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Article

Versatility of Dithiophosphates in the Syntheses of Copper(I) Complexes with Bis(diphenylphosphino)alkanes: Abstraction of Chloride from Dichloromethane

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Reactions of $[Cu(CH_3CN)_4]X$ (X = PF_6, BF_4) with bis(diphenylphosphino)methane (dppm = $Ph_2PCH_2PPh_2$) and ammonium dialkyldithiophosphates, $(NH_4)[S_2P(OR)_2]$ (R = Et, ^iPr), yield a series of novel Cu^I polynuclear complexes, trinuclear $[Cu_3(\mu\text{-}dppm)_3(\mu_3\text{-}Cl)\{S_2P(OEt)_2\}]$ (PF_6) **1** and $[Cu_3(\mu\text{-}dppm)_2\{S_2P(OR)_2\}_2](PF_6)$ (R = Et, **2**; ^iPr, **3**), tetranuclear $[Cu_4(\mu\text{-}dppm)_2\{S_2P(OEt)_2\}_4]$ **4**, and hexanuclear $[Cu_6(\mu\text{-}dppm)_2(\mu_4\text{-}Cl)\{S_2P(O^iPr)_2\}_4](BF_4)$ **5**. Similarly, the reaction of $[Cu_2(\mu\text{-}L-L)_2(CH_3CN)_2](PF_6)_2$ (L–L, dppm, dppe = $Ph_2PCH_2CH_2PPh_2$) with $(NH_4)[S_2P(OR)_2]$ yields dinuclear $[Cu_2(\mu\text{-}dppm)_2\{S_2P(OR)_2\}_2]$ **6** (R= ^iPr, **6A**; Et, **6B**), trinuclear $[Cu_3(\mu\text{-}dppe)_3(\mu\text{-}Cl)_2\{S_2P(O^iPr)_2\}]$ **9**, and polymeric $[Cu(\mu_2\text{-}dppe)\{S_2P(OR)_2\}]_n$ (R = Et, **7**; ^iPr, **8**) complexes. The formation of **1** and **5** involved the abstraction of chloride from dichloromethane when the $Cu/S_2P(OR)_2$ ratio exceeded 1, but when ratio was 1:1, no Cl abstraction occurred, as in compound **4**. Compound **9**, however, was obtained as a 12% byproduct in the synthesis of **8** using a 1:1:1 ratio of $Cu/dppe/S_2P(O^iPr)_2$. The chloride binds to Cu atoms in a μ_3-Cl mode by capping one face of the Cu_3 triangle of cluster **1**. A μ_4-Cl caps a single tetragonal face of the trigonal prism of cluster **5**, and in the cluster **9**, two chlorides bond in μ_2-Cl modes. Both clusters **2** and **3** exhibit the μ_3-S mode of bonding for dtp ligands. Only cluster **5** exhibited close Cu···Cu contacts (2.997–3.0238 Å). All of compounds were characterized by single-crystal X-ray diffraction and pertinent crystallographic data for **1**, **5**, and **9** are are follows: (**1**) $C_{79}H_{76}ClCu_3F_6O_2P_8S_2$, triclinic, $P\bar{1}$, a = 11.213(1) Å, b = 14.142(1) Å, c = 25.910(2) Å, α = 95.328(2)°, β = 99.594(2)°, γ = 102.581-(2)°, V = 3918.2(6) Å³, Z = 2; (**5**) $C_{74}H_{100}BClCu_6F_4O_8P_8S_8$, monoclinic, $P2_1/n$, a = 25.198(4) Å, b = 15.990(3) Å, c = 25.421(4) Å, β = 106.027(3)°, V = 9845(3)Å³, Z = 4; (**9**) $C_{84}H_{86}Cl_2Cu_3O_2P_7S_2$, monoclinic, $C2/c$, with a = 24.965(3) Å, b = 17.058(2) Å, c = 20.253(2) Å, β = 95.351(4)°, V = 8587.4(17)Å³, Z = 4.

Introduction

Dialkyldithiophosphates [dtp, $(RO)_2PS_2^-$] exhibit a variety of coordination modes (Scheme 1),[1–3] and their metal complexes have important analytical, biochemical, and

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# On leave (from January 18, 2005 to June 29, 2005) from the Guru Nanak Dev University, Amritsar 143005, India.

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Scheme 1
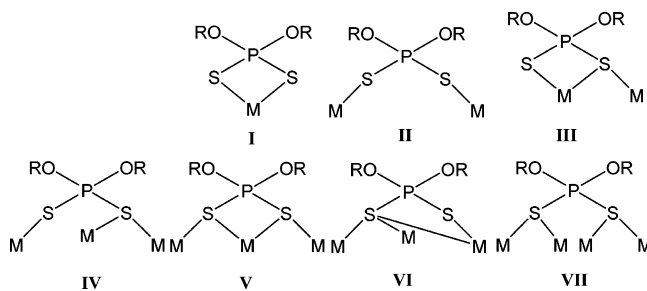
industrial applications.[4–15] Only a few Cu^I and Ag^I complexes of dtp which have tertiary phosphines as co-ligands are known, and none of them are bis(diphenylphosphino)alkanes, such as $PPh_2P(CH_2)_nPPh_2$ (n = 1, dppm; n = 2, dppe, and so on).[1–3] Given the ability of diphosphines to act as P,P-

bridging ligands, researchers recently reported the cluster cation, $[Ag_4(\mu\text{-dppm})_2\{S_2P(OEt)_2\}_3]^+$, which uniquely exhibited three coordination modes (III, V, and VI) of dtp.[16] Subsequently, the reaction that uses the dppe unit as the bridging ligand in the cluster synthesis yielded two kinds of polymeric species: the 1D zigzag chain, $[Ag(dppe)\{S_2P\text{-}(OR)_2\}]_n$, and an unusual 2D honeycomb-shaped network, $[Ag_4(\mu_3\text{-Cl})(dppe)_{1.5}\{S_2P(OR)_2\}_3]_n$.[17]

Copper(I) is an important metal ion with soft Lewis acid character. It has a strong tendency to form covalent bonds with soft ligands (such as P and S donor atoms) and make close Cu···Cu contacts (i.e., cuprophilicity,[18a-c] less than twice the van der Waals radius of Cu, 2.80 Å[18d]). These characteristics of Cu^I have resulted in the formation of oligomers and polymers with diverse coordination networks.[19] Studies of inorganic—organic coordination networks over the past decade have helped to develop new materials which exhibit conducting, catalytic, and magnetic exchange characteristics.[20-28] As part of our program to study the

interaction of dtp with metals, in this investigation, the influence of bis(diphenylphosphino)alkanes and the Cu/dtp molar ratio are examined. Nine new complexes are reported herein. These are trinuclear $[Cu_3(\mu\text{-dppm})_3(\mu_3\text{-Cl})\{S_2P\text{-}(OEt)_2\}](PF_6)$ **1** and $[Cu_3(\mu\text{-dppm})_2\{S_2P(OR)_2\}_2](PF_6)$ (R = Et, **2**; ^iPr, **3**), tetranuclear $[Cu_4(\mu\text{-dppm})_2\{S_2P(OEt)_2\}_4]$ **4**, hexanuclear $[Cu_6(\mu\text{-dppm})_2(\mu_4\text{-Cl})\{S_2P(O^iPr)_2\}_4](BF_4)$ **5**, dinuclear $Cu_2(\mu\text{-dppm})_2[S_2P(O^iPr)_2]_2$ **6**, polymeric $[Cu(\mu\text{-}dppe)\{S_2P(OR)_2\}]_n$ (R = Et, **7**; ^iPr, **8**), and trinuclear $[Cu_3(\mu\text{-}dppe)_3(\mu\text{-Cl})_2\{S_2P(O^iPr)_2\}]$ **9**. The formation of clusters **1**, **5**, and **9** involved the abstraction of chloride from CH_2Cl_2 or $CHCl_3$.

Experimental Section

Materials and Measurements. All chemicals and reagents obtained from commercial sources were purified and dried. CH_2Cl_2 and MeOH were distilled from P_4O_{10} and Mg, respectively. Hexane and diethyl ether were distilled from Na/K. All reactions were performed in oven-dried Schlenk glassware using standard inert-atmosphere techniques. The starting compounds, $[Cu(CH_3\text{-}CN)_4]X$ (X = PF_6,[29a] BF_4[29b]), $[Cu_2(\mu\text{-dppm})_2(CH_3CN)_2](PF_6)_2$,[30a] $[Cu_2(\mu\text{-dppe})_2(CH_3CN)_2](PF_6)_2$,[30b] and $(NH_4)[S_2P(OR)_2]$ (R = Et, ^iPr),[31] were prepared according to literature methods or purchased from Aldrich Chemicals. NMR spectra were recorded on Bruker AC-F200 and Advance-300 Fourier transform spectrometers. The $^{31}P\{^1H\}$ NMR spectra are referenced externally against 85% H_3PO_4. The elemental analyses (C, H, S) were done using a Perkin-Elmer 2400 analyzer.

