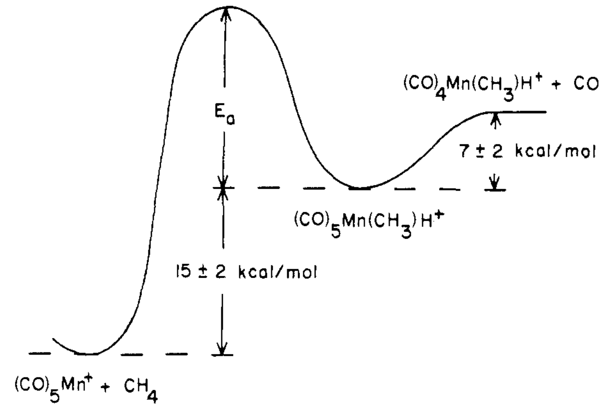

Figure 2. Energetic relationships between species resulting from reductive elimination of CH_4 or loss of CO from protonated $(CO)_5MnCH_3$.

kcal/mol. These results are summarized in Figure 2, where the activation energy E_a for elimination of methane from $(CO)_5Mn(CH_3)H^+$ is unknown.

Comparison of the present results to previous studies is rendered difficult by the absence of a detailed mechanistic picture for reductive elimination processes in solution. The kinetic stability of $(CO)_5Mn(CH_3)H^+$ is similar to that of *cis*-$(CO)_4Os(CH_3)H$, which slowly decomposes *inter*molecularly at room temperature.[18] In marked contrast is the unimolecular methane elimination from *cis*-$(PPh_3)_2Pt(CH_3)H$ which occurs with little activation energy.[19]

Further studies with $(CO)_5MnH$ and $(CO)_5ReCH_3$ should provide interesting mechanistic and thermochemical comparisons with the reactions of $(CO)_5MnCH_3$. Reaction of $(CO)_5ReCH_3$ with proton donors is analogous to that of $(CO)_5MnCH_3$, with methane elimination occurring for $PA(B) \leqslant 206 \pm 2$ kcal/mol and formation of $(CO)_5Re(CH_3)H^+$ observed for $PA(B) \leqslant 191 \pm 2$ kcal/mol. The question of site of protonation may be clarified by study of $(CO)_4Os(CH_3)H$, where deuteration on the metal prior to methane formation would be detected.

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Preparation of π-Allyl Metal Complexes by Direct Reaction of Highly Reactive Transition Metal Powders with Allylic Halides

Sir:

In 1972, we reported a general procedure for the preparation of highly reactive metal powders.[1] The basic procedure involved the reduction of a metal salt in a hydrocarbon or ethereal solvent.[1-10] We have noted that the reactivities and in some cases products are highly dependent on the reduction conditions, i.e., anion, reducing agent, solvent, temperature, and presence of added alkali salts, Lewis acids, or Lewis bases.[3-10] In this manuscript we report a general procedure for the preparation of highly reactive transition metal powders.[11] For example, reduction of nickel salts with various alkali metals yields finely divided nickel powders which react rapidly with allyl halides to give the corresponding $(\pi\text{-allyl NiX})_2$ compounds. Heretofore, this important organometallic intermediate[12-18] was accessible from the highly toxic nickel tetracarbonyl,[13] the bis(cycloocta-1,5-diene)nickel,[14] or by the metal atom vaporization technique.[15] In this manuscript we report reactions of highly reactive nickel, palladium, platinum, cobalt, and iron metal powders.

Reduction of anhydrous nickel(II) halides with 2 equiv of potassium in ethereal solvents yields a black metal slurry which reacts readily with allylic halides.[16] Reductions of transition metal salts have also been shown to readily occur with lithium, sodium, potassium, and sodium-potassium alloy. However, the use of an electron carrier, such as 5-10% naphthalene or anthracene based on the alkali metal, facilitates reduction thereby allowing reduction at room temperature or lower. These naphthalide reduced nickel slurries react with allylic halides to give deeply colored solutions which contain $(\pi\text{-allyl NiX})_2$, whereas no color is observed in the slurries produced without electron carriers.

