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Molecular Structure of $[CpFe(CO)_2]_2AlAr$ (Ar = 2-[(Dimethylamino)methyl]phenyl): An Alanediyl Complex with Two Fe−Al Bonds[†]

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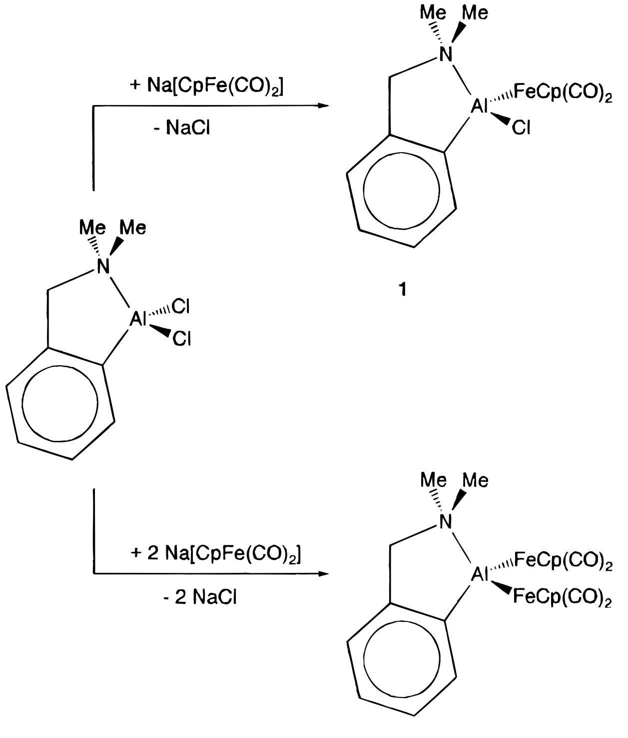
Introduction

Transition metal alanyl and alanediyl complexes are rare. There are only two examples, which have been characterized by single-crystal X-ray analyses: $[CpFe(AlR\textit{i}Bu)(CO)_2]$ [R = $Me_2N(CH_2)_3$][1] with a terminal alanyl group, which is intramolecularly stabilized by the 3-(dimethylamino)propyl substituent, and $[(CpNi)_2(C_5Me_5Al)_2]$[2] showing two bridging (η^5-C_5Me_5)Al ligands in a Ni_2Al_2 core.

Recently, we synthesized the intramolecular donor-stabilized dichloroalane $ArAlCl_2$ (Ar = 2-[(dimethylamino)methyl]phenyl) and examined some substitution reactions.[3] In this note, we wish to report the synthesis and spectroscopy of two alanes, having one and two $CpFe(CO)_2$ moieties, respectively.

Results and Discussion

The reaction of $ArAlCl_2$ with 1 or 2 equiv of $Na[CpFe(CO)_2]$ readily yields the corresponding complexes **1** and **2**.



1

2

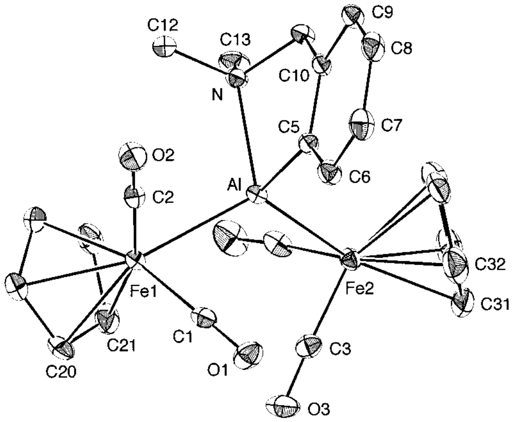


Figure 1. Moleculare structure of $ArAl[CpFe(CO)_2]_2$ (**2**) (thermal ellipsoids at 30% probability).

Table 1. Crystallographic Data for **2**

formula	$Fe_2AlO_4NC_{23}H_{22}$	space group (No.)	$P2_1/n$ (14)
f_w	515.11	Z	4
a, Å	11.259(7)	D_{calc}, g·cm^{-3}	1.565
b, Å	13.902(8)	μ, cm^{-1}	13.95
c, Å	14.049(4)	scan range, deg	3−26
β, deg	96.21(3)	scan mode	ω
V, Å^3	2186 (3)	R^a	0.032
T, K	203	R$_w$^{b}	0.039

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(F_o)$.

