**Experimental Details**

Time resolved IR spectra were obtained using a Bruker Vertex 80 FTIR equipped with step-scan and rapid-scan capabilities (2200-1800 $cm^{-1}$). Sample photolysis was conducted using the third harmonic (355 nm) of a Nd:YAG laser (Continuum Surelite I-10) operating at 1-10 Hz. A syringe pump was used to flow solution through a temperature controlled 0.5 mm pathlength IR cell with $CaF_2$ windows (Harrick Scientific) to ensure that a fresh solution was photolyzed with every shot of the laser. The temperature was monitored by a thermocouple located close to the photolysis solution and maintained by a water circulator to within ± 0.1 $^0$C. All spectra were obtained at 4 or 8 $cm^{-1}$ resolution.

Heptane solvent was of anhydrous grade (Aldrich) and > 99% purity. NMR spectra of triethylphosphite (Sigma-Aldrich, >98%) and borane triethylamine (Sigma-Aldrich, >97%) were obtained prior to the kinetic runs to rule out the presence of contaminants such as $OP(OEt)_3$ and free $NEt_3$. $BzCr(CO)_3$ (Strem) was used as received and $TpMn(CO)_3$ was synthesized according to a literature procedure.[1] The photolysis solution contained ≈ 1-3 mM of the parent metal tricarbonyl. All kinetic experiments were conducted under pseudo first-order conditions with the concentration of the incoming $P(OEt)_3$ ligand at least 10 times larger than that of the reactant complexes. The concentration of $H_3BNEt_3$ was held constant at either 0.27 M or 0.33 M during all kinetic runs. Observed rate constants ($k_{obs}$) were obtained from first order exponential fits to either the decay or growth of the reactant and product complexes, respectively, as a function of time. The errors in the reported rate constants and other kinetic parameters were obtained from least squares analysis of the data as implemented by the software program KaleidaGraph.

**Computational Details**

All calculations were performed in the development version of the Gaussian suite of programs using density functional theory.[2] Geometries were optimized using the wB97XD functional[3] which included the exact exchange in the long range and an empiric dispersion term. All atoms were described with the def2-TZVPP basis set,[4] while some elements in def2-TZVPP utilize effective core potentials, the elements considered in this study did not. The computed geometries were confirmed to be ground state structures according to their imaginary frequencies. If not stated otherwise, the energies reported in the text are enthalpies computed at 298.15 K and 1 atm, and are expressed in kcal/mol. Figures of computed geometries included in this work were rendered using CYLview.[5]

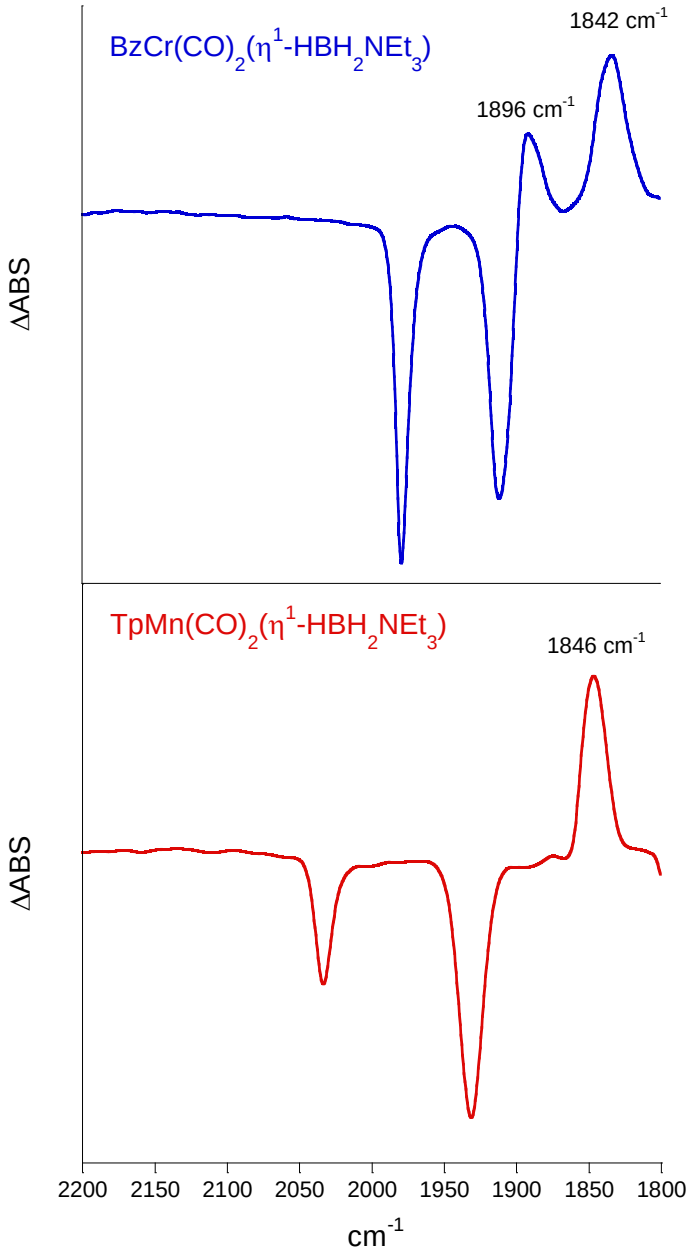


**Fig. S1**: Difference FTIR spectra obtained upon 355 nm photolysis of $BzCr(CO)_3$ (heptane solution) and $TpMn(CO)_3$ (toluene solution) in the presence of 0.26 M $H_3B{\cdot}NEt_3$ at 293 K. The second peak for the $TpMn(CO)_2(\eta^1\text{-}H_3B{\cdot}NEt_3)$ is obscured by the parent absorption at 1930 $cm^{-1}$.