$[Cu_3(dppm)_3(\mu_3\text{-Cl})\{S_2P(OEt)_2\}](PF_6)$ (1). The ligand $NH_4[S_2P(OEt)_2]$ (0.05 g, 0.27 mmol) was suspended in a solution of $[Cu(CH_3CN)_4](PF_6)$ (0.30 g, 0.81 mmol) and dppm (0.31 g, 0.81 mmol) in dichloromethane (30 mL) in a Schlenk flask (100 mL). The contents were stirred for 24 h at ambient temperature under a N_2 atmosphere; then the mixture was filtered to separate insoluble NH_4-PF_6 and unreacted ligand. The filtrate was transferred into a separating funnel, and water (20 mL) was added to it to remove water soluble unreacted ligand and NH_4PF_6; the dichloromethane extract was evaporated to dryness to give a white residue. This residue was then redissolved in dichloromethane (20 mL) and layered with hexane (10 mL) which yielded crystalline **1** (0.20 g, 44%; mp 183−186°C). Anal. Calcd for $C_{79}H_{76}ClCu_3O_2F_6S_2P_8$: C, 55.50; H, 4.48; S, 3.75. Found: C, 55.46; H, 4.45; S, 3.74. ^1H NMR $(CDCl_3)$: δ 0.82 (m, 6H, CH_3), 3.47 (s, br, 6H, PCH_2P), 4.62 (m, 4H, OCH_2), 6.80−7.24 (m, 60H, $P(C_6H_5)$). $^{31}P\{^1H\}$ NMR $(CDCl_3)$: δ 94.35 (s, $P(OC_2H_5)$), −15.98 (br, 6P, $P(C_6H_5)$), −143.7 (PF_6). $\Delta\delta = \delta_{Complex} - \delta_{Ligand(S_2P)} = -20.45$ ppm; $\Delta\delta = \delta_{Complex} - \delta_{Ligand(PPh_2)} = 3.52$ ppm.

The use of $CHCl_3$ in place of CH_2Cl_2 also gave the same compound, confirmed by NMR and elemental analysis.^1H NMR

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(CDCl$_3$): δ 0.86 (m, 6H, CH$_3$), 3.47 (s, br, 6H, PCH$_2$P), 4.62 (m, 4H, OCH$_2$), 6.80−7.24 (m, 60H, P(C$_6$H$_5$)). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 94.59 (s, P(OC$_2$H$_5$)), −15.85 (br, 6P, P(C$_6$H$_5$)), −143.7 (PF$_6$).

[Cu$_3$(dppm)$_2$\{S$_2$P(OEt)$_2$\}$_2$](PF$_6$) (2). This complex was prepared in a similar manner using THF in place of dichloromethane and reacting [Cu(CH$_3$CN)$_4$](PF$_6$) with dppm and (NH$_4$)[S$_2$P(OEt)$_2$] in a 3:2:2 molar ratio (0.18 g, 48%; mp 191−193 °C). Anal. Calcd for C$_{58}$H$_{64}$Cu$_3$O$_4$F$_6$S$_4$P$_7$: C, 47.23; H, 4.37; S, 8.70. Found: C, 46.35; H, 4.31; S, 8.93. ^{1}H NMR (acetone-d_6): δ 1.23 (d, 12H, CH$_3$), 3.24 (br, 4H, PCH$_2$P), 4.52 (m, 8H, OCH$_2$), 6.80−7.32 (m, 40H, P(C$_6$H$_5$)). ^{31}P{^{1}H} NMR (acetone-d_6): δ 93.90 (t, br, 2P, P(OEt)), −14.46 (t, br, 4P, P(C$_6$H$_5$)), −143.6 (PF$_6$). $\Delta\delta = \delta_{Complex} - \delta_{Ligand(S_2P)} = -20.90$ ppm; $\Delta\delta = \delta_{Complex} - \delta_{Ligand(PPh_2)} = 5.04$ ppm.

[Cu$_3$(dppm)$_2$\{S$_2$P(O^{i}Pr)$_2$\}$_2$](PF$_6$) (3). This complex was obtained by the same method as for **2** using (NH$_4$)[S$_2$P(O^{i}Pr)$_2$] (0.17 g, 42%; mp 192−194 °C). Anal. Calcd for C$_{62}$H$_{72}$Cu$_3$O$_4$F$_6$S$_4$P$_7$: C, 48.64; H, 4.74; S, 8.38. Found: C, 48.13; H, 4.83; S, 8.75. ^{1}H NMR (acetone-d_6), δ 1.22 (t, 24H, CH$_3$), 3.32 (br; 4H, PCH$_2$P), 4.72 (m; 4H, OCH), 6.88−7.48 (m; 40H, P(C$_6$H$_5$)). ^{31}P{^{1}H} NMR (acetone-d_6) δ 91.48 (s, br, 2P, P(O^{i}Pr)), −13.90 (t, br, 4P, P(C$_6$H$_5$)), −143.7 (PF$_6$). $\Delta\delta = \delta_{Complex} - \delta_{Ligand(S_2P)} = -19.90$ ppm; $\Delta\delta = \delta_{Complex} - \delta_{Ligand(PPh_2)} = 5.60$ ppm.

[Cu$_4$(dppm)$_2$\{S$_2$P(OEt)$_2$\}$_4$] (4). This complex was prepared by the method used for **1** by reacting [Cu(CH$_3$CN)$_4$](PF$_6$) with dppm and (NH$_4$)[S$_2$P(OEt)$_2$] in a 2:1:2 molar ratio (0.22 g, 62%; mp 189−192 °C). Anal. Calcd for C$_{66}$H$_{84}$Cu$_4$O$_8$S$_8$P$_8$: C, 44.94; H, 4.79; S, 14.51. Found: C, 44.87; H, 4.85; S, 14.52. ^{1}H NMR (CDCl$_3$): δ 1.33 (d, 24H, CH$_3$), 3.22 (br, 4H, PCH$_2$P), 4.23 (m, 16H, OCH$_2$), 7.10−7.41 (m, 40H, P(C$_6$H$_5$)). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 95.06 (s, br, 4P, P(OEt)), −11.95 (m, br, 4P, PPh$_2$). $\Delta\delta = \delta_{Complex} - \delta_{Ligand(S_2P)} = -19.74$ ppm; $\Delta\delta = \delta_{Complex} - \delta_{Ligand(PPh_2)} = 7.55$ ppm.

[Cu$_6$(dppm)$_2$(μ_4-Cl)\{S$_2$P(O^{i}Pr)$_2$\}$_4$](BF$_4$) (5). This complex was prepared by the same method as **1** by reacting [Cu(CH$_3$CN)$_4$](BF$_4$) with dppm and (NH$_4$)[S$_2$P(O^{i}Pr)$_2$] in a 3:1:2 molar ratio (0.10 g, 36%; mp 196−198 °C). Anal. Calcd for C$_{74}$H$_{100}$Cu$_6$O$_8$S$_8$P$_8$BF$_4$Cl: C, 41.83; H, 4.71; S, 12.07. Found: C, 42.29; H, 4.89; S, 11.85. ^{1}H NMR (CDCl$_3$): δ 1.32 (m, 48H, CH$_3$), 3.13 (m, 4H, PCH$_2$P), 4.82 (m, 8H, OCH), 6.80−7.34 (m, 40H, P(C$_6$H$_5$)). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 97.67, 92.68 (4P, P(O^{i}Pr)), −13.94 (s, 4P, P(C$_6$H$_5$)). $\Delta\delta = \delta_{Complex} - \delta_{Ligand(S_2P)} = -13.71, -18.70$ ppm; $\Delta\delta = \delta_{Complex} - \delta_{Ligand(PPh_2)} = 5.56$ ppm.

The use of CHCl$_3$ in place of CH$_2$Cl$_2$ also gave compound **5**, as confirmed by NMR and elemental analysis. ^{1}H NMR (CDCl$_3$): δ 1.31 (m, 48H, CH$_3$), 3.18 (br, 4H, PCH$_2$P), 4.88 (m, 8H, OCH), 6.90−7.21 (m, 40H, P(C$_6$H$_5$)). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 97.61, 92.62 (s, P(O^{i}Pr)), −12.60 (br, 4P, P(C$_6$H$_5$)).

