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Supplementary Material for

Solid-state NMR, X-ray diffraction and theoretical studies of neutral mononuclear molecular bis(triphenylphosphine)silver(I) mono-carboxylate and nitrate systems

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Table S1. Crystallographically established silver(I) atom environments in $[(Ph_3P)_2Ag(O_2XY)]$ complexes. (Relevant copper(I) analogues are also included for comparison.)

Anion (/mol.)	Ag-P/Å	Ag-O/Å	P-Ag-P/º	O-Ag-O/º	P-Ag-O/º
(a) *Silver(I) complexes*					
O_2CCH_2Ph (**1**)[a]	2.432(1)	2.436(1)	128.9(1)	53.4(1)	106.6(1)
	2.442(1)	2.458(1)			–118.3(1)
O_2CCHPh_2 (**2**)[a]	2.438(1)	2.441(2)	126.2(1)	52.8(1	98.1(1)
	2.465(1)	2.484(3)			–120.2(1)
$O_2CC(CH_3)_3$ (**3**)[a]	2.440(2)	2.392(4)	131.4(1)	53.8(1)	106.9(1)
	2.458(2)	2.499(4)			–118.3(1)
$O_2CCH_2C(CH_3)_3$ (**4**)/[a] 1	2.416(1)	2.384(3)	129.7(1)	53.5(1)	104.5(1)
	2.425(1)	2.497(2)			–116.0(1)
/2	2.439(1)	2.410(3)	125.8(1)	53.1(1)	111.1(1)
	2.450(1)	2.494(3)			–116.5(1)
O_2CCH_3 (**6**)/1[b]	2.4332(8)	2.420(2)	129.62(3)	53.33(7)	106.03(7)
(anhydrate)	2.4483(8)	2.438(2)			–114.83(7)
/2	2.4264(8)	2.379(3)	124.13(3)	52.3(1)	102.0(1)
	2.4608(8)	2.510(3)			–125.61(8)
(·EtOH·H_2O) (**7**)/1[c]	2.4461(8)	2.438(2)	127.72(3)	52.8(1)	110.75(8)
	2.4490(8)	2.451(3)			–115.25(7)
/2	2.4063(8)	2.431(2)	127.96(3)	53.5(1)	103.10(9)
	2.4582(8)	2.449(3)			–122.50(7)
$O_2CC(OH)CH_3$ (**8**)[d]	2.4345(9)	2.425(3)	126.15(3)	51.3(1)	104.7(1)
	2.4671(9)	2.508(4)			–126.5(1)
O_2CCF_3 (**5α**)[e] (orthorhombic)	2.423(1)	2.526(3)	142.18(4)	51.6(1)	97.13(9)
	2.445(1)	2.542(4)			–112.41(9)
(**5β**)[a] (monoclinic)	2.4367(7)	2.420(3)	129.35(5)	47.18(9)	99.73(7)
	2.4542(8)	2.894(4)			–126.97(8)
O_2CH[f]	2.426(1)	2.425(3)	127.37(3)	52.4(1)	112.53(9),
					114.36(8)
O_2CH(·HCO_2H)[f]	2.426(2)	2.550(7)	147.86(7)	49.5(2)	104.26(5)
		2.713(8)			104.84(5)

NO_3 (**9α**) (298 K)[a]		2.4379(6)	2.460(2)	138.26(2)	49.77(5)	100.42(4)
(unsolvated)						
		2.4357(7)	2.648(2)			–111.55(4)
	(200 K)[a]	2.4360(5)	2.4551(13)	138.58(1)	50.26(4)	100.11(3)
		2.4391(5)	2.6431(16)			–110.96(3)
	(120 K)[g]	2.4254(6)	2.4287(14)	138.14(2)	50.22(4)	99.38(4)
		2.4286(6)	2.6711(14)			–110.97(4)
(**10**)[h](triclinic, benzene solvate)		2.435(1)	2.463(2)	139.4(1)	50.4(1)	96.7(1)
		2.416(1)	2.572(2)			–114.9(1)
(**11α**)[a] (triclinic, toluene solvate)		2.4232(5)	2.468(2)	138.10(2)	51.35(5)	99.60(4)
		2.4366(5)	2.550(2)			–114.08(4)
(**11β**)[a] (monoclinic, toluene solvate)		2.411(3)	2.451(7)	135.85(9)	50.5(2)	98.4(2)
		2.430(2)	2.541(7)			–114.5(2)
(b) *Copper(I) complexes*						
O_2CH[i]		2.247(1)	2.226(3)	128.3(4)	58.05(8)	110.3(1), 114.6(1)
O_2CCH_3[j]		2.224(2), 2.232(2)	2.167(4), 2.227(3)	133.29(1)	60.3(1)	104.6(1), –116.4(1)
O_2CCH_2F[k]		2.222(3), 2.232(3)	2.144(6), 2.363(7)	135.0(1)	58.4(2)	101.7(2), –117.0(2)
O_2CCHF_2[k]		2.219(2), 2.234(2)	2.118(4), 2.465(6)	135.8(1)	56.7(2)	99.3(2) –117.0(2)
O_2CCF_3[k]		2.228(2), 2.235(2)	2.113(4), 2.545(5)	136.7(1)	55.4(1)	98.6(1) –116.3(1)
O_2NO[l]		2.231(4)	2.205(2)	130.9(1)	57.4(1)	108.3(1), 114.5(1)
O_2NO[m,†]		2.252(3), 2.252(3)	2.217(9), 2.184(9)	128.0(1)	56.2(4)	104.9(3) –117.2(3)

