Organometallics **1998,** *17,* 2373−2375

Synthesis, Structure, and Bonding of a Polyhedral Al_2Co_2 Cluster

Christoph Üffing, Achim Ecker, Ralf Köppe, and Hansgeorg Schnöckel*

Institute for Inorganic Chemistry, University of Karlsruhe, Box 6980,
D-76128 Karlsruhe, Germany

Received December 2, 1997

Summary: Bis(μ-(pentamethylcyclopentadienyl)aluminio)hexacarbonyldicobalt, (μ-$Cp^*Al)_2Co_2(CO)_6$, is formed in the reaction between $AlCp^*$ ($Cp^* = C_5Me_5$) and $Co_2(CO)_8$ in toluene. The bonding description as a polyhedral Al_2-Co_2 cluster in which $AlCp^*$ has completely lost its originally carbene-like character is based on X-ray data as well as on DFT calculations.

The synthetic potential of the carbene-analogue species $AlCp^*$ (**1**)[1a] has been demonstrated in main-group as well as in transition-metal chemistry.[1b] Here we report the synthesis of the polyhedral Al_2Co_2 cluster bis(μ-(pentamethylcyclopentadienyl)aluminum)hexacarbonyldicobalt, (μ-$Cp^*Al)_2Co_2(CO)_6$ (**3**), by the reaction of **1** with $Co_2(CO)_8$ (**2**). Its structure and bonding, especially with respect to three-center bonding (Al−Co−Al in addition to a Co−Al−Co contribution) and to direct Al−Co bonds, are discussed. The former situation is unique;[2] the latter have been observed only once before.[3] Moreover, a similar In_2Co_2 cluster, $\{\mu\text{-}(Me_3Si)_3CIn\}_2Co_2(CO)_6$, has been described recently.[4]

The reaction of **1** and **2** in toluene solution was carried out at 60 °C. Subsequent cooling to −20 °C gave yellow crystals of (μ-$Cp^*Al)_2Co_2(CO)_6$ (**3**) in about 22% yield. First evidence for the generation of **3** was given by its mass and IR spectra (see Experimental Section). The molecular structure of **3** as determined by X-ray diffraction is presented in Figure 1.

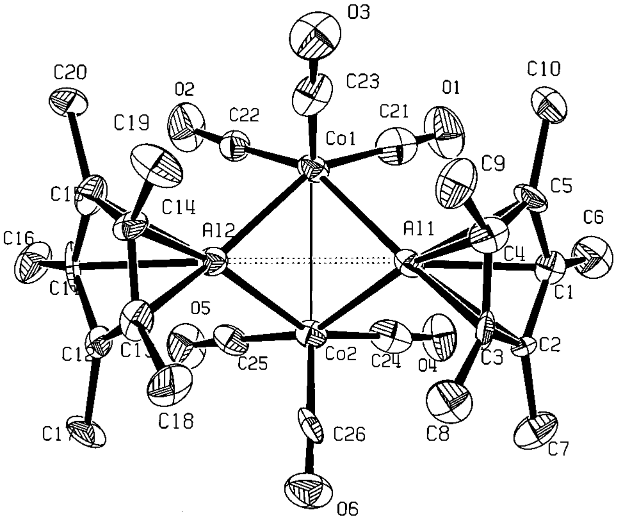

Figure 1. Molecular structure of (μ-$Cp^*Al)_2Co_2(CO)_6$ (**3**) (50% probability of the thermal ellipsoids; hydrogen atoms omitted for clarity). Selected distances (Å) and angles (deg) (maximum/mininum/average value): Al−Al = 3.121(3); Co−Co = 2.772(2); Al−Co = 2.384(3)/2.369(3)/2.377; Al−C = 2.240(8)/2.203(8)/2.221; Co−C = 1.775(10)/1.750(9)/1.760; C−O = 1.175(10)/1.142(9)/1.159; Al−Co−Al = 82.27(9)/81.97(9)/82.12; Co−Al−Co = 71.48(8)/71.22(8)/71.35.

