Homoleptic Cu–phosphorus and Cu–ethene complexes†

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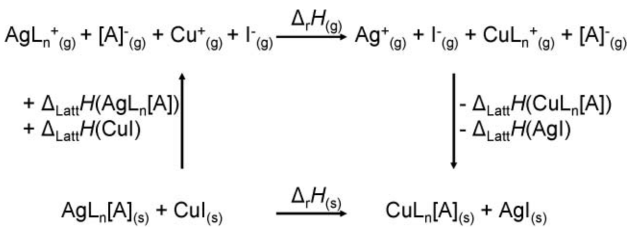
Stable salts of the first homoleptic Cu–phosphorus and Cu–ethene complexes, $[Cu(\eta^2\text{-}P_4)_2]^+$ and $[Cu(\eta^2\text{-}C_2H_4)_3]^+$, isolated by the aid of the weakly coordinating anion (WCA) $[Al(OC(CF_3)_3)_4]^-$, were obtained.

Currently known sources of Cu^I (*e.g.* with Cl^-, Br^-, I^-, BF_4^-, PF_6^-, counterions) are not suitable starting materials to extend the coordination chemistry of Cu^I with very weak bases due to the fact that Cu^+ often remains coordinated to the counterions.[1] "Naked" Cu^+ salts of large WCAs are unknown and the best approximation to "naked" Cu^I starting materials are $CuAsF_6$ and $CuSbF_6$.[2] Thus the preparation of a "naked" Cu^+ salt with a good WCA appears promising for coordination chemistry, catalysis and elsewhere.[3a] Our initial goal was the synthesis of a "naked" Cu^+ salt in analogy to the silver salt of the perfluoro-*tert*-butoxyaluminate $Ag[Al(pftb)_4]$ (pftb = $OC(CF_3)_3$),[3b] which we have previously used to investigate the rich $[AgL_n]^+$ coordination chemistry of Ag^+ with weak ligands, *e.g.* L = P_4, S_8, C_2H_4, C_2H_2, $P_3N_3Cl_6$.[4] Although we have been unable to synthesise a "naked" Cu^+ salt, we describe here a general route to the synthesis of Cu^+ complexes of very weak ligands as exemplified by the first homoleptic Cu–phosphorus and Cu–ethene complexes containing the weak ligands P_4 and C_2H_4.

Theoretical calculations[5] of an isodesmic reaction in combination with a suitable Born–Fajans–Haber cycle (Scheme 1), suggest that the formation of $Cu[Al(pftb)_4]$ from CuX (X = Cl, Br, I) and $Ag[Al(pftb)_4]$ should not proceed, as the reaction is always unfavourable by at least +73 kJ mol^{-1} (X = Br, L = nothing).



Scheme 1 Born–Fajans–Haber cycle to assess the accessibility of Cu salts.

However, if a suitable ligand is added to the system (*e.g.* L = P_4 or C_2H_4), $\Delta H^\circ_{(solid)}$ for the formation of $[Cu(P_4)_2][Al(pftb)_4]$ (**1**) and $[Cu(C_2H_4)_3][Al(pftb)_4]$ (**2**) from $[Ag(P_4)_2][Al(pftb)_4]$ or $[Ag(C_2H_4)_3][Al(pftb)_4]$, respectively, becomes negative (−8 and −17 kJ mol^{-1} respectively; see ESI†). This is due to the stronger Cu^+–L *vs.* Ag^+–L interactions.[6] According to eqn (1):

$$M^+ + 2L \rightarrow ML_2{}^+;\ M = Cu, Ag;\ L = P_4 \text{ or } C_2H_4 \quad (1)$$

the complexation enthalpy for the copper–phosphorus and copper–ethene complexes was shown[6] to be 143 and 126 kJ mol^{-1} more favourable than that for the corresponding silver complexes. To our knowledge, the obtained $[Cu(\eta^2\text{-}P_4)_2]^+$ and $[Cu(\eta^2\text{-}C_2H_4)_3]^+$ complexes described here are the first examples of homoleptic Cu–phosphorus and Cu–ethene species to be observed.

