Appendix J

# Supplemental Data for Table 13-4. Supraicosahedral Transition Element Metallacarboranes

| Compound[a] | Information[b] | References |
|---|---|---|
| **Synthesis and Characterization** | | |
| **Yttrium** | | |
| ***13-vertex $YC_2B_{10}$ clusters*** | | |
| $Cp(THF)\mathbf{Y}\{C_6H_4(CH_2)_2]C_2B_{10}H_{10}\}$ | S, H, B, C, IR | [1294] |
| $ClL_3\mathbf{Y}[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]$ **Y**—N L = THF, MeCN | S, X(MeCN), H, B, C, IR | [544] |
| $\{(THF)\mathbf{Y}[(Me_2NCH_2CH_2)C_2B_{10}H_{11}]Na(THF)_2\}_n$ **Y**—N | S, X, H, B, C, IR | [1297] |
| $\{\mathbf{Y}[(Me_2NCH_2CH_2)C_2B_{10}H_{10}]Na(MeCN)_2\}_n$ | S, X, H, B, C, IR | [1297] |
| Other $\mathbf{Y}C_2B_{10}$ clusters | S, X, H, B, C, IR | [1293,1295,1297] |
| **Lanthanide and Actinide Metals** | | |
| ***13-vertex $LnC_2B_{10}$ clusters*** | | |
| $[(THF)\mathbf{Er}[(1\text{-}C_9H_6)(\eta^7\text{-}C_2B_{10}H_{11})]_2(\mu\text{-}BH_4)^-$ | S, X, H, IR | [1298] |
| $[(THF)\mathbf{Er}[(1\text{-}C_9H_6)(\eta^7-C_2B_{10}H_{11})]_2{}^{4-}\ Na_4(THF)_6{}^{4+}$ | S, X, H, IR | [1298] |
| $HB(\mu\text{-}H)_3(THF)_3\mathbf{Nd}\{[C_6H_4(CH_2)_2]C_2B_{10}H_{10}\}$ | S, X, H, B, C, IR | [1294] |
| $(THF)_2(C_5H_4\text{-}CMe_2{}^-)\mathbf{Er}(C_2B_{10}H_{11})$ | S | [1300] |
| $[(C_5H_4\text{-}CMe_2{}^-)\mathbf{Er}\ (\eta^7-C_2B_{10}H_{11})]_2{}^{4-}(THF)_9{}^{4+}$ | S, X | [1300] |
| $[(C_5H_4\text{-}CMe_2{}^-)\mathbf{Er}\ (\eta^7\text{-}C_2B_{10}H_{11})\mathbf{Er}(\mu\text{-}Cl)(THF)_3]_2$ | S, X | [1300] |
| $(THF)_2\mathbf{Ln}(C_5H_4\text{-}CMe_2)(\eta^7\text{-}C_2B_{10}H_{11})$ **Ln** = **Er**, **Sm** | S, H, B, C, IR | [1301] |
| $\mathbf{Ln}_2[(PhCH_2)_2(C_2B_{10}H_{10})]_4Na_4$ **Ln** = **Sm**, **Yb** | S, H, B, C, IR, MS | [1302] |
| $(THF)_2(\eta^5\text{-}C_9H_6{}^-)\mathbf{Sm}(\text{-}SiMe_2\text{-}C_2B_{10}H_{11})$ $C_9H_6$ = indenyl | S, X, H, B, C, IR | [1304] |
| $[(MeCN)_3\mathbf{Eu}(C_2B_{10}H_{10})]_n$ polymer | S | [1307] |
| $[L_3\mathbf{Eu}(C_2B_{10}H_{12})]_n$ L = THF, MeCN polymer | S, X(MeCN), H, B, IR | [1306] |
| $[(C_5H_4CMe_2{}^-)\mathbf{Ln}(\eta^7-C_2B_{10}H_{11})]_2{}^{4-}\ (Na^+)_4(THF)_9$ **Ln** = **Er**, **Dy** | S, X, H, B, C, IR | [1301] |
| $\{[(MeO(CH_2)_2)_2C_2B_{10}H_{10}]\mathbf{Er}\}_2{}^{2-}$ | S, X, H, B, C, IR | [1295] |

