Facile Synthesis and Ambident Coordination of Cyclohexylbis-(2-pyridyl)phosphane: Novel Dinuclear Complexes of Cu^{+1}, Ag^{+1}, and Co^{+2} Ions

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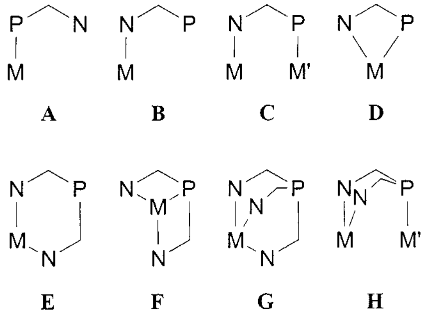
The title compound cyclohexylbis(2-pyridyl)phosphane (**1**) was synthesized by a Pd^0-catalyzed cross-coupling reaction from 2-bromopyridine and cyclohexylphosphane in 98% yield. Compound **1** formed colorless crystals that were moderately air-stable. It reacted, in CH_3CN, with CuOTf (OTf = OSO_2CF_3), $AgBF_4$, and $Co(BF_4)_2$ to form the complexes $[Cu_2\{CyP(2\text{-}Py)_2\}_2(NCCH_3)_2](OTf)_2$ (**2**), $[Ag_2\{CyP(2\text{-}Py)_2\}_2(NCCH_3)_2](BF_4)_2$ (**3**), and $[Co_2\{CyP(2\text{-}Py)_2\}_2(NCCH_3)_2](BF_4)_4$ (**4**), respectively. In these complexes, the pyridylphosphane ligands coordinate to two metal centers in a head-to-tail fashion involving both the P and the N atoms simultaneously. The compounds represent the first structurally characterized examples of dimeric dinuclear pyridylphosphane complexes showing the *P,N,N′* coordination. Reactions of **1** with other salts containing Cu^{+1} and Co^{+2} centers and coordinating anions resulted in different coordination modes. Thus, CuI reacted with **1** to form the complex $[Cu_2\{CyP(2\text{-}Py)_2\}_2I_2]$ (**5**) with both coordinated P and N donor centers and a terminal iodide. In contrast, the reaction of **1** with $CoCl_2$ afforded the mononuclear complex $[Co\{CyP(2\text{-}Py)_2\}Cl_2]$ (**6**) in which only the pyridyl N atoms and the chlorine ligands were coordinated to the metal center. X-ray analyses of the compounds **1**, **2**, **3**, **5**, and **6** are reported.

Introduction

Since 2-pyridylphosphanes can act as monodentate (*P*-coordinated), bidentate (*P,N*- or *N,N′*-chelating or *P,N*-bridging), or tridentate (*P,N,N′*-chelating or *N,N′,N′′′*-chelating) ligands with both hard (N) and soft (P) donor centers, they have been a topic of interest in the last 30 years.[1,2] Scheme 1 shows the various possible coordination modes for pyridylphosphanes **A**−**H**. All displayed modes have been described, except the coordination mode **H**.



Scheme 1. Some possible coordination modes **A**−**H** for pyridylphosphanes toward metal centers

Apart from the interesting structural features, pyridylphosphane metal complexes have been shown to act as good catalysts for reactions like the carbonylation of alkynes to form methacrylate,[3] showing surprisingly high turnover rates combined with an excellent product selectivity.

In contrast to the extensive use of diphenyl-2-pyridylphosphane[4] and its derivatives,[5] and the numerous complexes described with tris(2-pyridyl)phosphane,[6] the knowledge of bis-2-pyridylphosphanes is scarce.[7,8] Only recently, Ag^{+1} and Au^{+1} complexes of 1,2-bis(dipyridylphosphanyl)ethane have been shown to provide a promising approach in cancer research for their potent and selective antitumor activity.[9]

Usually, the synthesis of 2-pyridylphosphanes is achieved by the reaction of the 2-lithium pyridine with the appropriate chlorophosphane at very low temperatures (less than −90 °C). In searching for a convenient and more selective way of synthesizing pyridylphosphanes with varying alkyl substituents we have found that the reaction of cyclohexylphosphane with 2-bromopyridine in acetonitrile in a Pd^0-catalysed cross-coupling reaction[10] furnished cyclohexyl(2-pyridyl)phosphane (**1**) in 98% yield. This reaction type, which resembles the Stille coupling reaction,[11] has been extended to phosphanes without silyl or stannyl groups by Stelzer et al., and tolerates a number of functional groups that limit the versatility of the lithium pyridyl method.[12] Reactions of cyclohexylbis(2-pyridyl)phosphane (**1**) in acetonitrile with different Cu^{+1}, Ag^{+1}, and Co^{+2} salts containing weakly coordinating anions ($CF_3OSO_2^-$, BF_4^-) furnished the dinuclear complexes **2**, **3**, and **4**, respectively. In these complexes, the pyridylphosphane ligands coordinate in a head-to-tail bridging mode involving both the P and the N donor centers. To the best of our knowledge, these are the first structurally characterized complexes of (2-pyridyl)phosphanes that represent the coordination mode **H** (Scheme 1). CuI with the stronger coordinating iodide anion reacted with **1** to form the isostructural complex **5**, while $CoCl_2$ lead to the mononuclear complex **6**, which represents the coordination mode **E**, involving only the pyridyl

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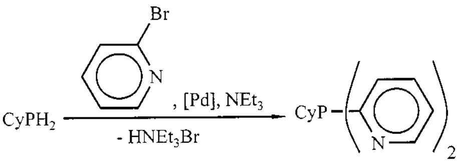
N atoms and the two chlorine atoms as donor centers toward the Co atom.

