

Tris(phosphino)borato Silver(I) Complexes as Precursors for Metallic Silver Aerosol-Assisted Chemical Vapor Deposition

Matthew N. McCain[†], Sven Schneider[‡], Michael R. Salata[†], Tobin J. Marks^{†*}

[†] *Department of Chemistry and the Materials Research Center, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113*

[‡] *Current address: Technische Universität München, Anorganisch-Chemisches Institut, Lichtenbergstraße 4, 85747 Garching, Germany*

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The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$
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The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$
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Table S1. Crystallographic data for complexes **1** and **2**.

	1	2
Empirical formula	C ₅₁ H ₅₆ AgBP ₄	C ₄₉ H ₆₀ AgBP ₄
Formula weight, g/mol	910.25	890.28
Temperature, °C	-153 ± 2	-153 ± 2
λ(Mo k _α) radiation, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n
Unit cell dimensions (Å)		
<i>a</i>	12.1245(12)	12.470(3)
<i>b</i>	20.281(2)	20.474(4)
<i>c</i>	19.020(3)	18.660(4)
Unit cell angles (deg.)		
α	90	90
β	100.334(7)	101.785(4)
γ	90	90
V, Å ³	4601.2(10)	4663.9(16)
Z	4	4
D _{calc'd} , g/cm ³	1.316	1.270
F(000)	1896	1864
Reflns collected/unique	42666/11231 (R _{int} = 0.0369)	42642/11196 (R _{int} = 0.116)
Largest diff peak and hole, (e ⁻ /Å ³)	1.404 and -0.848	1.972 and -1.322
R ₁	0.0421	.0868
R _w	0.0958	.2259
$R_1 = \frac{\sum F_o - F_c }{\sum F_o }$ $\text{and } wR^2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}, \text{ where } w = \frac{1}{[\sigma^2(F_o^2) + (0.1551P)^2 + 0.0000P]} \text{ and } P = (F_o^2 + 2F_c^2)/3$		

Table S2. Crystal data and structure refinement for complex 1.

Empirical formula	$C_{51} H_{56} Ag B P_4$
Formula weight	911.52
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	$a = 12.1245(12)$ Å $\alpha = 90$ deg. $b = 20.281(2)$ Å $\beta = 100.334(7)$ deg. $c = 19.020(3)$ Å $\gamma = 90$ deg.
Volume	4601.2(10) Å ³
Z, Calculated density	4, 1.316 Mg/m ³
Absorption coefficient	0.611 mm ⁻¹
F(000)	1896
Crystal size	0.202 x 0.180 x 0.092 mm
Theta range for data collection	1.48 to 28.92 deg.
Limiting indices	$-16 \leq h \leq 16$, $-27 \leq k \leq 26$, $-24 \leq l \leq 25$
Reflections collected / unique	42666 / 11231 [R(int) = 0.0369]
Completeness to theta = 28.92	92.5 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11231 / 0 / 533
Goodness-of-fit on F ²	1.080
Final R indices [I > 2σ(I)]	R1 = 0.0421, wR2 = 0.0958
R indices (all data)	R1 = 0.0585, wR2 = 0.1047

Largest diff. peak and hole 1.404 and -0.848 e.A⁻³

Table S3. Atomic coordinates (x 10⁴) and equivalent isotropic Displacement parameters (A² x 10³) for complex **1**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ag(1)	4528(1)	3085(1)	7549(1)	24(1)
B(1)	7291(2)	2351(1)	8149(1)	22(1)
C(1A)	1541(6)	3176(4)	7507(3)	52(1)
C(1B)	1729(8)	3623(6)	7733(5)	49(2)
C(2A)	1666(5)	3337(3)	8314(3)	52(1)
C(2B)	1225(9)	2992(5)	7733(6)	49(2)
C(3)	2097(3)	3340(2)	6193(2)	48(1)
C(4)	2754(3)	3581(2)	5648(2)	41(1)
C(5A)	2501(7)	4381(4)	7129(4)	45(2)
C(5B)	2983(10)	4571(5)	7094(6)	45(2)
C(6A)	1395(8)	4682(4)	6767(4)	65(2)
C(6B)	2002(10)	4973(5)	6741(6)	65(2)
C(7)	7439(2)	2925(1)	7540(1)	24(1)
C(8)	5088(2)	2245(1)	5952(1)	32(1)
C(9)	6092(2)	2581(1)	6172(1)	25(1)
C(10)	6984(2)	2443(1)	5825(1)	34(1)
C(11)	6877(3)	1979(2)	5280(2)	41(1)
C(12)	5876(3)	1646(1)	5078(2)	43(1)
C(13)	4989(3)	1775(1)	5415(2)	40(1)
C(14)	6597(2)	3937(1)	6507(1)	27(1)
C(15)	7692(2)	4163(1)	6607(2)	34(1)
C(16)	7942(3)	4774(1)	6337(2)	40(1)
C(17)	7101(3)	5163(1)	5971(2)	43(1)
C(18)	6006(3)	4943(2)	5868(2)	49(1)
C(19)	5764(3)	4333(1)	6136(2)	42(1)
C(20)	6421(2)	1744(1)	7801(1)	22(1)
C(21)	4214(2)	1223(1)	7164(1)	23(1)
C(22)	4766(2)	662(1)	6992(1)	29(1)
C(23)	4217(2)	205(1)	6507(2)	36(1)
C(24)	3108(3)	296(2)	6199(2)	40(1)

