1992 *Organometallics* **2003,** *22,* 1992−1994

Salts of the Cation $[(Cp^*Cr)_4(\mu\text{-Cl})_3(\mu\text{-CH}_2)_3AlMe]^+$ with the Oxo- and Methine-Based Aluminum Anions $[(Me_2Al)_2(\mu\text{-CH})(AlCl_2Me)_2]^-$ and $[(Me_2Al)(\mu_3\text{-O})(AlCl_2Me)(AlMe_2Cl)]^-$

Pingrong Wei and Douglas W. Stephan*

Department of Chemistry and Biochemistry, University of Windsor,
Windsor, Ontario, Canada N9B 3P4

Received March 7, 2003

Summary: Reactions of $(Cp^*CrCl_2)_2$ (**1**) *and* $Cp^*Cr(HNP\text{-}i\text{-}Pr_3)Cl_2$ (**3**) *with excess* $AlMe_3$ *gave* $[(Cp^*Cr)_4(\mu\text{-Cl})_3(\mu\text{-CH}_2)_3AlMe][(Me_2Al)(\mu_3\text{-O})(AlCl_2Me)(AlMe_2Cl)]$ (**2**) *and* $[(Cp^*Cr)_4(\mu\text{-Cl})_3(\mu\text{-CH}_2)_3AlMe][(Me_2Al)_2(\mu\text{-CH})(AlCl_2Me)_2]$ (**4**)*, respectively. Although the cations are the same, the former salt has a* Al_3O*-based anion, whereas the latter contains an* Al_4*−methine anion.*

The development of single-site olefin polymerization catalysts has become an increasingly broad area of pursuit, involving studies of early- and late-transition-metal derivatives[1−4] as well as main-group compounds.[3,5−8] While much of this work targets new catalysts, the examination of deactivation pathways has also revealed unique reactivity. For example, Ti−phosphinimide complexes yield highly active catalysts,[9−11] yet reactions with $AlMe_3$ result in multiple C−H activations and the formation of unprecedented Ti−Al−carbide clusters.[12−14] These reactions are mediated by interaction of the Lewis acid with the phosphinimide nitrogen donor atom. The $TiCAl_3$ core of these species has proven to be extremely robust, as efforts to liberate Al−carbide species have failed. While the groups of Marks,[1,15−17] Bochmann,[18−20] and Piers[21,22] have developed effective new anions for polymerization, we sought unique Al-based anions derived from C−H activation. We speculated that reactions of Cr−$AlMe_3$ systems could provide an alternative pathway for C−H activation chemistry. In this communication, we describe the structures of two salts, each containing Cr_4Al-based cations with the oxo- and methine-based Al anions $[(Me_2Al)(\mu_3\text{-O})(AlCl_2Me)(AlMe_2Cl)]^-$ and $[(Me_2Al)_2(\mu\text{-CH})(AlCl_2Me)_2]^-$. While the former anion is a methylaluminoxane derivative, the latter is an unprecedented Al−methine-based anion.

The species $(Cp^*CrCl_2)_2$ (**1**) was generated in situ and subsequently reacted with excess $AlMe_3$ at 25 °C for 3 days. Subsequent workup gave very small crystals of **2** in 23% yield. A crystallographic study revealed that **2** is the salt $[(Cp^*Cr)_4(\mu\text{-Cl})_3(\mu\text{-CH}_2)_3AlMe][(Me_2Al)(\mu_3\text{-O})(AlCl_2Me)(AlMe_2Cl)]$.[23] The singly charged cation is comprised of four Cp^*Cr units arranged in an approximately tetrahedral arrangement (Figure 1). One of the Cr atoms, subsequently referred to as the basal Cr, is bonded to three Cl atoms. The geometry about this basal Cr is that of a so-called piano stool, with Cl−Cr−Cl angles ranging from 95.80(11) to 98.22(11)°. These chlorides bridge to each of the other three Cr atoms in the cation. The average Cr−Cl distance to the basal Cr atom is 2.360(3) Å, which is comparable to that seen in $[(CpCr(\mu\text{-Cl}))_3(\mu\text{-CH})]$ ($Cr-Cl_{av} = 2.355(5)$ Å)[24] but significantly longer than the terminal Cr−Cl distances found in $[Cp^*{}_4Cr_4(\mu\text{-F})_5Cl_2]PF_6$ ($Cr-Cl_{av} = 2.271(3)$ Å).[25] The average Cr−Cl distance to the other Cr atoms is 2.434(3) Å. This difference presumably reflects the

---

* To whom correspondence should be addressed. Fax: 519-973-7098. E-mail: Stephan@uwindsor.ca.