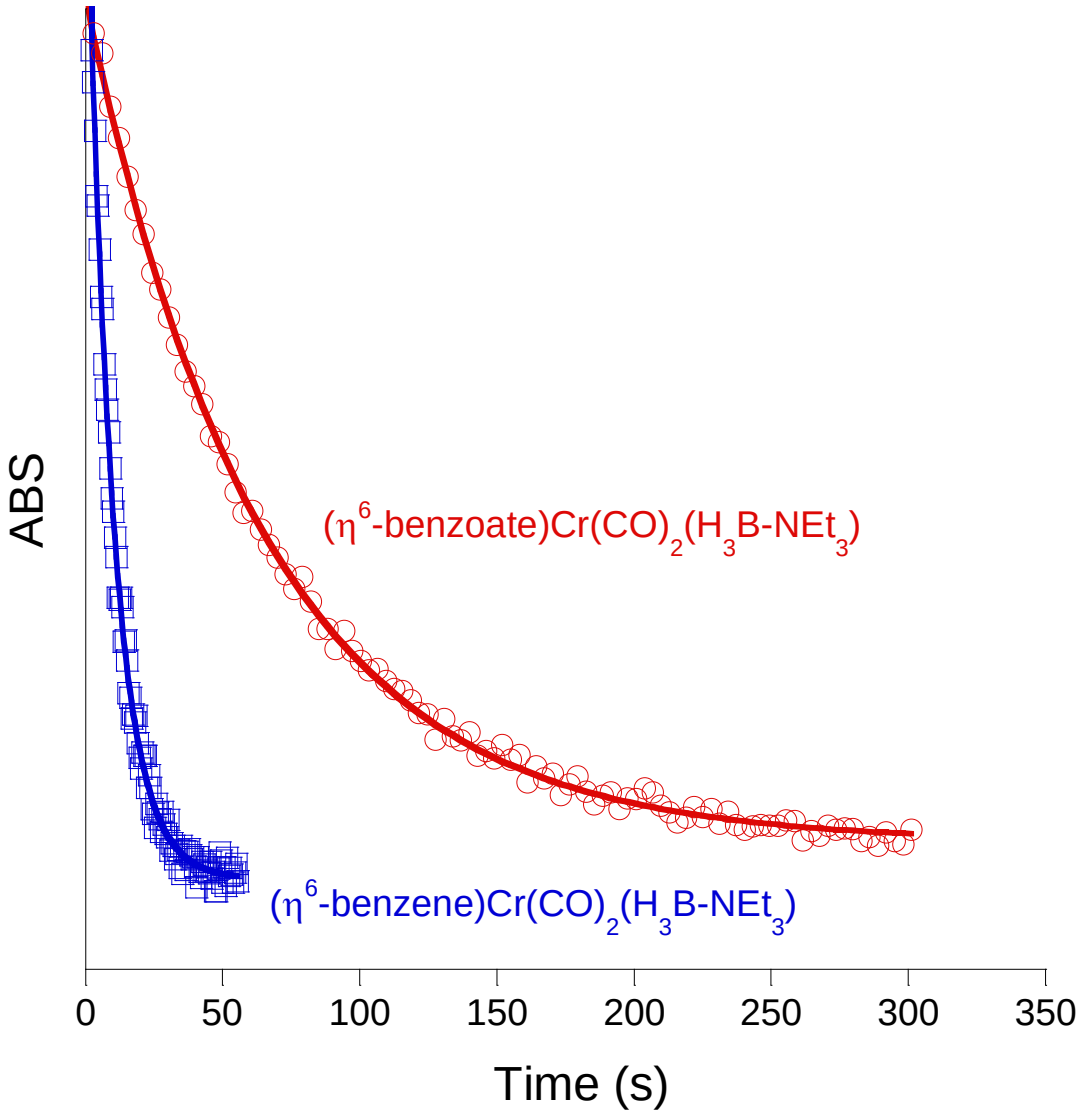


**Fig. S2**: Difference in reactivity between the $BzCr(CO)_2(\eta^1\text{-}H_3B{\cdot}NEt_3)$ and ($\eta^6$-methylbenzoate)$Cr(CO)_2(\eta^1\text{-}H_3B{\cdot}NEt_3)$ complexes under identical conditions of $[H_3B{\cdot}NEt_3]$ = 0.27M and $[P(OEt)_3]$ = 0.12M at 303 K.