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C(25)	2549(3)	845(2)	6370(2)	44(1)
C(26)	3096(2)	1309(1)	6845(2)	35(1)
C(27)	4619(2)	1593(1)	8624(1)	25(1)
C(28)	5280(2)	1140(1)	9060(2)	34(1)
C(29)	4995(3)	932(2)	9698(2)	45(1)
C(30)	4049(3)	1178(2)	9913(2)	51(1)
C(31)	3398(3)	1636(2)	9498(2)	49(1)
C(32)	3685(2)	1848(2)	8855(2)	39(1)
C(33)	6913(2)	2689(1)	8869(1)	23(1)
C(34)	6591(2)	4101(1)	8699(1)	24(1)
C(35)	6293(2)	4540(1)	8134(1)	30(1)
C(36)	6876(3)	5132(1)	8112(2)	37(1)
C(37)	7741(3)	5290(1)	8656(2)	39(1)
C(38)	8045(2)	4861(1)	9228(2)	37(1)
C(39)	7472(2)	4274(1)	9244(1)	30(1)
C(40)	5330(2)	3436(1)	9574(1)	23(1)
C(41)	5415(2)	2956(1)	10100(1)	30(1)
C(42)	4999(2)	3065(1)	10730(2)	36(1)
C(43)	4498(2)	3659(1)	10838(1)	33(1)
C(44)	4393(2)	4137(1)	10318(2)	34(1)
C(45)	4798(2)	4029(1)	9691(1)	30(1)
C(46)	8524(2)	1995(1)	8364(1)	25(1)
C(47)	9136(2)	1936(1)	9060(1)	29(1)
C(48)	10166(2)	1616(2)	9208(2)	40(1)
C(49)	10623(2)	1336(2)	8664(2)	45(1)
C(50)	10056(2)	1384(2)	7973(2)	42(1)
C(51)	9027(2)	1708(1)	7830(2)	34(1)
P(1)	2712(1)	3556(1)	7115(1)	43(1)
P(2)	6195(1)	3171(1)	6912(1)	22(1)
P(3)	4922(1)	1870(1)	7759(1)	20(1)
P(4)	5820(1)	3324(1)	8722(1)	21(1)

Table S4. Bond lengths [Å] and angles [deg] for complex **1**.

Ag(1)-P(1)	2.4065(8)
Ag(1)-P(3)	2.5275(7)
Ag(1)-P(4)	2.5321(7)
Ag(1)-P(2)	2.5426(7)
B(1)-C(46)	1.645(4)
B(1)-C(33)	1.669(3)
B(1)-C(7)	1.674(4)
B(1)-C(20)	1.677(4)
C(1A)-C(2A)	1.550(8)
C(1A)-P(1)	1.881(7)
C(1B)-C(2B)	1.418(16)
C(1B)-P(1)	1.822(9)
C(3)-C(4)	1.498(4)
C(3)-P(1)	1.831(3)
C(5A)-C(6A)	1.521(11)
C(5A)-P(1)	1.694(8)
C(5B)-C(6B)	1.497(14)
C(5B)-P(1)	2.088(10)
C(7)-P(2)	1.818(2)
C(8)-C(13)	1.387(4)
C(8)-C(9)	1.392(4)
C(9)-C(10)	1.392(4)
C(9)-P(2)	1.835(3)
C(10)-C(11)	1.389(4)
C(11)-C(12)	1.383(5)
C(12)-C(13)	1.374(5)
C(14)-C(19)	1.381(4)
C(14)-C(15)	1.385(4)
C(14)-P(2)	1.838(2)
C(15)-C(16)	1.395(4)
C(16)-C(17)	1.376(4)
C(17)-C(18)	1.381(5)
C(18)-C(19)	1.389(4)
C(20)-P(3)	1.823(2)
C(21)-C(22)	1.387(3)
C(21)-C(26)	1.392(4)
C(21)-P(3)	1.843(2)
C(22)-C(23)	1.391(4)
C(23)-C(24)	1.379(4)

C(24)-C(25)	1.373(4)
C(25)-C(26)	1.389(4)
C(27)-C(32)	1.386(4)
C(27)-C(28)	1.391(4)
C(27)-P(3)	1.836(2)
C(28)-C(29)	1.386(4)
C(29)-C(30)	1.378(5)
C(30)-C(31)	1.372(5)
C(31)-C(32)	1.398(4)
C(33)-P(4)	1.832(2)
C(34)-C(35)	1.392(3)
C(34)-C(39)	1.393(4)
C(34)-P(4)	1.837(2)
C(35)-C(36)	1.398(4)
C(36)-C(37)	1.372(4)
C(37)-C(38)	1.391(4)
C(38)-C(39)	1.381(4)
C(40)-C(41)	1.387(3)
C(40)-C(45)	1.401(3)
C(40)-P(4)	1.837(2)
C(41)-C(42)	1.397(4)
C(42)-C(43)	1.382(4)
C(43)-C(44)	1.374(4)
C(44)-C(45)	1.386(4)
C(46)-C(47)	1.401(4)
C(46)-C(51)	1.402(4)
C(47)-C(48)	1.391(4)
C(48)-C(49)	1.379(4)
C(49)-C(50)	1.374(4)
C(50)-C(51)	1.393(4)

P(1)-Ag(1)-P(3)	125.19(3)
P(1)-Ag(1)-P(4)	127.57(3)
P(3)-Ag(1)-P(4)	88.73(2)
P(1)-Ag(1)-P(2)	124.47(3)
P(3)-Ag(1)-P(2)	89.91(2)
P(4)-Ag(1)-P(2)	89.31(2)
C(46)-B(1)-C(33)	110.33(19)
C(46)-B(1)-C(7)	105.79(19)
C(33)-B(1)-C(7)	111.13(19)
C(46)-B(1)-C(20)	104.78(19)
C(33)-B(1)-C(20)	112.35(19)
C(7)-B(1)-C(20)	112.05(19)