[1] Hlatky, G. G. *Coord. Chem. Rev.* **1999**, *181*, 243−296.

[2] Hlatky, G. G. *Coord. Chem. Rev.* **2000**, *199*, 235−329.

[3] Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem.* **1999**, *112*, 1354−1356; *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447.

[4] Kaminsky, W. *J. Chem. Soc. D* **1998**, *009*, 1413−1418.

[5] Thiyagarajan, B.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1999**, *18*, 5347−5359.

[6] Korolev, A. V.; Guzei, I. A.; Jordan, R. F. *Abstracts of Papers*, 218th National Meeting of the American Chemical Society, New Orleans, Aug 22−26, 1999; American Chemical Society: Washington, DC, 1999; INOR-618.

[7] Korolev, A. V.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 11605−11606.

[8] Dagorne, S.; Guzei, I. A.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 274−289.

[9] Stephan, D. W.; Stewart, J. C.; Harrison, D. G. In Eur. Pat. Appl. (Nova Chemicals (International) S.A., Switzerland). 1999; p 21ff.

[10] Stephan, D. W.; Stewart, J. C.; Guerin, F.; Spence, R. E. v. H.; Xu, W.; Harrison, D. G. *Organometallics* **1999**, *18*, 1116−1118.

[11] Stephan, D. W.; Guerin, F.; Spence, R. E. v. H.; Koch, L.; Gao, X.; Brown, S. J.; Swabey, J. W.; Wang, Q.; Xu, W.; Zoricak, P.; Harrison, D. G. *Organometallics* **1999**, *18*, 2046−2048.

[12] Kickham, J. E.; Guerin, F.; Stephan, D. W. *J. Am. Chem. Soc.* **2002**, *124*, 11486−11494.

[13] Kickham, J. E.; Guerin, F.; Stewart, J. C.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3263−3266.

[14] Kickham, J. E.; Guerin, F.; Stewart, J. C.; Urbanska, E.; Ong, C. M.; Stephan, D. W. *Organometallics* **2001**, *20*, 3209.

[15] Metz, M. V.; Sun, Y.; Stern, C. L.; Marks, T. J. *Organometallics* **2002**, *21*, 3691−3702.

[16] Lanza, G.; Fragala, I. L.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 12764−12777.

[17] Metz, M. V.; Schwartz, D. J.; Stern, C. L.; Nickias, P. N.; Marks, T. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 1312−1316.

[18] Lancaster, S. J.; Rodriguez, A.; Lara-Sanchez, A.; Hannant, M. D.; Walker, D. A.; Hughes, D. H.; Bochmann, M. *Organometallics* **2002**, *21*, 451−453.

[19] Zhou, J.; Lancaster, S. J.; Walker, D. A.; Beck, S.; Thornton-Pett, M.; Bochmann, M. *J. Am. Chem. Soc.* **2001**, *123*, 223−237.

[20] Lancaster, S. J.; Walker, D. A.; Thornton-Pett, M.; Bochmann, M. *Chem. Commun.* **1999**, 1533−1534.

[21] Piers, W. E.; Irvine, G. J.; Williams, V. C. *Eur. J. Inorg. Chem.* **2000**, 2131−2142.

[22] Williams, V. C.; Irvine, G. J.; Piers, W. E.; Li, Z.; Collins, S.; Clegg, W.; Elsegood, M. R. J.; Marder, T. B. *Organometallics* **2000**, *19*, 1619−1621.

[23] X-ray data (CCDC Nos. 191376 and 191377): **2**, $P\bar{1}$, $a = 12.544(7)$ Å, $b = 16.300(10)$ Å, $c = 19.394(11)$ Å, $\alpha = 103.034(12)°$, $\beta = 103.644(11)°$, $\gamma = 93.060(12)°$, $V = 3730(4)$ Å^3, $Z = 2$, $R = 0.0885$, $R_w = 0.2426$, GOF = 1.002; $\mathbf{4}\cdot 2C_6H_6$, *Pmmn*, $a = 14.198(8)$ Å, $b = 15.155(10)$ Å, $c = 18.926(11)$ Å, $V = 4072(4)$ Å^3, $Z = 4$, $R = 0.0739$, $R_w = 0.1752$, GOF = 0.843.

