○ B H ● C—CH₃

Figure 2. Possible structure for isomer B, formed by face-to-face fusion of two $(CH_3)_2C_2B_4H_4$ units. Distortion from regular icosahedral symmetry is suggested by broken lines.

no reasonable structure would have six equivalent borons, this resonance is assumed to arise from superposition of signals of areas 4 and 2. The 100-MHz ^1H nmr spectrum of A in CCl_4 contains methyl resonances of equal area at δ -1.70 and -1.62 ppm relative to $(CH_3)_4Si$, while the spectrum of B exhibits methyl peaks of equal area at δ -2.07 and -2.01.

The ^{11}B and ^1H nmr spectra of isomers A and B do not exhibit marked temperature dependence from -80 to $+20°$, the primary effect on cooling being moderate peak broadening at low temperature. On heating the solution, the two CH_3 peaks in the proton nmr spectrum of B coalesce, collapsing at $+40°$ to a singlet indicating equivalence of all four methyl groups; the proton spectrum of A, however, is basically unchanged at $+40°$, as are the ^{11}B spectra of both A and B.

Unequivocal structure assignments for isomers A and B cannot be given at this time but some reasonable inferences can be made. A $(CH_3)_4C_4B_8H_8$ cage is not expected to be a regular icosahedron (see above); however, the nmr data do not support a polyhedral-fragment structure like that of the isoelectronic $(C_6H_5)_2$-$C_2B_{10}H_{11}^-$ ion previously described. The large range of ^{11}B nmr chemical shifts for isomer A suggests a relatively open structure, possibly consisting of two pyramidal $(CH_3)_2C_2B_4H_4$ units linked at the edges[12,13] (viable localized-bond valence structures based on Lipscomb's approach[14,15] can be written for such a species). The simplicity and small range of the ^{11}B spectrum of B are consistent with a more compact icosahedral-like cage (Figure 2). Distortion from regular icosahedral geometry could occur via cooperative stretching of several bonds[16] such that a high degree of symmetry is preserved, as required by the nmr spectra of B. The proposed structure of B is compatible with the observed nmr equivalence of the methyl groups at $+40°$, since a fluxional rearrangement involving rela-

(12) The structure proposed[13] for $(C_2B_9H_{11})_2$, consisting of edge-bonded $C_2B_9H_{11}$ icosahedral fragments, contains hydrogen bridges and borons lacking terminal hydrogens; both features are absent in $(CH_3)_4$-$C_4B_8H_8$.
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(14) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.
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tive twisting of the two $(CH_3)_2C_2B_4H_4$ pyramids is readily visualized.

Compound I reacts readily with $Mo(CO)_6$ in refluxing heptane, yielding the first known four-carbon metallocarborane system, $(CO)_3Mo(CH_3)_4C_4B_8H_8$ (II). This complex, a dark green, air-stable crystalline solid, has been characterized from its mass spectrum (calcd for $^{12}C_{11}^{16}O_3^{100}Mo^{11}B_8^1H_{21}^+$ (protonated parent ion), 389.1321; found, 389.1311), the ^{11}B nmr spectrum, which contains resonances ($J = 162 \pm 6$ Hz) at δ -50.9, -43.7, -41.0 (asymmetric), and -29.5, with relative areas $3:1:2:2$, and the ^1H nmr spectrum, which exhibits methyl peaks of equal area at δ -1.45, -1.88, -1.99, and -2.17. The molecule satisfies the electronic requirements[16-20] ($2n + 2$ rule) for a closed 13-vertex polyhedron and is electronically analogous to the known $[(CO)_3MoC_2B_{10}H_{12}]^{2-}$ dicarbon system.[21] Since a number of possible structures have the total asymmetry indicated by the nmr spectra, an unambiguous assignment must await X-ray studies.

Compound II and its tungsten analog, similarly prepared, are the first metallocarboranes containing an electrically neutral carborane ligand. The ability of I, a formal six-electron donor, to function as an acceptor of metals may open the way of the preparation of heretofore inaccessible metallocarboranes of electron-poor transition metals such as vanadium and titanium or of metals in unusually low oxidation states. This and other implications of the present work are under investigation.