Their synthesis was achieved in quantitative yields by sonicating (≈48 h) a threefold excess of CuI, $Ag[Al(pftb)_4]$ and equimolar amounts of P_4 or an atmosphere of C_2H_4 in CH_2Cl_2 according to eqn (2):

$$3CuI + nL + Ag[Al(pftb)_4] \xrightarrow{-2CuI} [Cu(L)_n][Al(pftb)_4] + AgI \quad (2)$$
$$(L = P_4,\ n = 2;\ L = C_2H_4,\ n = 3)$$

The presence of three equivalents of CuI appears to be necessary. Upon filtration clear solutions of the moisture- and oxygen-sensitive compounds were obtained. Both complexes were characterized spectroscopically[7] as well as crystallographically.[8] $[Cu(\eta^2\text{-}P_4)_2][Al(pftb)_4]$ (**1**) crystallises in the orthorhombic space group $P2_12_12_1$ (Fig. 1)[8] and the asymmetric unit contains two isolated anions and cations. The ethene complex, $[Cu(\eta^2\text{-}C_2H_4)_3][Al(pftb)_4]$ (**2**), crystallizes in the monoclinic space group $P2_1/c$ (Fig. 2) and there are three pairs of isolated anions and cations in the asymmetric unit.[8]

Just like $[Ag(P_4)_2]^+$,[9] the Cu^+ ion in (**1**) binds two tetrahedral P_4 molecules in an η^2-fashion so that the local coordination of the central Cu atom is nearly planar and the cation approaches D_{2h} symmetry. The $P_{1,2}$–Cu–$P_{1',2'}$ planes are tilted by 6.2 and 14.1° for the two independent cations respectively, *cf.* 8.1° on average for the Ag compound (see Table 1). The Cu–P distance is on average

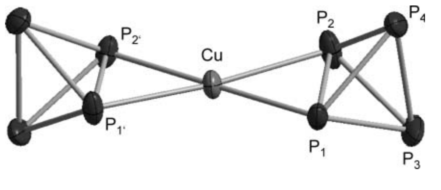


Fig. 1 The $[Cu(P_4)_2]^+$ cation in the solid state. Thermal ellipsoids are drawn at 50% probability.

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† Electronic supplementary information (ESI) available: Born–Fajans–Haber cycles and theoretical calculations; crystallization procedures, overall crystal structures and weak F–M and F–H interactions for $[Cu(P_4)_2]^+$ and $[Cu(C_2H_4)_3]^+$; model for extracting C=C distances; d_{xz}–σ^* interactions for $[M(P_4)_2]^+$; Raman spectra and experimental section. See DOI: 10.1039/b710899k

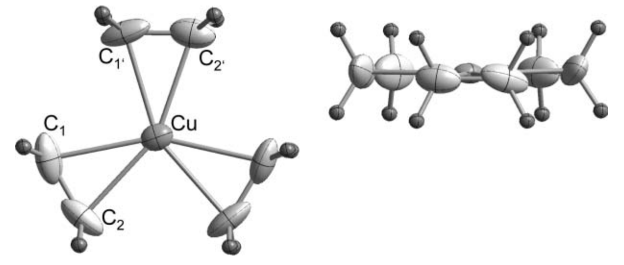

Fig. 2 Molecular structure of one of the three $[Cu(C_2H_4)_3]^+$ cations in the asymmetric unit. View through and perpendicular to the almost perfect C_3-axis of the planar spoke-wheel structure. Thermal ellipsoids are drawn at 50% probability.

