First Copper(I) and Silver(I) complexes containing phosphanylphosphido ligands

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**Abstract:** Three new complexes with phosphanylphosphido ligands, $[Cu_4\{\mu_2\text{-P(SiMe}_3)\text{-P}t\text{Bu}\}_4]$ (**1**), $[Ag_4\{\mu_2\text{-P(SiMe}_3)\text{-P}t\text{Bu}_2\}_4]$ (**2**) and $[Cu\{\eta^1\text{-P(SiMe}_3)\text{-P}i\text{Pr}_2\}_2]^-[Li(Diglyme)_2]^+$ (**3**) have been synthesized and structurally characterized by X-ray diffraction, NMR spectroscopy and elemental analysis. Complexes **1** and **2** were obtained in the reactions of lithium derivative of diphosphane $t\text{Bu}_2\text{P-P(SiMe}_3)\text{Li·2.7THF}$ with CuCl and $[t\text{Bu}_3\text{PAgCl}]_4$ respectively. The X-ray diffraction analysis revealed that the complexes **1** and **2** present macrocyclic, tetrameric form with Cu_4P_4 and Ag_4P_4 core. Complex **3** was prepared in the reaction of CuCl with a different derivative of lithiated diphosphane $i\text{Pr}_2\text{P-P(SiMe}_3)\text{Li·2(Diglyme)}$. Surprisingly, the X-ray analysis of **3** revealed that in this reaction instead of the tetramer the monomeric form, ionic complex $[Cu\{\eta^1\text{-P(SiMe}_3)\text{-P}i\text{Pr}_2\}_2]^-[Li(Diglyme)_2]^+$ was formed.

Introduction

Until now a relatively large number of late transition metal complexes with phosphido ligands has been investigated. Ongoing research reflects the importance of these compounds as synthetic intermediates.[1] The modification of phosphido moiety by expanding the ligand with additional phosphorus atom leads to the formation of phosphanylphosphido ligand. The P-P moiety gives the opportunity to obtain a new and different ligand coordinations. Additionally, the presence of the –SiMe₃ on the phosphido phosphorus atom provides a possibility of reactivity studies. The phosphanylphosphido $(RR'P\text{-P(SiMe}_3)$; R = tBu, iPr; R' = tBu, iPr, Ph) complexes have been only obtained for early and middle transition metals: titanium,[2] iron,[3] hafnium,[4] zirconium,[4-5] molybdenum[6] and tungsten[7] so far. Moreover, it should be emphasized that all reported works of metal complexes with $RR'P\text{-P(SiMe}_3)$ moiety present only the mononuclear forms. It should be also mentioned, that in these complexes the phosphanylphosphido ligands exhibit the monodentate (terminal) and bidentate (side-on) coordination to the metal center, but never bridging coordination. The bridging coordination of $RR'P\text{-P(SiMe}_3)$ ligands are only known for

dimeric and tetrameric forms observed in the derivatives of lithium salts: $[Li(THF)(Me_3Si)P\text{-P}t\text{Bu}_2]_2$ and $[Li(THF)(Me_3Si)P\text{-P}t\text{Bu}_2]_4$.[8] The solvent used to crystallization process of these compounds is significant. The applying of THF solution promotes the formation of cyclical forms, while the chelating solutions (TMEDA, 12-Crown-4) lead to the monomeric, ionic forms: $[Li(TMEDA)_2]^+[(Me_3Si)P\text{–P}t\text{Bu}_2]^-$ and $[Li(12\text{-Crown-}4)_2]^+[(SiMe_3)P\text{–P}t\text{Bu}_2]^-$.[8] Surprisingly, up to now the complexes of late transition metal with phosphanylphosphido ligands have never been synthesized and described.

