Mössbauer spectroscopy, see G. Garcin, P. Imbert, and G. Jehanno, *Solid State Commun.*, **21**, 545 (1977). (c) The X-ray powder pattern recorded at 80 K is different from that recorded at 293 K, but no thermal event is observed by low temperature DTA in agreement with a second-order phase transition around 170 K (Dr. J. Pannetier, private communication).

(15) (a) We could characterize η^5-$C_5(CH_3)_5Fe$–η^6-C_6H_6 as an Fe(I) monomeric green species by the Mössbauer spectrum of a frozen DME solution at 77 K: IS = 0.73 mm s^{-1}; QS = 0.82 mm s^{-1}. Dimer (η^5-$C_5(CH_3)_5Fe$–η^5-C_6H_6–$)_2$: ^{1}H NMR (δ, C_6D_6), CH_3 at 1.60 (s, 15), cyclohexadienyl at 1.60–1.80 (m, 3), 3.60 (m, 2), and 5.12 (m, 1). (b) d^7 $CpFePh(CH_3)_n$ can be isolated as solids at −20 °C and characterized by Mössbauer spectroscopy (n = 1, 5; parameters are in the same range as for d^7 Fe(I) sandwiches noted in text). Dimerization (in the solid state, not in solution) is slow (~10 min) for n = 1, 5 at −10 °C and for n = 2, 3, 4 at −20 °C.

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(17) For instance, $[\eta^6\text{-}C_6(CH_3)_6]_2M$ (Re, Te) dimerize spontaneously at low temperature in spite of the hypermethylation (E. O. Fischer and M. F. Schmidt, *Chem. Ber.*, **99**, 2206 (1966)) as Cp_2M (Ir, Rh) (E. O. Fischer and H. Waversick, *J. Organomet. Chem.*, **5**, C59 (1966)).

(18) The efficiency of this redox catalysis is still enhanced on solubilization of both 1 and **1**$^+$ by means of introducing a carboxylate group on the Cp ring; then $k(NO_3^- \rightarrow NH_3) = 10^2$ mol^{-1} L s^{-1}. (a) D. Astruc, A. Darchen, and C. Moinet, Colloque D.G.R.S.T., Paris, Dec 15th, 1978; (b) A. Buhet, A. Darchen, and C. Moinet, *J. Chem. Soc.*, *Chem. Commun.*, 447 (1979).

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Mechanism of the Reaction between Organo Transition Metal Alkyls and Hydrides. A Model for the Aldehyde-Forming Step in the Oxo Process

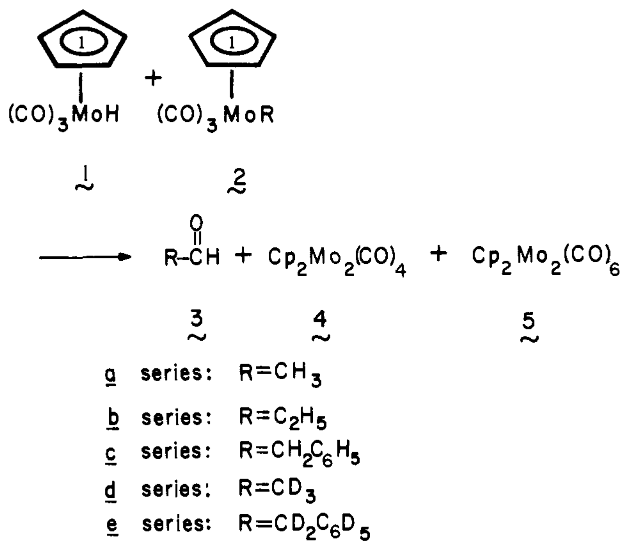
Sir:

The identification of primary reaction steps in organo transition metal chemistry (e.g., oxidative addition, reductive elimination, β-elimination, etc.) was an important advance in understanding organometallic reaction mechanisms.[1] These steps, characteristic of processes which occur at a single metal center, are now being augmented by the identification of steps which involve more than one metal.[2] One such process which has appeared repeatedly recently is the reaction of a metal hydride and a metal alkyl (or acyl) to give a product containing a new C–H bond:

