Coinage Metal Coordination Chemistry of Stable Primary, Secondary and Tertiary Ferrocenylethyl-Based Phosphines

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Coinage Metal Coordination Chemistry of Stable Primary, Secondary and Tertiary Ferrocenylethyl-Based Phosphines†

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Ferrocene-based phosphines constitute an important auxiliary ligand in inorganic chemistry. Utilizing the (ferrocenylethyl)phosphines (FcCH$_2$CH$_2$)$_{3\text{-}n}$H$_n$P (Fc = ferrocenyl; n = 2, **1**; n = 1, **2**; n = 0, **3**) the synthesis of a series of coordination complexes [(FcCH$_2$CH$_2$)$_{3\text{-}n}$H$_n$PCuCl]$_4$ (n = 2, **1-CuCl**; n = 0, **3-CuCl**), [(FcCH$_2$CH$_2$)$_2$HPCuCl] (**2-CuCl**), {[(FcCH$_2$CH$_2$)H$_2$P]$_2$AgCl}$_2$ (**1-AgCl**), [(FcCH$_2$CH$_2$)$_2$HPAgCl] (**2-AgCl**), [(FcCH$_2$CH$_2$)$_3$PAgCl]$_4$ (**3-AgCl**), [(FcCH$_2$CH$_2$)$_3$PM(OAc)]$_4$ (M = Cu, **3-CuOAc** M = Ag, **3-AgOAc**), [(FcCH$_2$CH$_2$)$_{3\text{-}n}$H$_n$PAuCl] (n = 1, **2-AuCl**; n = 0, **3-AuCl**), via the reaction between the free phosphine and MX (M = Cu, Ag and Au; X = Cl, OAc), is described. The reaction between the respective phosphine with a suspension of metal-chloride or -acetate in a 1:1 ratio in THF at ambient temperature affords coordinated phosphine-coinage metal complexes. Varying structural motifs are observed in the solid state, as determined via single crystal X-ray analysis of **1-CuCl**, **3-CuCl**, **1-AgCl**, **3-AgCl**, **3-CuOAc**, **3-AgOAc**, **2-AuCl** and **3-AuCl**. Complexes **1-CuCl** and **3-CuCl** are tetrameric Cu(I) cubane-like structures with a Cu$_4$Cl$_4$ core, whereas silver complexes with primary and tertiary phosphine reveal two different structural types. The structure of **1-AgCl**, unlike the rest, displays the coordination of two phosphines to each silver atom and shows a quadrangle defined by two Ag and two Cl atoms. In contrast, **3-AgCl** is distorted from a cubane structure via elongation of one of the Cl···Ag distances. **3-CuOAc** and **3-AgOAc** are isostructural with step-like cores, while complexes **2-AuCl** and **3-AuCl** reveal a linear geometry of a phosphine gold(I) chloride devoid of any aurophilic interactions. All of the complexes were characterized in solution by multinuclear ^{1}H, ^{13}C{^{1}H} and ^{31}P NMR spectroscopic techniques; the redox chemistry of the series of complexes was examined using cyclic voltammetry. This class of complexes has been found to exhibit one reversible Fe(II)/Fe(III) oxidation couple, suggesting the absence of electronic communication between the ferrocenyl units on individual phosphine ligands as well as between different phosphines on the polymetallic cores.

Introduction

While there is extensive literature that deals with the coordination chemistry of *tertiary* phosphines with coinage metal complexes, primary and secondary phosphines have been less employed in the syntheses of similar complexes.[1],[2],[3] This may be due in part to the toxicity, high reactivity and air-sensitive nature of R$_2$PH and RPH$_2$. Only a few coinage metal species containing secondary phosphines are known[4] and similarly, despite an impressive range of applications of primary phosphines as asymmetric ligand precursors,[5] biomedicines,[6] polymers,[7] and macrocycles,[8] their coordination chemistry still remains under-developed. Recently, there has been burgeoning interest in the development of some remarkably air-stable primary phosphines.[9] In this regard introducing the ferrocenyl fragment to the primary phosphine ligand by means of a saturated alkyl linker can provide air stability to the phosphine.[10] Additionally, the ferrocenyl moiety can play a significant role as a backbone or substituent in phosphine ligands introducing: (i) specific and unique geometries (flexibility and sterics), (ii) electronic (redox) properties (electron rich), and (iii) relative ease of derivatization.[11]

Currently, a large number of coinage metal complexes and clusters incorporating ferrocene-containing phosphines are known, including coinage metal chalcogenides.[12] In most of these ligands the phosphine group is linked directly by a P-C bond to the cyclopentadienyl ring of the ferrocene.[13] In contrast, the coordination chemistry of ferrocenyl phosphines derivatives in which the phosphorus atom is not directly bonded to the cyclopentadienyl ring is rare.[14] The (ferrocenylmethyl)phosphine, FcCH$_2$PH$_2$, a primary alkyl phosphine that is air stable both in the solid and solution states, was first reported by Henderson's group.[10a] A few molybdenum,[10a, 15] tungsten,[15-16] ruthenium[10b, 17] and rhenium[18] coordination compounds incorporating this phosphine have been reported. Englert and Mastrorilli showed the reactivity of FcCH$_2$PH$_2$ toward Pd and Pt chlorides, which led to the novel Pd(II) and Pt(II) tetramers of the general formula [M(PH$_2$CH$_2$Fc)Cl(μ-PHCH$_2$Fc)]$_4$ (M = Pd, Pt) via activation of P-H bonds.[19] The reactive character of the primary phosphines via the cleavage of the P-H bond upon metal coordination permits chemical flexibility in the synthesis of transition metal phosphinidene complexes. Recently Yam and co-workers have reported a series of hexanuclear gold(I) μ_3-(ferrocenylmethyl)phosphinidene complexes stabilized by bidentate phosphines through the reaction of the deprotonated primary (ferrocenylmethyl)phosphine FcCH$_2$PH$_2$ with (P$^\cap$P)Au$_2$Cl$_2$.[20] Hey-Hawkins and co-workers extended this chemistry to the sterically demanding, air-stable, secondary

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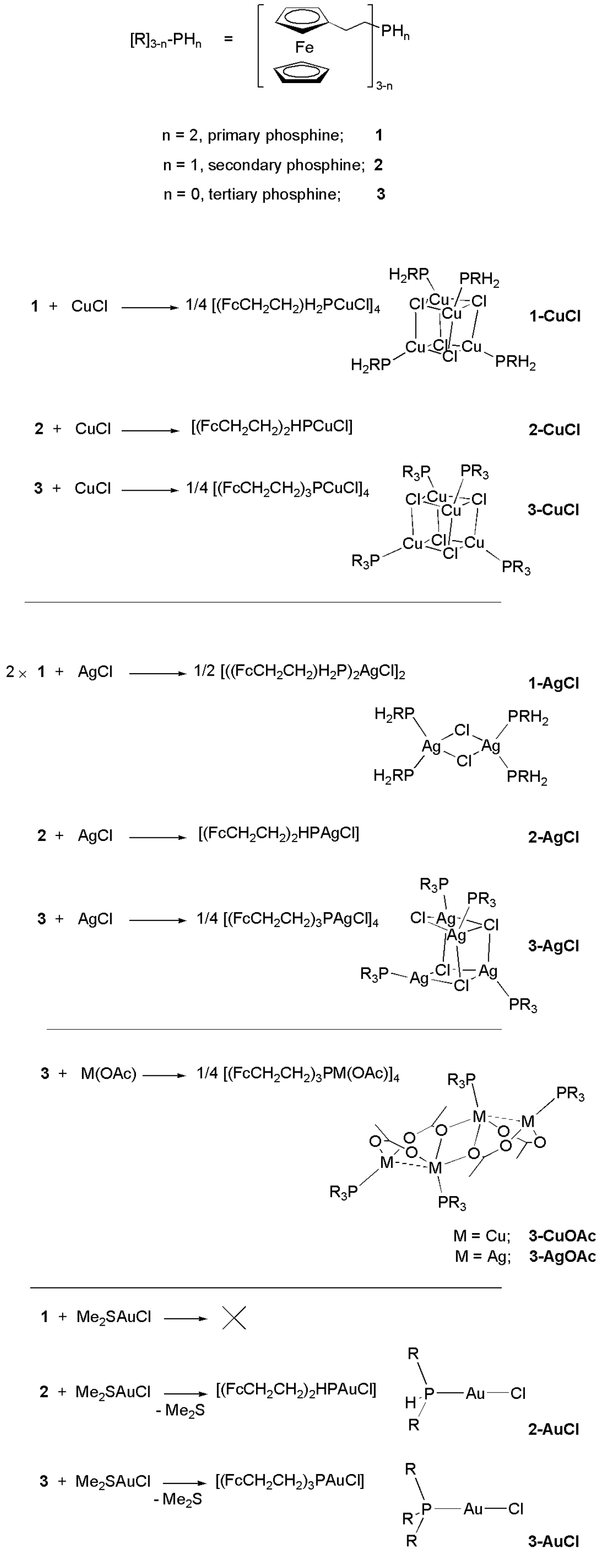
† Electronic Supplementary Information (ESI) available: X-ray crystallographic data for complexes **1-CuCl**, **3-CuCl**, **1-AgCl**, **3-AgCl**, **3-CuOAc**, **3-AgOAc**, **2-AuCl** and **3-AuCl** in CIF format, molecular structure of **3-AgOAc** and cyclic voltammograms for complexes **1-CuCl**, **3-CuCl**, **1-AgCl**, **3-AgCl**, **3-CuOAc** and **3-AgOAc**. See DOI: 10.1039/x0xx00000x

