Electronic Supporting Information

Mono- and Polynuclear Ag(I) Complexes of *N*-functionalized Bis(diphenylphosphino)amine DPPA-type Ligands: Synthesis, Solid-State Structures and Reactivity‡

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‡ Electronic Supporting Information (ESI) available: $^{31}P\{^{1}H\}$ NMR spectra (Figures S1-S6) and crystallographic and experimental details for all the structures (Tables S1-S7). The Crystallographic information files (CIF) of **2a**·BF_4, **2b**·BF_4, **3b**·$(BF_4)_2$, **3c**·$(BF_4)_2$, **3c**·$(BF_4)_2$·$(THF)_3$, **4a**·BF_4·$3(CH_2Cl_2)$, **4c**·BF_4·CH_2Cl_2 have been deposited to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K., and can be obtained on request free of charge, by quoting the publication citation and deposition numbers 1497150-1497155 and 1497157. See DOI: 10.1039/x0xx00000x.

Content:

Tables S1-S7. Crystallographic data for coumpounds **2a**·BF_4, **2b**·BF_4, **3b**·$(BF_4)_2$, **3c**·$(BF_4)_2$, **3c**·$(BF_4)_2$·$(THF)_3$, **4a**·BF_4·$3(CH_2Cl_2)$, **4c**·BF_4·CH_2Cl_2.

Table S1.

Identification code	Compound **2a**·BF_4	
Empirical formula	$C_{60}H_{50}AgBF_4N_2P_4$	
Formula weight	1117.58 g.mol^{-1}	
Temperature	173(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.9021(3) Å	α = 90 °
	b = 19.5151(9) Å	β = 99.519(2) °
	c = 14.0811(6) Å	γ = 90 °
Volume	2683.57(19) Å^3	
Z	2	
Density (calculated)	1.383 Mg/m^3	
Absorption coefficient	0.549 mm^{-1}	
F(000)	1144	
Theta range for data collection	2.33 to 26.00 °	
Index ranges	-12<=h<=12, -24<=k<=23, -17<=l<=17	
Reflections collected	24752	
Independent reflections	10058 [R(int) = 0.0869]	
Completeness to theta = 26.00°	185 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10058 / 57 / 644	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2σ(I)]	R1 = 0.0755, wR2 = 0.1198	
R indices (all data)	R1 = 0.1098, wR2 = 0.1300	
Largest diff. peak and hole	-0.563 and 0.779 e.Å^{-3}	

Table S2.

Identification code	Compound **2b**·BF_4	
Empirical formula	$C_{62}H_{54}AgBF_4N_2P_4S_2$	
Formula weight	1209.75 g.mol^{-1}	
Temperature	173(2) K	
Wavelength	0.71069 Å	
Crystal system	Tetragonal	
Space group	$P4_3$	
Unit cell dimensions	a = 11.9470(2) Å	α = 90 °
	b = 11.9470(2) Å	β = 90 °
	c = 41.0063(7) Å	γ = 90 °
Volume	5852.86(17) Å^3	
Z	4	
Density (calculated)	1.373 Mg/m^3	
Absorption coefficient	0.578 mm^{-1}	
F(000)	2480	
Theta range for data collection	1.70 to 27.50 °	
Index ranges	-10<=h<=15, -15<=k<=10, -44<=l<=53	
Reflections collected	40141	
Independent reflections	11820 [R(int) = 0. 0775]	
Completeness to theta = 26.00°	173 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11820/ 1 / 682	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2σ(I)]	R1 = 0.0571, wR2 = 0.1250	
R indices (all data)	R1 = 0. 1258, wR2 = 0.1688	
Largest diff. peak and hole	-1.112 and 0.853 e.Å^{-3}	

Table S3.

