Supporting Information for

Coinage Metal Complexes Supported by a "PN^{3}P" Scaffold.

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Contents

Cartesian coordinates (Å) for **1** optimized at the B3LYP/TZVP level of theory.

Cu	-0.000032	-0.877874	-0.334304
P	-2.119169	0.085000	-0.099144
P	2.119146	0.084935	-0.099149
N	0.000001	-0.145547	1.795636
N	-2.309481	-0.080056	1.651797
N	2.309484	-0.080248	1.651782
C	-1.169582	-0.212099	2.437171
C	-1.212914	-0.380624	3.830504
C	-0.000004	-0.468882	4.499062
C	1.212908	-0.380725	3.830497
C	1.169582	-0.212195	2.437164
C	-3.610231	-0.112117	2.314451
C	3.610239	-0.112484	2.314418
C	-3.644690	-0.727712	-0.751264
C	-3.582853	-2.108740	-0.971245
C	-4.693549	-2.785502	-1.464040
C	-5.865179	-2.094505	-1.756727
C	-5.927350	-0.718944	-1.553749
C	-4.823757	-0.037346	-1.051955
C	-2.428094	1.886385	-0.398124
C	-2.427200	2.343455	-1.721377
C	-2.578653	3.694992	-2.002032
C	-2.714189	4.614290	-0.964235
C	-2.695243	4.171470	0.352831
C	-2.551926	2.815092	0.635403
C	3.644642	-0.727763	-0.751341
C	3.582803	-2.108787	-0.971352
C	4.693480	-2.785529	-1.464214
C	5.865093	-2.094518	-1.756940
C	5.927264	-0.718961	-1.553934
C	4.823690	-0.037381	-1.052073
C	2.428122	1.886334	-0.398011
C	2.552248	2.814942	0.635567
C	2.695652	4.171329	0.353078
C	2.714400	4.614254	-0.963955
C	2.578570	3.695055	-2.001802
C	2.427024	2.343512	-1.721226
H	4.633652	-3.853851	-1.632144
H	6.725313	-2.624019	-2.148677
H	6.834666	-0.174492	-1.786387
H	4.881379	1.033219	-0.903019
H	2.663057	-2.649184	-0.772652
H	3.694127	0.682140	3.061829
H	3.776738	-1.075055	2.805901

H	4.397896	0.025135	1.580904
H	2.531039	2.482247	1.664989
H	2.792351	4.880639	1.166332
H	2.826130	5.669121	-1.182706
H	2.582608	4.032778	-3.031127
H	2.309467	1.640221	-2.538227
H	2.143571	-0.446917	4.370502
H	-0.000007	-0.608126	5.573709
H	-2.143579	-0.446743	4.370515
H	-3.693990	0.682511	3.061870
H	-4.397879	0.025626	1.580951
H	-3.776864	-1.074670	2.805925
H	-2.530555	2.482476	1.664848
H	-2.791714	4.880856	1.166045
H	-2.825848	5.669151	-1.183052
H	-2.582852	4.032632	-3.031384
H	-2.309879	1.640084	-2.538342
H	-4.881447	1.033258	-0.902926
H	-6.834767	-0.174486	-1.786170
H	-6.725414	-2.624021	-2.148412
H	-4.633721	-3.853827	-1.631949
H	-2.663094	-2.649128	-0.772577
Br	-0.000028	-3.284144	-0.575233

Cartesian coordinates (Å) for **2** optimized at the B3LYP/TZVP level of theory.

Cu	-0.050613	-0.174145	-0.547083
P	-2.276034	0.296698	-0.172365
P	1.959004	0.949416	-0.203594
N	-2.378782	-0.180733	1.522307
N	-0.073544	0.053410	1.624900
N	2.204306	0.487534	1.483176
C	-1.204029	-0.282318	2.258141
C	-1.175606	-0.677127	3.604183
C	0.056226	-0.688482	4.239991
C	1.221525	-0.309978	3.587511
C	1.113783	0.064151	2.240650
C	3.512997	0.531002	2.131370
C	-3.760117	-0.512314	-0.916402
C	-3.738217	-1.904054	-1.072053
C	-4.809829	-2.553054	-1.673239
C	-5.901387	-1.826233	-2.140765
C	-5.923801	-0.443674	-1.995204
C	-4.859848	0.213154	-1.383740
C	3.535539	0.447661	-1.022007
C	3.588172	-0.841183	-1.565180
C	4.747529	-1.286519	-2.191584
C	5.853016	-0.449098	-2.299201
C	5.800817	0.839553	-1.775495
C	4.649012	1.287190	-1.138198
C	2.050517	2.796781	-0.169117
C	2.004339	3.523077	1.020895
C	1.988546	4.915441	0.997606
C	2.014355	5.595561	-0.213919
C	2.046519	4.877362	-1.407064
C	2.055581	3.488840	-1.385883
C	-3.636058	-0.538779	2.176116
C	-2.713735	2.095772	-0.166246
C	-3.194617	2.760717	0.962080
C	-3.477215	4.122930	0.909655
C	-3.284003	4.832879	-0.270113
C	-2.792479	4.179304	-1.396854
C	-2.498021	2.822532	-1.341589
H	-6.729892	-2.335642	-2.617824
H	-4.781892	-3.629861	-1.785036
H	-2.896128	-2.481747	-0.709573
H	-4.892949	1.288698	-1.273859
H	-6.769918	0.128832	-2.355745
H	2.722649	-1.489627	-1.504025
H	4.777883	-2.287226	-2.604182

