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Article

Preparation and Characterization of the Argentates: $[Ag\{P(CF_3)_2\}_2]^-$, $[Ag\{(\mu\text{-}P(CF_3)_2)M(CO)_5\}_2]^-$ (M = Cr, W), and $[Ag\{(\mu\text{-}P(C_6F_5)_2)W(CO)_5\}_2]^-$: X-ray Crystal Structure of $[K(18\text{-crown-}6)][Ag\{(\mu\text{-}P(CF_3)_2)Cr(CO)_5\}_2]$[||]

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The first example of a mononuclear diphosphanidoargentate, bis{bis(trifluoromethyl)phosphanido}argentate, $[Ag\{P(CF_3)_2\}_2]^-$, is obtained via the reaction of $HP(CF_3)_2$ with $[Ag(CN)_2]^-$ and isolated as its [K(18-crown-6)] salt. When the cyclic phosphane $(PCF_3)_4$ is reacted with a slight excess of $[K(18\text{-crown-}6)][Ag\{P(CF_3)_2\}_2]$, selective insertion of one PCF_3 unit into each silver phosphorus bond is observed, which on the basis of NMR spectroscopic evidence suggests the $[Ag\{P(CF_3)P(CF_3)_2\}_2]^-$ ion. On treatment of the phosphane complexes $[M(CO)_5PH(CF_3)_2]$ (M = Cr, W) with $[K(18\text{-crown-}6)][Ag(CN)_2]$, the analogous trinuclear argentates, $[Ag\{(\mu\text{-}P(CF_3)_2)M(CO)_5\}_2]^-$, are formed. The chromium compound $[K(18\text{-crown-}6)][Ag\{(\mu\text{-}P(CF_3)_2)Cr(CO)_5\}_2]$ crystallizes in a noncentrosymmetric space group *Fdd*2 (No. 43), $a = 2970.2(6)$ pm, $b = 1584.5(3)$ pm, $c = 1787.0(4)$, $V = 8.410(3)$ nm^3, $Z = 8$. The C_2 symmetric anion, $[Ag\{(\mu\text{-}P(CF_3)_2)Cr(CO)_5\}_2]^-$, shows a nearly linear arrangement of the P–Ag–P unit. Although the bis(pentafluorophenyl)phosphanido compound $[Ag\{P(C_6F_5)_2\}_2]^-$ has not been obtained so far, the synthesis of its trinuclear counterpart, $[K(18\text{-crown-}6)][Ag\{(\mu\text{-}P(C_6F_5)_2)W(CO)_5\}_2]$, was successful.

Introduction

Nucleophilic bis(perfluoroorganyl)phosphanide sources are essential for the synthesis of chiral, bidentate, strong π-acidic bis(perfluoroorganyl)phosphane ligands. The bis(trifluoromethyl)phosphanide ion exhibits negative hyperconjugation which results in C−F activation and therefore favors the decomposition.

To obtain nucleophilic $P(CF_3)_2$ group transfer reagents it is essential to reduce the negative hyperconjugation in the free ion by addition of weak Lewis acids such as transition metals. The resulting terminal bis(perfluoroorganyl)phosphanido transition metal complexes are potential nucleophilic $P(CF_3)_2$ group transfer reagents.[1−3]

To the best of our knowledge, no binary bis(phosphanido)argentate of the general formula $[Ag(PR_2)_2]^-$ (R = noncyclic univalent group) has been identified so far. The trinuclear counterparts $[Ag\{(\mu\text{-}PR_2)M(CO)_5\}_2]^-$ (R = Ph, C_6H_{11} and M = Cr, Mo, W) have been characterized by ^{31}P NMR spectroscopy and by elemental analysis.[4] The novel gold complex $[Ag\{(\mu\text{-}PPh_2)Au(C_6F_5)_5\}_2]^-$ has also been structurally characterized.[5]

Experimental Section

Materials and Apparatus. All chemicals were obtained from commercial sources and used without further purification. Literature methods were used for the synthesis of $HP(C_6F_5)_2$, $[W(CO)_5PH(C_6F_5)_2]$, $[W(CO)_5PH(CF_3)_2]$,[6] and $[Cr(CO)_5PH(CF_3)_2]$.[7] Solvents

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Table 1. Crystal Data and Structure Refinement Parameters for $[\mathrm{K(18\text{-}crown\text{-}6)}][\mathrm{Ag}\{\mu\text{-}\mathrm{P(CF_3)_2Cr(CO)_5}\}_2]$

empirical formula	$C_{26}H_{24}AgCr_2F_{12}KO_{16}P_2$
formula mass	1133.36
T [K]	170(2)
space group	*Fdd*2 (No. 43)
a [pm]	2970.2(6)
b [pm]	1584.5(3)
c [pm]	1787.0(4)
V [nm^3]	8.41(3)
Z	8
ρ_{calc} [g cm^{-3}]	1.79
μ [mm^{-1}]	1.26
R indexes [$I > 2\sigma(I)$]	R1^a = 0.0280, $wR2^b$ = 0.0516
R indexes (all data)	R1^a = 0.0359, $wR2^b$ = 0.0530
goodness of fit (S_{obs})	1.014
Flack's parameter	−0.04(2)

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

Table 2. Selected Bond Distances and Bond Angles for $[\mathrm{K(18\text{-}crown\text{-}6)}][\mathrm{Ag}\{\mu\text{-}\mathrm{P(CF_3)_2Cr(CO)_5}\}_2]$

	Bond Lengths (pm)		
Ag(1)−P(1)	239.1(1)	Cr(1)−C(7)	183.6(5)
Cr(1)−C(5)	188.4(5)	Cr(1)−C(6)	189.2(5)
Cr(1)−C(3)	189.3(5)	Cr(1)−C(4)	190.7(6)
Cr(1)−P(1)	238.9(1)		
	Bond Angles (deg)^a		
P(1)−Ag(1)−P(1)$^{\mathrm{a}}$	169.17(6)	C(2)−P(1)−C(1)	95.1(2)
C(2)−P(1)−Cr(1)	111.5(2)	C(1)−P(1)−Cr(1)	114.9(1)
C(2)−P(1)−Ag(1)	107.3(1)	C(1)−P(1)−Ag(1)	105.3(1)
Cr(1)−P(1)−Ag(1)	119.68(4)	C(7)−Cr(1)−P(1)	177.7(2)
C(5)−Cr(1)−P(1)	89.9(1)	C(6)−Cr(1)−P(1)	92.1(1)
C(3)−Cr(1)−P(1)	87.4(1)	C(4)−Cr(1)−P(1)	92.4(1)

[a] a = $^3/_2 - x$, $^1/_2 - y$, z.

were purified by standard methods.[8] Standard high-vacuum techniques were employed throughout all preparative procedures. Nonvolatile compounds were handled under a dry N_2 atmosphere by using Schlenk techniques.

