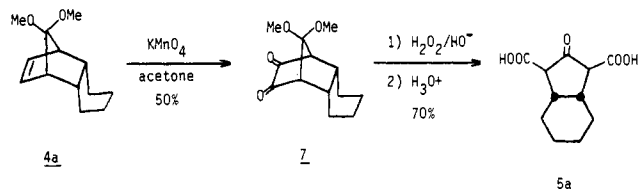
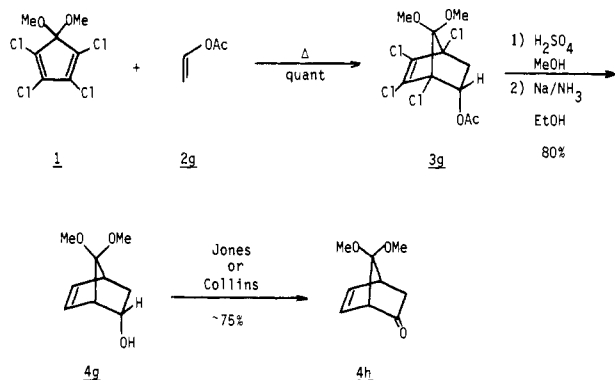


we assume that these are also endo by analogy to the many endo adducts of this type known in the literature.<sup>12</sup>

Other methods for oxidation of the norbornene double bond in **4a-f** were attempted ( $O_3$ , Jones;  $KMnO_4$ ,  $NaIO_4$ ,  $H_2O_2$ ,  $-OH$ ; etc.), but in all cases the overall yields of the keto diacids **5a-f** were lower than those with the conditions described above. Furthermore, in some cases different products were obtained. For example, treatment of the reduced cyclohexene adduct **4a** with  $KMnO_4$  in acetone afforded in 50% yield the  $\alpha$ -diketone **7** (mp 91–92 °C; IR 1760, 1820  $cm^{-1}$ ). Further oxidation of **7** to the diacid **5a** could be accomplished in 70% yield by treatment with hydrogen peroxide followed by aqueous acidic workup.



The intermediates in this sequence can be converted into other functionalized molecules which may be useful for further synthetic transformations. For example, the Diels–Alder reaction between **1** and vinyl acetate **2g** ( $R = OAc$ ;  $R' = H$ ) afforded the crude endo<sup>14</sup> acetate **3g** in quantitative yield. Acid-catalyzed hydrolysis and dissolving metal reduction gave the dechlorinated alcohol **4g** in 80% yield. Collins or Jones oxidation of **4g** furnished the ketone **4h** in  $\approx 75\%$  yield. The use of highly functionalized molecules of this type is under investigation in our laboratories.



**Acknowledgement.** We wish to acknowledge support of this project by a Frederick G. Cottrell Grant from the Research Corporation.

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- All new compounds had spectral properties in complete accord with the assigned structures. The keto diacids **5a-f** were unstable solids with large melting point ranges. For identification they were converted ( $CH_2N_2$ , ether) into their trimethylated (tetramethylated for **5e**) derivatives (enol ether diesters). These had properties in accord with the assigned structures.
- 3d**: NMR ( $CCl_4$ )  $\delta$  6.9–7.3 (m, 5 H), 3.65 (dd, 1 H), 3.63 (s, 3 H), 3.53 (s, 3 H), 2.72 (dd, 1 H), 2.16 (dd, 1 H). **3e**: NMR ( $CDCl_3$ )  $\delta$  3.67 (s, 3 H), 3.59 (s, 3 H), 3.53 (s, 3 H), 3.4 (dd, 1 H), 2.51 (dd, 1 H), 2.20 (dd, 1 H). **3f**: NMR ( $CDCl_3$ )  $\delta$  4.23 (dd, 1 H), 3.58 (q, 2 H,  $J = 7$  Hz), 3.58 (s, 3 H), 3.55 (s, 3 H), 2.58 (dd, 1 H), 1.69 (dd, 1 H), 1.20 (t, 3H,  $J = 7$  Hz). **3g**: NMR ( $CCl_4$ )  $\delta$  5.39 (dd, 1 H), 3.63 (s, 3 H), 3.58 (s, 3 H), 2.81 (dd, 1 H), 2.06 (s, 3 H), 1.68 (dd, 1 H).
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Michael E. Jung,\* James P. Hudspeth