[a] This work; [b] ref. [24]; [c] ref. [25]; [d] ref. [26]; [e] ref. [27]; [f] ref. [5(a)]; [g] ref. [35(c)]; [h] ref. [36]; [i]ref. [30]; [j] ref. [31(c)]; [k] ref. [32]; [l] ref. [33(c)]; [m] ref. [33(d)]. [†]a $(p\text{-tol})_3P$ adduct.

Table S2. Unit cell descriptors of $[(Ph_3P)_2M(O_2XY)]$ (unsolvated)

M(O,X,Y)[Ref]	CCDC code*	Space group	T(K)	*a* (Å)	*b*(Å)	*c*(Å)	α (º)	β(º)	γ(º)	*V*(Å^3)
Mononuclear forms										
$Cu(O_2CH)$[a]	BOMFUE	*C*2/*c*	RT	24.582(9)	9.100(5)	15.469(7)		116.10(10)		3107
$Cu(O_2CCH_3)$[b]	ACPHCU02	$P2_1/c$	193	18.085(5)	10.977(2)	17.979(5)		115.62(2)		3218
$Cu(O_2CCF_3)$[c]	WEPKAD	$P2_1/a$	RT	18.123(9)	11.357(5)	19.340(10)		122.04(6)		3374
$Cu(O_2N)$[d]	HIBPUD	*C*2/*c*	RT	24.443(9)	9.102(2)	15.356(5)		116.01(3)		3070
$Cu(O_2NO)$[e]	NITPPC01	*C*2/*c*	RT	24.558(5)	9.185(3)	15.420(3)		116.43(2)		3115
$Ag(O_2CH)$[f]	KIXCAV02	*C*2/*c*	RT	24.884(3)	9.189(1)	15.283(6)		116.05(2)		3140
$Ag(O_2CCH_3)$[g]	ACPSAG01	$P\bar{1}$	RT	10.078(1)	13.775(1)	24.167(3)	92.05(1)	90.67(1)	100.19(1)	3299
$Ag(O_2CCF_3)$[h]	NOZPIB	*Pbca*	153	16.964(3)	18.972(4)	21.063(3)				6779
$Ag(O_2CCF_3)$[i]	NOZPIB01	*C*2/*c*	150	23.403(14)	12.0965(7)	23.3957(14)		94.0440(10)		6607
$Ag(O_2NO)$[i]	HIPVEH01	$P2_1/c$	150	11.908(2)	18.364(2)	14.761(2)		101.12(1)		3167
$Ag(O_2N)$[j]	DUSZOG02	$P\bar{1}$	120	11.682(2)	11.833(2)	13.569(2)	102.64(1)	112.14(1)	105.65(1)	1561
$Ag(O_2COH)$[k]	OTAHUN	$P\bar{1}$	100	10.2351(3)	11.9944(3)	13.8661(3)	85.949(2)	87.989(2)	65.093(3)	1540
$Ag(O_2NO)(C_6H_6)$[l]	SAYZAT	$P\bar{1}$	RT	12.279(1)	16.260(1)	11.134(1)	102.51(1)	114.28(1)	101.79(1)	1868
(C_7H_8)[i]	This work	$P\bar{1}$	200	11.2434(4)	12.3381(6)	16.2534(6)	106.398(4)	96.842(3)	115.208(4)	1881