Infrared spectra were recorded on a Nicolet-5PC-FT-IR spectrometer as KBr pellets. Raman spectra were measured on a Bruker FRA-106/s spectrometer with a Nd:YAG laser operating at λ = 1064 nm.

The NMR spectra were recorded on Bruker model AMX 300 (^{31}P, 121.50 MHz; ^{19}F, 282.35 MHz; ^{13}C 75:47 MHz) and Bruker AC200 spectrometers (^{31}P, 81.01 MHz; ^{19}F, 188.31 MHz; ^{1}H, 200.13 MHz). Fluorine decoupled phosphorus spectra were measured on a Bruker DRX 500 spectrometer (^{31}P, 202.40 MHz) with positive shifts being downfield from the external standards (85% orthophosphoric acid (^{31}P), CCl_3F (^{19}F), and TMS (^{1}H)). Higher order NMR spectra were calculated with the program gNMR.[9]

Single-crystal X-ray diffraction studies were performed at 170-(2) K using a STOE IPDS I diffractometer using graphite-monochromatized Mo Kα radiation (λ = 71.073 pm). Details of the structural parameters are listed in Table 1. Selected bond lengths, bond angles, and torsion angles are listed in Table 2. A complete summary of structure solution and refinement is deposited as Supporting Information. The structure was solved in the space group *Fdd*2 using the Patterson method and refined with SHELXTL V6.10.[10] The positions of the silver and potassium atoms were located on special positions (2-fold axis), and the chromium atom was found to occupy a general position. Further structure expansion revealed the remaining atoms of the $[\mathrm{Ag}\{(\mathrm{P(CF_3)_2})\mathrm{Cr(CO)_5}\}]^-$ anion. Since the silver atom sits on a special position, the complete anion could be generated using the symmetry operation ($^3/_2 - x$, $^1/_2 - y$, z). From a disordered array of electron density around the potassium atom in the shape of a "half-fan", six oxygen positions were identified, which constituted the two-component half-crown ether structure. Two terminal carbon atoms of this half-crown configuration, later named C12 and C18, were subsequently located and found to occupy special positions. The two-component disordered 18-crown-6 was then generated using the symmetry operation ($^3/_2 - x$, $^3/_2 - y$, $+z$). One of these components was retained and used for further refinement after moving C12 and C18 off the special position and refining the symmetry generated equivalents with an occupancy factor of 0.5 using the PART -1 command in SHELXL. During this refinement, the C−C and C−O distances of the 18-crown-6 moiety were restrained to be equal with a maximum allowable deviation of 1 pm. Similarly, thermal parameters of the disordered atoms were also restrained using SIMU and DELU commands. Finally, all non-hydrogen atoms were refined anisotopically and hydrogen atoms were added to the carbon atoms at calculated positions. Since the structure belongs to a noncentrosymmetric space group *Fdd*2, the absolute configuration was determined by refining the Flack's parameter to 0.04(2), which confirms the corrected "handedness" of the molecular structure.

Preparation of $[\mathbf{K(18\text{-}crown\text{-}6)}][\mathbf{Ag}\{\mathbf{P(CF_3)_2}\}_2]$. A 1.75 g (10.28 mmol) amount of $HP(CF_3)_2$ was condensed on a solution of 1.89 g (4.08 mmol) of $[\mathrm{K(18\text{-}crown\text{-}6)}][\mathrm{Ag(CN)_2}]$ in 10 mL of acetone at −196 °C. The mixture was stirred at −78 °C for 1 h, prior to allowing the solution to rise to room temperature and evaporate to dryness. The residue was extracted several times with hexane, yielding 2.45 g (3.27 mmol, 80%) of $[\mathrm{K(18\text{-}crown\text{-}6)}][\mathrm{Ag}\{\mathrm{P(CF_3)_2}\}_2]$ as a colorless solid. Elemental anal. (calcd for $C_{16}H_{24}AgF_{12}KO_6P_2$): C 25.50 (25.65); H 3.42 (3.23). Infrared spectrum (cm^{-1}, KBr pellet): 3854 vw, 3445 w, 2891 s, 2829 m, 2748 vw, 1720 w, 1475 m, 1456 m, 1435 w, 1354 s, 1286 m, 1251 s, 1163 vs, 1109 vs, 962 s, 839 m, 734 vw, 559 w, 530 w, 459 m. Raman (cm^{-1}): 2956 (2), 2917 (5), 2889 (100), 2848 (27), 2811 (13), 2150 (20), 2136 (6), 1476 (44), 1274 (37), 1246 (11), 1183 (7), 1146 (17), 1068 (10), 873 (30), 832 (18), 736 (64), 549 (15), 534 (2), 465 (22), 294 (13), 275 (36), 240 (5), 140 (4), 105 (29). Negative ESI mass spectrum (acetone; 10^{-3} M) {m/z (%) [assignment]}: 999 (38) $[\mathrm{Ag_3}\{\mathrm{P(CF_3)_2}\}_4]^-$, 723 (100) $[\mathrm{Ag_2}\{\mathrm{P(CF_3)_2}\}_2]^-$, 573 (18) $[\mathrm{Ag_2}\{\mathrm{P(CF_3)_2}\}_2\mathrm{F}]^-$, 445 (35) $[\mathrm{Ag}\{\mathrm{P(CF_3)_2}\}_2]^-$. NMR data (THF; 298 K): $\delta(^{31}\mathrm{P})$ 2.8 ppm; $\delta(^{19}\mathrm{F})$ −39.4 ppm; $\delta(^{13}\mathrm{C})$ 138.0 ppm; ^1J(CF) 317 Hz; ^2J(PF) 57.9 Hz; ^1J(PC) 49 Hz; ^3J(CF) 9 Hz; ^4J(FF) 8 Hz. The NMR data of $[\mathrm{K(18\text{-}crown\text{-}6)}]^+$ are unaffected by the counterion ($\delta(^{13}\mathrm{C})$ 71 ppm, $\delta(^1\mathrm{H})$ 3 ppm).

Preparation of $[\mathbf{K(18\text{-}crown\text{-}6)}][\mathbf{Ag}\{(\boldsymbol{\mu}\text{-}\mathbf{P(CF_3)_2})\mathbf{W(CO)_5}\}_2]$. $[\mathrm{W(CO)_5PH(CF_3)_2}]$ (1.06 g, 2.14 mmol) and 0.48 g (1.02 mmol) of $[\mathrm{K(18\text{-}crown\text{-}6)}][\mathrm{Ag(CN)_2}]$ were dissolved in 5 mL of DMF and stirred for 2 h at room temperature. After evaporation of the solution, the residue was extracted with diethyl ether, giving 0.99 g (0.71 mmol, 70%) of $[\mathrm{K(18\text{-}crown\text{-}6)}][\mathrm{Ag}\{(\mu\text{-}\mathrm{P(CF_3)_2})\mathrm{W(CO)_5}\}_2]$ as a green powder. TG analysis: decomposition at 250 °C. Elemental analysis (calcd for $C_{26}H_{24}AgF_{12}KO_{16}P_2W_2$): C 22.63 (22.35); H 1.78 (1.73); N 0.15 (0.00). Infrared spectrum (cm^{-1}, KBr pellet): 3435 m, 2914 w, 2072 m, 2017 w, 1981 m, 1946 vs, 1931 vs, 1903 vs, 1903 vs, 1630 w, 1475 vw, 1456 vw, 1353 w, 1286 vw, 1251 w, 1168 s, 1110 s, 1086 m, 963 w, 841 vw, 598 m,