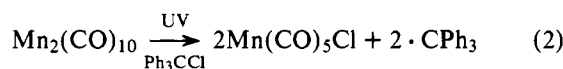
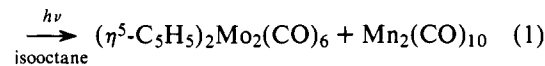
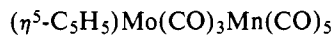
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Received April 21, 1977

## Ordering the Reactivity of Photogenerated, 17 Valence Electron, Metal Carbonyl Radicals

Sir:

We report herein the first ordering of reactivity of metal carbonyl radicals generated by the photoinduced cleavage of metal–metal bonds. There now exist a number of reports<sup>1–7</sup> showing the importance of photoinduced homolytic metal–metal bond cleavage in complexes like  $M_2(CO)_{10}$  and  $MM'(CO)_{10}$  ( $M, M' = Mn, Re$ );<sup>1–4</sup>  $(\eta^5-C_5H_5)_2M_2(CO)_6$  ( $M = Mo, W$ );<sup>5,6</sup>  $M(CO)_5M'(CO)_3(\eta^5-C_5H_5)$ <sup>7</sup> ( $M = Mn, Re; M' = Mo, W$ ); and  $(\eta^5-C_5H_5)_2Fe_2(CO)_4$ .<sup>8</sup> In these and related systems<sup>9</sup> radical cross coupling and halogen atom abstraction reactions have been used to implicate the photogeneration of 17e metal radicals such as  $M(CO)_5$  and  $M(CO)_3(\eta^5-C_5H_5)$  and the like; reactions 1<sup>7</sup> and 2<sup>1b</sup> are illustrative.



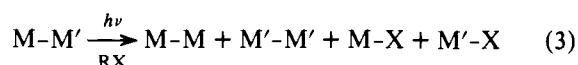
Coupling of the radicals has been shown to occur at an essentially diffusion controlled rate.<sup>6</sup> Photogenerated  $W(CO)_3(\eta^5-C_5H_5)$  radicals have been shown<sup>10</sup> to react bimolecularly with  $CCl_4$ ,  $CHCl_3$ , and  $CH_2Cl_2$  with bimolecular rate constants of  $1.5 \times 10^4$ ,  $\sim 21$ , and  $< 0.6 M^{-1} s^{-1}$ , respectively. In this communication we present results for the irradiation of heterodinuclear complexes which enable us to conveniently order the reactivity of 17e metal carbonyl radicals toward halogen atom donors.

We have studied the photochemistry of the M–M' bonded complexes listed in Table I, and the chemistry is largely as schemed in reaction 3

**Table I.** Irradiation of Heterodinuclear M-M' Bonded Complexes<sup>a</sup>

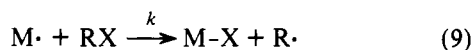
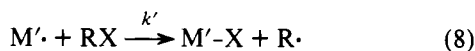
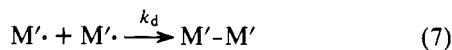
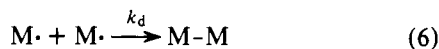
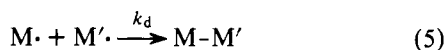
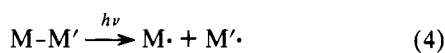
M-M' <sup>b</sup>	RX	Products <sup>c</sup>				Conclusion <sup>d</sup>	k'/k <sup>e</sup>
		M <sub>2</sub>	M-X	M' <sub>2</sub>	M'-X		
Mo-Co	1-C <sub>5</sub> H <sub>11</sub> I	0.52	0.48	0.95	0.00	Mo > Co	<0.08
W-Co	1-C <sub>5</sub> H <sub>11</sub> I	0.00	1.00	0.92	0.00	W > Co	<0.008
W-Mo	1-C <sub>5</sub> H <sub>11</sub> I	0.47	0.53	0.89	0.11	W > Mo	0.15
Mn-Mo	1-C <sub>5</sub> H <sub>11</sub> I	0.04	0.98	0.72	0.30	Mn > Mo	0.07
Mn-W	1-C <sub>5</sub> H <sub>11</sub> I	0.12	0.88	0.25	0.75	Mn > W	0.59
Mo-Fe	1-C <sub>5</sub> H <sub>11</sub> I	0.61	0.39	0.87	0.13	Mo > Fe	0.28
Re-Mn	1-C <sub>5</sub> H <sub>11</sub> I	0.00	0.99	0.36	0.64	Re > Mn	<0.1
W-Co <sup>f</sup>	CCl <sub>4</sub>	0.77	0.23	0.96	0.00	W > Co	<0.16
Re-W <sup>f</sup>	CCl <sub>4</sub>	0.00	1.00	0.28	0.68	Re > W	<0.13
Mn-W <sup>f</sup>	CCl <sub>4</sub>	0.75	0.24	0.86	0.14	Mn > W	0.54

