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$Ag(P_4)_2^+$: The First Homoleptic Metal−Phosphorus Cation

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Due to the unique structure and unusual bonding situation of the tetrahedral tetraphosphorus molecule its chemistry has attracted much attention over the past decades. However, little is known about the coordination behavior of the undistorted P_4 molecule and only few solid-state structures of end-on or side-on coordinated tetrahedral P_4 molecules have been determined.[1] In fact, upon reaction with transition metal fragments the decomposition and incorporation of the tetrahedral P_4 molecule is frequently observed and the phosphidic degradation appears to be the usual reaction pathway of P_4.[2] This led to the question, as to whether very weak and simple complexes between a univalent metal cation such as Ag^+ and the P_4 molecule are accessible.[3,4] We succeeded in preparing such a superweak silver−phosphorus complex by using very *w*eakly *c*oordinating *a*nions (WCA's)[5] of the type $Al(OR_F)_4^-$ (OR_F = polyfluoroalkoxy).[6,7]

When P_4 (in CS_2) was given to $AgAl[OC(CF_3)_3]_4$ and CH_2Cl_2 was added, a clear solution (over a small amount of an unidentified brown precipitate) resulted from which solid **1** was obtained (eq 1). The nature of **1** was established by Raman,

$$2P_4 + AgAl[OC(CF_3)_3]_4 \rightarrow [Ag(\eta^2\text{-}P_4)_2^{\ +}][Al(OC(CF_3)_3)_4^{\ -}] \quad (1)$$

solution NMR, and ^{31}P MAS NMR spectroscopy as well as single-crystal X-ray crystallography. The colorless compound is highly soluble in CH_2Cl_2, $CHCl_3$, and 1,2-$Cl_2C_2H_4$ and ignites spontaneously in air. In the room temperature ^{31}P NMR spectra of **1** (CD_2Cl_2) the chemical shift of the P_4 molecule is only very slightly shifted to lower field and appeared as a sharp singlet at $\delta^{31}P = -497$ (free P_4: $\delta^{31}P = -527$). A room temperature solid-state ^{31}P MAS NMR of **1** showed essentially the same shift at $\delta^{31}P$ = 511.[8] We note that available ^{31}P NMR resonances of species containing coordinated P_4 molecules usually appear considerably shifted to lower field, i.e., at −282 ppm (av) in $(P_4)Rh(PPh_3)_2(Cl)$,[1b] at −391 (1P) and −489 (3P) ppm in $[(triphos)Re(CO)_2(\eta^1\text{-}P_4)]^+$,[1d] or at −422 (1P) and −473 (3P) ppm in $(\eta^1\text{-}P_4)W(CO)_3P(C_6H_{11})_3$.[1c] Recording the ^{31}P NMR spectrum of **1** at low temperature led to a small shift to lower field ($\Delta\delta$ = 11 ppm at −100 °C) and to a broadening of the line, but no evidence for an AB_3 or A_2B_2 spin system was found in agreement with a fluxional system. Since the ^{31}P NMR chemical shift of **1** is nearly unchanged compared to free P_4, the coordination to the Ag^+ ion appears to be very weak.

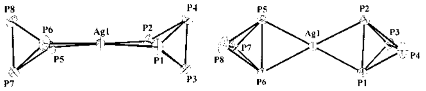

Figure 1. The solid-state structure of the $Ag(P_4)_2^+$ cation in **1**. Thermal ellipsoids were drawn at the 25% probability level; the $Al(OC(CF_3)_3)_4^-$ counterion was omitted for clarity. Selected distances [Å] and angles [deg]: Ag1−P1 2.540(2), Ag1−P2 2.548(1), Ag1−P5 2.536(2), Ag1−P6 2.539(1), P1−P2 2.328(2), P1−P3 2.152(2), P1−P4 2.149(2), P2−P3 2.160(2), P2−P4 2.157(2), P3−P4 2.172(2), P5−P6 2.330(2), P5−P7 2.155(2), P5−P8 2.163(2), P6−P7 2.150(2), P6−P8 2.145(2), P7−P8 2.174(2), P1−Ag1−P2 54.47(5), P5−Ag1−P6 54.65(5), P5−Ag1−P1 173.60(5), P5−Ag1−P2 126.63(5), P6−Ag1−P1 124.68(5), P6−Ag1−P2 176.67(5).

