Metal–Alkene Complexes

A Stable Salt of the Tris(ethene)silver Cation: Structure and Characterization of $[Ag(\eta^2\text{-}C_2H_4)_3]^+[Al\{OC(CF_3)_3\}_4]^-$**

Ingo Krossing and Andreas Reisinger*

Since the discovery of Zeise's salt $K[PtCl_3(C_2H_4)]$ in 1827[1] the investigation of simple ethene–metal complexes is an area of continuing interest in all fields of chemistry, fueled by the interest in transformations of the coordinated C_2H_4 molecule. Several ethene–metal coordination modes including $\mu,\eta^2{:}\eta^2$ are known,[2] and ethene–silver complexes with no or very little back-bonding served to formulate the Dewar–Chatt–Duncanson model for the binding of olefins to transition-metal atoms.[3] However, there is still much controversy about the nature of the bonding in $[Ag(\eta^2\text{-}C_2H_4)_x]^+$ ions ($x = 1$–3) with proposals ranging from mainly electrostatic[4] to mainly covalent[5] and mixtures thereof.[6,7] Several weak addition compounds $[Ag(C_2H_4)_x]^+[Y]^-$ ($x = 1$–3; e.g., $Y = BF_4$) were prepared by applying C_2H_4 pressure on solid Ag[Y] salts. They were characterized by complexation constants, NMR, and vibrational spectroscopy.[8] In addition, the experimental silver complexation enthalpies for the binding of one ($-142\ kJ\,mol^{-1}$) and two ($-136\ kJ\,mol^{-1}$) equivalents of C_2H_4 in the gas phase were determined by FT-ICR mass spectrometry;[9] Ag^+ complexes with three ethene molecules are unknown in the gas phase and were only once reported in a recent computational study.[7] However, although silver–ethene complexes are textbook compounds, no solid-state structure of a $[Ag(C_2H_4)_x]^+$ moiety ($x > 0$) has been determined. This is possibly due to the instability of the compounds already prepared. The complexation of one gaseous C_2H_4 molecule to a silver salt at 298 K diminishes the Gibbs energy of the $Ag{-}C_2H_4$ bond compared to its bond-dissociation enthalpy by $65\ kJ\,mol^{-1}$, owing to the loss of entropy. In contrast, a huge quantity of silver complexes with less volatile and/or chelating (di-)olefins is known, some of which contain a silver atom coordinated by three or four C=C double bonds (see for example $2\,Ag[ClO_4]\cdot 3\,C_6H_{10}$[10] or $Ag[SO_3CF_3]\cdot C_{24}H_{32}$[11]). These olefins are solids or liquids and, therefore, the entropic contribution to dissociation (and thus decomposition) is much smaller than that for the lightest parent C_2H_4 olefin.

Recently we prepared the silver salt of the very weakly coordinating $[Al\{OC(CF_3)_3\}_4]^-$ ($[A]^-$) ion [12,13] and reported its use in stabilizing silver complexes of very weak Lewis bases such as S_8,[14] P_4,[15] and P_4S_3,[16] as well as reactive cations such as CI_3^+,[17] $P_3I_6^+$, and $P_5X_2^+$ (X = Br, I).[18] Large weakly coordinating anions (WCAs[19]) such as $[A]^-$ stabilize weakly bound Lewis acid–base adducts through their ability to produce "pseudo-gas-phase conditions"[14] in condensed phases, which were used herein to prepare and characterize a stable $[A]^-$ salt of the $[Ag(\eta^2\text{-}C_2H_4)_3]^+$ ion, a weakly bound isoelectronic cation analogue of the neutral tris(ethene)-nickel,[20] -palladium, and -platinum molecules.[21]

When three equivalents of C_2H_4 were added to Ag[A] in CH_2Cl_2, cooling of the concentrated clear colorless solution to +7 °C resulted in the precipitation of an almost quantitative amount of large colorless blocks of a compound that was identified by NMR, IR, and X-ray studies as $[Ag(\eta^2\text{-}C_2H_4)_3]^+[A]^-$ [Eq. (1)].[22]

$$\begin{aligned}&Ag[A] + 3\,C_2H_4 \xrightarrow[+7^{\circ}C]{CH_2Cl_2} Ag(\eta^2\text{-}C_2H_4)_3^+[A]^- \\ &[A]^- = [Al(OC(CF_3)_3)_4]^-\end{aligned} \tag{1}$$