[24] Richeson, D. S.; Hsu, S.-W.; Fredd, N. H.; Van Duyne, G. D.; Theopold, K. H. *J. Am. Chem. Soc.* **1986**, *108*, 8273−8274.

10.1021/om030169w CCC: $25.00 © 2003 American Chemical Society
Publication on Web 04/05/2003

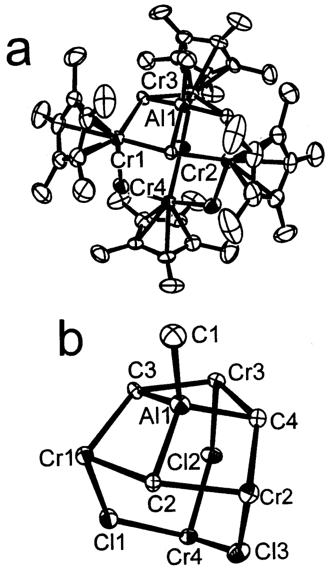

Figure 1. ORTEP drawings of (a) the cation of **1**, with hydrogen atoms omitted and (b) the core of the cation of **1**. Thermal ellipsoids at the 30% level are shown. Selected distances (Å) and angles (deg): Cr(1)−C(2) = 2.235(8), Cr(1)−C(3) = 2.252(8), Cr(1)−Cl(1) = 2.432(3), Cr(2)−C(4) = 2.191(10), Cr(2)−C(2) = 2.208(9), Cr(2)−Cl(3) = 2.434(3), Cr(3)−C(4) = 2.190(9), Cr(3)−C(3) = 2.228(8), Cr(3)−Cl(2) = 2.434(3), Cr(4)−Cl(2) = 2.353(3), Cr(4)−Cl(3) = 2.365(3), Cr(4)−Cl(1) = 2.364(3), Al(1)−C(1) = 1.990(10), Al(1)−C(2) = 2.032(9), Al(1)−C(3) = 2.032(9), Al(1)−C(4) = 2.031(10); C(2)−Cr(1)−C(3) = 94.0(3), C(2)−Cr(1)−Cl(1) = 94.6(2), C(3)−Cr(1)−Cl(1) = 94.2(2), C(4)−Cr(2)−C(2) = 94.1(3), C(4)−Cr(2)−Cl(3) = 94.8(3), C(2)−Cr(2)−Cl(3) = 94.7(2), C(4)−Cr(3)−C(3) = 94.4(3), C(4)−Cr(3)−Cl(2) = 94.7(3), C(3)−Cr(3)−Cl(2) = 93.8(2), Cl(2)−Cr(4)−Cl(3) = 98.22(11), Cl(2)−Cr(4)−Cl(1) = 95.80(11), Cl(3)−Cr(4)−Cl(1) = 97.53(11), $C{-}Al(1){-}C_{av}$ = 109.4(4), $Cr{-}Cl{-}Cr_{av}$ = 128.30(13), $Al(1){-}C{-}Cr_{av}$ = 77.6(3), $Cr{-}C{-}Cr_{av}$ = 138.7(4).

proximity of the three Cr atoms to the Lewis acidic Al center. In addition, three methylene units bridge the three Cr atoms, forming a Cr_3C_3 six-membered ring, which adopts a pseudo-chair conformation. Capping the carbons of this six-membered ring is a single AlMe fragment. The Cr−C distances to the triply bridging carbons average 2.217(9) Å, which is significantly longer than the Cr−methine distance seen in $[(CpCr(\mu\text{-}Cl))_3(\mu\text{-}CH)]$ ($Cr{-}C_{av}$ = 1.942(10) Å).[24] The piano-stool geometry of the Cp^*CrClC_2 environment about these three Cr atoms is similar to that of the basal Cr with Cl−Cr−C and C−Cr−C angles averaging 94.5(3) and 94.1(3)°, respectively. The geometry about the capping Al atom is approximately tetrahedral, with C−Al−C angles ranging from 104.9(4) to 114.9(5)°. The Al−C distances average 2.031(9) Å, while the Al−C distance to the terminal methyl group is 1.990(10) Å. This geometry dictates an average Cr−Al distance of 2.665(3) Å. As expected, this is longer than the Cr−Al distance seen in $Cp^*AlCr(CO)_5$ (2.3761(6) Å).[26]