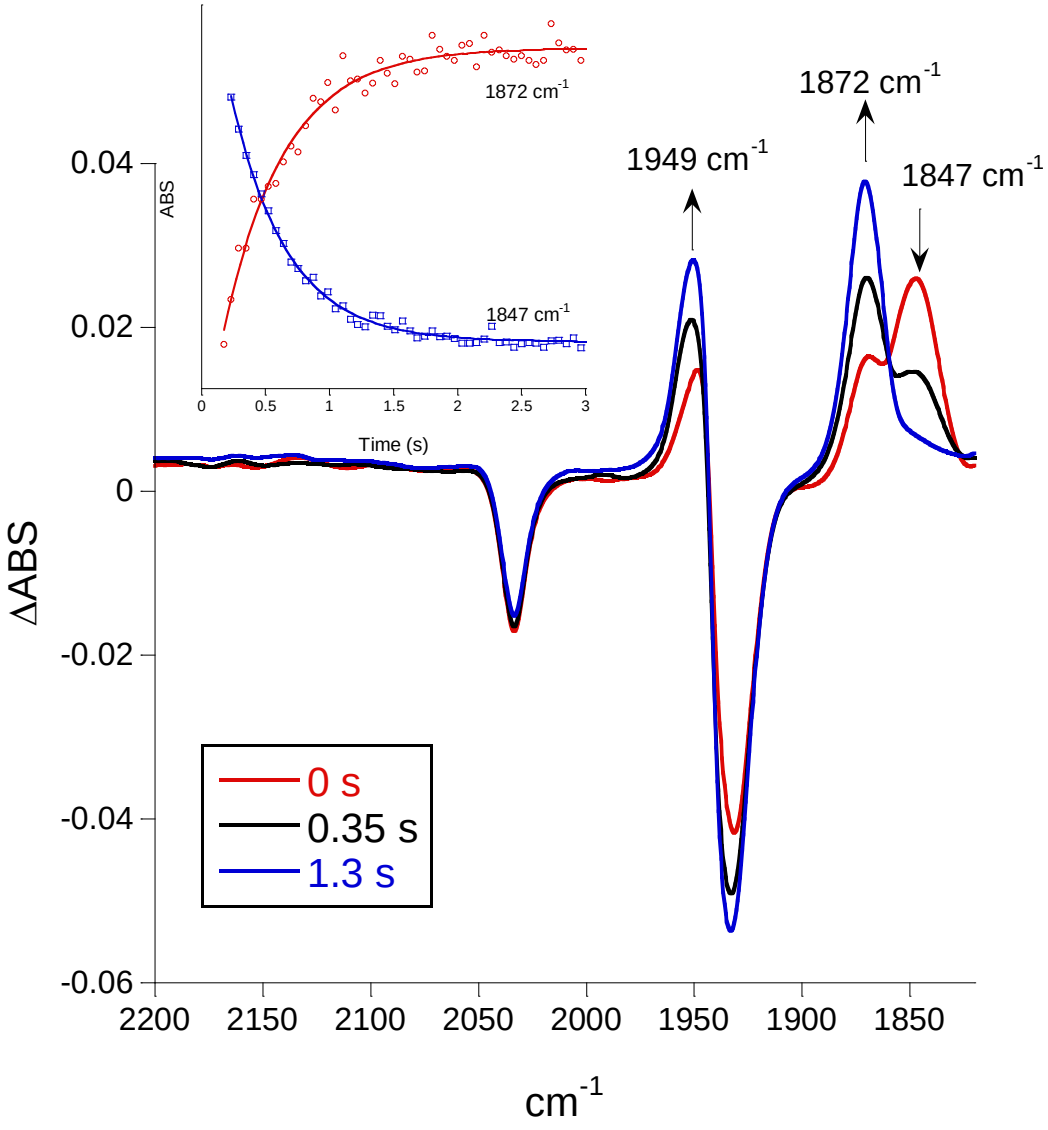


**Fig. S3:** Difference FTIR spectra obtained following 355 nm photolysis of a toluene solution containing 2 mM $TpMn(CO)_3$ with $[H_3B{\bullet}NEt_3]$ = 0.68M and $[P(OEt)_3]$ = 0.12M at 283K. The second CO absorption for **2** is obscured by the negative parent absorption band at 1930 $cm^{-1}$. The inset shows decay and growth of the reactant and product complexes, respectively.