$PH(CH_2Fc)_2$ and tertiary $P(CH_2Fc)_3$ (ferrocenylmethyl)phosphines, from the reaction between $P(CH_2OH)_3$ and $[FcCH_2NMe_3]I$ in a multistep procedure.[21] The synthesis of the primary, secondary and tertiary (ferrocenylmethyl)phosphines $[(FcCH_2)_{3-n}H_nP$, n = 0, 1, 2] series has been reinvestigated by the Glueck group, although their coordination potential remains little explored.[22]

Applying the longer $-CH_2CH_2-$ as a spacer between ferrocene and phosphorus, the high yield synthesis of primary, secondary, and tertiary (ferrocenylethyl)phosphine $[(FcCH_2CH_2)_{3-n}H_nP$ (n = 2, n = 1, n = 0, respectively)] was described recently, prepared via the radical-catalyzed hydrophosphination of vinylferrocene.[23] The tertiary phosphine $(FcCH_2CH_2)_3P$ was used to produce metal-containing phosphonium, redox-active polyelectrolytes.[23a] Henderson and co-workers have already reported the synthesis of the primary phosphine $(FcCH_2CH_2)PH_2$ through methylation of phosphonic acid $FcCH_2CH_2P(O)(OH)_2$ with excess diazomethane CH_2N_2, followed by $LiAlH_4/Me_3SiCl$ reduction.[10b] The coordination behaviour of these ferrocene-based phosphines has not yet been studied and we are particularly interested in exploring their simple coordination chemistry with d-block metals. The straightforward preparation of $(FcCH_2CH_2)_{3-n}H_nP$ (n = 2 **1**, n = 1 **2**, n = 0 **3**) permits a systematic investigation of the ligand chemistry of this class of phosphine with the Group 11 coinage metals Cu(I), Ag(I) and Au(I). The preparation of such basic coordination complexes can form the foundation for poly(ferrocenylphosphine) stabilized semiconductor nanocluster materials via subsequent reactions with chalcogen reagents..[24] The detailed preparation, structural characterization, spectroscopic behaviour and electrochemical properties of an extended series of Cu(I), Ag(I) and Au(I) ligated to **1**-**3** are described.

Results and Discussion

All complexes were obtained from the direct treatment of a phosphine solution with a metal salt suspended in an organic solvent, yielding various structures in the solid state based on the metal(I) source used as well as the 1° (**1**), 2° (**2**) or 3° (**3**) nature of the phosphine (Scheme 1). Thus the 1:1 reaction of the (ferrocenylethyl)phosphines with a suspension of copper chloride in tetrahydrofuran leads to the solubilisation of copper salts through coordination and yields $[(FcCH_2CH_2)H_2PCuCl]_4$ **1-CuCl**, $[(FcCH_2CH_2)_2HPCuCl]$ **2-CuCl** and $[(FcCH_2CH_2)_3PCuCl]_4$ **3-CuCl**, respectively. Similar reactions with silver chloride proceed over longer periods of time to yield $\{[(FcCH_2CH_2)H_2P]_2AgCl\}_2$ **1-AgCl**, $[(FcCH_2CH_2)_2HPAgCl]$ **2-AgCl** and $[(FcCH_2CH_2)_3PAgCl]_4$ **3-AgCl**. In the case of the tertiary phosphine $(FcCH_2CH_2)_3P$, it can be reacted with Cu(OAc) and Ag(OAc) to yield isostructural $[(FcCH_2CH_2)_3PMOAc]_4$ (M = Cu, **3-CuOAc**; M = Ag, **3-AgOAc**). Attempts at similar reactions with the primary or secondary phosphines **1** and **2** do not lead to selective complex formation, likely due to P-H bond breaking reactions; these were not pursued further due to the formation of complex reaction mixtures. Similarly, although the reaction of chloro(dimethylsulfide)gold(I) with **2** or **3** yields $[(FcCH_2CH_2)_2HPAuCl]$ **2-AuCl** and $[(FcCH_2CH_2)_3PAuCl]$ **3-AuCl**, respectively whereas similar treatment of $(Me_2S)AuCl$ with **1** does not proceed selectively and was not pursued further. Eight molecular structures emerged from the



Scheme 1 Synthesis and schematic representation of crystallographically determined structures.

current study. Crystal data and the details of the structure determinations are summarized in Table S1. Selected bond lengths and bond angles are given in Tables S2 and S3. All attempts to grow suitable crystals from **2-CuCl** and **2-AgCl** failed. Although these complexes have not been characterized by X-ray diffraction, elemental analyses are consistent with the expected chemical formula of a 1:1 phosphine-to-metal ratio. The ^{1}H, $^{13}C\{^{1}H\}$ and proton coupled ^{31}P NMR spectral data of complexes **1-CuCl**, **2-CuCl**, **3-CuCl**, **1-AgCl**, **2-AgCl**, **3-AgCl**, **3-CuOAc**, **3-AgOAc**, **2-AuCl**, **3-AuCl** and the free phosphines are summarized in Table 1.

Coinage metal phosphine complexes with a d^{10} electronic configuration of the type $(R/Ar/H)_nP\text{-}M\text{-}X$ (n = 3) (M = Cu, Ag, Au, X = halide, acetate etc.) have a remarkable tendency to form a range of fascinating architectures and clusters[25] relating to the d^{10} closed-shell metallophilic attraction and their ability to adopt variable nuclearities.[26] When coinage metal halides and acetates are combined with monodentate phosphine ligands, halide[27] and acetate[28] bridging interactions produce a wide array of cluster structural types. These complexes are frequently found to aggregate in the solid state into dimers or higher molecular species, which are produced by increasing the coordination number of the metal centres via additional metal-halogen or metal-oxygen bonds.[29] Previous results have shown that the coordination mode of the halide centers is controlled in part by the metal-to-PR_3 ratio as well as steric considerations.[30]

Single crystals of **1-CuCl** and **3-CuCl** were obtained by diffusion of a hydrocarbon solvent, at ambient temperature, into their reaction solutions. **1-CuCl** and **3-CuCl** crystallize in the monoclinic space groups *C*2/*c* and triclinic $P\bar{1}$, respectively. X-ray crystallographic determination of these two complexes revealed two distorted cubane-like tetrameric $(P\text{-}Cu)_4C1_4$ frameworks for both complexes, with the alternating corners of the cubes being occupied by copper and chlorine, and with each phosphorus atom projecting radially from a copper center (Figures 1 and 2). In other words each copper(I) has a distorted Cl_3P tetrahedral coordination environment. Such a heterocubane structure is well-known for both phosphine and phosphite complexes of copper(I) halides.[31]

Despite the approximate tetrahedral symmetry imparted by the cubane frameworks in **3-CuCl**, the cluster lacks such symmetry elements and it crystallizes with two crystallographically independent molecules in the asymmetric unit. In the case of **1-CuCl**, one of the two cubane units has an exact C_2 symmetry, residing on this crystallographic symmetry element. In both structures each tetranuclear copper(I) complex produces an 18-electron configuration at each copper atom. The Cu···Cu separations vary from 2.972(1) to 3.294(1) Å for **1-CuCl** compared to 3.139(1)–3.348(2) Å for **3-CuCl**. These distances are sufficiently longer than the sum of the van der Waals radii (2.80 Å) to preclude the possibility of any significant direct Cu···Cu interaction.[31b, 32] The averages of the Cu-Cl bond lengths (**1-CuCl**; 2.446 Å, **3-CuCl**; 2.438 Å) are in good agreement with previously reported cubane-like $[(L\text{-}Cu)_4(\mu_3\text{-}Cl)_4]$ clusters (L = PR_3).[32] Angles within the Cu_4Cl_4 cube vary significantly from the idealized value of 90°. The Cl-Cu-Cl angles range from 88.00(6)° to 106.64(6)° for **1-CuCl** and from 91.16(3)° to 102.93(3)° for **3-CuCl**, whereas the Cu-Cl-Cu angles are smaller and range from 72.23(5)° to 88.86(6)° for **1-CuCl** and from 78.02(3)° to 88.14(3)° for **3-CuCl**.

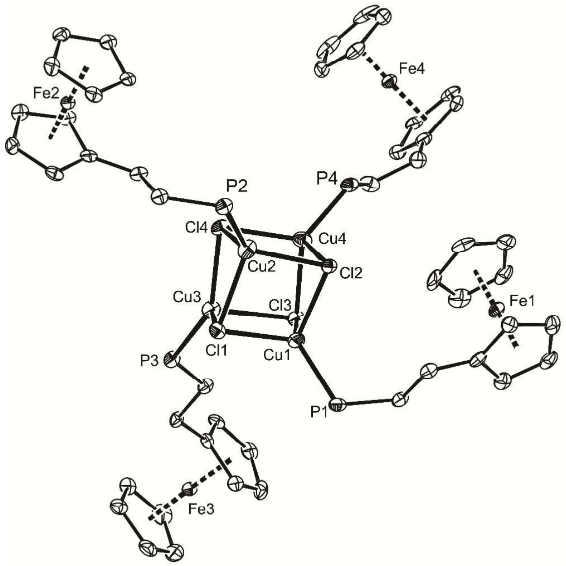


Fig. 1. ORTEP plot of the molecular structure of complex **1-CuCl** (40% probability, hydrogen atoms are omitted for clarity).