	This work	$P2_1/c$	RT	16.637(2)	19.265(4)	12.1100(13)	102.661(9)	3787
Binuclear forms								
$Cu(\mu\text{-}O.CO.OH)_2Cu$[l]	ZIMNAK	$P2_12_12$	RT	14.721(2)	21.113(2)	9.2130(10)		3135
$Ag(\mu\text{-}O.NO_2)_2Ag$[m]	WANFAS	$P2_12_12$	178	14.904(5)	23.169(7)	9.262(3)		3198
$Ag(\mu\text{-}O.CO.OH)_2Ag$[k]	OTAHEX	$P2_12_12$	RT	14.990(2)	23.435(7)	9.296(3)		3266

*Cambridge Structural Database, 2019. [a] Ref. [30]; [b] ref. [31(c)]; [c] ref. [32]; [d] ref. [59]; [e] ref. [33(b)]; [f] ref. [5]; [g] ref. [24]; [h] ref. [27]; [i] this work; [j] ref. [35(c)]; [k] ref. [23]; [l] ref. [36]; [m] ref. [37].

Table S3. ^{31}P NMR parameters measured from the 1D ^{31}P CPMAS and 2D ^{31}P-^{31}P CPCOSY MAS NMR data of **1**, **2**, **3**, **4**, **5β**, **9α**, **11α** and **11β** reported in this work, compared with values measured from previously reported bidentate carboxylate systems.

Compound	**δ(^{31}P)/ppm (±0.2 ppm)**	**^{1}J($^{107/109}$Ag,^{31}P)/Hz** [a] **(±3 Hz)**	**^{2}J(^{31}P,^{31}P)/Hz (±2 Hz)**	**Ref.**
$[(Ph_3P)_2Ag(O_2CCH_2Ph)]$ **1**	5.9 8.5	443 439	125	this work
$[(Ph_3P)_2Ag(O_2CCHPh_2)]\cdot EtOH$ **2**	3.8 11.0	414 470	125	this work
$[(Ph_3P)_2Ag(O_2CC(CH_3)_3)]$ **3** (molecule 1, larger component from disorder)	7.1 8.5	426 455	124	this work
$[(Ph_3P)_2Ag(O_2CC(CH_3)_3)]$ **3** (molecule 2, smaller component from disorder)	7.5 10.6	422 438	140	
$[(Ph_3P)_2Ag(O2CCH_2C(CH_3)_3)]$ **4** (molecule 1)	6.3 8.8	426 455	125	this work
$[(Ph_3P)_2Ag(O2CCH_2C(CH_3)_3)]$ **4** (molecule 2)	4.4 7.6	419 423	134	
$[(Ph_3P)_2Ag(O_2CCF_3]$, **5β**	9.0 11.4	461 506	112	this work
$[(PPh_3)_2AgNO_3]$ **9α**	7.5 9.3	489 492	127	this work
$[(PPh_3)_2AgNO_3]\cdot$toluene **11α**	6.8 13.7	482 505	126	this work
$[(PPh_3)_2AgNO_3]\cdot$toluene **11β**	6.0 10.5	471 510	136	this work
$[(Ph_3P)_2Ag(C_6H_7O_7)]\cdot EtOH$ dihydrogen citrate	7.6 12.9	412 501	134	9
$[(Ph_3P)_2Ag(O_2C(OH)CHCH_2)]$ lactate (molecule 1)	2.5 9.0	390 478	144	26
$[(Ph_3P)_2Ag(O_2C(OH)CHCH_2)]$ lactate (molecule 2)	4.1 7.1	389 471	144	
$[(Ph_3P)_2Ag(O_2CH)]$ formate				6
$[(Ph_3P)_2Ag(O_2CCH_3)]$ acetate (molecule 1)	4.7 9.5	385 459	146	65
$[(Ph_3P)_2Ag(O_2CCH_3)]$ acetate (molecule 1)	6.3 9.1	420 439	131	
$[(Ph_3P)_2Ag(O_2CCH_3)]\cdot H_2O\cdot 0.5EtOH$ acetate (molecule 1)	7.0 9.8	382 487	133	25
$[(Ph_3P)_2Ag(O_2CCH_3)]\cdot H_2O\cdot 0.5EtOH$ acetate (molecule 1)	16.23 17.78	426 427	133	
$[[(PPh_3)_2Ag(O_2CNC_5H_4)]_2]_n$ nicotinate (molecule 1)	6.5 10.3	433 457	140	[b]
$[[(PPh_3)_2Ag(O_2CNC_5H_4)]_2]_n$ nicotinate (molecule 1)	7.3 9.2	437 439	135	
$[(PPh_3)_2Ag(O_2CC_6H_4OH)]_4$ hydroxybenzoate	7.3 9.7	416 451	125	[c]

[a] average value of ^{1}J(^{107}Ag,^{31}P) and ^{1}J(^{109}Ag,^{31}P) couplings.