[Cu$_2$(dppm)$_2$\{S$_2$P(O^{i}Pr)$_2$\}$_2$] (6a). The NH$_4$S$_2$P(O^{i}Pr)$_2$ (0.13 g, 0.46 mmol) ligand was suspended in a solution of [Cu$_2$(dppm)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$ (0.30 g, 0.23 mmol) in dichloromethane (30 mL) in a Schlenk flask (100 mL). The contents were stirred for 24 h at ambient temperature and filtered to separate insoluble NH$_4$PF$_6$ and unreacted ligands. The resulting solution was evaporated to dryness at room temperature and recrystallized using CH$_3$OH (20 mL) at room temperature, which gave a white precipitate of **6a** in a short period of time (0.23 g, 79%; mp 176−179 °C). Anal. Calcd for C$_{62}$H$_{72}$Cu$_2$O$_4$S$_4$P$_6$·0.5CH$_2$Cl$_2$: C, 55.00; H, 5.39; S, 9.39. Found: C, 55.13; H, 5.69; S, 9.11. ^{1}H NMR (CDCl$_3$): δ 1.23 (d, 24H, CH$_3$), 2.94 (br, 4H, PCH$_2$P), 4.62 (m, 4H, OCH), 6.80−7.32 (m, 40H, P(C$_6$H$_5$)). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 94.90 (s, 2P, P(O^{i}Pr)),

−19.43 (br, 4P, P(C$_6$H$_5$)). $\Delta\delta = \delta_{Complex} - \delta_{Ligand(S_2P)} = -16.48$ ppm; $\Delta\delta = \delta_{Complex} - \delta_{Ligand(PPh_2)} = 2.12$ ppm.

[Cu$_2$(dppm)$_2$\{S$_2$P(OEt)$_2$\}$_2$] (6b). Compound **6b** was prepared using the same method that was used for the preparation of **6a** (0.203 g, 70%; mp 173−174 °C). Anal. Calcd for C$_{58}$H$_{64}$Cu$_2$O$_4$S$_4$P$_6$: C, 55.13; H, 5.09; S, 10.13. Found: C, 54.70; H, 5.31; S, 10.06. ^{1}H NMR (CDCl$_3$): δ 1.15 (d, 12H, CH$_3$), 3.03 (t, 4H, PCH$_2$P), 3.90 (m, 8H, OCH$_2$), 6.93−7.38 (m, 40H, P(C$_6$H$_5$)). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 96.70 (s, 2P, P(OEt)), −17.38 (s, 4P, P(C$_6$H$_5$)). $\Delta\delta = \delta_{Complex} - \delta_{Ligand(S_2P)} = -18.10$ ppm; $\Delta\delta = \delta_{Complex} - \delta_{Ligand(PPh_2)} = 0.07$ ppm.

[Cu(dppe)\{S$_2$P(OEt)$_2$\}]$_n$ (7). This complex was prepared by the method used to prepare compound **6** with dppm replaced by dppe (0.11 g, 78%; mp 175−177 °C). Anal. Calcd. for C$_{30}$H$_{34}$CuO$_2$S$_2$P$_3$·CH$_2$Cl$_2$: C, 50.85; H, 4.96; S, 8.76. Found: C, 50.43; H, 5.35; S, 8.62. ^{1}H NMR (CDCl$_3$): δ 1.33 (d, 6H, CH$_3$), 2.34 (br, 4H, PCH$_2$CH$_2$P), 4.12 (m, 4H, OCH$_2$), 7.20−7.62 (m, 20H, P(C$_6$H$_5$)). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 92.28 (s, 1P, P(OEt)), −12.04 (s, br, 2P, P(C$_6$H$_5$)). $\Delta\delta = \delta_{Complex} - \delta_{Ligand(S_2P)} = -22.52$ ppm; $\Delta\delta = \delta_{Complex} - \delta_{Ligand(PPh_2)} = 0.66$ ppm.

[Cu(dppe)\{S$_2$P(O^{i}Pr)$_2$\}]$_n$ (8). This complex was prepared by the method used to prepare **7** with (NH$_4$)[S$_2$P(O^{i}Pr)$_2$] (0.10 g, 68%; mp 173−175 °C). Anal. Calcd for C$_{32}$H$_{38}$CuO$_2$S$_2$P$_3$·CH$_2$Cl$_2$: C, 52.14; H, 5.30; S, 8.43. Found: C, 51.55; H, 5.35; S, 8.79. ^{1}H NMR (CDCl$_3$): δ 1.33 (d, 12H, CH$_3$), 2.34 (br, 4H, PCH$_2$CH$_2$P), 4.82 (m, 2H, OCH), 7.10−7.62 {m, 20H, P(C$_6$H$_5$)}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 90.04 (s, 1P, P(O^{i}Pr)), −12.11 {br, 2P, P(C$_6$H$_5$)}. $\Delta\delta = \delta_{Complex} - \delta_{Ligand(S_2P)} = -21.34$ ppm; $\Delta\delta = \delta_{Complex} - \delta_{Ligand(PPh_2)} = 0.59$ ppm.

[Cu$_3$(μ-dppe)$_3$(μ-Cl)$_2$\{S$_2$P(O^{i}Pr)$_2$\}] (9). After the formation of **8**, new crystals were obtained from the filtrate in a 12% (0.07 g) yield (mp 189−192 °C). Anal. Calcd for C$_{84}$H$_{86}$Cu$_3$O$_2$S$_2$P$_7$Cl$_2$: C, 60.41; H, 5.19; S, 3.84. Found: C, 58.79; H, 5.35; S, 4.02. ^{1}H NMR (CDCl$_3$): δ 1.31 (d, 12H, CH$_3$), 3.14 (br, 12H, PCH$_2$CH$_2$P), 4.82 (m, 2H, OCH), 7.04−7.27 {m, 60H, P(C$_6$H$_5$)}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 92.41 (s, 1P, P(O^{i}Pr)), 8.76 (br, 6P, P(C$_6$H$_5$)). $\Delta\delta = \delta_{Complex} - \delta_{Ligand(S_2P)} = -18.93$ ppm; $\Delta\delta = \delta_{Complex} - \delta_{Ligand(PPh_2)} = 21.46$ ppm.

Alternative Method for 9. The NH$_4$[S$_2$P(O^{i}Pr)$_2$] (0.06 g, 0.27 mmol) ligand was suspended in a solution of [Cu(CH$_3$CN)$_4$](PF$_6$) (0.30 g, 0.81 mmol) and dppe (0.320 g, 0.81 mmol) in dichloromethane (30 mL) in a Schlenk flask (100 mL). The contents were stirred for 24 h at ambient temperature under a N$_2$ atmosphere; then the mixture was filtered to separate insoluble NH$_4$PF$_6$ and unreacted ligand. Then the filtrate was evaporated to dryness to give a white residue. This residue was treated with methanol (10 mL) and filtered, and the solid obtained was dried (0.300 g, 40%; mp 189−192 °C). ^{1}H NMR (CDCl$_3$): δ 1.33 (d, 12H, CH$_3$), 3.20 (br, 12H, PCH$_2$CH$_2$P), 4.82 (m, 2H, OCH), 7.1−7.27 {m, 60H, P(C$_6$H$_5$)}. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 92.62 (s, 1P, P(O^{i}Pr)), 8.89 (br, 6P, P(C$_6$H$_5$)).

X-ray Structure Determination. The structures of **1−9** were obtained by single-crystal X-ray diffraction. Crystals of **1**, **4**, **5**, and **6−9** were grown using dichloromethane−hexane solvents, while crystal of **2** and **3** were grown from a thf−hexane mixture. The crystals were mounted on the tips of glass fibers with epoxy resin. Data for compounds **7** and **8** were collected at 293 K on a Siemens P4 diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å). The data were collected using the $2\theta-\omega$ scan technique. The data reduction was performed with SAINT,[32] which

(32) *SAINT*, version 4.043; Bruker Analytical X-ray System: Madison, WI, 1995.

Table 1. Crystallographic Data for Compounds **1**−**9**

	1	**2**	**3**	**4**	**5**
formula	$C_{79}H_{76}ClCu_3F_6O_2P_8S_2$	$C_{58}H_{64}Cu_3F_6O_4P_7S_4$	$C_{62}H_{72}Cu_3 F_6O_4P_7S_4$	$C_{66}H_{84}Cu_4 O_8P_8S_8$	$C_{74}H_{100}BCl Cu_6F_4O_8P_8S_8$
fw	1709.35	1474.74	1530.85	1763.73	2125.40
cryst syst	triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	11.213(1)	12.812(2)	12.896(2)	13.473(1)	25.198(4)
b (Å)	14.142(1)	15.221(3)	16.661(2)	23.888(1)	15.990(3)
c (Å)	25.910(2)	17.100(3)	16.876(2)	24.648(1)	25.421(4)
α (deg)	95.328(2)	82.275(3)	81.230(2)	90	90
β (deg)	99.594(2)	83.963(3)	84.472(2)	95.986(1)	106.027(3)
γ (deg)	102.581(2)	89.726(3)	87.297(2)	90	90
V (Å^3)	3918.2(6)	3285.8(9)	3564.9(8)	7889.7(6)	9845(3)
Z	2	2	2	4	4
ρ_{calcd} (g cm^{-3})	1.449	1.491	1.426	1.485	1.456
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	1.117	1.320	1.219	1.487	1.675
T (K)	298(2)	298(2)	298(2)	298(2)	298(2)
R1[a]	0.0391	0.0484	0.0456	0.0348	0.0609
wR2[b]	0.0996	0.1186	0.1140	0.0859	0.1615

