Weakly Coordinating Anions

DOI: 10.1002/ange.201408019

$Ag[Fe(CO)_5]_2^+$: A Bare Silver Complex with $Fe(CO)_5$ as a Ligand**

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Abstract: *Attempts to prepare $Fe(CO)_5^+$ from $Ag[Al(OR^F)_4]$ ($R^F = C(CF_3)_3$) and $Fe(CO)_5$ in CH_2Cl_2 yielded the first complex of a neutral metal carbonyl bound to a simple metal cation. The $Ag[Fe(CO)_5]_2^+$ cation consists of two $Fe(CO)_5$ molecules coordinating Ag^+ in an almost linear fashion. The ν(CO) modes are blue-shifted compared to $Fe(CO)_5$, with one band above 2143 cm^{-1} indicating that back-bonding is heavily decreased in the $Ag[Fe(CO)_5]_2^+$ cation.*

Since their unexpected discovery in 1890 by Mond, metal carbonyls have played an important role for chemistry and chemical engineering development, from applications in metallurgy (for example, $Ni(CO)_4$), as petroleum additives, and as precursors of finely dispersed metal or oxide particles (including nanoparticles).[1,2] Metal carbonyls can be easily reduced, yielding anionic carbonyl metalates such as $[Fe(CO)_4]^{2-}$ or $[Co(CO)_4]^-$.[3,4] Oxidation gives the much rarer homoleptic metal carbonyl cations, including $[Ir(CO)_6]^{3+}$,[5] $[M(CO)_6]^{2+}$ (M = Fe, Ru, Os),[6,7] $[M(CO)_6]^+$ (M = Mn, Tc, Re),[8] $[Pd_2(CO)_6]^{2+}$,[9] $[M(CO)_4]^{2+}$ (M = Pd, Pt),[10,11] $[Rh(CO)_4]^+$,[12] $[Co(CO)_5]^+$,[13] $[Au(CO)_2]^+$,[14] $[Hg_y(CO)_2]^{2+}$ ($y = 1,2$),[15] and also unstable $[Ag(CO)_x]^+$ ($x = 1,2$) or $[Cu(CO)_x]^+$ ($x = 1$–4).[16–18] The interest in those arises from their relative scarceness, interesting electronic structure, and their potent catalytic activity.[12,19–22] Owing to their reactivity, it is often required to use inert anions for their stabilization, that is, advanced weakly coordinating anions (WCA).[13,17,18] Such WCAs enabled the isolation of compounds either previously only known from the gas phase or matrix isolation studies[18,23,24] (thus, the term "pseudo-gas phase conditions" was coined), or not known at all.[25–28] A common reagent in WCA chemistry are Ag^+ salts that for example oxidize metallic gallium or nickel to form Ga^I or Ni^I complexes.[29,30] As the first ionization potential of Ag (7.58 eV)[31] is comparable to that of $Fe(CO)_5$ (7.96 eV),[32] and the evaporation enthalpy of $Fe(CO)_5$ (40 kJ mol^{-1})[33] is much smaller than the atomization energy of Ag (285 kJ mol^{-1}),[33] we tested whether $Ag[Al(OR^F)_4]$ might oxidize $Fe(CO)_5$.

However, upon addition of an excess of the pentacarbonyl to a CH_2Cl_2 solution of $Ag[Al(OR^F)_4]$ at room temperature, dark orange $Ag[Fe(CO)_5]_2^+[Al(OR^F)_4]^-$ (**1**; **1**$^+$ abbreviates the bare cation) precipitated immediately [Eq. (1)]:

$$2\,Fe(CO)_5 + Ag[Al(OR^F)_4] \rightarrow Ag[Fe(CO)_5]_2[Al(OR^F)_4]\downarrow \qquad (1)$$

After work-up, the salt is a pale yellow powder. The purity and phase homogeneity of the obtained samples were confirmed by IR/Raman measurements as well as phase analysis by powder X-ray diffraction measurements (see the Supporting Information). Compound **1** decomposes endothermally only above 150 °C (TGA/DSC; for details, see the Supporting Information) and shows no signs of decomposition after months of exposure to daylight.