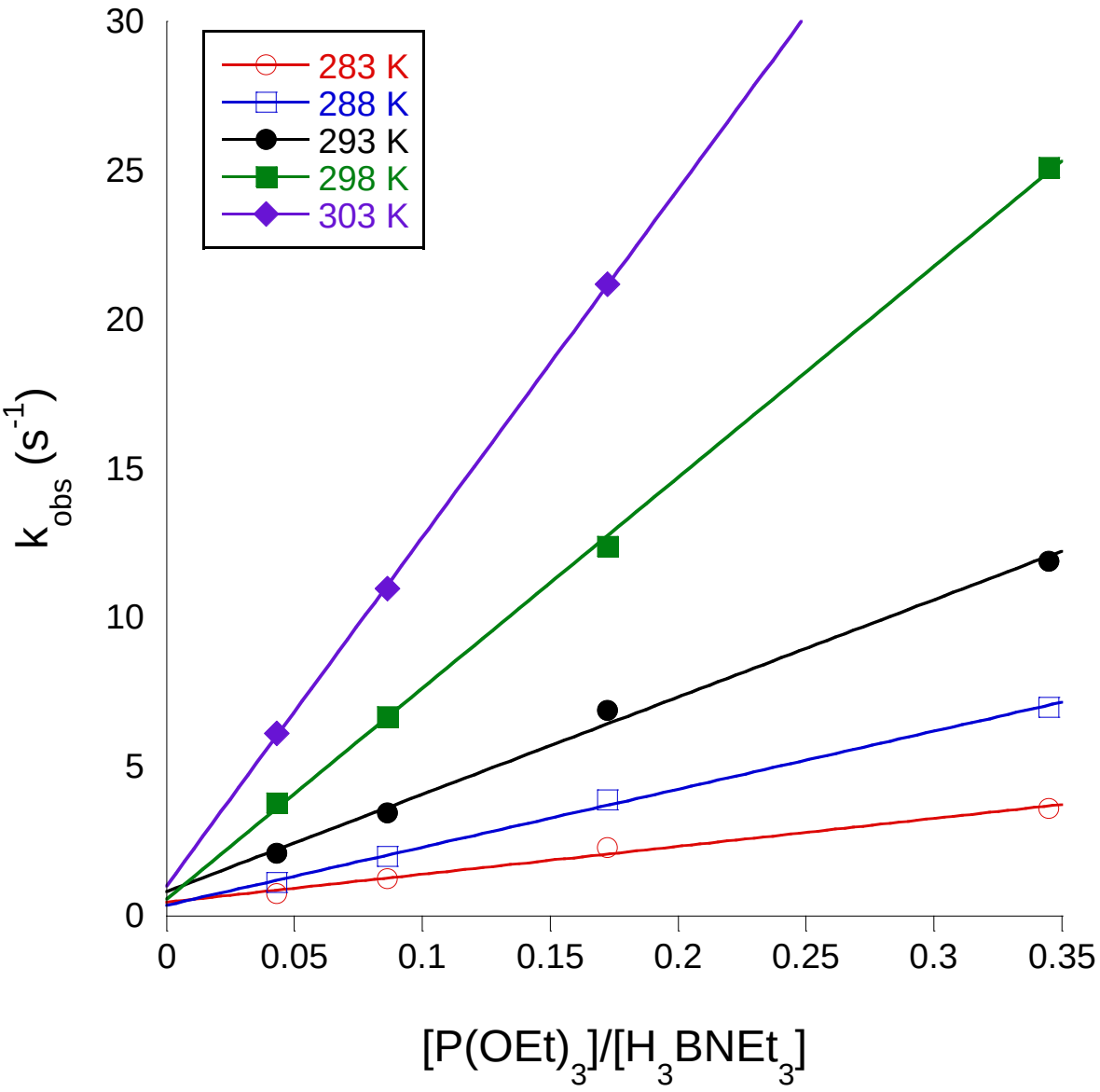


**Figure S4**: A plot of $k_{obs}$ vs $[P(OEt)_3]/[H_3B{\cdot}NEt_3]$ at different temperatures.

**Kinetic Analysis**

The saturation behavior observed in the reaction of **1** with $P(OEt)_3$ is consistent with a dissociative mechanism of borane exchange (Scheme 2). Applying the steady state assumption to the $BzCr(CO)_2$ intermediate yields the following dependence of $k_{obs}$ on $[P(OEt)_3]$.

$$k_{obs} = \frac{k_1 k_2 [P(OEt)_3]}{k_{-1}[H_3BNEt_3] + k_2[P(OEt)_3]} \qquad (1)$$

A non-linear fit of the $k_{obs}$ vs. $[P(OEt)_3]$ data therefore yields $k_1$ and the selectivity ratio, $k_2/k_{-1}$ (Table S2)

In the case of **2**, the displacement reaction was much faster than in the Cr system and therefore concentrations of $P(OEt)_3$ large enough to observe saturation could not be used. Under conditions where $k_2[P(OEt)_3] << k_{-1}[H_3B{\cdot}NEt_3]$, equation 1 reduces to:

$$k_{obs} = \frac{k_1 k_2 [P(OEt)_3]}{k_{-1}[H_3BNEt_3]} \qquad (2)$$

A plot of $k_{obs}$ vs. $[P(OEt)_3]/[H_3B{\cdot}NEt_3]$ in this case is expected to be linear as observed (Fig. S4). The slope is expected to yield the collection of rate constants $k_1k_2/k_{-1}$. As mentioned in the paper, since the reaction of $TpMn(CO)_2$ with either borane or $P(OEt)_3$ is expected to be almost barrierless, an Eyring analysis yields the activation enthalpy associated with the $k_1$ step and hence an estimate for the Mn-H-B BDE in complex 2. The close agreement between the experimental and calculated BDE's lends support to the kinetic analysis.

## TABLES

**Table S1**: Experimental CO stretching frequencies for [M]-($\eta^1$-$H_3B{\cdot}NEt_3$) complexes. Unscaled calculated values are in parenthesis for [M]-($\eta^1$-$H_3B{\cdot}NMe_3$).

| [M] | $\nu_{CO}$ ($cm^{-1}$) |
|---|---|
| $BzCr(CO)_2$ | 1842 (1976)<br>1896 (2022) |
| (benzoate)$Cr(CO)_2$ | 1859(1998)<br>1912(2049) |
| $TpMn(CO)_2$ | 1847 (2029)<br>≈1930 (2094) |
| $CpMn(CO)_2$ | 1862 (2018)<br>1923 (2076) |