	6·CH$_2$Cl$_2$	**7·^{1}/$_2$CH$_2$Cl$_2$**	**8·CH$_2$Cl$_2$**	**9**
formula	$C_{63}H_{74}Cl_2Cu_2 O_4P_6S_4$	$C_{30.5}H_{35}Cl CuO_2P_3S_2$	$C_{33}H_{40}Cl_2 CuO_2P_3S_2$	$C_{84}H_{86}Cl_2 Cu_3O_2P_7S_2$
fw	1407.36	689.64	760.12	1669.96
cryst syst	orthorhombic	triclinic	monoclinic	monoclinic
space group	$Pbcn$	$P\bar{1}$	$C2/c$	$C2/c$
a (Å)	18.5958(11)	11.752(2)	19.672(4)	24.965(3)
b (Å)	15.5449(9)	13.127(2)	17.197(2)	17.058(2)
c (Å)	24.486(2)	13.268(3)	13.680(5)	20.253(2)
α (deg)	90	61.126(2)	90	90
β (deg)	90	76.858(8)	126.67(2)	95.351(4)
γ (deg)	90	68.480(1)	90	90
V (Å^3)	7078.3(7)	1664.2(6)	3711.9(16)	8587.4(17)
Z	4	2	4	4
ρ_{calcd} (g cm^{-3})	1.319	1.375	1.360	1.292
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	0.972	1.032	1.002	1.021
T (K)	298(2)	293(2)	293(2)	298(2)
R1[a]	0.0474	0.0663	0.0622	0.0422
wR2[b]	0.1311	0.1642	0.1342	0.0945

[a] R1 = $||F_o| - |F_c||/|F_o|$. [b] wR2 = $[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]^{1/2}$.

corrects for Lorentz and polarization effects. An empirical absorption correction (Ψ scans) was applied. The crystal data for compounds **1**−**6** and **9** were collected at 298 K on a Siemens SMART CCD diffractometer. The data were measured with ω scans of 0.3^o per frame for 60 s. A total of 1271 frames were collected with a maximum resolution of 0.84 Å. Cell parameters were retrieved with SMART software[33] and refined with SAINT software on all observed reflections ($I > 10\sigma(I)$). Data reduction was performed with SAINT, which corrects for Lorentz and polarization effects. An empirical absorption correction was applied for all compounds. All structures were solved by the use of direct methods, and the refinement was performed by the least-squares methods on F^2 with the SHELXL-97 package,[34] incorporated in SHELXTL/PC, version 5.10.[35] Selected crystal data for the compounds (**1**−**9**) are summarized in Table 1.

Results and Discussion

Synthesis. Schemes 2 and 3 show the formation of Cu^I polynuclear complexes by the reaction of copper(I) salts with bisphosphines and dtp ligands. The reaction of [Cu(CH$_3$CN)$_4$]-

(33) *SMART*, version 4.043; Bruker Analytical X-ray System: Madison, WI, 1995.

(34) Sheldrick, G. M. *SHELXL-97: Program for the Refinement of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1997.

(35) *SHELXL: Program Library for Structure Solution and Molecular Graphics*, version 5.10 *(PC version)*; Bruker Analytical X-ray System: Madison, WI, 1998.

Scheme 2^a
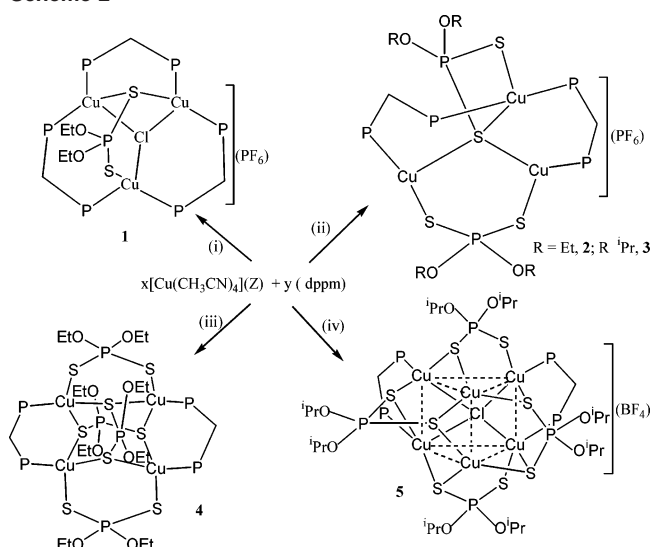
^{a} The following synthetic conditions apply: (i) (NH$_4$)[S$_2$P(OEt)$_2$], x = y = 3, Z = PF$_6$, CH$_2$Cl$_2$, RT (**1**); (ii) 2 (NH$_4$)[S$_2$P(OR)$_2$], x = 3, y = 2, Z = PF$_6$, THF, RT (**2**, **3**); (iii) 4(NH$_4$)[S$_2$P(OEt)$_2$], x = 4, y = 2, Z = PF$_6$, CH$_2$Cl$_2$, RT (**4**); and (iv) 4(NH$_4$)[S$_2$P(O^{i}Pr)$_2$], x = 6, y = 2, Z = BF$_4$, CH$_2$Cl$_2$, RT (**5**).

(PF$_6$) with dppm and (NH$_4$)[S$_2$P(OEt)$_2$] in dichloromethane with a 3:3:1 molar ratio yielded the trinuclear cluster [Cu$_3$-

Scheme 3^a
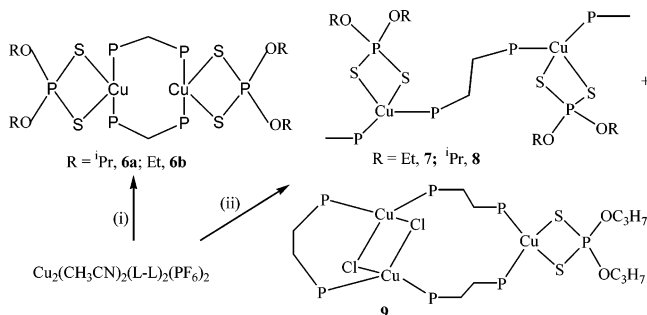
^{a} The following synthetic conditions apply: (i) 2(NH$_4$)[S$_2$P(OR)$_2$], L−L = dppm, CH$_2$Cl$_2$, RT (**6**) and (ii) 2(NH$_4$)[S$_2$P(OR)$_2$], L−L = dppe, CH$_2$Cl$_2$, RT (**6−9**).

(μ-dppm)$_3$(μ_3-Cl){S$_2$P(OEt)$_2$}](PF$_6$), **1**, and the reaction involved the abstraction of chloride from CH$_2$Cl$_2$. When [Cu(CH$_3$CN)$_4$](PF$_6$) was reacted with dppm and (NH$_4$)[S$_2$P-(OR)$_2$] (R = Et, ^{i}Pr) in a 3:2:2 molar ratio in THF solvent, the analogous [Cu$_3$(μ-dppm)$_2${S$_2$P(OR)$_2$}$_2$](PF$_6$) (R = Et, **2**; ^{i}Pr, **3**) clusters were produced. Tetranuclear [Cu$_4$(μ-dppm)$_2$-{S$_2$P(OEt)$_2$}$_4$], **4**, was formed by reacting [Cu(CH$_3$CN)$_4$](PF$_6$) with dppm and (NH$_4$)[S$_2$P(OEt)$_2$] in a 2:1:2 molar ratio in dichloromethane. Similarly, the reaction of [Cu(CH$_3$CN)$_4$]-(BF$_4$) with dppm and (NH$_4$)[S$_2$P(O^{i}Pr)$_2$] in CH$_2$Cl$_2$ in a 3:1:2 molar ratio yielded a hexanuclear cluster, [Cu$_6$(μ-dppm)$_2$-(μ_4-Cl){S$_2$P(O^{i}Pr)$_2$}$_4$](BF$_4$) **5**, and its formation also involved the abstraction of one chloride. The photoinduced extraction of chloride from a chlorocarbon solvent by iron complexes has also been reported.[36]