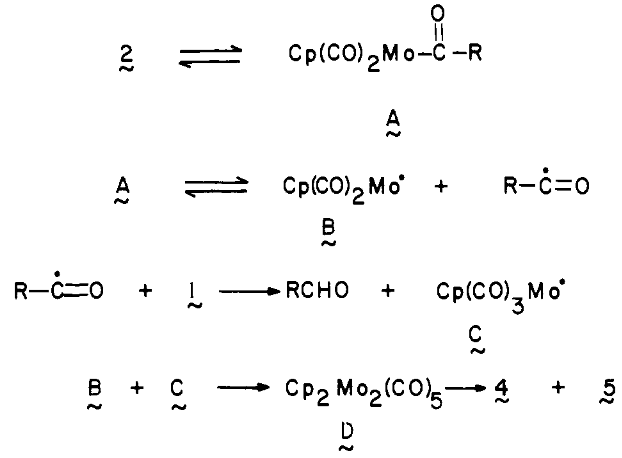
$$M\text{-}H + M'\text{-}R \rightarrow R\text{-}H + M\text{-}M' \qquad (1)$$

An early example was the observation made by Breslow and Heck[3] that $HCo(CO)_4$ and $CH_3COCo(CO)_4$ led rapidly to acetaldehyde, a process which was, however, discounted (perhaps prematurely[4]) as the source of aldehyde in the hydroformylation reaction. Later Schwartz uncovered another example in an iridium system.[5] Norton and his co-workers have investigated such a process in an osmium alkyl hydride, a study which led to the unusual postulate of reductive elimination of *alkane* from an acyl hydride intermediate.[6] More recently still, Halpern and co-workers have shown that benzylpentacarbonylmanganese and hydridopentacarbonylmanganese react to give toluene in a process for which they have proposed a mechanism involving initial homolysis of the benzylmanganese bond, followed by rapid hydrogen transfer from $HMn(CO)_5$ to the benzyl radical intermediates so formed.[7]

Scheme I



Scheme II



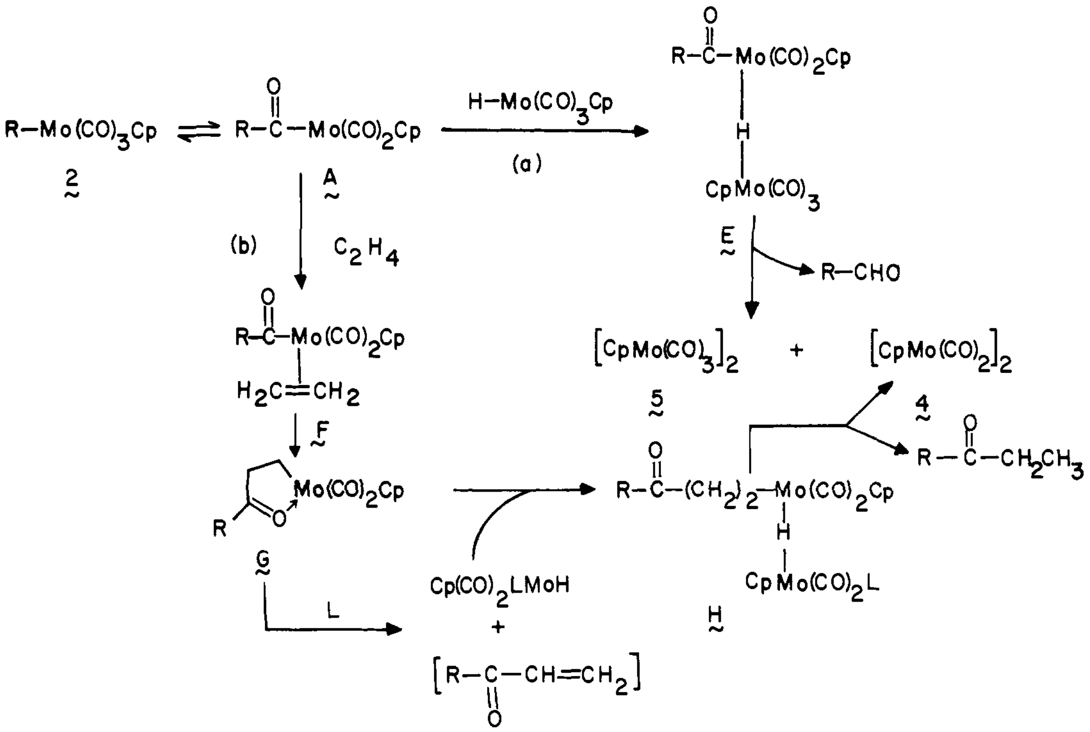
The growing ubiquity and apparent facility of metal hydride-metal alkyl reactions makes it important to have good mechanistic information available on these processes. After briefly surveying the reactions of several well-characterized hydrides and alkyls, we discovered that molybdenum hydride **1** and corresponding alkyls **2** undergo an especially clean and quantitative reaction which leads to aldehyde **3** and dimers **4** and **5** (Scheme I). The methyl and ethyl complex **2a** and **2b** are converted into aldehydes **3a** and **3b** at temperatures between 25 and 50 °C, **2b** reacting substantially more rapidly. Yields are quantitative and no trace of alkanes are observed. These reactions give clean second-order kinetics; rate constants are listed in Table I.