Herein we report on the synthesis and molecular structures of the phosphanylphosphido copper(I) **1** and **3** and silver(I) **2** complexes. To the best of our knowledge, these compounds are the first structurally characterized homoleptic phosphanylphosphido complexes of late transition metals. As in the case of the synthesis of other metal complexes with phosphanylphosphido ligands, for the preparation of silver and copper complexes we used lithium derivatives of diphosphanes: $t\text{Bu}_2\text{P-P(SiMe}_3)\text{Li·2.7THF}$ and $i\text{Pr}_2\text{P-P(SiMe}_3)\text{Li·2(Diglyme)}$ (Scheme 1).
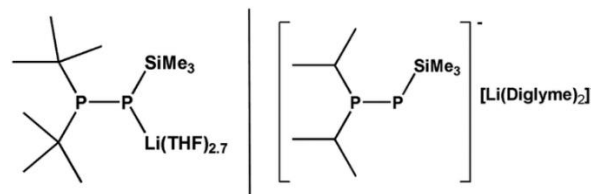

Scheme 1. Lithium derivatives of diphosphanes used in the reaction with CuCl and $[t\text{Bu}_3\text{PAgCl}]_4$; left: $t\text{Bu}_2\text{P-P(SiMe}_3)\text{Li·2.7THF}$; right: $i\text{Pr}_2\text{P-P(SiMe}_3)\text{Li·2(Diglyme)}$.

Both used diphosphorus reactants differ in the substituents on the phosphanyl phosphorus atom (tBu or iPr groups) and solvent coordinated to the lithium cation (THF and Diglyme respectively).

Results and Discussion

The reactions of $t\text{Bu}_2\text{P-P(SiMe}_3)\text{Li·2.7THF}$ with CuCl or $[t\text{Bu}_3\text{PAgCl}]_4$ were initiated at low temperature (-30°C). After over 2 hours, during which the temperature increased to -10°C, the solvent (THF) was evaporated and the solid residue was dissolved in different non-polar solvents at room temperature. Good single crystals of **1** for X-ray analysis were obtained from pentane, while crystals of **2** were obtained from toluene solution at +4°C (Scheme 2). Initially we attempted to prepare silver complex **2** with the use of AgCl but we observed that during the reaction the silver ion was reduced to metallic silver, while the

diphosphorus ligand was oxidized, which was not observed for CuCl.
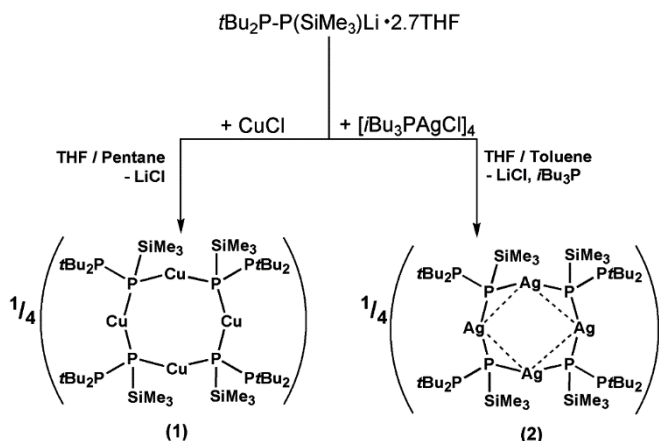
Scheme 2. The reactions of tBu_2P-$P(SiMe_3)Li·2.7THF$ with CuCl and $[iBu_3PAgCl]_4$.

