Synthesis and X-ray Crystal Structure of $(tmp)_2Al{-}Fe(cp)(CO)_2$: An Alanyl-Containing Iron Complex with a Tricoordinated Aluminum Atom

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Synthesis of the tricoordinated alanyl-containing iron complex $(tmp)_2Al{-}Fe(cp)(CO)_2$ (**1**) (tmp = 2,2,6,6-tetramethylpiperidino) has been achieved in a straightforward salt elimination reaction of $(tmp)_2AlBr$ with $Na[(cp)Fe(CO)_2]$. **1** crystallizes in the triclinic space group $P\bar{1}$ ($a = 8.347(4)$ Å, $b = 10.044(5)$ Å, $c = 15.087(8)$ Å, $\alpha = 94.01(1)°$, $\beta = 91.18(1)°$, $\gamma = 102.50(1)°$) and is an unassociated monomer with an Al−Fe bond length of 2.450(1) Å.

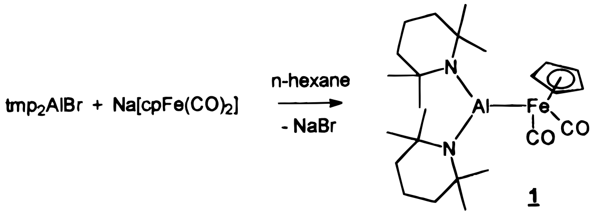
Introduction

Transition metal aluminum σ-bonds are scarcely described in the literature. Only three of them (e.g. $[(R)(^{i}Bu)Al{-}Fe(cp)(CO)_2]$ ($R = Me_2N(CH_2)_3$),[1] $[((cp)Ni)_2(AlC_5Me_5)_2]$,[2] and $ArAl{-}[Fe(cp)(CO)_2]_2$ (Ar = 2-[(dimethylamino)methyl]phenyl)[3]) have been characterized by X-ray single-crystal structure determination. The first and the last compound possess an intramolecular donor-stabilized tetracoordinated aluminum center, whereas the second compound contains two pentahapto-coordinating cp* moieties at the aluminum nuclei. So, in contrast to the higher homologue gallium (e.g. in $^{t}Bu_2Ga{-}Fe(cp)(CO)_2$[4] and others), no tricoordinated alanyl group bonded to a transition metal center has been prepared to the best of our knowledge.

Recently, we synthesized the series of monomeric, tricoordinated bis(2,2,6,6-tetramethylpiperidino)aluminum halides (Cl, Br, I)[5] and indicated their usefulness in the preparation of new aluminum compounds with coordination number 3. In this note we wish to report on the synthesis, characterization and X-ray crystal structure analysis of the unassociated alanyl-containing iron compound $(tmp)_2Al{-}Fe(cp)(CO)_2$ (**1**).

Synthesis and Spectroscopic Characterization

Nucleophilic substitution reaction of $Na[(cp)Fe(CO)_2]$ with $(tmp)_2AlBr$ in *n*-hexane (1:1 ratio) yielded the salt elimination product $(tmp)_2Al{-}Fe(cp)(CO)_2$ (**1**), as described in eq 1.



(1)

1

^{27}Al-NMR spectra for this compound revealed a chemical shift of 212 ppm. This chemical shift lies in the same range as these reported by Fischer et al. for Al−Fe compounds with tetracoordinated Al atoms.[1] In comparison to the starting material $(tmp)_2AlBr$ ($\delta(^{27}Al) = 130$ ppm, $h_{1/2} = 9.100$ Hz) the substitution of the bromine atom by the $(cp)Fe(CO)_2$ entity leads to a deshielding of 82 ppm. The monomeric nature of **1** in solution can in particular be readily deduced from its broad ^{27}Al-NMR signal (half-width 9.000 Hz). These half-widths have also been observed for the tricoordinated bis(tmp)aluminum halides[5] (9.100−13.700 Hz), and as monomeric **1** exhibits the same local symmetry as the compounds $(tmp)_2AlX$ (X = Cl, Br, I), we take this as evidence of its monomeric state in solution. This conclusion is further supported by the proton NMR spectrum: A single set of resonances for the cp ring and the tmp group has been observed. Oligomeric structures are likely to lead to a more complicated NMR spectrum. In the ^{13}C-NMR spectrum, the signal of the tmp-methyl groups is split into two signals of equal intensities. Therefore, due to the steric demand of the tmp ligand, free rotation about the Al−N bond is hindered.