C(2A)-C(1A)-P(1)	111.1(5)
C(2B)-C(1B)-P(1)	105.3(8)
C(4)-C(3)-P(1)	114.2(2)
C(6A)-C(5A)-P(1)	120.8(6)
C(6B)-C(5B)-P(1)	115.5(7)
B(1)-C(7)-P(2)	117.84(16)
C(13)-C(8)-C(9)	120.9(3)
C(8)-C(9)-C(10)	118.1(2)
C(8)-C(9)-P(2)	119.0(2)
C(10)-C(9)-P(2)	122.9(2)
C(11)-C(10)-C(9)	120.9(3)
C(12)-C(11)-C(10)	119.9(3)
C(13)-C(12)-C(11)	119.9(3)
C(12)-C(13)-C(8)	120.2(3)
C(19)-C(14)-C(15)	118.3(2)
C(19)-C(14)-P(2)	118.7(2)
C(15)-C(14)-P(2)	122.8(2)
C(14)-C(15)-C(16)	120.6(3)
C(17)-C(16)-C(15)	120.4(3)
C(16)-C(17)-C(18)	119.5(3)
C(17)-C(18)-C(19)	119.8(3)
C(14)-C(19)-C(18)	121.4(3)
B(1)-C(20)-P(3)	117.70(16)
C(22)-C(21)-C(26)	118.3(2)
C(22)-C(21)-P(3)	122.50(19)
C(26)-C(21)-P(3)	119.18(19)
C(21)-C(22)-C(23)	120.6(2)
C(24)-C(23)-C(22)	120.4(3)
C(25)-C(24)-C(23)	119.6(3)
C(24)-C(25)-C(26)	120.3(3)
C(25)-C(26)-C(21)	120.8(3)
C(32)-C(27)-C(28)	118.2(2)
C(32)-C(27)-P(3)	118.4(2)
C(28)-C(27)-P(3)	123.3(2)
C(29)-C(28)-C(27)	121.1(3)
C(30)-C(29)-C(28)	120.0(3)
C(31)-C(30)-C(29)	119.9(3)
C(30)-C(31)-C(32)	120.2(3)
C(27)-C(32)-C(31)	120.6(3)
B(1)-C(33)-P(4)	117.48(16)
C(35)-C(34)-C(39)	118.1(2)
C(35)-C(34)-P(4)	120.3(2)
C(39)-C(34)-P(4)	121.62(19)
C(34)-C(35)-C(36)	120.6(3)

C(37)-C(36)-C(35)	120.0(3)
C(36)-C(37)-C(38)	120.2(3)
C(39)-C(38)-C(37)	119.5(3)
C(38)-C(39)-C(34)	121.6(3)
C(41)-C(40)-C(45)	117.6(2)
C(41)-C(40)-P(4)	123.78(19)
C(45)-C(40)-P(4)	118.53(19)
C(40)-C(41)-C(42)	121.1(2)
C(43)-C(42)-C(41)	120.0(3)
C(44)-C(43)-C(42)	119.7(2)
C(43)-C(44)-C(45)	120.4(2)
C(44)-C(45)-C(40)	121.1(2)
C(47)-C(46)-C(51)	115.1(2)
C(47)-C(46)-B(1)	125.2(2)
C(51)-C(46)-B(1)	119.7(2)
C(48)-C(47)-C(46)	122.3(2)
C(49)-C(48)-C(47)	120.5(3)
C(50)-C(49)-C(48)	119.3(3)
C(49)-C(50)-C(51)	119.8(3)
C(50)-C(51)-C(46)	123.0(3)
C(5A)-P(1)-C(1B)	78.3(5)
C(5A)-P(1)-C(3)	102.4(3)
C(1B)-P(1)-C(3)	115.8(3)
C(5A)-P(1)-C(1A)	105.7(4)
C(1B)-P(1)-C(1A)	31.6(3)
C(3)-P(1)-C(1A)	94.4(2)
C(5A)-P(1)-C(5B)	18.2(4)
C(1B)-P(1)-C(5B)	93.6(5)
C(3)-P(1)-C(5B)	104.8(3)
C(1A)-P(1)-C(5B)	122.9(4)
C(5A)-P(1)-Ag(1)	121.2(3)
C(1B)-P(1)-Ag(1)	118.2(3)
C(3)-P(1)-Ag(1)	115.08(12)
C(1A)-P(1)-Ag(1)	114.25(18)
C(5B)-P(1)-Ag(1)	105.1(3)
C(7)-P(2)-C(9)	104.99(11)
C(7)-P(2)-C(14)	104.90(12)
C(9)-P(2)-C(14)	102.52(11)
C(7)-P(2)-Ag(1)	107.70(8)
C(9)-P(2)-Ag(1)	111.74(8)
C(14)-P(2)-Ag(1)	123.45(9)
C(20)-P(3)-C(27)	106.02(11)
C(20)-P(3)-C(21)	106.09(11)

C(27)-P(3)-C(21)	100.75(11)
C(20)-P(3)-Ag(1)	107.65(8)
C(27)-P(3)-Ag(1)	112.15(8)
C(21)-P(3)-Ag(1)	122.92(8)
C(33)-P(4)-C(40)	106.98(11)
C(33)-P(4)-C(34)	104.43(11)
C(40)-P(4)-C(34)	99.27(11)
C(33)-P(4)-Ag(1)	108.44(8)
C(40)-P(4)-Ag(1)	123.62(8)
C(34)-P(4)-Ag(1)	112.35(8)

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for complex **1**.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
Ag(1)	24(1)	23(1)	23(1)	2(1)	2(1)	3(1)
B(1)	22(1)	22(1)	22(1)	1(1)	3(1)	0(1)
C(1A)	60(3)	66(3)	36(2)	14(2)	25(2)	21(2)
C(1B)	47(4)	60(5)	40(4)	2(3)	8(3)	12(3)
C(2A)	60(3)	66(3)	36(2)	14(2)	25(2)	21(2)
C(2B)	47(4)	60(5)	40(4)	2(3)	8(3)	12(3)
C(3)	34(2)	60(2)	45(2)	18(2)	-7(1)	-4(1)
C(4)	43(2)	46(2)	32(2)	-1(1)	1(1)	2(1)
C(5A)	68(6)	31(4)	33(2)	-2(3)	2(4)	16(3)
C(5B)	68(6)	31(4)	33(2)	-2(3)	2(4)	16(3)
C(6A)	83(6)	57(5)	50(3)	-3(3)	-1(4)	38(3)
C(6B)	83(6)	57(5)	50(3)	-3(3)	-1(4)	38(3)
C(7)	24(1)	26(1)	21(1)	-1(1)	5(1)	-1(1)
C(8)	37(2)	31(1)	26(1)	5(1)	-1(1)	-4(1)
C(9)	30(1)	22(1)	21(1)	4(1)	2(1)	0(1)
C(10)	39(2)	35(2)	26(1)	-3(1)	4(1)	1(1)
C(11)	49(2)	41(2)	31(2)	-5(1)	4(1)	10(1)