Identification code	Compound **3b**·$(BF_4)_2$	
Empirical formula	$C_{62}H_{54}Ag_2B_2F_8N_2P_4S_2$	
Formula weight	1404.43 $g.mol^{-1}$	
Temperature	298(2) K	
Wavelength	0.71069 Å	
Crystal system	Orthorhombic	
Space group	*P*bcn	
Unit cell dimensions	a = 17.893(5) Å	α = 90 °
	b = 19.791(5) Å	β = 90 °
	c = 17.617(5) Å	γ = 90 °
Volume	6239(3) $Å^3$	
Z	4	
Density (calculated)	1.495 Mg/m^3	
Absorption coefficient	0.861 mm^{-1}	
F(000)	2832	
Theta range for data collection	3.10 to 26.00 °	
Index ranges	-21<=h<=22, -24<=k<=24, -21<=l<=21	
Reflections collected	55530	
Independent reflections	6092 [R(int) = 0.1010]	
Completeness to theta = 26.00°	99.3 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6092 / 327 / 369	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2σ(I)]	R1 = 0.0665, wR2 = 0.1414	
R indices (all data)	R1 = 0.1121, wR2 = 0.1574	
Largest diff. peak and hole	- 0.791 and 1.025 $e.Å^{-3}$	

Table S4.

Identification code	Compound **3c**·$(BF_4)_2$	
Empirical formula	$C_{62}H_{54}Ag_2B_2F_8N_2O_2P_4$	
Formula weight	1372.31 g.mol^{-1}	
Temperature	173(2) K	
Wavelength	0.71069 Å	
Crystal system	Orthorhombic	
Space group	*P*bcn	
Unit cell dimensions	a = 19.6121(4) Å	α = 90 °
	b = 17.0360(3) Å	β = 90 °
	c = 17.8281(2) Å	γ = 90 °
Volume	5956.58(17) Å^3	
Z	4	
Density (calculated)	1.530 Mg/m^3	
Absorption coefficient	0.835 mm^{-1}	
F(000)	2768	
Theta range for data collection	1.583 to 25.999 °	
Index ranges	-22<=h<=23, -18<=k<=18, -18<=l<=21	
Reflections collected	49665	
Independent reflections	5749 [R(int) = 0.0742]	
Completeness to theta = 26.00°	98.2 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5749 / 9 / 278	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2σ(I)]	R1 = 0.0953, wR2 = 0.2609	
R indices (all data)	R1 = 0.1095, wR2 = 0.2740	
Largest diff. peak and hole	-2.184 and 3.046 e.Å^{-3}	

Table S5.

Identification code	Compound **3c**$\cdot(BF_4)_2\cdot(THF)_3$	
Empirical formula	$C_{74}H_{78}Ag_2B_2F_8N_2O_5P_4$	
Formula weight	1588.62 g.mol^{-1}	
Temperature	173(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.2883(2) Å	α = 90 °
	b = 23.0676(4) Å	β = 101.8914(10) °
	c = 27.7279(3) Å	γ = 90 °
Volume	7065.20(19) Å^3	
Z	4	
Density (calculated)	Mg/m^3	
Absorption coefficient	1.494 mm^{-1}	
F(000)	3248	
Theta range for data collection	1.92 to 26.00 °	
Index ranges	-13<=h<=13, -28<=k<=28, -34<=l<=34	
Reflections collected	25030	
Independent reflections	13754 [R(int) = 0.0641]	
Completeness to theta = 26.00°	99.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13754 / 61 / 858	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2σ(I)]	R1 = 0.0621, wR2 = 0.1233	
R indices (all data)	R1 = 0.1013, wR2 = 0.1352	
Largest diff. peak and hole	- 0.946 and 1.555 e.Å^{-3}	

Table S6.

Identification code	Compound **4a**·BF_4·3(CH_2Cl_2)	
Empirical formula	$C_{93}H_{81}Ag_3BCl_8F_4N_3P_6$	
Formula weight	2120.45 g.mol^{-1}	
Temperature	173(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 22.5824(7) Å	α = 90 °
	b = 23.1008(7) Å	β = 116.2390(10) °
	c = 21.1189(7) Å	γ = 90 °
Volume	9881.9(5) Å^3	
Z	4	
Density (calculated)	1.425 Mg/m^3	
Absorption coefficient	0.953 mm^{-1}	
F(000)	4272	
Theta range for data collection	1.41 to 31.04 °	
Index ranges	-32<=h<=32, -33<=k<=33, -30<=l<=30	
Reflections collected	126093	
Independent reflections	31563 [R(int) = 0.0452]	
Completeness to theta = 26.00°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	31563 / 0 / 1063	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2σ(I)]	R1 = 0.0540, wR2 = 0.1305	
R indices (all data)	R1 = 0.0903, wR2 = 0.1464	
Largest diff. peak and hole	- 1.081 and 1.540 e.Å^{-3}	

Table S7.