H	6.751508	-0.796657	-2.794623
H	6.656825	1.497838	-1.862494
H	4.618311	2.293577	-0.740599
H	3.508251	1.204350	2.993533
H	3.816281	-0.465073	2.463570
H	4.257805	0.885865	1.426822
H	-3.797788	0.066704	3.072608
H	-4.463128	-0.366115	1.494775
H	-3.644543	-1.595251	2.456001
H	-3.340510	2.220245	1.887781
H	-3.848773	4.628196	1.793014
H	-3.506480	5.892149	-0.309972
H	-2.626637	4.728794	-2.315412
H	-2.094827	2.326666	-2.217643
H	2.073605	2.942433	-2.322180
H	2.060270	5.400043	-2.355821
H	2.004043	6.678423	-0.231166
H	1.955468	5.466502	1.929714
H	1.976158	3.003252	1.969476
H	-2.067665	-0.975007	4.130468
H	0.110880	-0.999089	5.276559
H	2.166895	-0.320500	4.104960
S	0.046389	-3.429916	-0.658891
C	1.468827	-4.064697	0.430733
F	1.702310	-3.216654	1.448273
F	1.173500	-5.262780	0.942860
F	2.600827	-4.174897	-0.281771
O	0.589969	-2.081039	-1.103603
O	-1.094428	-3.305456	0.280179
O	-0.057832	-4.414069	-1.746511

Cartesian coordinates (Å) for **3** used for single-point calculations at the B3LYP/TZVP (DGDZVP for Ag) level of theory.

Ag	-0.00607600	-0.40654300	-0.66269800
P	-2.40660600	0.34644700	0.00176500
P	2.06302600	1.15470800	-0.02507500
N	-0.18613100	0.63379500	1.84404200
N	2.07768900	1.18463800	1.72923300
N	-2.46381900	0.18012600	1.75056700
C	0.99811200	0.68074300	2.46312000
C	1.13917100	0.28223000	3.80056000
C	0.00489600	-0.16821800	4.45902500
C	-1.22244300	-0.22856600	3.81980500
C	-1.27458300	0.18280200	2.47831100
C	3.29510800	1.54534400	2.45629900
C	-3.70772800	-0.10976800	2.46497200
C	3.75322100	0.55486400	-0.47709300
C	4.88369500	1.37549000	-0.56316500
C	6.11746300	0.83736500	-0.90807700
C	6.23673900	-0.52522700	-1.17061600
C	5.11671500	-1.34551300	-1.09809500
C	3.87695400	-0.81016500	-0.76114500
C	2.08749600	2.94527300	-0.47993700
C	1.67399200	3.93104600	0.41701300
C	1.60217400	5.26249000	0.01694600
C	1.93227100	5.62172100	-1.28463600
C	2.33001700	4.64136600	-2.19033500
C	2.40203200	3.31192600	-1.79384000
C	-3.91759700	-0.55798200	-0.54959500
C	-3.81313600	-1.94878400	-0.67328500
C	-4.90905400	-2.69149700	-1.09899500
C	-6.10465400	-2.05750400	-1.42315500
C	-6.20760600	-0.67386500	-1.31532500
C	-5.12006200	0.07543200	-0.87870900
C	-2.81127300	2.12455800	-0.30001300
C	-3.07647500	3.02333100	0.73248500
C	-3.33434600	4.36238000	0.45059900
C	-3.32797900	4.81479700	-0.86378900
C	-3.05164500	3.92532600	-1.89912700
C	-2.78536600	2.59121100	-1.61846700
H	3.03673200	2.09203000	3.36464800
H	3.89451100	0.67076200	2.72611400
H	3.90774200	2.19779100	1.84111200
H	2.09363400	0.29359100	4.30177900
H	0.08462000	-0.49931100	5.48752800
H	-2.09056400	-0.60463500	4.33616500