The phosphine ligands show varying cone angles in the solid state, due to the flexibility of ethylferrocene and differing rotation of the pendant ferrocenyl groups which direct away from the

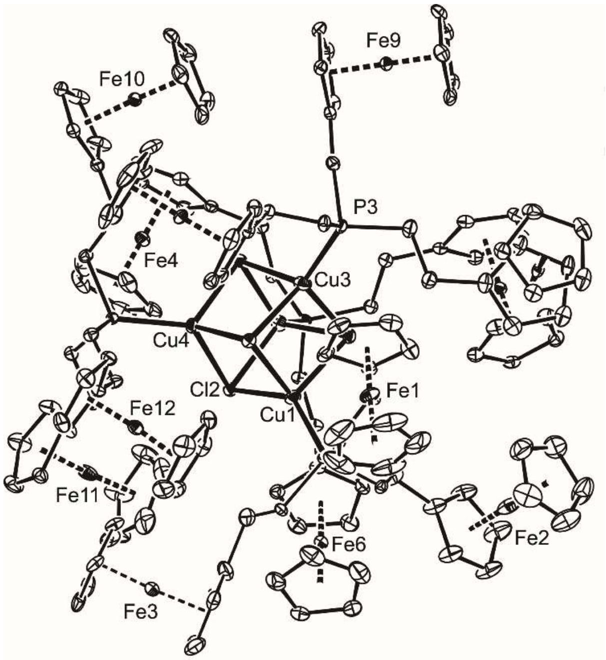


Fig. 2. ORTEP plot of the molecular structure of complex **3-CuCl** (40% probability, hydrogen atoms are omitted for clarity).

Cu_4Cl_4 cores [**1-CuCl**; 58-69°, **3-CuCl**; 155-190°][33]. The P–Cu bond lengths [**1-CuCl**; 2.159(2)–2.176(2)Å, **3-CuCl**; 2.168(1)–2.188(1)Å] compare well with those reported for the $[(L)CuI]_4$ complexes obtained from phosphine donor ligands.[32,34] A very slight elongation in the Cu-P distances in **3-CuCl** (av. 2.179(1) Å) compared to **1-CuCl** [av. 2.169(2) Å] is observed, likely caused by the higher steric demands of the tertiary phosphine ligands.

The ^{1}H NMR spectra of **1-CuCl**, **2-CuCl** and **3-CuCl**, as well as those for other reported compounds in this paper, show the typical pattern of a monosubstituted ferrocene and two inequivalent methylene groups. Signals for the PH protons in the complexes containing the primary (**1-CuCl** and **1-AgCl**) or secondary (**2-CuCl** and **2-AgCl**) phosphines are clearly observed. In the ^{1}H NMR spectra of complexes **1-CuCl**, **2-CuCl** and **3-CuCl**, $-CH_2CH_2-$ protons of the phosphine ligands resonate as two multiplets in the range of 1.86–1.97 and 2.60–2.69 ppm. Ferrocenyl groups exhibit one singlet for the unsubstituted Cp ring and two singlets for H_α and H_β of the substituted Cp ring in the range 4.06–4.18 ppm. The ^{1}H NMR spectra of **1-CuCl** and **2-CuCl** exhibit a doublet of multiplets for the P-H groups, with higher $^1J_{HP}$ values (**1-CuCl** 306.4, **2-CuCl** 306.5 Hz) than observed in the corresponding free phosphines (**1**, 194.2; **2**, 198.1 Hz). The $^{13}C\{^1H\}$ NMR spectra of **1-CuCl** - **3-CuCl** show the expected signals of the phosphine ligands. In the $^{13}C\{^1H\}$ NMR spectrum of **1-CuCl**, one of the signals of the methylene groups and *ipso*-C_5 of the substituted Cp ring resonates as a doublet due to J_{PC} coupling, while in $^{31}C\{^1H\}$ NMR spectra of **3-CuCl** the peaks of the both $C_\alpha H_2$ and $C_\beta H_2$ of the methylene groups and *ipso*-C_5 display coupling to phosporus. In the $^{13}C\{^1H\}$ NMR spectrum of **2-CuCl**, in addition to the methylene groups and *ipso*-C_5, an additional carbon atom of the substituted Cp ring resonates as a doublet, similar to what is observed in the spectra of the corresponding free phosphine.

^{31}P NMR spectroscopy has been shown to yield useful information about the phosphine bonding in coinage metal complexes.[35] As summarized in Table 1, ^{31}P chemical shifts of the coordinated phosphines are generally downfield from those of the free ligand. Phosphine bonding to copper resulted in large changes in the chemical shifts, together with broad ^{31}P NMR signals, likely arising due to the presence of quadrupolar ^{65}Cu and ^{63}Cu nuclei.[23a,36]

The ^{31}P NMR spectrum of **1-CuCl** at –60 °C shows a broad triplet signal at –112.4 ppm ($^1J_{HP}$ = 306 Hz), while in **2-CuCl**, the ^{31}P NMR spectrum at room temperature exhibits a broad doublet at –55.1 ppm ($^1J_{HP}$ = 306 Hz) (Figure 3). These are shifted to higher field versus the free phosphine, from δ = –137.6 (J_{HP} = 194.2 Hz) for **1** and –68.2 ($^1J_{HP}$ = 198.1 Hz) for **2**. Two aspects confirm the coordination of the phosphine: the high value of the PH coupling constant observed in the ^{1}H and ^{13}P NMR spectra,[23a] relating to increased s character in the P-H bonds,[37] and the line broadening of the signal observed in the ^{31}P NMR spectra which is interpreted due to the high quadrupole moment of copper.[36] Unlike **1-CuCl** and **2-CuCl**, the ^{31}P NMR spectrum of the tertiary phosphine complex **3-CuCl** shows a broadened resonance (–11.0 ppm, $W_{1/2}$ = ~72 Hz) at ambient temperature, which is at lower field compared to that for the free ligand **1** (δ = –28.0 ppm) (Figure 3).[23a,36]

The silver complex $\{[(FcCH_2CH_2)H_2P]_2AgCl\}_2$ **1-AgCl** crystallizes in the space group *P*2$_1$/*c*, crystals forming via slow evaporation of methanol solutions. The solid state structure of **1-AgCl** (Figure 4) consists of rhombus-shaped Ag_2Cl_2 center with distorted tetrahedral coordination of the two Ag(I). In this structure, which is common in silver halide complexes with mono- and bidentate phosphine ligands $[L_4Ag_2(\mu\text{-}Cl)_2]$ (L = mono- or ½-bidendate phosphine ligand),[38] each of the two silver atoms is four coordinate, forming two bonds with the P atoms of the two independent primary phosphine ligands and the two doubly and 2.465(2) Å] compare well with those obtained for bridging chloride atoms. Each of the molecules in the unit cell has an inversion centre, so that the $AgCl_2Ag$ core is strictly planar. The Cl-Ag-Cl and Ag-Cl-Ag angles in **1-AgCl** are 97.13(4)° and 82.87(4)°, respectively with the Ag-Ag separation [3.469(2) Å] close to the sum of the van der Waals radii (3.44 Å).[39] The Ag-P distances [2.444(2)

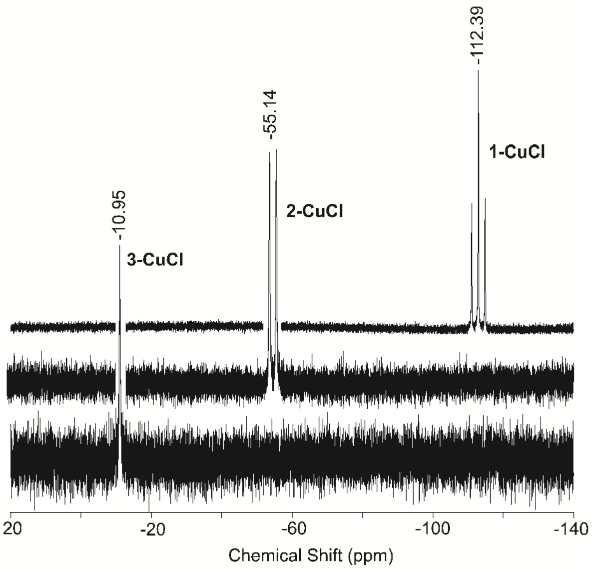


Fig. 3. ^{31}P NMR spectrum of **1-CuCl** at –60 °C and **2-CuCl** and **3-CuCl** at 25 °C in CD_2Cl_2.

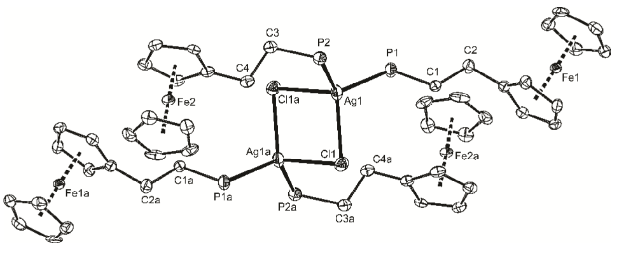


Fig. 4. ORTEP plot of the molecular structure of complex **1-AgCl** (40% probability, hydrogen atoms are omitted for clarity).

