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Homoleptic and Heteroleptic Gallium(III) Compounds Containing Monosubstituted Cyclopentadienyl Ligands: $Ga(C_5H_4Me)_3$, $Ga(C_5H_4SiMe_3)_3$ and $R_2Ga(C_5H_4Me)$ (R = Me, Et).

by

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Supporting Information

$Ga(C_5H_4Me)_3$: IR (neat, cm^{-1}): 3082 (sh, w), 3062 (m), 2961 (m), 2928 (sh, m), 2915 (m), 2885 (m), 2860 (m), 2730 (vw), 1775 (vw, br), 1621 (w, br), 1554 (sh,w), 1530 (w, br), 1442 (m, br), 1374 (m), 1353 (w), 1302 (w), 1227 (sh, w), 1209 (w), 1195 (sh, w), 1167 (w), 1070 (m), 1028 (w), 1013 (w), 988 (m), 965 (m), 918 (m), 883 (sh, m), 842 (vs), 828 (vs), 787 (vs), 751 (m), 724 (s), 654 (m, br), 605 (m), 521 (w), 402 (s), 353 (w), 311 (m).

$Ga(C_5H_4SiMe_3)_3$: IR (neat, cm^{-1}): 3910 (w), 3795 (w), 3730 (w), 3645 (w), 3170 (w), 3090 (m,sh), 3065 (m), 2960 (vs), 2900 (s), 2795 (w, sh), 2655 (vw), 2485 (vw), 2090 (vw), 2005 (vw), 1935 (vw), 1875 (vw), 1800 (vw, br), 1630 (w), 1550 (w), 1525 (w), 1490 (w), 1460 (m, sh), 1440 (m), 1415 (m, sh), 1405 (m), 1360 (w), 1345 (m), 1320 (w), 1250 (vs), 1210 (m), 1145 (m), 1120 (m, sh), 1105 (m), 1075 (s), 1035 (m), 985 (vs), 960 (m,sh), 895 (vs), 830 (vs, br), 750 (vs), 730 (vs, sh), 690 (s), 645 (s, sh), 625 (vs), 605 (m, sh), 595 (m, sh), 535 (m, sh), 490 (w), 465 (w), 410 (vs), 305 (m).

$Me_2Ga(C_5H_4Me)$: ^1H NMR (C_6D_{12}, δ): 5.94 (s, 1.1, ring-H), 5.87 (s, 1.1, ring-H), 2.13 (s, 3.0, ring-CH_3), -0.33 (s–br, 5.3, Me_3Ga/Me_2GaCp), -1.11 (s, 0.2, $MeGaCp_2$); (d_8-Tol, δ): 5.94 (s, 1.2, ring-H), 5.77 (s, 1.3, ring-H), 2.09 (s, 3.0, ring-CH_3), -0.44

(s–br, 7.5, $\underline{Me}_3Ga/\underline{Me}_2GaCp$), -1.07 (s, 0.5, $\underline{Me}GaCp_2$); ($CDCl_3$, δ): 6.02 (s, 1.1, ring-$\underline{H}$), 5.98 (s, 1.0, ring-$\underline{H}$), 2.16 (s, 3.0, ring-$C\underline{H}_3$), -0.26 (s–br, 6.4, $\underline{Me}_3Ga/\underline{Me}_2GaCp$); ($CD_2Cl_2$, δ): 6.08 (s, 1.2, ring-$\underline{H}$), 5.95 (t, 1.0, ring-$\underline{H}$), 2.15 (s, 3.0, ring-CH_3), -0.30 (s–br, 5.6, $\underline{Me}_3Ga/\underline{Me}_2GaCp$), -1.12 (s, 0.3, $\underline{Me}GaCp_2$). IR (Nujol mull, cm^{-1}): 3033 (m), 2713 (w), 1238 (w), 1192 (m), 1184 (sh, m), 1150 (sh, vw), 1098 (vw), 1069 (vw), 1020 (sh, w), 996 (m), 967 (w), 922 (w), 870 (sh, w), 838 (sh, m), 789 (vs), 755 (s, br), 719 (s), 611 (m), 588 (m), 575 (sh, m), 530 (m), 373 (m), 352 (w), 307 (w).

$Et_2Ga(C_5H_4Me)$: ^1H NMR (d_8-Tol, δ): 6.01 (s, 1.2, ring-$\underline{H}$), 5.86 (t, 1.2, ring-$\underline{H}$)), 2.13 (s, 3.0, ring-$C\underline{H}_3$), 1.04 (s–br, 8.2, Et_3Ga/Et_2GaCp-$C\underline{H}_3$), 0.82 (t, 0.5, $EtGaCp_2$-$C\underline{H}_3$), 0.25 (s-br, 6.0, Et_3Ga/Et_2GaCp-$C\underline{H}_2$), -0.22 (q, 0.3, $EtGaCp_2$-$C\underline{H}_2$); (d_8-Tol, δ, -50 °C): 6.01 (s, ring-$\underline{H}$), 5.90 (s, ring-$\underline{H}$), 2.13 (s, ring-$C\underline{H}_3$), 1.01 (s–br, Et_3Ga/Et_2GaCp-$C\underline{H}_3$), 0.62 (t, $EtGaCp_2$ -$C\underline{H}_3$), 0.13 (s–br, Et_3Ga/Et_2GaCp-$C\underline{H}_2$); ($CDCl_3$, δ): 6.10 (s, 1.2, ring-$\underline{H}$), 6.05 (t, 1.2, ring-$\underline{H}$), 2.20 (s, 3.0, ring-$C\underline{H}_3$), 1.08 (t, 6.3, Et_2GaCp-$C\underline{H}_3$), 0.38 (s–br, 3.9, Et_2GaCp-$C\underline{H}_2$); (C_6D_{12}, δ): 6.00 (s, 1.3, ring-$\underline{H}$), 5.94 (t, 1.3, ring-$\underline{H}$), 2.15 (s, 3.0, ring-$C\underline{H}_3$), 1.17 (t, 0.1, $GaEt_3$ -$C\underline{H}_3$), 1.07 (t, 6.0, Et_2GaCp'-$C\underline{H}_3$), 0.89 (t, -,$EtGaCp_2$-$C\underline{H}_3$), 0.55 (q, -, $GaEt_3$-$C\underline{H}_2$), 0.35 (s–br, 3.7, Et_2GaCp-$C\underline{H}_2$), -0.21 (s–br, -,$EtGaCp_2$-$C\underline{H}_2$). IR (neat, cm^{-1}): 3031 (w), 2919 (vs), 2900 (s), 2882 (vs), 2805 (w), 2713 (w), 1595 (w, br), 1524 (w), 1457 (m), 1412 (m), 1369 (m), 1328 (w), 1228 (w), 1216 (sh, w), 1183 (w), 1085 (vw), 1020 (sh, w), 995 (s), 957 (w), 928 (w), 890 (sh, w), 870 (w), 840 (m), 792 (vs), 731 (m), 646 (sh, m), 621 (sh, s), 612 (s), 595 (sh, m), 503 (m), 370 (m), 354 (m), 310 (m).

Note: Multiple, exceedingly closely spaced lines, possibly due to fine splitting, were observed frequently for the cyclopentadienyl ring protons in the ^1H NMR spectra (400 MHz) of pure samples of $Me_2Ga(C_5H_4Me)$ and $Et_2Ga(C_5H_4Me)$ in d_8-THF and $Ga(C_5H_4Me)_3{\bullet}NMe_3$ in C_6D_6.