Alanyl complex **1** shows two strong bands in the solution IR spectrum (*n*-hexane: 1982 and 1927 cm^{-1}). These values are comparable to those reported for the known organoaluminum compounds bonded to a $(cp)Fe(CO)_2$ fragment.[1,3] Moreover, the tricoordinated gallium compound $^{t}Bu_2Ga{-}Fe(cp)(CO)_2$ shows absorptions at 1980 and 1928 cm^{-1}.[4] These are almost identical to **1** and thus prove the assumption of the unassociated nature of $(tmp)_2Al{-}Fe(cp)(CO)_2$.

Attempts to volatalize **1** as such in the mass spectrometer failed due to decomposition.

According to the fragmentation pattern delineated in Figure 1, the compound **1** decomposes into $[(cp)Fe(CO)_2]_2$ (**2**) and $(tmp)_4Al_2$ (**3**). While **2**, with the lower formula weight, volatizes at 55 °C and shows stepwise loss of CO groups followed by loss of one iron atom to result in the $(cp)_2Fe^+$ cation as base peak, $(tmp)_4Al_2$ (**3**) volatizes at 110 °C (high vacuum) and is ionized with fragmentation yielding the $(tmp)_2Al^+$ fragment, which is the only major signal observed at an energy of 70 eV.[6]

Crystal Structure

The X-ray crystal structure determination was performed not only to characterize the new compound but also to ascertain its nature in the solid state and to obtain bonding parameters on the still rare class of transition metal alanyls. **1** crystallizes in

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(6) Unpublished results. The synthesis and characterization of $(tmp)_4Al_2$ was achieved, and it showed a similar fragmentation pattern in the 70 eV mass spectrum.

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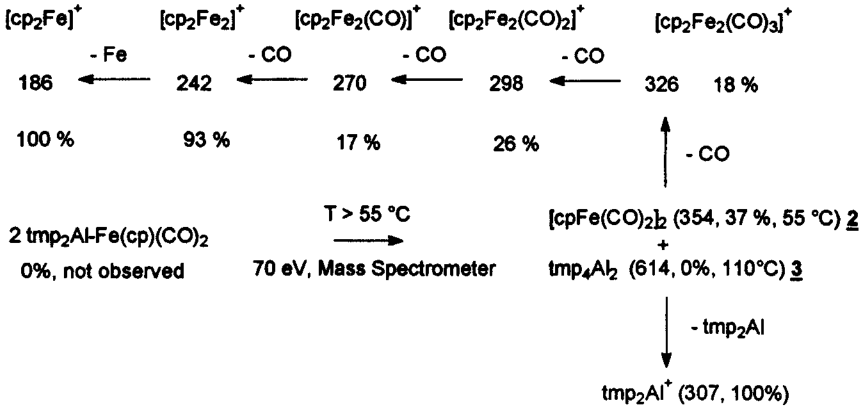

Figure 1. Thermal decomposition and succeeding fragmentation of **1** observed in the mass spectrometer (70 eV).