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578 m, 469 w, 459 w, 428 w. Raman (cm^{-1}, as a result of fluorescence, some of the intensities are uncertain): 2951 (8), 2918 (12), 2893 (10), 2879 (10), 2847 (8), 2071 (60), 1979 (100), 1917 (50), 1475 (5), 974 (20) 958 (20), 870, 798, 737, 449, 428 (40), 405, 349, 331, 222, 94 (60). Negative ESI mass spectrum (acetone; 10^{-3} M) {*m*/*z* (%) [assignment]}: 1094 (100) [$Ag\{P(CF_3)_2W(CO)_5\}_2]^-$. NMR data (CDCl$_3$/DMF; 298 K): $\delta(^{31}P)$ 13.8 ppm; $\delta(^{19}F)$ −48.5 ppm; $^1J(^{109/107}AgP)$ 424.6/369.4 Hz; $^1J(^{183}WP)$ 155.6 Hz; $^2J(PP)$ 100.7 Hz; $^2J(PF)$ 63.3 Hz; $^4J(PF)$ 2.5 Hz.

Preparation of [K(18-crown-6)][Ag{(μ-P(C$_6$F$_5$)$_2$)W(CO)$_5$}$_2$]. A solution of 2.00 g (2.90 mmol) of [W(CO)$_5$PH(C$_6$F$_5$)$_2$] dissolved in 5 mL of acetone was added dropwise to a solution of 0.55 g (1.18 mmol) [K(18-crown-6)][Ag(CN)$_2$] dissolved in 10 mL of acetone at −50 °C. After the temperature was allowed to rise to room temperature over a period of 1 h, the reaction mixture was evaporated to dryness. After recrystallization from diethyl ether/hexane the product [K(18-crown-6)][Ag{(μ-P(C$_6$F$_5$)$_2$)W(CO)$_5$}$_2$] (1.09 g, 0.61 mmol, 50%) was obtained as a yellow powder. TG analysis: decomposition at 180 °C. Elemental analysis (calcd for $C_{46}H_{24}AgF_{20}KO_{16}P_2W_2$): C 31.71 (30.88); H 1.84 (1.35). Infrared spectrum (cm^{-1}, KBr pellet): 2918 m, 2880 w, 2930 vw, 2066 s, 1977 s, 1937 vs, 1921 vs, 1887 s, 1638 w, 1624 vw, 1514 s, 1468 s, 1379 vw, 1352 w, 1284 w, 1250 w, 1111 s, 1080 s, 972 s, 837 w, 826 w, 760 vw, 750 vw, 725 vw, 634 w, 598 m, 577 m, 532 vw, 503 vw, 426 vw, 413 vw. Raman (cm^{-1}): 2954 (8), 2920 (12), 2895 (11), 2848 (10) 2810 (7), 2067 (33), 1971 (100), 1944 (23), 1930 (25), 1903 (50), 1639 (22), 1514 (5), 1475 (9), 1381 (12), 1275 (8), 1246 (4), 1141 (5), 873 (4), 827 (15), 584 (19), 503 (10), 457 (30), 432 (28), 387 (10), 345 (8), 332 (6), 281 (4), 102 (60). Positive ESI mass spectrum (acetone/THF; 10^{-3} M) {*m*/*z* (%) [assignment]}: 303 (100) [K(18-crown-6)]$^+$. Negative ESI mass spectrum (acetone/THF; 10^{-3} M) {*m*/*z* (%) [assignment]}: 1486 (1) $[AgP_2(C_6F_5)_4W_2(CO)_{10}]^+$, 1403 (18) $[AgP_2(C_6F_5)_4W_2(CO)_7]^+$, 1374 (6) $[AgP_2(C_6F_5)_4W_2(CO)_6]^+$, 1346 (26) $[AgP_2(C_6F_5)_4W_2(CO)_5]^+$, 1318 (8) $[AgP_2(C_6F_5)_4W_2(CO)_4]^+$, 1290 (100) $[AgP_2(C_6F_5)_4W_2(CO)_3]^+$, 1262 (7) $[AgP_2(C_6F_5)_4W_2(CO)_2]^+$, 1234 (36) $[AgP_2(C_6F_5)_4W_2(CO)]^+$, 1206 (95) $[AgP_2(C_6F_5)_4W_2]^+$, 1088 (10) $[AgP_2(C_6F_5)_4W(CO)_2]^+$, 1022 (9) $[AgP_2(C_6F_5)_4W]^+$. NMR data (CDCl$_3$; 298 K): $\delta(^{31}P)$ −126.5 ppm; $\delta(^{19}F_o)$ −128.0 ppm (m, 2F); $\delta(^{19}F_m)$ −162.8 ppm (m, 2F); $\delta(^{19}F_p)$ −156.3 ppm (m, 1F); $^1J(^{109/107}AgP)$ 437.4/380.4 Hz; $^1J(^{183}WP)$ 167.7 Hz; $^2J(PP)$ 142.4 Hz; $^3J(PF)$ 9.0 Hz; $^4J(PF)$ 8.4 Hz.

Preparation of [K(18-crown-6)][Ag{(μ-P(CF$_3$)$_2$)Cr(CO)$_5$}$_2$]. A solution of 1.40 g (3.02 mmol) of [K(18-crown-6)][Ag(CN)$_2$] dissolved in 10 mL of acetone was treated with a slight excess of [Cr(CO)$_5$PH(CF$_3$)$_2$] (7 mmol) at −30 °C. After the temperature was allowed to rise to room temperature (2 h), the reaction mixture was evaporated to dryness. The red oily product, [K(18-crown-6)][Ag{(μ-P(CF$_3$)$_2$)Cr(CO)$_5$}$_2$], was extracted several times with hexane. Colorless single crystals were obtained after slow condensation of hexane onto a diethyl ether solution at −45 °C. Infrared spectrum (cm^{-1}, THF solution, 1700−2400 cm^{-1}): 2064 m, 1946 vs, 1926 s. NMR data (CDCl$_3$; 298 K): $\delta(^{31}P)$ 64.8 ppm; $\delta(^{19}F)$ −45.5 ppm; $^1J(^{109/107}AgP)$ 412/359 Hz; $^2J(PP)$ 94 Hz; $^2J(PF)$ 55 Hz; $^4J(PF)$ 3 Hz.