It is noteworthy that the affinity of the dissolved Ag[A] silver ion towards the C_2H_4 molecule is so high that a stoichiometric amount of ethene is sufficient to prepare the $[Ag(\eta^2\text{-}C_2H_4)_3]^+[A]^-$. The latter salt is stable in a closed nitrogen-filled container at room temperature and may be handled quickly in the atmosphere of a glove box. Compared to free C_2H_4, the ^1H and ^{13}C NMR spectra of a CD_2Cl_2 solution of $[Ag(\eta^2\text{-}C_2H_4)_3]^+[A]^-$ showed a downfield shift of $\Delta(\delta^1H) = +0.49$ ppm and an upfield shift of $\Delta(\delta^{13}C) = -6.9$ ppm, which is in good agreement with the DFT-calculated[23–28] NMR shifts of $[Ag(\eta^2\text{-}C_2H_4)_3]^+$ and free C_2H_4 ($\Delta(\delta^1H) = +0.3$ ppm; $\Delta(\delta^{13}C) = -7.3$ ppm; Table 1).

Table 1: Comparison of experimental and DFT-calculated properties of $[Ag(\eta^2\text{-}C_2H_4)_3]^+$ and free C_2H_4.

	$[Ag(\eta^2\text{-}C_2H_4)_3]^+$		C_2H_4	
Property	expt	calcd	expt	calcd
δ^1H [ppm]	5.77	5.3[a]	5.28	5.0[a]
$\delta^{13}C$ [ppm]	116.4	114.4[a]	123.3	121.7[a]
d(C=C) [Å]	1.307[b]	1.364[c]	1.313[b]	1.333[c]
d(Ag–C) [Å]	2.396	2.388[c]	–	–
ν(C=C) [cm^{-1}]	1581 (vw; e′) 1575 (3 km mol^{-1}, e′)[a]	1610 (vw; a_1′) 1577 (0 km mol^{-1}, a_1′)[a]	1623	1656[a]

[a] BP86/SV(P). [b] In the solid state, corrected for libration. [c] BP86/TZVPP. vw = very weak.

This agreement suggests that the planar spoke-wheel structure of solid $[Ag(\eta^2\text{-}C_2H_4)_3]^+[A]^-$ may be retained in solution (see below).

In the solid state[29] $[Ag(\eta^2\text{-}C_2H_4)_3]^+[A]^-$ forms an ionic lattice with the almost planar $[Ag(\eta^2\text{-}C_2H_4)_3]^+$ ions in a spoke-wheel arrangement (Figure 1). Short C=C bond lengths of 1.30(1) to 1.309(9) Å (av 1.304 Å) were found in the $[Ag(\eta^2\text{-}C_2H_4)_3]^+$ ion. An additional correction for libration elongates the C=C bonds by 0.003 to 0.005 Å[30] (av 1.307 Å). These C=C bond lengths compare well to those in solid ethane (1.313 Å, corrected for libration).[31] In conclusion it may be

---

[*] Priv.-Doz. Dr. I. Krossing, Dipl.-Chem. A. Reisinger
Universität Karlsruhe, Institut für Anorganische Chemie
Engesserstrasse Geb. 30.45, 76128 Karlsruhe (Germany)
Fax: (+49) 721-608-4854
E-mail: krossing@chemie.uni-karlsruhe.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Prof. H. Schnöckel and Dr. H.-J. Himmel for valuable discussions.