The anion $[(Me_2Al)(\mu_3\text{-}O)(AlCl_2Me)(AlMe_2Cl)]^-$ of **2** contains three Al atoms bound to a central O atom in a trigonal-planar geometry (Figure 2a). Each of these Al centers is distinct, being $AlMe_2$, $AlMe_2Cl$, and $AlCl_2Me$, respectively; however, a 50:50 disorder of two of the three Al centers suggests that facile bridging and exchange of chloride between Al centers result in a dynamic stability of this anion. The disorder notwithstanding, the average Al−O, Al−Cl, and Al−C distance averages were found to be 1.78(1), 2.22(1), and 1.99(1) Å, respectively. The Al−O distance is comparable to the "in-plane" Al−O distances found in $[t\text{-}BuAl(\mu\text{-}O)]_6$ (Al−O = 1.782(7) Å)[27] but shorter than those found by Barron et al. in $[t\text{-}Bu_2Al(\mu\text{-}OH)]_3$ (Al−O = 1.846(3) Å)[27] and $[t\text{-}Bu_6Al_6O_6Me_2]^{2-}$ (Al−O = 1.83(1) Å),[28] consistent with the greater steric congestion in these species. This anion may be related to portions of the Al-containing anions derived from the reactions of methylalumoxane (MAO) with metal chlorides; however, the source of the oxygen in **2** is uncertain. Activation of residual THF from the preparation of $(Cp^*CrCl_2)_2$ and the intervention of adventitious water are possibilities that could not be dismissed or confirmed.

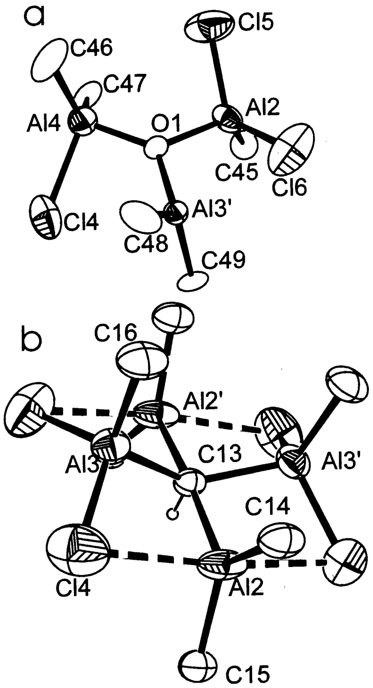

Figure 2. ORTEP drawings of anions of (a) **2** (one orientation of disorder) and (b) **4**. Thermal ellipsoids at the 30% level are shown. Only the methine H atom is shown. Selected distances (Å) and angles (deg) are as follows. (a) **2**: Al(2)−O(1) = 1.817(8), Al(2)−C(45) = 1.966(12), Al(2)−Cl(6) = 2.076(10), Al(2)−Cl(5) = 2.144(8), Al(3)′−O(1) = 1.773(17), Al(3)′−C(49) = 1.919(18), Al(3)′−C(48) = 1.983(19), Al(4)−O(1) = 1.822(10), Al(4)−C(46) = 1.983(18), Al(4)−C(47) = 2.070(16), Al(4)−Cl(4) = 2.349(10); Al(3)′−O(1)−Al(4) = 127.5(7), Al(3)′−O(1)−Al(2) = 103.4(7), Al(4)−O(1)−Al(2) = 129.1(5). (b) **4**: Al(2)−C(14) = 1.926(14), Al(2)−C(15) = 1.958(14), Al(2)−C(13) = 2.029(5), Al(3)−C(16) = 1.954(14), Al(3)−C(13) = 2.020(8), Al(3)−C(14) = 2.159(6); Al(2)−C(13)−Al(2) = 173.0(11), Al(2)−C(13)−Al(3) = 91.20(16), Al(3)−C(13)−Al(3) = 140.1(10).