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Transition Metal Catalyzed Single Electron Transfer in Grignard Reagent Addition to Ketones

Sir:

Since 1968 evidence has been accumulating to indicate that Grignard reagent addition to ketones can proceed through a single electron transfer (SET) mechanism.[1] It is felt that the nature of the solvent, ketone, R group of the Grignard reagent, purity of magnesium used to prepare the Grignard reagent, and mode of preparation of the Grignard reagent are all influential

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Table I. Reaction of Methyl Magnesium Bromide with Benzophenone

Expt	Magnesium purity[a]	Grignard prepared in excess	Solvent	Grignard concn (M)	G/K ratio	% 1,2-addition	% benzo-pinacol	% benzhydrol	FeCl₃ catalyst(ppm)
1	GGT	Mg	Ether	0.178	1.42	98.0	2.0	0	
2	SC	CH₃Br	Ether	0.213	1.17	>99.4	0.6	0	
3	GGT	Mg	Ether	1.38	125	90.6	9.4	0	
4	SC	CH₃Br	Ether	0.048	0.05	>99.2	0.8	0	
5	SC	CH₃Br	Ether	0.188	1.5	99.0	1.0	0	4
6	SC	CH₃Br	Ether	0.188	1.5	97.4	2.6	0	40
7	SC	CH₃Br	Ether	0.188	1.5	81:3	18.7	0	400
8	SC	CH₃Br	Ether	0.188	1.5	54.0	46.0	0	4000
9	SC	CH₃Br	Ether	0.188	1.5	29.5	70.5	0	40,000
10	GGT	Mg	Ether	0.188	1.5	27.5	72.5	0	40,000
11	SC	CH₃Br	THF	0.188	1.5	99.2	0.8	0	
12	SC	CH₃Br	THF	0.188	1.5	27.0	72.0	<1.0	4000
13	SC	CH₃Br	HMPA	0.187	1.5	96.6	0.8	2.6	4000
14	SC	CH₃Br	HMPA	0.187	1.5	95.2	0.8	4.0	

[a] Key: GGT = Grignard Grade turnings, SC = single crystal, G = Grignard, K = ketone.

in determining the course of the reaction.[1c,f,2] It has also been recognized that the reaction of some Grignard reagents with ketones are highly influenced by the addition of the salts of some transition metals.[3]

In the present study we have investigated the relationship between polar and single electron transfer mechanisms in the reaction of Grignard reagents with benzophenone in an attempt to determine the influence of magnesium metal purity (or the addition of trace transition metal impurities) on the reaction pathway.

$$RMgX + Ph_2C{=}O \xrightarrow[NH_4Cl]{H_2O}$$

(1,2-addition)　(1,6-addition)　(pinacol)　(benzhydrol)
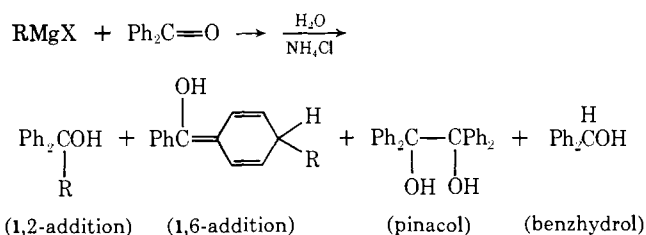
Each of the four products could be formed through a single electron transfer (SET) pathway. While it is well known that the 1,2-addition product can be formed through a polar mechanism, it is far less likely that the other products would be formed in that manner, especially benzopinacol, which is generally accepted to be the coupling product of ketyl radical anions. For this reason, it is likely that a change in mechanism (or in the ratio of two competing mechanisms) would be indicated by a change in the ratio of products.