Table 1. ^{1}H, ^{31}P and ^{13}C{^{1}H} NMR spectroscopic data.

	^{31}P NMR (δ, ppm), T / °C		$^1J_{HP}$ / Hz	^{1}H NMR (δ / ppm), 25 °C (phosphine peaks)			^{13}C {^{1}H} NMR (δ / ppm), 25 °C (phosphine only)	
				P*H*	Fc	-C*H*$_2$C*H*$_2$-	Fc	-*C*H$_2$-
1	–137.6(t)	25	194.2	2.70(d-m, 2H)[c]	4.09(s,5H), 4.07(s,2H), 4.04(s,2H)	2.54(m,2H), 1.70(m,2H)	89.7(d, J_{CP} = 6.1 Hz), 69.0(s), 68.5(s), 67.8(s)	33.7(d, J_{CP} = 3.1 Hz), 16.0(d, J_{CP} = 8.4 Hz)
2	–68.2(d)	25	198.1	3.12(d-m, 1H)	4.10(s,10H), 4.09(s,4H), 4.05(s,4H)	2.50(m,4H), 1.78(d-m,4H)	90.2(d, J_{CP} = 10.0 Hz), 69.0(s), 68.5(d, J_{CP} = 3.1 Hz), 67.7(s)	29.0(d, J_{CP} = 9.2 Hz), 22.4(d, J_{CP} = 10.0 Hz)
3	–28.0(s)	25	-	-	4.11(s,15H), 4.10(s,6H), 4.06(s,6H)	2.48(m,6H), 1.66(m,6H)	90.6(d, J_{CP} = 11.5 Hz), 69.0(s), 68.4(s), 67.7(s)	29.0(d, J_{CP} = 15.0 Hz), 26.5(d, J_{CP} = 15.0 Hz)
1-CuCl	–112.4(t-br)[a]	-60	306.4	3.78(d-m, 2H)	4.13(s,2H), 4.12(s,5H), 4.06(s,2H)	2.66(m,2H), 1.96(m,2H)	88.4(d, J_{CP} = 11.5 Hz), 69.2(s), 68.7(s), 68.0(s)	30.4(s), 17.4(d, J_{CP} = 22.2 Hz)
2-CuCl	–55.1(d-br)[b]	25	306.5	4.08(d-m, 1H)	4.17(s,4H), 4.14(s,10H), 4.07(s,4H)	2.69(m,4H), 1.97(m,4H)	89.0(d, J_{CP} = 13.0 Hz), 69.2(s), 68.6(d, J_{CP} = 13.8 Hz), 68.0(s)	27.5(d, J_{CP} = 3.8 Hz), 22.4(d, J_{CP} = 20.7 Hz)
3-CuCl	–11.0(br)	25	-	-	4.18(s,6H), 4.16(s,15H), 4.12(s,6H)	2.60(m,6H), 1.86(m,6H)	89.2(d, J_{CP} = 15.0 Hz), 69.4(s), 68.7(s), 68.3(s)	26.8(d, J_{CP} = 21.9 Hz), 26.1(d, J_{CP} = 4.6 Hz)
1-AgCl	–124.6(t) –112.5(t)	25 –75	242.8	3.20(d-m, 4H)	4.09(s,10H),4.08(s,4H), 4.04(s,4H)	2.58(m,4H), 1.82(m,4H)	88.8(d, J_{CP} = 8.4 Hz), 69.1(s), 68.6(s), 67.9(s)	32.4(s), 16.8(d, J_{CP} = 3.8 Hz)
2-AgCl	–48.9(d), –49.6(br)	25 –60	307.7	4.20(d-m, 1H)	4.15(s,4H), 4.14(s,10H), 4.07(s,4H)	2.68(m,4H), 2.00(m,4H)	88.6(d, J_{CP} = 13.8 Hz), 69.2(s), 68.7(d, J_{CP} = 8.4 Hz), 68.0(s)	8.0(d, J_{CP} = 4.6 Hz), 22.6(d, J_{CP} = 16.9 Hz)
3-AgCl	-4.2(br),	25	-	-	4.13(s,15H), 4.12(s,6H), 4.10(s,6H)	2.62(m,6H), 1.91(m,6H)	88.7(d, J_{CP} = 15.3 Hz), 69.2(s), 68.5(s), 68.2(s)	27.4(d, J_{CP} = 16.9 Hz), 26.4(d, J_{CP} = 6.1 Hz)
3-CuOAc	–13.2(br)	25	-	-	4.14(s,6H), 4.13(s,15H), 4.09(s,6H)	2.60(m,6H), 1.84(m,6H)	89.1(d, J_{CP} = 15.3 Hz), 69.2(s), 68.5(s), 68.1(s)	27.0(d, J_{CP} = 20.7 Hz), 25.9(d, J_{CP} = 4.6 Hz)
3-AgOAc	–1.0(2 d)	-60	-	-	4.12(s,15H), 4.11(s,6H), 4.09(s,6H)	2.58(m,6H), 1.86(m,6H)	88.2(d, J_{CP} = 15.3 Hz), 69.2(s), 68.5(s), 68.3(s)	27.5(d, J_{CP} = 19.9 Hz), 26.7(d, J_{CP} = 5.4 Hz)
2-AuCl	–18.7(d-br)	25	378.3	5.06(d-m, 1H)	4.12(s,10H), 4.11(s,4H), 4.10(s,4H)	2.65(m,4H), 2.09(m,4H)	87.2(d, J_{CP} = 13.8 Hz), 69.3(s), 68.8(d J_{CP} = 10.7 Hz), 68.4(s)	27.6(s), 24.2(d, J_{CP} = 36.0 Hz)
3-AuCl	22.0(s)	25	-	-	4.13(s,15H), 4.12(s,6H), 4.11(s,6H)	2.64(m,6H), 2.00(m,6H)	87.8(d, J_{CP} = 16.1 Hz), 69.2(s), 68.6(s), 68.3(s)	28.1(d, J_{CP} = 34.5 Hz), 26.3(s)

[a] t-b: broad triplet, [b] d-br: broad doublet, [c] d-m: double of multiplet

and 2.465(2) Å] compare well with those obtained for $[(R/Ar)_3P]_2AgCl_2Ag[(R/Ar)_3P]_2$ and $(P^{\cap}P)AgCl_2Ag(P^{\cap}P)$ structures.[38a, b, 40] In contrast, the structure of $[(FcCH_2CH_2)_3PAgCl]_4$ **3-AgCl** in the solid state consists a secocubane structure, which is usually observed in mixed metal clusters,[41] featuring two different bridging chlorides and two different silver centers, where the Ag1-Cl3 bond is broken. The μ_2-Cl3 bridges Ag3 and Ag4 while the other three chloride atoms bridge three Ag centres. Ag1 assumes a disordered trigonal planar geometry, coordinated by one phosphine and two μ_3-Cl atoms. The other vertices (Ag2, Ag3 and Ag4) adopt four-coordinate geometry by coordinating to three chlorides and one phosphine ligand. The constituent atoms on "bottom" face of the cluster are nearly coplanar, the dihedral angle Ag1Cl1Cl2/Ag2Cl1Cl2 being 168.33°, while the top face obviously is more hinged (Cl3Ag3Ag4/Cl4Ag3Ag14 = 162.17°) (Figure 5, insert). Atom Cl1 has moved substantially out of the plane, so a portion of the top face is bent away resulting in a very long Ag1···Cl3 separation of 3.1791(7) Å. The finding that the Ag1-Cl2 bond distance at 2.4737(8) Å is shorter than the other Ag-Cl bond lengths in the range 2.5148(8)–2.8308(6) Å may be accounted for by the coordinatively unsaturated, electron-deficient Ag1. The Cl-Ag-Cl and Ag-Cl-Ag bond angles vary between 87.91(2)-105.60(2)° and 81.44(2)–93.51(2)° respectively. The difference in the solid-state structures of **3-CuCl** and **3-AgCl** is in accordance with the tendency that the 16-electron complexes are more readily available for Ag than for Cu under similar conditions. The Ag–P bond distances in **3-AgCl** [2.3711(8)–2.3839(8) Å] compare well to those found in related complexes such as $[(H_{11}C_6)_3PAgCl]_4$[35b] or $[Et_3PAgCl]_4$.[42] There is no significant metal-metal interaction between the silver atoms [3.4709(7)–3.8192(9) Å] which are longer than the sum of their van der Waals radii (3.44 Å).[39] Similar to **3-CuCl**, the ferrocenylethyl groups are directed into structural voids away from the $(P\text{-}Ag)_4Cl_4$ core.

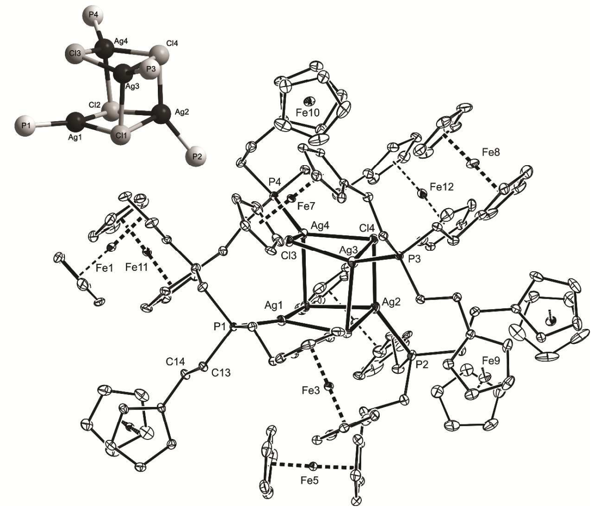


Fig. 5. ORTEP plot of the molecular structure of complex **3-AgCl** (40% probability, hydrogen atoms are omitted for clarity).