DOI: 10.1002/ange.200352080

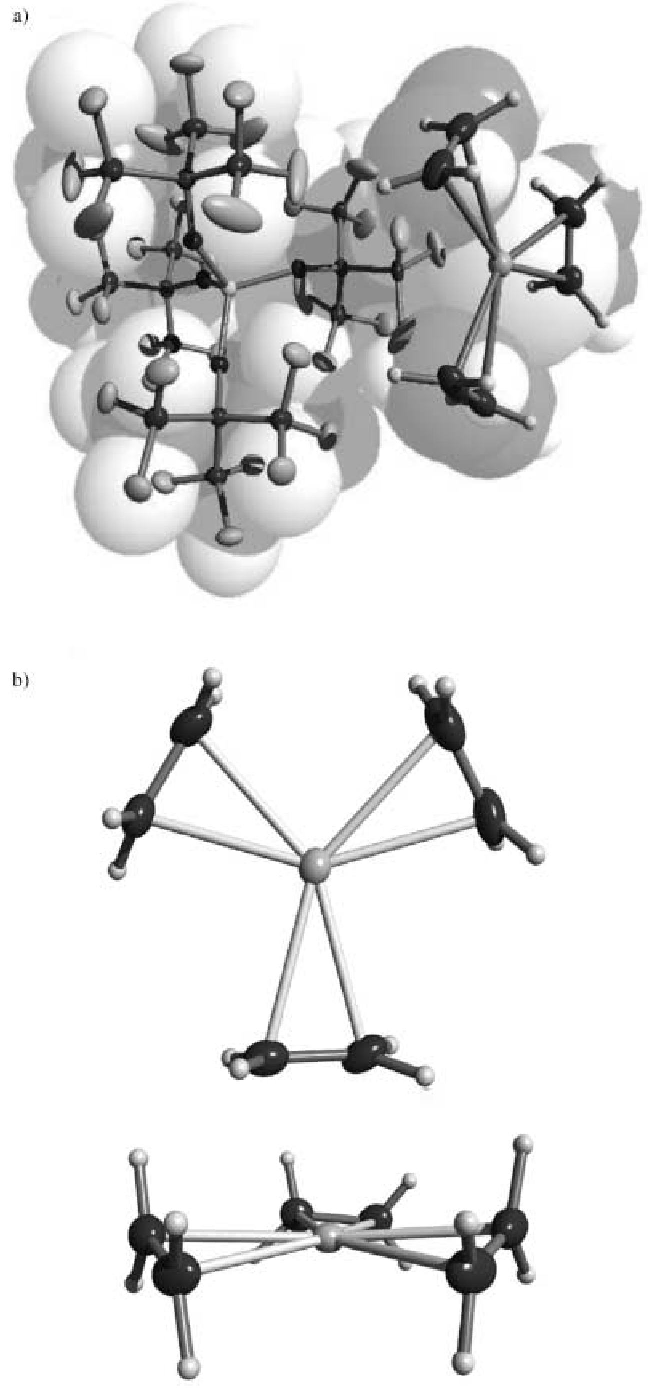

Figure 1. a) Section of the solid-state structure of $[\mathrm{Ag}(\eta^2\text{-C}_2\mathrm{H}_4)_3]^+[\mathrm{A}]^-$. Superposition of a space-filling (faint in gray scale) and a 25% probability ellipsoid model; b) two additional views of the cation. The positions of the hydrogen atoms were found in the difference Fourier map.