Results and Discussion

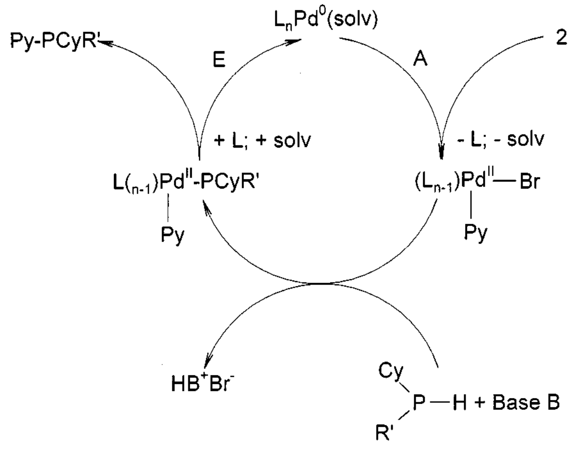
Synthesis of Cyclohexylbis(2-pyridyl)phosphane (1)

If cyclohexylphosphane is allowed to react with two molar equivalents 2-bromopyridine and triethylamine in the presence of catalytic amounts of tetrakis(triphenylphosphane)palladium(0) in acetonitrile for 24 hours, the desired cyclohexylbis(2-pyridyl)phosphane (**1**) is formed in 98% yield. The reaction can easily be monitored by ^{31}P-NMR spectroscopy, and proceeds stepwise via cyclohexyl-2-pyridylphosphane as the initial product. The latter can be identified by its diagnostic ^{31}P NMR signal ($\delta = -26.8$, $^1J_{PH} = 212.6$ Hz).



1 : Cy = C_6H_{11}

This type of Pd-catalyzed cross-coupling reaction has been described previously by Stelzer et al.,[10] and resembles the Stille coupling reaction.[11] The synthesis of **1** is the first example in which a primary aliphatic phosphane and 2-bromopyridine have been successfully coupled. The mechanism of the reaction involves the oxidative addition of 2-bromopyridine to the palladium catalyst, followed by the substitution of one triphenylphosphane ligand by cyclohexylphosphane or cyclohexyl-2-pyridylphosphane, respectively. Finally, the product is formed through a P−C bond formation in a reductive-elimination step (Scheme 2).[12]



Scheme 2. Proposed mechanism for the Pd^0-catalyzed synthesis of **1** based on previous results, starting from $CyPH_2$, 2-bromopyridine, and a Base. R′ = H, L = PPh_3, solv = solvent

Compound **1** forms colorless, fairly air-stable crystals that are soluble in most organic solvents. The ^{31}P NMR spectrum of **1** in C_6D_6 shows a singlet at $\delta = -3.2$, similar to the values observed for tris(2-pyridyl)phosphane ($\delta = -1.3$), phenylbis(2-pyridyl)phosphane ($\delta = -2.9$), and diphenyl(2-pyridyl)phosphane ($\delta = -1.9$).[13]

Crystal Structure of 1

Crystals of **1** suitable for an X-ray diffraction analysis were obtained from solutions in hexane. A view of its molecular structure is shown in Figure 1 and the crystallographic details are given in the Experim. Section.

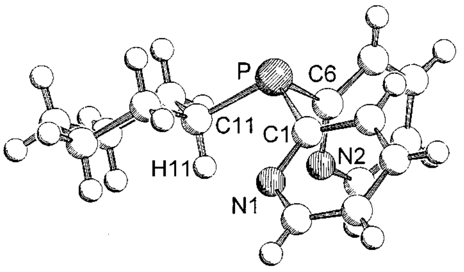


Figure 1. Molecular structure of cyclohexylbis(2-pyridyl)phosphane **1**. Selected distances [Å] and angles [°]: P1−C11 1.847(4), P1−C6 1.851(4), P1−C1 1.854(5), C11−P−C6 101.6(1), C11−P−C1 101.4(1), C6−P−C1 97.6(1)

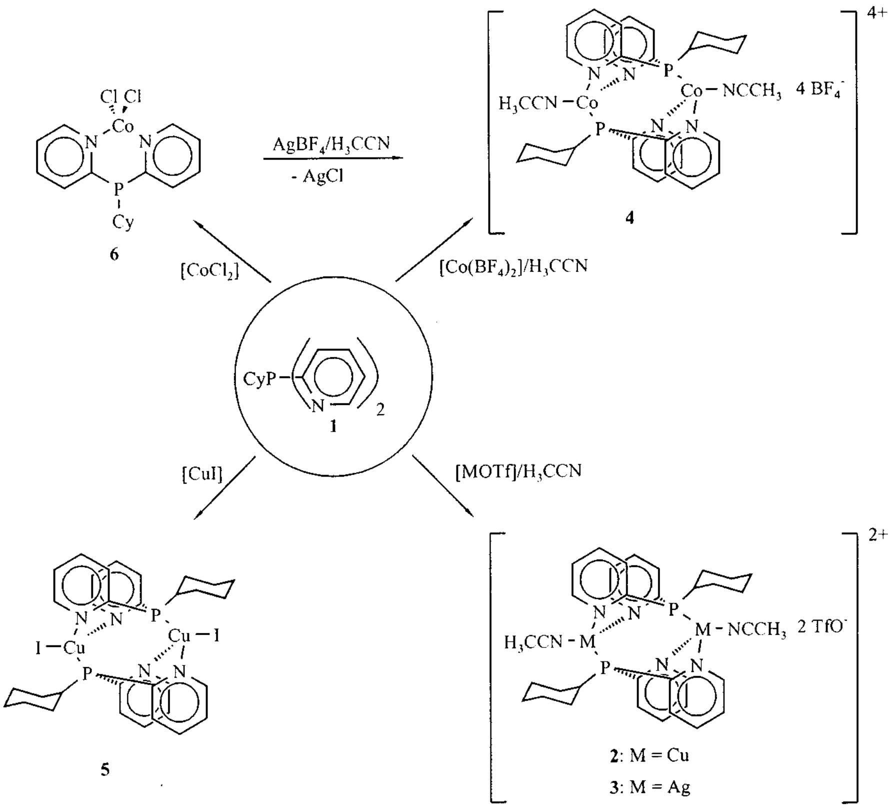
The P−C distance of 1.847(4) Å in **1** is similar to those in tris(2-pyridyl)phosphane (1.83 Å and 1.82 Å). As expected, the P atom has a pyramidal coordination, with the sum of bond angles at phosphorus of 300.6°. The latter value is only slightly smaller than that in tris(2-pyridyl)phosphane (305.6°).

