and is consistent with the larger activation barriers that frequently impede association reactions between singlets and triplets.[41,42] It is noteworthy in this regard that the reactions of $^3O_2$ with the odd electron, radical anions $Fe(CO)_4^-$, $Cr(CO)_5^-$, and $Mo(CO)_5^-$ are surprisingly slow (Table I), despite the favorable energetics and kinetic factors that might otherwise be expected for their direct reaction. The origin of this effect may lie in unfavorable spin localization requirements or inaccessible spin states of the product polyoxide ions and is presently under investigation. We are also currently examining the gas-phase reactions of the polyoxide ions with a series of neutral substrates and will report these results in a future publication.

Acknowledgment. We gratefully acknowledge Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support in the construction of our instrument.

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Bimetallic Solvated Metal Atom Dispersed Catalysts. New Materials with Low-Temperature Catalytic Properties

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During 1974–1976 we reported the first examples of solvated metal atom dispersion (SMAD).[1-3] In this process metal atoms such as Mg, Ni, Co, Fe, etc. are solvated at low temperature in toluene or some other appropriate solvent, and upon warming metal atom nucleation begins, but this nucleation process (cluster growth) competes with a reaction channel where the growing clusters react with the host solvent.[4] These reactions, even with alkanes, can occur extensively as low as 140 K (−130 °C).[5] This observation in itself indicates that these small growing clusters are *fundamentally different and more reactive* than clean metal surfaces.[5] Appropriate theoretical rationale for this variant behavior are not currently available.

These growing clusters incorporate carbonaceous fragments and stabilize as amorphous "pseudoorganometallic" powders, which represent a special new class of materials. We have provided many examples showing where these materials behave as novel heterogeneous catalysts.[6] Contrary to popular current thought, the incorporated carbonaceous fragments do not poison but instead *aid* the catalytic action[7] and apparently even provide a better means of attachment of the metal particles to catalyst support surfaces.[6c]

In our earlier paper we also suggested that the SMAD procedure would be useful for the preparation of bimetallic particles.[3] Herein we report our initial results in this area and show that Mn–Co pseudoorganometallic particles possess catalytic activities that allow alkene hydrogenation at −60 °C at diffusion-controlled rates, which represents considerably increased activity over all other SMAD monometallic catalysts we have prepared, including Ni, Co, Fe, Mn, and Cr.[8]

Table I. Initial Reaction Rates for 1-Butene Isomerization, 1-Butene Hydrogenation, and 1,3-Butadiene Hydrogenation over Monometallic and Bimetallic SMAD Catalysts

		initial rates, molecule/(M atom s)		
catalyst[b]	atom %[c]	isom 1-$C_4{}'$	hydrog 1-$C_4{}'^{e}$	hydrog 1.3-$C_4{}''^{f}$
2.6% Co–1.5% Fe	39.4	0.017	0.44[g]	0.14 (0.41)[h]
1.5% Co–3.4% Fe	70.5	0.0096	0.0063	0.029 (0.96)[h]
2.4% Co–6.8% Fe	74.9	0.00087	0.00016	0.0049 (0.96)[h]
4.1% Co–0.1% Mn	2.5	0.018	0.35[g]	0.18 (0.57)[h]
3.6% Co–0.8% Mn	19.3	0.084	0.45[g]	
2.0% Co–1.1% Mn	37.6	0.018	0.79[g]	
3.3% Co–2.6% Mn	45.8	0.024	0.53[g]	
3.4% Co–3.3% Mn	51.0	0.021	0.50[g]	0.083 (0.56)[h]
1.7% Co–5.1% Mn	76.3	0.016	0.016	0.0053 (0.95)[h]
3.6% Co–0.7% Cr	18.1	0.0034	0.0051	0.011 (0.96)[h]
2.0% Co–2.2% Cr	55.5	0.00022	0.0028	0.011 (0.94)[h]
0.6% Co–3.7% Cr	87.5	0	0.0047	0.011 (0.95)[h]
4.7% Fe		0.00053	0.00022	0.0048 (0.97)[h]
2.3% Co		0.0063	0.029	0.012 (0.98)[h]
3.4% Mn		0	0.000013	0.00030 (1.0)[h]
3.8% Cr		0	0	0

[a] Based on 100% Co dispersion neglecting second metal contribution. [b] SiO_2 support, wt %. [c] Atom % of second metal, not including support. [d] $P_{rea} = 30$ torr, without H_2, 253 K. [e] $H_2/HC = 1.67$, $P_{tot} = 80$ torr, 213 K. [f] $H_2/HC = 2$, $P_{tot} = 60$ torr, 273 K. [g] The rate was controlled by diffusion. [h] Ratios of butene to (butenes + butane).

