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## Notes

## Understanding Electronic Effects in Organometallic Complexes. Electron Donation by the Trimethylsilyl Group

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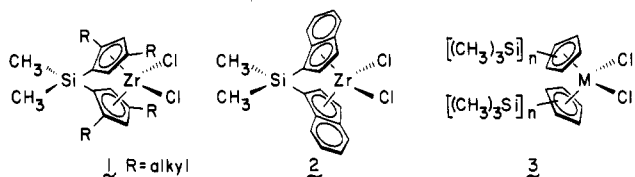
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**Summary:** Electron donation by the trimethylsilyl group has been determined, through X-ray photoelectron spectroscopic analysis of the transition-metal center of zirconocenes, hafnocenes, and ferrocenes having trimethylsilyl substituents on the cyclopentadienide rings, to decrease the binding energy of the inner-shell electrons of the complexed transition metal by 0.10 eV/trimethylsilyl group. The trimethylsilyl group is slightly more electron donating than the methyl group in these systems.

Much attention has been given to the electronic influence of silyl substituents in the literature.<sup>2</sup> In general, trialkylsilyl groups have been suggested to have inductive effects which range from less electron donating than methyl to more electron donating than *tert*-butyl.<sup>2</sup> Although Cradock and co-workers have evaluated the electronic influence of the silyl group (-SiH<sub>3</sub>) on cyclopentadiene,<sup>3</sup> relatively little is known about the electronic effect of the trialkylsilyl group on cyclopentadiene and more importantly on cyclopentadienide-complexed transition metals. This becomes particularly interesting in view of recent syntheses and uses of trialkylsilyl-substituted cyclopentadienide-complexed transition metals. Of special concern are recent reports that describe the superior properties of dimethylsilyl-bridged *ansa*-zirconocene derivatives, such as 1 and 2, as catalysts for Ziegler-Natta



polymerizations of propylene.<sup>4-7</sup> Several groups have

**Table I. Binding Energies of Inner-Shell Electrons of Zirconocenes, Hafnocenes, and Ferrocenes as a Function of Trimethylsilyl or Methyl Substitution**

compd	electron	binding energy, ±0.1 eV
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ZrCl <sub>2</sub>	3d <sub>5/2</sub>	181.7 <sup>9</sup>
(Me <sub>3</sub> SiC <sub>5</sub> H <sub>4</sub> ) <sub>2</sub> ZrCl <sub>2</sub> <sup>13</sup>	3d <sub>5/2</sub>	181.5
[(Me <sub>3</sub> Si) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> ] <sub>2</sub> ZrCl <sub>2</sub> <sup>13</sup>	3d <sub>5/2</sub>	181.4
[(Me <sub>3</sub> Si) <sub>3</sub> C <sub>5</sub> H <sub>2</sub> ] <sub>2</sub> ZrCl <sub>2</sub> <sup>14</sup>	3d <sub>5/2</sub>	181.2
(Me <sub>5</sub> C <sub>5</sub> ) <sub>2</sub> ZrCl <sub>2</sub>	3d <sub>5/2</sub>	181.0 <sup>9</sup>
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> HfCl <sub>2</sub>	4f <sub>7/2</sub>	17.1 <sup>9</sup>
[(Me <sub>3</sub> Si) <sub>3</sub> C <sub>5</sub> H <sub>2</sub> ] <sub>2</sub> HfCl <sub>2</sub> <sup>14</sup>	4f <sub>7/2</sub>	16.5
(Me <sub>5</sub> C <sub>5</sub> ) <sub>2</sub> HfCl <sub>2</sub>	4f <sub>7/2</sub>	16.5 <sup>9</sup>
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Fe	2p <sub>3/2</sub>	708.0 <sup>9</sup>
[(Me <sub>3</sub> Si) <sub>3</sub> C <sub>5</sub> H <sub>2</sub> ] <sub>2</sub> Fe <sup>15</sup>	2p <sub>3/2</sub>	707.3
(Me <sub>5</sub> C <sub>5</sub> ) <sub>2</sub> Fe	2p <sub>3/2</sub>	707.1 <sup>9</sup>

demonstrated that increased steric effects can dramatically impede the efficiency of the polymerization process.<sup>4-8</sup> However, Ewen reported that monomethylation of both cyclopentadienide rings of zirconocene dichloride resulted in a catalyst with increased activity, while pentamethylation of both rings dramatically decreased activity.<sup>8</sup> Since methyl group substitution on the cyclopentadienide results in significant electron donation to the complexed transition metal,<sup>9</sup> it is clear that the properties of zirconocenes as Ziegler-Natta polymerization catalysts<sup>10</sup> are a function of both electronic and steric effects. Relative to the indenide moiety of 2, we have previously demonstrated that indenide is electronically equivalent to dimethyl-

(5) Herrmann, W. A.; Rohrmann, J.; Herdtweck, E.; Spaleck, W.; Winter, A. *Angew. Chem.* 1989, 101, 1536; *Angew. Chem. Int. Ed. Engl.* 1989, 28, 1511. Antberg, M.; Böhm, L. L.; Dolle, V.; Löker, H.; Rohrmann, J.; Spalek, W.; Winter, A. Presented at the 44th Southwest Regional Meeting of the American Chemical Society, 1988; Abstract No. 48.