*Continued*

| Compound | Information | References |
|---|---|---|
| {(THF)**Er**[$\eta^7$-$(PhCH_2)_2C_2B_{10}H_{10}$)]}$_2$[Li(THF)$_4$]$_2$ | S, X, H, B, C, IR | [1293] |
| [(THF)[ClNa(THF)$_2$]**Er**{[$(C_9H_6)Me_2Si$]$C_2B_{10}H_{11}$}]$_n$ indenyl | S, X, H, B, C, IR | [1296] |
| {(THF)**Er**[$(ArCH_2)_2$]$C_2B_{10}H_{10}$]}$_2$Na$_2$(THF)$_6$ Ar = $C_6H_4(OMe)_2$, pyrenyl | S, X, H, B, C, IR | [1296] |
| {(THF)**Er**[$(Me_2NCH_2CH_2)C_2B_{10}H_{11}$]Na(THF)$_3$}$_2$ | S, X, H, B, C, IR | [1297] |
| $(NC_5H_5)_3$**Yb** {1,2-[$(C_6H_4(CH_2)_2]C_2B_{10}H_{10}$} {Na$(NC_5H_5)_2]_{0.5}$}$_2$(μ-Cl) | S, X, H, B, C, IR | [1294] |
| Other **Ln**$C_2B_{10}$ clusters | | [1301] |
| **Zirconium** | | |
| ***13-vertex closo-ZrC$_2$B$_{10}$ clusters*** | | |
| 1,2,4-(THF)Cl**Zr**[$(RNSiMe_2)C_2B_{10}H_{11}$] N—M | S, H, B, C, IR | [1311] |
| {Na$_3$(THF)$_4$(Et$_2$N)$_2$**Zr**[$(C_5H_4$-$SiMe_2)C_2B_{10}H_{11}$]}$_n$ | S, X, H, B, C, IR | [1312] |
| {[o-$C_6H_4(CH_2)_2C_2B_{10}H_{10}]_2$**Zr**Cl$_2$}$^{2-}$ [Na(THF)$_3$ $^+$]$_2$ | S, X, H, B, C, IR | [1313] |
| (μ-Cl)**Zr**[$(Me_2NCH_2CH_2)(RCH_2CH_2)C_2B_{10}H_{10}$] Zr—O, Zr—N R = MeO, $Me_2N$ | S, X, H, B, C, IR | [1314] |
| **Molybdenum** | | |
| ***13-vertex MoC$_2$B$_{10}$ clusters*** | | |
| 4,1,6-(*n*-$C_3H_5$)(CO)$_2$**Mo**$(C_2B_{10}H_{12})_2^-$ | S(insertion into $RhSB_9$), X, H, B | [1318] |
| (μ-$MeC_6H_4C$)(CO)$_2$Cp*Co═**Mo**$(Me_2C_2B_{10}H_{10})^-$ | S, H, C, IR | [641] |
| (Ph$_3$P)Au(μ-$MeC_6H_4C$)(CO)$_2$Cp*Co**Mo**$(Me_2C_2B_{10}H_{10})$ | S, H, C, IR | [641] |
| (μ-$MeC_6H_4C$)(CO)$_2$($C_4Me_4$)Co═**Mo**$(Me_2C_2B_{10}H_{10})$ | S, X, H, B, C, IR | [641] |
| 1,2,4-(CO)$_3$**Mo**$(Me_2C_2B_{10}H_{10})^-$ | S, H, B, C, IR | [1319] |
| 1,2,4-$(C_8H_{12})_2Pt_2$(CO)$_3$**Mo**$(Me_2C_2B_{10}H_{10})$ | S, H, B, C, IR | [1319] |
| 1,2,4-$(C_8H_{12})_2Pt_2$(CO)$_3$**W**$(Me_2C_2B_{10}H_{10})$ | S, H, B, C, P, IR | [1319] |
| 1,2,4-$(Me_3P)_2CpPt_2W$(μ-$CC_6H_4Me$)(CO)$_5$**Mo**-$(Me_2C_2B_{10}H_8$-12-OC) | S, X, H, B, C, P, IR | [1319] |
| ($\eta^3$-$C_3H_5$)(CO)$_2$**Mo**(7,9-$Me_2C_2B_{10}H_{10})^-$ | S, H, B, C, IR | [1320] |
| **Tungsten** | | |
| ***13-vertex WC$_2$B$_{10}$ clusters*** | | |
| (CO)$_3$**W**$(C_2B_{10}H_{12})_2^-$ | S, H, B, IR | [730] |
| ($\eta^1$-$C_3H_5$)(CO)$_3$**W**(7,9-$Me_2C_2B_{10}H_{10})^-$ | S, H, IR | [1320] |
| ($\eta^3$-$C_3H_5$)(CO)$_2$**W**(7,9-$Me_2C_2B_{10}H_{10})^-$ | S, H, B, C, IR | [1320] |
| ($\eta^7$-$C_7H_7$)Mo(μ-$MeC_6H_4C$)(CO)$_2$**W**$(Me_2C_2B_{10}H_{10})$ | S, H, B, C, IR | [621] |
| (μ-$MeC_6H_4C$)(CO)$_2$Cp*Co═**W**$(Me_2C_2B_{10}H_{10})^-$ | S, H, C, IR | [641] |
| (μ-$MeC_6H_4C$)(CO)$_2$Cp*Co═**W**$(Me_2C_2B_{10}H_9)$ (Co–B linked) | S, H, B, C, IR | [641] |
| (μ-$MeC_6H_4C$)(CO)$_2$($C_4Me_4$)Co═**W**$(Me_2C_2B_{10}H_{10})$ | S, H, B, C, IR | [641] |
| LL′Pt═**W**(CO)$_3$$(Me_2C_2B_{10}H_{10})$ L = $Ph_3P$, $Et_3P$; L′ = $Ph_3P$, CO | S, H, B, C, P, IR | [600] |
| (Ph$_3$P)(CO)Pt═**W**(CO)$_3$$(Me_2C_2B_{10}H_9)^-$ Pt—B linked | S, H, B, C, P, IR | [600] |
| 1,2,4-$(C_8H_{12})_2Pt_2$(CO)$_3$**W**$(Me_2C_2B_{10}H_{10})$ | S, H, B, C,IR | [1319] |