The formation of compounds **6a** and **6b** from Cu$_2$(dppm)$_2$-(CH$_3$CN)$_2$(PF$_6$)$_2$ and (NH$_4$)[S$_2$P(OR)$_2$] (R= ^{i}Pr, **6a**; Et, **6b**) involves the replacement of weakly coordinated CH$_3$CN by chelating [S$_2$P(OR)$_2$]$^-$ ligands; the central P,P-bridged dinuclear Cu(μ-P,P-dppm)$_2$Cu framework is retained (Scheme 3). Finally, the reaction of Cu$_2$(dppe)$_2$(CH$_3$CN)$_2$(PF$_6$)$_2$ with (NH$_4$)[S$_2$P(OR)$_2$] in a 1:1 molar ratio yielded [Cu(μ-dppe)-{S$_2$P(OR)$_2$}]$_n$ (R = Et, **7**; ^{i}Pr, **8**) polymers, as well as a trinuclear cluster, [Cu$_3$(μ-dppe)$_3$(μ-Cl){S$_2$P(O^{i}Pr)$_2$}] **9**, with a yield of ~12%. The formation of **9** involved the abstraction of two chloride ions from the solvent, and the structure thus produced is analogous to that of [Cu$_3$(μ-dppe)$_3$(μ_2-I)$_2$(I)(2-SC$_5$H$_4$NH)],[28] which was isolated from the reaction of Cu^I with pyridine-2-thione in the presence of dppe. This is in sharp contrast to the above-mentioned silver work where CH$_2$Cl$_2$ acts as a source of capping chlorine atoms in the formation of starburst clusters, [Ag$_4$(μ_3-Cl)(dppe)$_{1.5}${S$_2$P-(OR)$_2$}$_3$], which in turn propagate to produce a 2D hexagonal network.[17]

The above reactions indicate dppm typically favors the formation of clusters, and when the Cu/dtp ratio exceeds 1, the abstraction of chloride from CH$_2$Cl$_2$ yields [M$_n$]$^+$ (n = 3, 6) cations balanced by PF$_6$ or BF$_4$ counteranions. It is

found to be true in the formation of clusters **1** and **5** and in the formation of **9**; after the polymeric species have been isolated, a low dtp content, which again favors the chloride abstraction, is present. Notably, replacing CH$_2$Cl$_2$ with CHCl$_3$ in the synthesis of **1** and **5**, also resulted in the abstraction of chloride from CHCl$_3$, as verified by NMR spectroscopy and elemental analyses (see Experimental Section). Cluster **9** was also obtained by reacting [Cu(CH$_3$CN)$_4$](PF$_6$), dppe, and (NH$_4$)[S$_2$P(O^{i}Pr)$_2$] in a 3:3:1 molar ratio with a 40% yield, determined by NMR spectroscopy. Compounds **6−8** included CH$_2$Cl$_2$ in the lattice (vide infra); this fact further supports the claim that the complexes are stable in CH$_2$Cl$_2$ and that abstraction occurs when necessitated by a low molar ratio of dithiophosphate. All clusters and polymers discussed above are colorless, stable to air and moisture, and do not melt; rather, they decompose in the range of ~170−200 °C.

Molecular Structures of 1−9. Table 1 presents the crystallographic data of the compounds, while Table 2 lists some important bond parameters of the compounds. The Supporting Information includes the bond parameters of compounds **3** and **8**, which are isostructural with compounds **2** and **7**, respectively. Figures 1−7 display the molecular structures of the compounds. The compounds crystallize in triclinic (**1**, **2**, **3**, and **7**), monoclinic (**4**, **5**, **8** and **9**), and orthorhombic (**6a**) crystal systems.

Clusters 1−3, 5, and 9. The formation of clusters **1**, **5**, and **9** involves the abstraction of chloride from dichloromethane. Three Cu atoms of cluster **1** form a Cu$_3$ triangle bridged by three dppm ligands (Figure 1). The dithiophosphate anion, [S$_2$P(OEt)$_2$]$^-$ adopts bonding Mode IV; accordingly, S(1) binds to Cu(1) [Cu(1)−S(1), 2.464(1) Å], and S(2) bridges the other two Cu atoms [Cu(2)−S(2), 2.3902-(9) Å; Cu(3)−S(2), 2.352(1) Å]. The chloride abstracted from CH$_2$Cl$_2$ connects three Cu atoms in a μ_3-Cl mode with approximately equal Cu−Cl bond lengths [2.4603(8), 2.4782-(8), 2.4988(8) Å], and bond angles at Cl(1) [92.21(3), 91.63-(3), 76.57(2)°], suggesting a face-capped Cu$_3$ triangle. The Cu−Cl bond distances are less than the sum of the covalent radii, 2.58 Å,[18d] and other Cu^I complexes with μ_3-Cl (e.g., (2.408−2.589 Å)[37,38] in [Cu$_3$(μ-dppm)$_3$(μ_3-SR)(μ_3-Cl)](PF$_6$) and [Cu$_3$(μ-dppm)$_3$(μ_3-η^1-C≡C^{t}Bu)(μ_3-Cl)]$^+$ have similar bond lengths. The geometry around each Cu center is distorted tetrahedral.

Cluster **9** is composed of three dppe ligands that bridge the Cu$_3$ triangle, and the S$_2$P(O^{i}Pr)$_2$ anion chelates with the Cu(1) center (Mode I) (Figure 2). The 2-fold rotational axis passes through the Cu(1) and P(1) atoms. Interestingly, two chloride anions extracted from CH$_2$Cl$_2$ bridge two Cu centers, Cu(2) and Cu(2A) [Cu(2)−Cl(1) = 2.398(1) Å, Cu(2)−Cl-(1A) = 2.472(1) Å], to achieve tetracoordination for both Cu atoms. As before, the geometry around each Cu center is distorted tetrahedral. The Cu$_2$Cl$_2$ core does not lie in a plane but is bent with a dihedral angle of 17.07° between

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Table 2. Bond Lengths (Å) and Angles(deg) for Compounds 1−9[a]