Results and Discussion

On the basis of the successful synthesis of bis(perfluoroorganyl)phosphanide salts[11] and bis(perfluoroorganyl)phosphanido complexes,[2,12] by reacting bis(perfluoroorganyl)phosphanes, HP(R$_F$)$_2$ (R$_F$ = CF$_3$, C$_6$F$_5$), with cyanide compounds, we further investigated the reactions of HP(CF$_3$)$_2$, HP(C$_6$F$_5$)$_2$ and their comparable [M(CO)$_5$PH(R$_f$)$_2$] complexes (M = Cr, W) with dicyanoargentates.

To obtain dicyanoargentate salts that are soluble in most organic solvents, we first reacted K[Ag(CN)$_2$] with 18-crown-6 in methanol. After the solvent was evaporated, the product [K(18-crown-6)][Ag(CN)$_2$] was isolated as a colorless solid in quantitative yield.

$$K[Ag(CN)_2] + \text{18-crown-6} \rightarrow [K(\text{18-crown-6})][Ag(CN)_2] \quad (1)$$

By treatment of a [K(18-crown-6)][Ag(CN)$_2$] acetone solution with a slight excess of HP(CF$_3$)$_2$, a complete conversion to [Ag{P(CF$_3$)$_2$}$_2$]$^-$ is achieved:

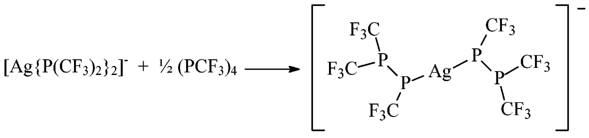
$$[Ag(CN)_2]^- + 2HP(CF_3)_2 \rightarrow 2HCN + [Ag\{P(CF_3)_2\}_2]^- \quad (2)$$

$$\text{counterion} = [K(\text{18-crown-6})]^+$$

Removal of all the volatile components at room temperature, and extracting the residue several times with hexane, gives [K(18-crown-6)][Ag{P(CF$_3$)$_2$}$_2$] in a 80% yield. An analysis of the Raman spectrum indicates the presence of cyano compounds as minor impurities. To our knowledge, the bis(bis(trifluoromethyl)phosphanido)argentate is the first isolated example of a binary di(phosphanido)argentate salt.

Attempts to use the [Ag{P(CF$_3$)$_2$}$_2$]$^-$ ion in various nucleophilic displacement reactions was unsuccessful. On treatment of [K(18-crown-6)][Ag{P(CF$_3$)$_2$}$_2$] solutions with ethyl iodide, the expected product C$_2$H$_5$P(CF$_3$)$_2$ could be obtained only in minor amounts (<5%). Several attempts of this reaction in different solvents proved unsuccessful. Further extending the reaction time or increasing the reaction temperature favored the formation of a number of unidentified side products.

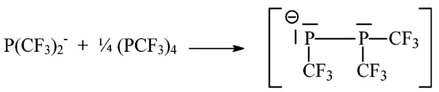
The reaction of cyclic phosphane (PCF$_3$)$_4$[13] with a slight excess of [K(18-crown-6)][Ag{P(CF$_3$)$_2$}$_2$] was found to be selective and proceed to the formation of the [Ag{P(CF$_3$)P(CF$_3$)$_2$}$_2$]$^-$ ion, as evidenced by NMR spectroscopic studies.



(3)

counterion = [K(18-crown-6)]$^+$

The nucleophilic cleavage of the phosphorus−phosphorus bond in cyclic (PCF$_3$)$_4$ is comparable to the observed reactions with [K(18-crown-6)]P(CF$_3$)$_2$, which allowed the NMR spectroscopic characterization of the novel tris(trifluoromethyl)diphosphanide ion, P(CF$_3$)P(CF$_3$)$_2$$^-$.



(4)

counterion = [K(18-crown-6)]$^+$

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Table 3. NMR Spectroscopic Data for Phosphanide Derivatives and $(PCF_3)_4$[a]

	phosphanide unit			phosphane unit			
	$\delta(^{31}P)$	$\delta(^{19}F)$	$^2J(PF)$	$\delta(^{31}P)$	$\delta(^{19}F)$	$^2J(PF)$	$^1J(PP)$
$P(CF_3)_2^-$ [b]	−1.9	−31.4	47.2				
$[Ag\{P(CF_3)_2\}_2]^-$ [c]	2.8	−39.4	57.9				
$(PCF_3)_4$[d]				−74.8	−51	*e*	100.6
$P(CF_3)P(CF_3)_2^-$ [f]	−92.0	−26.6	39.2	35.5	−51.4	62.0	339.7
$[Ag\{P(CF_3)P(CF_3)_2\}_2]^-$ [f]	−79.5	−32.1	44.7	21.9	−53.0	65.9	286.7
$P(C_2H_5)P(C_2H_5)(C_6H_5)^-$ [g]	−112.8			−17.2			396

[a] Chemical shifts in ppm; coupling constants in Hz. [b] Reference 11. [c] See Experimental Section. [d] Reference 14. [e] Not resolved. [f] THF; 243 K. [g] Reference 15.

Both diphosphanide compounds (cf. eqs 3 and 4) are selectively generated in THF at −30 °C. The neat [K(18-crown-6)] salts, which were expected to be stable at room temperature, could not be isolated. The NMR spectroscopic data of the diphosphanide compounds (cf. eqs 3 and 4) are summarized in Table 3 and compared to the data of the starting material $[Ag\{P(CF_3)_2\}_2]^-$, $P(CF_3)_2^-$, and the cyclic phosphane $(PCF_3)_4$.

The ^{31}P NMR resonances of the phosphanide units of the $P(CF_3)P(CF_3)_2^-$ ion (cf. Table 3) and $[Ag\{P(CF_3)P(CF_3)_2\}_2]^-$ ions exhibit expected shifts to higher field with respect to $(PCF_3)_4$ of about 17 and 5 ppm, respectively.[14] The ^{31}P NMR resonances of the phosphane units (cf. Table 3) are shifted by 110 and 97 ppm, respectively, to lower field with respect to $(PCF_3)_4$. These characteristic shifts allow an unambiguous assignment.

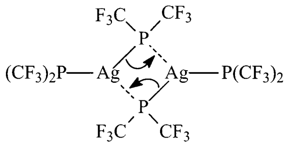
The $^1J(PP)$ coupling constants of 340 and 287 Hz for $P(CF_3)P(CF_3)_2^-$ and $[Ag\{P(CF_3)P(CF_3)_2\}_2]^-$ exhibit strong increased magnitudes as compared to the coupling of 101 Hz for $(PCF_3)_4$.[14] Both values are in the expected range, reduced by 55 and 110 Hz with respect to the 1,2-diethylphenyldiphosphanide ion, $P(C_2H_5)P(C_2H_5)(C_6H_5)^-$; synthesized by reacting $LiP(C_2H_5)(C_6H_5)$ with $(PC_2H_5)_4$.[15]

The low nucleophilicity of the $[Ag\{P(CF_3)_2\}_2]^-$ ion is surprising as compared to $[Hg\{P(CF_3)_2\}_2]$, which reacts smoothly to give $CH_3CH_2P(CF_3)_2$ on treatment with ethyl iodide. Because bis(perfluororganyl)argentates $[Ag(R_f)_2]^-$ are stronger nucleophiles than $[Hg(R_f)_2]$,[16] we expected the phosphanido argentate, $[Ag\{P(CF_3)_2\}_2]^-$, to be an even stronger nucleophilic agent.