The tetranuclear complex $[Cu_4\{\mu_2$-$P(SiMe_3)$-$PtBu_2\}_4]$ (1) crystallizes in the monoclinic space group $C2/c$ with four molecules in the unit cell. The asymmetric unit of 1 contains a half of the molecule, which obeys point group 2 symmetry (Schoenflies notation: C_2). Approximated point group symmetry for the tetramer molecule is $\bar{4}$ (S_4). $[Ag_4\{\mu_2$-$P(SiMe_3)$-$PtBu_2\}_4]$ (2) crystallizes in the triclinic space group P-1 with two molecules in the unit cell. The molecule of 2 has also approximated point group symmetry $\bar{4}$ (S_4). In both complexes the M_4P_4 core is practically planar (rms deviation from the planarity is 0.0111(2) for 1 and 0.342(3) for 2). The molecular structures of 1 and 2 are depicted on the Figures 1 and 2 respectively.
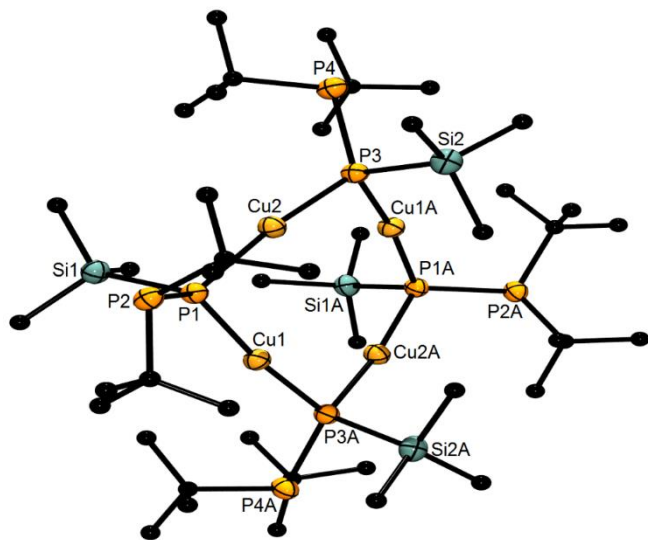
Figure 1. Molecular structures of $[Cu_4\{\mu_2$-$P(SiMe_3)$-$PtBu_2\}_4]$ (1) (thermal ellipsoids 50%; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Cu1-P1 2.1990(10), Cu1-P3 2.2025(10), Cu2-P1 2.2173(10), Cu2-P3 2.2181(10), P1-P2 2.2099(13), P1-Si1 2.2437(13), P3-P4 2.2139(13), P3-Si2 2.2375(14); P1-Cu-P3A 171.37(4), P1-Cu2-P3 170.51(4), Cu1-P1-Cu2 95.88(4), Cu1-P3A-Cu2A 98.27(4), Cu1-P1-P2 122.15(5), Cu2-P3-P4 121.82(5), ΣP2 = 317.46(14) and ΣP4 = 319.19(15).
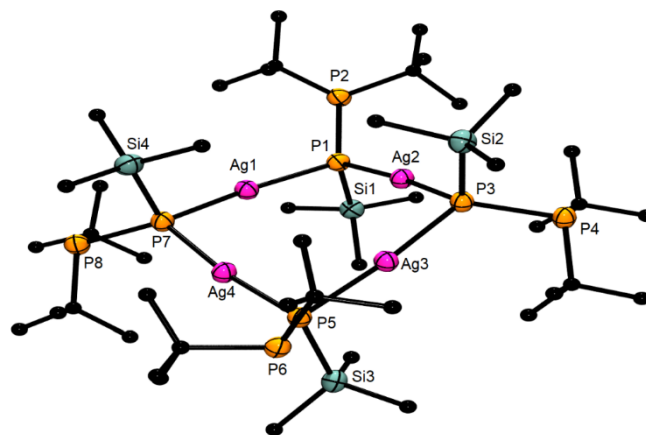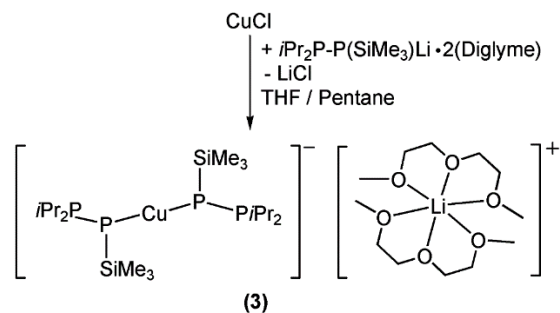

Figure 2. Molecular structure of $[Ag_4\{\mu_2$-$P(SiMe_3)$-$PtBu_2\}_4]$ (2) (thermal ellipsoids 50%, hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ag1-P1 2.3817(15), Ag1-P3 2.3878(15), Ag2-P3 2.3810(16), Ag2-P1 2.3910(16), Ag3-P5 2.3838(16), Ag3-P3 2.3874(16), Ag4-P7 2.3925(15), Ag4-P5 2.3969(15), P1-P2 2.199(2), P3-P4 2.206(2), P5-P6 2.198(2), P7-P8 2.204(2), P1-Si1 2.238(2), P3-Si2 2.231(2), P5-Si3 2.230(2), P7-Si4 2.228(2); P1-Ag1-P7 174.06(5), P3-Ag2-P1 169.90(6), P5-Ag3-P3 172.24(5), P7-Ag4-P5 171.91(5), Ag1-P1-Ag2 95.76(5), Ag2-P3-Ag3 95.68(6), Ag3-P5-Ag4 95.41(5), Ag1-P7-Ag4 94.41(5), P2-P1-Ag1 121.67(7), P2-P1-Ag2 119.51(8), P4-P3-Ag2 124.68(8), P4-P3-Ag3 121.92(8), P6-P5-Ag3 122.15(8), P6-P5-Ag4 119.26(8), P8-P7-Ag1 121.08(8), P8-P7-Ag4 121.92(8), ΣP2 = 318.4(2), ΣP4 = 320.9(3), ΣP6 = 317,1(3) and ΣP8 = 319.1(2), Ag···Ag interactions: Ag1···Ag2 3.5400(6), Ag2···Ag3 3.5346(6), Ag3···Ag4 3.5363(6), Ag4···Ag1 3.5077(6).