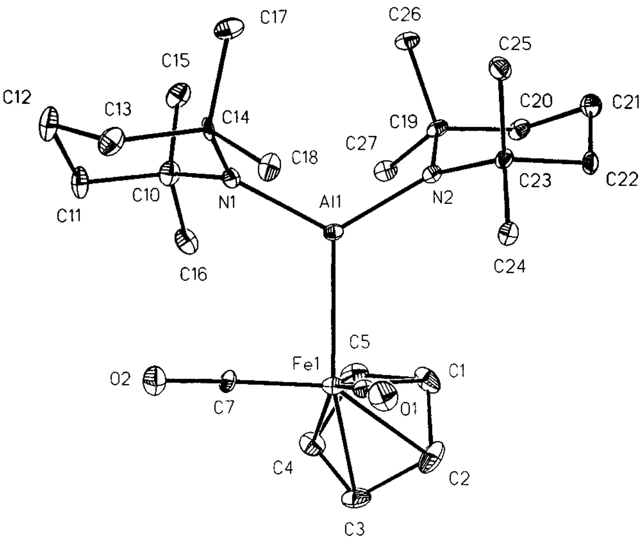

Figure 2. Molecular structure of **1** in the solid state. Thermal ellipsoids are shown at a 25% probability level.

Table 1. Crystallographic Data for **1**

chem formula	$C_{25}H_{41}AlFeN_2O_2$	$F(000)$	520
fw	484.43	index range	$-10 \le h \le 10$, $-12 \le k \le 12$, $-16 \le l \le 19$
cryst size (mm)	0.1 × 0.2 × 0.2		
cryst system	triclinic	2θ (deg)	54.86
space group	$P\bar{1}$	temp (K)	173
a (Å)	8.347(4)	reflcns collcd	4819
b (Å)	10.044(5)	unique reflcns	3387
c (Å)	15.087(8)	reflcns obsd (4σ)	2683
α (deg)	94.015(12)	R(int)	0.0450
β (deg)	91.184(8)	no. of variables	288
γ (deg)	102.496(13)	GOOF	1.179
V (Å^3)	1231.0(10)	final R (4σ)^a	0.0399
Z	2	final wR2	0.1281
ρ(calc) (Mg/m^3)	1.307	larg resid peak (e/Å^3)	0.355
μ (mm^{-1})	0.672		

[a] Weighting scheme: $w^{-1} = \sigma^2(F_o^2) + (0.0689P)^2 + 2.1826P$; $P = (F_o^2 + 2F_c^2)/3$.

the triclinic space group $P\bar{1}$. Its molecular structure is depicted in Figure 2, which shows **1** to be a monomer.

The aluminum atom resides in a planar environment (sum of bond angles 360.0°), coordinated by two tmp ligands in the half-chair conformation containing planar nitrogen atoms (sum of bond angles 359.3 and 359.9°, respectively) and the iron atom. As indicated by the N−Al−N (121.9(1)°) and the N−Al−Fe bond angles (117.5(1) and 120.6(1)°), the trigonal planar environment of the aluminum atom is almost undistored. Complex **1** exhibits two different bond lengths Al−N which are quite long taking the tricoordinated state of both Al and N into account.

Table 2. Selected Bond Distances and Angles for $(tmp)_2Al-Fe(cp)(CO)_2$ (**1**)

	Bond Lengths (Å)		
Fe1−Al1	2.450(1)	Al1−N1	1.847(4)
Al1−N2	1.862(4)	Fe1−C1	2.089(6)
Fe1−C2	2.113(6)	Fe1−C3	2.133(5)
Fe1−C4	2.112(4)	Fe1−C5	2.101(5)
Fe1−C6	1.745(4)	Fe1−C7	1.725(7)
C6−O1	1.155(5)	C7−O2	1.169(6)
	Bond Angles (deg)		
N1−Al1−N2	121.85(15)	N1−Al1−Fe1	117.5(1)
N2−Al1−Fe1	120.6(1)	Al1−Fe1−C6	88.1(1)
Al1−Fe1−C7	86.9(1)	C6−Fe1−C7	88.9(2)
	Torsion Angles (deg)		
cp−Fe1−Al1−N1	53.2	cp−Fe1−Al1−N2	54.4

The main feature of interest of compound **1** is of course the Al−Fe bond. Due to the possible π-interaction between Al and Fe one could expect a shorter distance as compared with the expected value of 2.51 Å for an Al−Fe single bond (covalent radii: Al, 1.25 Å;[7] Fe, 1.26 Å [8]). The observed bond length of 2.450(1) Å is shorter than the predicted value, but comparison with the four other published Al−Fe bond distances (see Table 3) gives massive evidence against any Al−Fe π-bonding but for the presence of an Al−Fe σ-bond.