H	-3.79759900	0.53429900	3.34286700
H	-4.55583300	0.08086100	1.81581300
H	-3.75765900	-1.15433500	2.78515900
H	3.00673400	-1.45638400	-0.74455000
H	5.19668200	-2.40282200	-1.31747500
H	7.19917400	-0.94245100	-1.44108300
H	6.98555200	1.48216600	-0.97438000
H	4.80331700	2.43874300	-0.37472400
H	1.40425000	3.65697300	1.42872100
H	2.71218800	2.56005100	-2.51029200
H	2.58369800	4.91182500	-3.20814900
H	1.87665100	6.65793200	-1.59476800
H	1.28471200	6.01815600	0.72526200
H	-2.55974600	1.91069200	-2.43238600
H	-3.03441300	4.27285700	-2.92484800
H	-3.53011200	5.85624900	-1.08191900
H	-3.54034700	5.05096700	1.26124600
H	-3.07431500	2.68030900	1.75887900
H	-2.88216000	-2.45551900	-0.44162000
H	-4.81675300	-3.76646600	-1.19130900
H	-6.95232200	-2.63885700	-1.76525200
H	-7.13442100	-0.17504400	-1.57197500
H	-5.21076300	1.15097500	-0.79970500
C	1.44029300	-4.62462300	0.16293100
F	2.58329500	-4.87724400	-0.49189500
F	1.73867500	-3.88996400	1.24834200
F	0.92224200	-5.78693200	0.57260200
S	0.21347500	-3.70112500	-0.95493500
O	-0.94779300	-3.43395100	-0.06431600
O	0.00223200	-4.59473000	-2.10379200
O	0.98806200	-2.43428600	-1.26962100

Fragment orbital analysis of the metal-ligand interactions in the [2,6-{Ph_2PNMe}$_2$(NC_5H_3)]Cu^+ cation (**1**). Fragment 1 is Cu^+ and fragment 2 is the ligand.

FO Contributions (%) to occupied and unoccupied MOs.
The sixth column in the output below indicates
the FO occupancies * 100% in the molecule.

Frag #	Orb #	Initial Occupancy	E(eV)	Symmetry	FO Contribution (%) to -->OMOs	-->UMOs
1	1	1	-8797.33	na	100.00	0.00
1	2	1	-1063.36	na	100.06	-0.06
1	3	1	-932.91	na	100.00	0.00
1	4	1	-932.91	na	100.00	-0.01
1	5	HOFO-9 1	-932.91	na	100.00	0.00
1	6	HOFO-8 1	-124.53	na	100.49	-0.48
1	7	HOFO-7 1	-83.60	na	100.03	-0.04
1	8	HOFO-6 1	-83.60	na	100.09	-0.09
1	9	HOFO-5 1	-83.60	na	100.03	-0.03
1	10	HOFO-4 1	-15.49	na	97.73	2.27
1	11	HOFO-3 1	-15.49	na	99.30	0.71
1	12	HOFO-2 1	-15.49	na	97.68	2.32
1	13	HOFO-1 1	-15.49	na	97.20	2.80
1	14	HOFO 1	-15.49	na	98.17	1.83
1	15	LUFO 0	-10.69	na	35.52	64.58
1	16	LUFO+1 0	-4.82	na	4.70	95.31
1	17	LUFO+2 0	-4.82	na	12.29	87.67
1	18	LUFO+3 0	-4.82	na	4.08	95.90
1	19	LUFO+4 0	-2.07	na	0.32	99.68
1	20	LUFO+5 0	11.70	na	0.09	99.91
1	21	LUFO+6 0	11.70	na	0.14	99.86
1	22	LUFO+7 0	11.70	na	0.34	99.67
1	23	LUFO+8 0	11.70	na	0.28	99.72
1	24	LUFO+9 0	11.70	na	0.42	99.58
2	119	HOFO-14 1	-8.48	na	99.85	0.15
2	120	HOFO-13 1	-8.00	na	94.30	5.71
2	121	HOFO-12 1	-7.70	na	92.05	7.97
2	122	HOFO-11 1	-7.38	na	98.21	1.80
2	123	HOFO-10 1	-7.27	na	99.67	0.33
2	124	HOFO-9 1	-7.18	na	99.79	0.20
2	125	HOFO-8 1	-7.14	na	99.79	0.21
2	126	HOFO-7 1	-7.12	na	99.88	0.12
2	127	HOFO-6 1	-6.98	na	96.49	3.50
2	128	HOFO-5 1	-6.95	na	99.72	0.28
2	129	HOFO-4 1	-6.88	na	99.94	0.06
2	130	HOFO-3 1	-6.32	na	99.34	0.65
2	131	HOFO-2 1	-5.84	na	93.55	6.46
2	132	HOFO-1 1	-5.48	na	82.22	17.81
2	133	HOFO 1	-5.24	na	95.08	4.91
2	134	LUFO 0	-0.85	na	0.40	99.60
2	135	LUFO+1 0	-0.85	na	0.27	99.73
2	136	LUFO+2 0	-0.64	na	0.41	99.59
2	137	LUFO+3 0	-0.56	na	0.12	99.88
2	138	LUFO+4 0	-0.55	na	0.32	99.68
2	139	LUFO+5 0	-0.35	na	0.46	99.54
2	140	LUFO+6 0	-0.26	na	0.37	99.63
2	141	LUFO+7 0	-0.22	na	0.19	99.80
2	142	LUFO+8 0	-0.14	na	0.04	99.96
2	143	LUFO+9 0	0.48	na	0.16	99.84