stated that the C=C bond in $\mathrm{C}_2\mathrm{H}_4$ is unaffected upon coordination in the $[\mathrm{Ag}(\eta^2\text{-C}_2\mathrm{H}_4)_3]^+$. This stands in sharp contrast to the solid-state structure of the isoelectronic $[\mathrm{Pt}(\eta^2\text{-C}_2\mathrm{H}_4)_3]$ molecule, in which the average C=C bond length is elongated to 1.402(7) Å.[21d] The Ag–C separations range from 2.385(5) to 2.410(5) Å (av 2.396 Å) and are ≈0.22 Å longer than those in $[\mathrm{Pt}(\eta^2\text{-C}_2\mathrm{H}_4)_3]$.[21d] However d(Ag–C) is in good agreement with other Ag–C bonds in silver complexes, for example, in $[\mathrm{Ag(toluene)}_2\{\mathrm{Al(OR)}_4\}]$ (2.363(5)–2.647(6) Å; R = C(H)(CF$_3$)$_2$).[12a] The overall structure of the $[\mathrm{Ag}(\eta^2\text{-C}_2\mathrm{H}_4)_3]^+$ ion approaches D_{3h} symmetry, but the three individual AgC$_2$ planes deviate from the mean plane defined by the silver atom and all carbon atoms by 11.7 to 17.5°. This distortion is attributed to packing effects, which are underlined by 10 weak H···F contacts between the cation and the anion that range from 2.56 to 2.93 Å (av 2.79 Å; sum of van der Waals radii: 2.90 Å). In contrast, no contacts between fluorine and carbon atoms were observed, while the silver atom forms two weak contacts to fluorine atoms at 3.07 and 3.19 Å (sum of van der Waals radii: 3.20 Å). By employing the bond valence method of Brown,[32] the nature of the two Ag···F contacts correspond to a partial charge of +0.14 v.u. residing on the silver atom. The remainder (+0.86 v.u.) is distributed over the hydrogen atoms only, since no close contacts between carbon and fluorine atoms were observed. The latter assignment of positive partial charges to hydrogen but no (or even negative) charge to the carbon atoms is in agreement with the trends concluded from ^{1}H and ^{13}C NMR spectroscopy of $[\mathrm{Ag}(\eta^2\text{-C}_2\mathrm{H}_4)_3]^+[\mathrm{A}]^-$ (Table 1).

The infrared spectra of $[\mathrm{Ag}(\eta^2\text{-C}_2\mathrm{H}_4)_3]^+[\mathrm{A}]^-$ contain the bands of the isolated nondistorted $[\mathrm{A}]^-$ ion as well as some less intense bands assigned to the almost D_{3h}-symmetric $[\mathrm{Ag}(\eta^2\text{-C}_2\mathrm{H}_4)_3]^+$ ion. The C=C stretches are expected to be intense in the Raman spectrum, however, all attempts to obtain such a spectrum of $[\mathrm{Ag}(\eta^2\text{-C}_2\mathrm{H}_4)_3]^+[\mathrm{A}]^-$ failed and led to immediate decomposition of several independently prepared samples. Nevertheless, two very weak C=C stretches at 1581 and 1610 cm^{-1} assigned to the e′- and a$_1$′-modes were observed in the IR spectrum and fit with the DFT-calculated[23,33] frequencies (Table 1). The weighted average[34] of those two bands is 1591 cm^{-1} and $\Delta\nu$ with respect to free ethene (1623 cm^{-1}) is -32 cm^{-1}. This is in line with earlier reports on $[\mathrm{Ag}(\mathrm{C}_2\mathrm{H}_4)_2]^+$ ($\Delta\nu = -37$)[8] and $[\mathrm{Ag}(\mathrm{C}_2\mathrm{H}_4)]^+$ ($\Delta\nu = -44$).[8] As expected, $\Delta\nu$ decreases with an increasing number of coordinated C$_2$H$_4$ molecules, which is indicative of weaker interactions.[35] It should be noted that although the observed average C=C frequency fits very well with the trend of other $[\mathrm{Ag}(\mathrm{C}_2\mathrm{H}_4)_x]^+$ cations ($x = 1, 2$), the DFT-calculated frequencies as well as the calculated C=C bond distance indicate a greater weakening of the C=C bond in $[\mathrm{Ag}(\eta^2\text{-C}_2\mathrm{H}_4)_3]^+$ than expected from the experimental data (compare $\Delta\nu$ and d(C=C) in Table 2).