However, the Al−Fe distance observed in **1** is definitely shorter than any of the other known Al−Fe bonds (see Table 3). Moreover, all these mentioned compounds contain a tetracoordinated aluminum atom, and their Al−Fe bonds are expected to be longer. Actually it is surprising that the Al−Fe bond lengths differences are small, particularly for the recently reported compound **4**. The $[(cp)(CO)_2Fe]^+$ fragment has been a subject to theoretical studies concerning its capability to form π-bonds with carbenes[9] (which are related to the $(tmp)_2Al$ fragment). The most efficient π-overlap involves the a″ orbital at the iron atom, which is oriented parallel to the cp-ring plane. For a 0 (or 180) deg torsion angle between cp(centroid)−Fe−Al−N this overlap is achieved best. As in the alanyl-containing iron complex **1**, torsion angles of 53.2 and 54.4° are observed and only very weak π-bonding can be present (as also proved by the above mentioned explanation). Furthermore the IR bands of **1** exhibit lower frequencies than the related $(cp)Fe(CO)_2$ alkyl

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Table 3. Comparison of All Reported Al−Fe Bond Lengths

	compound			
	(tmp)$_2$Al−Fe(cp)(CO)$_2$] (**1**)	[(cp)Fe(AlR^{i}Bu)(CO)$_2$] (**4**) (R = Me$_2$N(CH$_2$)$_3$)	ArAl[Fe(cp)(CO)$_2$]$_2$ (**5**) (Ar = 2-[(Me$_2$NCH$_2$)C$_6$H$_4$)	[(cp)Fe(AlPh$_3$)(CO)$_2$]$^-$ (**6**)
d(Al−Fe) (Å)	2.450(1)	2.456(1)	2.468(1); 2.496(1)	2.510(1)
Al coord no.	3	4	4	4

(about 2010 and 1960 cm^{-1}) or silyl compounds (about 2000 and 1945 cm^{-1}).[10,11] However, the aluminum atom is more electropositive than C or Si, and therefore the iron atom in **1** may have more electron density than the one in these compounds. This may result in an increased back-donation into the π*-CO orbital and thus lower the IR frequencies of **1**. The absorption at lower wavenumbers also suggests a quite weak π-interaction, if at all, as the electron density seems not to be involved into π-bonding (if this is present, one would expect higher frequencies like in the related boryliron complexes R$_2$B−Fe(cp)(CO)$_2$ (R$_2$ = Ph$_2$ or catecholyl),[12] where B−Fe π-interaction is believed to occur).

If we turn to the Al−N bond, only very few compounds, tricoordinated at Al and N, exhibit such long distances (e.g. ^{t}Bu$_2$AlN(1-Ad)SiPh$_3$ (Ad = adamantyl) with 1.849(4) Å [13]). In comparison to the (tmp)$_2$Al halides these are elongated from 1.782(6) and 1.812(6) Å ((tmp)$_2$AlBr[5]) to 1.847(4) and 1.862(4) Å. This is accompanied by a decreased bond angle N−Al−N (121.85(15)°), which are about 130° for the halides. Compared to these, as explained in ref 5, the charge density at the aluminum center is decreased and thus the long Al−N bonds result.

Conclusion

The highly air- and moisture-sensitive alanyl-containing iron complex **1** was prepared by a salt elimination reaction. The steric requirement of the tmp ligands prevents the system from oligomerization and, moreover, is sterically shielding the Al−Fe single bond. **1** is a rare example of a complex with the iron atom bonded to a tricoordinated Al atom and demonstrates the utility of the (tmp)$_2$Al group to stabilize this complex. Since many alane derivatives of type (tmp)$_2$AlY (Y = Al(NR$_2$)$_2$, alkyl, aryl, SiR$_3$, NR$_2$, PR$_2$, AsR$_2$, OR, BH$_4$) are accessible,[14] it is most likely that compound **1** is one, though yet the finest representative of transition metal alanyl complexes. Extension of this principle is under investigation, as well as the chemistry of main group metal and transition metal alanyl complexes.