Table 2. Selected Bond Distances (pm) and Angles (deg) for **2**

Fe1−Al	246.8(1)	O1−C1	115.2(3)
Fe2−Al	249.6(1)	O2−C2	115.0(3)
Fe1−C1	173.8(3)	O3−C3	115.0(3)
Fe1−C2	174.0(3)	O4−C4	114.9(3)
Fe2−C3	174.0(3)	Al−N	213.2(2)
Fe2−C4	173.4(3)	Al−C5	199.3(3)
Fe1−Al−Fe2	119.89(3)	Al−Fe2−C3	86.67(9)
N−Al−C5	84.22(9)	Al−Fe2−C4	83.0(1)
N−Al−Fe1	111.67(6)	C3−Fe2−C4	90.9(1)
N−Al−Fe2	109.79(6)	Al−N−C11	103.4(1)
C5−Al−Fe1	113.01(7)	Al−N−C12	111.0(2)
C5−Al−Fe2	112.67(7)	Al−N−C13	118.0(2)
Al−Fe1−C1	78.18(9)	C12−N−C13	107.8(2)
Al−Fe1−C2	84.65(9)		

These compounds were isolated upon crystallization from hexane solutions in good yields (61 and 59% for **1** and **2**, respectively). The molecular structure of the disubstituted product **2** was determined by single-crystal X-ray analysis.

Compound **2** crystallizes in the space group $P2_1/n$ with no unusual intermolecular contacts (Figure 1, Table 1). The Al atom is distorted tetrahedrally surrounded by a set of two irons, a carbon, and a nitrogen atom. The deviations from a regular polyhedron may be illustrated by the six "tetrahedral angles" which vary between 84.2 and 119.9° (Table 2). Five of the six "tetrahedral angles" fall in the narrow range 109.8−119.9°, while the angle which is part of the five-membered heterocycle (N−Al−C5) is significantly smaller (84.2°). This value is the consequence of the steric requirements of the chelating Ar− ligand, and similar acute angles are found for the known alanes $ArAlBr_2$ (89.3°),[4] $ArAlCl_2{\cdot}H_2N\textit{i}Pr$ (82.0°), and Ar_2AlMe (79.6 and 78.9°),[3] respectively. The five-membered ring of **2** shows the expected envelope conformation, with the nitrogen atom displaced 61 pm outside the least-squares plane defined by Al−C5−C10−C11.[5]

[†] This paper is dedicated to Professor G. E. Herberich on the occasion of his 60th birthday.

(1) Fischer, R. A.; Priermeier, T. *Organometallics* **1994**, *13*, 4306.
(2) Dohmeier, C.; Krautscheid, H.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2482.
(3) Müller, J.; Englert, U. *Chem. Ber.* **1995**, *128*, 493.
(4) Isom, H. S.; Cowley, A. H.; Decken, A.; Sissingh, F.; Corbelin, S.; Lagow, R. J. *Organometallics* **1995**, *14*, 2400.

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Concerning a rotation around the two Al−Fe bonds, one can imagine several conformations. The one adopted by **2** in the solid state can be described by looking at the two Fe−Al bonds. In the Fe1−Al direction, the aromatic ring is staggered with the two carbonyl ligands of Fe1, whereas with the other iron−aluminum bond (Fe2−Al), the CpFe1(CO)$_2$ fragment is arranged in a staggered way with respect to the OC−Fe2−CO unit.

The Al−N distance of 213 pm found for the complex **2** is just outside the common range 194−210 pm for simple amine adducts.[6] The recently published compound ArAlBr$_2$ shows an Al−N distance of 200 pm.[4] To our knowledge, this dibromoalane is the only known alane containing the same chelating ligand as **2** and tetracoordinated aluminum where structural details are available. Concerning electronic effects of the ligands on the Al center, the complex [CpFe(AlR*i*Bu)(CO)$_2$] [R = Me$_2$N(CH$_2$)$_3$] is a much better basis for comparison, where 209 pm was measured for the Al−N bond.[1] Compound **2** exhibits two different Fe−Al distances of 246.8 and 249.6 pm. These values are comparable to those reported for [CpFe(AlPh$_3$)(CO)$_2$]$^{1-}$ (251.0 pm)[7] and [CpFe(AlR*i*Bu)(CO)$_2$] [R = Me$_2$N(CH$_2$)$_3$] (245.6 pm).[1]