Fragment orbital analysis of the metal-ligand interactions in the [2,6-{Ph_2PNMe}$_2$(NC_5H_3)]Cu^+ cation (**2**). Fragment 1 is Cu^+ and fragment 2 is the ligand.

FO Contributions (%) to occupied and unoccupied MOs.
The sixth column in the output below indicates the FO occupancies * 100% in the molecule.

Fr #	Orb #	Initial Occupancy	E(eV)	Symmetry	FO Contribution (%) to -->OMOs	-->UMOs
1	1	1	-8797.33	na	100.00	0.00
1	2	1	-1063.36	na	100.07	-0.07
1	3	1	-932.91	na	100.00	0.00
1	4	1	-932.91	na	100.00	0.00
1	5	HOFO-9 1	-932.91	na	100.01	-0.01
1	6	HOFO-8 1	-124.53	na	100.51	-0.49
1	7	HOFO-7 1	-83.60	na	100.04	-0.05
1	8	HOFO-6 1	-83.60	na	100.03	-0.04
1	9	HOFO-5 1	-83.60	na	100.08	-0.09
1	10	HOFO-4 1	-15.49	na	99.05	0.95
1	11	HOFO-3 1	-15.49	na	97.49	2.51
1	12	HOFO-2 1	-15.49	na	97.50	2.50
1	13	HOFO-1 1	-15.49	na	96.36	3.64
1	14	HOFO 1	-15.49	na	98.91	1.09
1	15	LUFO 0	-10.69	na	36.47	63.63
1	16	LUFO+1 0	-4.82	na	5.63	94.36
1	17	LUFO+2 0	-4.82	na	2.11	97.89
1	18	LUFO+3 0	-4.82	na	14.17	85.84
1	19	LUFO+4 0	-2.07	na	0.38	99.62
1	20	LUFO+5 0	11.70	na	0.08	99.92
1	21	LUFO+6 0	11.70	na	0.24	99.76
1	22	LUFO+7 0	11.70	na	0.12	99.88
1	23	LUFO+8 0	11.70	na	0.23	99.77
1	24	LUFO+9 0	11.70	na	0.64	99.36
2	119	HOFO-14 1	-8.49	na	99.77	0.23
2	120	HOFO-13 1	-8.00	na	94.62	5.36
2	121	HOFO-12 1	-7.70	na	91.99	8.03
2	122	HOFO-11 1	-7.41	na	98.20	1.79
2	123	HOFO-10 1	-7.27	na	99.62	0.38
2	124	HOFO-9 1	-7.17	na	99.45	0.55
2	125	HOFO-8 1	-7.12	na	99.67	0.34
2	126	HOFO-7 1	-7.09	na	99.58	0.42
2	127	HOFO-6 1	-6.97	na	98.36	1.63
2	128	HOFO-5 1	-6.95	na	97.68	2.32
2	129	HOFO-4 1	-6.90	na	99.93	0.07
2	130	HOFO-3 1	-6.37	na	99.12	0.87
2	131	HOFO-2 1	-5.86	na	93.90	6.10
2	132	HOFO-1 1	-5.45	na	82.75	17.29
2	133	HOFO 1	-5.22	na	93.93	6.06
2	134	LUFO 0	-0.88	na	0.35	99.65
2	135	LUFO+1 0	-0.79	na	0.43	99.57
2	136	LUFO+2 0	-0.64	na	0.42	99.57
2	137	LUFO+3 0	-0.57	na	0.21	99.79
2	138	LUFO+4 0	-0.55	na	0.25	99.75
2	139	LUFO+5 0	-0.37	na	0.49	99.50
2	140	LUFO+6 0	-0.26	na	0.36	99.64
2	141	LUFO+7 0	-0.22	na	0.20	99.80
2	142	LUFO+8 0	-0.14	na	0.05	99.95
2	143	LUFO+9 0	0.46	na	0.16	99.84

Fragment orbital analysis of the metal-ligand interactions in the [2,6-{Ph_2PNMe}$_2$(NC_5H_3)]Ag+ cation (**3**). Fragment 1 is Ag^+ and fragment 2 is the ligand.