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1-AgCl** – **3-AgCl** show the similar pattern to their copper analogues (**1-CuCl** – **3-CuCl**). The ^1H NMR spectra of **1-AgCl** exhibit a doublet of multiplets for the P-H groups as well, but at lower chemical shift (3.20 pm) and with smaller $^1J_{HP}$ value (242.8 Hz) than observed for **1-CuCl** (3.78 ppm, 306.4 Hz). Room-temperature ^1H-coupled ^{31}P NMR spectra of **1-AgCl** and **2-AgCl** contain sharp triplet and doublet signals at –124.6 ($^1J_{HP}$ = 242.8 Hz) and –48.9 ppm ($^1J_{HP}$ = 307.7 Hz,) respectively. However, these resonances do not exhibit any Ag-P coupling at room temperature due to rapid intramolecular exchange due to ligand dissociation/reassociation. Low temperature ^{31}P NMR spectra of **2-AgCl** broaden at –49.6 ppm, although ^{107}Ag-P or ^{109}Ag-P was not resolved.[2b] Spectra of **1-AgCl** are unchanged at lower temperatures. Its ^{31}P NMR spectrum at room temperature shows one broad signal at -4.2 ppm, a feature observed for labile complexes such as $(R_3P)_nAgX$,[43] where fast ligand-exchange is possible.

The complexes **3-CuOAc** and **3-AgOAc** are isostructural and both crystallized in the triclinic space group $P\bar{1}$. **3-CuOAc** and **3-AgOAc** form a metal(I) carboxylate complex having an interesting tetranuclear structure in which the near linear arrangement of four metals is maintained with bridging carboxylates.[44] The tertiary phosphine ligands coordinate to two type of metal(I) centres. These centrosymmetric complexes exist as dimers of dimers: two acetate ligands bridge in μ_2-O fashion where two copper (silver) centers are 3.239(2) Å (3.682(3) Å) apart (Figures 6 and S1). Two additional $CH_3CO_2^-$ bridge in κ*O*: κ*O*′ fashion, with both shorter Cu1-Cu2 (2.799(2) Å) and Ag1-Ag2 length [2.959(2) Å] that is significantly shorter than the sum of their van der Waals radii (2.80 Å for Cu-Cu and 3.44 Å for Ag-Ag),[45] suggesting the existence of metallophilic interactions for copper and silver centres, respectively. Atom Cu1 atom adopts a distorted tetrahedral geometry, whereas atom Cu2 exhibits a distorted trigonal planar geometry (sum. of bond angles around the metal: 347.9°). The atoms Cu1 and Ag1 have an 18 electron count around the metal, while Cu2 and Ag2 have 16 electrons each. The M-P lengths in cluster **3-CuOAc** (M = Cu) are 2.151(2) and 2.165(1) Å and in cluster **3-AgOAc** (M = Ag) are 2.348(3) and 2.369(1) Å.

In the solution ^1H NMR spectra of **3-CuOAc** and **3-AgOAc**, the resonance for the protons of the acetate moiety are observed as single broad peak ~2.0 ppm. Compared to the chloride complexes, the $^{13}C\{^1H\}$ spectra of **3-AgOAc** display two additional peaks at 22.9 and 179.5 from -OAc, although these signals are not resolved for **3-CuOAc**. The ^{31}P NMR resonance of **3-CuOA**, which is markedly broadened ($W_{1/2}$ = ~830 Hz), is observed at –13.2 ppm, close to that of **3-CuCl** (–11.0 ppm). At room temperature the silver complex **3-AgOAc** shows a broad doublet at –1.0 ppm with an average coupling constant $^1J_{PAg}$ = 710 Hz. Upon lowering the temperature to –60 °C, the signal is shifted to –2.3 ppm and sharpened to give two well resolved doublets (Figure 7),[46] which correspond to the two spin ½ isotopes ^{109}Ag (48.18 %) ^{107}Ag (51.82 %).[47] The magnitude of these coupling constants in **3-AgOAc** (at –60 °C), P-^{107}Ag (^1J = 668 Hz) and P-^{109}Ag (^1J = 770 Hz), are in the expected range.[35b, 47, 48]

The structural chemistry of the corresponding Au(I) complexes with these phosphines is dominated by near linear gold(I) centres. Complexes **2-AuCl** and **3-AuCl** crystallize in $P\bar{1}$ with two

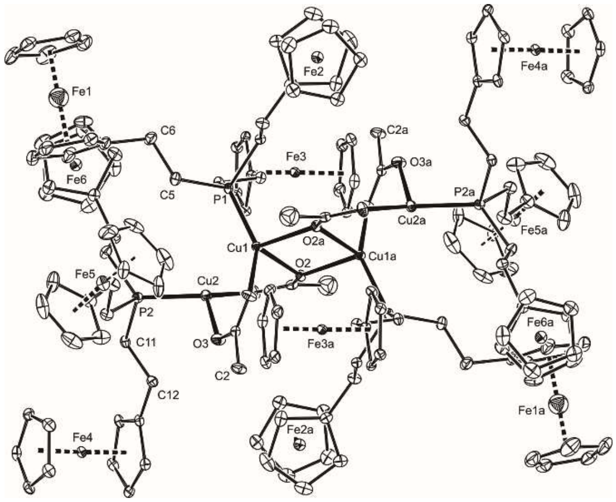


Fig. 6. ORTEP plot of the molecular structure of complex **3-CuOAc** (40% probability, hydrogen atoms are omitted for clarity).

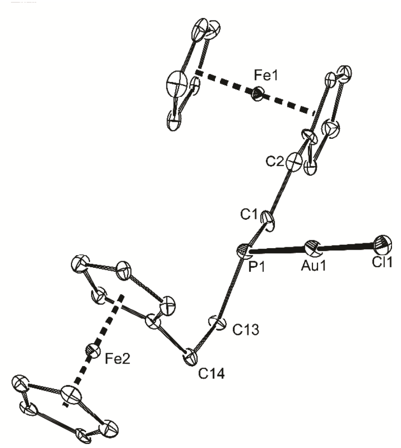


Fig. 8. ORTEP plot of the molecular structure of complex **2-AuCl** (40% probability, hydrogen atoms are omitted for clarity).

independent molecules in the asymmetric unit; the data below describe parameters for one of the two independent molecules (Figures 8 and 9). Phosphine gold analogues of the type R_3PAuX are well known to show near linear, two coordinate metal atoms that, depending on the nature and the size of the substituents R and the ligand X, may dimerize via Au···Au interactions:[49] short (sub-van der Waals) intermolecular Au-Au contacts of *ca.* 3.1 Å in length.[4a]. In **2-AuCl** and **3-AuCl**, the gold centres exhibit almost linear geometry, with P-Au-Cl angles of 178.8(1)° for **2-AuCl** and 178.02(9)° for **3-AuCl**. In the crystal packing of **2-AuCl**, in order to minimise the steric repulsion between the phosphine substituents while at the same time maximizing intermolecular $Cl\cdots H_2P$ interactions (Cl···H-P = 2.791(4) and 2.788(4) Å), the molecules are arranged in a head to tail fashion, with an Au···Au distance of 3.948(1) A˚, ruling out any significant aurophilic interaction.[49,50] In **3-AuCl** the cone-shaped molecules are packed with a one dimensional tandem array arrangement with repeating intermolecular Cl-Au separation of 4.037(4) Å (phosphine cone angle: 140°). The ^{31}P NMR spectrum of **2-AuCl** features a broad

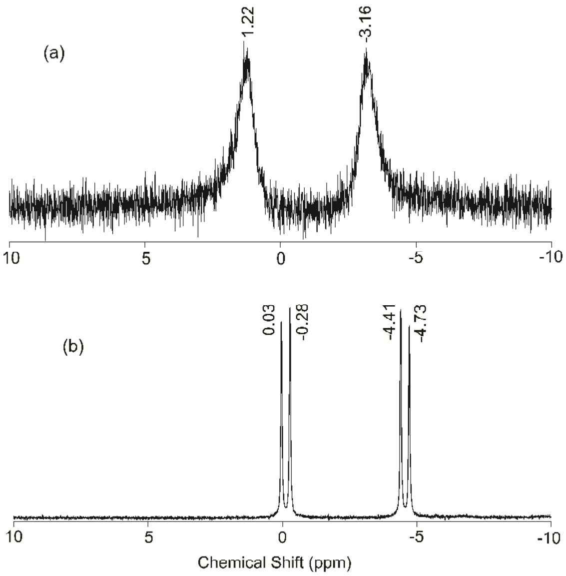


Fig. 7. ^{31}P NMR spectrum of **3-AgOAc** at (a) 25 and (b) -60 °C in CD_2Cl_2.