Table 1 Comparison of the $[M(P_4)_2]^+$ moieties and Raman frequencies [cm^{-1}]. Theoretical values[6] in { }. Average bond lengths in pm

	$[Cu(P_4)_2]^+$	$[Ag(P_4)_2]^+$
$M–P_{exp/\{calc\}}$[a]	234.2(2)/{234.9}	255.4 (2)/{256.7}
$P_1–P_2$[b]**$_{exp/\{calc\}}$**[a]	234.2(2)/{238.7}	233.8 (3)/{239.0}
$P_3–P_4$[b]**$_{exp/\{calc\}}$**[a]	219.7(3)/{225.0}	219.8 (3)/{225.0}
$P_{1,2}–P_{3,4}$[b]**$_{exp/\{calc\}}$**[a]	217.3(3)/{220.8}	217.3 (3)/{220.6}
$\tau(P_{1,2}–M–P_{1',2'})$[b]**/°**	6.2, 14.1	8.1
Raman[c] **(*I* %)**	599 [100], 468 [19], 459 [37], 409 [20], 373 [6], 361 [7]	601, 473, 458, 413, 381, 374[d]

[a] BLYP/IV′-R: see ref. 6. [b] See Fig. 1. [c] See endnote 11. [d] See ref. 9.

234.2(2) pm (range: 233.6(2) to 234.5(2) pm), 21 pm shorter than in $[Ag(P_4)_2]^+$ (see Table 1, the difference of the Cu^+ and Ag^+ ionic radii is 21 pm for C.N. 2[10]). The P–P bond lengths in the P_4 cages range from 215.4(3) to 235.0(3) pm. Previous DFT calculations using relativistic basis sets,[6] have predicted a copper–phosphorus bond length of 234.9 pm and phosphorus–phosphorus bonds which range from 220.8 to 238.7 pm.[6]

The coordinated edge of the P_4 cage is on average 234.2(2) pm (predicted value: 238.7 pm),[6] *i.e.* 13 pm longer than free P_4 [d(P–P) = 221 pm)][10] while all other P–P distances shrunk by 1 to 6 pm, suggesting a weak coordination of the ligand to the central atom. There are 14 and 16 weak P–F interactions ranging from 326 to 340 pm (*cf.* sum of the P and F van der Waals radii: 340 pm)[10] for each of the independent cations in the asymmetric unit respectively and the shortest intramolecular Cu–F distance is 320 pm (see ESI†). In the published structure of $[Ag(P_4)_2]^+$ there are no Ag–F contacts below 400 pm.[9a,b] For better comparison to the 100 K data set of (**1**), we included in Table 1 the data of a new modification[9c] of $[Ag(P_4)_2]^+$ for which data collection was also performed at 100 K and which has Ag–F contacts down to 321 pm. In solution, even at −90 °C, no coupling between the individual phosphorus atoms or to the NMR active ^{63}Cu atom was observed in the NMR. ^{31}P NMR gave only a sharp singlet, indicating that all phosphorus atoms are equivalent. A similar observation was made for $[Ag(P_4)_2]^+$, which was dynamic even in the solid state at 153 K.[9a,b]

The P–Cu–P angle in the four independent (two for each cation) P_4-cages is on average 60°. Deubel and co-workers predicted a P–Cu–P angle of 61°.[6] They suggested that this larger P–metal–P angle (compared to 54° in the silver complex[9c]) likely favours the overlap of the corresponding σ*(P–P) orbitals with the lobes of the metal d_{xz} orbital (see ESI†), making the Cu complex a better back donor and therefore more stable than the respective silver cation.[6] (see ref. 6. for details of the bonding in $[M(P_4)_2]^+$).

Table 2 Experimental and theoretical bond lengths for $[Cu(C_2H_4)_3)]^+$. All values in pm. Average values in { }. Theoretical values in [ ]

	$[Cu(C_2H_4)_3]^+$
Cu–C/{av.} [ ][a]	209.5(1.0)–217.3(0.7)/{214.7} [218.9]
C=C/{av.} [ ][a,b]	131.1(1.7)–134.0(1.5)/{133.1} [135.3]
$\tau(C_{1,2}–M–C_{1',2'})$[c]**/°**	{6.0} [0]

[a] pbe0/TZVPP. [b] Libration correction analysis:[14] +0.1 pm. [c] See Fig. 2.