To understand the formation of a planar, almost D_{3h}-symmetric $[\mathrm{Ag}(\eta^2\text{-C}_2\mathrm{H}_4)_3]^+$ ion and relate its structure and bonding to the (known) isoelectronic $[\mathrm{Pd}(\eta^2\text{-C}_2\mathrm{H}_4)_3]$ molecule, as well as the hypothetic $[\mathrm{Na}(\eta^2\text{-C}_2\mathrm{H}_4)_3]^+$ ion, additional DFT[23] and ab initio[23,36] calculations were performed on spoke-wheel D_{3h} molecules, as well as trigonal-prismatic barrel-like $[\mathrm{M}(\eta^2\text{-C}_2\mathrm{H}_4)_3]$ (M = Ag$^+$, Pd, and Na$^+$) with all C$_2$H$_4$ molecules perpendicular to the mean central plane (Table 2). From Table 2 it is evident that the planar form of $[\mathrm{M}(\eta^2\text{-C}_2\mathrm{H}_4)_3]$ is highly favored for M = Pd (by 186.5 kJ mol^{-1}), with M = Ag$^+$ (44.4 kJ mol^{-1}) being intermediate, while for M = Na$^+$ both the planar and prismatic arrangements are isoenergetic within 1.5 kJ mol^{-1}. The sodium structure contains the longest M–C separations and the structural/vibrational parameters of the coordinated C$_2$H$_4$

Table 2: Experimental and calculated properties of $[M(\eta^2\text{-}C_2H_4)_3]$ ($M = Ag^+$, Pd, Na^+). ΔE represents the energy difference between the planar spoke-wheel and the prismatic barrel structure and $\Delta\tilde{\nu}$ is the difference between the C=C stretching frequency of free ethene and $[M(\eta^2\text{-}C_2H_4)_3]$.

Property (Level or expt)	$Pd(C_2H_4)_3$	$[Ag(C_2H_4)_3]^+$	$[Na(C_2H_4)_3]^+$	$C_2H_{4\,free}$
ΔE [kJ mol^{-1}] (MP2/TZVPP)	186.5	44.4	1.5	–
d(M–C) [Å] (BP86/TZVPP)	2.216	2.388	2.852	–
d(C=C) [Å] (BP86/TZVPP)	1.389	1.364	1.340	1.333
d(C=C) [Å] (expt)	–	1.307[a]	–	1.313[a]
ν (C=C) [cm^{-1}] (BP/SV(P))	1522[b]	1576[b]	1631	1656
ν (C=C) [cm^{-1}] (expt)	1522[b]	1591[b]	–	1623
$\Delta\nu$ [cm^{-1}] (computed/expt)	134/101	80/32	24/–	–

[a] In the solid state, corrected for libration. [b] weighted average of the e′ and a$_1$′ modes.[33]

molecule are least affected upon coordination to M. Therefore the Na–C bonding in $Na(\eta^2\text{-}C_2H_4)_3^+$ is best described as being of electrostatic nature. In contrast, Ag^+ and Pd have an accessible $4d^{10}$ shell. The large energetic differences ΔE of the planar versus the prismatic form, as well as the short M–C separation, suggest that d-orbital bonding contributions are most important for the Pd complex but are, to a lesser extent, also important for the Ag complex.[37] A full analysis of the nature of this bonding is in progress.[35]

The synthesis and full characterization of a stable $[Ag(\eta^2\text{-}C_2H_4)_3]^+[A]^-$ salt gives the first structural information on the $[Ag(C_2H_4)_x]^+$ textbook ions ($x > 0$). It is rather remarkable that a tris(ethene)silver cation can be stabilized in condensed phases considering the fact that in the gas phase this was hitherto impossible.[9] This is certainly due to the low binding energy of the third C_2H_4 molecule of $\Delta G_{298} = -55$ kJ mol^{-1} in the gas phase (MP2/TZVPP).[23] According to an estimation of the lattice potential enthalpies in a suitable Born–Fajans–Haber cycle, solid $[Ag(\eta^2\text{-}C_2H_4)_3]^+[A]^-$ is stable against the loss of one gaseous C_2H_4 molecule by only 17 kJ mol^{-1}.[38] Therefore we consider the preparation of $[Ag(\eta^2\text{-}C_2H_4)_3]^+[A]^-$ as a further proof for the validity of the concept of pseudo-gas-phase conditions[14] in condensed phases.