Identification code	Compound **4c**·BF_4·CH_2Cl_2
Empirical formula	$C_{94}H_{83}Ag_3BCl_4F_4N_3O_3P_6$
Formula weight	2040.67 g.mol^{-1}
Temperature	173(2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 10.25800(10) Å α = 90 °
	b = 34.9966(5) Å β = 105.1040(10) °
	c = 29.4055(4) Å γ = 90 °
Volume	10191.8(2) Å^3
Z	4
Density (calculated)	1.330 Mg/m^3
Absorption coefficient	0.822 mm^{-1}
F(000)	4128
Theta range for data collection	2.08 to 26.00 °
Index ranges	-12<=h<=12, -43<=k<=43, -36<=l<=36
Reflections collected	98194
Independent reflections	19790 [R(int) = 0.1035]
Completeness to theta = 26.00°	98.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	19790 / 1024 / 1049
Goodness-of-fit on F^2	1.073
Final R indices [I>2σ(I)]	R1 = 0.0793, wR2 = 0.2433
R indices (all data)	R1 = 0.1276, wR2 = 0.2630
Largest diff. peak and hole	- 1.331 and 1.445 e.Å^{-3}

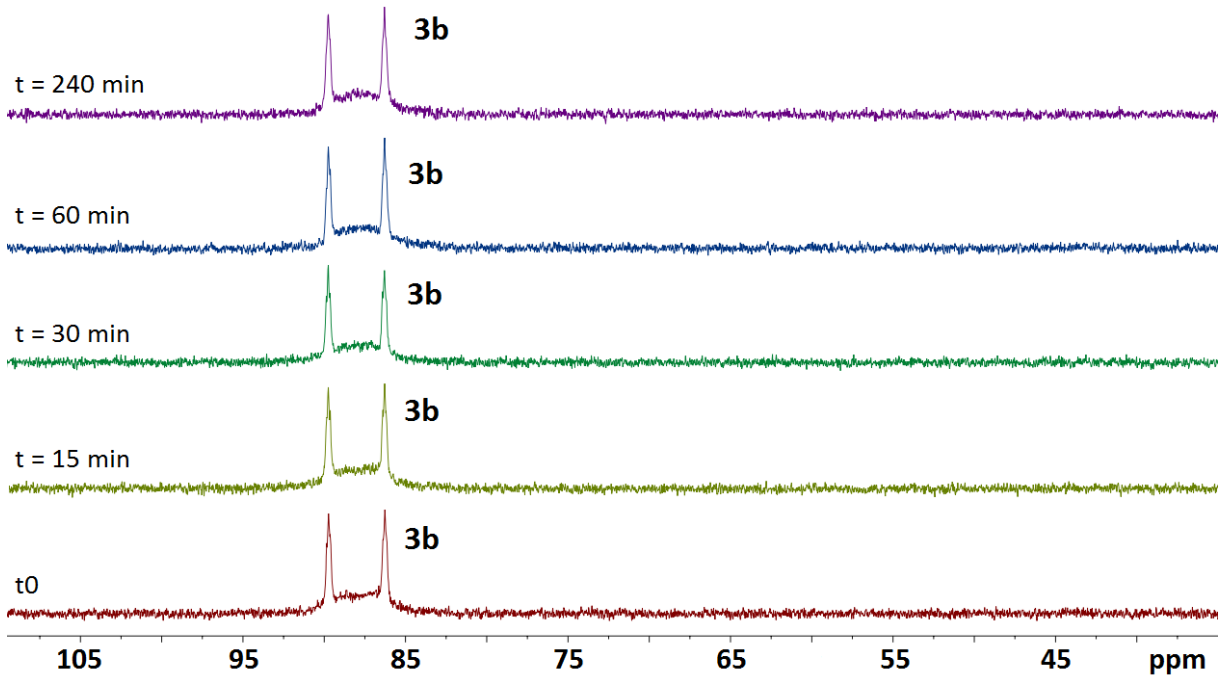

Figure S1. $^{31}P\{^{1}H\}$ NMR control experiment illustrating the stability of **3b**·$(BF_4)_2$ in CD_2Cl_2. Conditions: 10 mg of **3b**·$(BF_4)_2$ dissolved in 0.6 mL of CD_2Cl_2 and kept under inert atmosphere, in the absence of light, at room temperature and analysed over a period of 4 h.

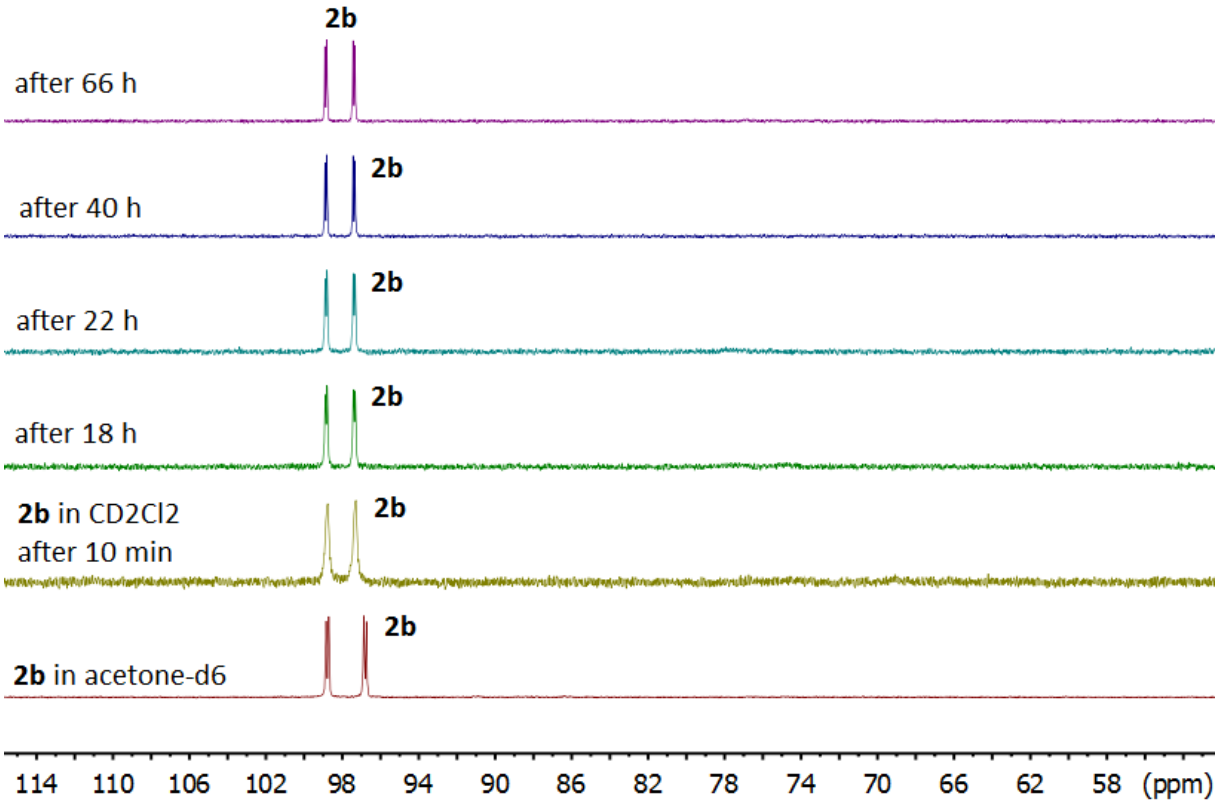

Figure S2. $^{31}P\{^{1}H\}$ NMR control experiment illustrating the stability of **2b**·BF_4 in CD_2Cl_2. Conditions: 10 mg of **2b**·BF_4 dissolved in 0.6 mL of CD_2Cl_2 and kept under inert atmosphere, in the absence of light, at room temperature and analysed over a period of 66 h.