In 1 the Cu-P-Cu angles are 98.27(4)° and 95.88(4)°, while the P-Cu-P angles are 171.37(4)° and 170.51(4)°. The present values are comparable to these observed in tetranuclear copper complex $[CuPtBu_2]_4$ (Cu-P-Cu 100.6(2)° and P-Cu-P 169.4(2)°).[1c] The Cu-P bond lengths in 1 (2.1990(10) Å, 2.2025(10) Å) are similar as in complex $[CuPtBu_2]_4$ and are slightly shorter than these observed in complex $[Cu_4\{cyclo$-$(P_4tBu_3)PtBu\}_4]$ (2.2144(8) Å and 2.2265(8) Å).[9] In 2 the values of angles Ag-P-Ag are successively 95.76(5)°, 95.68(6)°, 95.41(5)°, 94.41(5)° and are the smallest known values for similar compounds with Ag_4P_4 core: 102.32(2)° in $[Ag_4\{cyclo$-$(P_4tBu_3)PtBu\}_4]$ [9] and 105.61(2)°, 105.39(2)°, 104.99(2)°, 105.09(2)° in $Ag_4P[(C_6F_5)N(SiMe_3)Si(SiMe_3)_2Cl]_4$.[10] The P-Ag-P angles 174.06(5)°, 169.90(6)°, 172.24(5)°, 171.91(5)° are more obtuse than these presented in following complexes $[Ag_4\{cyclo$-$(P_4tBu_3)PtBu\}_4]$ (160.31(3)°, 162.83(3)°) and $Ag_4P[(C_6F_5)N(SiMe_3)Si(SiMe_3)_2Cl]_4$ (160.38(2)°, 160.96(2)°, 160.78(2)°, 160.33(2)°). Moreover, all P-Ag-P and Ag-P-Ag angles are consistent with values of Cu_4P_4 core in the complex 1. The P-P distances in the phosphanylphosphido ligands in both complexes (2.198(2) Å – 2.2139(13) Å) are located in the range of single P-P bond and are comparable to distances in complexes with monodentate coordination of phosphanylphosphido ligands to the metal center.[2b, 5a]

In **1** and **2** the phosphanyl groups (PtBu$_2$) are located in the equatorial and the trimethylsilyl groups in axial positions of the slightly folded metallocycles (Cu$_4$P$_4$ and Ag$_4$P$_4$ respectively). The Cu-Cu distances 3.3430(6) Å and 3.2790(6) Å indicate a lack of interaction between copper atoms, while the distances of neighboring silver atoms in the Ag$_4$P$_4$ metallocycle (3.5400(6) Å, 3.5346(6) Å, 3.5363(6) Å, 3.5077(6) Å) may point to the presence of metallophilic interactions. The NBO analysis revealed the weak interactions between adjacent silver atoms (10-15 kcal/mol). The distances in **2** are comparable to these observed in [Ag$_2$(NO$_3$)$_2$-{C$_4$H$_2$S(CONMe-4-C$_5$H$_4$N)$_2$}$_2$], [Ag$_2$(CF$_3$CO$_2$)$_2${C$_4$H$_2$S(CONMe-4-C$_5$H$_4$N)$_2$}$_2$] (intermolecular Ag···Ag = 3.48 Å)[11] and are longer than these observed in [Ag$_4${Fe(CO)$_4$}$_4$]$^{4-}$ (3.036(1) Å – 3.334(1) Å).[12] The geometry around P2 and P4 atoms in **1** (ΣP2 = 317.46(14)° and ΣP4 = 319.19(15)°) and P2, P4, P6 and P8 in **2** (ΣP2 = 318.4(3)°, ΣP4 = 320.9(3)°, ΣP6 = 317.1(3)° and ΣP8 = 319.1(2)°) is clearly pyramidal.