compound 1							
Cu(1)−P(7)	2.2783(9)	Cu(2)−P(4)	2.2909(8)	P(7)−Cu(1)−P(2)	137.42(3)	P(3)−Cu(2)−P(4)	124.39(3)
Cu(1)−P(2)	2.2795(8)	Cu(2)−S(2)	2.3902(9)	P(7)−Cu(1)−Cl(1)	103.94(3)	P(3)−Cu(2)−S(2)	119.86(3)
Cu(1)−Cl(1)	2.4603(8)	Cu(2)−Cl(1)	2.4782(8)	P(2)−Cu(1)−Cl(1)	103.36(3)	P(4)−Cu(2)−S(2)	101.69(3)
Cu(1)−S(1)	2.4643(10)	Cu(3)−Cl(1)	2.4988(8)	P(7)−Cu(1)−S(1)	96.26(3)	P(3)−Cu(2)−Cl(1)	110.64(3)
Cu(2)−P(3)	2.2606(8)	Cu(3)−S(2)	2.3515(9)	P(2)−Cu(1)−S(1)	95.38(3)	P(4)−Cu(2)−Cl(1)	98.69(3)
P(1)−S(1)	1.9514(13)	P(1)−S(2)	2.0198(12)	Cl(1)−Cu(1)−S(1)	123.24(3)	S(1)−Cu(2)−Cl(1)	96.24(3)
				Cu(1)−Cl(1)−Cu(2)	92.21(3)	Cu(2)−Cl(1)−Cu(3)	76.57(2)
				Cu(1)−Cl(1)−Cu(3)	91.63(3)		
compound 2							
Cu(1)−P(3)	2.2256(13)	Cu(3)−S(1)	2.6968(14)	P(3)−Cu(1)−S(3)	122.42(5)	P(6)−Cu(3)−S(2)	108.69(6)
Cu(2)−P(5)	2.2120(12)	Cu(1)−S(3)	2.2676(13)	P(3)−Cu(1)−S(1)	131.03(5)	P(4)−Cu(3)−S(1)	114.40(4)
Cu(3)−P(4)	2.2694(13)	Cu(2)−S(4)	2.2629(14)	S(3)−Cu(1)−S(1)	106.39(5)	S(2)−Cu(3)−S(1)	81.35(5)
Cu(3)−P(6)	2.2760(14)	Cu(3)−S(2)	2.4697(15)	P(5)−Cu(2)−S(4)	128.10(5)	P(1)−S(1)−Cu(1)	116.25(6)
Cu(1)−S(1)	2.2785(13)	P(1)−S(1)	2.0369(16)	P(5)−Cu(2)−S(1)	123.12(5)	P(1)−S(1)−Cu(2)	121.26(7)
Cu(2)−S(1)	2.2873(13)	P(1)−S(2)	1.953(2)	S(4)−Cu(2)−S(1)	108.78(5)	Cu(1)−S(1)−Cu(2)	111.94(5)
P(2)−S(3)	1.982(2)	P(2)−S(4)	1.993(2)	P(4)−Cu(3)−P(6)	124.55(5)	Cu(2)−S(1)−Cu(3)	76.76(4)
				P(4)−Cu(3)−S(2)	100.94(5)	P(1)−S(1)−Cu(3)	75.64(6)
				P(6)−Cu(3)−S(1)	115.60(4)	Cu(1)−S(1)−Cu(3)	85.47(4)
compound 4							
Cu(1)−P(12)	2.2532(8)	Cu(4)−S(2)	2.3980(8)	P(12)−Cu(1)−S(1)	107.30(3)	P(10)−Cu(3)−S(2)	104.17(3)
Cu(1)−S(1)	2.307(8)	Cu(4)−S(3)	2.3358(8)	P(12)−Cu(1)−S(4)	114.10(3)	P(10)−Cu(3)−S(4)	116.44(3)
Cu(1)−S(4)	2.3714(8)	Cu(4)−S(5)	2.3479(9)	P(12)−Cu(1)−S(8)	109.79(3)	P(10)−Cu(3)−S(7)	105.21(3)
Cu(1)−S(8)	2.3462(8)	P(7)−S(4)	1.9907(10)	S(4)−Cu(1)−S(1)	113.73(3)	S(4)−Cu(3)−S(2)	111.66(3)
Cu(2)−S(1)	2.3926(8)	P(7)−S(3)	1.9962(11)	S(8)−Cu(1)−S(1)	105.41(3)	S(7)−Cu(3)−S(2)	114.90(3)
Cu(2)−S(3)	2.3334(8)	P(13)−S(1)	2.0005(11)	S(8)−Cu(1)−S(4)	106.13(3)	S(7)−Cu(3)−S(4)	104.66(3)
Cu(2)−S(6)	2.3579(9)	P(13)−S(2)	2.0076(10)	P(9)−Cu(2)−S(1)	103.29(3)	P(14)−Cu(4)−S(2)	106.28(3)
Cu(3)−P(10)	2.2499(9)	P(17)−S(8)	1.9825(12)	P(9)−Cu(2)−S(3)	113.66(3)	P(14)−Cu(4)−S(3)	115.95(3)
Cu(3)−S(7)	2.3393(8)	P(17)−S(7)	1.9896(12)	P(9)−Cu(2)−S(6)	106.07(3)	P(14)−Cu(4)−S(5)	108.89(3)
Cu(3)−S(4)	2.3450(9)	P(19)−S(5)	1.9730(12)	S(3)−Cu(2)−S(1)	116.60(3)	S(3)−Cu(4)−S(2)	114.85(3)
Cu(4)−P(14)	2.2656(8)	P(19)−S(6)	1.9915(12)	S(3)−Cu(2)−S(6)	105.79(3)	S(3)−Cu(4)−S(5)	105.33(3)
				S(6)−Cu(2)−S(1)	111.08(3)	S(5)−Cu(4)−S(2)	104.90(3)
compound 5							
Cu(1)−P(5)	2.2276(18)	Cu(2)−S(5)	2.2675(19)	P(5)−Cu(1)−S(3)	106.33(7)	S(3)−Cu(1)−Cl(1)	100.08(6)
Cu(1)−S(3)	2.3444(19)	Cu(2)···Cu(4)	3.0238(12)	P(5)−Cu(1)−S(1)	115.49(6)	S(1)−Cu(1)−Cl(1)	100.48(5)
Cu(1)−S(1)	2.3531(17)	Cu(3)−P(7)	2.2370(17)	S(3)−Cu(1)−S(1)	109.02(6)	P(7)−Cu(3)−S(6)	97.11(6)
Cu(1)−Cl(1)	2.5029(17)	Cu(3)−S(4)	2.2925(17)	P(5)−Cu(1)−Cl(1)	123.93(6)	S(4)−Cu(3)−S(6)	109.14(6)
Cu(2)−S(4)	2.2551(17)	Cu(3)−S(6)	2.4008(19)	S(4)−Cu(2)−S(1)	122.32(6)	P(7)−Cu(3)−Cl(1)	116.11(6)
Cu(2)−S(1)	2.2624(17)	Cu(3)−Cl(1)	2.7078(18)	S(4)−Cu(2)−S(5)	115.77(6)	S(4)−Cu(3)−Cl(1)	98.85(5)
Cu(4)−S(7)	2.2466(17)	Cu(2)−S(2)	2.2501(17)	S(1)−Cu(2)−S(5)	119.17(6)	S(6)−Cu(3)−Cl(1)	101.05(5)
Cu(4)−S(5)	2.2648(17)	Cu(5)−P(8)	2.2446(16)	P(7)−Cu(3)−S(4)	131.04(6)		
Cu(5)−S(7)	2.2948(18)	Cu(5)−S(6)	2.4811(17)				
Cu(6)−P(6)	2.2360(18)	Cu(6)−S(8)	2.3338(19)				
Cu(6)−S(2)	2.4263(17)	Cu(3)···Cu(5)	2.9971(13)				
Cu(5)−Cl(1)	2.6955(18)	Cu(6)−Cl(1)	2.5894(17)				
S(1)−P(1)	2.0195(19)	S(2)−P(1)	2.0049(19)				
S(3)−P(2)	1.951(2)	S(4)−P(2)	2.022(2)				
S(5)−P(3)	2.010(2)	S(6)−P(3)	2.002(2)				
S(7)−P(4)	2.035(3)	S(8)−P(4)	1.934(3)				
compound 6							
Cu(1)−P(1)	2.2726(9)	Cu(1)−S(1)	2.3990(11)	P(1)−Cu(1)−P(2)	111.00(4)	P(2)−Cu(1)−S(2)	106.35(4)
Cu(1)−P(2)	2.2748(10)	Cu(1)−S(2)	2.5070(10)	P(1)−Cu(1)−S(1)	121.15(4)	P(1)−Cu(1)−S(2)	104.76(4)
S(1)−P(3)	1.9776(13)	S(2)−P(3)	1.9815(14)	P(2)−Cu(1)−S(1)	122.13(4)	S(1)−Cu(1)−S(2)	83.89(4)
compound 7							
Cu(1)−P(3)	2.291(2)	Cu(1)−S(1)	2.466(2)	P(3)−Cu(1)−P(2)	112.32(7)	P(3)−Cu(1)−S(1)	112.59(8)
Cu(1)−P(2)	2.297(2)	Cu(1)−S(2)	2.451(2)	P(3)−Cu(1)−S(2)	114.49(8)	P(2)−Cu(1)−S(1)	112.62(8)
S(1)−P(1)	1.979(3)	S(2)−P(1)	1.964(3)	P(2)−Cu(1)−S(2)	117.82(8)	S(1)−Cu(1)−S(2)	84.03(8)
compound 9							
Cu(1)−P(2)	2.2626(10)	Cu(2)−Cl(1)	2.3976(10)	P(3)−Cu(2)−P(4)	127.44(4)	P(2)#1−Cu(1)−S(1)	113.17(4)
Cu(2)−P(3)	2.2551(9)	Cu(2)−Cl(1)#1	2.4715(9)	P(3)−Cu(2)−Cl(1)	107.85(3)	P(2)#1−Cu(1)−P(2)	114.89(5)
Cu(2)−P(4)	2.2606(9)	S(1)−P(1)	1.9656(15)	P(4)−Cu(2)−Cl(1)	111.15(3)	P(2)−Cu(1)−S(1)	114.47(4)
Cu(1)−S(1)	2.4615(11)			P(3)−Cu(2)−Cl(1)#1	111.88(3)	S(1)−Cu(1)−S(1)#1	82.72(6)
				P(4)−Cu(2)−Cl(1)#1	99.05(3)	Cu(2)−Cl(1)−Cu(2)#1	83.34(3)
				Cl(1)−Cu(2)−Cl(1)#1	94.17(3)		

[a] Symmetry transformations used to generate equivalent atoms: #1 −x, y, −z + 1/2.

the planes formed by Cu(2), Cl(1), and Cl(1A) and Cu(2A), Cl(1), and Cl(1A). The structure of 9 is analogous to that of Cu$_3$I$_3$(dppe)$_3$(2-SC$_5$H$_4$NH).[28]

In cluster 2, two sides of the Cu$_3$ triangle are bridged by dppm ligands and the third side is bridged by a dtp anion (Mode II) (Figure 3). The second dtp anion exhibits mode
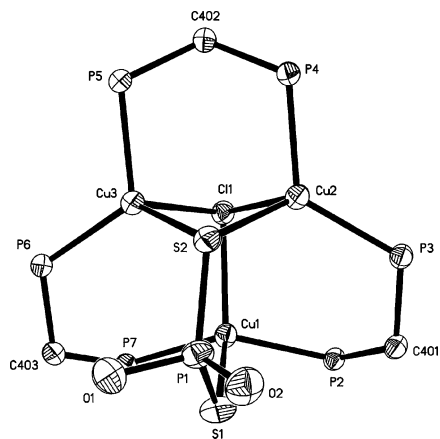
Figure 1. Thermal ellipsoid drawing (30% probability level) of **1** with atomic numbering scheme (with phenyl rings and ethyl groups omitted for clarity).
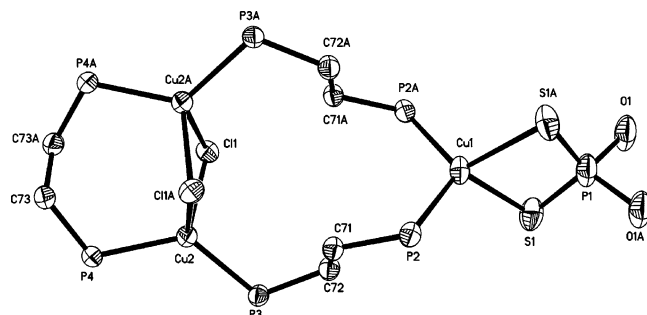