The weak coordination also follows from the X-ray crystal structure of one colorless platelet of **1**.[9] In the solid state (150 K) **1** is a salt and the Ag^+ ion binds two tetrahedral P_4 molecules in η^2 fashion so that the local coordination sphere of the Ag atom is nearly planar and the two AgP_2 planes are tilted by only 10.6° (see Figure 1). There is only one family of ions known that shows an isolobal topology to **1**—$[M\{M'(tppme)(P_3)\}_2]PF_6$ (M = Cu, Au; M′ = Co, Rh, Ir)—in which the local coordination of the M atom is between planar and tetrahedral (the two MP_2 planes include an angle of about 51°; in **1**, 10.6°).[10]

In fact, at 200 K an order−disorder phase transition occurred and the $Ag(P_4)_2^+$ cation was perfectly D_{2h} symmetric while all $OC(CF_3)_3$ groups of the $Al[OC(CF_3)_3]_4^-$ anion were disordered and freely rotating.[11] Upon cooling to 150 K, this rotation was hindered by the formation of 11 weak P- -F contacts at 3.12 to 3.36 Å (sum of the P and F van der Waals radii: 3.40 Å) and these weak contacts slightly distort the D_{2h} symmetric conformation. There are no Ag- -F contacts below 4 Å. Compared to free P_4 [d(P−P) = 2.21 Å] the coordinated edge of the P_4 tetrahedron is elongated by 0.12 Å to 2.329(2) Å (av) while all other P−P distances shrunk by 0.04 to 0.06 Å. In contrast, the coordinated P−P edge in the $(\eta^2\text{-}P_4)Rh(PPh_3)_2(Cl)$ molecule[1b] is elongated to 2.462(2) Å, i.e., 0.25 Å longer than in P_4. The Rh−P_4 bonds in the latter species are short (average: 2.293 Å; cf. 2.542 Å on average in **1**), even shorter than the strong dative Rh−PPh_3 bonds in the same molecule (2.333 Å on average). This appears rare considering the low nucleophilcity of the neutral P_4 molecule.[12] One would expect a difference of about 0.1 Å between Ag−P and Rh−P bonds since the atomic and ionic radii of silver and rhodium differ by this amount and not by the about 0.25 Å difference between **1** and $(P_4)Rh(PPh_3)_2(Cl)$.[1b] This again underlines the weak coordination of the tetrahedral P_4 molecule in **1** and raises the question, if the P_4 moiety in $(P_4)Rh(PPh_3)_2(Cl)$[1b] should be formulated as being derived from Rh^{III} and P_4^{2-}

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(3) Such compounds may be viewed as primary steps on the usual pathway leading to the phosphidic degradation of P_4 and, in agreement with this picture, older investigations showed that the final product of the reaction of silver salts with P_4 is Ag_3P.[4]

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(8) This solid state room temperature shift is in agreement with a loosely bound flexible P_4 molecule and suggests that the observed solution ^{31}P NMR shift is due to **1** and not to a fast equilibrium between $Ag(P_4)_2^+$, P_4, and Ag^+.

(9) Data collection was performed at 150 K on a STOE IPDS diffractometer [Mo Kα (0.71073 Å) radiation]. A colorless platelet (0.5 × 0.5 × 0.2 mm) was mounted from perfluoroether oil; the structure was solved (SHELX93) by the Patterson heavy atom method and successive interpretation of the difference Fourier maps, followed by least-squares refinement. All atoms were refined anisotropically (697 parameters). a = 14.455(3) Å, b = 17.385(4) Å, c = 15.693(3) Å, β = 100.88(3)°, V = 3872.8(13) Å^3. ρ_{calcd} = 2.269 g cm^{-3}, Z = 4; space group $P2_1/n$; 15374 reflections collected, 7202 unique (R_{int} = 0.037) and 4102 observed ($F > 4\sigma$); μ(Mo Kα) = 1.078 mm^{-1}; numeric absorption correction (min/max = 0.861, 0.752); $R1$ = 0.0569 and $wR2$ (all data) = 0.1572, GOOF = 0.858, max/min larg. res. peak, 1.165/−0.465 e/Å^3.

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(11) At 200 K the lattice constants of **1** are the following: a = 9.704 Å, b = 17.408 Å, c =11.683 Å, monoclinic crystal system, β = 94.78°, V = 1977 Å^3.