C(12)	67(2)	29(1)	27(1)	-5(1)	-6(1)	2(1)
C(13)	49(2)	34(2)	32(2)	2(1)	-8(1)	-13(1)
C(14)	37(1)	22(1)	21(1)	-1(1)	7(1)	-5(1)
C(15)	33(1)	30(1)	41(2)	7(1)	11(1)	0(1)
C(16)	42(2)	32(2)	48(2)	2(1)	13(1)	-11(1)
C(17)	60(2)	26(1)	41(2)	7(1)	7(2)	-11(1)
C(18)	55(2)	35(2)	50(2)	16(1)	-7(2)	-6(1)
C(19)	41(2)	34(2)	45(2)	13(1)	-6(1)	-8(1)
C(20)	21(1)	22(1)	23(1)	-1(1)	5(1)	1(1)
C(21)	26(1)	23(1)	20(1)	2(1)	5(1)	-4(1)
C(22)	29(1)	27(1)	30(1)	-3(1)	6(1)	-4(1)
C(23)	43(2)	30(1)	37(2)	-7(1)	14(1)	-6(1)
C(24)	49(2)	38(2)	32(2)	-7(1)	5(1)	-15(1)
C(25)	31(2)	46(2)	47(2)	0(1)	-9(1)	-8(1)
C(26)	31(1)	31(1)	41(2)	0(1)	0(1)	0(1)
C(27)	27(1)	23(1)	24(1)	-1(1)	5(1)	-3(1)
C(28)	38(2)	29(1)	34(1)	3(1)	9(1)	1(1)
C(29)	61(2)	38(2)	33(2)	6(1)	5(1)	-11(2)
C(30)	61(2)	66(2)	28(2)	-1(2)	16(2)	-28(2)
C(31)	36(2)	77(2)	38(2)	-11(2)	19(1)	-12(2)
C(32)	30(1)	52(2)	36(2)	1(1)	11(1)	6(1)
C(33)	26(1)	20(1)	22(1)	-1(1)	3(1)	3(1)
C(34)	28(1)	20(1)	25(1)	1(1)	10(1)	2(1)
C(35)	40(2)	25(1)	26(1)	0(1)	8(1)	4(1)
C(36)	62(2)	21(1)	35(2)	4(1)	24(1)	4(1)
C(37)	48(2)	26(1)	50(2)	-6(1)	29(2)	-8(1)
C(38)	29(1)	36(2)	46(2)	-9(1)	10(1)	-7(1)
C(39)	28(1)	28(1)	33(1)	0(1)	3(1)	1(1)
C(40)	22(1)	24(1)	24(1)	-2(1)	4(1)	-2(1)
C(41)	32(1)	32(1)	28(1)	4(1)	10(1)	8(1)
C(42)	36(2)	44(2)	30(1)	9(1)	14(1)	8(1)
C(43)	30(1)	44(2)	30(1)	-4(1)	15(1)	1(1)
C(44)	34(1)	30(1)	41(2)	-6(1)	15(1)	1(1)
C(45)	33(1)	26(1)	33(1)	2(1)	11(1)	4(1)
C(46)	22(1)	25(1)	25(1)	-4(1)	2(1)	-2(1)
C(47)	27(1)	31(1)	27(1)	-5(1)	2(1)	3(1)
C(48)	29(1)	46(2)	39(2)	-5(1)	-9(1)	7(1)
C(49)	26(1)	50(2)	54(2)	-10(2)	-2(1)	10(1)
C(50)	31(2)	52(2)	44(2)	-15(1)	7(1)	9(1)
C(51)	31(1)	40(2)	29(1)	-9(1)	2(1)	5(1)
P(1)	36(1)	65(1)	28(1)	14(1)	8(1)	25(1)
P(2)	24(1)	22(1)	20(1)	2(1)	4(1)	-2(1)
P(3)	21(1)	19(1)	21(1)	1(1)	3(1)	1(1)
P(4)	25(1)	19(1)	19(1)	0(1)	3(1)	2(1)

Table S6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for complex **1**.

	x	y	z	U(eq)
H(1A1)	814	3347	7252	62
H(1A2)	1547	2692	7441	62
H(1B1)	2127	3739	8218	59
H(1B2)	1156	3964	7570	59
H(2A1)	2416	3208	8560	78
H(2A2)	1099	3093	8517	78
H(2A3)	1562	3811	8376	78
H(2B1)	682	2933	7289	73
H(2B2)	841	2956	8142	73
H(2B3)	1805	2651	7766	73
H(3A)	2031	2854	6155	58
H(3B)	1331	3526	6081	58
H(4A)	2784	4064	5659	62
H(4B)	2390	3434	5172	62
H(4C)	3517	3403	5756	62
H(5A1)	2622	4517	7637	54
H(5A2)	3100	4591	6916	54
H(5B1)	3210	4728	7592	54
H(5B2)	3618	4654	6843	54
H(6A1)	1244	4555	6261	97
H(6A2)	1439	5163	6806	97
H(6A3)	788	4520	7000	97
H(6B1)	1813	4854	6235	97
H(6B2)	2194	5442	6786	97
H(6B3)	1358	4885	6973	97
H(7A)	7998	2761	7261	28
H(7B)	7759	3324	7799	28
H(8)	4462	2340	6173	38
H(10)	7675	2668	5964	40
H(11)	7491	1892	5046	49
H(12)	5802	1327	4706	51
H(13)	4304	1541	5280	48
H(15)	8279	3899	6861	41
H(16)	8697	4922	6407	48
H(17)	7273	5580	5790	51

H(18)	5420	5208	5616	59
H(19)	5008	4185	6062	50
H(20A)	6639	1339	8083	26
H(20B)	6549	1658	7309	26
H(22)	5526	590	7208	34
H(23)	4608	-173	6387	43
H(24)	2734	-19	5870	48
H(25)	1783	907	6162	52
H(26)	2704	1690	6955	42
H(28)	5936	971	8918	40
H(29)	5453	620	9988	54
H(30)	3847	1031	10347	61
H(31)	2750	1809	9648	58
H(32)	3237	2170	8574	46
H(33A)	7590	2885	9164	28
H(33B)	6655	2331	9154	28
H(35)	5688	4435	7759	36
H(36)	6674	5425	7721	45
H(37)	8133	5694	8642	46
H(38)	8643	4970	9605	44
H(39)	7683	3982	9635	36
H(41)	5761	2547	10032	36
H(42)	5060	2729	11083	43
H(43)	4228	3737	11269	40
H(44)	4041	4544	10388	40
H(45)	4714	4363	9335	36
H(47)	8836	2121	9444	34
H(48)	10558	1591	9686	48
H(49)	11321	1112	8767	54
H(50)	10366	1198	7593	50
H(51)	8648	1736	7348	41

Table S7. Crystal data and structure refinement for complex **2**.