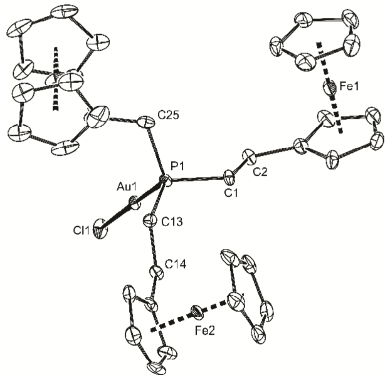


Fig. 9. ORTEP plot of the molecular structure of complex **3-AuCl** (40% probability, hydrogen atoms are omitted for clarity).

doublet at –18.7 ppm (${}^{1}J_{HP}$ = 378 Hz), while the ^{31}P{^{1}H} NMR of **3-AuCl** shows a sharp singlet (22.0 ppm), shifted to considerably lower field from the signal observed for the free phosphine.

Generally, the cyclic voltammograms (CVs) of all complexes are comprised of single, reversible oxidation waves at potentials ($E_{1/2}$) between –10 and 15 mV relative to the Fc$^{0/+}$ redox couple, with a ΔE_p value varying between 70–80 mV (**1-CuCl**, **2-CuCl** and **3-CuCl**, Figure S2; **1-AgCl**, **2-AgCl** and **3-AgCl**, Figure S3; **3-CuOAc** and **3-AgOAc**, Figure S4; **2-AuCl** and **3-AuCl**, Figure 10) (Table 2). The data reveal that the iron oxidation processes between separated (inter- and intra-phosphine) ferrocenyl moieties seem to coincide at one potential. The cyclic voltammograms collected for the secondary and tertiary free phosphines under identical conditions reveal a small, irreversible oxidation peak at ca. −100 mV relative to the ferrocene/ ferrocenium redox couple.[23a] This electrochemical feature, which may associated with redox reactivity and/or electrode interactions associated with the phosphorus lone pair, no longer exits due to the coordination of the phosphines to the metal atoms. Some broadening and shoulder peaks for the copper complex **2-CuCl** and the silver complex **2-AgCl**, each ligated with the secondary phosphine, are present (see Supporting Information); these are not observed for the gold complex **2-AuCl** (Fig 11). This latter fact, combined with the absence of such features in the CV of all complexes bearing the tertiary ferrocenyl phosphines, suggests that the broadening does not arise from electronic communication between the ferrocenyl centres. However, both ^{1}H and ^{31}P NMR spectra indicate that only one phosphine species is present in solution; thus the origin of these additional features in the CVs of **2-CuCl** and **2-AgCl** is unclear at present. When scanning over a wider potential range for **1-CuCl, 2-CuCl, 3-CuCl** and **3-CuOAc ,** CVs display broad tails / unresolved peaks at higher potential that are likely due to the redox behaviour of copper(I) in these complexes (see Supporting Information).

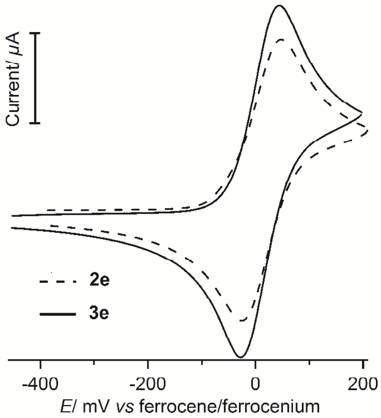


Fig. 10. Cyclic voltammograms of a 1 mM solution of **2-AuCl** and **3-AuCl** (scan rate 100 m Vs^{-1}) (0.1 mol dm^{-3} of ^{n}Bu$_4$N[PF$_6$] in 2:1 DCM:acetonitrile) at 298 K.

Table 2. Cyclic voltammetry data.[a]

	$E_{1/2}$ (mv *vs* Fc/Fc.)	ΔE_p[b] (mV)
1-CuCl	0	80
2-CuCl	5	80
3-CuCl	10	80
1-AgCl	10	70
2-AgCl	15	70
3-AgCl	–5	80
3-CuOAc	–10	70
3-AgOAc	0	80
2-AuCl	10	70
3-AuCl	10	75

[a] Recorded in 2:1 CH$_2$Cl$_2$:CH$_3$CN/0.1M Bu$_4$NPF$_6$ at 100 mVs^{-1} and 298 K.

[b] Difference between anodic and cathodic peak potentials.

Conclusions

A particularly interesting class of ferrocene-based phosphine ligands was studied with a focus on coordination to coinage metals. In this regard the set of ten complexes of copper(I), silver (I) and gold(I) {(FcCH$_2$CH$_2$)H$_2$PCuCl}$_4$ (**1-CuCl**), [(FcCH$_2$CH$_2$)$_2$HPCuCl] (**2-CuCl**), {(FcCH$_2$CH$_2$)$_3$PCuCl}$_4$ (**3-CuCl**), {[(FcCH$_2$CH$_2$)H$_2$P]$_2$AgCl}$_2$ (**1-AgCl**), [(FcCH$_2$CH$_2$)$_2$HPAgCl] (**2-AgCl**), [(FcCH$_2$CH$_2$)$_3$PAgCl]$_4$ (**3-AgCl**), [(FcCH$_2$CH$_2$)$_3$PCu(OAc)]$_4$ (**3-CuOAc**), [(FcCH$_2$CH$_2$)$_3$PAg(OAc)]$_4$ (**3-AgOAc**), [(FcCH$_2$CH$_2$)$_2$HPCuCl] (**2-AuCl**) and [(FcCH$_2$CH$_2$)$_3$PAgCl] (**3-AuCl**) are readily obtained through treatment of the selected phosphine with the corresponding metal salt in an appropriate organic solvent. Since phosphine ligated coinage metal-halides and -acetates are among the most important starting material for metal based clusters and nanoclusters,[51] these complexes represent a convenient entry into a wide variety molecules/materials bearing multiple redox-active ferrocenyl sites. These reactions are being developed currently.

One of the interesting features of these complexes is the diversity in the molecular structures in the solid state, a reflection of the varying steric requirements of the phosphine, together with the flexible coordination geometries of Cu(I) and Ag(I). Both the primary phosphine-copper(I) chloride **1-CuCl** and the tertiary phosphine-copper(I) chloride **3-CuCl** reveal tetrameric Cu(I) cubane-like structures, whereas silver chloride forms quadrangle and secocubane structure types with the primary and tertiary phosphine, respectively. The tertiary phosphine reveals step-like clusters with both copper(I) acetate and silver(I) acetate (**3-CuOAc** and **3-AgOAc** complexes, respectively). Gold(I) chloride displays a linear coordination geometry with both the secondary and tertiary phosphine.

Experimental Section

All syntheses and electrochemical analyses were carried out under an atmosphere of high-purity dried nitrogen using standard double-manifold Schlenk line techniques and nitrogen-filled glove boxes unless otherwise stated. Solvents were dried and collected using an MBraun MB-SP Series solvent purification system with tandem activated alumina (tetrahydrofuran) and an activated alumina/copper redox catalyst (pentane). Chlorinated solvent (dichloromethane) was dried and distilled over P_2O_5, while for methanol and acetonitrile, CaH_2 was used as the absorbent. Dichloromethane-d$_2$ was purchased from Cambridge Isotope Laboratories (CIL).

Other chemicals were used as received from commercial sources (Caledon, Strem and Aldrich). $(FcCH_2CH_2)PH_2$ **1**,[23a] $(FcCH_2CH_2)_2PH$ **2**,[23a] $(FcCH_2CH_2)_3P$ **3**,[23a] (Fc = $(C_5H_5)Fe(C_5H_4)$), Cu(OAc)[52] and Me_2SAuCl[53] were synthesized according to literature procedures.

A Bas 100B\W Electrochemical Analyzer was used for cyclic voltammetry (CV) experiments. A homemade glassy carbon (GC, Tokai GC-20) working-electrode 3 mm in diameter was prepared by polishing over silicon carbide papers (500, 1200, 2400 and 4000) followed by diamond paste (Struers, 1 and 0.25 mm). The GC electrodes were stored in ethanol and polished before each set of experiments with the 0.25 mm diamond paste (Struers), rinsed with dry ethanol (Commercial Alcohols) and sonicated in dry ethanol for 5 min. Platinum wires served as the reference and counter electrodes. Electrochemical experiments were carried out in dry 2:1 dichloromethane:acetonitrile solutions of the analyte (~1 mM), containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte. Potentials are referenced internally to decamethylferrocene (~3 mM, -0.520 V *vs.* ferrocene/ferrocenium) added at the end of the experiments.

NMR spectra were recorded on Varian Mercury 400, Inova 400 and Inova 600 NMR spectrometers. ^{1}H and ^{13}C chemical shifts are referenced to $SiMe_4$, using solvent peak as a secondary peak, ^{31}P chemical shifts are referenced to 85% H_3PO_4. Elemental analysis was performed by Laboratoire d'Analyze Élementaire de l'Université de Montréal, Montréal, Canada.