**Table S2**: Rate constants for the reaction of **1** with $P(OEt)_3$

| Temp (K) | k1 (s-1) | k2/k-1 |
|---|---|---|
| 293 | 0.23±0.03 | 0.4±0.1 |
| 298 | 0.43±0.03 | 0.5±0.1 |
| 303 | 0.78±0.03 | 0.4±0.1 |
| 313 | 2.3±0.1 | 0.4±0.1 |
| 318 | 4.0±0.2 | 0.4±0.1 |
| $\Delta H^{\ddagger}$ = 20.3±0.3 kcal/mol, $\Delta S^{\ddagger}$ = 8±1 e.u | | |

**Table S3**: Rate constants for the reaction of **2** with $P(OEt)_3$

| Temp (K) | k1k2/k-1 |
|---|---|
| 283 | 9.35±0.80 |
| 288 | 19.5±0.7 |
| 293 | 32.6±1.6 |
| 298 | 70.7±1.3 |
| 303 | 117±2 |
| $\Delta H^{\ddagger}$ = 20.9±0.8 kcal/mol, $\Delta S^{\ddagger}$ = 20±3 e.u | |

**Table S4**: Calculated BDE's for several [M]-($\eta^1$-$H_3B{\cdot}NMe_3$) complexes

| **[M]** | **BDE (kcal/mol)** |
|---|---|
| $BzCr(CO)_2$ | 23.1 |
| (benzoate)$Cr(CO)_2$ | 25.1 |
| $TpMn(CO)_2$ | 20.3 |
| $CpMn(CO)_2$ | 26.3 |

**Table S5**: Relevant geometric parameters from computed geometries for several [M]-($\eta^1$-$H_3B{\cdot}NMe_3$) complexes

| [M] | $BzCr(CO)_2$ | ($\eta^6$-methylbenzoate)$Cr(CO)_2$ | $TpMn(CO)_2$ | $CpMn(CO)_2$ |
|---|---|---|---|---|
| **Distances (in Å)** | | | | |
| **M-CO** | 1.841 | 1.856 | 1.797 | 1.782 |
| **M-CO** | 1.837 | 1.841 | 1.792 | 1.779 |
| **M-H** | 1.764 | 1.749 | 1.766 | 1.681 |
| **H-B** | 1.244 | 1.242 | 1.238 | 1.255 |
| **M-B** | 2.750 | 2.812 | 2.776 | 2.635 |
| **B-H** | 1.201 | 1.201 | 1.200 | 1.199 |
| **B-H** | 1.211 | 1.204 | 1.206 | 1.209 |
| **Angles (in °)** | | | | |
| **∠(M-H-B)** | 131.4 | 139.5 | 134.3 | 127.0 |

**Cartesian coordinates of the calculated geometries and energies (in hartree)**

**$BzCr(CO)_2(H_3B{\cdot}NMe_3)$**

E= -1704.61599926

H= -1704.318041

| | | | |
|---|---|---|---|
| C | -2.956555 | 0.258701 | -0.554330 |
| C | -2.848400 | 0.062330 | 0.833944 |
| C | -2.168130 | -1.076188 | 1.338539 |
| C | -1.541765 | -1.955334 | 0.458172 |
| C | -1.633420 | -1.749395 | -0.944176 |
| C | -2.359632 | -0.666229 | -1.441949 |
| H | -3.468080 | 1.127409 | -0.939420 |

| | | | |
|---|---|---|---|
| H | -3.284155 | 0.777280 | 1.515033 |
| H | -2.064204 | -1.214288 | 2.404336 |
| H | -0.938858 | -2.764662 | 0.841635 |
| H | -1.107982 | -2.407354 | -1.619142 |
| H | -2.401140 | -0.491078 | -2.506985 |
| Cr | -0.877441 | 0.084112 | -0.005797 |
| C | -0.366989 | 1.169691 | 1.390883 |
| O | -0.100357 | 1.857639 | 2.276796 |
| C | -0.430837 | 1.424132 | -1.181022 |
| O | -0.185582 | 2.275157 | -1.922446 |
| H | 1.430122 | -1.160049 | 1.519851 |
| H | 1.671340 | -2.280666 | -0.145550 |
| H | 0.704074 | -0.596723 | -0.387355 |
| B | 1.546552 | -1.172263 | 0.324983 |
| N | 2.902053 | -0.354943 | -0.037778 |
| C | 3.063705 | -0.268627 | -1.504437 |
| H | 3.989951 | 0.253267 | -1.749157 |
| H | 2.216227 | 0.270618 | -1.919935 |
| H | 3.083872 | -1.274895 | -1.914972 |
| C | 2.855775 | 1.012107 | 0.526049 |
| H | 2.695086 | 0.947442 | 1.598589 |
| H | 2.025085 | 1.549894 | 0.079254 |
| H | 3.792134 | 1.531001 | 0.315452 |
| C | 4.049963 | -1.080657 | 0.543067 |
| H | 4.081514 | -2.083653 | 0.125750 |
| H | 3.913093 | -1.148232 | 1.619193 |
| H | 4.978593 | -0.553650 | 0.318843 |