The negative electrospray ionization (ESI) mass spectrum of a diluted acetone solution of $[K(18\text{-crown-6})][Ag\{P(CF_3)_2\}_2]$ provides an explanation for the low nucleophilicity of the argentate ion. Besides the monometallic ion, $[Ag\{P(CF_3)_2\}_2]^-$, with a relative intensity of 35% we detected a bimetallic and a trimetallic fragment ion. The fragment ions $[Ag_2\{P(CF_3)_2\}_3]^-$ and $[Ag_3\{P(CF_3)_2\}_4]^-$ are detected with relative intensities of 100% and 38% and exhibit the expected isotopic patterns for bi- and trinuclear silver compounds. The observation of fragment ions containing multiple silver atoms suggests a likely association of the $[Ag\{P(CF_3)_2\}_2]^-$ ion in solution. In the case of an association via bridging μ-phosphanido groups, the phosphorus lone electron pair is no longer available for nucleophilic displacement reactions.

The fast ligand exchange, based on the NMR time scale, of the $[Ag\{P(CF_3)_2\}_2]^-$ ion in solution further supports association of the argentate ion which involves bridging μ-phosphanido groups and the formation of oligomeric moieties:

E. g.



(5)

Fenske and co-workers provided X-ray structural evidence for the formation of bridging μ_2-phosphanido groups in the polymetallic mixed phosphanido phosphane silver complexes.[17]

While room temperature NMR spectra of the $[Ag\{P(CF_3)_2\}_2]^-$ ion exhibit sharp ^{19}F and ^{31}P NMR resonances, the low temperature NMR spectra (THF; −90 °C) exhibit very complex spin systems, which were unable to be characterized. The room temperature ^{19}F and ^{31}P NMR spectra exhibit line widths of less than 4 Hz but show no indication of fluorine or phosphorus silver nuclear couplings. To obtain NMR spectroscopic evidence for the formation of a silver phosphorus bond, via the detection of the ^{31}P nuclear couplings with the two NMR active silver isotopes (^{109}Ag and ^{107}Ag), it was necessary to slow down the ligand exchange process.

The coordination of both phosphanido ligands in the $[Ag\{P(CF_3)_2\}_2]^-$ ion to a $M(CO)_5$ moiety prevents the involvement of the phosphorus lone pair with association. As a consequence, blocking of the phosphorus lone pair should slow down the ligand exchange process, allowing the detection of phosphorus silver nuclear couplings.

$[W(CO)_5PH(CF_3)_2]$[7] and $[Cr(CO)_5PH(CF_3)_2]$[7] react selectively with $[K(18\text{-crown-6})][Ag(CN)_2]$ to form the corresponding trinuclear argentates, $[Ag\{(\mu\text{-}P(CF_3)_2)M(CO)_5\}_2]^-$ (M = W and Cr) at −50 °C in acetone.

$$[Ag(CN)_2]^- + 2[M(CO)_5PH(CF_3)_2] \rightarrow 2HCN + [Ag\{(\mu\text{-}P(CF_3)_2)M(CO)_5\}_2]^- \quad (6)$$

$$M{=}Cr,W;counterion{=}[K(18\text{-crown-6})]^+$$

Upon removal of all volatile materials in vacuo at room temperature followed by extraction of the residue with diethyl ether, the product $[K(18\text{-crown-6})][Ag\{(\mu\text{-}P(CF_3)_2)W(CO)_5\}_2]$ was obtained as a green powder. The trinuclear argentate ion, $[Ag\{(\mu\text{-}P(CF_3)_2)W(CO)_5\}_2]^-$, exhibits no ESI mass spectrometric or NMR spectroscopic evidence for association in solution. The ESI mass spectrum reveals only one

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(13) Mahler, W.; Burg, A. B. *J. Am. Chem. Soc.* **1958**, *80*, 6161−6167.
(14) Albrand, J. P.; Cogne, A.; Robert, J. B. *J. Am. Chem. Soc.* **1978**, *100*, 2600−2604.
(15) Fluck, E.; Issleib, K. *Z. Anorg. Allg. Chem.* **1965**, *339*, 274−280.
(16) For example: Naumann, D.; Wessel, W.; Hahn, J.; Tyrra, W. *J. Organomet. Chem.* **1997**, *547*, 79−88 and references therein.
(17) Eisenmann, J.; Fenske, D.; Simon, F. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1681−1688. Eichhöfer, A.; Eisenmann, J.; Fenske, D.; Simon, F. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1360−1368.

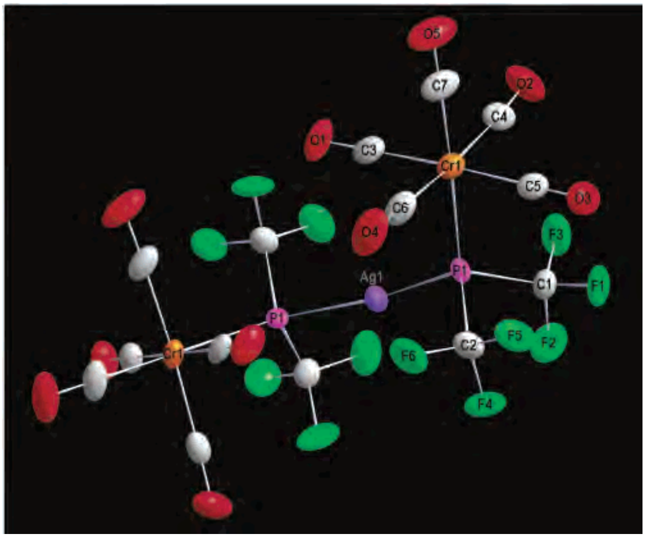

Figure 1. Central projection of the C_2 symmetric $[Ag\{(\mu\text{-}P(CF_3)_2)Cr(CO)_5\}_2]^-$ ion in the compound $[K(18\text{-crown-}6)][Ag\{(\mu\text{-}P(CF_3)_2)Cr(CO)_5\}_2]$ showing the atom numbering scheme of the asymmetric unit and thermal ellipsoids (40%).

fragment at $m/z = 1094$ assigned to the $[Ag\{(\mu\text{-}P(CF_3)_2)W(CO)_5\}_2]^-$ ion.