The Co−Co bond (2.772(2) Å) is significantly longer than in $Co_2(CO)_8$ (**2**) (2.5290(8) Å),[5] and the Al−Al distance (3.121(3) Å) is longer than that of a typical Al−Al bond (2.660(1) Å),[6] as well as those in **1** (2.769 Å (2.773(4)−2.767(5) Å)),[1a] by about 13%. On the other hand, the Al−Co interactions (2.377 Å) are of strength similar to that in the only other known example containing an Al−Co bond, $\{Cp^*(\eta^2\text{-}C_2H_4)Co\text{−}AlEt\}_2$ (**4**),[3] possessing a central planar Al_2Co_2 ring with a Al−Co bond length of 2.333(1) Å. The Co−C bonds in **3** (1.76 Å) are shorter than those in $Co_2(CO)_8$ by about 0.07 Å. Furthermore, the Al−C distances in **3** (2.221 Å) are significantly shorter than those in monomeric or tetrameric **1** (2.388(7) or 2.334 Å (2.292(13)−2.378(11) Å) respectively).[7]

From these experimental results the following bonding description can be concluded. The negatively polarized Co atoms (cf. Table 1) repel each other, the consequence being a long Co−Co bond and a short Co−CO distance due to Co−CO back-bonding. Moreover, the Al atoms are positively polarized, which is evident from the extremely short Al−C distance. In Al(III) containing $(Cp^*AlCl_2)_2$[8] almost identical Al−C distances are observed (2.227 Å (2.184(3)−2.284(3) Å)). However,

---

* To whom correspondence should be addressed. Tel.: +49 (0) 721 608 2981. Fax: +49 (0) 721 608 4854. E-mail: hg@achpc9.chemie.uni-karlsruhe.de.

[1] (a) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 564. (b) Dohmeier, C.; Loos, D.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 129−149.

[2] The structure of an $AlCo_3(CO)_9$ cluster compound is not based on an X-ray study but has been concluded from spectroscopic data: Schwarzhans, K. E.; Steiger, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 535.

[3] In the Co_2Al_2 system $[\{Cp^*(\eta^2\text{-}C_2H_4)Co\text{−}AlEt\}_2]$ planarity and two additional framework electrons result in different bonding with a strong AlCoAl contribution but without CoAlCo three-center bonding. In another Co_2Al_2 compound $[(Cp^{**}CoH)_2\text{-}\mu\text{-}\{\eta^2\text{:}\eta^2\text{-}cis\text{-}\mu\text{-}[Et_2AlCH{=}CHAlEt_2]\}]$, where $Cp^{**} = C_5Me_4Et$, the bonding is completely different, as evidenced by the extremely long Al−Al (3.503 Å) and Co−Co bonds (3.338 Å). Furthermore, long Al−Co bonds (2.604(1) and 2.591(2) Å), which are an indication of missing three-center bonding (AlCoAl, CoAlCo), are observed: Schneider, J. J.; Krüger, C.; Nolte, M.; Abraham, I.; Ertel, T. S.; Bertagnolli, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2435.

[4] Uhl, W.; Keimling, S. U.; Hiller, W.; Neumayer, M. *Chem. Ber.* **1996**, *129*, 397−400.

[5] (a) Sumner, G. G.; Klug, H. P.; Alexander, L. E. *Acta Crystallogr.* **1964**, *17*, 732−742. (b) Leung, P. C.; Coppens, P. *Acta Crystallogr.* **1983**, *B39*, 535−542.

[6] Uhl, W. *Z. Naturforsch.* **1988**, *43B*, 1113−1118.

[7] (a) Haaland, A.; Martinsen, K.-G.; Shlykov, S. A.; Volden, H. V.; Dohmeier, C.; Schnöckel, H. *Organometallics* **1995**, *14*, 3116−3119. (b) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 564−565.

S0276-7333(97)01057-1 CCC: $15.00

Table 1. Results of DFT Calculations for the Compounds 1−3, 5−7, $Fe(CO)_5$, and $Fe(CO)_4{}^{2-}$ [a]

	Q(Al)	d(Al−C)	Q(M)	$Q(CO)_{terminal}$	$d(M-C)_{terminal}$	d(C−O)
CpAlO (**7b**)	+0.42	2.230				
AlCp (**1b**)	+0.16	2.388				
$[AlCp_2]^+$ (**6b**)	+0.36	2.190				
$[AlCp*_2]^+$ (**6a**)	+0.71	2.194				
$[CpAlCo(CO)_3]_2$ (**3b**)	+0.54	2.251	−0.99	+0.12/+0.15	1.754/1.769	1.167/1.170
$Co_2(CO)_8$ (**2**)			−0.95	+0.24	1.799/1.812	1.156
$CpAlFe(CO)_4$ (**5b**)	+0.7	2.240	−1.01	+0.06	1.776/1.780	1.163/1.171
$Fe(CO)_5$			−0.99	+0.2	1.802/1.804	1.157/1.160
$Fe(CO)_4{}^{2-}$			−0.58	−0.36	1.753	1.207