| Compound | Information | References |
|---|---|---|
| μ-($Ph_3P$)Au-μ-RC-$(CO)_2$**W**($Me_2C_2B_{10}H_{10}$) R = $MeC_6H_4$, $Me_2C_6H_3$ | S, H, C, IR | [1321] |
| μ-$(Ph_3P)_2$Rh-μ-RC-$(CO)_2$**W**($Me_2C_2B_{10}H_{10}$) R = $MeC_6H_4$, $Me_2C_6H_3$) | S, H, P, IR | [1321] |
| μ-$(CO)_2$Fe-μ-($Me_2C_6H_3C$)-$(CO)_2$**W**($Me_2C_2B_{10}H_{10}$)$^-$ | S, H, C, IR | [1321] |
| (μ-$Ph_3PAu$)(RC)$(CO)_2$**W**($Me_2C_2B_{10}H_{10}$) R = $MeC_6H_4$, $Me_2C_6H_3$ | S, H, C, P, IR | [1322] |
| (μ-CO)[$(Ph_3P)_2$Rh](μ-R)(CO)**W**($Me_2C_2B_{10}H_{10}$) R = $MeC_6H_4$, $Me_2C_6H_3$ | S, H, B, C, P, IR | [1322] |
| (μ-$MeC_6H_4C$)[$(CO)_6Fe_2$]$(CO)_2$**W**($Me_2C_2B_{10}H_{10}$)$^-$ | S, H, B, C, IR | [1322] |
| $(CO)_3$(RC)**W**(7,9-R′$_2C_2B_{10}H_{10}$)$^-$ R = $MeC_6H_4$, Me; R′ = H, Me | S, H, C, IR | [1323] |
| $(CO)_4$**W**(7,9-$Me_2C_2B_{10}H_9$-$CH_2C_6H_4Me$) | S, H, B, C, P, IR | [1323] |
| $(CO)_2$(PhC═CPh)**W**(7,9-$Me_2C_2B_{10}H_9$-$CH_2$R R = $C_6H_4Me$, Me | S, H, B, C, P, IR | [1323] |
| $(CO)_2L_2$**W**(7,9-$R_2C_2B_{10}H_{10}$) L = CO, $PPh_3$; R = H, Me | S, H, B, C, P, IR | [1323] |
| $(CO)_2$(PhC═CPh)**W**(7,9-$Me_2C_2B_{10}H_{10}$) | S, H, B, C, P, IR | [1323] |
| **Ruthenium** | | |
| ***13-vertex $RuC_2B_{10}$ clusters*** | | |
| 4,1,*n*-(*p*-$MeC_6H_4CHMe_2$)**Ru**($C_2B_{10}H_{12}$) *n* = 10, 12 | S, X, H, B, IR, MS | [1327] |
| 4,1,6-(*p*-$MeC_6H_4CHMe_2$)**Ru**($R_2C_2B_{10}H_{10}$) R = H, Ph | S, X, H, B, MS | [1328] |
| 4,1,11/4,1,10-(*p*-$MeC_6H_4CHMe_2$)**Ru**($Ph_2C_2B_{10}H_{10}$) | S, X, H, B | [1331] |
| 4,1,*n*-($MeC_6H_4$-$CMe_3$)**Ru**($MeC_2B_{10}H_{10}$) *n* = 2, 6, 12 | S, X, H, B, MS | [1599] |
| 4,1,*n*-($C_{10}H_8$)**Ru**($C_2B_{10}H_{12}$) *n* = 6, 8, 10, 12 | S, X, H, B, MS | [1480] |
| 1,2,*n*-($MeC_6H_4CHMe_2$)**Ru**{[$(Me_2Si(CH_2)_2]C_2B_{10}H_{10}$} *n* = 3, 8 | S{double desilylation of 1,2-[$Me_3Si(CH_2)_2$]$C_2B_{10}H_{10}$}, X, H, B, MS | [1602] |
| 4,1,2-($MeC_6H_4CHMe_2$)**Ru**{$Me[Me_3SiCH_2]C_2B_{10}H_{10}$} | S{double desilylation of 1,2-[$Me_3Si(CH_2)_2$]$C_2B_{10}H_{10}$}, X, H, B, MS | [1602] |
| **Cobalt** | | |
| ***13-vertex $CoC_2B_{10}$ clusters*** | | |
| Cp**Co**($C_2B_{10}H_{12}$) three isomers | S, E | [431] |
| **Co**$(C_2B_{10}H_{12})_2^-$ isomers; oxidation to $C_2B_{10}H_{12}$ isomers | | [1339,1340] |
| 1,2,3-Cp**Co**[$(NC)C_2B_{10}H_{11}$] | S, X, H, B, C, IR, MS | [797] |
| 4,1,2-Cp**Co**[$(CH_2)_3C_2B_{10}H_{10}$] henicosahedral | S, X, H, B, IR, MS | [1329] |
| μ-$Co(Et_3P)_2$-μ-$H_2$-1,2,4-($Et_3P$)**Co**($MeC_2B_{10}H_{10}$) | X | [1341] |
| 4,1,6-($F_3C$-$C_6F_3$-$C_5H_4$)**Co**($C_2B_{10}H_{10}$) | S, X, H, B, MS | [1549] |
| Cp**Co**[(*cyclo*-$CH_2C_6H_4C(O)$]$C_2B_{10}H_{10}$} | S, X, H, B, C, IR | [1479] |
| Cp**Co**[(*cyclo*-$CH_2C_6H_4C(OH)$]$C_2B_{10}H_{10}$} | S, X, H, B, C, IR | [1479] |
| ***13-vertex $CoC_4B_8$ clusters*** | | |
| H**Co**($Et_4C_4B_8H_7$)$_2$$(OMe_2)_2$ | S, H, B, IR, MS | [434] |
| **Co**($Et_4C_4B_8H_7$)$_2$(OH) 2 isomers | S, B, IR, MS | [434] |
| ($Et_2C_2B_4H_4$)**Co**($Et_4C_4B_8H_8$-$OC_4H_8$) | S, H, B(2d), IR, MS | [58] |
| ($Et_4C_4B_8H_8$)**Co**($Et_4C_4B_8H_7$-$OC_4H_8$) | S, IR, MS | [434] |