Colorless crystals of the chromium compound, $[K(18\text{-crown-}6)]^+$ $[Ag\{(\mu\text{-}P(CF_3)_2)Cr(CO)_5\}_2]^-$, were obtained by slow condensation of hexane onto a saturated diethyl ether solution at −45 °C. This compound crystallizes in the noncentrosymmetric space group *Fdd*2. The asymmetric unit shows the silver atom on a 2-fold axis with only half of the anionic structure. The complete C_2 symmetric structure of $[Ag\{(\mu\text{-}P(CF_3)_2)Cr(CO)_5\}_2]^-$ anion is generated using the symmetry operation ($a = {}^3/_2 - x, {}^1/_2 - y, z$) yielding a $P1^a$−Ag1−P1 bond angle of 169.17(6)°, an Ag−P distance of 239.1(1) pm and a P′−Ag−P−Cr torsion angle of 39.02(4)° (Figure 1). A survey of the CCSD[18] reveals only one example of an analogous, isolated Ag(I) anion, $[Ag\{(\mu\text{-}P(C_6H_5)_2)Au(C_6F_5)_3\}_2]^-$, which contains a linear P−Ag−P bond (180°) with an Ag−P distance of 238.6 pm.[5] This distance is similar to those in other linear or cyclic P−Ag−P complexes (238−241 pm).[5,17,19]

In the compound $[K(18\text{-crown-}6)][Ag\{(\mu\text{-}P(CF_3)_2)Cr(CO)_5\}_2]$, the potassium atom lies on a 2-fold axis and is encapsulated by a severely disordered 18-crown-6 ring. The disordered component of the crown ether is generated by symmetry (${}^3/_2 - x, {}^3/_2 - y, z$) (see Experimental Section), and the two conformations are rotated by ∼22.4° with respect to each other as shown in Figure 2. An analysis of the mean plane formed by the oxygen atoms of the crown ether shows a near-planar arrangement with a deviation of 19.3(5) pm with the potassium atom almost coplanar at 2.6(3) pm with this mean plane. The maximum deviations from the mean plane described are shown by the O8 and O9 atoms +22.5(5) and −24.8(5) pm, respectively.

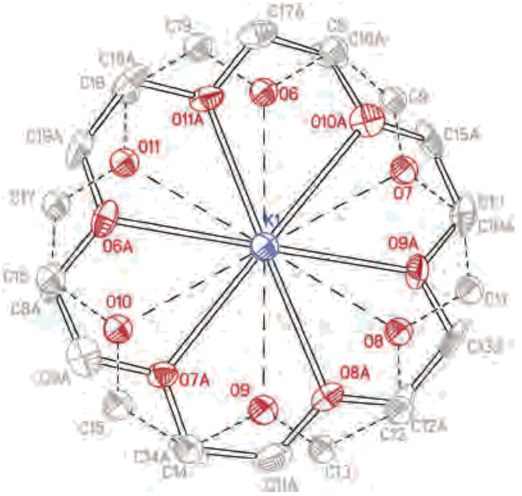

Figure 2. Figure showing an ORTEP plot for the two components of the disordered 18-crown-6 ring. The thermal ellipsoids are at the 30% probability level.

In addition to hexacoordination from the oxygen atoms of the 18-crown-6 ring, the potassium atom further coordinates to one fluorine atom, (F5) of the $P(CF_3)_2$ group (K···F = 3.052(5) pm), and one oxygen atom, (O3) of the $Cr(CO)_5$ (K···O = 3.287(3)pm), as well as their symmetry equivalents, $O3^b$ and $F5^b$ ($b = {}^3/_2 - x, {}^3/_2 - y, z$). These distances are shorter than the sum of the van der Waals radii of K and O (427 pm), and K and F (422 pm), and result in the formation of a seven-membered ring which increases the coordination number of potassium to ten. Only two [K(18-crown-6)] structures containing both K···O and K···F contacts could be found in the CCSD. For these compounds, the K···O and K···F distances lie in the range 267.6−288.0 pm and 289.5−333.1 pm, respectively.[20] Further, in these oxagermetanide anions containing 18-crown-6 complexes, the potassium atom lies 15 and 121 pm above the crown ring.[20]

The crystal packing diagram (Figure 3) shows the formation of two Ag···O5 contacts at 321.9(5) pm, which are comparable to the sum of the van der Waals radii for Ag and O (324 pm). The O−Ag−O arrangement is almost linear at 169.4° and twists 81.9° with respect to the $P1^a$−Ag1−P1 bond (Figure 3).

As a result of slowing down the ligand exchange silver phosphorus coupling constants ${}^1J({}^{109/107}AgP)$ were determined in the ${}^{31}P$ NMR spectrum to be 425 and 369 Hz, respectively, which lies within the expected range.[21] As a result of the ${}^2J(PF)$ and long range ${}^4J(PF)$ coupling with values of 55 Hz and of 2 Hz, the fluorine and the phosphorus NMR spectra show the magnetic nonequivalence of the two $P(CF_3)_2$ units. This allows the determination of the ${}^2J(PP)$ coupling via the calculation of the center signal as an $[A_6X]_2$ ($A_6A'_6XX'$) spin system. With the knowledge that ${}^2J(PF)$ couplings—in contrast to the always negative ${}^1J(PF)$ couplings—are always

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[18] Conquest 1.5, Cambridge Crystal Structure Database, CCDC, Cambridge, U.K.

[19] Blanco, M. C.; Fernandez, E. J.; Lopez-de-Luzuraga, J. M.; Olmos, M. E.; Crespo, O.; Gimeno, M. C.; Laguna, A.; Jones, P. G. *Chem. Eur. J.* **2000**, *6*, 4116−4123.

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[21] Odendorf, D.; Peringer, P. *J. Organomet. Chem.* **1987**, *326*, 375−380. Odendorf, D.; Peringer, P. *J. Organomet. Chem.* **1986**, *299*, 127−130.

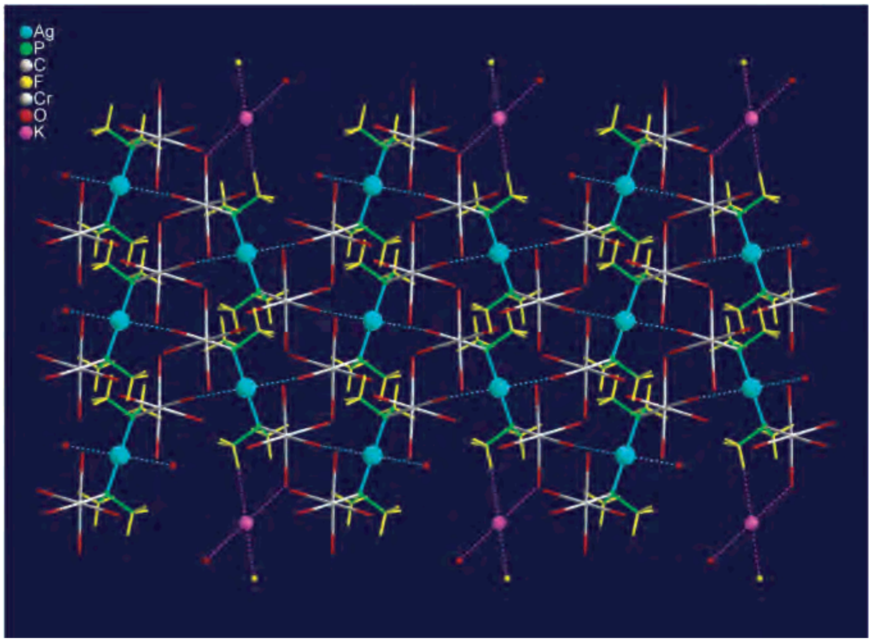

Figure 3. Crystal packing diagram of [K(18-crown-6)][Ag{(μ-P(CF$_3$)$_2$)Cr(CO)$_5$}$_2$] viewed along the *c*-axis showing the K···O/F and Ag···O contacts. The 18-crown-6 rings are omitted and the potassium atoms are only shown on the periphery for figure clarity.