[b] N. R. A Rahazat, R. A. Haque, S.-W. Ng, M.R. Razali, *J. Coord. Chem.* **2015**, *68*, 1317.

[c] M. Poyraz, C. N. Banti, N. Kourkoumelis, V. Dokorou, M. J. Manos, M. Simcic, S. Golic-Grdadolnik, T. Mavromoustakos, A. D. Giannoulis, I. I. Verginadis, K. Charalabopoulos, S. K. Hadjikakou, *Inorg. Chim. Acta* **2011**, *375*, 114.

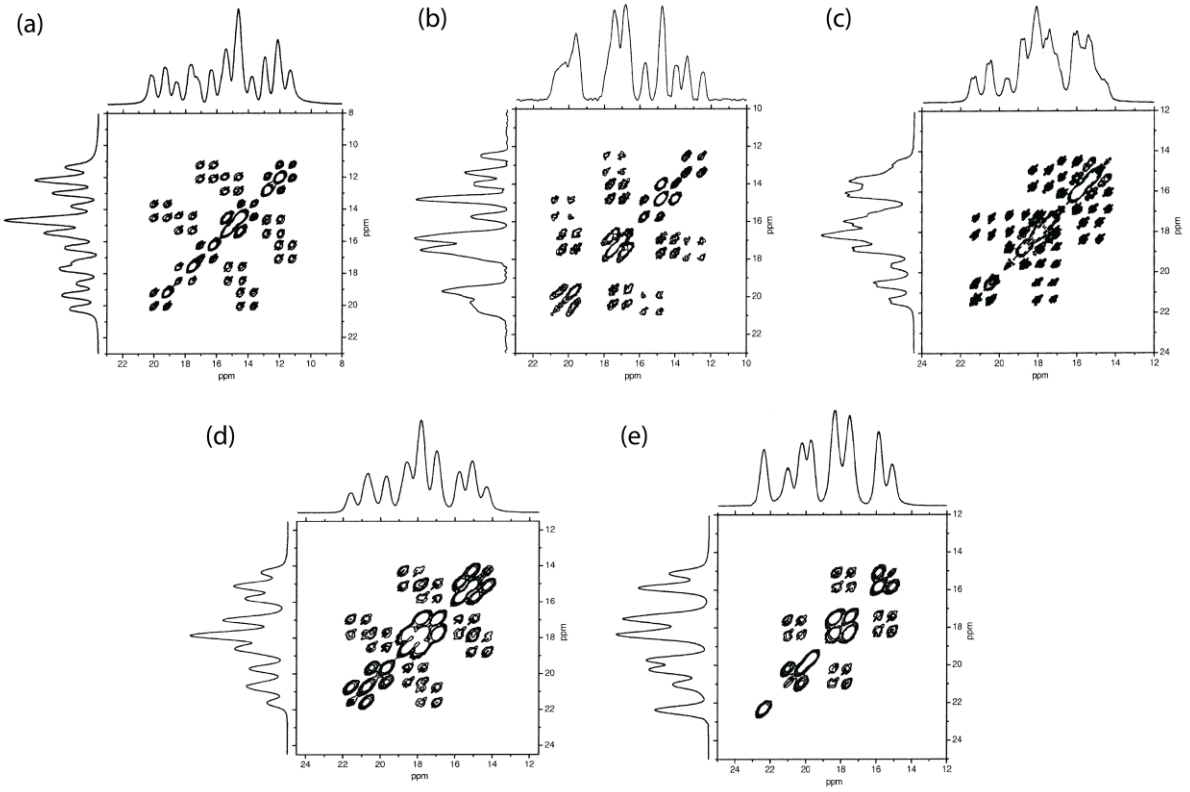
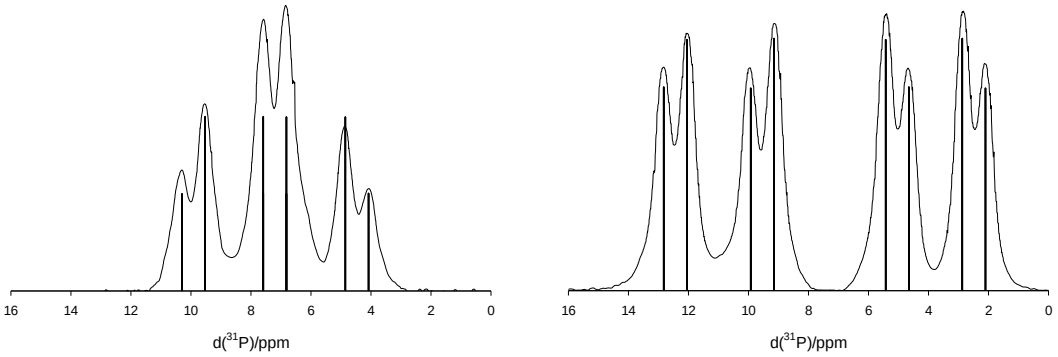
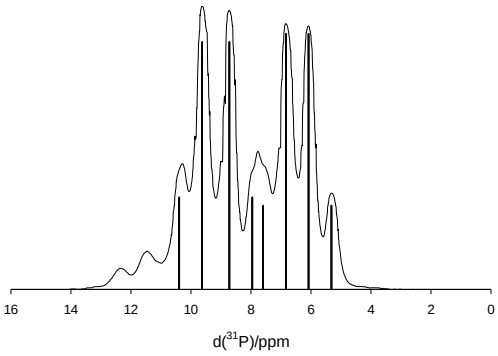