Experimental Section

All manipulations were performed using grease-free Schlenk or drybox techniques and a dinitrogen or argon atmosphere. CH_2Cl_2 was rigorously dried by multiple additions of 20-g quantities of P_2O_5, followed by distillation and degassing prior to use. Solvents were added by condensation techniques. Stoichiometric quantities of ethene were added by condensation techniques from flasks with a known volume and pressure of ethene. Ag[A] was prepared as previously described.[12a]

Received: June 6, 2003
Revised: July 21, 2003 [Z52080]

Keywords: alkenes · cations · density functional calculations · silver

---

[1] Crystal structure: M. Black, R. H. B. Mais, P. G. Owston, *Acta. Crystallogr. Sect. B* **1969**, *25*, 1753.

[2] a) F. A. Cotton, P. A. Kibala, *Polyhedron* **1987**, *6*, 645; b) F. A. Cotton, E. V. Dikarev, M. A. Petrukhina, R. E. Taylor, *J. Am. Chem. Soc.* **2001**, *123*, 5831.

[3] a) M. J. S. Dewar, *Bull. Soc. Chim. Fr.* **1951**, *79*, 18; b) J. Chatt, L. A. Duncanson, *J. Chem. Soc.* **1953**, 2939.

[4] a) M. Sodupe, C. W. Bauschlicher, *J. Phys. Chem.* **1991**, *95*, 8640; b) J. Miralles-Sabater, M. Merchan, I. Nebot-Gil, P. M. Viruela-Martin, *J. Phys. Chem.* **1996**, *100*, 4853.

[5] a) G. Frenking, N. Froehlich, *Chem. Rev.* **2000**, *100*, 717; b) R. H. Hertwig, W. Koch, D. Schröder, H. Schwarz, J. Hrušák, P. Schwerdtfeger, *J. Phys. Chem.* **1996**, *100*, 12253.

[6] a) T. Ziegler, A. Rauk, *Inorg. Chem.* **1979**, *18*, 1558; b) D. V. Deubel, *J. Am. Chem. Soc.* **2002**, *124*, 12312; c) J. C. Ma, D. A. Dougherty, *Chem. Rev.* **1997**, *97*, 1303; d) G. W. Gokel, S. L. De Wall, E. S. Meadows, *Eur. J. Org. Chem.* **2000**, 2967.

[7] J. Kaneti, L. de Smet, R. Boom, H. Zuilhof, E. Sudhölter *J. Phys. Chem. A* **2002**, *106*, 11197.

[8] a) H. W. Quinn, J. S. McIntyre, *Can. J. Chem.* **1965**, *43*, 2896; b) D. B. Powell, J. G. V. Scott, N. Sheppard, *Spectrochim. Acta Part A* **1972**, *28*, 327; c) H. W. Quinn, D. N. Glew, *Can. J. Chem.* **1962**, *40*, 1103.

[9] a) B. C. Guo, A. W. Castleman, Jr., *Chem. Phys. Lett.* **1991**, *181*, 16; b) D. Schröder, R. Wesendrup, R. H. Hertwig, T. K. Dargel, H. Grauel, W. Koch, B. R. Bender, H. Schwarz, *Organometallics* **2000**, *19*, 2608.

[10] I. W. Bassi, G. Fagherazzi, *J. Organomet. Chem.* **1968**, *13*, 535.

[11] J. McMurry, G. J. Haley, J. R. Matz, J. C. Clardy, J. Mitchell, *J. Am. Chem. Soc.* **1986**, *108*, 515.

[12] a) I. Krossing, *Chem. Eur. J.* **2001**, *7*, 490; b) I. Krossing, H. Brands, R. Feuerhake, S. König, *J. Fluorine Chem.* **2001**, *112*, 83; c) M. Gonsior, I. Krossing, N. Mitzel, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1821.

[13] S. M. Ivanova, B. G. Nolan, Y. Kobayashi, S. M. Miller, O. P. Anderson, S. H. Strauss, *Chem. Eur. J.* **2001**, *7*, 503.

[14] T. S. Cameron, A. Decken, I. Dionne, M. Fang, I. Krossing, J. Passmore, *Chem. Eur. J.* **2002**, *8*, 3386.

[15] a) I. Krossing, *J. Am. Chem. Soc.* **2001**, *123*, 4603; b) I. Krossing, L. van Wüllen, *Chem. Eur. J.* **2002**, *8*, 700.