While the C11−P−C6 and the C11−P−C1 angles [101.6(1) and 101.4(1)°] are practically identical to the corresponding angles in tris(2-pyridyl)phosphane, the C6−P1−C1 angle of 97.6(1)° is notably smaller. The N centers are directed away from the lone pair at the P atom. A similar orientation is also found for two pyridyl groups in tris(2-pyridyl)phosphane, while the third pyridyl substituent in the latter compound is rotated away from the other two.[14]

Coordination Reactions of 1 with Cu^{+1}, Ag^{+1}, and Co^{+2} Salts

Treatment of acetonitrile solutions of $Cu(O_3SCF_3)$, $AgBF_4$, and $Co(BF_4)_2$ with **1** at room temperature affords the dinuclear complexes **2**, **3**, and **4**, respectively. All three complexes form colorless (**2**, **3**) or pink (**4**) crystals from acetonitrile solution and are practically insoluble in other common solvents.

A ligand exchange of acetonitrile by other solvent molecules, as has been found in similar complexes,[15,16] could therefore not be achieved. The ^{31}P-NMR spectra show singlet signals at $\delta = 0.2$ for **2** and at $\delta = 23.6$ for **3**, thus confirming the coordination of the phosphorus atom by a downfield shift with respect to the value for the "free" ligand **1**. These values compare well with those in similar Cu and Ag complexes with bridging pyridylphosphanes, as observed in $[Cu_2(\mu\text{-}Ph_2P\text{-}Py)_3CH_3CN]^{2+}$ ($\delta = 5.45$)[15] and $[Ag_2(Ph_2P{-}Py)_2]^{2+}$ ($\delta = 25.7$), respectively.[17]



In order to investigate the influence of the anion on the coordination mode, and also to overcome the poor solubility properties of the ion pairs **2**, **3**, and **4**, CuI was allowed to react with **1** in THF at 50 °C. Yellow crystals of **5** precipitated as the desired product from the reaction mixture. Compound **5** turned out to be well soluble in THF, CH_2Cl_2, $CHCl_3$, and acetone. Its ^{31}P-NMR spectrum reveals a singlet at $\delta = 1.5$, very similar to that chemical shift observed for **2**. The crystal structure, which is described below, indeed shows that **5** is isostructural with the cation in **2**, except that the terminal acetonitrile ligands were replaced by iodine ions.

In contrast, the reaction of $CoCl_2$ with **1** yielded the complex **6** in good yields, which implies a different coordination mode of the dipyridylphosphane **1**, involving only the pyridyl N donor atoms and the Cl ligands as donor centers. As expected for a Co^{+2} complex, **6** is paramagnetic and unlike the other complexes, which are rather sensitive to air and water, is indefinitely resistant in air and moisture. It is soluble in most organic solvents and reacts with two equiv. of $AgBF_4$ in acetonitrile giving the separated ion pair **4** and AgCl.

Crystal Structures of 2, 3, and 4

The molecular structures of **2** and **3** are shown in Figure 2 and 3, while experimental details of the X-ray analyses are described in the Experim. Section and in Table 2. In all three complexes, the metal centers are held together in close proximity by the two bridging ligands that coordinate in a head-to-tail fashion and resemble the dimeric form of the coordination mode **H**, according to Scheme 1. In addition, both metal centers bear an acetonitrile ligand to achieve a distorted tetrahedral coordination sphere. Espinet et al. have merely described several dipyridylphosphane Mo^0 complexes for one of which the *P*,*N*,*N′*-coordination mode **F** was postulated, but crystallographic evidence could not be achieved.[18]

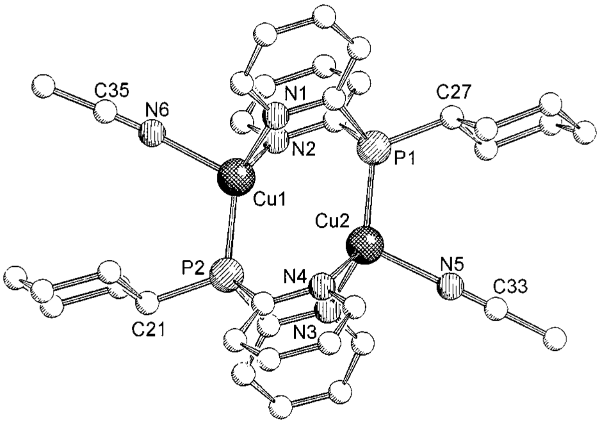


Figure 2. Molecular structure of the dication in **2**. For the sake of clarity, the H atoms have been omitted. Selected distances [Å] and angles [°]: Cu2···Cu1 3.225(2), Cu−N(Py, average) 2.077(3), Cu−N (acetonitrile, average) 2.093(3), Cu1−P2 2.202(1), Cu2−P1 2.186(1); N2−Cu1−N1 94.2(1), N2−Cu1−P2 123.7(1), N1−Cu1−P2 126.2(1), N3−Cu2−N4 90.7(1), N3−Cu2−P1 125.2(1), N4−Cu2−P1 127.9(1), Cu2−N5−C33 171.0(4), Cu1−N6−C35 171.5(4)