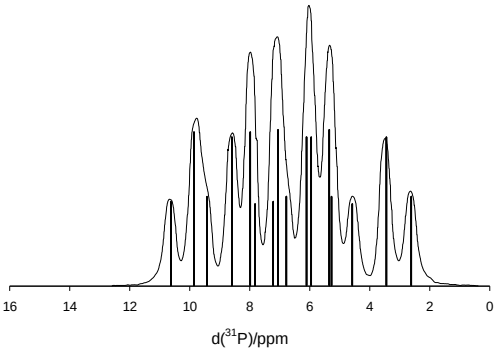
Figure S1. 1D ^{31}P CPMAS (F1 & F2 projections) and 2D ^{31}P-^{31}P CPCOSY MAS NMR data from previously reported carboxylate-based systems, (a) $[(Ph_3P)_2AgO_2C(OH)CHCH_2]$ (lactate), (b) $[(Ph_3P)_2Ag(O_2CCH_3)]$ (acetate), (c) $[(Ph_3P)_2Ag(O_2CCH_3)]\cdot H_2O\cdot 0.5EtOH$ (acetate solvate), (d) $[[(PPh_3)_2Ag(O_2CNC_5H_4)]_2]_n$ (nicotinate) and (e) $[(PPh_3)_2Ag(O_2CC_6H_4OH)]_4$ (hydroxybenzoate).



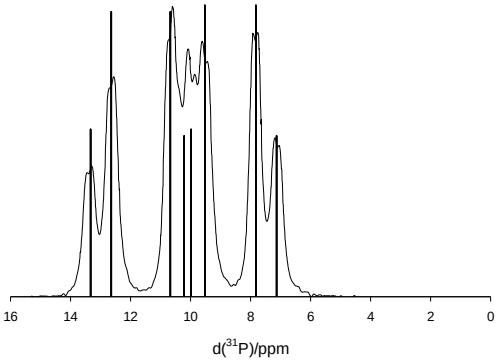
(a) compound **1** (b) compound **2**



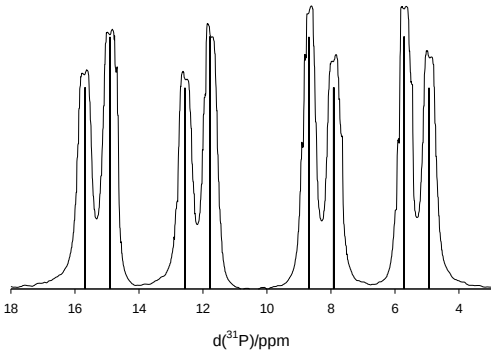
(c) compound **3**



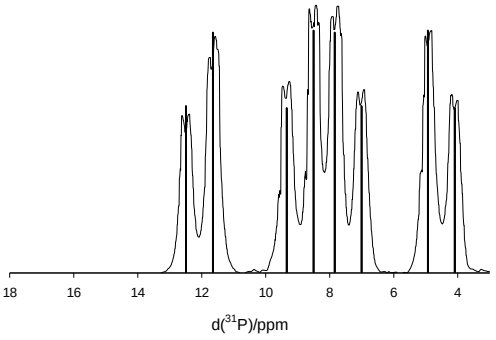
(d) compound **4**



(e) compound **5β**



(f) compound **11α**



(g) compound **11β**

Figure S2. ^{31}P CPMAS NMR spectra of compound **1**, **2**, **3**, **4**, **5β**, **11α** and **11β** and stick diagrams of the simulated spectra as the AB part of an ABX system.