The crystal structure[34] of **1** at 100 K contains one symmetry-independent $Ag[Fe(CO)_5]_2[Al(OR^F)_4]$ ion pair in the asymmetric unit. The Ag atom of **1**$^+$ is coordinated by two Fe atoms aligned almost linearly (174.31(2)°) and almost equally distant (Ag–Fe 2.5965(6) Å and 2.5998(6) Å; Figure 1).

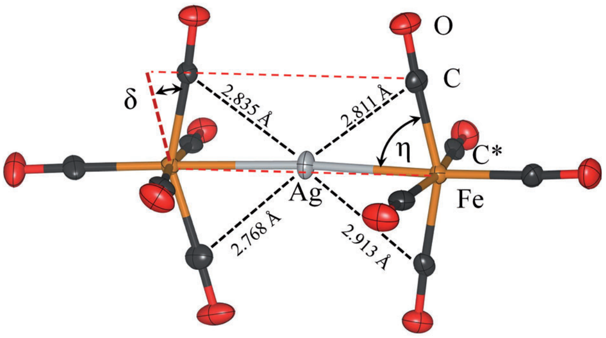

Figure 1. View of cation **1**$^+$ observed in the crystal structure of **1**; contacts with d_{AgC} below 2.92 Å are included. Definition of C^t, C*, the torsion angle δ and the η angle are shown; ellipsoids are set at 50% probability.

Especially d_{FeC} to the carbonyls in the Fe-Ag-Fe axis ("C^t": 1.842–1.855 Å, cf. d_{FeC}(avg.) 1.834 Å) is elongated as compared to solid $Fe(CO)_5$ (1.801–1.811 Å),[35] but shorter than in $[Fe(CO)_6]^{2+}$ (1.903–1.917 Å).[7] Analogously, d_{CO}(avg.) (1.128 Å) is similar to $Fe(CO)_5$,[35] but longer than in $[Fe(CO)_6]^{2+}$ (1.096–1.119 Å).[7] This points to an electron density at the central atom intermediate between neutral iron

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[**] The authors would like to acknowledge the Mobility Plus programme (project 895/MOB/2012/0) and ERC project UniChem for financial support that enabled the research. We would like to thank also Dr. Daniel Himmel and Dr. Daniel Kratzert for fruitful discussions concerning computational and single crystal data processing issues.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201408019.

carbonyl and $[Fe(CO)_6]^{2+}$. Four CO ligands perpendicular to the Fe-Ag-Fe axis are significantly bent towards the Ag atom (C-Fe-Ag angle $\eta = 75$–$80.2°$), resulting in long Ag–C contacts at 2.832 Å (avg.) (cf. 2.156 Å in $[Ag(CO)_2]^+$).[17] The angles η to the remaining four CO ligands are between 83° and 88° and the Ag–C distances more than 3 Å (avg. 3.044 Å). The opposing carbonyls are almost perfectly eclipsed, with the C-Fe-Fe-C torsion angle δ being below 3°. DFT calculations reproduce the structure of $\mathbf{1}^+$ only in D_{2h} symmetry (but not D_{4h}!) with both BP86/def2-TZVPP and PBE/def2-TZVPP functionals and the use of the DFT-D3 dispersion correction.[36] Importantly also the four bent carbonyls with $d_{AgC} = 2.784$ Å (BP86, $\delta = 0°$) are reproduced (cf. $d_{AgC*} = 3.131$ Å), suggesting that the Ag–C interactions are an intrinsic property of $\mathbf{1}^+$, and not just a packing effect in the crystal. There are no significant cation–anion contacts ($d_{FO} > 2.8$ Å).

The thermodynamic stability of $\mathbf{1}^+$ with respect to $[Ag(CH_2Cl_2)_3]^+$ and $Fe(CO)_5$ is not high, being only 31 to 65 kJ mol^{-1} (BP86/def2-TZVPP/D3, corrected to 298 K):

$$[Ag(CH_2Cl_2)_3]^+ + 2\,Fe(CO)_5 \rightarrow [Ag[Fe(CO)_5]_2]^+ + 3\,CH_2Cl_2$$
$$\Delta_r H(g/CH_2Cl_2) = -30.9/-40.7\ \text{kJ mol}^{-1}$$
$$\Delta_r G\ (g/CH_2Cl_2) = -54.8/-64.7\ \text{kJ mol}^{-1}$$

