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Titanium NMR Data for Titanium Half-Sandwich Complexes Bearing Substituted Cyclopentadienyl Ligands

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Summary: Titanium NMR spectroscopic data for a series of trichlorotitanium complexes bearing a cyclopentadienyl ligand substituted with tert-butyl and/or trimethylsilyl groups have been collected. According to chemical shift values a weak electron-donating effect of trimethylsilyl groups is implied, whereas the line widths reflect the symmetry of the five-membered ring's substitution pattern.

In the context of understanding factors influencing the stereoselectivity of a class of cyclopentadienyldialkoxyallyltitanium complexes in enantioselective allylation of aldehydes, ^{49}Ti NMR spectroscopy was recently shown to be an effective method for probing the electronic environment at the titanium center.[1] Whereas chemical shift values for both ^{47}Ti and ^{49}Ti resonances display similar values for a series of related complexes, the line widths $\Delta\nu_{1/2}$ were found to reflect the (sterically induced) electronic asymmetry around the titanium atom.[2] The line width was interpreted as a qualitative, yet useful measure for the enantio-face-discrimination capability of a chiral titanium center. In addition, it was noted that substituents on the cyclopentadienyl ligand have a rather significant effect on the $\Delta\nu_{1/2}$ values.[1a] We present here titanium NMR spectroscopic data for a more extensive series of titanium half-sandwich complexes with sterically demanding ring substituents.[3]

Results and Discussion

Table I summarizes ^{47}Ti and ^{49}Ti chemical shifts and line widths measured for 0.4 M solutions of [η^5-C_5H_3-$(CMe_3)_2$-1,3]$TiCl_3$, [η^5-$C_5H_3(CMe_3)$-3-$(SiMe_3)$-1]$TiCl_3$, [η^5-$C_5H_5(SiMe_3)_2$-1,3]$TiCl_3$,[4] [η^5-$C_5H_3(SiMe_3)_3$-1,2,4]$TiCl_3$,[5] and [η^5-$C_5H_3(CMe_3)$-4-$(SiMe_3)_2$-1,2]$TiCl_3$[5] in $CDCl_3$ at 320 K along with previously published data[1a] for (η^5-C_5H_5)-$TiCl_3$, (η^5-C_5H_4Me)$TiCl_3$, (η^5-$C_5H_4SiMe_3$)$TiCl_3$, and (η^5-C_5Me_5)$TiCl_3$.

Table I. ^{49}Ti and ^{47}Ti NMR Chemical Shifts and Line Widths of Trichloro(η^5-cyclopentadienyl)titanium Complexes

compd[a]	δ^{49}Ti (ppm)[b]	$\Delta\nu_{1/2}(^{49}$Ti) (Hz)[c]	δ^{47}Ti (ppm)[b]	$\Delta\nu_{1/2}(^{49}$Ti) (Hz)[c]	λ_{max} (nm)[d]
$TiCl_4$	0	4 ± 0.5	0	11 ± 2.0	
$CpTiCl_3$	−390	60 ± 5.0	−390	160 ± 8.0	380
$Cp'TiCl_3$	−332	30 ± 2.5	−332	90 ± 5.0	395
$(SiCp)TiCl_3$	−361	70 ± 5.0	−361	190 ± 8.0	395
$(Si_2Cp)TiCl_3$	−332	20 ± 2.0	−332	75 ± 7.0	400
$(BuSiCp)TiCl_3$	−306	80 ± 5.0	−306	230 ± 10.0	415
$(Bu_2Cp)TiCl_3$	−280	20 ± 2.0	−280	55 ± 4.0	425
$(Si_3Cp)TiCl_3$	−298	35 ± 3.0	−298	100 ± 5.0	415
$(BuSi_2Cp)TiCl_3$	−271	45 ± 3.5	−271	140 ± 7.0	418
Cp^*TiCl_3	−85	10 ± 2.0	−85	27 ± 3.0	437