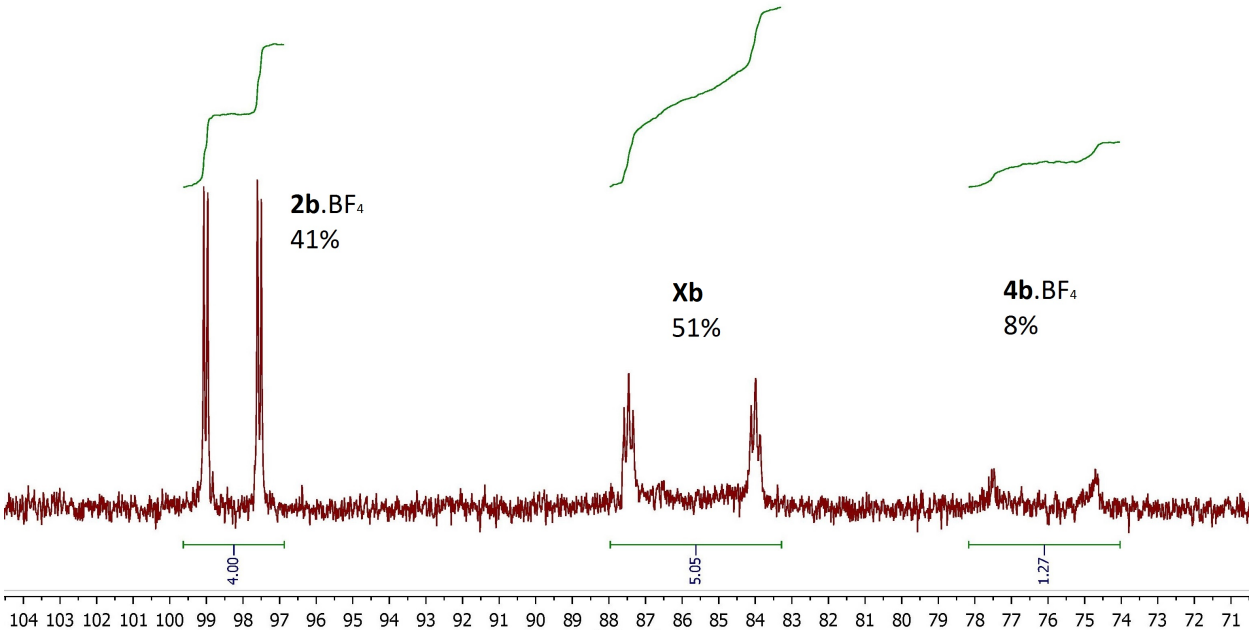

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction between ligand **1b** and $AgBF_4$ (1:1 molar ratio) in $CDCl_3$ after 10 min, with approximate integrations.