FO Contributions (%) to occupied and unoccupied MOs.
The sixth column in the output below indicates
the FO occupancies * 100% in the molecule.

Fr #	Orb #	Initial Occupancy	E(eV)	Symmetry	FO Contribution (%) to -->OMOs	-->UMOs
1	1	1	-24606.04	na	100.00	0.00
1	2	1	-3571.67	na	100.00	0.00
1	3	1	-3324.35	na	100.00	0.00
1	4	1	-3324.35	na	100.00	0.00
1	5	1	-3324.35	na	100.00	0.00
1	6	1	-665.04	na	100.03	-0.03
1	7	1	-564.68	na	100.01	-0.01
1	8	1	-564.68	na	100.00	0.00
1	9	1	-564.68	na	100.01	-0.01
1	10	1	-379.03	na	100.00	0.00
1	11	1	-379.03	na	100.00	0.00
1	12	1	-379.03	na	100.00	0.00
1	13	1	-379.03	na	100.00	0.00
1	14 HOFO-9	1	-379.03	na	100.00	0.00
1	15 HOFO-8	1	-100.12	na	99.81	0.18
1	16 HOFO-7	1	-68.15	na	99.97	0.03
1	17 HOFO-6	1	-68.15	na	99.92	0.07
1	18 HOFO-5	1	-68.15	na	99.86	0.15
1	19 HOFO-4	1	-17.43	na	99.88	0.12
1	20 HOFO-3	1	-17.43	na	99.61	0.39
1	21 HOFO-2	1	-17.43	na	99.79	0.21
1	22 HOFO-1	1	-17.43	na	99.80	0.20
1	23 HOFO	1	-17.43	na	99.69	0.31
1	24 LUFO	0	-9.97	na	24.87	75.14
1	25 LUFO+1	0	-5.51	na	10.52	89.35
1	26 LUFO+2	0	-5.51	na	3.44	96.53
1	27 LUFO+3	0	-5.51	na	2.44	97.56
1	28 LUFO+4	0	-1.56	na	0.00	100.00
1	29 LUFO+5	0	1.31	na	0.18	99.82
1	30 LUFO+6	0	1.31	na	0.51	99.50
1	31 LUFO+7	0	1.31	na	0.02	99.97
1	32 LUFO+8	0	1.31	na	0.40	99.61
1	33 LUFO+9	0	1.31	na	0.22	99.78
2	119 HOFO-14	1	-8.44	na	99.61	0.39
2	120 HOFO-13	1	-8.01	na	97.47	2.53
2	121 HOFO-12	1	-7.60	na	95.39	4.62
2	122 HOFO-11	1	-7.37	na	99.21	0.78
2	123 HOFO-10	1	-7.29	na	99.76	0.24
2	124 HOFO-9	1	-7.21	na	99.77	0.23
2	125 HOFO-8	1	-7.15	na	99.86	0.14
2	126 HOFO-7	1	-7.13	na	99.92	0.09
2	127 HOFO-6	1	-6.97	na	98.75	1.25
2	128 HOFO-5	1	-6.91	na	99.32	0.68
2	129 HOFO-4	1	-6.87	na	99.89	0.11
2	130 HOFO-3	1	-6.37	na	99.86	0.14
2	131 HOFO-2	1	-5.86	na	94.78	5.20
2	132 HOFO-1	1	-5.60	na	84.59	15.40
2	133 HOFO	1	-5.25	na	93.63	6.34
2	134 LUFO	0	-0.91	na	0.21	99.79
2	135 LUFO+1	0	-0.86	na	0.23	99.76
2	136 LUFO+2	0	-0.61	na	0.18	99.82
2	137 LUFO+3	0	-0.57	na	0.10	99.90
2	138 LUFO+4	0	-0.49	na	0.18	99.82
2	139 LUFO+5	0	-0.37	na	0.30	99.70
2	140 LUFO+6	0	-0.24	na	0.24	99.76
2	141 LUFO+7	0	-0.20	na	0.06	99.94
2	142 LUFO+8	0	-0.14	na	0.04	99.96
2	143 LUFO+9	0	0.39	na	0.12	99.88