Methylmagnesium bromide prepared by the reaction of single-crystal magnesium with excess CH₃Br (this method produces the purest Grignard[1f,2]) reacts with benzophenone (Grignard/ketone ratio ∼1.5) in diethyl ether to give more than 99.4% 1,2-addition, while the same reaction using a less "pure" Grignard reagent[1f,2] (prepared from Grignard Grade turnings employing excess magnesium) gave 98.0% 1,2-addition (Table I). (In the former case no benzopinacol was detected by nmr within the limits of detection, whereas in the latter case 2% was observed). At higher G/K ratios, larger amounts of by-product were observed. (At G/K =

125, CH₃MgBr (GGT, excess Mg) gave only 90.6% 1,2-addition and 9.4% benzopinacol.) There is obviously some impurity in the Grignard reagent prepared from Grignard Grade turnings whose effect is substantially increased as the G/K ratio is increased. Doping the ketone solution with FeCl₃ (4–40,000 ppm) followed by reaction with CH₃MgBr (SC, excess CH₃Br) gave by-product benzopinacol (1.0–70.5%) in amounts proportional to the amount of catalyst added. Since no detectable by-product is formed in experiment 2, whereas FeCl₃ causes significant quantities of by-product to be formed (experiments 5–9), it appears that the presence of iron causes a considerable shift in the mechanism of the reaction.[4] Since CH₃MgBr (SC, excess CH₃Br) has been clearly shown to react with benzophenone and 2-methylbenzophenone in a polar manner[1f,2] and since benzopinacol may be expected to occur through some sort of SET intermediate, it appears that the reaction of CH₃MgBr with benzophenone in diethyl ether normally proceeds via a polar mechanism except when catalyzed by a transition metal compound, at which time a SET pathway becomes predominant.

Similar observations were made when the solvent was changed to THF. CH₃MgBr (SC, excess CH₃Br) reacted with benzophenone to give 99.2% 1,2-addition and only 0.8% of the ketone was converted to benzopinacol. On the other hand, when the benzophenone solution was doped with 4000 ppm FeCl₃, benzopinacol accounted for 72.0% of the ketone and 1,2-addition for only 27.0% (the other 1.0% was benzhydrol). As may have been expected, the more polar solvent (THF) better stabilizes the ketyl; therefore, more by-product was observed than in the equivalent experiment in diethyl ether. When the solvent is further changed to HMPA, it would appear that the reaction must proceed entirely by one mechanism (no competition between polar and SET) since doping with FeCl₃ does not significantly change the product ratio. However, further investigation along these lines shows that HMPA inactivates the iron catalyst, hence, both reactions are proceeding by the same mechanism.

Holm and Crossland have clearly demonstrated that the reaction of t-C₄H₉MgCl (prepared from Dow sublimed magnesium in excess Mg) with benzophenone

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(3) (a) J. Hilden and J. Munch-Peterson, Acta Chem. Scand., 21, 1370 (1967); (b) M. S. Karasch and P. O. Tawney, J. Amer. Chem. Soc., 63, 2308 (1941); (c) M. S. Karasch and F. L. Lambert, ibid., 63, 2315 (1941); (d) M. S. Karasch and E. K. Fields, ibid., 63, 2316 (1941).

(4) It is not necessary, nor likely, that the active catalytic iron species is Fe(III). It may well be Fe(0) or Fe(I).

Table II. Reaction of *tert*-Butylmagnesium Chloride with Benzophenone

Expt	Magnesium purity[d]	Grignard prepared in excess	Solvent	Grignard concn (M)	G/K ratio	% 1,6-addition	% 1,2-addition	% benzopinacol
15	SC	*t*-BuCl	Ether	0.188	1.5	48.0	42.3	9.7
16	GGT	Mg	Ether	0.188	1.5	50.0	40.3	9.7
17	GGT	Mg	Ether	0.188	20	48.5	40.7	10.8
18	GGT	Mg	Ether	0.230	121	50.0	42.2	8.8
19	SC	*t*-BuCl	Ether	0.033	0.05	43.8	31.2	25.0
20	GGT	Mg[a]	Ether	0.188	1.5	49.1	38.2	12.7
21	SC	*t*-BuCl	THF	0.208	1.68	41.3	47.0	11.7
22	SC	*t*-BuCl[b]	THF	0.188	1.5	47.4	45.3	7.3
23	SC	*t*-BuCl	HMPA	0.188	1.5	26.0	72.3	<1.7
24	SC	*t*-BuCl[c]	HMPA	0.188	1.5	20.8	77.8	<1.4

[a] With 400 ppm $FeCl_3$. [b] With 4000 ppm $FeCl_3$ added. [c] With 2500 ppm $FeCl_3$, $CoCl_2$, $CuCl$, and $CrCl_3$ added. [d] Key: GGT = Grignard Grade turnings, SC = single crystal, G = Grignard, K = Ketone.