**($\eta^6$-methylbenzoate)Cr(CO)$_2$($H_3B{\cdot}NMe_3$)**

E= -1932.52157376

H= -1932.175981

| | | | |
|---|---|---|---|
| C | -1.555982 | 0.936340 | -0.624604 |
| C | -2.380729 | 0.370032 | 0.387647 |
| C | -2.908129 | -0.920305 | 0.245312 |
| C | -2.516472 | -1.707478 | -0.849375 |
| C | -1.743392 | -1.142385 | -1.901040 |
| C | -1.268870 | 0.158028 | -1.774946 |
| H | -2.588310 | 0.942000 | 1.278288 |
| H | -3.507122 | -1.346991 | 1.035154 |
| H | -2.840092 | -2.735380 | -0.914417 |
| H | -1.461791 | -1.741440 | -2.752945 |
| H | -0.591568 | 0.566249 | -2.509623 |
| Cr | -0.725312 | -0.946826 | 0.043438 |
| C | -0.212263 | -2.715277 | 0.277309 |
| O | 0.074131 | -3.815417 | 0.434339 |
| C | -0.300796 | -0.673143 | 1.813857 |
| O | -0.070050 | -0.492864 | 2.928641 |
| H | 1.739417 | 0.020041 | -2.124754 |
| H | 0.861194 | -0.346385 | -0.380907 |
| H | 2.038922 | -1.805105 | -1.289742 |
| B | 1.816309 | -0.637555 | -1.118775 |
| N | 3.031949 | -0.025483 | -0.239431 |
| C | -0.905287 | 2.248232 | -0.476766 |
| O | -0.127902 | 2.725937 | -1.267512 |
| O | -1.265384 | 2.873975 | 0.655406 |
| C | -0.650427 | 4.133259 | 0.887934 |
| H | -1.057083 | 4.493000 | 1.828462 |
| H | 0.431664 | 4.026700 | 0.962407 |
| H | -0.879323 | 4.830263 | 0.082934 |
| C | 4.252947 | -0.024099 | -1.070363 |
| H | 5.099611 | 0.346824 | -0.490797 |

| | | | |
|---|---|---|---|
| H | 4.088313 | 0.611556 | -1.936118 |
| H | 4.449991 | -1.039147 | -1.406259 |
| C | 2.707875 | 1.360284 | 0.166063 |
| H | 1.843315 | 1.336425 | 0.825065 |
| H | 2.453527 | 1.939061 | -0.718069 |
| H | 3.557965 | 1.805061 | 0.685538 |
| C | 3.257642 | -0.852340 | 0.965206 |
| H | 3.508062 | -1.863454 | 0.655815 |
| H | 2.344105 | -0.878848 | 1.552042 |
| H | 4.068449 | -0.430381 | 1.560927 |

**$TpMn(CO)_2(H_3B{\cdot}NMe_3)$**

E= -2281.37847406

H= -2280.971171

| | | | |
|---|---|---|---|
| Mn | 0.172304 | 1.003589 | -0.048851 |
| C | 0.298535 | 2.221711 | -1.357055 |
| O | 0.392740 | 3.012964 | -2.182544 |
| C | 0.260541 | 2.325328 | 1.165489 |
| O | 0.338103 | 3.177840 | 1.927251 |
| H | 2.192889 | -2.882437 | 0.114912 |
| B | 1.627300 | -1.823819 | 0.072900 |
| C | 3.973726 | -0.684980 | 0.033386 |
| N | 2.196570 | 0.613830 | -0.012762 |
| C | 4.432651 | 0.612660 | -0.005900 |
| H | 4.500870 | -1.622870 | 0.065613 |
| H | 5.453172 | 0.950336 | -0.012891 |
| H | 3.161095 | 2.459081 | -0.068020 |
| C | 0.592588 | -2.579562 | -2.207655 |
| N | 0.092040 | -0.581235 | -1.434814 |
| C | -0.190021 | -1.970402 | -3.166181 |

| | | | |
|---|---|---|---|
| H | 1.059664 | -3.549047 | -2.184643 |
| H | -0.497623 | -2.369259 | -4.115970 |
| H | -1.016099 | 0.111164 | -3.059821 |
| C | 0.602942 | -2.388708 | 2.403846 |
| N | 0.076998 | -0.466547 | 1.466459 |
| C | -0.177759 | -1.705550 | 3.311878 |
| H | 1.079439 | -3.352302 | 2.460285 |
| H | -0.476562 | -2.024070 | 4.294338 |
| H | -1.051420 | 0.338372 | 3.022083 |
| N | 2.632206 | -0.658787 | 0.028178 |
| N | 0.738415 | -1.625374 | 1.310955 |
| N | 0.743488 | -1.726687 | -1.185400 |
| C | 3.271374 | 1.388245 | -0.033861 |
| C | -0.472245 | -0.499157 | 2.673390 |
| C | -0.467442 | -0.711211 | -2.631388 |
| H | -1.569806 | 0.996299 | -0.338480 |
| B | -2.562311 | 1.263349 | 0.351944 |
| H | -2.412479 | 1.263405 | 1.542075 |
| H | -3.068443 | 2.270327 | -0.077189 |
| N | -3.576333 | 0.040115 | 0.004089 |
| C | -3.904056 | 0.044935 | -1.435941 |
| C | -2.974483 | -1.264627 | 0.358519 |
| C | -4.815610 | 0.236257 | 0.783602 |
| H | -2.991233 | -0.115069 | -2.001154 |
| H | -4.615859 | -0.750942 | -1.660987 |
| H | -4.327000 | 1.010697 | -1.698797 |
| H | -3.676996 | -2.068497 | 0.133021 |
| H | -2.058553 | -1.398027 | -0.210629 |
| H | -2.730402 | -1.268053 | 1.416878 |
| H | -5.531349 | -0.554618 | 0.553616 |
| H | -4.571485 | 0.219279 | 1.842202 |