[a] Cp = η^5-C_5H_5; Cp′ = η^5-C_5H_4Me; SiCp = $C_5H_4(SiMe_3)$; Si_2Cp = $C_5H_3(SiMe_3)_2$-1,3; Bu_2Cp = $C_5H_3(CMe_3)_2$-1,3; BuSiCp = $C_5H_3(CMe_3)$-3-$(SiMe_3)$-1; Si_3Cp = $C_5H_3(SiMe_3)_3$-1,2,4; $BuSi_2Cp$ = $C_5H_3(CMe_3)$-4-$(SiMe_3)_2$-1,2; Cp* = η^5-C_5Me_5. [b] ^{49}Ti and ^{47}Ti chemical shifts (error ± 1.0 ppm) are given relative to external $^{49}TiCl_4$ and $^{47}TiCl_4$, respectively. [c] Mean values and standard deviations of three independent measurements. [d] In $CHCl_3$.

Since chemical shifts are dominated by the paramagnetic shielding constant,[6] they cannot always be directly related to the ground-state charge density at a given nucleus. However, as first investigated by McGlinchey et al.[7a] for a series of titanocene dihalides, there is an inverse relationship between the titanium NMR shifts and the electronegativity of the halide ligands at titanium ("inverse halogen dependence"[7]). Gassman et al. later extended this peculiar finding to the effect of ring-methylation in titanocene dihalide complexes and established an inverse correlation between ^{49}Ti chemical shift and X-ray photoelectron binding energy for Ti($2p_{3/2}$).[8] In line with these and subsequent[9] reports the significant electron-donating influence of methyl and *tert*-butyl groups can clearly be detected from the downfield shift of titanium resonances upon introducing these substituents on the cyclopentadienyl ligand. There is a similarly consistent trend with regard to the effect of a trimethylsilyl group, but the absolute shift difference is comparably smaller. Likewise, the absorption maxima in the electronic spectra recorded in $CHCl_3$ are bathochromically shifted with increasing

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[1] (a) Hafner, A.; Duthaler, R. O.; Marti, R.; Rihs, G.; Rothe-Streit, P.; Schwarzenbach, F. *J. Am. Chem. Soc.* **1992**, *114*, 2321. (b) Duthaler, R. O.; Hafner, A.; Riediker, M. In *Organic Synthesis via Organometallics*; Dötz, K. H., Hofmann, R. W., Eds.; Vieweg: Braunschweig, Germany, 1991; p 285. (c) Duthaler, R. O.; Hafner, A. *Chem. Rev.* **1992**, *92*, 807.

[2] The line widths provide direct information about the symmetry of the electron distribution around the metal: Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pittman Books Ltd.: London, 1983.

[3] Okuda, J. *Top. Curr. Chem.* **1991**, *160*, 97. Janiak, C., Schumann, H. *Adv. Organomet. Chem.* **1991**, *33*, 291.

[4] (a) Jutzi, P.; Kuhn, M. *J. Organomet. Chem.* **1979**, *173*, 221. (b) Winter, C. H.; Zhou, X.-X.; Dobbs, D. A.; Heeg, M. J. *Organometallics* **1991**, *10*, 210.

[5] Okuda, J.; Herdtweck, E. *Inorg. Chem.* **1991**, *30*, 1516.

[6] *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983. A series of ring-substituted cobalt half-sandwich complexes have been studied by ^{59}Co NMR spectroscopy: Benn, R.; Cibura, K.; Hofmann, P.; Jonas, K.; Rufinska, A. *Organometallics* **1985**, *4*, 2214.

[7] (a) Hao, N.; Sayer, B. G.; Dénès, G.; Bickley, D. G.; McGlinchey, M. J. *J. Magn. Reson.* **1982**, *50*, 50. (b) Kidd, R. G.; Mathews, R. W.; Spinney, H. G. *J. Am. Chem. Soc.* **1972**, *94*, 6686. (c) Kidd, R. G. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: New York, 1980; Vol. 10a, p 12.

[8] Gassman, P. G.; Campbell, W. H.; Macomber, D. W. *Organometallics* **1984**, *3*, 385.