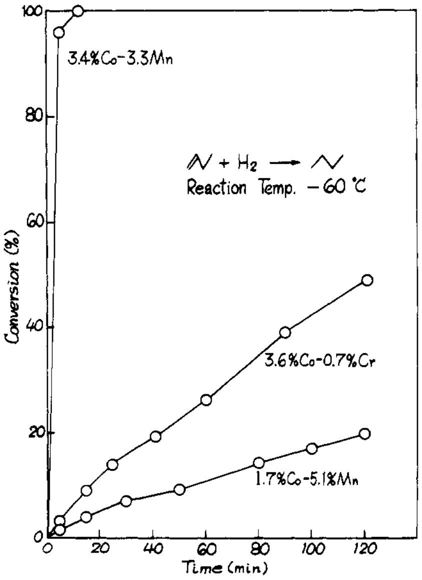

Figure 1. Effect of Mn addition on hydrogenation activity for a Co/SiO_2 SMAD catalyst.

An apparatus similar to those described previously[9] was constructed possessing four water-cooled copper electrodes, two $W\text{–}Al_2O_3$ metal vaporization crucibles, and two separate power supplies. Two metals were vaporized simultaneously as excess toluene solvent vapor was inletted. The liquid nitrogen cooled walls condensed the toluene and metal atoms into a frozen matrix. About 0.02–1.4 g of each metal and 100 mL of toluene were used in each experiment, which lasted about 2 h.

[†] On leave from the Kitami Institute, Hokkaido, Japan.

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After completion of the tri-deposition, the matrix was allowed to warm slowly to −95 °C whereapon it melted and formed a toluene-solvated metal atom solution. This solution was stirred and slowly warmed further in the presence of a powdered SiO_2 catalyst support (20 g, preheat treated at 500 °C for 3 h in dry air, cooled, and handled under pure nitrogen prior to and during transfer to the reaction chamber where it was placed under vacuum prior to the metal vapor reaction). During the warming period of about 2 h, the solution turned from dark red-brown to a clear solution. Major color change occurred in the −50 to −20 °C range, and we presume this is the range where metal nucleation/deposition along with toluene reaction occurred. After reaching room temperature the mixture was vacuum siphoned and placed under nitrogen in airless glassware. Toluene was removed under vacuum and the resultant dark powder placed in a reactor in the inert atmosphere box. The catalyst was then outgassed at room temperature to less than 1×10^{-5} torr and subsequently used without further treatment.

Initial rates for three catalysis reactions are summarized in Table I and Figure 1. The remarkable finding is that addition of Mn, itself an almost inactive catalyst, substantially increased the catalytic activity of the Co/SiO_2 system. Indeed, only 2.5 atom % Mn increased the activity for hydrogenation by 10^2. Even higher activities were obtained by adding more Mn, up to 51 atom %, where the rate for 1-butene hydrogenation at −60 °C was controlled by diffusion.[10] These data show that the activity of Mn/SiO_2 is 10^2 lower than that of Co/SiO_2[11] and at least 10^4 lower than $Co\text{-}Mn/SiO_2$.

Catalyst life was studied by repeating 1-butene hydrogenation experiments. After hydrogenation cycles such that each site was used over 470 times, no sign of deactivation was noted.

In summary, for 1-butene hydrogenation and isomerization as well as 1,3-butadiene hydrogenation, we have found small amounts of Mn greatly increase the activity of a Co/SiO_2 SMAD catalyst. Large amounts of Mn are detrimental, however, as is any amount of Cr. Addition of Fe caused a slight increase in activity.

To the best of our knowledge this type of *activation* of one metal on another has not been observed before for heterogeneous bimetallic systems, although Sinfelt and others have reported extensively on *selectivity* differences due to a second metal (eg., Cu-Ni).[12] Naturally we are actively trying to ascertain if this is an electronic effect, an ensemble effect, or simply a dispersion effect.

The discovery that Mn activates SMAD Co/SiO_2 catalysts is timely. There is a great deal of interest currently in both homogeneous cluster chemistry and heterogeneous catalysis in making "early-late" transition-metal clusters and catalysts, and this impetus is mainly based on the supposition that the combination of two such metals may lead to unusual CO activation mechanisms and hence affect selectivity in Fischer-Tropsch reduction products.

Although SMAD catalysts are new materials, and extrapolation of these data to other catalyst systems perhaps is not justified, we do believe our results at least show such activation procedures are possible. Currently we are investigating other catalytic reactions with these bimetallic SMAD materials and will report these data and physical characterization data at a later time.

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Registry No. Co, 7440-48-4; Fe, 7439-89-6; Mn, 7439-96-5; Cr, 7440-47-3; 1-butene, 106-98-9; 1,3-butadiene, 106-99-0; butene, 25167-67-3; butane, 106-97-8.