[a] Legend: Q, (atomic charge)/(sum of atomic charges) (Mulliken); *d*, bond length (Å); M, transition metal. In order to distinguish between Cp*- and Cp-substituted compounds, the abbreviations "**a**" (Cp*) and "**b**" (Cp) have been used.

a shorter Al−C bond has been observed in $Cp*AlFe(CO)_4$ (**5**) (2.147 Å (2.140(5)−2.153(5) Å)).[9] Al−C bonding in **5** can only be compared with that in the $[AlCp*_2]^+$ cation **6** (2.155 Å (2.137(8)−2.184(8) Å)),[10] which also contains Al(III). These examples demonstrate that in **3**, and especially in **5**, the AlCp* ligand has lost its carbene-like character by releasing electron density toward the transition metal. Therefore, from experimental data for **3**, and more drastically for **5**, a polar bonding description, $[Cp*Al]^{2+}[Fe(CO)_4]^{2-}$, is appropiate and, consequently, AlCp* must not be regarded as stabilized in a complex in both cases. This strong polar bonding is in line with the decrease of C−O bond strength by back-bonding in **5**. Therefore, the experimentally observed C−O frequencies in **5** are just between those of $Fe(CO)_5$ and the isolated tetrahedral anion $Fe(CO)_4{}^{2-}$ ($Fe(CO)_5$ (E′), 1989 cm^{-1}; **5** (E′), 1903 cm^{-1}; $Fe(CO)_4{}^{2-}$ (F_2), 1788 cm^{-1}).[11]

This bonding description is in line with a redox process, which is expected from the well-known strong reducing ability of AlCp* ($Al^+ \rightarrow Al^{3+}$).[12] To a certain degree the formation of **3** and **5** can be compared with the oxidation of **1** to the hypothetical compound Cp*Al=O (**7**); for which from DFT calculations (see Experimental Section) for **7** the Al−C shortening (2.38 → 2.23 Å) is accompanied by a strong increase of the positive charge on Al from 0.16 (**1**) to 0.42 (**7**).

This idea of a polar $Al^{\delta+}-Fe^{\delta-}$ bonding on the basis of experimental data is strongly supported by DFT calculations on the species presented in Table 1. Thus, "oxidation" of AlCp* in the above-mentioned compounds **3** and **5**, and more convincingly in **6**, is followed by a strengthening of the Al−C bonds and a dramatic increase of the positive charge on the Al atom which is even larger for **5b** (+0.7) than for **7b** (+0.42). However, the electron transfer in the direction of the transition metal does not lead to a more negatively charged Co or Fe atom (in comparison to **2** or $Fe(CO)_5$), since there is simultaneous electron transfer to the CO ligands. This is evident from the shorter M−C and the longer C−O bonds in **5b** and **3b**. For comparison also the charge distribution of the isolated anion $Fe(CO)_4{}^{2-}$ is listed in Table 1. For this anion it is remarkable that the negative charge is now concentrated at the CO ligands and that the charge at the Fe atom is less negative than in **5** or $Fe(CO)_5$. Although experimental data as well as ab initio calculations favor a polar bonding description, there are significant covalent contributions to justify the description of **3** as a cluster compound.

The SEN[13] (shared electron number) as a measure of covalent contributions shows a slight decrease in Co−Co bonding for **3** in comparison to **2** (0.91 instead of 0.99). On the other hand, the Al−Co bond is strong (SEN = 1.12)[14] and the Al−Al interaction is weak (SEN = 0.35). This 2c−2e SEN for Al−Al bonding is mainly a consequence of a strong 3c−2e SEN (Al−Co−Al) which is completely missing in the equivalent triangle C−Co−C in **2**.

According to the structural data, a similar bonding situation is observed for the above-mentioned In_2Co_2 cluster.[4] In this cluster the Co−Co bond is longer (2.8014(6) Å) than in **2** by about 0.27 Å and the In−In distance (3.3618(6) Å) is longer than in $[InC(SiMe_3)_3]_4$ (3.001(1) Å) by about 12%, which is in good agreement with our results. Furthermore, also the shorter In−C distances (2.183(3) Å), compared with the In_4 species (2.25(1) Å), and the shorter Co−CO bonds (1.773(3) Å), compared with 1.828(2) Å for **2**, can also be regarded as a consequence of charge transfer from the In to the Co atoms.