Figure 2. Thermal ellipsoid drawing (30% probability level) of **9** with atomic numbering scheme (with phenyl rings and isopropyl groups omitted for clarity).
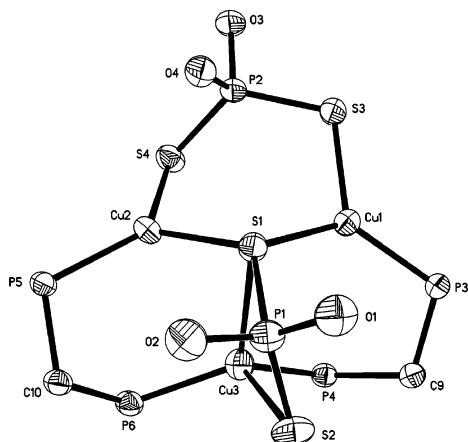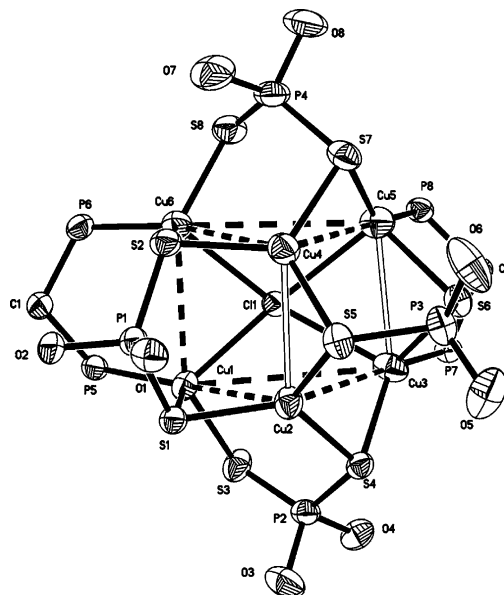

Figure 3. Thermal ellipsoid drawing (30% probability level) of **2** with atomic numbering scheme (with phenyl rings and alkyl groups omitted for clarity). The structure of **3** is similar.

VI of bonding, and replacing CH_2Cl_2 with THF stabilized trinuclear cluster **2** with two different geometries around the Cu centers. The geometry around each Cu(1) and Cu(2) center is distorted trigonal planar [106.39(5)−131.03(5)°] and that around the Cu(3) center is distorted tetrahedral (ca. 81−124°). The angles around the triply bridging sulfur atom of the dtp ligand are in the range of 75.64(6)−121.26(7)° (Table 2). The Cu−(μ_3-S) bond lengths are unequal and Cu(3)−S(1) distance, 2.6968(14) Å, is quite long, even exceeding 2.589(2)Å of the Cu−(μ_3-S) bond as determined from one

Figure 4. Thermal ellipsoid drawing (30% probability level) of **5** with atomic numbering scheme (with phenyl rings and isopropyl groups omitted for clarity).

of the monothiocarboxylato moieties in [$Cu_3(\mu$-dppm)$_3${μ_3-SC(O)Ph-*S*}{μ_3-SC(O)Ph-*S, O*}](ClO$_4$).[39]

Cluster **5** exhibits a trigonal prismatic arrangement of Cu$_6$ atoms; two dppm ligands bridge the two opposite sides of the tetragonal plane formed by the Cu1, Cu3, Cu5, and Cu6 atoms (Figure 4). Two dtp ligands bridge the top (Cu1, Cu2, Cu3) and bottom (Cu4, Cu5, Cu6) triangles of the prism, in tridentate mode IV. The other two dtp ligands act as tetradentates (Mode VII) and bind to four Cu atoms, each along the tetragonal planes formed by Cu1, Cu2, Cu4, and Cu6 and Cu2, Cu3, Cu5, and Cu4 atoms. Four copper atoms, Cu1, Cu3, Cu5, and Cu6, complete tetracoordination by abstracting a single chloride from the solvent; this chloride in fact caps (μ_4-Cl) the tetragonal plane. The Cu−μ_4-Cl bond lengths (mean 2.624; 2.503−2.708 Å) exceed the sum of covalent radii, 2.58 Å.[18d] The other two tricoordinated copper atoms, Cu2 and Cu4, form a relatively close Cu···Cu contact with a length 3.024(1) Å. Another close contact is between Cu3 and Cu5 [2.997(1) Å], but both of these contacts are longer than the sum of the van der Waals radii of the Cu atom, 2.80 Å.[18d]

The trigonal-prismatic metal core observed in **5** is extremely unusual in cluster chemistry. Most hexanuclear clusters or cage molecules prefer an octahedral metal core over a trigonal prismatic core. However, M$_6$ clusters that contain interstitial main group elements such as [$M_6(\mu_6$-C)(CO)$_{15}$]$^{2-}$ (M = Co, Rh),[40] [$M_6(\mu_6$-N)(CO)$_{15}$]$^-$ (M = Co, Rh),[41] [$Os_6(\mu_6$-P)(CO)$_{18}$]$^-$,[42] and [$H_2Ru_6(\mu_6$-B)(CO)$_{18}$]$^{-43}$ do

(39) Deivaraj. T. C.; Vittal, J. J. *J. Chem. Soc., Dalton Trans.* **2001**, 322.
(40) Martinengo, S.; Strumolo, D.; Chini, P.; Albano, V. G.; Braga, D. *J. Chem. Soc., Dalton Trans.* **1985**, 35. (b) Albano, V. G.; Sansoni, M.; Chini, P.; Martinengo, S. *J. Chem. Soc., Dalton Trans.* **1973**, 651.
(41) Martinengo, S.; Ciani, G.; Sironi, A.; Heaton, B. T.; Masion, J. *J. Am. Chem. Soc.* **1979**, *101*, 7095. (b) Bonfichi, R.; Ciani, G.; Sironi, A.; Martinengo, S. *J. Chem. Soc., Dalton Trans.* **1983**, 253.
(42) Colbran, S. P.; Lahor, F. J.; Raithby, P. R.; Lewis, J.; Johnson, B. F. G.; Cardin, C. J. *J. Chem. Soc., Dalton Trans.* **1988**, 173.
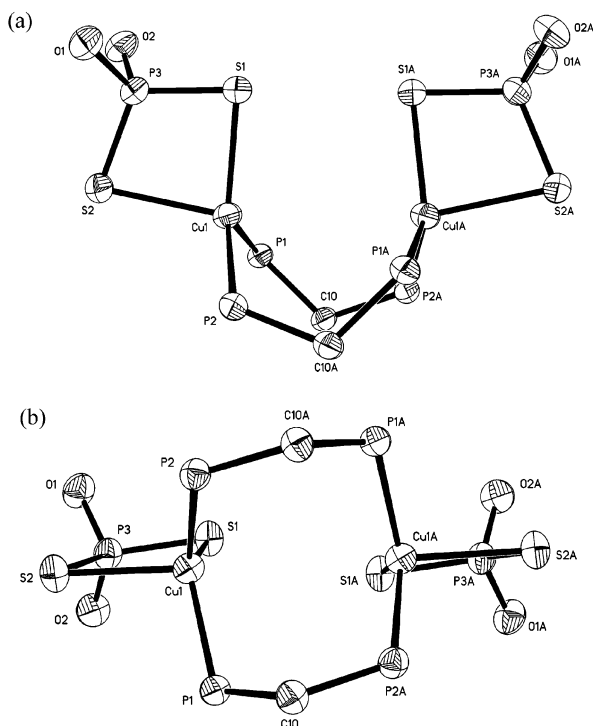
(a)

(b)

Figure 5. Thermal ellipsoid drawing (30% probability level) of **6** with atomic numbering scheme (with phenyl rings and ethyl groups omitted for clarity).

exhibit a trigonal-prismatic arrangement of six metal atoms. $[(\eta^3\text{-}C_4H_7)_6Pd_6Se_3]$ contains a slightly distorted Pd_6 trigonal prism whose Pd_4 tetragonal faces are capped by μ_4-Se ligands.[44] The anionic cluster, $[Cu_6(\mu_3\text{-phenylimido})_2(\mu\text{-phenyamido})_3]^-$,[45] also has a trigonal-prismatic Cu_6 core whose two triangular faces are capped by imido ligands. Therefore compound **5** is the first neutral M_6 cluster in which a chloro (μ_4-Cl) and four dtp ligands cap all five faces of a trigonal prism.