Empirical formula	C ₄₉ H ₆₀ Ag B P ₄
Formula weight	891.53
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	$a = 12.470(3)$ Å $\alpha = 90$ deg. $b = 20.474(4)$ Å $\beta = 101.785(4)$ deg. $c = 18.660(4)$ Å $\gamma = 90$ deg.
Volume	4663.9(16) Å ³
Z, Calculated density	4, 1.270 Mg/m ³
Absorption coefficient	0.601 mm ⁻¹
F(000)	1864
Crystal size	0.500 x 0.104 x 0.078 mm
Theta range for data collection	1.49 to 28.86 deg.
Limiting indices	-16 ≤ h ≤ 16, -26 ≤ k ≤ 26, -25 ≤ l ≤ 24
Reflections collected / unique	42642 / 11196 [R(int) = 0.1116]
Completeness to theta = 28.86	91.6 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11196 / 0 / 501
Goodness-of-fit on F ²	1.034
Final R indices [I > 2σ(I)]	R1 = 0.0868, wR2 = 0.2259
R indices (all data)	R1 = 0.1654, wR2 = 0.2629

Largest diff. peak and hole 1.972 and -1.322 e.A³

Table S8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **2**.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ag(1)	10414(1)	1954(1)	7440(1)	43(1)
B(1)	7756(8)	2669(4)	6727(5)	42(2)
C(1)	10395(6)	3410(4)	6336(4)	38(2)
C(2)	11302(8)	3136(5)	6136(5)	64(3)
C(3)	11650(9)	3317(6)	5509(6)	84(3)
C(4)	11049(9)	3775(5)	5043(5)	69(3)
C(5)	10138(8)	4051(4)	5232(4)	56(2)
C(6)	9840(7)	3874(4)	5865(4)	46(2)
C(7)	10717(6)	3795(3)	7809(4)	38(2)
C(8)	11825(7)	3714(4)	8136(5)	52(2)
C(9)	12365(8)	4172(4)	8614(5)	59(2)
C(10)	11830(9)	4723(4)	8784(5)	62(2)
C(11)	10751(8)	4806(4)	8460(5)	59(2)
C(12)	10196(7)	4342(4)	7986(4)	48(2)
C(13)	8577(6)	3284(3)	7087(4)	40(2)
C(14)	7575(7)	2135(4)	7362(4)	46(2)
C(15)	8894(7)	2489(3)	8780(4)	41(2)
C(16)	9887(8)	2796(4)	9037(5)	54(2)
C(17)	10006(9)	3266(4)	9579(5)	60(2)
C(18)	9131(9)	3429(4)	9891(5)	62(3)
C(19)	8134(9)	3121(5)	9651(5)	67(3)
C(20)	8005(8)	2662(4)	9100(5)	55(2)
C(21)	8306(7)	1163(4)	8513(4)	48(2)
C(22)	8945(10)	960(6)	9154(8)	126(6)
C(23)	8661(11)	380(7)	9489(10)	152(8)
C(24)	7798(9)	28(4)	9190(6)	70(3)
C(25)	7121(10)	251(5)	8572(5)	79(4)
C(26)	7404(9)	819(5)	8237(5)	73(3)
C(27)	8197(6)	2314(3)	6038(4)	40(2)
C(28)	8460(6)	925(3)	6256(4)	42(2)
C(29)	8791(8)	484(4)	6828(4)	50(2)
C(30)	8228(9)	-89(4)	6862(5)	61(2)

C(31)	7320(8)	-232(4)	6343(6)	63(3)
C(32)	6977(8)	190(5)	5760(6)	71(3)
C(33)	7541(7)	763(4)	5725(5)	53(2)
C(34)	9704(6)	1544(4)	5373(4)	41(2)
C(35)	10208(6)	952(4)	5251(4)	46(2)
C(36)	10573(7)	848(4)	4599(5)	51(2)
C(37)	10477(7)	1316(5)	4077(5)	59(2)
C(38)	10010(8)	1888(5)	4188(5)	60(2)
C(39)	9633(7)	2018(4)	4830(4)	51(2)
C(40)	6522(7)	2960(4)	6362(5)	54(2)
C(41)	5954(8)	3373(5)	6796(5)	70(3)
C(42)	4773(9)	3581(6)	6414(7)	83(3)
C(43A)	4170(13)	4037(9)	6844(10)	161(8)
P(1)	10029(2)	3155(1)	7197(1)	37(1)
P(2)	8761(2)	1882(1)	8047(1)	44(1)
P(3)	9227(2)	1679(1)	6220(1)	38(1)
P(4)	12229(2)	1506(1)	7925(1)	63(1)
C(44)	12308(9)	611(5)	7868(6)	76(3)
C(48)	12777(9)	1700(5)	8873(5)	70(3)
C(49)	12122(9)	1398(6)	9365(6)	83(3)
C(45)	13363(11)	279(6)	8211(6)	100(4)
C(46)	13342(9)	1785(5)	7491(7)	85(3)
C(47)	13317(13)	1641(6)	6684(6)	110(5)

Table S9. Bond lengths [Å] and angles [deg] for **2**.

Ag(1)-P(3)	2.512(2)
Ag(1)-P(4)	2.5287(19)
Ag(1)-P(2)	2.551(2)
Ag(1)-P(1)	2.439(2)
B(1)-C(40)	1.662(12)
B(1)-C(14)	1.663(11)
B(1)-C(27)	1.665(11)
B(1)-C(13)	1.674(12)
C(1)-C(2)	1.380(11)
C(1)-C(6)	1.380(10)
C(1)-P(4)	1.834(7)
C(2)-C(3)	1.380(13)
C(3)-C(4)	1.390(14)
C(4)-C(5)	1.378(13)
C(5)-C(6)	1.356(11)
C(7)-C(12)	1.370(10)
C(7)-C(8)	1.402(11)
C(7)-P(1)	1.831(7)
C(8)-C(9)	1.371(11)
C(9)-C(10)	1.381(13)
C(10)-C(11)	1.369(13)
C(11)-C(12)	1.384(11)
C(13)-P(4)	1.800(8)
C(14)-P(2)	1.822(8)
C(15)-C(16)	1.384(11)
C(15)-C(20)	1.408(12)
C(15)-P(2)	1.831(8)
C(16)-C(17)	1.383(12)
C(17)-C(18)	1.378(14)
C(18)-C(19)	1.385(14)
C(19)-C(20)	1.378(12)
C(21)-C(26)	1.338(12)
C(21)-C(22)	1.359(14)
C(21)-P(2)	1.857(8)
C(22)-C(23)	1.420(15)
C(23)-C(24)	1.322(16)
C(24)-C(25)	1.360(13)
C(25)-C(26)	1.400(12)
C(27)-P(3)	1.812(7)
C(28)-C(33)	1.393(11)
C(28)-C(29)	1.395(10)