[16] A. Adolf, M. Gonsior, I. Krossing, *J. Am. Chem. Soc.* **2002**, *124*, 7111

[17] A. Bihlmeier, I. Krossing, I. Raabe, N. Trapp, *Angew. Chem.* **2003**, *115*, 1569; *Angew. Chem. Int. Ed.* **2003**, *42*, 1531.

[18] a) I. Krossing, *J. Chem. Soc. Dalton Trans.* **2002**, 500; b) I. Krossing, I. Raabe, *Angew. Chem.* **2001**, *113*, 4544; *Angew. Chem. Int. Ed.* **2001**, *40*, 4406; c) M. Gonsior, I. Krossing, L. Müller, I. Raabe, M. Jansen, L. van Wüllen, *Chem. Eur. J.* **2002**, *8*, 4475; d) I. Krossing, I. Raabe, *Angew. Chem.* **2004**, *116*; *Angew. Chem. Int. Ed.* **2004**, *43*, in press.

[19] For recent reviews see: a) C. Reed, *Acc. Chem. Res.* **1998**, *31*, 133; b) S. H. Strauss, *Chem. Rev.* **1993**, *93*, 927; c) E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391.

[20] a) K. Fischer, K. Jonas, G. Wilke, *Angew. Chem.* **1973**, *85*, 620; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 565; b) J. Mink, M. Gal, P. L. Goggin, J. L. Spencer, *J. Mol. Struct.* **1986**, *142*, 467.

[21] a) M. Green, J. A. K. Howard, J. L. Spencer, F. G. A. Stone, *J. Chem. Soc. Chem. Commun.* **1975**, 449; b) M. Green, J. A. K. Howard, J. L. Spencer, F. G. A. Stone, *J. Chem. Soc. Dalton Trans.* **1977**, 271; c) P. Csaszar, P. L. Goggin, J. Mink, J. L. Spencer, *J. Organomet. Chem.* **1989**, *379*, 337; d) J. A. K. Howard, J. L. Spencer, S. A. Mason, *Proc. R. Soc. London Ser. A* **1983**, *386*, 145.

[22] Synthesis of $[Ag(C_2H_4)_3]^+[Al(OC(CF_3)_3)_4]^-$: $Ag^+[Al(OC(CF_3)_3)_4]^-$ (1.045 g, 0.901 mmol) was weighed into a two-bulb frit plate vessel with a glass stem that was closed with two J. Young valves. The salt was dissolved in CH_2Cl_2 (≈40 mL), cooled to 77 K, and the flask was evacuated. Next, ethene (76 mg, 2.70 mmol) was condensed onto the mixture. The vessel was allowed to reach ambient temperature where a small quantity of a gray precipitate was observed in the clear solution, which was then filtered. The filtrate was very slowly cooled to +7 °C and within about 12 h a large quantity of colorless blocks of $[Ag(C_2H_4)_3]^+[Al(OC(CF_3)_3)_4]^-$ had formed (0.892 g, 80 %). ^1H NMR (250 MHz, CD_2Cl_2, 300 K): $\delta = 5.77$ ppm (s); $^{13}C[^1H]$ NMR (63 MHz, CD_2Cl_2, 300 K): $\delta = 116.4$ (s, C_2H_4); 121.5 ppm (q, CF_3, $^1J_{CF} = 292.5$ Hz); ^{19}F NMR (235 MHz, CD_2Cl_2, 300 K): $\delta = -75.38$ (s); ^{27}Al NMR (78 MHz, CD_2Cl_2, 300 K): $\delta = 36.0$ ppm (s). IR (CsI plates, Nujol): $\tilde{\nu} = 206$ (mw), 285 (mw), 315 (m), 330 (w), 368 (mw), 379 (mw), 444 (ms), 536 (ms), 560 (m), 571 (w), 727 (s), 756 (mw), 833 (ms), 966 (vs), 999 (m), 1065 (mw), 1224 (vs), 1243 (vs), 1274 (vs), 1299 (s), 1354 cm^{-1} (ms); IR (CsI plates, perfluoropolyalkylether): $\tilde{\nu} =$ 1581 (vw), 1612 (vw), 3007(vw), 3114 cm^{-1} (vw).