<sup>a</sup> M-M' complexes (0.005–0.025 M) irradiated in deoxygenated benzene solutions of RX (0.1–0.8 M) at 25 °C using a GE Blacklite source equipped with two 15-W bulbs with output between 300 and 400 nm unless noted otherwise. <sup>b</sup> M-M' complexes; Co is Co(CO)<sub>4</sub>; Mo is Mo(CO)<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>); W is W(CO)<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>); Fe is Fe(CO)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>); Re is Re(CO)<sub>5</sub>; and Mn is Mn(CO)<sub>5</sub>. <sup>c</sup> Products from irradiation analyzed by IR (Perkin-Elmer Model 180, matched path NaCl cells) by comparison with authentic samples. M-X is metal carbonyl halide; M<sub>2</sub> is homodinuclear complex. The fractions are the fraction of M or M' containing products. The error is ± 15% of value given. The numbers given are the average of at least two determinations in every case. <sup>d</sup> Relative reactivity of M and M' radicals toward RX. <sup>e</sup> Approximate ratio of abstraction constants for M and M' toward RX; see expression 10 in text. Where one or more products are undetectable an upper limit on k'/k is given. <sup>f</sup> In these cases the solutions were flash photolyzed using a Xenon Corp. flash apparatus.



RX = CCl<sub>4</sub> or 1-C<sub>5</sub>H<sub>11</sub>I  
deoxygenated, C<sub>6</sub>H<sub>6</sub> solution

i.e., we can account for the major fraction (>90%) of M-M' starting material as metal radical coupling or halogen atom abstraction products.<sup>11</sup> We find that the distribution of products depends on M-M', Table I. Data in Table I are for low conversion (<15%) to avoid secondary photolysis of the homodinuclear products. Assuming the proposed<sup>10</sup> mechanistic scheme outlined in eq 4–9



we can determine the relative rate of reaction of M and M' with RX, k'/k, given the expression 10

$$k'/k = [M'-X/M-X][M-M/M'-M']^{1/2} \quad (10)$$

which relates relative abstraction rate and product distribution. The key assumptions in deriving eq 10 are (a) all metal radicals cross couple with the same rate constant, k<sub>d</sub>,<sup>6</sup> and (b) metal radicals react biomolecularly with RX.<sup>10</sup> A crucial fact is that, with the heterodinuclear starting materials, the rate of generation of the M· and M'· must be the same, and, consequently, one can draw conclusions concerning k'/k without regard for absolute quantum yield or light intensity, both of which can change the absolute rate of radical generation. However, variation in radical steady-state concentration by variation in light intensity and/or halocarbon concentration should allow the study of a wide range of radical reactivities.

From the data in Table I we can order the reactivity of several metal radicals toward 1-iodopentane and CCl<sub>4</sub>. For the 1-iodopentane the ordering is as follows: Re(CO)<sub>5</sub> > Mn(CO)<sub>5</sub> > W(CO)<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) > Mo(CO)<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) > Fe(CO)<sub>2</sub>-