In **2**, the copper centers are surrounded, in a distorted tetrahedral geometry, by one phosphorus and three nitrogen donors. The Cu centers lie about 48 pm outside of the P,N,N′-plane. The N(Py)−Cu−N(Py) bond angles of 90.7(1) and 94.2(1)°, respectively, are considerably smaller than those of the P−Cu−N(Py) angles, which vary between 123.7(1) and 127.9(1)°, respectively. Such a difference has also been observed in the $[Cu_2(\mu\text{-dppy})_3(CH_3CN)]^{2+}$ ion [dppy = diphenyl(2-pyridyl)phosphane],[15] in which one Cu center is also coordinated in a distorted tetrahedral arrangement. However, the differences between the N(Py)−Cu−N(Py)- and the P−Cu−N(Py) angles, respectively, are less significant in the latter complex, due to stronger geometric constraints in the ligand backbone in **2** than in dppy in $[Cu_2(\mu\text{-dppy})_3(CH_3CN)]^{2+}$. The Cu···Cu distance of 3.225(2) Å is larger than the respective distance in $[Cu_2(\mu\text{-dppy})_3(CH_3CN)]^{2+}$ (2.72 Å), in which one Cu center is tetrahedral and the other trigonal-planar coordinated.[19] It is, however, shorter than in $[Cu_2(\text{dppy})_2(CH_3CN)_2]^{2+}$ (3.58 Å) with both Cu atoms being trigonal coordinated.[19] The value is also considerably shorter than in $[Cu_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(CH_3CN)_4]^{2+}$ (3.75 Å),[20] in which both Cu centers are surrounded by four donor atoms. The close proximity between the Cu atoms in **2** compared with that in $[Cu_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(CH_3CN)_4]^{2+}$ probably reflects the higher ring strain induced by the relatively rigid threefold coordination within the ligand backbone rather than suggesting attractive intermetallic interactions. According to Figure 3, the dinuclear Ag complex **3** adopts the same core structure as **2**. However, the tetrahedral coordination geometry around the Ag centers is even more distorted than that in **2** with P−Ag−N(Py) angles varying between 126.6(1) and 135.2(1)°, while the N(Py)−Ag−N(Py) angles are 86.7(2) and 87.4(2)°, respectively.

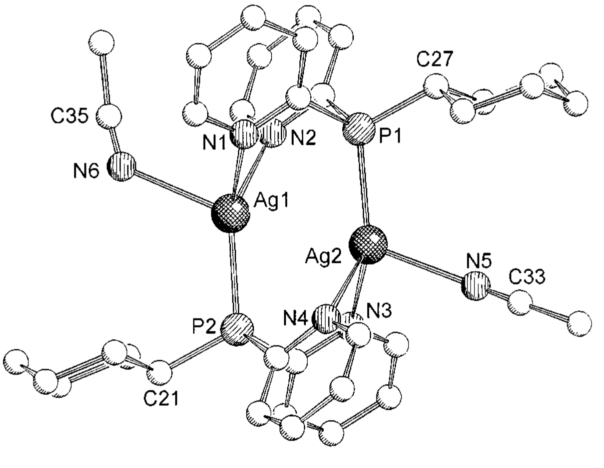


Figure 3. Molecular structure of the dication in **3**. For the sake of clarity, the H atoms have been omitted. Selected distances [Å] and angles [°]: Ag1···Ag2 2.932(4), Ag−N(Py, average) 2.397(5), Ag1−N6 2.466(7), Ag2−N5 2.373(6), Ag1−P2 2.390(1), Ag2−P1 2.383(2); N2−Ag1−N1 86.7(2), N1−Ag1−P2 129.5(1), N2−Ag1−P2 134.6(1), N3−Ag2−N4 87.4(2), N3−Ag2−P1 135.2(1), N4−Ag2−P1 126.6(1), Ag1−N6−C35 125.9(7), Ag2−N5−C33 158.9(5)

The Ag···Ag distance of 2.932(4) Å is shorter than that in other complexes with bridging pyridylphosphanes like $[Ag_2(Ph_2P\text{-}Py)_2](NO_3)_2$ (3.14 Å),[21] $[Ag_2(\eta^1\text{-}Ph_2P\text{-}Py)(\mu\text{-}Ph_2P\text{-}Py)_2](ClO_4)_2$ (3.07 Å),[17] $[Ag_2(Ph_2P\text{-}Py)_3]Cl_2$ (3.08 Å),[22] and $[Ag_2(\mu\text{-L})_2(CH_3CN)_2](ClO_4)_2$ [L = 2-(diphenylphosphanyl)-6-(pyrazol-1-yl)pyridine] (2.96 Å).[23]