[23] All quantum chemical calculations were carried out with the TUBOMOLE program of R. Ahlrichs.[24] The geometries of all species $[M(C_2H_4)_3]$ ($M = Pd$, Ag^+, Na^+) were fully optimized in D_{3h} symmetry in the spoke-wheel as well as the trigonal-prismatic barrel structure by DFT calculations using the BP86/SV(P) or BP86/TZVPP basis sets,[25–27] as well as the (RI-)MP2/TZVPP levels.[36] The nature of the obtained minima was verified by the calculation of vibrational frequencies[33] at the BP86/SV(P) level and, unless otherwise stated, all species are true minima. The 28 core electrons of Ag were replaced by a scalar relativistic effective core potential,[28] however, the entire $4d^{10}$ shell was explicitly treated in the MO calculations.

[24] a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165; b) M. von Arnim, R. Ahlrichs, *J. Chem. Phys.* **1999**, *111*, 9183.

[25] K. Eichkorn, O. Treutler, H. Oehm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652.

[26] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; b) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.

[27] K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119.

[28] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123.

[29] Crystal-structure determination of $[Ag(C_2H_4)_3]^+[Al(OC(CF_3)_3)_4]^-$: IPDS (Stoe), graphite-monochromated $Mo_{K\alpha}$ radiation, $T = 150(2)$ K, 5000 reflections, Lorentz, polarization, and numerical absorption corrections, $\mu = 0.807$ cm^{-1}, direct methods with SHELXS-97, refinement against F^2 with SHELXL-97; $P2_1/c$, $Z = 4$, $a = 11.2881(3)$, $b = 14.984(3)$, $c = 19.092(4)$ Å, $\beta = 103.47(3)°$; $V = 3469.4(12)$ Å^3, $\rho_{calcd} = 2.148$ $g\,cm^{-1}$, $2\theta_{max} = 50°$, reflections: 10365 collected, 6102 unique ($R_{int} = 0.0469$), 5586 observed (2σ), 654 parameter, $R_1 = 0.0548$, wR_2 (all data) = 0.1470, GOF = 1.019. CCDC-211689 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[30] Librational correction done with XP (SHELXTL suite of programs, LIBR keyword) based on the method of V. Schomaker, K. N. Trueblood, *Acta Crystallogr. Sect. B* **1968**, *24*, 63.

[31] G. H. van Nes, A. Vos, *Acta. Crystalogr. B* **1979**, *35*, 2593.

[32] The contacts s (in valency units v.u.) have been defined as $s = (R/R_0)^{-N}$, where R is the observed distance, R_0 is the covalent bond distance (bond order = 1) of the bond in question and N is an empirically derived constant. For $Ag^I\cdots F$ contacts $N = -6.5$ and $R_0 = 1.95$ Å. see: I. D. Brown in *Structure and Bonding in Crystals*, *Vol. 2* (Eds.: M. O'Keefe, A. Navrotsky), Academic Press, London, **1981**, p. 1.

[33] P. Deglmann, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2002**, *362*, 511.

[34] Weighted average: the e′ mode is degenerate and counts double, that is, 1591 $cm^{-1} = (2 \times 1581 + 1610)/3$.

[35] Full details and assignments of the vibrational spectrum as well as a full analysis of the bonding in $[Ag(\eta^2\text{-}C_2H_4)_3]^+$ and related species will appear in an upcoming full paper; A. Reisinger, I. Krossing, unpublished results.

[36] a) F. Weigend, M. Häser, *Theor. Chem. Acc.* **1997**, *97*, 331; b) F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *294*, 143.

[37] An analysis of the related $Ag-(\eta^2\text{-}C{=}C)$ bonding in Ag^+[2,2,2]cyclophane prismands is found in: P. Saarenketo, R. Suontamo, T. Jödicke, K. Rissanen, *Organometallics* **2000**, *19*, 2346.

[38] A. Reisinger, Diplomarbeit, Universität Karlsruhe **2003**.