The second reaction of CuCl was conducted with iPr$_2$P-P(SiMe$_3$)Li·2(Diglyme) in THF solution in molar ration 1 : 1 (Scheme 3). The new derivative of lithium salt contains the lithium atom chelated by two molecules of Diglyme [Li(Diglyme)$_2$]$^+$ and in result hampered the precipitation of LiCl. Consequently the lithium cation was presented both in the solution and the final molecular structure of complex [Cu{η^1-P(SiMe$_3$)-PiPr$_2$}$_2$]$^-$[Li(Diglyme)$_2$]$^+$ (**3**). Molecular structure of **3** indicates, that the stoichiometry of adducts should be 1 : 2 (excess of lithium derivative of diphosphane). Therefore, we carried out the reaction with the double excess of iPr$_2$P-P(SiMe$_3$)Li·2(Diglyme) and surprisingly we only obtained oil, but never a crystalline product (Scheme 3). The reaction of iPr$_2$P-P(SiMe$_3$)Li·2(Diglyme) with [iBu$_3$PAgCl]$_4$ was also conducted, however no crystals were isolated.

Scheme 3. The reaction of iPr$_2$P-P(SiMe$_3$)Li·2(Diglyme) with CuCl.

The ionic complex **3** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The presence of the chelating ligand (Diglyme) connected to the lithium atom causes that in the reaction the tetrameric moiety Cu$_4$P$_4$ is not formed. In this case the lithium ion crystallizes together with the monomeric ion of copper complex. The molecular structure of **3** is shown in Figure 3.
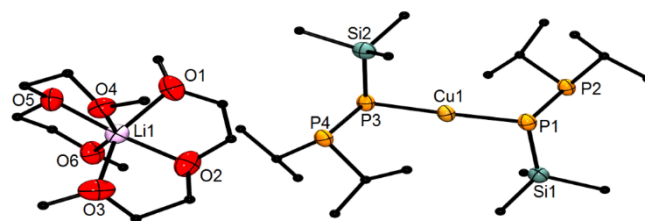
Figure 3. Molecular structure of **3** (thermal ellipsoids 50%, hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Cu1-P1 2.2080(13), Cu1-P3 2.2098(12), P1-P2 2.1864(17), P3-P4 2.1953(17), P1-Si1 2.2176(17), P3-Si2 2.2229(18); P1-Cu1-P3 177.23(5), Cu1-P1-P2 111.68(6), Cu1-P3-P4 110.45(6); ΣP1 = 312.02(6), ΣP2 = 307.82(14), ΣP3 = 303.3(6), ΣP4 = 309.10(13).

In **3** the P1-Cu1-P3 angle is approximately linear (177.23(7)°) and is comparable to other complexes with CuP$_2$ core: [Li(thf)$_2$][Cu(PtBu$_2$)$_2$] (176.5(6)°)[1c] and [Cu(PCy$_3$)$_2$][PF$_6$] 179.47(3)°.[13] The Cu-P distances in **3** (2.2080(13) Å and 2.2098(12) Å) are analogous to these found in complexes [Cu(PBz$_3$)$_2$][PF$_6$] (2.191(1) Å)[14] and [Cu(PCy$_3$)$_2$][PF$_6$] (2.213 (4) Å), while are slightly shorter that these occurring in complexes [Cu(PAdm$_2$Bz)$_2$][BF$_4$]·2CHCl$_3$ (2.228(2) Å, 2.239(3) Å)[15] and [Li(thf)$_2$][Cu(PtBu$_2$)$_2$] (2.246(5) Å and 2.266(4) Å).[1c] On the other hand, the P-P distances (2.1864(17) Å, 2.1953(17) Å) are much shorter than these in complex **1**, but they are still within the range of single P-P bond. All P atoms in complex **3** present pyramidal geometry (ΣP1 = 312.02(6)°, ΣP2 = 307.82(14)°, ΣP3 = 303.3(6)°, ΣP4 = 309.10(13)°).