The application of AlCp* in preparative chemistry is restricted because of its difficult synthesis, although a classical preparation method has been described.[12a] Nevertheless, in principle AlCp* seems to be an excellent precursor for new Al−transition-metal cluster compounds which incorporate strong Al−metal bonds.[15] On the basis of experimental and ab initio results, this interaction may be described better by polar than by multiple bonding. This interpretation is supported by

---

[8] Koch, H.-J.; Schulz, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Heine, A.; Herbst-Irmer, R.; Stalke, D.; Sheldrick, G. M. *Chem. Ber.* **1992**, *125*, 1107−1109.

[9] Weiss, J.; Stetzkamp, D.; Nuber, B.; Fischer, R. A.; Boehme, C.; Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 70−72.

[10] Dohmeier, C.; Schnöckel, H.; Robl, C.; Schneider, U.; Ahlrichs, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1655−1657.

[11] These vibrations have been selected because their symmetry-adapted force constants contain the same linear combination of internal force constants ($f_{CO} - f_{CO/CO}$): Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Cooordination Compounds*, 5th ed.; Wiley: New York, 1997.

[12] (a) Schulz, S.; Roesky, H. W.; Koch, H.-J.; Sheldrick, G. M.; Stalke, D.; Kuhn, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1729. (b) Dohmeier, C.; Schnöckel, H.; Robl, C.; Schneider, U.; Ahlrichs, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 199.

[13] The shared electron number (SEN) provides a reliable measure of the covalent bond strength. To give an idea of typical values found for SEN, we list some representative cases: strong bonds such as C−C or C−H (SEN = 1.4); double bonds such as C=C (SEN = 2.2); triple bonds such as C≡C and N≡N (SEN = 3.3). A reduced SEN is found for polar bonds as in NaF (SEN = 0.3) and for weak bonds such as in Cl_2 (SEN = 0.9) and in F_2 (SEN = 0.6). Ahlrichs, R.; Erhardt, C. *Chem. Unserer Zeit* **1985**, *19*, 120−124.

[14] For **5** the SEN is 1.48.

[15] However, preliminary reactions with simple carbonyls such as $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Mn_2(CO)_{10}$ have not been successful thus far.

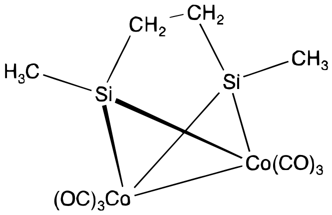

Figure 2. Molecular structure of $[(\mu\text{-MeSiCH}_2)_2\text{Co}_2(\text{CO})_6]$.

the structural data of the recently published compound **5** and to a lesser degree also of the Si−transition metal bond in $[(\mu\text{-MeSiCH}_2)_2\text{Co}_2(\text{CO})_6]$ (Figure 2).[16]

Experimental Section

General Comments. All manipulations were carried out under an argon (glovebox, MBraun) or dinitrogen atmosphere. Toluene was dried (sodium), distilled, and degassed prior to use. $\text{Co}_2(\text{CO})_8$ (Fluka) was used without further purification.

Physical Measurements. Mass spectra (EI, 70 eV) were run on a Finnigan MS 8230 instrument; NMR spectra were obtained using a Bruker AC 250 spectrometer (^{1}H, 250.134 MHz). These spectra were referenced to the residual protic impurities of the solvent (δ($\text{C}_6\text{D}_5\text{H}$) 7.16 ppm). IR spectra were obtained using KBr pellets on an IFS 113v FT-IR spectrometer (Bruker) and Raman spectra on a DILOR XY 800 instrument (vacuum-sealed glass capillary tubes; λ(excitation) = 514.532 nm).