The molecular structures of the organometallic complexes **1** and **2** in solution are derived from NMR and IR measurements. The NMR spectra of **1** are as expected for a C_1-symmetrical molecule; i.e., diastereotopic methylene protons (^{1}H NMR), diastereotopic *N*-methyl groups (^{1}H and ^{13}C NMR), and two resonances for the CO ligands at $\delta = 217.06$ and 217.34 in the ^{13}C NMR spectrum. In contrast, compound **2** gives only single resonances for the CH$_2$ and the NMe$_2$ group in the ^{1}H and ^{13}C NMR spectra. As with complex **1** the diastereotopic character of the CO ligands is revealed by two peaks in the ^{13}C NMR spectrum at $\delta = 219.18$ and 219.55. These data are only consistent with a C_s point-group symmetry of **2** with respect to the NMR time scale. The C_s symmetry can be rationalized by assuming two dynamic processes; i.e., a fast envelope inversion of the five-membered heterocycle and free rotations around the two Al−Fe bonds. Also, the detection of two different carbonyl ligands for complex **2** excludes a fast rotation for the Al−C bond. This is consistent with the picture of the “amine arm” bound to the aluminum center.

The ^{27}Al NMR shifts of **1** and **2** were detected at $\delta = 186$ and 232, respectively. Compounds with a similar substitution pattern like **1** are known to cover the range 180−215 ppm on the ^{27}Al NMR scale.[1] This is the low-field end of the common four-coordinated organoaluminum compounds. In comparison with the starting material ArAlCl$_2$ ($\delta = 127$),[3] the substitution of the first chloro ligand by a CpFe(CO)$_2$ moiety results in a deshielding of 59 ppm, while replacement of the second chlorine atom causes another change of 46 ppm.

Complex **1** shows two bands in the IR spectrum at 1968 and 1907 cm^{-1}. Substance **2** has four resonances, with two partly overlapped bands at higher energy (1965 and 1948 cm^{-1}) and another “doublet” at lower wavenumbers (1904 and 1890 cm^{-1}). These results are as expected for similar kinds of molecules with local C_s symmetries. The values are comparable to those of the known organoaluminum compounds with only one CpFe(CO)$_2$ substituent. From these published IR data the predominant σ-character of the aluminum−transition-metal bond has already been deduced in the literature.[1]

Experimental Section

All procedures were carried out under dry nitrogen atmosphere using conventional Schlenk techniques. Solvents were dried by standard procedures, distilled, and stored under nitrogen and molecular sieves (4 Å). ArAlCl$_2$[3] and Na[CpFe(CO)$_2$][8] were prepared according to the literature. NMR: Varian Unity 500 in C$_6$D$_6$ at 499.843 (^{1}H, internal standard: TMS), 130.195 (^{27}Al, external standard: [Al(acac)$_3$] in C$_6$D$_6$), 125.639 MHz (^{13}C{^{1}H}, APT, internal standard: TMS). IR: Perkin-Elmer FTIR 1720x in toluene. Elemental analyses (C, H, N): Carlo-Erba elemental analyzer, Model 1106. As a result of the electric quadrupole moment of the ^{27}Al nucleus, the ^{13}C NMR signals of the carbon atoms bound to aluminum could not be detected. Due to the reaction of **1** and **2** with traces of water the ν_{CO} bands for CpFe(CO)$_2$H (2015 and 1956 cm^{-1})[9] were found in the IR spectra.

Preparation of ArAl[CpFe(CO)$_2$]Cl (1). ArAlCl$_2$ (2.63 g, 11.4 mmol) was added to a suspension of Na[CpFe(CO)$_2$] (2.28 g, 11.4 mmol) in benzene (40 mL) at ambient temperature. The reaction mixture was stirred for 4 h and evaporated to dryness, and hexane (50 mL) was added to the solid residue. The solution was filtered, and crystallization at −30 °C gave pale orange **1** (2.60 g, 61%). Mp: 118 °C. ^{1}H NMR: $\delta = 2.02$ (s, 3 H, NCH$_3$), 2.34 (s, 3 H, NCH$_3$), 2.99 (d, $^2J_{HH} = 14.0$ Hz, 1 H, CH$_2$), 3.81 (d, $^2J_{HH} = 14.0$ Hz, 1 H, CH$_2$), 4.44 (s, 5 H, Cp), 6.85 (m, 1 H, 3-H), 7.24 (m, 2 H, 4,5-H), 7.73 (m, 1 H, 6-H). ^{13}C NMR: $\delta = 45.43$ (NCH$_3$), 46.64 (NCH$_3$), 67.30 (CH$_2$), 81.89 (Cp), 124.40, 127.55, 128.34, 136.06 (4 CH), 142.07 (C2), 217.06, 217.34 (2 CO). ^{27}Al NMR: $\delta = 186$ ($h_{1/2} = 2750$ Hz). IR (ν_{CO} cm^{-1}): 1968 (vs), 1907 (vs). Anal. Calcd for C$_{16}$H$_{17}$AlClFeNO$_2$: C, 51.44; H, 4.59; N, 3.75. Found: C, 51.49; H, 4.62; N, 3.73.