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[10] The reactions were carried out in a 496 cm^3 recirculation system. Usually 0.2 g of catalyst was employed. The ratio of 1-butene to Co metal was 76 in the case of 3.4 wt % Co-3.3 wt % Mn/SiO_2. Below −60 °C (213 K) experimental problems with butene liquefaction were encountered.

[11] Co/SiO_2 (SMAD) is a very effective hydrogenation catalyst itself compared with conventional Co or Ni systems. Such findings are not unusual for SMAD catalysts.[6]

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Metal-Induced Oxidative Fusion of Boranes. Synthesis of $B_{12}H_{16}$, the First Neutral Dodecaborane

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Transition-metal-promoted oxidative fusion of small *nido*-carborane anions to generate large, carbon-rich carborane cages was discovered several years ago[1] and has been elaborated in a series of synthetic, structural, and mechanistic investigations.[2,3] While the most success experienced thus far has involved the high-yield conversion of $R_2C_2B_4H_5^-$ ions to $R_4C_4B_8H_8$ via complexation with transition metals,[2a] fusion via metal complexation has been extended to other carborane and metallacarborane systems.[3] It has not, however, been employed in reactions of boron hydrides (although $PdCl_2$-induced coupling of B_5H_9 to give the linked-cage borane $1,2'\text{-}(B_5H_8)_2$, has been reported[4]). Metal-promoted fusion of boranes under mild conditions could furnish one-step, nonpyrolytic synthetic routes to known species such as $B_{10}H_{14}$[5] and also allow facile, "rational" syntheses of new boron hydrides that might not be otherwise accessible. In this communication we report the preparation of $B_{10}H_{14}$ from $B_5H_8^-$ and of $B_{12}H_{16}$, a new borane, from $B_6H_9^-$ via metal-induced fusion.

The reaction of $Na^+B_5H_8^-$ (obtained by treatment of B_5H_9 with NaH) with an approximately equimolar quantity of $RuCl_3$ in tetrahydrofuran solution at −78 °C for 3 h and then for 30 min at room temperature followed by extraction with CH_2Cl_2 and elution on a silica column gave $B_{10}H_{14}$ in 27% isolated yield (40 mg), identified from NMR and mass spectra. Fusion of $B_5H_8^-$ is not observed with $FeCl_2$ alone, but when both $FeCl_2$ and $FeCl_3$ are present, $B_{10}H_{14}$ and the linked-cage borane $2,2'\text{-}(B_5H_8)_2$[8] are obtained in about equal amounts (ca. 20% total isolated yield). When $FeCl_3$ alone is allowed to react with $B_5H_8^-$ in THF, $2,2'\text{-}(B_5H_8)_2$ but not $B_{10}H_{14}$ is obtained.

Treatment of $K^+B_6H_9^-$ (prepared from 9.2 mmol each of B_6H_{10} and KH) with 6.0 mmol $FeCl_2$ and 10.6 mmol $FeCl_3$ in dimethyl ether at −78 °C for 2 h followed by extraction with *n*-hexane, separation in a −78 °C trap, vacuum sublimation at 50-60 °C, and a final sublimation at room temperature gave colorless crystals characterized as $B_{12}H_{16}$ (140 mg, 43% yield based on B_6H_{10} consumed). No other borane products were detected. Dodecaborane(16), an air-stable solid (mp 64-66 °C dec), exhibits an electron-impact mass spectrum containing a cutoff at *m/e* 148 corresponding to the $^{11}B_{12}{}^1H_{16}^+$ parent ion and a parent envelope consistent with the presence of 12 boron atoms; extensive loss of hydrogen is evident (base peak at *m/e* 138). No significant intensities appear above *m/e* 148. The 115.8-MHz ^{11}B FT NMR spectrum in hexane consists of seven resonances in a 1:2:1:4:2:1:1 integrated area ratio, at δ 15.4, 13.4, 11.4, 4.6, −18.3, −40.7, and −43.0 relative to $BF_3 \cdot OEt_2$, respectively. This is consistent with a framework of C_s symmetry containing four borons on the mirror plane. From the $^{11}B-^{11}B$ two-dimensional (2D) NMR spectrum, the observed pattern of cross (off-diagonal) peaks reveals couplings (hence bonds) between specific boron atoms;[9a] the cage connec-

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[5] Improved multistep syntheses of $B_{10}H_{14}$, (a) via conversion of $B_5H_8^-$ to $B_9H_{14}^-$ and subsequent reaction with boron trihalides[6] and (b) from $B_{11}H_{14}^-$, which is in turn prepared from $NaBH_4$,[7] have been reported recently.

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