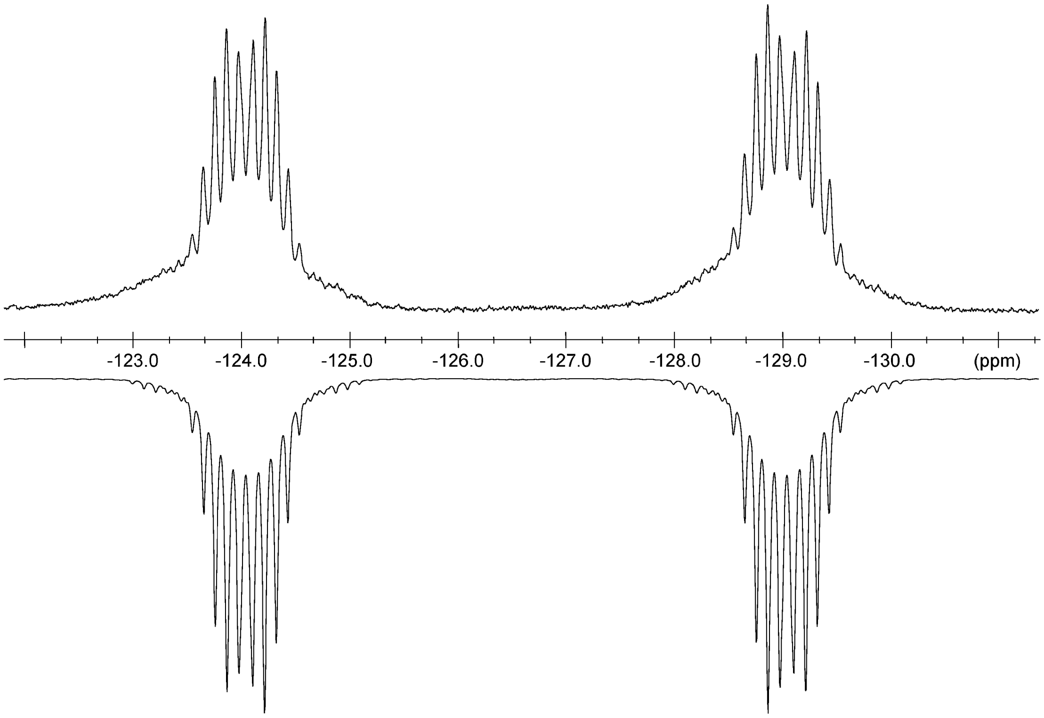

Figure 4. Experimental (top) and calculated (bottom) ^{31}P NMR spectrum (81.01 MHz) of [Ag{(μ-P(C$_6$F$_5$)$_2$)W(CO)$_5$}$_2$]$^-$.

positive,[22] the long range ^4J(PF) couplings can be assigned with a positive sign with respect to the interpretation of the experimental spectra as [A$_6$X]$_2$ spin systems. In general, for spin systems based on [AX]$_2$ only the relative signs of the AX and AX′ couplings can be determined by iteration of the obtained experimental spectrum.[23]

The magnitude of the ^2J(PP) couplings of 94 and 101 Hz for the C_2 symmetric chromium and tungsten compound is comparable to that found for the nonsymmetric compounds [Ag(μ-PR$_2$)M(CO)$_5$(μ-PR′$_2$)M′(CO)$_5$]$^-$ (R, R′ = Ph, Cyhex and M, M′ = Cr, Mo, W) with values of 130−150 Hz. These nonsymmetric compounds were obtained as a mixture via a synproportionation of the corresponding symmetric compounds.[4]

The ^2J(PP) coupling of 101 Hz for the tungsten derivative, [Ag{(μ-P(CF$_3$)$_2$)W(CO)$_5$}$_2$]$^-$, exactly matches the value

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(22) Berger, S.; Braun, S.; Kalinowski, H.-O. *NMR-Spektroskopie von Nichtmetallen*; Georg Thieme Verlag: Stuttgart, New York, 1993; p 147.

(23) Günther, H. *NMR-Spektroskopie*, 3rd ed.; Georg Thieme Verlag: Stuttgart, New York, 1992; p 175.