C(28)-P(3)	1.824(8)
C(29)-C(30)	1.375(12)
C(30)-C(31)	1.363(13)
C(31)-C(32)	1.386(14)
C(32)-C(33)	1.376(12)
C(34)-C(39)	1.393(11)
C(34)-C(35)	1.405(10)
C(34)-P(3)	1.821(8)
C(35)-C(36)	1.398(11)
C(36)-C(37)	1.353(12)
C(37)-C(38)	1.343(12)
C(38)-C(39)	1.399(12)
C(40)-C(41)	1.451(12)
C(41)-C(42)	1.558(14)
C(42)-C(43A)	1.525(16)
P(1)-C(48)	1.806(9)
P(1)-C(46)	1.834(12)
P(1)-C(44)	1.841(10)
C(44)-C(45)	1.502(14)
C(48)-C(49)	1.482(14)
C(46)-C(47)	1.528(16)
P(3)-Ag(1)-P(4)	90.03(6)
P(3)-Ag(1)-P(2)	90.56(7)
P(1)-Ag(1)-P(2)	89.73(7)
P(1)-Ag(1)-P(4)	124.04(6)
P(1)-Ag(1)-P(2)	125.91(7)
P(1)-Ag(1)-P(3)	125.59(7)
C(40)-B(1)-C(14)	106.2(7)
C(40)-B(1)-C(27)	105.3(6)
C(14)-B(1)-C(27)	112.2(6)
C(40)-B(1)-C(13)	109.5(6)
C(14)-B(1)-C(13)	111.7(6)
C(27)-B(1)-C(13)	111.5(7)
C(2)-C(1)-C(6)	116.2(7)
C(2)-C(1)-P(4)	119.0(6)
C(6)-C(1)-P(4)	124.9(6)
C(1)-C(2)-C(3)	122.4(9)
C(2)-C(3)-C(4)	119.3(9)
C(5)-C(4)-C(3)	118.9(8)
C(6)-C(5)-C(4)	120.0(8)
C(5)-C(6)-C(1)	123.1(8)
C(12)-C(7)-C(8)	117.7(7)
C(12)-C(7)-P(4)	123.4(6)

C(8)-C(7)-P(4)	118.8(6)
C(9)-C(8)-C(7)	120.8(8)
C(8)-C(9)-C(10)	120.8(9)
C(11)-C(10)-C(9)	118.5(8)
C(10)-C(11)-C(12)	121.0(8)
C(7)-C(12)-C(11)	121.1(8)
B(1)-C(13)-P(4)	117.0(5)
B(1)-C(14)-P(2)	118.6(6)
C(16)-C(15)-C(20)	117.8(7)
C(16)-C(15)-P(2)	120.3(6)
C(20)-C(15)-P(2)	121.9(6)
C(17)-C(16)-C(15)	121.6(9)
C(18)-C(17)-C(16)	120.1(9)
C(17)-C(18)-C(19)	119.3(8)
C(20)-C(19)-C(18)	120.8(10)
C(19)-C(20)-C(15)	120.4(9)
C(26)-C(21)-C(22)	118.3(8)
C(26)-C(21)-P(2)	123.4(6)
C(22)-C(21)-P(2)	118.2(7)
C(21)-C(22)-C(23)	119.2(11)
C(24)-C(23)-C(22)	121.7(12)
C(23)-C(24)-C(25)	119.1(9)
C(24)-C(25)-C(26)	119.2(9)
C(21)-C(26)-C(25)	122.2(9)
B(1)-C(27)-P(3)	120.1(5)
C(33)-C(28)-C(29)	117.5(8)
C(33)-C(28)-P(3)	122.5(6)
C(29)-C(28)-P(3)	120.0(6)
C(30)-C(29)-C(28)	120.9(8)
C(31)-C(30)-C(29)	120.5(9)
C(30)-C(31)-C(32)	120.1(9)
C(33)-C(32)-C(31)	119.4(9)
C(32)-C(33)-C(28)	121.5(9)
C(39)-C(34)-C(35)	116.6(7)
C(39)-C(34)-P(3)	122.8(6)
C(35)-C(34)-P(3)	120.5(6)
C(36)-C(35)-C(34)	120.5(7)
C(37)-C(36)-C(35)	121.4(8)
C(38)-C(37)-C(36)	118.9(9)
C(37)-C(38)-C(39)	122.0(8)
C(34)-C(39)-C(38)	120.5(8)
C(41)-C(40)-B(1)	119.8(8)
C(40)-C(41)-C(42)	115.3(8)
C(43A)-C(42)-C(41)	116.6(10)

C(13)-P(4)-C(7)	107.4(3)
C(13)-P(4)-C(1)	106.5(3)
C(7)-P(4)-C(1)	100.0(3)
C(13)-P(4)-Ag(1)	108.2(2)
C(7)-P(4)-Ag(1)	122.4(2)
C(1)-P(4)-Ag(1)	111.2(2)
C(14)-P(2)-C(15)	105.5(4)
C(14)-P(2)-C(21)	105.8(4)
C(15)-P(2)-C(21)	100.3(4)
C(14)-P(2)-Ag(1)	106.6(3)
C(15)-P(2)-Ag(1)	109.6(3)
C(21)-P(2)-Ag(1)	127.3(3)
C(27)-P(3)-C(34)	106.9(3)
C(27)-P(3)-C(28)	104.9(4)
C(34)-P(3)-C(28)	99.8(3)
C(27)-P(3)-Ag(1)	105.9(2)
C(34)-P(3)-Ag(1)	125.8(3)
C(28)-P(3)-Ag(1)	111.9(3)
C(48)-P(1)-C(46)	101.3(5)
C(48)-P(1)-C(44)	105.1(5)
C(46)-P(1)-C(44)	103.3(5)
C(45)-C(44)-P(1)	118.6(8)
C(49)-C(48)-P(1)	111.6(7)
C(47)-C(46)-P(1)	120.7(10)