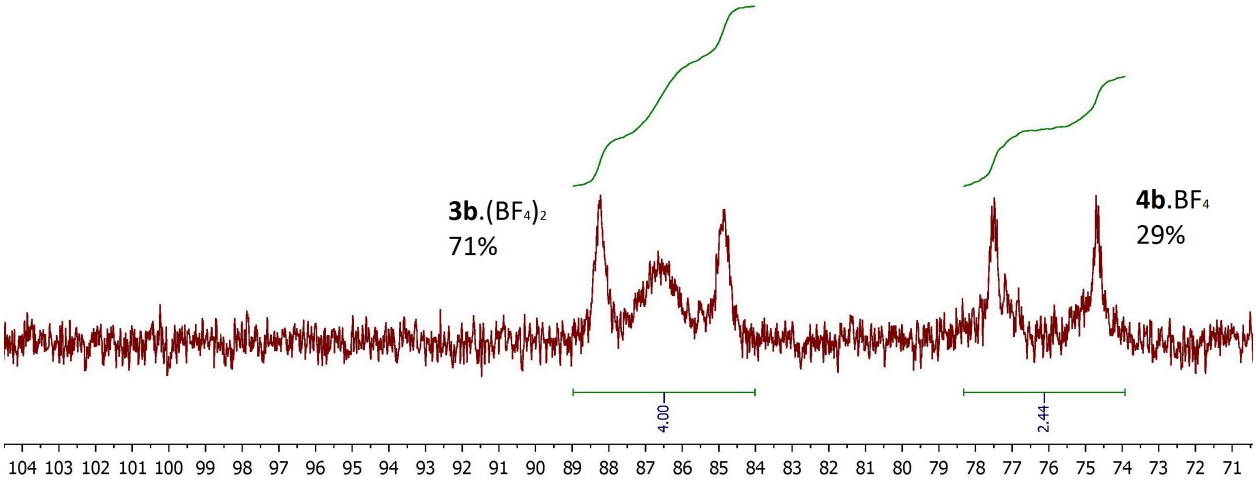

Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction between ligand **1b** and $AgBF_4$ (1:1 molar ratio) in $CDCl_3$ after 6 h, with approximate integrations.

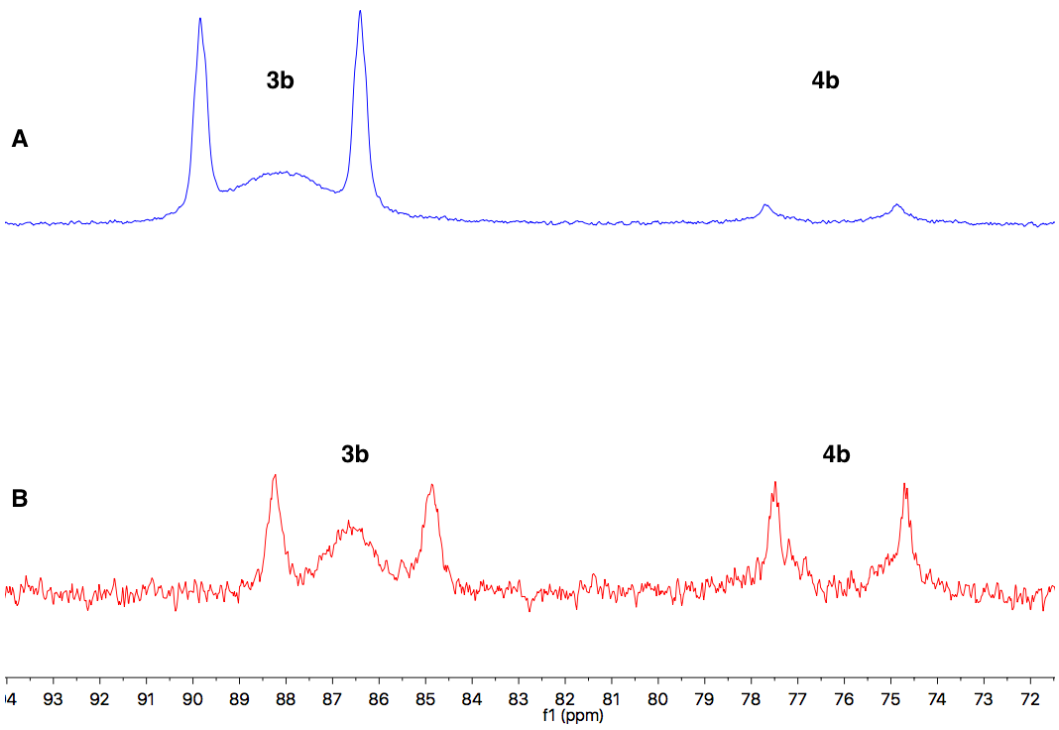

Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum showing the influence of the chlorinated solvent, CD_2Cl_2 (**A**) and $CDCl_3$ (**B**) on the relative formation of the complexes **3b**·$(BF_4)_2$ and **4b**·BF_4. Reaction conditions: ligand **1b**:$AgBF_4$ 1:1 ratio, in 0.6 mL of the corresponding deuterated solvent, time: 6 h.