Preparation of ArAl[CpFe(CO)$_2$]$_2$ (2). ArAlCl$_2$ (1.37 g, 5.9 mmol) was added to a suspension of Na[CpFe(CO)$_2$] (2.37 g, 11.8 mmol) in benzene (50 mL) at ambient temperature. The reaction mixture was stirred for 1 d and evaporated to dryness, and hexane (50 mL) was added to the solid residue. The solution was filtered, and crystallization at −30 °C gave dark orange **2** (1.80 g, 59%). Mp: >113 °C dec. ^{1}H NMR: $\delta = 2.22$ (s, 6 H, NCH$_3$), 3.72 (s, 2 H, CH$_2$), 4.40 (s, 10 H, Cp), 6.97 (m, 1 H, 3-H), 7.22 (m, 2 H, 4,5-H), 7.93 (m, 1 H, 6-H). ^{13}C NMR: $\delta = 48.55$ (NCH$_3$), 68.58 (CH$_2$), 82.66 (Cp), 124.16, 127.06, 127.35, 135.01 (4 CH), 140.21 (C2), 219.18, 219.55 (2 CO). ^{27}Al NMR: $\delta = 232$ ($h_{1/2} = 3800$ Hz). IR (ν_{CO} cm^{-1}): 1965 (vs), 1948 (vs), 1904 (vs), 1890 (vs). Anal. Calcd for C$_{23}$H$_{22}$AlFe$_2$NO$_4$: C, 53.63; H, 4.31; N, 2.72. Found: C, 53.90; H, 4.38; N, 2.64.

Crystal Structure Determination of 2. A crystal of approx. dimensions 0.60 × 0.40 × 0.20 mm was studied on an ENRAF-NONIUS CAD4 diffractometer with graphite-monochromized Mo Kα radiation ($\lambda = 0.710\,73$ Å). Crystal data and parameters of data collection and structure refinement are compiled in Table 1. The Fe atoms were located by direct methods using SHELX86[10] and the remaining atom positions resulted from subsequent cycles of refinement and difference Fourier syntheses.[11] An empirical absorption correction based on ψ-scans[12] was applied (maximum/minimum transmission 99.93/88.52%). In the final least-squares full-matrix refinement, on the basis of 3546 observed independent reflections for 280 variables, all non-hydrogen atoms refined anisotropically and all hydrogen atoms were treated as riding atoms. A final difference fourier synthesis showed a maximal residual electron density of 0.34 e Å^{-3}.

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Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, bond distances and angles, and data collection and refinement parameters and text giving experimental details of the structure determination for **2** (5 pages). Ordering information is given on any current masthead page.

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[5] Orthogonal distances from from the least-squares plane (pm): C11, 1.9(3); C10, −3.5(2); C5, 3.0(2); Al, −1.4(1).

[6] Haarland, A. In *Coordination Chemistry of Aluminum;* Robinson, G. H., Ed.; VCH: Weinheim, Germany, 1993; Chapter 1.

[7] Burlitch, J. M.; Leonowicz, M. E.; Petersen, R. B.; Hughes, R. E. *Inorg. Chem.* **1979**, *18*, 1097.

[8] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

[9] Bullock, R. M.; Samsel, E. G. *J. Am. Chem. Soc.* **1990**, *112*, 6886.

[10] Sheldrick, G. M. SHELXS-86, Program for Crystal Structure Solution. University of Göttingen, Germany, 1986.

[11] MolEN, An Interactive Structure Solution Procedure. Enraf-Nonius, Delft University: The Netherlands, 1990.

[12] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351.