(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) > Co(CO)<sub>4</sub>. A similar ordering seems to obtain for CCl<sub>4</sub>. From the approximate values of k'/k given in Table I we find that the bimolecular rate constants for radical reaction with RX vary by at least 10<sup>3</sup>. We do not place too much confidence in the exact values of k'/k, since in many cases we can only place limits on the amount of certain products. Further, the values of k'/k are likely to be in error owing to some small variation in metal radical coupling rate constants, and there is some evidence for generation of other intermediates as a minor component of the primary photoprocesses of metal-metal bonded complexes.<sup>6</sup> However, we feel that the reactivity ordering from a given experiment is certain, e.g., Mo > Co from Mo-Co, W > Co from W-Co, Mn > Mo from Mn-Mo, Mn > W from Mn-W, and Re > Mn from Mn-Re. Thus we are certain that the qualitative ordering of reactivities is very credible. Qualitatively, we find that CCl<sub>4</sub> is more reactive than 1-iodopentane. With the bimolecular rate constant of 1.5 × 10<sup>4</sup> M<sup>-1</sup> s<sup>-1</sup> for W(CO)<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) reacting with CCl<sub>4</sub>,<sup>10</sup> we conclude that for every metal radical studied here the rate constant for abstraction is substantially lower than that associated with diffusion controlled processes of ~5 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>. One final preliminary result is noteworthy; according to the simple scheme (eq 4–9), the reactivity of a metal radical toward two different RX species should be independent of the source of that radical. Within experimental error, (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub> was shown to give the same ratio of (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub>Cl and (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub>I when photo-generated from (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub>, (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>-Mo(CO)<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), or Co(CO)<sub>4</sub>Mo(CO)<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) in the presence of a solution containing both CCl<sub>4</sub> and 1-iodopentane.

Study of the variation in 17e metal radical reactivity will be elaborated in the full paper, but we note here that the ordering of reactivity found seems to correlate with the lability of the M-M bonded complexes. For example, Co(CO)<sub>4</sub> is the least reactive and Co<sub>2</sub>(CO)<sub>8</sub> has a labile Co-Co bond, while Re(CO)<sub>5</sub> is the most reactive and Re<sub>2</sub>(CO)<sub>10</sub> has a fairly inert Re-Re bond.

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## References and Notes

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 (11) As might be expected, we do see some evidence of coupling of the R- and M- species in certain cases. This will be elaborated in the full paper. These considerations do not influence the thrust of the conclusions to be made here. In the absence of RX the only products from irradiation of M-M' are M-M and M'-M'.  
 (12) National Science Foundation Predoctoral Fellow, 1975-present.  
 (13) Recipient of a Dreyfus Teacher-Scholar Grant, 1975-1980.

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## Rearrangement of 5-Methyl-closo-2,4-dicarbaheptaborane

Sir:

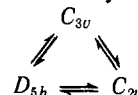
Except for  $(\eta\text{-C}_5\text{H}_5)_x\text{Co}_x\text{C}_2\text{B}_y\text{H}_{y+2}$  ( $x = 1, y = 4; x = 2, y = 3$ ),<sup>1</sup> cage rearrangements among seven-vertex closo deltahedra are unknown. Furthermore, temperature-dependent studies on *closo*- $\text{B}_7\text{H}_7^{2-}$  show no structural pliability up to 90 °C for this pentagonal bipyramidal polyhedron on the NMR time scale.<sup>2</sup>

We find that 5-methyl-*closo*-2,4-dicarbaheptaborane (5-( $\text{CH}_3$ )-2,4- $\text{C}_2\text{B}_5\text{H}_6$ )<sup>3</sup> rearranges to an equilibrium 38:34:28% ( $\pm 1\%$  for each value) mixture of 1-, 3-, and 5-( $\text{CH}_3$ )-2,4- $\text{C}_2\text{B}_5\text{H}_6$ , respectively, at 300 °C over a 2-h period with no significant side reactions evident. The identity of the product mixture was established by (a) GLC-MS which exhibits only one slightly broadened GLC peak having the mass spectrum (PP =  $m/e$  100) expected of a monomethyl derivative of  $\text{C}_2\text{B}_5\text{H}_7$ <sup>4</sup> with the only detectable impurity being a trace of a dimethyl derivative (PP =  $m/e$  114) appearing at the tail end of the GLC peak; (b) a <sup>11</sup>B NMR comparison with other methyl derivatives of  $\text{C}_2\text{B}_5\text{H}_7$ <sup>3</sup> (the proton decoupled <sup>11</sup>B NMR exhibits peaks at  $\delta +27.6, +20.6, +11.9, -3.9, -6.6, -8.3, -11.2$ , and  $-14.1$ , the pattern of which matched composite spectra for a mixture of 1-, 3-, and 5-Me $\text{C}_2\text{B}_5\text{H}_6$  based upon either known<sup>3,5</sup> or calculated<sup>3</sup> chemical shifts and assuming a 38:34:28 ratio for the three isomers, respectively; a similar comparison made using the undecoupled <sup>11</sup>B NMR spectra also supported the presence of all three B-Me $\text{C}_2\text{B}_5\text{H}_6$  isomers in the above quantity ratio); (c) a <sup>1</sup>H NMR spectrum containing three B-methyl peaks at  $\tau$  9.00 (3-Me), 9.28 (5-Me), and 10.50 (1-Me) in an area ratio of 1.25:1.00:1.39 (these shifts are nearly superimposable on the chemical shifts found for the 3-, 5-, and 1-methyl hydrogens, respectively, of a series of  $(\text{CH}_3)_x\text{C}_2\text{B}_5\text{H}_{7-x}$  ( $x = 1-5$ ) prepared by the Friedel-Crafts methylation of the parent carborane).<sup>3</sup>