Experimental Section

All manipulations were performed using Schlenk techniques under an argon atmosphere. All solvents were rigorously dried prior to use and stored under argon. (tmp)$_2$AlBr and Na[(cp)Fe(CO)$_2$] were prepared according to the reported methods.[5,14] NMR: Bruker ACP 200, Jeol GSX400, and Jeol GSX270. IR: Nicolet Model 6000 FT-IR spectrometer (NaCl cuvette, *n*-hexane solution). MS: Varian Atlas CH7 spectrometer (70 eV).

(Bis(2,2,6,6-tetramethylpiperidino)alanyl)cyclopentadienyldicarbonyliron (1). Na[CpFe(CO)$_2$] is prepared freshly according to the method as reported in the literature (1.28 g, 6.4 mmol).[14] From the resulting THF filtrate the solvent is evaporated under reduced pressure until constant weight is achieved. The residue is suspended in 100 mL of *n*-hexane. A solution of (tmp)$_2$AlBr (2.32 g, 6.0 mmol)[5] in 60 mL of *n*-hexane is added dropwise at ambient temperature. After the mixture was stirred overnight, the insoluble material was filtered off and the clear, brown-yellowish filtrate concentrated to 50 mL. Storing the solution for 24 h at −20 °C afforded 2.47 g (85%) of yellowish, air- and moisture-sensitive crystals of (tmp)$_2$AlFe(Cp)(CO)$_2$ (**1**), mp > 83 °C dec. ^{1}H-NMR (C$_6$D$_6$) (270 MHz; δ): 1.38 t (8 H, tmp-β-C*H*$_2$); 1.55 s (24 H, tmp-C*H*$_3$); 1.62−1.72 m (4 H, tmp-γ-C*H*$_2$); 4.72 s (5 H, cp-*H*). ^{13}C-NMR (C$_6$D$_6$) (100 MHz; δ): 18.7 (tmp-γ-*C*H$_2$); 37.1, 30.5, (tmp-*C*H$_3$); 41.0 (tmp-β-*C*H$_2$); 52.8 (N-*C*); 82.8 (cp-*C*). ^{27}Al-NMR (C$_6$D$_6$) (70 MHz; δ): 212 ($h_{1/2}$ = 9.000 Hz) IR [ν(C−O) range (hexane solution)]: 1982 (vs), 1927 (vs) cm^{-1}. MS: Decomposition at 55 °C into *m/z* (%) 354 [(cp)Fe(CO)$_2$]$_2^+$ (37), 326 (354 − CO) (18), 298 (354 − 2CO) (26), 270 (354 − 3CO) (17), 242 (354 − 4CO) (93), 186 (Cp$_2$Fe$^+$) (100); at 110 °C *m/z* (%) 307 (tmp)$_2$Al$^+$ (100). Anal. Calcd for C$_{25}$H$_{41}$N$_2$O$_2$AlFe (484.44): C, 61.98; H, 8.53; N, 5.78. Found: C, 59.84; H, 7.98; N, 5.42.

X-ray Crystal Structure Determination. Data collection for the X-ray structure determination was performed on a Syntex P4 four-circle diffractometer equipped with a smart CCD area detector using graphite-monochromated Mo Kα (0.710 73 Å) radiation. Crystal data and parameters of data collection and structure refinement are compiled in Tables 1 and 2. A single crystal was covered with polyfluoro ether oil and fixed on top of a glass fiber. The crystal was cooled to −100 °C, and data were collected at this temperature. All calculations were performed on Pc's and workstations using the program SAINT for data reduction and the Siemens SHELXTL-Plus or SHELX93 software packages for structure solution and refinement. The structure was solved by the heavy atom method and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in calculated positions using fixed isotropic parameters.

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Supporting Information Available: One X-ray crystallographic file, in CIF format, is availble on the Internet only. Access and ordering information is given on any current masthead page.

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