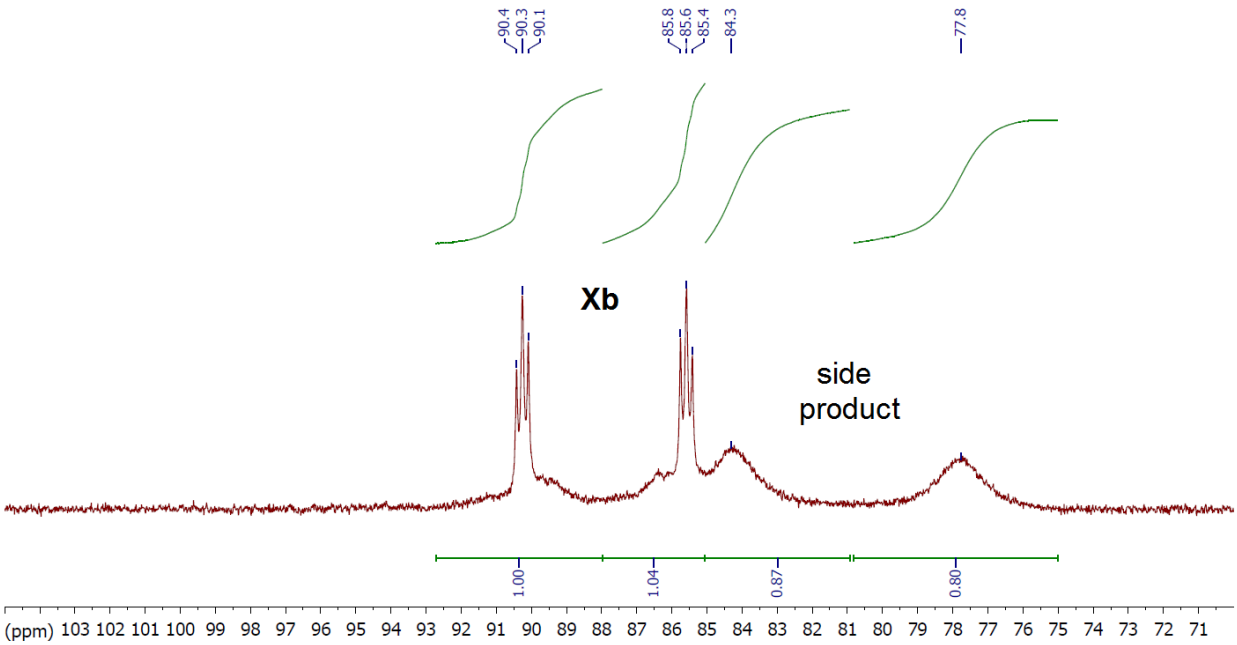

Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of the mixture resulting from the dissolution in CD_2Cl_2 of the solid obtained after solvent evaporation of the mixture **3b**·$(BF_4)_2$ and 1 equiv. $AgBF_4$ (unreacted) prepared in acetone. [53]

We note the presence of the expected **Xb** and of another product different from all other characterized complexes.