Surprisingly, the Ag···Ag distance in **3** is smaller than the Cu···Cu distance in **2**, and the same is true for the homologous complexes $[Ag_2(\mu\text{-L})_2(CH_3CN)_2](ClO_4)_2$ and $[Cu_2(\mu\text{-L})_2(CH_3CN)_2](ClO_4)_2$ [L = 2-(diphenylphosphanyl)-6-(pyrazol-1-yl)pyridine].[23,24] This observation may indicate attractive interactions between the Ag centers due to a larger contribution of relativistic effects. However, in the case of bridging ligands, it is difficult to distinguish between ligand-induced effects (strain) and true "metallophilic" d^{10}-d^{10} dispersion-type interactions.[25] It is also noteworthy that one of the acetonitrile molecules is coordinated to the Ag center with an Ag−N−C angle of 125.9(7)°, while the other Ag−N−C moiety adopts an angle of 158.9(5)°. A similar small Cu−N−C bond angle of 129.2° has also been observed in the case of the Cu(+1) complex [Cu(acac)(phen)(CH_3CN)](ClO_4) (acac = acetylacetonate; phen = 1,10-phenanthroline),[26] but **3** represents the first Ag^{+1} acetonitrile complexes with an Ag−N−C angle < 140° (Table 1).

Table 1. Comparison of Ag−N bond length and the Ag−N−C angle in different Ag(+1)-acetonitrile complexes

AgNC[a]	Ag−N[b]	compound	ref.
174.5	2.08	$[Ag\{CF(CF_3)_2\}(NCCH_3)]$	[30]
156.2	2.11	$[Ag_3L^1(NCCH_3)_3]$[c]	[31]
178.8	2.14	$[Rh_6C(CO)_{15}\{Ag(NCCH_3)_2\}_2]$	[32]
165.3	2.25	$[Ag(NCCH_3)_4]^+$	[33]
162.0	2.27	$[Ag_2L^2(NCCH_3)_2](BF_4)_2$[d]	[34]
146.1	2.27	$[Ag\{NCCH_3)_2\text{-}\{\mu_4\text{-}3,6\text{-}(Ph_2P)_2Pyr\}]_n$[e]	[23]
162.7	2.28	$[AgL^3(NCCH_3)_2]$ (SbF_5)[f]	[35]
152.5	2.28	$[AgL^3(NCCH_3)_2]$ (SbF_5)[f]	[23]
158.9	2.37	**3**, this work	
156.0	2.41	$[Ag\{\mu_2\text{-}2\text{-}(Ph_2P)\text{-}6\text{-}(Pyz)Py\}_2\text{-}(NCCH_3)]_2(ClO_4)_2$[g]	[23]
140.7	2.42	$[\{\mu_2\text{-}2,6\text{-}(Ph_2P)_2Py\}\text{-}Ag(NCCH_3)_2]$	[36]
125.9	2.47	**3**, this work	

[a] Ag−N−C angle at the coordinated CH_3CN (°). − [b] Bond length (Å). − [c] L^1 = μ_3-6,13,20-trimethoxycalix(3)pyridine. − [d] L^2 = μ_2-1,11-(1,2)Ph-3,6,9,13,16,19-hexathiacycloicosaphane. − [e] Pyr = pyridazine. − [f] L^3 = μ_2-3,7-di-*tert*-butyl-2,8-dioxa-5-aza-1-phosphabicyclo(3.3.0)octa-2,4,6-triene. − [g] Pyz = pyrazole

It has been proposed that the M−N−C angle of the acetonitrile ligand corresponds well with the M−N(acetonitrile) distance in such a way that longer M−N bonds imply a smaller M−N−C angle, thereby representing a rather early stage of acetonitrile coordination.[15] This trend is supported by the respective data of $CH_3CN\text{−}Ag^{+1}$ complexes that are summarized in Table 1. However, the $[AgL^3(NCCH_3)_2]$ cation [L^3 = μ_2-3,7-di-*tert*-butyl-2,8-dioxa-5-aza-1-phosphabicyclo(3.3.0)octa-2,4,6-triene] is an exception, revealing two different Ag−N−C angles (Δ = 10°), and at the same time, equidistant Ag−N bonds (2.28 Å).[32] Quantitative correlation of the Ag^{+1} complexes seems very difficult because a clear distinction between electronic effects, steric influences, and possible packing effects cannot be made. Nonetheless, the relatively small Ag−N−C angle of 125.6(1) at one Ag center and the much shorter Ag···Ag distance in **3** [2.932(4) Å] are consistent with the presence of metallophilic Ag(donor)−Ag(acceptor) interactions. This is because its Cu-homologue **2** is apparently different, possessing a much longer M···M distance of 3.225(2) Å and both acetonitrile ligands are inconspicuously coordinated to the Cu^{+1} centers [averaged Cu−N−C angle 171.2(4)°].

The paramagnetic dicobalt complex **4** shows basically the same core-structure as **2** and **3**. According to a preliminary X-ray structure analysis of moderate crystals of **4**, which crystallizes in the monoclinic space group $P2_1/c$ [$R1$ = 0.1319, $wR2$ (all data) = 0.3397], the Co···Co distance of 2.976(5) Å is larger than that in other dinuclear complexes like [Co^{I}Co^{0}(μ-Ph$_2$PPy)$_2$(μ-CO)(CO)Cl][27,34] and [Co$_2^0$(μ-Ph$_2$PPy)(η^2-μ-HC≡CSiMe$_3$)].[28,35] The latter complexes imply Co−Co bonds due to short intermetallic distances and electron deficiency. In the acetylene complex, the observed diamagnetism, shown by a ^{31}P-NMR spectrum, provides further proof of an antiferromagnetic coupling of the unpaired electrons at the Co centers. This is, however, not the case in **4**, which is reluctant to undergo direct- or ligand-induced coupling of the d^7-Co centers even at 15 K. This was proven by temperature-dependent magnetic susceptibility measurements and fitting of the observed data with the calculated values. The effective magnetic moment of η_{eff} = 5.5 B.M. at room temperature seems relatively large in comparison to mononuclear tetrahedral Co^{+2} complexes that show η_{eff} values in the range between 4.3 and 5.2 B.M. However, larger values can be expected due to the different nature of the ligands and their ligand fields.[36,37] In line with that, simulations of the magnetic moment of high-spin Co^{+2} ions in a tetrahedral ligand field revealed the η_{eff} value of 4.82 B.M., which can be increased using appropriate ligands. The results suggest that spin-spin coupling between the Co^{+2} ions in **4** is negligible.