When comparing the above observed equilibrium ratio with the statistical 40:20:40 (for 1-, 3-, 5-Me $\text{C}_2\text{B}_5\text{H}_6$ ) expected for a hypothetical situation where no enthalpy differences exist between the isomers, it is obvious from enthalpy considerations alone that the positional preference of the B-methyl group follows the order  $3 > 1, 7 > 5, 6$ . It is interesting to note that this is in reverse order to that observed for electrophilic methyl

substitution of the  $\text{C}_2\text{B}_5\text{H}_7$  cage,<sup>3</sup> but a reversal of this genre is also seen when comparing the kinetically controlled Friedel-Crafts methylation of  $\text{B}_5\text{H}_9$  (which exclusively favors the 1-, or apex, position)<sup>6</sup> with thermal equilibration results which favor the 2-, or basal, methyl isomer, 2-Me $\text{B}_5\text{H}_8$ .<sup>7</sup> These results suggest that the positional preference of the methyl group due to the enthalpy contribution is on the boron with greatest positive charge. This is in agreement with a simple electrostatic polarization model<sup>8</sup> as applied to a B-methyl group.

In the course of the rearrangement it is probable that the methyl group does not migrate from boron to boron atom but, instead, accompanies its attached boron as the cage atoms undergo skeletal shifts. This is based on (a) the absence of significant quantities of  $(\text{CH}_3)_x\text{C}_2\text{B}_5\text{H}_{7-x}$  ( $x = 0-7, x \neq 1$ ) as side products which tend to rule out an intermolecular exchange mechanism expected of severe Me-B cleavage; and (b) the previous suggestion of a very plausible intramolecular skeletal rearrangement mechanism for a seven-atom cluster involving the stylized structural cycle:<sup>9-15</sup>



It is to be noted that this mechanistic scheme can lead to all possible B-methyl isomers. The substituted  $\text{C}_{2v}$  intermediate, a capped trigonal prism, contains two square faces as a result of two broken "edge" bonds, whereas the substituted  $\text{C}_{3v}$  intermediate, a capped octahedron, has evolved from a single diamond-square-diamond (dsd)<sup>9</sup> transformation which, at most, involves the breaking of only one "edge" bond of the starting pentagonal bipyramidal  $D_{5h}$  structure. Both the  $D_{5h} \rightleftharpoons \text{C}_{3v}$  and the  $D_{5h} \rightleftharpoons \text{C}_{2v}$  mechanistic schemes can involve identical dsd transformations with the subtle difference that the  $D_{5h} \rightleftharpoons \text{C}_{2v}$  steps involve two concurrent dsd transformations occurring sequentially in the  $D_{5h} \rightleftharpoons \text{C}_{3v}$  mechanism. Another plausible mechanistic scheme involving a rotating triangle rearrangement mechanism<sup>1,15-18</sup> may also account for the observed results.

The 5,6-di-, 1,5,6-tri-, and 1,5,6,7-tetramethyl derivatives of 2,4- $\text{C}_2\text{B}_5\text{H}_7$  also rearrange at 300 °C to isomers which, when analyzed, reinforce the stability trend  $3 > 1, 7 > 5, 6$  (for methyl-substituent placement) found for the monoethyl derivative. Related to these observations we note that the positional preference of the methyl group in a mixture of B,B'-( $\text{CH}_3$ )<sub>2</sub>-2,4- $\text{C}_2\text{B}_5\text{H}_5$  isomers formed from cage expansion of *closo*-1,6- $\text{C}_2\text{B}_4\text{H}_6$  with  $\text{B}(\text{CH}_3)_3$  is nearly identical with that experienced from the rearrangement of 5,6-( $\text{CH}_3$ )<sub>2</sub>-2,4- $\text{C}_2\text{B}_5\text{H}_5$  at 300 °C.

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## References and Notes

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