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10.1021/ja002007m CCC: $20.00

Table 1. Experimental Raman Spectrum of **1**, Calculated Scaled[13,17] Raman Spectrum of $Ag(P_4)_2^+$ (D_{2h}), and Experimental Raman Frequencies of P_4 and $(P_4)Rh(PPh_3)_2(Cl)$[1b] [in cm^{-1}]

1	$Ag(P_4)_2^+$	$RH(P_4)^a$	P_4^b
ν_{exp} (I %)	ν_{calcd} (I %) sym	ν_{exp} (I)	ν_{exp} (I %) sym
601 (100)	595 (100) A_g	571 (w)	598 (100) A_1
473 (18)	468 (21), B_{2g}	438 (m)	
458 (16)	465 (13), B_{1g}	386 (m)	457 (37) T_2
413 (5)	413 (15), A_g	374 (sh)	
381 (sh)	366 (7), B_{3g}	344 (w)	360 (9) E
374 (9)	361 (12), A_g		

^{a} RH = $Rh(PPh_3)_2(Cl)$. ^{b} In the solid state on our spectrometer.

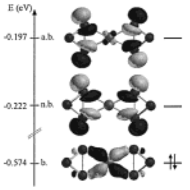

Figure 2. $d_{x^2-y^2} \rightarrow \sigma^*$ interaction in $Ag(P_4)_2^+$.

including two covalent Rh−P bonds. We note the structural similarity between the $Ag(\eta^2\text{-}P_4)$ moiety in **1** and the calculated geometry of the HP_4^+ cation.[12]

The FT-Raman spectrum of **1** also showed the weak coordination to the Ag^+ ion. Upon coordination of P_4 the local symmetry is lowered from T_d (in P_4) to D_{2h} in $Ag(P_4)_2^+$, and therefore the three A_1, T_2, and E Raman bands of P_4 split into six Raman active modes. All observed frequencies of **1** are collected in Table 1 and were assigned based on the HF-DFT calculated frequencies.[13−16]

The Raman frequencies of **1** are only slightly shifted if compared to those of free P_4 indicating the nearly undistorted and therefore weak coordination of the P_4 molecule. In contrast, the P−P Raman frequencies of the $(P_4)Rh(PPh_3)_2(Cl)$ molecule[1b] are shifted by 27 to 72 cm^{-1} to lower energy in agreement with considerable weakening of the P−P bonds and a strong coordination to the rhodium center. Moreover, the symmetric A_1 breathing mode of P_4, which in free P_4 and **1** is the most intense band, is only weakly scattering in $(P_4)Rh(PPh_3)_2(Cl)$.[1b] This again raises the question as to whether one has to regard the latter $\eta^2\text{-}P_4$ moiety as neutral P_4 or rather P_4^{2-}.

How is the P_4 molecule in **1** bonded to the Ag^+ ion with a $[Kr]4d^{10}$ electron configuration? Initially a Lewis acid base adduct is formed as may be seen by the similar energies of the LUMO of the Ag^+ ion at −0.322 eV ($5s^0$ orbital) and the HOMO of the P_4 molecule at −0.300 eV. However, in this picture one would expect a tetrahedral conformation of the $Ag(P_4)_2^+$ cation. The observed planar conformation of the silver atom in **1** suggested d-orbital contributions to the $Ag(\eta^2\text{-}P_4)$ bonding, and indeed, inspection of the calculated molecular orbitals of $Ag(P_4)_2^+$ showed that the planar conformation is induced by a $d_{x^2-y^2}(Ag) \rightarrow \sigma^*(P-P)$ interaction of the highest lying filled $d_{x^2-y^2}$ orbital of the Ag^+ ion donating electron density into the empty σ^* orbital of the coordinated P−P bond of the P_4 tetrahedron, shown in Figure 2.

The three sets of orbitals [1 $d_{x^2-y^2}$ and 2 $\sigma^*(P-P)$] transform to one bonding (b.), one nonbonding (n.b.), and one antibonding (a.b.) molecular orbital, only the bonding combination of which is occupied. In principle a similar interaction should also be feasible in a tetrahedral ligand field; however, in a planar ligand field the five degenerate atomic d orbitals transform into four sets of orbitals, the $d_{x^2-y^2}$ orbital of which is shifted to highest energy (to +12.28 Dq),[18] in fact, to much higher energy than the three t_2 orbitals in a tetrahedral ligand field (to +1.78 Dq).[18] Therefore, the $d_{x^2-y^2}$ orbital of the Ag^+ ion of $Ag(P_4)_2^+$ is found at sufficiently high energy to interact with the σ^* orbital of the coordinated P−P bond as shown in Figure 2. Moreover, only one d orbital is at high energy (the next orbital (d_{xy}) is found at +2.28 Dq)[18] thus explaining the planar arrangement.