proceeds predominantly, if not entirely, through a SET mechanism.[1e] Since the purity of the magnesium was shown to be important with CH_3MgBr, it was considered necessary to determine whether or not their findings were the result of a transition metal catalyzed reaction. We have found that the reaction of *t*-C_4H_9-MgCl with benzophenone in diethyl ether gives from 48.0 to 50.0% conversion to 1,6-addition products, 38.2 to 42.3% conversion to 1,2-addition product, and 8.8 to 12.7% conversion to benzopinacol, regardless of the grade of Grignard reagent used, the ratio of G/K (if Grignard is in excess), or the presence of 400 ppm $FeCl_3$ (Table II). This is sufficient indication that the reaction of *t*-BuMgCl with benzophenone in diethyl ether proceeds predominantly through a SET mechanism even in the most favorable case when the Grignard reagent was prepared from single crystal magnesium in excess *t*-C_4H_9Cl. Again, experiment 19 shows that in a reaction which is already proceeding predominantly through SET, the presence of a more polar compound in the ether (in this case the excess benzophenone) evidently stabilizes the ketyl radical anion and aids in escape from the solvent cage, forming a larger percentage of benzopinacol. In THF solvent, 41.3% 1,6-addition product, 47.0% 1,2-addition product, and 11.7% benzopinacol was formed. The same reaction in HMPA gave 26.0% 1,6-addition product, >72.3% 1,2-addition product, and <1.7% benzopinacol. No real information can be drawn from the iron doped experiment in HMPA. The doped experiment in THF (experiment 22) gives less 1,2-addition product than the undoped one (experiment 21). This trend is in the right direction to indicate a shift away from a polar mechanism, but the magnitude of the change is too small to be significant and most likely the mechanism is SET in each case. The importance of the *t*-BuMgCl–Ph_2C=O reaction lies in the fact that in ether the product ratio does not depend on the "purity" of the magnesium used to prepare the Grignard reagent. It appears, then, that the reaction, when compared to the work of Holm and Crossland,[1e] proceeds through a SET mechanism, even when the best grade of magnesium available is used to prepare the Grignard.

It is clear from all these data that CH_3MgBr addition to benzophenone in ether solvent is proceeding predominantly, if not entirely, by a polar mechanism whereas the reaction of *t*-C_4H_9MgCl under the same conditions is proceeding by a SET pathway. It is also clear that a reaction that would normally proceed by

a polar mechanism can proceed by a SET pathway, if the magnesium used to prepare the Grignard reagent contains parts per million of transition metal impurities. Further work is underway to determine the effect of other transition metals and the nature of the ketone in affecting the mechanism of reaction of Grignard reagents with ketones.

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Reduction of Coordinated O_2 by Organic Substrates

Sir:

The recent preparation[1] of functionally active cobalt-containing analogs of hemoglobin (Hb) and myoglobin (Mb) suggests that further study of the reactions of mononuclear $Co–O_2$ adducts (best formulated as $Co^{III}O_2^-$, but here written $Co^{II}O_2$ for the sake of simplicity) may contribute to an understanding of the mechanisms whereby the protein can either "stabilize" the O_2 coordinated to iron(II) porphyrins, as in Hb and Mb, or conversely "activate" it, as in the enzyme cytochrome oxidase. We report here some results on the "activation" of O_2 coordinated to Co(II) complexes.

We have previously noted[2a] that the autoxidation of the Co(II) corrinoid vitamin B_{12r} in aqueous solution at room temperature is accelerated by the addition of *p*-dihydroxybenzene (QH_2), thiols, ferrocyanide, and other reducing agents and have ascribed this to the occurrence of the following type of reaction involving a transient $Co^{II}O_2$ complex

$$Co^{II}O_2 + QH_2 \longrightarrow Co^{III}O_2H^- + QH\cdot \quad (1)$$
$$\text{(or } QH^-) \qquad\qquad \text{(or } Q\cdot^-)$$
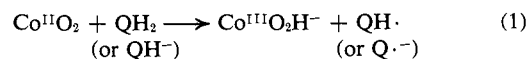
We have now studied directly the reaction of QH_2, etc., with the fully formed O_2 adducts of [Co(II) 3-methoxy-

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