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters ($\text{Å}^2 \times 10^2$) for **2**.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ag(1)	56(1)	32(1)	36(1)	4(1)	-5(1)	3(1)
B(1)	57(6)	32(4)	37(5)	4(4)	7(4)	9(4)
C(1)	45(4)	41(4)	29(4)	-1(3)	11(3)	6(3)
C(2)	65(6)	76(7)	54(5)	18(5)	20(4)	29(5)
C(3)	72(7)	116(9)	75(7)	21(7)	39(6)	23(7)
C(4)	86(7)	82(7)	45(5)	9(5)	25(5)	-15(6)
C(5)	80(7)	45(5)	39(4)	9(4)	4(4)	-5(4)
C(6)	60(5)	40(4)	37(4)	5(3)	9(4)	5(4)
C(7)	60(5)	30(4)	27(4)	6(3)	15(3)	-2(3)
C(8)	59(5)	40(4)	55(5)	2(4)	8(4)	3(4)
C(9)	60(6)	57(6)	53(5)	-2(4)	-2(4)	-9(4)
C(10)	85(7)	44(5)	52(5)	-11(4)	1(5)	-15(5)
C(11)	67(6)	38(5)	71(6)	-12(4)	12(5)	-3(4)
C(12)	53(5)	37(4)	53(5)	-3(4)	10(4)	1(4)
C(13)	56(5)	25(3)	45(4)	6(3)	20(4)	10(3)
C(14)	56(5)	38(4)	44(4)	5(3)	6(4)	0(4)
C(15)	58(5)	32(4)	33(4)	8(3)	6(3)	1(3)
C(16)	67(6)	47(5)	49(5)	3(4)	15(4)	-10(4)
C(17)	80(7)	49(5)	48(5)	-2(4)	5(5)	-13(5)
C(18)	93(8)	45(5)	43(5)	-10(4)	4(5)	-10(5)
C(19)	87(7)	61(6)	55(5)	-5(5)	19(5)	4(5)
C(20)	60(6)	47(5)	54(5)	-3(4)	3(4)	-3(4)
C(21)	59(5)	33(4)	50(5)	11(3)	8(4)	-3(4)
C(22)	83(8)	100(10)	164(14)	80(9)	-44(8)	-40(7)
C(23)	90(9)	128(12)	205(17)	125(12)	-46(10)	-40(9)
C(24)	81(7)	41(5)	88(7)	25(5)	20(6)	-8(5)
C(25)	140(10)	55(6)	37(5)	-1(4)	4(6)	-51(6)
C(26)	105(8)	60(6)	42(5)	13(4)	-14(5)	-38(6)
C(27)	49(5)	32(4)	35(4)	7(3)	2(3)	8(3)
C(28)	52(5)	30(4)	42(4)	-3(3)	6(4)	6(3)
C(29)	83(6)	32(4)	35(4)	5(3)	9(4)	2(4)
C(30)	106(8)	38(4)	45(5)	0(4)	30(5)	2(5)
C(31)	79(7)	45(5)	79(7)	-20(5)	50(6)	-12(5)

C(32)	48(6)	57(6)	107(9)	-11(6)	17(5)	-4(4)
C(33)	45(5)	44(5)	68(6)	5(4)	5(4)	3(4)
C(34)	42(4)	36(4)	40(4)	-3(3)	-3(3)	5(3)
C(35)	52(5)	34(4)	52(5)	0(3)	8(4)	4(3)
C(36)	54(5)	41(4)	60(5)	-10(4)	13(4)	7(4)
C(37)	58(6)	65(6)	55(5)	-4(5)	11(4)	1(5)
C(38)	73(6)	62(6)	48(5)	11(4)	17(4)	16(5)
C(39)	68(6)	40(4)	44(4)	5(4)	7(4)	17(4)
C(40)	65(6)	41(5)	58(5)	14(4)	16(4)	15(4)
C(41)	77(7)	67(6)	64(6)	-20(5)	8(5)	3(5)
C(42)	72(7)	82(8)	93(8)	-10(6)	14(6)	17(6)
C(43A)	113(12)	188(18)	171(16)	-104(14)	-1(11)	40(12)
P(1)	72(2)	41(1)	61(2)	8(1)	-17(1)	4(1)
P(2)	59(1)	32(1)	39(1)	3(1)	5(1)	-6(1)
P(3)	51(1)	26(1)	34(1)	-1(1)	-2(1)	8(1)
P(4)	52(1)	25(1)	34(1)	0(1)	10(1)	2(1)
C(44)	99(8)	56(6)	63(6)	-3(5)	-2(6)	21(6)
C(48)	79(7)	71(6)	50(5)	9(5)	-8(5)	-12(5)
C(49)	85(8)	107(9)	54(6)	-4(6)	8(5)	13(7)
C(45)	153(12)	89(8)	51(6)	2(6)	1(7)	56(8)
C(46)	77(7)	66(7)	116(10)	2(6)	28(7)	22(6)
C(47)	181(14)	84(8)	60(7)	12(6)	15(8)	50(9)

Table S11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **2**.

	x	y	z	U(eq)
H(2)	11701	2810	6442	76
H(3)	12294	3131	5397	101
H(4)	11262	3896	4601	83
H(5)	9718	4365	4920	67
H(6)	9219	4079	5989	55
H(8)	12207	3337	8026	63
H(9)	13116	4109	8831	70
H(10)	12202	5038	9118	75
H(11)	10377	5189	8562	71
H(12)	9440	4404	7780	57
H(13A)	8420	3387	7574	48
H(13B)	8378	3674	6774	48
H(14A)	7242	1737	7108	56
H(14B)	7031	2322	7624	56
H(16)	10502	2680	8837	65
H(17)	10691	3478	9736	72
H(18)	9212	3749	10267	74
H(19)	7531	3228	9869	81
H(20)	7312	2460	8936	66
H(22)	9574	1204	9375	151
H(23)	9103	242	9941	182
H(24)	7652	-375	9403	84
H(25)	6465	23	8371	95
H(26)	6939	966	7798	88
H(27A)	8485	2664	5763	47
H(27B)	7548	2128	5705	47
H(29)	9414	581	7199	61
H(30)	8474	-388	7250	73
H(31)	6922	-622	6380	76
H(32)	6359	85	5389	85
H(33)	7298	1055	5329	64
H(35)	10302	620	5614	56
H(36)	10895	441	4521	62
H(37)	10735	1241	3640	71
H(38)	9934	2215	3820	72
H(39)	9326	2433	4897	61