*Continued*

| Compound | Information | References |
|---|---|---|
| **Rhodium** | | |
| *13-vertex $RhC_2B_{10}$ clusters* | | |
| 4,1,6-($C_8H_{12}$)**Rh**($C_2B_{10}H_{10}$)-(μ-H)$_2$-$RhL_2$ L = $PPh_3$, 0.5 $C_8H_{12}$ | S, X, H, B, C, P | [1344] |
| 4,1,6-($C_8H_{12}$)**Rh**($C_2B_{10}H_9$)-(μ-H)$_3$-$RuCl(PPh_3)_2$ | S, X, H, B, C, P | [1344] |
| 4,1,6-($\eta^3$-$C_8H_{13}$)**Rh**($C_2B_{10}H_{11}$)-7-R R = H, $O(CH_2)_4$ | S, X, H, B, C, P | [1344] |
| **Nickel** | | |
| *13-vertex $NiC_2B_{10}$ clusters* | | |
| 1,2,4-($\eta^3$-$C_3H_5$)**Ni**($R_2C_2B_{10}H_{10}$) R = H, Me | S, X(Me), H, B, C | [1345] |
| 4,1,6-($Ph_2PCH_2CH_2PPh_2$)**Ni**($C_2B_{10}H_{12}$) | S, X, H, B, P | [1318] |
| 4,1,6-($\eta^3$-$C_3H_5$)**Ni**($R_2C_2B_{10}H_{10}$)-3,8-$Rh(PPh_3)_2$-3,8-(μ-H)$_2$ | S, X, H, B, C, P | [1181] |
| 4,1,6-($\eta^3$-$C_3H_5$)**Ni**($C_2B_{10}H_9$)-3,7,8-$RuCl(PPh_3)_2$-3,7,8-(μ-H)$_3$ | S, X, H, B, C, P | [1181] |

[a] *Transition metals and other heteroatoms (other than carbon) incorporated into the cluster framework are in* ***boldface****.*
[b] *S, synthesis; X, X-ray diffraction; H, $^1$H NMR; B, $^{11}$B NMR; C, $^{13}$C NMR; P, $^{31}$P NMR; 2d, two-dimensional (COSY) NMR; IR, infrared data; MS, mass spectroscopic data; UV, UV-visible data; E, electrochemical data; ESR, electron spin resonance data; MAG, magnetic susceptibility.*