All complexes were also investigated using the NMR spectroscopy technique. Unfortunately, we noticed, that all complexes were very poorly soluble in common organic solvents (THF-d$_8$, C$_6$D$_6$, Toluene-d$_8$), moreover the complexes decomposed and hydrolyzed during dissolution (doublets in the range of 19.04 ppm and -197.35 ppm with J_{PP} = 188.9 Hz from tBu$_2$P-P(SiMe$_3$)H and singlet at 19.62 ppm from tBu$_2$PH for **1** and **2**; doublets in the range of -8.86 ppm and -201.82 ppm with J_{PP} = 188.9 Hz from iPr$_2$P-P(SiMe$_3$)H and singlet at -16.38 ppm from iPr$_2$PH for **3**). The signals of complex **1** were visible in ^{31}P{^{1}H}-NMR at room temperature as two very broad doublets at 47 ppm (PtBu$_2$) and -203 ppm (P(SiMe$_3$)). The VT NMR investigation of **1** indicates that in the solution there is a multicomponent dynamic equilibrium with highly flexible structures. The spectrum obtained at 223 K revealed a few geometric isomers. The two main ones (Scheme 4) can be seen as doublets at 43.82, 39.69, -203.69, -203.88 ppm (J_{PP} = 328.0 Hz) and as two doublets at 54.16, -208.92 (J_{PP} = 386.2 Hz) and at 53.49 ppm, -209.33 ppm (J_{PP} = 381.3 Hz). In comparison, the NMR spectrum of **2** at 298 K revealed only two broad doublets in the range of 43.05 ppm and -212.72 ppm (J_{PP} ≈ 358 Hz).
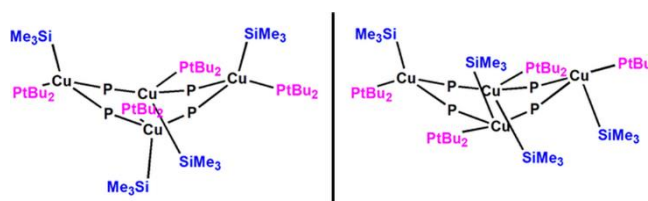
Scheme 4. Two main geometrical isomers of [Cu$_4$(μ_2-P(SiMe$_3$)-PtBu$_2$)$_4$] **(1)**. left: -SiMe$_3$ groups lying opposite each other have the same direction; right: -SiMe$_3$ groups lying next to each other have the same direction.

In the case of **2**, no dynamic equilibrium was observed during the VT NMR measurement, only the quality of the signals was improved. The differences in spectra of **1** and **2** may result from stabilization of the Ag$_4$P$_4$ core by the metallophilic interactions. Moreover, the improvement of the quality of NMR spectrum of **2** recorded at 223 K allowed to assign the coupling constant $^1J(^{107}$Ag-^{31}P) = 328.6 Hz (observed also at 298 K, see SI, Figure S12 and S14). Definitely, among the studied compounds **1-3**, the crystals of **3** were the most unstable in the deuterated solutions. During the ^{1}H and ^{31}P{^{1}H}-NMR measurement at 298 K we observed broad signals at 16.08 ppm and -221.60 ppm.

Conclusions

The reactions of lithium derivatives of diphosphanes with CuCl and [iBu$_3$PAgCl]$_4$ salts lead to new copper and silver complexes with phosphanylphosphido ligands. Furthermore, both forms of complexes, tetrameric and monomeric contain the reactive trimethylsilyl group on the phosphido phosphorus atom. Thus, we believe, the compounds will be convenient starting materials for further modifications and for the synthesis of organometallic polymers (mono- and heterometallic). The obtained results are only the first stage of further scientific research.

Experimental Section

Materials and Methods: THF and toluene were dried over Na/benzophenone, pentane was dried over Na/K and distilled under argon. All reactions were performed under argon atmosphere and were carried out using standard Schlenk techniques. Literature method were used to prepare for tBu$_2$P-P(SiMe$_3$)Li·2.7THF,[16] iPr$_2$P-P(SiMe$_3$)Li·2(Diglyme)[17] and [iBu$_3$PAgCl]$_4$.[18] CuCl was commercially purchased. ^{1}H and ^{31}P{^{1}H} spectra in solution were recorded on Bruker AV300 MHz and Bruker AV400 MHz (external standard tetramethylsilane for ^{1}H, 85% H$_3$PO$_4$ for ^{31}P).