Crystal Structure of 5

Crystals of **5** suitable for an X-ray diffraction analysis were obtained by recrystallization in CH$_2$Cl$_2$. Its structure is shown in Figure 4. As expected, the structure of **5** is identical with that of **2**, but in place of the terminal acetonitrile ligands, iodine ions are coordinated to the Cu centers of **5**. This can be explained by the superior coordinating ability of the iodine ions compared to the triflate anion. The Cu···Cu distance of 3.333(3) Å is ca. 0.1 Å longer than that in **2**, and the tetrahedral coordination geometry of the Cu centers is notably distorted. The two N(Py)−Cu−N(Py) angles of 93.9(2) and 100.8(2)° are considerably different from the corresponding values in **2** [90.7(1) and 94.2(1)°]. Several attempts to exchange the iodine atoms at copper by organo substituents, through reaction of **5** with MeLi, BuLi, and lithium phenylacetylide, did not lead to any isolable product.

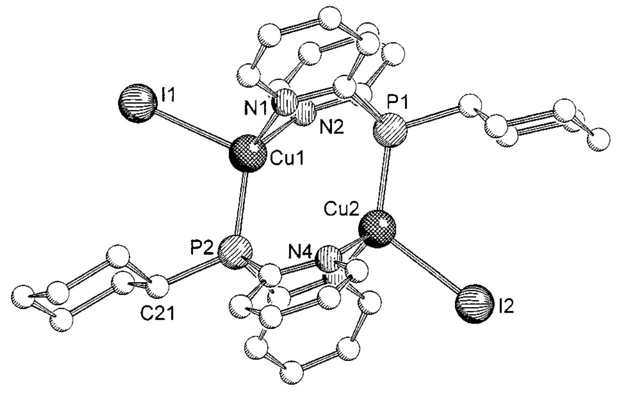


Figure 4. Molecular structure of **5**. For the sake of clarity, the H atoms have been omitted. Selected distances [Å] and angles [°]: Cu1···Cu2 3.333(3), Cu1−I1 2.7201(8), Cu2−I2 2.6978(8), Cu−N(Py, average) 2.052(4), Cu1−P2 2.189(2), Cu2−P1 2.218(2); N2−Cu1−N1 100.8(2), N2−Cu1−P2 114.6(1), N1−Cu1−P2 122.5(1), N3−Cu2−N4 93.9(2), N3−Cu2−P1 116.6(1), N4−Cu2−P1 127.5(1)

Crystal Structure of 6

The CoCl$_2$ complex **6** affords dark-blue crystals that could be recrystallized in most organic solvents. According to its X-ray diffraction analysis, the ligand **1** adopts a different coordination mode in the mononuclear complex than in the dimeric acetonitrile complex **4**, which is also apparent from their different color. Crystallographic details for **6** are summarized in Table 2 and Figure 5 shows a model of its crystal structure. In **6**, both N donor atoms of the ligand coordinate to the Co^{+2} center, affording a distorted tetrahedral N$_2$Cl$_2$ coordination geometry around the Co atom, while the P atom is only a spectator, bridging center. The ligand and the metal form a six-membered CoN$_2$C$_2$P ring that prefers the thermodynamically favorable chair conformation. As expected, the structure is similar to that of [Co(N,N′-PhPPy$_2$)Cl$_2$].[38] The Co−N distances are identical with those in other Co(+2) dipyridyl complexes like

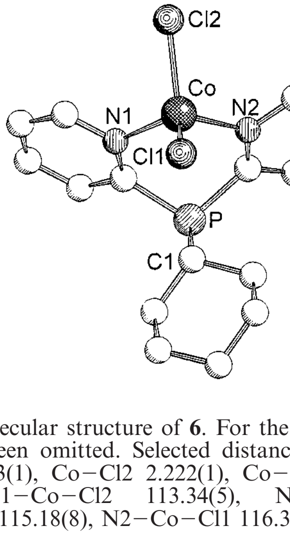


Figure 5. Molecular structure of **6**. For the sake of clarity, the H atoms have been omitted. Selected distances [Å] and angles [°]: Co−Cl1 2.213(1), Co−Cl2 2.222(1), Co−N1 2.034(3), Co−N2 2.028(3); Cl1−Co−Cl2 113.34(5), N1−Co−N2 99.5(1), N1−Co−Cl1 115.18(8), N2−Co−Cl1 116.32(8)

[Co(4-vinylpyridine)$_2$Cl$_2$][29,39] and [Co(4-methyl pyridine)$_2$Cl$_2$], respectively.[40] The tetrahedral coordination geometry at the Co(+2) center is somewhat more distorted than in the latter because of the phosphane linkage between the pyridyl rings in the *meta* positions. The N−Co−N angle of 99.5° in **6**, especially, shows a considerable deviation from the ideal tetrahedral angle. An even smaller N−Co−N angle of 94.8° is observed in [Co(*N*,*N*′-PhPPy$_2$)Cl$_2$].[38]