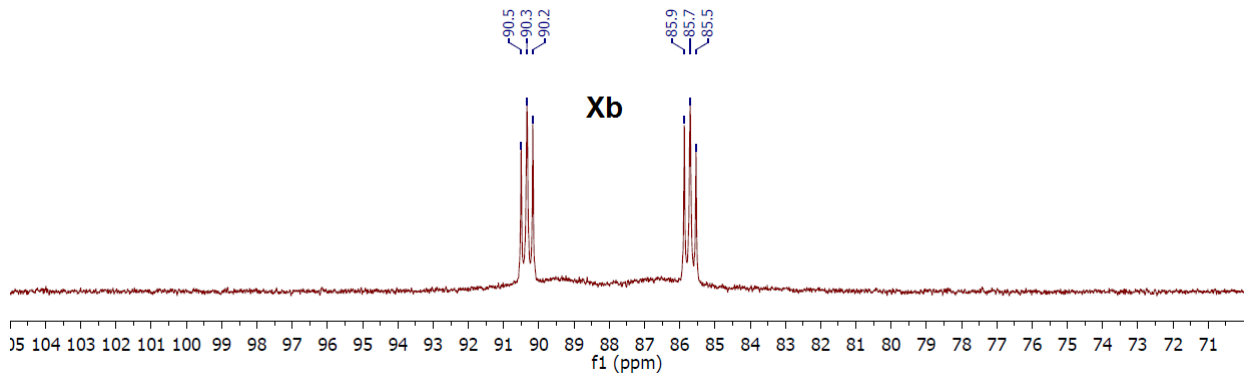

Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of complex **Xb** in CD_2Cl_2.

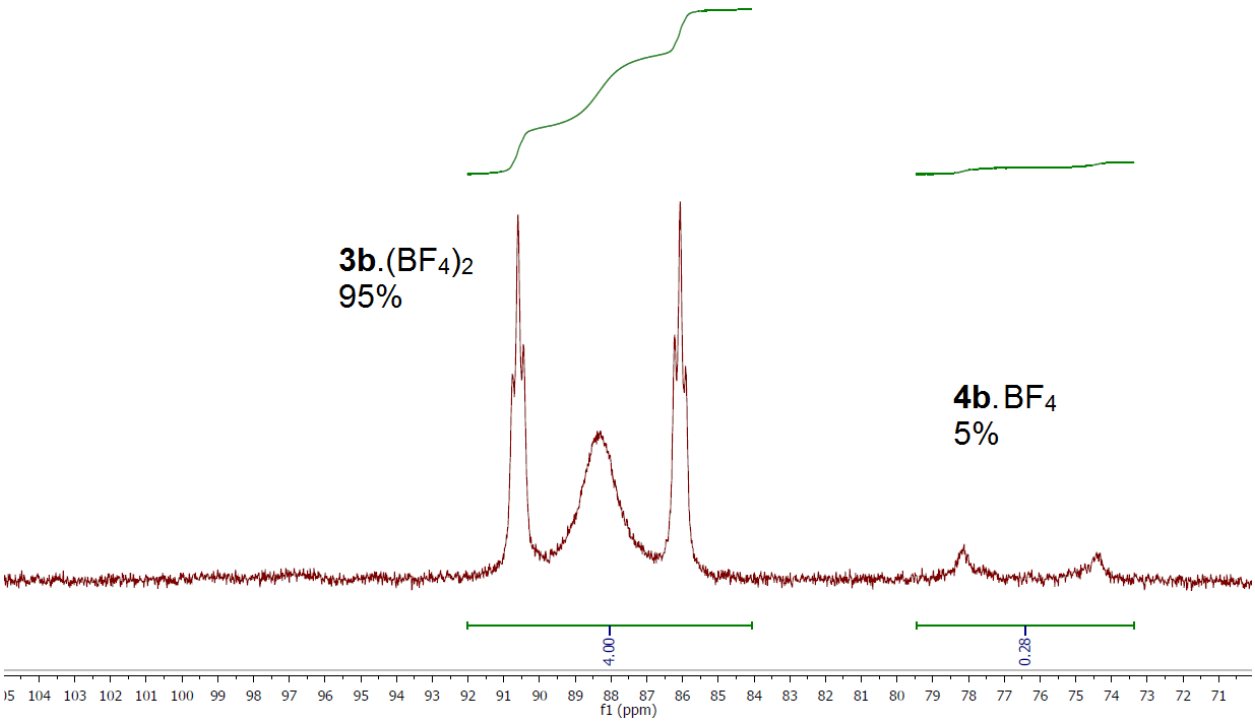

Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of the mixture of **3b**·$(BF_4)_2$ (≈ 95%) and **4b**·BF_4 (≈5%) resulting from the addition of 2 equiv. **2b**·BF_4 to 1 equiv. **Xb** in CD_2Cl_2.