The WCA $Al[OC(CF_3)_3]_4^-$ allowed a superweak complex of the Ag^+ ion and two nearly undistorted tetrahedral P_4 molecules to stabilize giving the unusual D_{2h} symmetric $Ag(P_4)_2^+$ cation, the planar bonding situation of which is induced by a $d_{x^2-y^2} \rightarrow \sigma^*$ interaction. On the basis of the available experimental NMR, Raman and structural information on the related $(P_4)Rh(PPh_3)_2$-Cl compound,[1b] we cast doubt on the earlier conclusion that the latter species contains a coordinated tetrahedral P_4 molecule which, in agreement with a comment made by Scheer,[1c] possibly should be reassigned as formally being derived from Rh^{III} and a tetraphosphabicyclo-butane-P_4^{2-} structure. However, this is the focus of current investigations that will be reported in an upcoming full paper.

Experimental Section: All manipulations were performed using standard grease free (J. Young valves) Schlenk or drybox techniques and a dinitrogen or argon atmosphere. Solvents were rigorously dried and degassed prior to use and stored under N_2. Sublimed yellow phosphorus was added by syringe techniques as a CS_2 stock solution. $Ag[Al(OC(CF_3)_3)_4]$ was prepared according to the literature.[6] The Raman spectrum was obtained from a solid sample sealed in a melting point capillary. The NMR spectra of a sealed sample were run in CD_2Cl_2 and referenced toward the solvent (^1H, ^{13}C) or external H_3PO_4 (^{31}P) and aqueous $AlCl_3$ (^{27}Al). The ^{31}P MAS NMR was run by L. van Wüllen at the MPI in Stuttgart, Germany.

$[Ag(P_4)_2]\{Al[OC(CF_3)_3]_4\}$, 1: A stock solution of P_4 in CS_2 (4.57 mL, 1.566 M, 7.152 mmol) was added to solid $Ag(CH_2Cl_2)Al[OC(CF_3)_3]_4$ (4.148 g, 3.576 mmol) at ambient temperature (= room temperature). This suspension was dissolved by addition of 10 mL of CH_2Cl_2 giving a clear colorless solution over a little dark brown precipitate. After the dark material had settled (approximately 2 h), the mixture was filtered through a fine glass frit and all volatiles were removed in vaccuo leaving a beige microcrystalline and pyrophoric material (3.984 g, 84%). Crystals of **1** suitable for X-ray crystallography were obtained by recristallization of part of the highly soluble beige material in about 0.5 mL of CH_2Cl_2.

^{13}C NMR (63 MHz, CD_2Cl_2, 25 °C) δ 121.6 (q, CF_3, J_{CF} = 293.1 Hz); ^{27}Al NMR (78 MHz, CD_2Cl_2, 25 °C), 36.0 (s, $\nu_{1/2}$ = 14 Hz); ^{31}P NMR (101 MHz, CD_2Cl_2, 25 °C) δ −497 (s, P_4, $\nu_{1/2}$ = 25 Hz); ^{31}P NMR (101 MHz, CD_2Cl_2, −100 °C) δ −486 (s, P_4, $\nu_{1/2}$ = 220 Hz); ^{31}P MAS NMR δ −510; FT-Raman ν(%) = 798 (7, Al−O), 746 (7, Al−O), 601 (100, P_4−A_g), 473 (18, P_4−B_{2g}), 458 (16, P_4−B_{1g}), 413 (5, P_4−A_g), 381 (sh, P_4−B_{3g}), 374 (9, P_4−A_g), 322 (5, Al−O).

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Supporting Information Available: Thermal ellipsoid of **1** and tables of crstal data and data collection parameters of **1**, atomic coordinates, and anisotropic displacement parameters (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) All calculations have been performed using the Gaussian98W suite of programs. The geometry of $Ag(P_4)_2^+$ was optimized at the hybrid HF-DFT MPW1PW91/TZV(df) level.[15,16] For silver the standard 3-21G* basis set augmented with one set of uncontracted diffuse and f-polarization functions each was used [=3-21+G(df)]. The frequency analysis showed the $Ag(P_4)_2^+$ cation (D_{2h} symmetry) to be a true minimum. d(Ag−P) = 2.642 Å, d(P1−P2) 2.339 Å, d(P1−P3) 2.195 Å, d(P3−P4) = 2.234 Å, P−Ag−P = 52.5 and 127.5°; total energy = −7907.14895 au.

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