Preparation of [Cu$_4$(μ_2-P(SiMe$_3$)-PtBu$_2$)$_4$] (1): To a suspension of CuCl (0.150 g, 1.515 mmol) in 15 ml of THF cooled to -30°C a solution of tBu$_2$P-P(SiMe$_3$)Li·2.7THF (0.680 g, 1.515 mmol) was dropwise added. The resulting light-green solution was stirred for 2 h and during this time the temperature increase to -10°C. After that, the THF was slowly evaporated and the oily residue was dissolved in 40 ml of pentane. The light-yellow mixture was filtered and concentrated to 5 ml of volume (the colour of concentrated solution: light-brown). The solution was stored in +4°C and after 24 h the yellow crystals were grown. Yield of obtained product: 0.400 g (21 %). Anal. Calcd for C$_{44}$H$_{108}$Cu$_4$P$_8$Si$_4$: C, 42.22; H, 8.69 %. Found: C, 42.34; H, 8.74 %. ^{1}H-NMR (298 K, THF-d$_8$) δ 1.44 (J_{PH} = 12.3 Hz, 72H, P(SiMe$_3$)-PtBu$_2$), 0.38 (J_{PH} = 4.2 Hz, J_{PH} = 1.9 Hz, 36 H, P(SiMe_3)-PtBu$_2$); ^{31}P-NMR (298 K, THF-d$_8$) δ 47 (br s, P(SiMe$_3$)-**P**tBu$_2$), -203 (br s, **P**(SiMe$_3$)-PtBu$_2$) ppm.

Synthesis of [Ag$_4$(μ_2-P(SiMe$_3$)-PtBu$_2$)$_4$] (2): To a solution of [iBu$_3$PAgCl]$_4$ (0.400 g, 0.290 mmol) in 15 ml of THF cooled to -30°C a solution of tBu$_2$P-P(SiMe$_3$)Li·2.7THF (0.520 g, 1.158 mmol) was slowly added and the resulting light-yellow mixture was stirring for 2 h. At the time the mixture became turbid. Next, the THF was slowly evaporated and the oily residue was dissolved in 30 ml of toluene. The mixture was filtered and concentrated to 25 ml of volume. The yellow solution was stored to +4°C and after 12 h the colorless crystals were obtained. Yield of obtained product: 0.320 g (19 %). Anal. Calcd for C$_{44}$H$_{108}$Ag$_4$P$_8$Si$_4$: C, 36.98; H, 7.62 %. Found: C, 37.22; H, 7.75 %. ^{1}H-NMR (298 K, THF-d$_8$) δ 1.40 (broad d, 72H, J_{PH} = 11.4 Hz, 72H, P(SiMe$_3$)-PtBu$_2$), 0.38 (broad singlet, 36 H, P(SiMe_3)-PtBu$_2$), ^{31}P-NMR (298 K, THF-d$_8$) δ 43 (br d, P(SiMe$_3$)-**P**tBu$_2$), -212 (br d, $^1J(^{107}$Ag-^{31}P) = 328.6 Hz, **P**(SiMe$_3$)-PtBu$_2$) ppm.

Synthesis of [Cu{η^1-P(SiMe$_3$)-PiPr$_2$}$_2$]$^-$[Li(Diglyme)$_2$]$^+$ (3): To a suspension of CuCl (0.150 g, 1.515 mmol) in 15 ml of THF cooled to -30°C a solution of iPr$_2$P-P(SiMe$_3$)Li·2(Diglyme) (0.763 g, 1.515 mmol) was dropwise added. The resulting light-green mixture was stirring for 2 h. Afterwards the THF was removed under vacuum and the residue was dissolved in 40 ml of pentane. The yellow mixture was filtered and concentrated to 30 ml of volume. After 24 h at +4°C crystals were formed from clear yellow solution. Yield of obtained product: 0.232 g (19 %). Anal. Calcd for C$_{30}$H$_{74}$CuLiO$_6$P$_4$Si$_2$: C, 46.10; H, 9.54 %. Found: C, 45.58; H, 9.32 %. ^{1}H-NMR (298 K, Toluene-d$_8$) δ 3.23 (s, 12H, MeO, Diglyme), 3.12 (m, 8H, MeOCH_2, Diglyme), 2.98 (m, 8H, CH_2OCH_2, Diglyme), 2.09 (broad m, 4H, CHMe$_2$), 1.54 – 1.25 (broad m, 12H, CHMe_2), 0.58 (broad dd, J_{PH} = 12.1 Hz, 18H, J_{PH} = 3.3 Hz, SiMe_3); ^{31}P-NMR (298 K, Toluene-d$_8$) δ 16 (br d, P(SiMe$_3$)-**P**tBu$_2$), -222 (br d, **P**(SiMe$_3$)-PtBu$_2$) ppm.