Vibrational spectra show significantly blue-shifted CO stretches as compared to $Fe(CO)_5$. The highest ν_{CO} mode (2150 cm^{-1}) lies above free CO (2143 cm^{-1}), which qualifies **1** as a "non-classical" or "sigma-only" metal carbonyl complex. As expected, it is lower than the value for $[Fe(CO)_6]^{2+}$, for which all ν_{CO} bands lie above 2200 cm^{-1}.[6,7] The positions and intensities obtained from DFT BP86/def2-TZVPP/D3 calculations[37] (scaling by 1.0065) are in a very good agreement with the observed values in both IR and Raman, lending credibility to the assignment of the visible bands (Table 1; Supporting Information).

Table 1: Observed and calculated ν_{CO} in the vibrational spectra of $\mathbf{1}^+$.[a]

IR (calc.)	IR (obs.)	Raman (obs.)	Raman (calc.)
2137 (38)	2137 (m, sh)	2150 (s)	2151 (12)
2093 (39)	2093 (sh)	2099 (vs)	2094 (38)
2081 (100)	2084 (vs)	2092 (sh)	2093 (3.2)
2076 (28)	2076 (sh)	2072 (vs)	2076 (1.4)
2066 (14)	2066 (sh)		2069 (26)
	2063 (sh)	2061 (sh)	2066 (8.7)
2053 (78)	2048 (sh)	2043 (vw)	2043 (0.1)
2043 (9.5)	2038 (s, br)		

[a] Relative intensities in % are given in parentheses. A full list of all modes together with their assignment is included in the Supporting Information. Band descriptions: vs very strong, s strong, m medium, w weak, vw very weak, sh shoulder, br broad.

The structure, bonding, and symmetry of $\mathbf{1}^+$ was investigated. Screening the potential energy of $\mathbf{1}^+$ as a function of the δ angle (see Figure in the Supporting Information), reveals that the energy difference between the highest and lowest conformation is below 0.6 kJ mol^{-1} (at 0 K), pointing at an almost barrier-free rotation of $Fe(CO)_5$ around the Ag–Fe bond. Therefore, the eclipsed conformation found in the crystal may be the result of packing effects. The Ag–$Fe(CO)_5$ interaction in $\mathbf{1}^+$ (D_{2h})[38] is a Ag-Fe-C multi-center bond with 3d(Fe)→5s(Ag) and 2p(C)→5s(Ag) contributions. There is also a share of 4d(Ag) character in the orbital (Figure 2a), similar to the situation in the $Ag(CO)_2^+$ cation.[17] The probable reason for breaking the expected fourfold symmetry in $\mathbf{1}^+$ is the LUMO+1 orbital of $[Ag–Fe(CO)_5]^+$ **2** (0.724 eV above LUMO), which has C_{2v} symmetry (Figure 2c; contrary to the C_{4v} symmetry of **2** and its LUMO in Figure 2b). Upon coordination of a Lewis base and filling the Ag(5s) orbital, it interacts with the 2p(C) orbitals. Different signs for the 2p(C) lobes result in a shortening of the Ag–C and an elongation of the Ag–C* bond lengths. To support this hypothesis, we have examined the interaction of **2** with NH_3 as a base. The approach of N along the Fe–Ag axis also caused a shortening of d_{AgC} to 2.768 Å and an elongation of d_{AgC*} to 3.097 Å (see the Supporting Information).

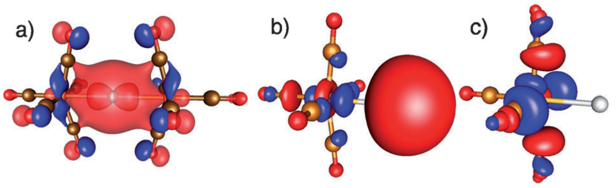

Figure 2. a) Multi-center Ag-Fe–C bonding MO (26 a_g) of $\mathbf{1}^+$ (D_{2h}); the inner orbital represents the negative lobe of 4d(Ag). b) LUMO of **2**. c) (LUMO+1) of **2** with 2-fold 2p(C) orbital symmetry. Isodensity surfaces cut-offs at 0.03 eÅ^{-3} (a), 0.04 eÅ^{-3} (b), and 0.05 eÅ^{-3} (c).

