = 0.0177, wR_2 = 0.0447	R_1 = 0.0321, wR_2 = 0.0580
Largest diff. peak/hole / e Å^{-3}	0.34/-0.22	1.12/-1.20	2.17/-0.74	0.92/-0.52	1.36/-0.77	0.66/-0.74

Table 2 Crystal data and structure refinement for $\mathbf{L_3}$, $\mathbf{L_4}$, $\mathbf{L_{5a}}$ and $\mathbf{L_{5b}}$.

Compound	$\mathbf{L_3}$	$\mathbf{L_4}$	$\mathbf{L_{5a}}$	$\mathbf{L_{5b}}$
Empirical formula	$C_{15}H_{20}NO_3P$	$C_{14}H_{19}N_2O_3P$	$C_{16}H_{22}NO_3P$	$C_{16}H_{22}NO_3P$
Formula weight	293.29	294.28	307.31	307.31
Temperature/K	100.01	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	*C*2/*c*	*C*2/*c*	$P2_1/c$	*P*-1
a/Å	7.9601(3)	13.9879(8)	16.3067(5)	8.0709(8)
b/Å	14.7432(5)	8.0408(5)	12.0198(4)	9.2900(9)
c/Å	24.8613(8)	25.4615(14)	7.7629(3)	11.0652(10)
α/°	90	90	90	78.954(7)
β/°	93.416(3)	99.511(3)	92.552(2)	84.366(7)
γ/°	90	90	90	76.677(7)
Volume/Å^3	2912.47(18)	2824.4(3)	1520.04(9)	791.10(13)
Z	8	8	4	2
ρ_{calc}g/cm^3	1.338	1.384	1.343	1.290
μ/mm^{-1}	0.196	0.204	0.191	0.183
F(000)	1248.0	1248.0	656.0	328.0
Crystal size/mm^3	0.36 × 0.28 × 0.17	0.33 × 0.27 × 0.23	0.33 × 0.29 × 0.2	0.32 × 0.3 × 0.21
Radiation	MoKα λ = 0.71073	MoKα λ = 0.71073	MoKα λ = 0.71073	MoKα λ = 0.71073
2Θ range for data collection/°	3.282 to 53.65	5.864 to 56.066	2.5 to 53.522	3.756 to 55.964
Index ranges	-9 ≤ h ≤ 10, -18 ≤ k ≤ 18, -31 ≤ l ≤ 31	-11 ≤ h ≤ 18, -10 ≤ k ≤ 10, -33 ≤ l ≤ 33	-20 ≤ h ≤ 20, -15 ≤ k ≤ 15, -9 ≤ l ≤ 9	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14
Reflections collected	11677	12722	12114	12496
R_{int}	0.0449	0.0314	0.0290	0.0399
Data/restraints/parameters	3126/0/185	3422/0/185	3227/0/195	3788/0/195
Goodness-of-fit on F^2	1.023	1.028	1.040	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0367, wR_2 = 0.0804	R_1 = 0.0328, wR_2 = 0.0784	R_1 = 0.0323, wR_2 = 0.0796	R_1 = 0.0424, wR_2 = 0.1036
Final R indexes [all data]	R_1 = 0.0553, wR_2 = 0.0881	R_1 = 0.0410, wR_2 = 0.0834	R_1 = 0.0378, wR_2 = 0.0832	R_1 = 0.0549, wR_2 = 0.1109
Largest diff. peak/hole / e Å^{-3}	0.33/-0.26	0.41/-0.28	0.39/-0.25	0.55/-0.31

Table 3 Crystal data and structure refinement for $\mathbf{L_{6a}}$, $\mathbf{L_{6b}}$, $\mathbf{L_{7a}}$ and $\mathbf{L_{7b}}$.

Identification code	$\mathbf{L_{6a}}$	$\mathbf{L_{6b}}$	$\mathbf{L_{7a}}$	$\mathbf{L_{7b}}$
Empirical formula	$C_{16}H_{19}F_3NO_3P$	$C_{16}H_{19}F_3NO_3P$	$C_{18}H_{28}NO_3PSi$	$C_{18}H_{28}NO_3PSi$
Formula weight	361.29	361.29	365.47	365.47
Temperature/K	170(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$C2/c$	$P2_1/n$	$Pca2_1$
a/Å	7.5819(9)	35.1058(14)	9.2174(4)	11.9811(8)
b/Å	10.5008(12)	7.3423(3)	11.5325(5)	12.8561(11)
c/Å	22.185(3)	13.5142(6)	18.7960(7)	12.8375(10)
α/°	90	90	90	90
β/°	99.305(5)	105.839(3)	99.645(2)	90
γ/°	90	90	90	90
Volume/Å^3	1743.1(4)	3351.1(2)	1969.77(14)	1977.4(3)
Z	4	8	4	4
ρ_{calc}g/cm^3	1.377	1.432	1.232	1.228
μ/mm^{-1}	1.815	0.209	0.216	0.215
F(000)	752.0	1504.0	784.0	784.0
Crystal size/mm^3	0.38 × 0.3 × 0.19	0.47 × 0.32 × 0.21	0.58 × 0.35 × 0.31	0.48 × 0.28 × 0.23
Radiation	CuKα λ = 1.54178	MoKα λ = 0.71073	MoKα λ = 0.71073	MoKα λ = 0.71073
2Θ range for data collection/°	8.076 to 133.618	4.824 to 55.86	4.16 to 54.198	3.168 to 55.968
Index ranges	-9 ≤ h ≤ 6, -12 ≤ k ≤ 12, -25 ≤ l ≤ 26	-44 ≤ h ≤ 46, -9 ≤ k ≤ 9, -17 ≤ l ≤ 17	-11 ≤ h ≤ 11, -14 ≤ k ≤ 7, -24 ≤ l ≤ 24	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -16 ≤ l ≤ 7
Reflections collected	33931	14898	16282	17162
R_{int}	0.0504	0.0255	0.0246	0.0531
Data/restraints/parameters	3071/60/267	4011/0/221	4336/0/224	3582/1/224
Goodness-of-fit on F^2	1.040	1.034	1.047	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0431, wR_2 = 0.1099	R_1 = 0.0328, wR_2 = 0.0817	R_1 = 0.0299, wR_2 = 0.0733	R_1 = 0.0385, wR_2 = 0.0926
Final R indexes [all data]	R_1 = 0.0463, wR_2 = 0.1133	R_1 = 0.0400, wR_2 = 0.0862	R_1 = 0.0373, wR_2 = 0.0778	R_1 = 0.0436, wR_2 = 0.0963
Largest diff. peak/hole / e Å^{-3}	0.34/-0.54	0.36/-0.33	0.46/-0.22	0.64/-0.25