DFT calculations: Single point calculations for complexes **1** and **2** were carried out on geometries obtained from X-ray analysis at the ωB97XD/Def2TZVP level of theory by using Gaussian09 program packaged with imple-mented NBO 3.1 module.[19] Second Order perturbation theory analysis of Fock matrix in NBO basis was used to estimate the strength and type of interactions between metal atoms (Ag···Ag).

Crystal Structure Determination and Refinement: Diffraction data of **1**, **2** and **3** were collected on a diffractometer equipped with a STOE image plate detector system IPDS2T using Mo-Kα (λ = 0.71073 Å) radiation with graphite monochromatization. Good quality single-crystal specimens were selected for the X-ray diffraction experiments at 120 K. The structures were solved by direct methods and refined against F^2 using the Shelxs-2008 and Shelxl-2008 programs[20] run under WinGX.[21] Non-hydrogen atoms were refined with anisotropic displacement parameters: hydrogen atoms were usually refined using the isotropic model with U_{iso}(H) values fixed at 1.5 U_{eq} of the C atoms for CH$_3$ and 1.2 U_{eq} for CH, CH$_2$. Details of the crystals data, data collection, structure solution and refinement parameters of **1-3** are summarized in Table 1.

Crystallographic data for the structures of **1**, **2** and **3** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1880914-1880916. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic and experimental data for [Cu$_4$(μ_2-P(SiMe$_3$)-PtBu$_2$)$_4$] (**1**), [Ag$_4$(μ_2-P(SiMe$_3$)-PtBu$_2$)$_4$] (**2**) [Cu{η^1-P(SiMe$_3$)-PiPr$_2$}$_2$]$^-$[Li(Diglyme)$_2$]$^+$ (**3**).

	1	2	3
Empirical formula	$C_{44}H_{108}Cu_4P_8Si_4$	$C_{44}H_{108}Ag_4P_8Si_4$	$C_{30}H_{74}CuLiO_6P_4Si_2$
Formula weight/g·mol^{-1}	1251.58	1428.9	781.43
Crystal System	monoclinic	Triclinic	monoclinic
Space group	$C2/c$	P-1	$P2_1/c$
a /Å	28.4981(18)	9.7109(6)	19.4250(5)
b /Å	9.7372(3)	15.1607(7)	14.2190(3)
c /Å	26.2037(15)	24.8086(11)	16.6171(5)
α /°	90	79.557(4)	90
β /°	115.967(4)	79.394(4)	92.603(2)
γ /°	90	72.438(2)	90
V /Å^3	6537.2(6)	3391.8(3)	4585.0(2)
Z	4	2	4
D_c /g·cm^{-1}	1.272	1.399	1.132
T [K]	120(2)	120(2)	120(2)
μ /mm^{-1}	1.579	1.423	0.700
F(000)	2656	1472	1688
2Θ Range /°	2.24-29.53	2.25-29.67	2.10-29.02
Reflections, collected	8834	16140	11030
Reflections, independent	5613	11466	5936
Parameters	271	577	397
Goodness-of-fit on F^2	1.024	1.068	1.024
R_{int}	0.0717	0.0650	0.0841
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0516$	$R_1 = 0.0711$	$R_1 = 0.0702$
	$wR_2 = 0.1011$	$wR_2 = 0.2013$	$wR_2 = 0.1691$
R indices (all data)	$R_1 = 0.1023$	$R_1 = 0.0924$	$R_1 = 0.1454$
	$wR_2 = 0.1211$	$wR_2 = 0.2161$	$wR_2 = 0.2111$
Largest diff peak/hole /e·Å^3	0.768 / -0.628	3.399 / -1.85	0.847 / -0.623
CCDC	1880916	1880914	1880915

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