In the case of activated palladium, reduction using lithium

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Table I. Coupling Reactions of Allylic Halides with Ni[a]

allylic halide	temp, °C	% yield (min)[b]	product(s)[c,d]
allyl bromide	85	73 (15)	1,5-hexadiene
allyl chloride	85	25 (15)	1,5-hexadiene
2-methallyl chloride	85	91 (120)	2,5-dimethyl-1,5-hexadiene
crotyl chlorides[e]	85	93 (120)	A[f] (12) B (43) C (44)
crotyl bromides[e]	85	100 (20)	A[f] (0) B (31) C (69)

[a] All reactions used nickel prepared by reduction of 1 equiv of appropriate NiX_2 with 2 equiv of K in refluxing glyme. Concentrations were kept the same throughout. Allylic halides used were >95% pure and 1 equiv was used. [b] Yields are GC yields based on internal standards and corrected for response factors. Separations were effected using 55 mL/min of He on a 3-m, ⅛-in. 5% SE-30 on Chromosorb GAW 60/80. Yields indicated are maximum yields which are observed at the time reported. [c] Products were identified by matching GC retention times and also by GC–mass spectrum, when necessary. [d] Bicrotyls were seen as well-resolved peaks and the ratios of the structural isomers are given in parentheses. [e] Used commercial mixture of ~20% secondary and 80% primary halides. [f] A, 3,4-dimethyl-1,5-hexadienes; B, 3-methyl-1,5-heptadienes; C, 2,6-octadienes.

with naphthalene appears so far to give the most reactive powder. For example, such a powder reacts at room temperature with an excess of allyl chloride to afford (π-allyl $PdCl)_2$ in 47% yield. Palladium powder prepared by potassium reduction in refluxing glyme reacts with allyl chloride under the same conditions to yield <6% of the corresponding compound. Palladium powders produced by potassium reduction in refluxing ethers or via alkali metal–naphthalene reductions readily react with allyl bromide at room temperature to yield (π-allyl $PdBr)_2$ in >90% yield. The reaction between stoichiometric amounts of allyl iodide and palladium metal reduced via lithium–naphthalene is 60% complete in 2 min and essentially quantitative in 30 min. Fischer and Bürger[17] obtained (π-allyl $PdBr)_2$ from finely divided palladium and neat refluxing allyl bromide in 46% yield. Under similar conditions they reported that a reaction occurred with allyl iodide but no compound was isolated, and with allyl chloride no reaction of the metal was observed after several days.

The lithium–naphthalene reduction has been successfully extended to other metals. Platinum metal so prepared reacts at room temperature with allyl iodide. Cobalt metal reacts with allyl bromide to yield 1,5-hexadiene without any evidence of an organocobalt compound. Iron powder reacts very vigorously with allyl bromide at room temperature to yield 1,5-hexadiene.

A very useful procedure for the preparation of nickel powders involves the use of a support. The reduction of nickel salts with lithium and naphthalene in the presence of alumina[18] yields nickel powders which react with allyl, 2-methallyl, and crotyl halides to give solutions of the corresponding organonickel compounds. [π-$CH_2C(CH_3)CH_2NiBr]_2$ has been isolated and identified by its NMR spectrum.[19] The (π-allylic $NiX)_2$ compounds which from allylic halides and nickel powders produced in glyme are stable for ~30–60 min; however, in xylene-glyme (~80–20%) the organonickel compounds are stable for at least 24 h. The reductions in this mixed solvent system are inconvenient because they require several days for complete reduction, whereas glyme reductions are usually complete in <12 h. A superior method is to reduce the metal salt in glyme and then substitute xylene or the desired solvent for the glyme before forming the organonickel compound.

The (π-allyl $NiX)_2$ compound existing in this reduction environment will undergo cross-coupling reactions as have been reported by Corey and co-workers[13,20,21] for various pure (π-allyl $NiX)_2$ compounds. We have obtained a 20% yield of the cross-coupled product formed between (π-2-methallyl $NiBr)_2$ and iodobenzene. With (π-allyl $NiBr)_2$ and iodobenzene a yield of 7% allylbenzene has been obtained.[22] The competing reaction in these systems is the coupling of the allylic groups to form the corresponding biallyl compounds. Use of the more active slurries appears to allow the (π-allyl $NiX)_2$ compounds to accumulate to a significant concentration which slowly decomposes to give the biallyl compounds. We believe that in the reactions of our nickel slurries with allylic halides, the (π-allyl $NiX)_2$ is an intermediate even though it has not been observed and isolated in every case. We are presently working to increase the yields of the cross coupled products.

Coupling of the allylic halides is a competing reaction in the cross-coupling experiments. When these nickel slurries are allowed to react with allylic halides in ethereal solvents, even with a large excess of alkyl iodides or carbonyl compounds present, selective coupling of the allylic groups is observed in good yields and no cross-coupling occurs. At present the selectivity of this reaction appears to be dependent on the solvent; however, the reactivity of the nickel may prove to be an important factor in this selectivity.[23] The order of reactivity of the allylic halides is, as expected, I > Br > Cl and temperature can greatly alter the overall yield. For example, the reaction of allyl bromide at 25 °C yields a maximum of 45% 1,5-hexadiene after several hours, whereas at 85 °C the yield is at least 73% in a few minutes.