| | | | |
|---|---|---|---|
| H | -5.239217 | 1.205605 | 0.533248 |

**$CpMn(CO)_2(H_3B{\cdot}NMe_3)$**

E= -1772.45244966

H= -1772.172621

| | | | |
|---|---|---|---|
| C | -2.904959 | -0.027829 | -0.737812 |
| C | -2.911175 | -0.225500 | 0.658665 |
| C | -2.157166 | -1.404576 | 0.938886 |
| C | -1.696887 | -1.915599 | -0.290012 |
| C | -2.149025 | -1.077161 | -1.335286 |
| H | -3.393621 | 0.776901 | -1.261549 |
| H | -3.406953 | 0.397828 | 1.383699 |
| H | -1.971126 | -1.826518 | 1.911785 |
| H | -1.053382 | -2.772100 | -0.407855 |
| H | -1.970870 | -1.216239 | -2.387734 |
| Mn | -0.913185 | 0.082086 | -0.006091 |
| C | -0.459699 | 0.917699 | 1.501419 |
| O | -0.233100 | 1.452861 | 2.493827 |
| C | -0.571346 | 1.505545 | -1.017758 |
| O | -0.393362 | 2.428680 | -1.682656 |
| H | 1.248031 | -1.385654 | 1.291683 |
| H | 1.504788 | -2.208048 | -0.534563 |
| H | 0.572977 | -0.497692 | -0.535918 |
| B | 1.387263 | -1.196304 | 0.115971 |
| N | 2.763740 | -0.357606 | -0.086701 |
| C | 2.966582 | -0.052498 | -1.519164 |
| H | 3.908321 | 0.480064 | -1.658618 |
| H | 2.141443 | 0.562417 | -1.869371 |
| H | 2.979437 | -0.984436 | -2.078159 |
| C | 2.734025 | 0.907285 | 0.679166 |

| | | | |
|---|---|---|---|
| H | 2.540178 | 0.684158 | 1.724650 |
| H | 1.932037 | 1.532570 | 0.298387 |
| H | 3.688349 | 1.425507 | 0.575451 |
| C | 3.881886 | -1.192180 | 0.400755 |
| H | 3.900126 | -2.121428 | -0.162369 |
| H | 3.719085 | -1.416985 | 1.451519 |
| H | 4.826605 | -0.661177 | 0.275786 |

**$H_3B{\cdot}NMe_3$**

E=-201.158575751

H= -200.994822

| | | | |
|---|---|---|---|
| H | -1.970377 | 0.988319 | 0.625375 |
| H | -1.971641 | -1.033621 | 0.542004 |
| H | -1.971051 | 0.049522 | -1.167385 |
| B | -1.643716 | 0.001210 | -0.000030 |
| N | -0.004554 | 0.000015 | -0.000011 |
| C | 0.486903 | -1.174790 | -0.743762 |
| H | 1.578925 | -1.190800 | -0.753090 |
| H | 0.106621 | -1.128550 | -1.760775 |
| H | 0.105500 | -2.074230 | -0.267703 |
| C | 0.488748 | 1.230990 | -0.645173 |
| H | 0.108974 | 2.089062 | -0.096933 |
| H | 0.108254 | 1.268897 | -1.662455 |
| H | 1.580792 | 1.245896 | -0.653491 |
| C | 0.487726 | -0.057278 | 1.388959 |
| H | 0.106513 | -0.960621 | 1.857726 |
| H | 0.107923 | 0.805294 | 1.930082 |
| H | 1.579755 | -0.058857 | 1.406729 |

**$BzCr(CO)_2$**

E= -1503.41732138

H= -1503.286423

| | | | |
|---|---|---|---|
| C | 0.799787 | -0.703560 | 1.386584 |
| C | 0.799822 | 0.703841 | 1.386430 |
| C | 1.359519 | 1.410123 | 0.293255 |
| C | 1.854821 | 0.710591 | -0.812328 |
| C | 1.854694 | -0.710803 | -0.812234 |
| C | 1.359338 | -1.410078 | 0.293505 |
| H | 0.361022 | -1.242517 | 2.212243 |
| H | 0.361085 | 1.242986 | 2.211985 |
| H | 1.333987 | 2.489607 | 0.278041 |
| H | 2.212856 | 1.252730 | -1.675392 |
| H | 2.212785 | -1.253122 | -1.675158 |
| H | 1.333696 | -2.489563 | 0.278479 |
| Cr | -0.151136 | 0.000012 | -0.398033 |
| C | -1.439589 | 1.336713 | -0.203623 |
| O | -2.192693 | 2.177488 | -0.002830 |
| C | -1.439487 | -1.336748 | -0.203630 |
| O | -2.192507 | -2.177600 | -0.002814 |