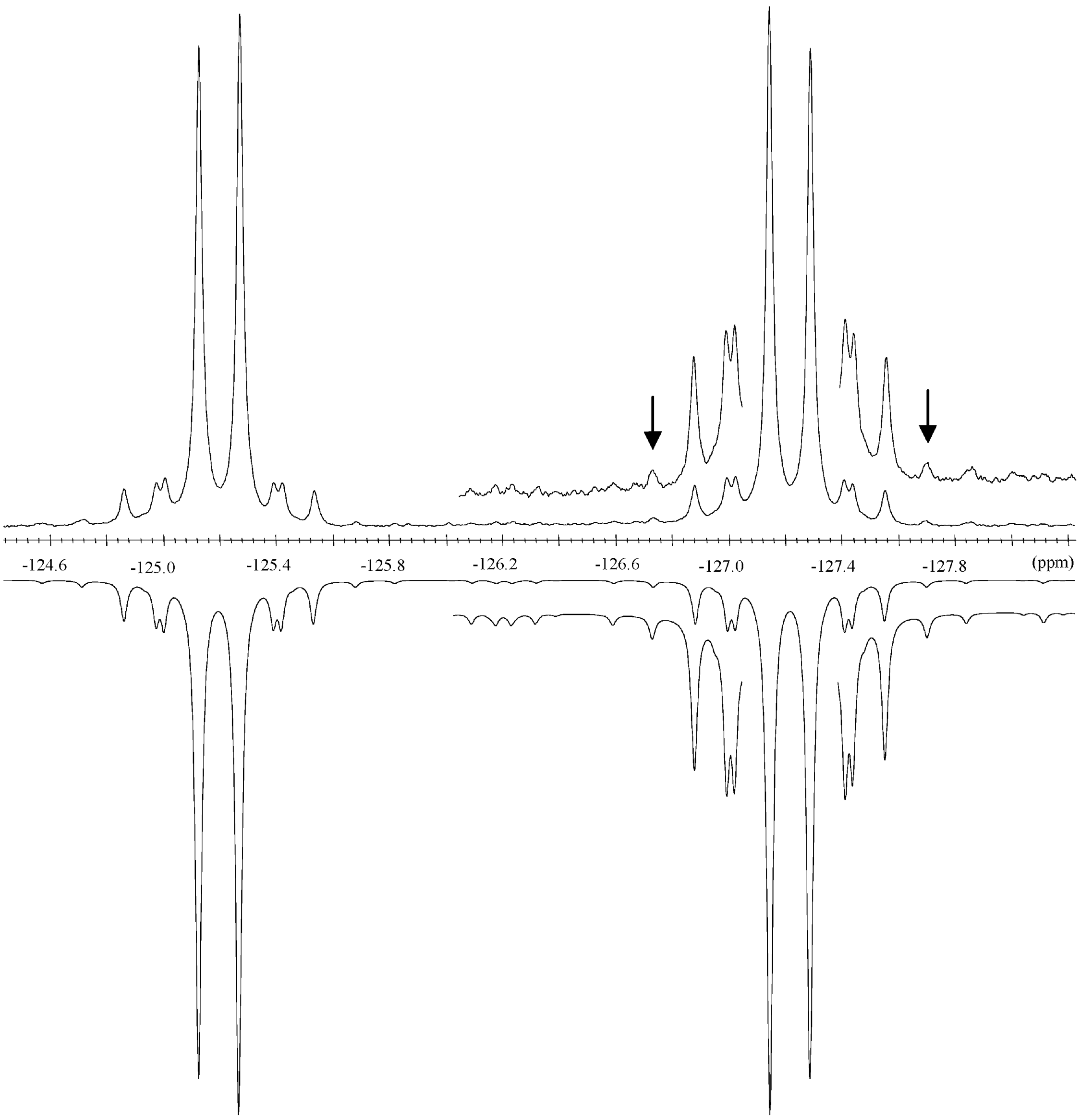

Figure 5. Experimental (top) and calculated (bottom) $^{31}P\{^{19}F\}$ NMR spectrum (202.4 MHz) of $[Ag\{(\mu\text{-}P(C_6F_5)_2)W(CO)_5\}_2]^-$ (compare text).

obtained from the tungsten satellites of the fluorine decoupled phosphorus spectrum. The isotopomer of the W−P−Ag−P−W unit with one NMR active ^{183}W isotope gives rise to a magnetic nonequivalence of the two phosphorus atoms. The theoretical chemical difference of the two phosphorus atoms, caused by the isotopic shift, can be neglected in this case. The calculation of the two resulting $[A]_2MX$ (AA′MX) spin systems with A = P, M = ^{183}W, and X = ^{109}Ag and ^{107}Ag allows the determination of the ^2J(PP) and the ^1J(WP) coupling constants. Because the ^3J(WP) coupling has a value close to zero, it is not possible to determine the relative signs of the ^2J(PP) and the ^1J(WP) coupling constants by iteration of the obtained experimental $^{31}P\{^{19}F\}$ NMR spectrum.

While the reaction of $[K(18\text{-crown-}6)][Ag(CN)_2]$ with $[W(CO)_5PH(C_6F_5)_2]$ allows the isolation of the trinuclear product, $[K(18\text{-crown-}6)][Ag\{(\mu\text{-}P(C_6F_5)_2)W(CO)_5\}_2]$, as a bright yellow powder in 50% yield after recrystallization from a diethyl ether hexane mixture, unfortunately, the reaction with $HP(C_6F_5)_2$ did not yield a uniform product.

$$[Ag(CN)_2]^- + 2[W(CO)_5PH(C_6F_5)_2] \rightarrow 2HCN + [Ag\{(\mu\text{-}P(C_6F_5)_2)W(CO)_5\}_2]^- \quad (7)$$

$$\text{counterion} = [K(18\text{-crown-}6)]^+$$

The experimental first order ^{31}P NMR spectrum of the trinuclear ion is depicted in Figure 4, showing a ^3J(PF) and a ^4J(PF) coupling of 9.0 and 8.4 Hz, respectively. The coupling constants were determined by an iteration of the experimental spectrum (bottom trace of Figure 4).

As a result of the chemical and magnetic equivalence of the two $P(C_6F_5)_2$ units, the ^2J(PP) coupling constant cannot be determined from the fluorine decoupled phosphorus spectrum. In the case of the fluorine decoupled phosphorus spectrum, the tungsten satellites could be resolved (upper trace of Figure 5). As already discussed for the CF_3 derivative, the isotopomer of the W−P−Ag−P−W unit with one NMR active ^{183}W isotope gives rise to a magnetic nonequivalence of the two phosphorus atoms. The tungsten satellites are therefore a combination of two $[A]_2MX$ spin systems (A = P, X = ^{183}W, M = ^{109}Ag and ^{107}Ag), one for each NMR active silver isotope. The calculation and iteration of the two spin systems allows the determination of the $^{2}J(PP)$ coupling constant to 142.4 Hz.

Only four lines for the isotopomer of the W−P−Ag−P−W unit with two NMR active ^{183}W isotopes could be assigned in the experimental fluorine decoupled ^{31}P NMR spectrum by the calculation of two sets of an $[AX]_2M$ spin system. Two of them are marked with an arrow in the enlargement of Figure 5.

The highest CO stretching frequencies of the compounds $[W(CO)_5PH(CF_3)_2]$,[7] $[Ag\{(\mu\text{-}P(CF_3)_2)W(CO)_5\}_2]$, and $[W\{P(CF_3)_2\}(CO)_5]^{-}$[24] with about 2093, 2072, and 2065 cm^{-1}, respectively, exhibit the expected shift to lower frequencies. These findings can be explained by the increasing electron density at the phosphorus atoms which causes a reduced π-back-bonding effect for the W−P bonds while the π-back-bonding effect for the W−C bonds increases in the opposite direction.

The highest CO valence mode of a comparable mercury complex $[Hg\{(\mu\text{-}P(CF_3)_2)W(CO)_5\}_2]\cdot 2DMF$,[3] located at 2081 cm^{-1}, might be interpreted in terms of a stronger Lewis acidity of the mercury center in comparison to the silver center in $[Ag\{(\mu\text{-}P(CF_3)_2)W(CO)_5\}_2]^{-}$.

The highest infrared CO stretching frequency of the trinuclear anion, $[Ag\{(\mu\text{-}P(C_6F_5)_2)M(CO)_5\}_2]^{-}$, located at 2066 cm^{-1}, is shifted by 12 cm^{-1} to higher frequencies and by 18 cm^{-1} to lower frequencies in comparison to $[W\{P(C_6F_5)_2\}(CO)_5]^{-}$ and $[W(CO)_5PH(C_6F_5)_2]$, respectively, and therefore describes the weaker and stronger, respectively, π acidity of the comparable phosphorus moieties.

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Supporting Information Available: Crystallographic file in CIF format for $[K(18\text{-crown-6})][Ag\{(\mu\text{-}P(CF_3)_2)Cr(CO)_5\}_2]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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