Substituents on the allyl group appear not to significantly influence the rate of the reaction of the allylic halides with the nickel powders. The coupling reaction can be driven to completion with a significant excess of either nickel or allylic halide. Some examples of coupling reactions of nickel and allylic halides in stoichiometric amounts are shown in Table I.

As shown in Table I, excellent yields of the coupled products can be readily obtained using our activated nickel. We obtain the same compounds as are obtained in coupling reactions with nickel tetracarbonyl[24] and with Grignard reagents.[25] In the case of the bicrotyls, we observe quite different ratios of products. Initially the reaction of activated nickel with crotyl halides yields mainly 3-methyl-1,5-heptadienes, similar to the product distribution of the Grignard reaction. As the coupling reaction proceeds, the quantity of the 2,6-octadienes increases relative to the amounts of 3-methyl-1,5-heptadienes produced until the distributions in Table I are reached. With nickel tetracarbonyl and crotyl halides, the product distribution is reported to be 78% 2,6-octadienes and 22% 3-methyl-1,5-heptadienes in an overall 81% yield.[24]

The finely divided nickel powders were tested for catalytic activity in hydrogenation reactions and were found to compare favorably with W-6 Raney nickel.[26] The catalytic hydrogenation studies demonstrated very dramatically how changing the reduction conditions changes the properties of the resulting metal powders. Nickel powders generated by reducing $NiCl_2$ were at least twice as good as those obtained by reducing $NiBr_2$. Furthermore addition of KF prior to the reduction of the nickel salts yielded better catalysts while addition of LiF prior to reduction yielded a nickel powder with no catalytic activity. These nickel catalysts should prove to be of general value as they are easier to prepare than the Raney nickel catalysts.

The results presented in this manuscript indicate that highly reactive transition metal powders can be prepared and that the reactivity and selectivity of the metal powders can be drastically changed by changing the reduction conditions. We are continuing our studies of the chemistry of these highly reactive transition metal powders and these studies will be reported shortly.

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(19) The ^1H NMR spectrum in $CDCl_3$ (internal Me_4Si) shows three singlets at δ 1.93 (2 H), 2.33 (3 H), and 2.85 (2 H) and is consistent with that obtained by M. Semmelhack, Ph.D. Thesis. In benzene (internal Me_4Si) the spectrum shows three singlets at δ 1.65 (2 H), 1.90 (3 H), and 2.64 (2 H). This spectrum is different from that reported in two conflicting citations, both of which are probably in error.[13,21]

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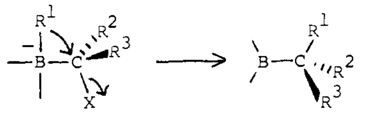
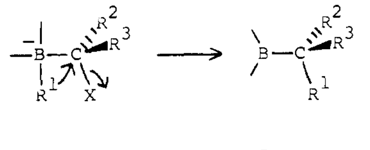
Stereochemistry at the Migration Terminus in the Base-Induced Rearrangement of α-Haloorganoboranes

Sir:

Using a stereochemically defined α-iodo- or α-bromoorganoborane we have found that the base-induced migration of an alkyl group from boron to the α-halo carbon in the absence of solvent is stereospecific and occurs with essentially complete inversion at the migration terminus. Remarkably, in the presence of the normal hydroboration solvents, tetrahydrofuran (THF) or dimethyl sulfide, the α-halo carbon suffers complete loss of stereochemistry.

The ability to form carbon–carbon bonds is one of the outstanding features of organoborane chemistry. Many of these carbon–carbon (and carbon–heteroatom) bond-forming reactions are believed to proceed through an organoborate anion which undergoes a facile 1,2 migration of an alkyl group from boron to an adjacent atom containing an appropriate leaving group.[1] Particularly important in this process is that the stereochemistry of the boron–carbon bond is maintained in the final product.[2] However, despite the wide number and utility of these reactions, very little is known about the stereochemistry of the carbon containing the leaving group.[3] The rearrangement could occur by three distinct pathways. In a concerted process ($\mathrm{S_N2}$ like) the alkyl group could displace the leaving group from the back side giving inversion of configuration on carbon (eq 1). Also in a concerted process the migration could lead to retention of configuration on carbon (eq 2). Finally in a stepwise process ($\mathrm{S_N1}$ like) the intermediate could first ionize with a consequent loss of stereochemistry at the migration terminus (eq 3). To test the stereochemistry of the reaction we have investigated the base-induced alkyl-transfer reaction of a stereochemically defined α-iodo- and α-bromoorganoborane.


(1)


(2)


(3)

Cis hydroboration[4] from the top or bottom of (*Z*)-1-iodo-[5] or (*Z*)-1-bromo-2-methyl-1-butene[6] with diethylborane[7] produces two enantiomeric α-haloorganoboranes. A migration