Conclusion

We reported here on an economical and at the same time facile synthesis of (cyclohexyl)bis(2-pyridyl)phosphane (**1**). The formation of its new complexes **2**−**5** proves the existence of the missing *P*,*N*,*N*′-coordination mode **H** for dipyridylphosphanes. Apparently, this coordination mode supports the formation of dinuclear complexes. The metals in **2**−**5** are in close proximity, which in general permits intermetallic interactions influenced by the terminal ligands at the metal center. The formation of the mononuclear Co complex **6** illustrates the directing influence of the hardness of the anion and its coordination ability on the coordination properties of the metal toward the chelate ligand **1**. Further investigations to synthesize related water-soluble dinuclear complexes and to probe their use in metal-assisted organic synthesis are in progress.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques unless otherwise stated. Solvents and reagents were dried by standard methods and distilled prior to use. − The ^{31}P- and ^{1}H-NMR spectra were measured on a Bruker Avance 250 spectrometer at 250 MHz (^{1}H) and 101.3 MHz (^{31}P), respectively. Chemical shifts are given in ppm relative to respective standards. External standards for ^{1}H NMR: SiMe$_4$; ^{31}P NMR: H$_3$PO$_4$ (85% aq. solution). − Elemental analyses were performed on an Elementar VarioEL microanalyser.

Synthesis of CyP(2-Py)$_2$ (1): A solution of 1.0 g (8.6 mmol) of cyclohexylphosphane, 2.7 g (17.2 mmol) of 2-bromopyridine, 1.8 g (17.8 mmol) of triethylamine, and ca. 0.1 g of tetrakis(triphenylphosphanyl)palladium(0) in 20 mL of acetonitrile were degassed thoroughly in a Schlenk tube and sealed under vacuum. The reaction mixture was heated under reflux for 36 h, monitoring the progress of the reaction by ^{31}P-NMR spectroscopy. Then the solvent was evaporated in vacuo at 25 °C and the residue was taken up with 30 mL of hexane. The triethylammonium bromide was then filtered off and washed with two 5 mL portions of hexane. The filtrates were combined and the solvent removed in vacuo. Distillation gave the crude product that was recrystallized in hexane at −20 °C and dried in vacuo to give 2.25 g (8.4 mmol, 98%) of the colorless crystalline product. − ^{31}P NMR: δ = 3.2 (s). − ^{1}H NMR: δ = 1.2−2.2 [m, 10 H, C*H*(C*H*$_2$)$_5$], 3.2 [m, 1H, C*H*(CH$_2$)$_5$], 6.7 (m, 2 H, Py), 7.1 (m, 2 H, Py), 7.5 (m, 2 H, Py), 8.6 (m, 2 H, Py). − MS (EI, 70 eV): *m*/*z* (%) = 270 (35) [M$^+$], 193 ([M − C$_6$H$_4$N]$^+$, 80), 187 ([M − C$_6$H$_{11}$]$^+$, 100), 109 ([M − C$_6$H$_{11}$-C$_6$H$_4$N], 75). − HR-MS: calcd. *m*/*z* = 270.1283 for C$_{16}$H$_{19}$N$_2$P, found 270.1281.

Synthesis of {Cu$_2$[CyP(2-Py)$_2$]$_2$(NCCH$_3$)$_2$}(OTf)$_2$ (2): A solution of 0.33 g (0.7 mmol) of (CuOTf)$_2$·C$_6$H$_6$ in 10 mL of acetonitrile was allowed to react with 0.35 g (1.3 mmol) of **1** in 5 mL of acetonitrile at room temperature. After stirring the mixture overnight, a white precipitate formed that was recrystallized in acetonitrile to afford slightly yellowish crystals in 79% yield (1.0 g). − ^{31}P NMR: δ = 0.2 (s); elemental analysis calcd. (%): calcd. C 43.55, H 4.23, N 8.02; found (%) C 43.05, H 4.18, N 7.90.

Synthesis of {Ag$_2$[CyP(2-Py)$_2$]$_2$(NCCH$_3$)$_2$}(BF$_4$)$_2$ (3): To 0.20 g (1.0 mmol) of AgBF$_4$ in 10 mL of acetonitrile a solution of 0.30 g (1.0 mmol) of **1** in 5 mL of acetonitrile was added at room temperature. After stirring the mixture overnight, a white precipitate was formed that was recrystallized in acetonitrile to form colorless crystals in 85% yield (0.86 g). − ^{31}P NMR: δ = 0.2 (s); elemental analysis calcd. (%): calcd. C 42.72, H 4.38, N 8.30; found (%) C 43.21, H 4.35, N 8.35.

Synthesis of {Co$_2$[CyP(2-Py)$_2$]$_2$(NCCH$_3$)$_2$}(BF$_4$)$_4$ (4): A blue solution of 0.26 g (1.0 mmol) of CoCl$_2$ in 20 mL of CH$_3$CN was added to 0.40 g (2.0 mmol) of AgBF$_4$ at room temperature, from which the color of the solution turned pink and AgCl precipitated. The latter was filtered off and the clear filtrate allowed to react with 0.30 g (1.0 mmol) of **1** in 10 mL of CH$_3$CN at room temperature. After stirring the pink solution for 12 h, the reaction mixture was reduced to 2 mL in vacuo and stored at −25 °C. The product precipitated in the form of pink crystals in 58% yield (0.34 g, 0.58 mmol). Elemental analysis of the mono-solvate with CH$_3$CN, calcd. (%): calcd. C 39.77, H 3.95, N 7.74; found (%): C 39.36, H 4.19, N 7.51.