Single-crystal X-ray diffraction measurements were completed on Bruker APEX-II CCD diffractometers equipped with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Single crystals of the complexes were carefully selected, immersed in paraffin oil and mounted on MiteGen micromounts. The structures were solved using direct methods and refined by the full-matrix least-squares procedure of SHELXTL.[54] All non-hydrogen atoms, with the exception of some disordered carbon centers, were refined with anisotropic thermal parameters. Hydrogen atoms were included as riding on their respective carbon or phosphorus (for primary and secondary phosphine) atoms. For **2-AuCl**, the TWIN command in SHELXTL was used to refine the structure. The ORTEP program was used to prepare molecular illustrations.[55] Files CCDC 1429835 (**1-CuCl**), 1429842 (**3-CuCl**), 1429840 (**1-AgCl**), 1429844 (**3-AgCl**), 1429839 (**3-CuOAc**), 1429848 (**3-AgOAc**), 1429841 (**2-AuCl**), 1429843 (**3-AuCl**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 1-CuCl. A solution of 116 mg primary phosphine **1** (0.471 mmol) in 5 mL anhydrous tetrahydrofuran was added to 47 mg CuCl (0.47 mmol). The mixture was stirred for 30 min at room temperature resulting in a clear orange solution, followed by filtration over a filter paper. The filtrate was layered with 20–25 mL of pentane. Orange plate crystals suitable for X-ray diffraction were obtained after a few days. The crystals were washed with 3 × 10 mL of pentane and dried under dynamic vacuum for further analyses (79.6% yield); m.p. 88–91 °C. ^{1}H NMR (CD_2Cl_2, 400.1 MHz, 25 °C): δ 4.13 (s, 2H, β-C_5H_4R), 4.12 (br s, 5H, C_5H_5), 4.06 (br s, 2H, α-C_5H_4R), 3.78 (d of m, $^1J_{HP}$ = 306.4 Hz, 2H, PH_2), 2.66 (m, 2H, $C_5H_4CH_2$), 1.96 (m, 2H, CH_2PH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.6 MHz, 25 °C): δ 88.4 (d, $^3J_{CP}$ = 11.5 Hz, *ipso*-C_5H_4R), 69.2(s, C_5H_5), 68.7 (s, β-C_5H_4R), 68.0 (s, α-C_5H_4R), 30.4 (s, $C_5H_4CH_2$), 17.4 (d, $^1J_{CP}$ = 22.2 Hz, CH_2PH_2); ^{31}P NMR (CD_2Cl_2,161.8 MHz, –60 °C): δ -112.4 (t-br, $^1J_{PH}$ = 306.4 Hz) ppm. Anal. Calcd for $C_{12}H_{15}ClCuFeP$: C, 41.77; H, 4.38. Found: C, 42.49; H, 4.60.

Synthesis of 2-CuCl. 165 mg of the secondary phosphine **2** (0.296 mmol) was dissolved in 5 mL tetrahydrofuran. This solution was added to 0.296 mmol, 29 mg of CuCl. After stirring for 30 min at room temperature the solution was filtered over a filter paper. The solvent was removed under vacuum to yield a greasy orange solid. The product was washed with 3 × 10 mL of pentane and dried under vacuum (47.1% yield); m.p. 52–54 °C. ^{1}H NMR (CD_2Cl_2, 399.8 MHz, 25 °C): δ 4.17 (br s, 4H, β-C_5H_4R), 4.14 (s, 10H, C_5H_5), 4.07 (br s, 4H, α-C_5H_4R), 4.08 (d of m, $^1J_{HP}$ = 306.5 Hz, 1H, P*H*), 2.69 (m, 4H, $C_5H_4CH_2$), 1.97 (m, 4H, CH_2PH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.5 MHz, 25 °C): δ 89.0 (d, $^3J_{CP}$ = 13.0 Hz, *ipso*-C_5H_4R), 69.2(s, C_5H_5), 68.6 (d, $^4J_{CP}$ = 13.8 Hz, β-C_5H_4R), 68.0 (s, α-C_5H_4R), 27.5 (d, $^2J_{CP}$ = 3.8 Hz, $C_5H_4CH_2$), 22.4 (d, $^1J_{CP}$ = 20.7 Hz, CH_2PH_2); ^{31}P NMR (CD_2Cl_2,161.8 MHz, –60 °C): δ -55.1 (d-br, $^1J_{PH}$ = 306.5 Hz) ppm. Anal. Calcd for $C_{24}H_{27}ClCuFe_2P$: C, 51.74; H, 4.88. Found: C, 50.24 H, 4.70.

Synthesis of 3-CuCl. 113 mg of the tertiary phosphine **3** (0.169 mmol) was reacted with one equivalent (17 mg) of CuCl in 5 mL tetrahydrofuran as described for the preparation of **1-CuCl** (74.5% yield); m.p. 193–198 °C. Orange block single crystals suitable for X-ray diffraction were obtained after a few days by layering the reaction solution with 20 mL of pentane 74.5% yield); m.p. 193-198 °C. ^{1}H NMR (CD_2Cl_2, 599.4 MHz, 25 °C): δ 4.18 (br s, 6H, β-C_5H_4R), 4.16 (s, 15H, C_5H_5), 4.12 (br s, 6H, α-C_5H_4R), 2.60 (m, 6H, $C_5H_4CH_2$), 1.86 (m, 6H, CH_2PH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 150.7 MHz, 25 °C): δ 89.2 (d, $^3J_{CP}$ = 15.0 Hz, *ipso*-C_5H_4R), 69.4(s, C_5H_5), 68.7 (s, β-C_5H_4R), 68.3 (s, α-C_5H_4R), 26.8 (d, $^2J_{CP}$ = 21.9 Hz, $C_5H_4CH_2$), 26.1 (d, $^1J_{CP}$ = 4.6 Hz, CH_2PH_2); ^{31}P NMR (CD_2Cl_2, 155
61.9 MHz, 25 °C): δ –11.0 (br) ppm. Anal. Calcd for $C_{36}H_{39}ClCuFe_3P$: C, 56.21; H, 5.11. Found: C, 56.29; H, 5.27.

Synthesis of 1-AgCl. A solution of 143 mg primary phosphine **1** (0.581 mmol) in 10 mL of tetrahydrofuran was added to 83 mg of AgCl (0.58 mmol). The mixture was stirred for 12 h at room temperature resulting in the formation of a light orange precipitate. The solvent was removed under vacuum and 20 mL of MeOH was added to the residue with vigorous stirring for 1 h at room temperature. The resulting orange suspension in MeOH was filtered over a filter paper to yield a clear, orange solution. Orange, plate-like single crystals suitable for X-ray diffraction were obtained by slow evaporation of the filtrate. The crystals were washed with 3 × 10 mL of pentane and dried under dynamic vacuum for further analyses (32.0% yield); m.p. 57–62 °C. ^{1}H NMR (CD_2Cl_2, 399.8 MHz, 25 °C): δ 4.09 (s, 10H, C_5H_5), 4.08 (br s, 4H, β-C_5H_4R), 4.04 (br s, 4H, α-C_5H_4R), 3.20 (d of m, $^1J_{HP}$ = 242.8 Hz, $^3J_{HH}$ = 7.4 Hz, 4H, PH_2), 2.58 (m, 4H, $C_5H_4CH_2$), 1.82 (m, 4H, CH_2PH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.6 MHz, 25 °C): δ 88.8 (d, $^3J_{CP}$ = 8.4 Hz, *ipso*-C_5H_4R), 69.1 (s, C_5H_5), 68.6 (s, β-C_5H_4R), 67.9 (s, α-C_5H_4R), 32.4 (s, $C_5H_4CH_2$), 16.8 (d, $^1J_{CP}$ = 3.8 Hz, CH_2PH_2); ^{31}P NMR (CD_2Cl_2,161.8 MHz, –75 °C): δ –112.5 (t, $^1J_{PH}$ = 275.4 Hz, no sign of Ag-P coupling in solution at -75 °C) ppm. Anal. Calcd for $C_{24}H_{30}ClAgFe_2P2$: C, 45.36; H, 4.76. Found: C, 46.60 H, 4.95.

Synthesis of 2-AgCl. 94 mg of the secondary phosphine **2** (0.205 mmol) was reacted with one equivalent of AgCl, 29 mg (in 5 mL tetrahydrofuran). After stirring for 10-12 h, the mixture was filtered over a filter paper. The filtrate was dried under vacuum to yield a greasy orange solid. The product was washed with 3×10 mL of pentane and dried under vacuum (46.5% yield); m.p. 56–60 °C. ^{1}H NMR (CD_2Cl_2, 399.8 MHz, 25 °C): δ 4.20 (d of m, $^1J_{HP}$ = 307.7 Hz, 1H, PH), 4.15 (br s, 4H, β-C_5H_4R), 4.14 (s, 10H, C_5H_5), 4.07 (br s, 4H, α-C_5H_4R), 2.68 (m, 4H, $C_5H_4CH_2$), 2.00 (m, 4H, CH_2PH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.6 MHz, 25 °C): δ 88.6 (d, $^3J_{CP}$ = 13.8 Hz, *ipso*-C_5H_4R), 69.2(s, C_5H_5), 68.7 (d, $^4J_{CP}$ = 8.4 Hz, β-C_5H_4R), 68.0 (s, α-C_5H_4R), 28.0 (d, $^2J_{CP}$ = 4.6 Hz, $C_5H_4CH_2$), 22.6 (d, $^1J_{CP}$ = 16.9 Hz, CH_2PH_2); ^{31}P NMR (CD_2Cl_2,161.9 MHz, 25 °C): δ –48.9 (d, $^1J_{PH}$ = 307.7 Hz, no sign of Ag-P coupling in solution at 25 °C); ^{31}P NMR (CD_2Cl_2,161.8 MHz, –60 °C): δ –49.6 (br, no recognizable $^1J_{PH}$ or $^1J_{PAg}$ at -60 °C) ppm. Anal. Calcd for $C_{24}H_{27}AgClFe_2P$: C, 47.93; H, 4.52. Found: C, 48.60; H, 4.73.