To conclude, we have shown that a novel complex of the silver cation with two $Fe(CO)_5$ molecules serving as ligands can be easily obtained in the reaction between $Fe(CO)_5$ and the silver salt of the weakly coordinating anion $[Al(OR^F)_4]^-$. There are weak bonds between the Ag ion and the carbonyl molecules in combination with a very low rotational barrier around the Ag–Fe bond. The complex exhibits an unusual structure with symmetry lower than the expected fourfold, and the reason appears to be the symmetry of the acceptor orbital in **2**. The Ag^+–$Fe(CO)_5$ complex is yet another example for the unusual chemistry that is achievable by advanced WCAs.[13–18,25–30] It will be interesting to see the effect of this unusual carbonyl in catalytic applications.[41]

Experimental Section

All operations on the substrates and products were carried out in a glass Schlenk line or in MBraun glovebox filled with Ar (O_2, H_2O < 1 ppm). All reactions were performed in double-Schlenk flasks as described elsewhere.[39] $Ag[Ag(OR^F)_4]$ was synthesized according to a previously reported procedure.[40] $Fe(CO)_5$ (BASF) was dried over molecular sieves and distilled prior to use. An excess of $Fe(CO)_5$ (2.4 g) was condensed above the frozen (LN_2 temperature) solution of the silver salt (950 mg) in CH_2Cl_2 (ca. 6 mL). The reaction mixture was vigorously stirred while the melting of the substrates proceeded. The reaction occurs immediately upon contact of the carbonyl and the

Ag salt solution, yielding a yellow solution and a dark precipitate. The product was purified by repeated extraction (7 times) with CH_2Cl_2 (ca. 4 mL) and subsequent drying of the solution under dynamic vacuum. The yield of the pure product recovered from the flask is 0.7 g (55%). Note: the CH_2Cl_2 solution of **1** shows signs of decomposition at RT after 24 h, so the above described procedure has to be performed on the same day as the synthesis. Crystals of **1** were grown from a concentrated CH_2Cl_2 solution by slow cooling (ca. 24 h) from room temperature down to −40 °C and additional two weeks at that temperature to improve the quality of the obtained crystals. Hardware and software details are presented in the Supporting Information.

Received: August 6, 2014
Revised: September 11, 2014

Keywords: carbonyl ligands · pentacarbonyliron · silver · weakly coordinating anions

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[34] Crystal structure determination of **1** at 100 K: $C_{26}AgAlF_{36}Fe_2O_{14}$, $M_r = 1466.81$, $a = 9.4410(4)$ Å, $b = 15.4283(7)$ Å, $c = 15.9943(7)$ Å, $\alpha = 97.318(2)°$, $\beta = 106.015(3)°$, $\gamma = 104.689(3)°$, $V = 2116.75(16)$ Å^3 $Z = 2$, $\rho_{calcd} = 2.301\ g\,cm^{-1}$; $\mu_{exp} = 1.377\ mm^{-1}$; $T = 100(2)$ K; Mo-Kα1 (0.71073 Å); $2\Theta_{min} = 4.938°$, $2\Theta_{max} = 57.398°$; measured reflections: 10116 (8255 with $I > 2\sigma(I)$), unit cell determination: 9936 reflections, $R_1 = 0.0522$, $wR_2 = 0.0928$ (for $I > 2s(I)$: $R_1 = 0.0381$, $wR_2 = 0.0879$); GooF = 1.046; residual electron density: min = −0.624, max = 0.946. CCDC 1014975 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[38] The situation is similar for staggered carbonyl ligands in D_2 symmetry, but is easier to depict and explain in D_{2h}.

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[41] The authors would like to add that there has been a manuscript published almost parallel to this work in which neutral $Fe(CO)_5$ acts as a ligand to the metal atom in $GaCl_3$, forming a neutral adduct: H. Braunschweig, R. D. Dewhurst, F. Hupp, C. Kaufmann, A. K. Phukan, C. Schneider, Q. Ye, *Chem. Sci.* **2014**, *5*, 4099 – 4104. In this respect, a Review towards metal-only Lewis pairs has to be acknowledged: J. Bauer, H. Braunschweig, R. D. Dewhurst, *Chem. Rev.* **2012**, *112*, 4329 – 4346.