Dinuclear 6, Cluster 4, and Polymer 7. Dinuclear compound **6** has bridging dppm and chelating dtp ligands with tetracoordinated Cu atoms. The lattice contains one CH_2Cl_2 molecule. The eight-membered ring, consisting of two bridging dppm ligands and two copper atoms adopts the boat conformation, as shown in Figure 5a. The angles at Cu vary over a wide range: the S−Cu−S angle is the smallest and the other angles lie in a wide range, ca. 104−122° (Table 2), and the geometry is distorted tetrahedral (Figure 5). The literature reports similar P,P-bridged dimers with the dithiocarboxylate ligand, $[Cu_2(\mu\text{-dppm})_2\{S_2C\text{−}C_6H_4\text{-X }\}_2](X= H, o\text{-}, m\text{-}, \text{and } p\text{-CH}_3)$.[46]

In cluster **4**, four copper atoms forms a tetragon with sides that are alternatively bridged by dppm and dtp ligands in the two-up and two-down conformation (Figure 6). Thus each
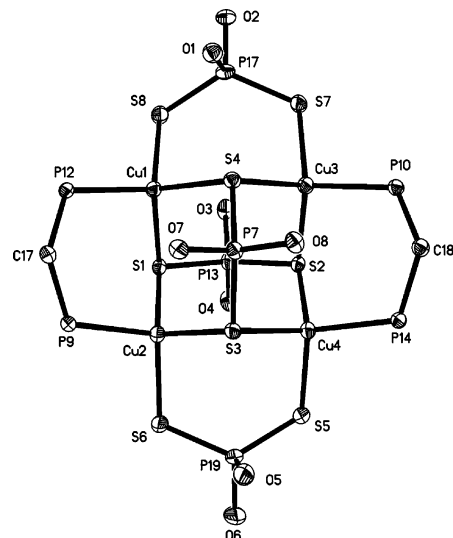
(43) Housecroft, C. E.; Matthews, D. M.; Rheingold, A. L.; Song, X. *J. Chem. Soc., Chem. Comm.* **1992**, 842.

(44) Fenske, D.; Hollnagel, A.; Merzweiler, K. *Z. Naturforsch., B: Chem. Sci.* **1988**, *43*, 634.

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(46) (a) Manotti, L.; Anna, M.; Ugozzli, F.; Camus, A.; Marsich, N. *Inorg. Chim. Acta* **1985**, *99*, 111. (b) Camus, A.; Marsich, N.; Pellizer, G. *J. Organomet. Chem.* **1983**, *259*, 367. (c) Pellizer, G.; Marsich, N.; Camus, A. *Inorg. Chim. Acta* **1989**, *155*, 167.

Figure 6. Thermal ellipsoid drawing (30% probability level) of **4** with atomic numbering scheme (with phenyl rings and ethyl groups omitted for clarity).
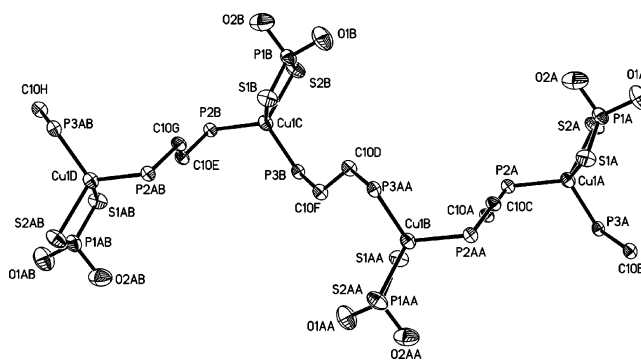

Figure 7. Thermal ellipsoid drawing (30% probability level) of **7** with atomic numbering scheme (with phenyl rings and alkyl groups omitted for clarity). The structure of **8** is similar.

Cu atom is bonded to one P and three S atoms. The other two dtp ligands bond to the four Cu atoms by the front and back face of the square, according to bonding mode VII. The angles around the Cu centers lie in the range of 103−116°, forming a shape that was closer to the tetrahedron than the several near-tetragonal copper centers discussed above. No close Cu···Cu contact is shorter than ca. 3.50 Å. The core geometry in **4** is similar to those of $[Cu_4(dppm)_4\{S_2CC(CN)P(O)(OEt)_2\}_2]$[47] and $[Cu_4(dppm)_4(CS_3)_2]$.[48]

In polymers **7** and **8**, dtp ligands chelate to Cu centers, and dppe serves as a bridging ligand; CH_2Cl_2 molecules are present in the lattice. Because of the difference in the number of CH_2 groups connecting the Ph_2P moieties in dppm and dppe, the latter ligand formed the polymers and trinuclear cluster **9**, obtained at low yield. The geometry around each Cu center is distorted tetrahedral and the zigzag chain structure (Figure 7) is similar that of its silver analogues, $[Ag(dppe)\{S_2P(OR)_2\}]_n$.[17]

Table 2 demonstrates that the mean P−(μ_3-S) bond length (2.038(2) Å) of all complexes that exhibit μ_3-S bonding

(47) Liu, C. W.; Liaw, B. J.; Wang, J. C.; Liou, L. S.; Keng, T. C. *J. Chem. Soc., Dalton Trans.* **2002**, 1058.

(48) Lanfredi, A. M. M.; Tiripicchio, A.; Camus, A.; Marish, N. *J. Chem. Soc., Chem. Comm.* **1983**, 1126.

exceeds that of those with P$-(\mu_2$-S) bonding (2.004(2) Å), which in turn exceeds that of those with P$-(\eta^1$-S) bonding (1.968(2) Å).

NMR Spectroscopy. The proton NMR data of compounds **1**−**9** show peaks attributed to the ethyl and isopropyl groups of dtp and the $-(CH_2)-$ and phenyl groups of dppm and dppe in their characteristic groups, as indicated in the Experimental Section. ^{31}P NMR spectroscopy is more interesting and provides valuable information about the complexes. The spectrum of **1** includes a sharp peak at 94.35 ppm because of $-S_2P(OEt)_2$ with a upfield coordination shift ($\Delta\delta = \delta_{Complex} - \delta_{Ligand(S_2P)}$) of −20.45 ppm relative to the dtp ligand itself. The dppm component undergoes a downfield coordination shift ($\Delta\delta = \delta_{Complex} - \delta_{Ligand(Ph_2P)}$) of 3.52 ppm. Other compounds, **2**−**9**, showed coordination shifts in the range of −16.5 to −22.5 ppm for $S_2P(OR)_2$ groups; dppm/dppe components revealed the coordination shift ranges: (i) 3.5−7.5 ppm for **1**−**5**, (ii) 0.07−2.12 ppm for **6**−**8**, and (iii) 21.5 ppm for **9**. Complexes **2** and **3** have two types of copper atoms so PPh$_2$ groups are expected to be in the form of a pair of doublet of doublets in each case; however, the lack of resolution causes the peaks to appear as a partially resolved broad triplet for **3** and a well resolved broad triplet for **2**. Likewise, unresolved broad signals from the $-S_2P(OR)_2$ groups were obtained. The spectrum of **4** also shows broad signals for both types of ligands, revealing that in solution it probably dissociates and more than one species, the identities of which are not yet clear, are present. Two types of dtp groups in compound 5 show clear sharp signals in each type at 92.68 and 97.67 ppm. Thus, complex

5 exhibits remarkable stability in solution and its structure matches well with that in the solid state. Polymers **7** and **8** show singlet but somewhat broad signals for the dtp and dppe ligands. Finally, cluster **9** exhibits a very broad signal associated with dppe resulting from unresolved peaks from different chemical environments of this ligand, and the $-S_2P(O^iPr)_2$ group showed a very sharp signal. However, the large coordination shift for the dppe component ($\Delta\delta = \delta_{Complex} - \delta_{Ligand(PPh_2)} = 21.46$ ppm) implies that this ligand binds copper atoms very strongly and appears to be responsible for the stability of such triangular clusters.[28]

In conclusion, dithiosphosphates in copper(I) compounds **1**−**9** exhibit a variety of coordination modes. The modes, with the corresponding compounds in parentheses, are as follows: Mode I (**6**−**9**), Mode II (**2**−**4**), Mode IV (**1, 5**), Mode VI (**2, 3**), and Mode VII (**4, 5**). Clusters **2** and **3** exhibit a μ_3-S bonding for dtp. This finding is the first of its kind in copper chemistry. The ratio of metal salt to dtp ligand appears to affect the abstraction of a chloride ion from the CH$_2$Cl$_2$ or CHCl$_3$ solvent. Cluster **5** with the capping of the tetragonal face of the trigonal prism by μ_4-Cl, is a rare structure in cluster chemistry.

Supporting Information Available: X-ray crystallographic files in CIF format for compounds **1**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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