H(40 ^a)	6589	3211	5919	65
H(40B)	6041	2582	6195	65
H(41 ^a)	6395	3773	6933	84
H(41B)	5913	3139	7254	84
H(42 ^a)	4813	3796	5945	100
H(42B)	4327	3180	6295	100
H(43A)	4057	3816	7288	242
H(43B)	3458	4155	6541	242
H(43C)	4606	4433	6978	242
H(44 ^a)	11722	426	8094	91
H(44B)	12134	489	7343	91
H(48 ^a)	13542	1542	9008	84
H(48B)	12785	2180	8939	84
H(49 ^a)	11410	1616	9300	125
H(49B)	12512	1443	9874	125
H(49C)	12011	933	9245	125
H(45 ^a)	13937	406	7949	151
H(45B)	13262	-196	8181	151
H(45C)	13577	410	8725	151
H(46 ^a)	13396	2264	7554	102
H(46B)	14031	1598	7775	102
H(47 ^a)	13388	1170	6616	164
H(47B)	13926	1868	6532	164
H(47C)	12622	1794	6387	164

Figure S1. Room temperature and low temperature (-103 °C) ^{31}P NMR of complexes **1** (A), **2** (B), **3** (C), **4** (D) in d_8 -thf.

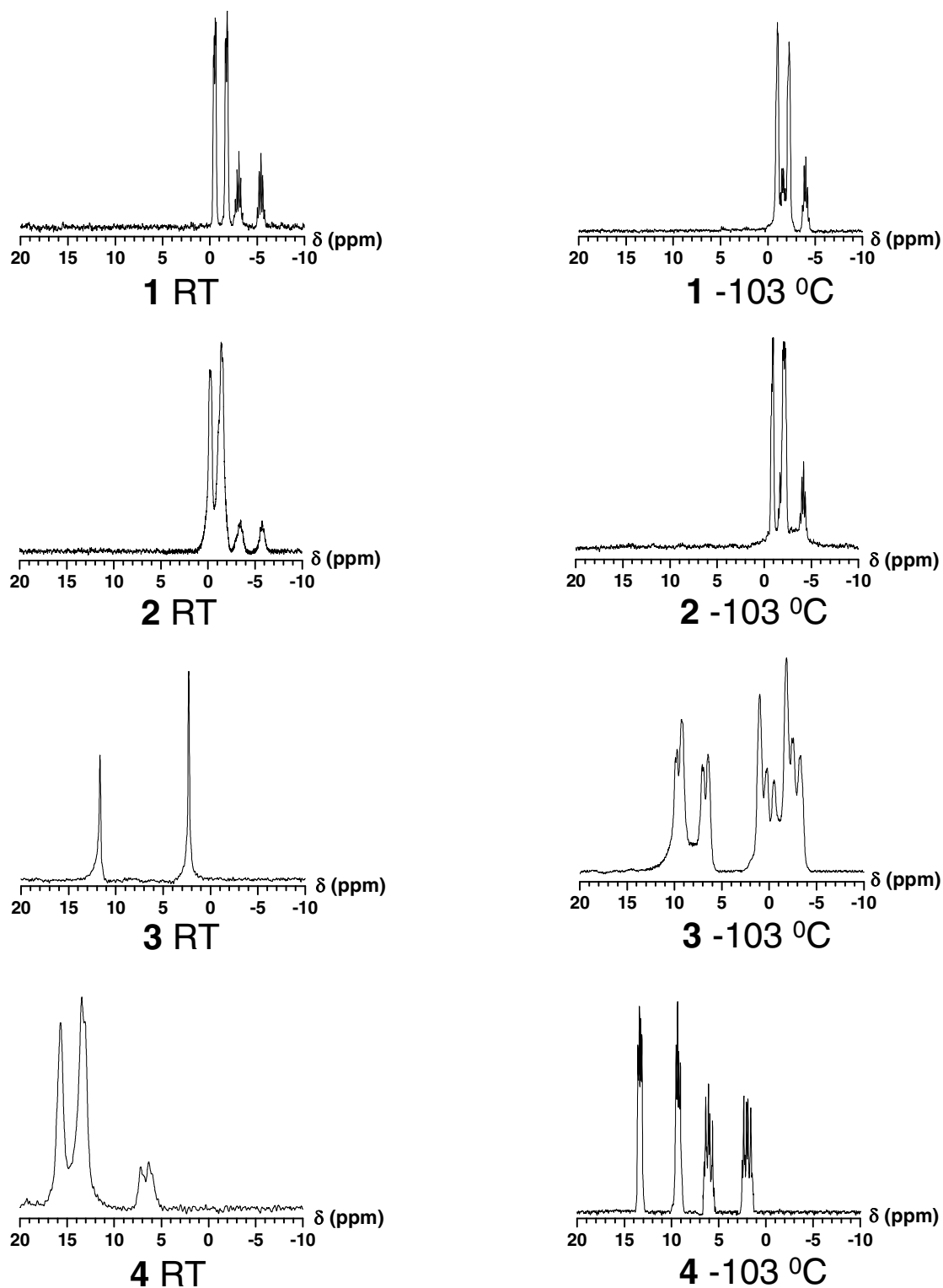


Figure S2. ^{31}P NMR of complex **3** at $-103\text{ }^{\circ}\text{C}$ (A), $-90\text{ }^{\circ}\text{C}$ (B), $-80\text{ }^{\circ}\text{C}$ (C), $-60\text{ }^{\circ}\text{C}$ (D), $-20\text{ }^{\circ}\text{C}$ (E), and $20\text{ }^{\circ}\text{C}$ (F) in d_8 -thf.