Synthesis of {Cu$_2$[CyP(2-Py)$_2$]$_2$I$_2$} (5): CuI (0.70 g, 3.7 mmol) was dissolved in 120 mL of THF at 50 °C and a solution of 0.99 g (3.7 mmol) of **1** in 30 mL of THF was added with vigorous stirring. The reaction mixture turned yellow and standing of the solution at room temperature yielded, after 3 d, 1.75 g (1.64 mmol, 89%) of the product in the form of yellow crystals. − ^{31}P NMR (CDCl$_3$): δ = 1.5 (s, *w*1/2 = 22.8 Hz). − ^{1}H NMR (CDCl$_3$): δ = 1.2−2.2 [m, 20 H, CH(C*H*$_2$)$_5$], 3.1 [m, 2 H, C*H*(CH$_2$)$_5$], 7.5 (m, 4 H, Py), 7.8 (m, 8 H, Py), 9.1 (m, 4 H, Py); elemental analysis (solvate with two molecules THF) calcd. (%): calcd. C 45.08, H 5.12, N 5.26; found (%) C 44.14, H 5.10, N 5.36.

Synthesis of {Co[CyP(2-Py$_2$]Cl$_2$] (6): CoCl$_2$ (0.13 g, 1.0 mmol) was dissolved in 20 mL of CH$_3$CN at room temperature. To this deep-blue mixture a solution of **1** (0.27 g, 1.0 mmol) in 10 mL of CH$_3$CN was added, and the reaction mixture was stirred for 12 hours. Solvent was removed in vacuo to leave 5 mL of a dark-blue solution from which **6** crystallized in the form of dark-blue crystals. Yield: 0.37 g (0.93 mmol, 93%). − MS (EI, 70 eV): *m*/*z* (%) = 399 ([M]$^+$, 0.5), 364 ([M − Cl]$^+$, 3), 327 ([M − 2Cl]$^+$, 10), 270 ([CyPpy$_2$]$^+$, 80), 193 ([CyPpy$_2$-C$_6$H$_4$N]$^+$, 82), 187 ([CyPpy$_2$-C$_6$H$_{11}$]$^+$, 100), 109 ([CyPpy$_2$ -C$_6$H$_{11}$-C$_6$H$_4$N], 78); elemental analysis calcd. (%): calcd. C 48.03, H 4.79, N 7.00; found (%): calcd. C 47.80, H 5.22, N 6.99.

X-ray Structural Determinations: The intensities were measured with a Bruker-axs-SMART diffractometer (Mo-K_α radiation, λ = 0.7170 Å, ω scan). The structures were solved by direct methods (SHELXS97), and refined against F^2 with all measured reflections (SHELXL97). All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were introduced in calculated positions. Other experimental details are summarized in Table 2.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary

Table 2. Experimental data of the X-ray analyses

	1	**2**	**3**	**5**	**6**
empirical formula	$C_{16}H_{19}N_2P$	$C_{38}H_{44}Cu_2F_6N_6O_6P_2S_2$	$C_{36}H_{44}Ag_2B_2F_8N_6P_2$	$C_{32}H_{38}Cu_2I_2N_4P_2$	$C_{16}H_{19}Cl_2CoN_2P$
molecular mass	270.30	1654.01	1012.07	921.526	400.13
temperature [K]	203(2)	203(2)	203(2)	203(2)	203
crystal system	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic
space group	*Pn*	$P\bar{1}$	$P2_1/c$	*Pbca*	$P2_1/c$
unit cell dimensions [Å, °]	$a = 8.776(2)$	$a = 9.667(2)$	$a = 11.170(4)$	$a = 17.473(8)$	$a = 8.997(4)$
	$b = 10.057(2)$	$b = 15.321(4)$	$b = 10.083(3)$	$b = 20.397(2)$	$b = 14.310(6)$
	$c = 9.193(2)$	$c = 25.610(6)$	$c = 38.18(1)$	$c = 21.314(6)$	$c = 13.967(6)$
	$\alpha = 90$	$\alpha = 81.904(5)$	$\alpha = 90$	$\alpha = 90.00$	$\alpha = 90.00$
	$\beta = 115.45(3)$	$\beta = 84.210(4)$	$\beta = 90.478(1)$	$\beta = 90.00$	$\beta = 97.16(1)$
	$\gamma = 90$	$\gamma = 72.204(5)$	$\gamma = 90$	$\gamma = 90.00$	$\gamma = 90.00$
volume [Å^3]	732.8(3)	3569.0(1)	4301(2)	7596.8	1784.2(1)
Z	2	2	4	8	4
calcd. density [Mg/m^3]	1.225	1.539	1.536	1.756	1.490
crystal size [mm]	0.3 × 0.3 × 0.5	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.3	0.2 × 0.2 × 0.3	0.3 × 0.3 × 0.5
Θ range [°]	2.68 to 25.11	1.61 to 25.17	2.10 to 25.09		2.05 to 25.11
reflections collected	3619	18765	20385	40105	9210
independent reflections	2090	12478	7552	4875	3172
parameters	172	897	507	406	275
$R1[I > 2\sigma(I)]$[a]	$R = 0.0610$	$R = 0.0502$	$R = 0.0552$	$R1 = 0.0410$	$R1 = 0.0374$
$wR2$(all data)[b]	$wR2 = 0.1680$	$wR2 = 0.1424$	$wR2 = 0.1162$	$wR2 = 0.1098$	$wR2 = 0.0843$

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

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