Synthesis of 3-AgCl. A solution of 153 mg of the tertiary phosphine **3** (0.228 mmol) in 10 mL of tetrahydrofuran was added to one equivalent of AgCl (33 mg). The mixture was stirred for 2 h at room temperature resulting in an orange solution with yellow suspension that was filtered over filter paper. The filtrate was layered with ~25 mL of pentane. Orange block crystals suitable for X-ray diffraction were obtained after two days. The crystals were washed with 3 × 10 ml of pentane and dried under dynamic vacuum for further analyses (37.7% yield); m.p. 182–187 °C. ^{1}H NMR (CD_2Cl_2, 400.1 MHz, 25 °C): δ 4.13 (s, 15H, C_5H_5), 4.12 (br s, 6H, β-C_5H_4R), 4.10 (br s, 6H, α-C_5H_4R), 2.62 (m, 6H, $C_5H_4CH_2$), 1.91 (m, 6H, CH_2PH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.6 MHz, 25 °C): δ 88.7 (d, $^3J_{CP}$ = 15.3 Hz, *ipso*-C_5H_4R), 69.2 (s, C_5H_5), 68.5 (s, β-C_5H_4R), 68.2 (s, α-C_5H_4R), 27.4 (d, $^2J_{CP}$ = 16.9 Hz, $C_5H_4CH_2$), 26.4 (d, $^1J_{CP}$ = 6.1 Hz, CH_2PH_2); ^{31}P NMR (CD_2Cl_2,161.8 MHz, 25 °C): δ -4.2 (br); ^{31}P NMR (CD_2Cl_2,161.8 MHz, –60 °C): δ –3.1 (d-br, $^1J_{107Ag/109Ag\text{-}P}$ = 665 Hz), -8.5 (d-br, $^1J_{107Ag/109Ag\text{-}P}$ = 436 Hz) ppm. Anal. Calcd for $C_{36}H_{39}ClAgFe_3P$: C, 53.15; H, 4.83. Found: C, 53.64 H, 5.08.

Synthesis of 3-CuOAc. 219 mg of the tertiary phosphine **3** (0.327 mmol) in 10 mL of tetrahydrofuran was reacted with one equivalent (40 mg) of Cu(OAc) as described for the preparation of **1-CuCl** (60.0% yield); m.p. 114–120 °C. Orange block single crystals suitable for X-ray diffraction were obtained after a couple of days by layering the reaction solution with 35 mL of pentane. ^{1}H NMR (CD_2Cl_2, 599.4 MHz, 25 °C): δ 4.14 (s, 6H, β-C_5H_4R), 4.13 (s, 15H, C_5H_5), 4.09 (s, 6H, α-C_5H_4R), 2.60 (m, 6H, $C_5H_4CH_2$), 2.01 (br, 3H, CH_3-acetate), 1.84 (m, 6H, CH_2P); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.6 MHz, 25 °C): δ 89.1 (d, $^3J_{CP}$ = 15.3 Hz, *ipso*-C_5H_4R), 69.2(s, C_5H_5), 68.5 (s, β-C_5H_4R), 68.1 (s, α-C_5H_4R), 27.0 (d, $^2J_{CP}$ = 20.7 Hz, $C_5H_4CH_2$), 25.9 (d, $^1J_{CP}$ = 4.6 Hz, CH_2P); ^{31}P NMR (CD_2Cl_2,161.8 MHz, 25 °C): δ –13.2 (br) ppm. Anal. Calcd for $C_{38}H_{42}CuFe_3O_2P$: C, 57.57; H, 5.34. Found: C, 57.61; H, 5.53.

Synthesis of 3-AgOAc. 151 mg of tertiary phosphine **3** (0.225 mmol) was dissolved in 10 mL tetrahydrofuran and reacted with one equivalent (37 mg) of Ag(OAc). The reaction mixture was stirred for 30 min at room temperature followed by filtration over a filter paper to yield a clear, dark red solution. The filtrate was layered with ~25 mL hexane. Orange block single crystals suitable for X-ray diffraction were obtained after three days. The crystals were washed with 3 × 10 mL of pentane and dried under dynamic vacuum for further analyses (72.4% yield); m.p. 100-105 °C. ^{1}H NMR (CD_2Cl_2, 399.8 MHz, 25 °C): 4.12 (s, 15H, C_5H_5), 4.11 (br s, 6H, β-C_5H_4R), 4.10 (br s, 6H, α-C_5H_4R), 2.58 (m, 6H, $C_5H_4CH_2$), 1.99 (s, 3H, OC(O)CH_3-acetate), 1.86 (m, 6H, CH_2P); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.5 MHz, 25 °C): δ 179.5 (s, CH_3-acetate), 88.2 (d, $^3J_{CP}$ = 15.3 Hz, *ipso*-C_5H_4R), 69.2 (s, C_5H_5), 68.5 (s, β-C_5H_4R), 68.3 (s, α-C_5H_4R), 27.5 (d, $^2J_{CP}$ = 19.9 Hz, $C_5H_4CH_2$), 26.7 (d, $^1J_{CP}$ = 5.4 Hz, CH_2P), 22.9 (s, CH_3-acetate); ^{31}P NMR (CD_2Cl_2,161.8 MHz, –60 °C): δ –1.0 (two doublets from P-Ag coupling, $^1J_{P\text{-}}{}^{107}{}_{Ag}$ = 668 Hz, $^1J_{P\text{-}}{}^{109}{}_{Ag}$ = 770 Hz) ppm. Anal. Calcd for $C_{38}H_{42}AgFe_3O_2P$: C, 54.52; H, 5.06. Found: C, 54.82; H, 5.32.

Synthesis of 2-AuCl. 70 mg of the secondary phosphine **2** (0.153 mmol) was added to one equivalent of 45 mg (0.15 mmol) Me_2SAuCl followed by the addition of 5 mL of acetone. Stirring the reaction mixture for 60 min at room temperature yielded an orange solution with a fine suspension which was filtered over a filter paper to yield a clear orange solution. The filtrate was layered with ~25 mL pentane. Orange, plate-like single crystals suitable for X-ray diffraction were obtained after two days. The crystals were washed with 3×10 mL pentane and dried under vacuum (65.1% yield); m.p. 162–165 °C. ^{1}H NMR (CD_2Cl_2, 400.1 MHz, 25 °C): δ 5.06 (d of m, $^1J_{HP}$ = 378.3 Hz, 1H, PH), 4.12 (s, 10H, C_5H_5), 4.11 (br s, 4H, β-C_5H_4R), 4.10 (br s, 4H, α-C_5H_4R, slightly overlapped with the peak at 4.12), 2.65 (m, 4H, $C_5H_4CH_2$), 2.09 (m, 4H, CH_2PH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.6 MHz, 25 °C): δ 87.2 (d, $^3J_{CP}$ = 13.8 Hz, *ipso*-C_5H_4R), 69.2 (s, C_5H_5), 68.8 (d, $^4J_{CP}$ = 10.7 Hz, β-C_5H_4R), 68.4 (s, α-C_5H_4R), 27.6 (s, $C_5H_4CH_2$), 24.2 (d, $^1J_{CP}$ = 36.0 Hz, CH_2PH_2); ^{31}P NMR (CD_2Cl_2,161.8 MHz, 25 °C): δ –18.7 (d-br, $^1J_{PH}$ = 378 Hz) ppm.

Synthesis of 3-AuCl. A solution of 127 mg of the tertiary phosphine **3** (0.189 mmol) in 5 mL of tetrahydrofuran was added to one equivalent of Me_2SAuCl (56 mg). The reaction mixture was stirred for 12 hrs to give **3-AuCl** in the form of a yellow precipitate. The light yellow solid, separated by centrifuge, was twice washed with 10 mL tetrahydrofuran. The solid was dissolved in 5 mL dichloromethane and layered with 20 mL pentane to yield yellow, plate-like single crystals of **3-AuCl** after three days; (48.8 % yield); m.p. 182–185 °C). ^{1}H NMR (CD_2Cl_2, 400.1 MHz, 25 °C): δ 4.13 (s, 15H, C_5H_5), 4.12 (br s, 6H, β-C_5H_4R), 4.11 (br s, 6H, α-C_5H_4R), 2.64 (m, 6H, $C_5H_4CH_2$), 2.0 (m, 6H, CH_2PH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.6 MHz, 25 °C): δ 87.8 (d, $^3J_{CP}$ = 16.1 Hz, *ipso*-C_5H_4R), 69.2 (s, C_5H_5), 68.6 (s, β-C_5H_4R), 68.3 (s, α-C_5H_4R), 28.1 (d, $^1J_{CP}$ = 34.5 Hz, CH_2PH_2), 26.3 (s, $C_5H_4CH_2$); ^{31}P NMR (CD_2Cl_2,161.9 MHz, 25 °C): δ 22.0 (s) ppm. Anal. Calcd for $C_{36}H_{39}AuClFe_3P$: C, 47.90; H, 4.36. Found: C, 48.40 H, 4.47.

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