**(benzoate)$Cr(CO)_2$**

E= -1731.31986195

H= -1731.141127

| | | | |
|---|---|---|---|
| C | -0.961975 | -0.558629 | 0.492584 |
| C | -0.149338 | -0.032075 | 1.533977 |
| C | 1.130959 | -0.543192 | 1.780677 |
| C | 1.657063 | -1.522351 | 0.919384 |

| | | | |
|---|---|---|---|
| C | 0.848242 | -2.105187 | -0.094091 |
| C | -0.436851 | -1.603581 | -0.312288 |
| H | -0.542033 | 0.783496 | 2.122814 |
| H | 1.746383 | -0.112047 | 2.554984 |
| H | 2.674663 | -1.859240 | 1.049411 |
| H | 1.246613 | -2.877848 | -0.733151 |
| H | -1.023949 | -1.971429 | -1.141203 |
| Cr | 0.936865 | 0.060083 | -0.312877 |
| C | 2.693961 | 0.164944 | -0.942386 |
| O | 3.792827 | 0.191135 | -1.262809 |
| C | 0.903262 | 1.920836 | -0.080280 |
| O | 0.886446 | 3.043560 | 0.133348 |
| C | -2.296804 | 0.039018 | 0.270386 |
| O | -2.910769 | -0.475848 | -0.804301 |
| O | -2.785704 | 0.886967 | 0.969790 |
| C | -4.201732 | 0.055178 | -1.088723 |
| H | -4.142481 | 1.126579 | -1.274372 |
| H | -4.546454 | -0.465496 | -1.977016 |
| H | -4.880635 | -0.122270 | -0.256071 |

**TpMn(CO)$_2$**

E= -2080.18446603

H= -2079.943968

| | | | |
|---|---|---|---|
| Mn | -0.895219 | 0.000060 | -0.798677 |
| C | -2.174179 | 1.265418 | -0.916904 |
| O | -3.007207 | 2.048763 | -0.968806 |
| C | -2.174243 | -1.265224 | -0.917011 |
| O | -3.007315 | -2.048517 | -0.968980 |
| H | 2.623704 | -0.000117 | 1.715003 |
| B | 1.660808 | -0.000068 | 0.999427 |

| | | | |
|---|---|---|---|
| C | 0.202910 | -0.000162 | 3.159742 |
| N | -0.844639 | -0.000028 | 1.226114 |
| C | -1.145532 | -0.000174 | 3.439627 |
| H | 1.060971 | -0.000207 | 3.809435 |
| H | -1.617422 | -0.000234 | 4.405343 |
| H | -2.805351 | -0.000062 | 1.932319 |
| C | 2.511640 | 2.256362 | -0.025245 |
| N | 0.624626 | 1.408442 | -0.766802 |
| C | 2.038716 | 3.124696 | -0.987433 |
| H | 3.395231 | 2.292943 | 0.588449 |
| H | 2.485991 | 4.042878 | -1.322438 |
| H | 0.138246 | 2.896933 | -2.150118 |
| C | 2.511533 | -2.256463 | -0.025408 |
| N | 0.624562 | -1.408399 | -0.766911 |
| C | 2.038566 | -3.124709 | -0.987655 |
| H | 3.395121 | -2.293129 | 0.588284 |
| H | 2.485795 | -4.042891 | -1.322722 |
| H | 0.138109 | -2.896771 | -2.150328 |
| N | 0.360476 | -0.000074 | 1.827819 |
| N | 1.649049 | -1.239403 | 0.085060 |
| N | 1.649105 | 1.239337 | 0.085155 |
| C | -1.758604 | -0.000087 | 2.185883 |
| C | 0.845367 | -2.545504 | -1.417408 |
| C | 0.845487 | 2.545581 | -1.417222 |

**$CpMn(CO)_2$**

E= -1571.24867806

H= -1571.135954

| | | | |
|---|---|---|---|
| C | -1.093994 | 0.705047 | 1.164078 |
| C | -1.093886 | -0.704776 | 1.164316 |

| | | | |
|---|---|---|---|
| C | -1.640247 | -1.150979 | -0.078118 |
| C | -1.969077 | -0.000261 | -0.827792 |
| C | -1.640414 | 1.150763 | -0.078499 |
| H | -0.748520 | 1.335510 | 1.966276 |
| H | -0.748329 | -1.334920 | 1.966727 |
| H | -1.795103 | -2.173820 | -0.376650 |
| H | -2.366269 | -0.000462 | -1.831614 |
| H | -1.795435 | 2.173477 | -0.377380 |
| Mn | 0.138852 | -0.000020 | -0.407309 |
| C | 1.331034 | -1.320108 | -0.124321 |
| O | 2.039911 | -2.177799 | 0.141456 |
| C | 1.330898 | 1.320190 | -0.124332 |
| O | 2.039648 | 2.177980 | 0.14146 |

## References

1. a) Trofimenko, S. *J. Am. Chem. Soc.* **1969**, *91*, 588; b) Joachim, J. E.; Apostolidis, C.; Kanellakopulos, B.; Maier, R.; Marques, N.; Meyer, D.; Mueller, J.; Pires de Matos, A.; Nuber, B.; Rebizant, J.; Ziegler, M. L. *J. Organomet. Chem.* **1993**, *448*, 119-129.

2. Gaussian Development Version, Revision H.13, Frisch M. J. et.al. *Gaussian, Inc.*, Wallingford CT, 2009.

3. Chai, J. -D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615.

4. Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

5. CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, **2009** (http://www.cylview.org).