[9] (a) Dormond, A.; Fauconet, M.; Leblanc, J. C.; Moise, C. *Polyhedron* **1984**, *3*, 897. (b) McGlinchey, M. J.; Bickley, D. G. *Polyhedron* **1985**, *4*, 1147. (c) Finch, W. C.; Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2406.

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number of substituents, but the increment for the trimethylsilyl group is again smaller than that for the *tert*-butyl group. For a series of ferrocene derivatives with the same set of substituted cyclopentadienyl ligands,[10] a similar trend was observed for electrochemical, UV/vis, and Mössbauer spectroscopic data. Interestingly, it was recently reported that trimethylsilyl groups in ring-substituted metallocene dihalides of zirconium and hafnium are *more* electron-donating than methyl groups, when binding energy values of the inner-shell electron of the metal center, as determined by X-ray photoelectron spectroscopy, are examined.[11] These observations appear to be in agreement with the literature evidence that the electron-donating effect of a trimethylsilyl group may vary depending on the system under consideration.[12]

On inspection of the line width values $\Delta\nu_{1/2}$ for both ^{47}Ti and ^{49}Ti, a correlation with the symmetry of the substitution pattern can be recognized. Thus, (η^5-C_5Me_5)$TiCl_3$ with a permethylated five-membered ring exhibit the lowest value in the series, whereas derivatives having an apparently more unsymmetrical substitution pattern of the cyclopentadienyl ligand show higher values. Most strikingly, [η^5-$C_5H_3(CMe_3)$-3-$(SiMe_3)$-1]$TiCl_3$ reveals the highest value, whereas electronically related symmetrical complexes with the $C_5H_3(CMe_3)_2$-1,3 and $C_5H_3(SiMe_3)_2$-1,3 ligands give rise to significantly smaller line widths. The noticeably exceptionally high value for the parent compound (η^5-C_5H_5)$TiCl_3$ appears to be due to the ligand field effect that influences the line widths.[13]

Despite the scarcity of reports on titanium NMR spectroscopic data[7-9,14] the above observations suggest that line widths of titanium NMR resonances are fairly responsive to even peripheral substituent effects of the ancillary ligand. These data therefore serve as a useful tool for assessing the electron distribution around the titanium center in a series of structurally analogous complexes.

Experimental Section

^{47}Ti and ^{49}Ti NMR spectra at 22.571 and 22.577 MHz, respectively, were measured on a Bruker AM-400 spectrometer with a 10-mm diameter broad-band probe (20–100 MHz). All samples were measured as 0.4 M solutions in 10-mm tubes sealed under argon in $CDCl_3$ at 320 ± 1 K. To suppress acoustic ringing and (if necessary) the overlapping ^{47}Ti signal, a preacquisition delay of 140 μs was used. Errors in line widths and chemical shifts due to temperature differences were avoided by not using ^{1}H decoupling. To optimize the accuracy of peak positions, spectra were Gaussian-broadened between one-fifth and one-tenth of their natural line widths. Chemical shifts were recorded on the δ scale relative to external $TiCl_4$. [η^5-$C_5H_3(SiMe_3)_2$-1,3]$TiCl_3$,[4a] [η^5-$C_5H_3(SiMe_3)_3$-1,2,4]$TiCl_3$,[5] and [η^5-$C_5H_3(CMe_3)$-4-$(SiMe_3)_2$-1,2]$TiCl_3$[5] were prepared according to literature procedures.