In $[Cu(C_2H_4)_3]^+$, each Cu^+ binds three C_2H_4 molecules in a η^2-fashion so that the local coordination sphere of the central atom is trigonal-planar and approaches D_{3h} symmetry (Fig. 2).

The displacement of the central atom above the mean of the ligand C atoms is no more than 1 pm for any of the independent cations. To the best of our knowledge this is the first example of a homoleptic Cu–C_2H_4 complex, furthermore, it shows an almost ideal trigonal-planar environment (Fig. 2). The closest approximation to our complex (**2**) is $Cu(C_2H_4)_2[AlCl_4]$, which contains coordinated $[AlCl_4]^-$ anions blocking the third ligand position and preventing the formation of a homoleptic complex.[12]

For (**2**), the Cu–C bonds range from 209.5(1.0)–217.3(0.7) pm with an average d(Cu–C) of 214.7 pm (Table 2, *cf.* predicted values:[6] 213.0–215.4 pm and $[Ag(C_2H_4)_3]^+$,[4d] 240.6 pm) and the shortest intramolecular F–H distance is 234.3 pm (sum of van der Waals radii: 290 pm,[10] see ESI†). These weak F–H interactions are probably responsible for the distortion from the ideal D_{3h} symmetry (average deviation of 6.0° of the individual $C_{1,2}$–Cu–$C_{1',2'}$ planes from planarity, see ESI†). For the heavier and more weakly bound Ag analogue[4d] this deviation of the $C_{1,2}$–M–$C_{1',2}$ planes was reported to be 11.7 to 17.5°.[4d]

On the other hand, the description of the C=C bond is not as straightforward as the description of the Cu–C bond and it is somehow delicate. The average C=C bond length is 133.1(1.8) pm, slightly shorter than that of gaseous ethene (133.3 pm).[13a] From the observed Raman C=C stretching frequency (ν = 1577 cm^{-1} in (**2**), compared to 1623 cm^{-1} for free ethene[13b] and 1516 cm^{-1} for isoelectronic, but stronger bound $Ni(C_2H_4)_3$[13c]) one would expect a longer C=C bond than in free ethene. But in fact, the C=C bond length obtained by X-ray single-crystal analysis even with a libration correction[14] is not longer than in free ethene. So the description of the C=C bond with our data "appears" to be somehow incorrect.

However, we[4d] have recently shown with high-resolution X-ray data at different temperatures that the C=C bond lengths in $[Ag(C_2H_4)_3]^+$ are always shorter than that of gaseous ethene. This discrepancy observed (attributed to various systematic errors, see ESI†and ref. 4d for details) is also expected for $[Cu(C_2H_4)_3]^+$, *i.e.* a seemingly shorter d(C=C) than in free ethene.

Nevertheless, (using the methodology described in ref. 4*d*) the elongation of the C=C bond (compared to free ethene) upon complexation to any metal can be easily calculated. Using this model[4d] (see ESI†) and the stretching frequency of the C=C bond observed by Raman spectroscopy we would expect a d(C=C) of ∼135.0 pm.

In fact, Deubel and co-workers predicted for the related $[Cu(C_2H_4)_2]^+$ cation C=C bond lengths between 135.0–135.6 pm[6] and we predicted for (**2**) a value of 135.3 pm (Table 2). These findings support our assignment of the most likely C=C distance in (**2**) as 135 pm (and not 133.1 pm as observed experimentally).