(6) Miya, S.; Yoshimura, T.; Mise, T.; Yamazaki, H. *Polym. Prepr. Jpn.* 1988, 37, 285. Mise, T.; Miya, S.; Yamazaki, H. *Chem. Lett.* 1989, 1853.

(7) For selected examples of carbon-bridged *ansa*-zirconocenes and *ansa*-hafnocenes in Ziegler-Natta polymerization, see: Kaminsky, W.; Külpel, K.; Brintzinger, H.-H.; Wild, F. R. W. P. *Angew. Chem.* 1985, 97, 507; *Angew. Chem., Int. Ed. Engl.* 1985, 24, 507. Ewen, J.; Haspelslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* 1987, 109, 6544. Ewen, J. A. *J. Am. Chem. Soc.* 1984, 106, 6355. Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* 1987, 109, 6189. Kaminsky, W.; Ahlers, A.; Möller-Lindenhof, N. *Angew. Chem.* 1989, 101, 1304; *Angew. Chem., Int. Ed. Engl.* 1989, 28, 1216.

(8) Ewen, J. A. In *Catalytic Polymerizations of Olefins*; Keii, T.; Soga, K., Eds.; Elsevier-Kodansha: Tokyo, 1986; p 271. See also: Kaminsky, W.; Külpel, K.; Niedoba, S. *Makromol. Chem. Symp.* 1986, 3, 377.

(9) Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* 1983, 2, 1470. Gassman, P. G.; Campbell, W. H.; Macomber, D. W. *Organometallics* 1984, 3, 385.

(10) For a detailed mechanistic analysis of zirconocene-catalyzed Ziegler-Natta polymerization, see: Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* 1987, 109, 7875.

(1) National Science Foundation Predoctoral Fellow, 1987-1990.

(2) For selected references to trialkylsilyl substituent effects, see: Eaborn, C.; Thompson, A. R.; Walton, D. R. M. *J. Organomet. Chem.* 1969, 17, 149. Bock, H.; Seidl, H. *J. Am. Chem. Soc.* 1968, 90, 5694. Heilbronner, E.; Hornung, V.; Bock, H.; Alt, H. *Angew. Chem., Int. Ed. Engl.* 1969, 8, 524. Kaim, W.; Tesmann, H.; Bock, H. *Chem. Ber.* 1980, 113, 3221. Heilbronner, E.; Hornung, V.; Pinkerton, F. H.; Thames, S. F. *Helv. Chim. Acta* 1972, 55, 289. See, also; Shiner, V. J., Jr.; Ensinger, M. W.; Kritiz, G. S. *J. Am. Chem. Soc.* 1986, 108, 842. Schiavelli, M. D.; Jung, D. M.; Vaden, A. K.; Stang, P. J.; Fisk, T. E.; Morrison, D. S. *J. Org. Chem.* 1981, 46, 92.

(3) Cradock, S.; Findley, R. H.; Palmer, M. H. *J. Chem. Soc., Dalton Trans.* 1974, 1650. Cradock, S.; Ebsworth, E. A. V.; Moretta, H.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* 1975, 390.

(4) Röhl, W.; Brintzinger, H.-H.; Rieger, B.; Zolk, R. *Angew. Chem.* 1990, 102, 339; *Angew. Chem., Int. Ed. Engl.* 1990, 29, 279. Wiesenfeldt, H.; Reinmuth, A.; Barsties, E.; Evertz, K.; Brintzinger, H.-H. *J. Organomet. Chem.* 1989, 369, 359.

cyclopentadienide when complexed to a transition metal.<sup>11</sup> However, quantitative data on the electronic effect of the trialkylsilyl moiety on systems such as 1 and 2 are not available.

With utilization of X-ray photoelectron spectroscopy,<sup>9</sup> a series of derivatives of 3 ( $n = 1-3$ ;  $M = \text{Zr, Hf}$ ) and of ferrocene were studied. Table I lists the binding energies for these compounds and for appropriate reference compounds. Examination of the series of zirconocene derivatives showed that the binding energies of the  $3d_{5/2}$  electrons decreased by an average of 0.1 eV/trimethylsilyl group. Two, four, and six trimethylsilyl groups gave an orderly decrease in binding energy. The electronic impact of six trimethylsilyl groups on hafnocene dichloride and on ferrocene again averaged -0.1 eV/trimethylsilyl group.

Investigation of a large variety of transition-metal complexes of methylated cyclopentadienides showed that the methyl substituent averaged an electron donation of 0.08 eV to the complexed metal.<sup>9,12</sup> In comparison, the trimethylsilyl group is ca. 1.25 times more electron donating than the methyl moiety. Thus, in systems such as 1 and 2, we can confidently predict that the silyl substituent will be more electron donating than hydrogen to the complexed zirconium atom and that the zirconium atoms of 1 and 2 will be electron rich relative to zirconocene dichloride.