Synthesis of $(\mu\text{-Cp*Al})_2\text{Co}_2(\text{CO})_6$ (3). A mixture of $\text{Co}_2(\text{CO})_8$ (37 mg; 0.11 mmol) and $(\text{Cp*Al})_4$ (35 mg; 0.05 mmol) was dissolved in toluene (15 mL) and the solution heated to 60 °C for about 24 h. After it was cooled to room temperature and subsequently filtered, the dark solution was stored at −20 °C. At this temperature yellow crystals formed over several days of standing (about 22% yield). IR (KBr; cm^{-1} (relative intensity)): 2017 (2); 1977 (2); 1943 (3); 1932 (3); 1926 (3); 1922 (3); 1916 (2); 1910 (2); 1883 (1); 561 (10); 540 (10); 518 (7); 488 (8); 429 (3); 416 (2); 304 (2). During the preparation of the KBr pellet **3** may be partially decomposed. Raman (solid; (cm^{-1} (relative intensity)): 2931.3 (1); 2020.2 (1); 1946.1 (1); 1915.5 (2); 1789.3 (2); 1420.4 (1); 894.0 (1); 592.6 (3); 555.8 (2); 487.9 (3); 434.8 (7); 389.6 (1); 262.6 (2); 187.1 (6); 92.5 (10). ^{1}H NMR (C_6D_6, room temperature): 1.60 ppm (s, Cp*). MS (EI, 70 eV, 150 °C; m/z (relative intensity)): 609.9 (14.7; M$^+$); 582.0 (27.1; M$^+$ − CO); 553.9 (30.7; M$^+$ − 2 CO); 498.0 (100; M$^+$ − 4 CO); 468 (32.3); 377.0 (99.2); 277.0 (63.1). When it is heated to 200 °C in a vacuum-sealed glass capillary tube **3** slightly sublimes and partially decomposes to a mixture of orange-red ($\text{Co}_2(\text{CO})_8$?), green, and colorless products.

Table 2. Data for the X-ray Structural Study of $(\mu\text{-Cp*Al})_2\text{Co}_2(\text{CO})_6$

formula	$\text{C}_{26}\text{H}_{30}\text{Al}_2\text{Co}_2\text{O}_6$
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
fw	610.33
a, Å	17.434(5)
b, Å	8.927(5)
c, Å	17.450(5)
α, deg	90
β, deg	93.41(3)
γ, deg	90
Z	4
V, Å^3	2711.0(19)
ρ(calcd), g cm^{-3}	1.459
cryst dimens, mm	0.01 × 0.1 × 0.5
F(000)	1256
μ, mm^{-1}	1.286
T, K	200(2)
2θ range, deg	4.68−47.78
index ranges	$-19 \le h \le 19$
	$-2 \le k \le 10$
	$-19 \le l \le 19$
no. of rflns collct	5614
no. of indepd rflns	4174 ($R_{\text{int}} = 0.0630$)
no. of reflns obsd	2453 ($F > 4\sigma(F)$)
no. of params	335
GOF	1.176
wR2 (all data)	0.1666
R1	0.0585
largest diff peak, e Å^{-3}	0.473
deepest diff peak, e Å^{-3}	−0.390

X-ray Data Collection and Solution and Refinement of the Structure. The crystals were selected under argon in perfluorinated polyethers. The oil-coated crystals were manipulated onto a glass fiber and transferred to the cold nitrogen stream of the Stoe Stadi IV diffractometer (Mo Kα radiation (graphite monochromated, $\lambda = 0.710\,69$ Å); ω scan mode). The structure was solved by direct methods (SHELXS-90)[17a] and refined (SHELXL-93)[17b] by full-matrix least squares on F^2 (hydrogen atoms: riding model, fixed isotropic U); weighting scheme $w^{-1} = \sigma^2 F_o^2 + (0.0332P)^2 + 4.9312P$, $P = (F_o^2 + 2F_c^2)/3$. Crystallographic data are given in Table 2.

Quantum Chemical Calculations. The DFT calculations were performed using the RI-DFT module (B−P parametrization)[18a] of the TURBOMOLE program package.[18b] The basis sets were of SV(P) quality. The electronic distribution was obtained from Roby−Davidson and Mulliken population analyses.[13,18c] To save computational time, the calculations were restricted to unsubstituted C_5H_5 systems.

Supporting Information Available: Tables giving crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles and two additional ORTEP views of $(\mu\text{-Cp*Al})_2\text{Co}_2(\text{CO})_6$ (10 pages). Ordering information is given on any current masthead page.

OM9710576

---

[16] Bourg, S.; Boury, B.; Carré, F.; Corriu, R. J. P. *Organometallics* **1997**, *16*, 3097−3099.

[17] (a) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473. (b) Sheldrick, G. M. Universität Göttingen, 1993.

[18] (a) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *240*, 283; **1995**, *242*, 652. (b) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165−169. (c) Heinzmann, R.; Ahlrichs, R. *Theor. Chim. Acta* **1976**, *42*, 33−45.