With this work we have analyzed the energetics of the formation of Cu^I complexes with very weak ligands L from CuI, a silver salt and L. This methodology has previously been employed,[15] but its underlying thermodynamics was never investigated. As this method allowed the preparation of even delicate complexes of very weak bases, we suggest that this is a general method applicable to many weak ligands. In this work, this procedure has been used for the preparation of the first homoleptic copper–phosphorus and copper–ethene complexes. We plan to further investigate the coordination chemistry of Cu^+ with very weak ligands and continue to investigate possible routes to naked Cu^+ salts of very good WCAs.

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7 NMR measurements were performed on a Bruker 400 MHz instrument. **$[Cu(P_4)_2]^+$** (CD_2Cl_2, −90 °C): ^{31}P NMR: δ −460 ppm (s, 8P), ^{19}F NMR: δ −76.8 ppm (s, 36F), ^{27}Al NMR: δ 34.8 ppm (s, 1Al). **$[Cu(C_2H_4)_3]^+$** (CD_2Cl_2): ^{19}F NMR: δ −75.7 ppm (s, 36F), ^{27}Al NMR: δ 31.9 ppm (s, 1Al), $^{13}C\{^1H\}$ NMR: δ 110.0 ppm (s, 6C), δ 122.0 ppm (q, 16C, $^1J_{C\text{–}F}$ = 294.4 Hz). ^{1}H NMR: δ 5.47 ppm (s, 12H). FT-Raman measurements were performed on a Bruker Ram II module for the Vertex 70 spectrometer equipped with a highly sensitive Ge detector. ν/cm^{-1} (I %): **$[Cu(P_4)_2]^+$** 599 (100), 468 (19), 459 (37), 409 (20), 373 (6), 361 (7). **$[Cu(C_2H_4)_3]^+$**: 3147 (6), 3096 (19), 3045 (4), 3013 (100), 1577 (65), 1483 (2), 1321 (78), 1009 (29) and 495 (6). Original spectra in ESI†.

8 Data collection was performed on a Nonius Kappa goniometer equipped with a Bruker APEX II CCD (Mo-Kα (0.70173 Å) radiation). **$[Cu(P_4)_2]^+$**: Data collection was done at 100 K. A colourless platelet, very sensitive to air and moisture which ignites spontaneously in air was mounted at low temperature using a stream of cold gaseous N_2. **$[Cu(C_2H_4)_3]^+$**: Data collection was performed at various temperatures (for a detailed description, see ESI†). Colourless blocks, very sensitive to air and moisture were mounted at low temperature using a stream of cold gaseous N_2. Both structures were solved (SHELX 6.14 8/6/00) by the Patterson heavy atom or direct methods and successive interpretation of the difference Fourier maps, followed by least-square refinement. All non H-atoms were refined anisotropically. H atoms were fixed by a HFIX command. **$[Cu(P_4)_2]^+$**: orthorhombic, space group $P2_12_12_1$, a = 11.7609, b = 16.9425, c = 38.2658, V = 7624.81 Å^3, D_c = 2.227 g cm^{-3}, Z = 8, 80549 reflections collected (13407 unique), $R1$ = 0.0506 for 11418 $F_o > 4\sigma(F_o)$ and 0.0671 for all 13407 data and 1190 parameters, $wR2$ = 0.1152, GooF = 1.187, restrained GooF = 1.187 for all data, $\Delta\rho_{max,\ min}$ = 0.76/−0.56 e Å^{-3}, CCDC 654312. **$[Cu(C_2H_4)_3]^+$** (at 153 K): monoclinic, space group $P2_1/c$, a = 12.8455, b = 44.8620, c = 18.9555 Å, β = 102.506°, V = 10664.39 Å^3, D_c = 2.083 g cm^{-3}, Z = 4, 145068 reflections collected (15367 unique), $R1$ = 0.0727 for 8402 $F_o > 4\sigma(F_o)$ and 0.1495 for all 15367 data, $wR2$ = 0.1759, GooF = 1.033, restrained GooF = 1.034 for all data, $\Delta\rho_{max,\ min}$ = 0.68/−0.67 e Å^{-3}, CCDC 654311. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b710899k.

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