(η^5-1,3-Di-*tert*-butylcyclopentadienyl)trichlorotitanium. This compound was synthesized by treating $TiCl_4$ with 1,3-di-*tert*-butyl-1-(trimethylsilyl)cyclopentadiene[16] analogously to a procedure described for [η^5-$C_5H_3(SiMe_3)_2$-1,3]$TiCl_3$.[4a] Orange red crystals were isolated in 75% yield; mp 140 °C. ^{1}H NMR (C_6D_6): δ 1.11 (s, 18 H, CH_3), 6.23 [d, ^4J(H,H) = 2.4 Hz, 2 H, C_5H_2], 6.65 [t, ^4J(H,H) = 2.4 Hz, 1 H, C_5H]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 30.58 (CCH_3), 30.65 (CCH_3), 118.49, 119.56, 157.15 (ring C). IR (KBr): ν 3114 (m), 3094 (w), 2969 (s), 2908 (m), 2875 (m), 2867 (w), 1493 (m), 1465 (m), 1432 (m), 1372 (m), 1362 (m), 1251 (s), 1173 (ms), 1065 (m), 930 (m), 892 (w), 849 (vs), 770 (m), 682 (w), 666 (mw), 474 (mw), 437 (mw), 406 (mw) cm^{-1}. EI MS (70 eV): *m/z* (%) 330 (8, M^+), 315 (20, $M^+ - Me$), 279 (40, $M^+ - Me - Cl$), 57 (100, $C_4H_9^+$). Anal. Calcd for $C_{13}H_{21}Cl_3Ti$: C, 47.09; H, 6.38; Cl, 32.08. Found: C, 47.09; H, 6.37; Cl, 32.13.

(η^5-3-*tert*-Butyl-1-(trimethylsilyl)cyclopentadienyl)trichlorotitanium. Orange crystals were obtained in 80% yield following an procedure analogous to that above by using 3-*tert*-butyl-1,1-bis(trimethylsilyl)cyclopentadiene;[15] mp 104 °C. ^{1}H NMR (C_6D_6): δ 0.21 (s, 9 H, $SiCH_3$), 1.12 (s, 9 H, CCH_3), 6.46, 6.53, 6.93 (s br, 1 H, ring H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −0.69 ($SiCH_3$), 30.75 (CCH_3), 34.24 (CCH_3), 126.44, 123.73, 128.86, 143.93, 159.63 (ring C). IR (KBr): ν 3091 (m), 2960 (m), 2934 (w), 2904 (w), 2872 (w), 1486 (m), 1250 (s), 1183 (ms), 1088 (ms), 907 (m), 840 (vs), 758 (m), 454 (mw) cm^{-1}. CI MS: *m/z* (%) 348 (2, M^+), 333 (58, $M^+ - CH_3$), 311 (100, $M^+ - Cl$). Anal. Calcd for $C_{12}H_{21}Cl_3SiTi$: C, 41.46; H, 6.09; Cl, 30.59. Found: C, 41.37; H, 6.00; Cl, 30.20.

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(10) Okuda, J.; Albach, R. W.; Herdtweck, E.; Wagner, F. E. *Polyhedron* **1991**, *10*, 1741.

(11) Gassman, P. G.; Deck, P. A.; Winter, C. H.; Dobbs, D. A.; Cao, D. H. *Organometallics* **1992**, *11*, 959.

(12) Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 893.

(13) (a) Reference 9a reports slightly smaller (incorrectly assigned, cf. ref 9b) $\Delta\nu_{1/2}$ values: 36 Hz (^{49}Ti), 80 Hz (^{47}Ti). The previously reported chemical shifts for $CpTiCl_3$ and Cp^*TiCl_3 are comparable.[8,9] (b) Sayer, B. G.; Hao, N.; Dénès, G.; Bickley, D. G.; McGlinchey, M. J. *Inorg. Chim. Acta* **1981**, *48*, 53.

(14) (a) Chi, K. M.; Frerichs, S. R.; Philson, S. B.; Ellis, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 303. (b) Traill, P. R.; Young, C. G. *J. Magn. Reson.* **1990**, *90*, 551. (c) Berger, S.; Bock, W.; Marth, C. F.; Raguse, B.; Reetz, M. T. *Magn. Reson. Chem.* **1990**, *28*, 559.

(15) Okuda, J. *Chem. Ber.* **1989**, *122*, 1075.

(16) Abu-Orabi, S. T.; Jutzi, P. *J. Organomet. Chem.* **1987**, *329*, 169.