### Experimental Section

X-ray photoelectron spectra were recorded on a Physical Electronics Model 555 ESCA-Auger-SIMS spectrometer, equipped with a retarding-grid cylindrical mirror analyzer operating at a pass energy of 25 eV. Samples were irradiated with Mg K $\alpha$  X-rays. Samples<sup>13-15</sup> were finely dispersed on the surface

(11) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* 1988, 110, 6130.

(12) Gassman, P. G.; Winter, C. H.; Macomber, D. W. Unpublished results.

of a polyethylene film, and all data were calibrated against the C(1s) signal of polyethylene.

Peak positions reported are the centroids of Gaussian + Lorentzian functions obtained via a standard nonlinear least-squares regression technique. Binding energies are corrected for sample charging by adjusting the C(1s) signal of polyethylene to 284.6 eV. While the C(1s) signal arose mainly from polyethylene, we observed small, unresolved shoulders on the low binding energy side of the signals, which we believe to have resulted from carbon atoms directly attached to the electropositive silicon atoms in the complexes studied. This interference was subtracted from the spectra as follows. The intensity of the shoulder signal arising from silicon-bound carbon atoms was calculated from the integrated area of the metal core electron signal using published tables of atomic sensitivities.<sup>16</sup> The shoulder binding energy was determined from spectra of heavily loaded samples, in which polyethylene was completely obscured and in which silicon-bound carbon atoms dominated the sample. After subtraction of the shoulder, the remaining C(1s) signal had a fwhm of less than 1.7 eV and was used as the internal charging standard.

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**Registry No.** 3 ( $M = \text{Zr}, n = 1$ ), 60938-59-2; 3 ( $M = \text{Zr}, n = 2$ ), 137964-45-5; 3 ( $M = \text{Zr}, n = 3$ ), 137917-28-3; 3 ( $M = \text{Hf}, n = 3$ ), 137917-29-4;  $[(\text{Me}_3\text{Si})_3\text{C}_2\text{H}_5]_2\text{Fe}$ , 137917-30-7.

(13) Tolstikov, G. A.; Miftakhov, M. S.; Monakhov, Y. B. *Zh. Obshch. Khim.* 1976, 46, 1778.

(14) Winter, C. H.; Dobbs, D. A.; Zhou, X.-X. *J. Organomet. Chem.* 1991, 403, 145.

(15) Okuda, J.; Herdtweck, E. *Chem. Ber.* 1988, 121, 1899. Miftakhov, M. S.; Tolstikov, G. A. *Zh. Obshch. Khim.* 1976, 46, 930.

(16) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. *Handbook of X-Ray Photoelectron Spectroscopy*; Perkin-Elmer Corp.: Eden Prairie, MN, 1979; p 188.

## Synthesis and Characterization of Novel Aluminum-Arsenic Compounds. Crystal Structure of $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$

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**Summary:** The viability of dehalosilylation and lithium chloride elimination reactions for use in the preparation of compounds containing core rings of the type Al-As-Al-As and Al-As-Al-Cl was investigated. The second fully characterized aluminum-arsenic dimer,  $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$  (1), was isolated from a coupling reaction between  $\text{Et}_2\text{AlCl}$  and  $\text{LiAs}(\text{SiMe}_3)_3$  carried out at  $-78^\circ\text{C}$ . Reactions between  $\text{Et}_2\text{AlCl}$  and  $\text{As}(\text{SiMe}_3)_3$  in 1:1 and 2:1 mole ratios at ambient temperature failed to give the expected dehalosilylation products, instead yielding the adduct  $\text{Et}_2(\text{Cl})\text{Al}\cdot\text{As}(\text{SiMe}_3)_3$  (2). As evidenced by  $^1\text{H}$  NMR spectra, an NMR tube sample of 2 in benzene- $d_6$  did undergo internal dehalosilylation to give 1 when heated to  $87^\circ\text{C}$  in an oil bath. X-ray crystallographic analysis of 1 confirms its dimeric solid-state structure and shows the Al-As-Al-As ring to be planar. Compound 1 crystallizes

in the monoclinic system, space group  $C2/c$  ( $C_{2h}^6$ ), with four molecules in a unit cell of dimensions  $a = 18.214$  (2) Å,  $b = 9.542$  (1) Å,  $c = 20.453$  (2) Å, and  $\beta = 99.89$  (1) $^\circ$ .

Of late, there has been heightened interest in the preparation of compounds that may serve as single-source precursors to group 13-15 semiconductor materials.<sup>1,2</sup> Two methods have been developed in our laboratories to fabricate compounds that may prove useful to this end: (a) dehalosilylation between tris(trimethylsilyl)arsine and a group 13 halide and (b) coupling reactions involving lithium bis(trimethylsilyl)arsenide and a group 13 halide. These methodologies have been applied to systems involving the heavier group 13 elements to prepare com-

(1) Cowley, A. H.; Jones, R. A. *Angew. Chem., Intl. Ed. Engl.* 1989, 28, 1208.

(2) Cole-Hamilton, D. J. *Chem. Brit.* 1991, 852.