The related reaction of the species $Cp^*Cr(HNP\text{-}i\text{-}Pr_3)Cl_2$ (**3**) with $AlMe_3$ proceeded with a color change similar to that seen in the formation of **2**, giving dark

---

(25) Thomas, B. J.; Mitchell, J. F.; Theopold, K. H.; Leary, J. A. *J. Organomet. Chem.* **1988**, *348*, 333−342.

(26) Yu, Q.; Purath, A.; Donchev, A.; Schnockel, H. *J. Organomet. Chem.* **1999**, *584*, 94−97.

(27) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971−4984.

(28) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 6465−6474.

purple crystals of product **4** in 31% yield. An X-ray crystallographic study confirmed the formulation of **4** as $[(Cp^*Cr)_4(\mu\text{-Cl})_3(\mu\text{-CH}_2)_3AlMe][(Me_2Al)_2(\mu\text{-CH})(AlCl_2Me)_2]$.[23] The cation of **4** is precisely the cation observed in **2**; however, in this case the Cr atoms sit on mirror site symmetry. Thus, two Cp*Cr positions are symmetry-related to the other two. Thus, the bridging Cl and C atoms as well as the AlMe fragment are disordered over four positions. This disorder was successfully modeled.

The anion of **4** (Figure 2b) involves four Al atoms about a central methine fragment which adopts a pseudo-trigonal-bipyramidal geometry. The methine hydrogen atom was located in the difference Fourier map, and its position and thermal parameter were fully refined. The symmetry about this anion dictates an almost linear arrangement of the axial Al−C−Al angle (173.0(11)°), while the Al−C−Al angle in the equatorial plane was found to be 140.1(10)°, resulting in Al−C−H angles of 109.9(10)°. The distances between the Al and the central methine carbons are 2.029(5) and 2.020(8) Å. The two “axial” Al atoms are bound to two methyl groups and are trigonal planar. The two other Al atoms in the “equatorial plane” bear two chlorides and one methyl group. The average Al−methyl carbon distance is 2.01(1) Å. The Al−Cl distance is 2.159(6) Å, while these Cl atoms also approach the axial Al atoms at a distance of 2.731(6) Å. Such bridging may provide stabilization of this unique anion. To our knowledge, the characterization of **4** provides the first structural data for an Al-based anion centered on a methine carbon.

C−H activation clearly takes place in the formation of the cations **2** and **4**. However, the mechanisms involved are unknown and difficult to follow because of the paramagnetic nature of Cr. In the case of **4**, the formation of the Al_4−methine-based anion prompts speculation about the role of the phosphinimine ligand. It may be that, similar to related Ti chemistry yielding Ti−Al−carbide aggregates of the form $CpTi(\mu\text{-Me})(\mu\text{-NPR}_3)(\mu_4\text{-C})(AlMe_2)_3$,[12,13,29] interaction of **3** with $AlMe_3$ proceeds through the anionic species $[Cp^*Cr(NPR_3)Me_2]^-$, which templates C−H bond activation. Liberation of the observed methine-based anion could result from the weaker nature of Cr−C bonds in comparison to analogous Ti−C systems. Ultimately, the phosphinimine ligand is thought to be sequestered by $AlMe_3$, as has been inferred in the formation of Zr−methine clusters.[30]

The characterizations of **2** and **4** infer that unique C−H activation pathways occur in the presence of phosphinimine ligand. The Al_3O anion of **2** may offer some structural insight into anionic fragments of MAO, while the formation of the unprecedented Al_4−methine-based anion in **4** provides a new approach for unique Lewis acid based anions. Independent synthetic routes to these anions as well as the role of phosphinimine or phosphinimide ligands in mediating C−H activation are subjects of ongoing investigations.

Acknowledgment. Financial support from the NSERC of Canada and NOVA Chemicals Corp. is gratefully acknowledged. D.W.S. is also grateful to AvHumboldt Stiftung for a Research Award.

Supporting Information Available: Synthetic and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030169W

---

(29) Kickham, J. E.; Guerin, F.; Stewart, J. C.; Urbanska, E.; Stephan, D. W. *Organometallics* **2001**, *20*, 1175−1182.

(30) Yue, N.; Hollink, E.; Guérin, F.; Stephan, D. W. *Organometallics* **2001**, *20*, 4424−4433.