Table I. Rate Constants for Reaction between $CpMo(CO)_3H$ and $CpMo(CO)_3R$ in THF-d_8[a]

alkyl	T, °C	k, M^{-1} s^{-1}
2a	50	2.5×10^{-4}
2b	50	4.0×10^{-3}
2b	25	8.5×10^{-4}
2c	50	2.5×10^{-5}
6a	50	2.3×10^{-4}

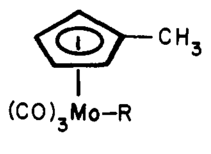
[a] Rates measured by monitoring disappearance of starting material resonances in the 180-MHz NMR spectrum.

Scheme III



These initial observations are consistent with a mechanism involving a rapid preequilibrium between the alkyl and corresponding unsaturated acyl complex, followed by direct reaction of the acyl with molybdenum hydride. However, metal-acyl may be lower than metal-alkyl bond energies and, in view of Halpern's recent result,[7] it is imperative to rule out the possibility that alkyl migration in **2** is followed, as shown in Scheme II, by reversible metal-acyl bond cleavage and scavenging of acyl radicals by hydride.

Because **2** is stable in the absence of hydride, and our observed kinetics are second order, the only way this homolysis mechanism can operate is if the homolysis step is rapid and reversible, and the subsequent reaction of radicals with **1** is rate determining. In an experiment designed to rigorously test this possibility, we examined the behavior of complexes **2** and **6**. The metal-bound methyl resonances in **2a** and **6a** are nicely resolved in the NMR, making it possible to analyze effectively solutions containing **6a, 6d, 2a,** and **2d.** We first demonstrated that **6a** and **2a** are each converted into aldehyde by **1** at nearly identical rates (see Table I). If these complexes are in rapid, reversible equilibrium first with acyl complexes and then with acyl radicals, in mixtures of **2a** and **6d** one should see the methyl resonance of **6a** rapidly growing into the NMR spectrum. However, no such behavior is observed. When hydride **1** is added to the solution containing **2a** and **6d,** conversion into aldehyde takes place at the normal rate, still without any sign of crossover.



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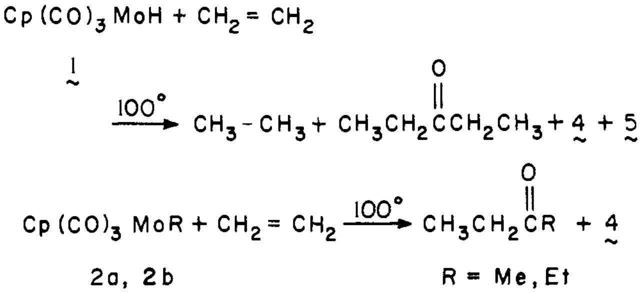
The behavior of the analogous benzyl complex **2c** is somewhat more complicated. As one might expect if alkyl migration is the first step, **2c** reacts with **1** more slowly than **2a** or **2b** (Table I). In addition, R-H (toluene) is now formed as well as aldehyde. Furthermore, the RCHO:RH ratio is dependent upon initial hydride concentration, increases in [**1**] giving rise to a higher yield of aldehyde. This result may be rationalized by assuming that CO insertion in **2c** is slow enough,[8a,b] and the benzyl radical is stable enough,[8c] that CO insertion and simple metal-carbon bond cleavage are now competitive. Again this result was tested by mixing compound **2c** with **6e** and examining the NMR spectrum for signs of the methylene resonance of **6c.** In this case slow appearance of the methylene was observed, at a rate comparable with that of toluene formation in the reaction of **6c** with **1**.

It has been reported[9] that **1** reacts with ethylene to give ethyl complex **2b.** Given that **1** and **2** are converted efficiently into aldehyde, it appeared that, if dimer **5** could be reconverted into **1** with H_2, the reactions reported here could be used to design a catalytic hydroformylation system. We have found, however, that, contrary to the earlier report, **1** and ethylene do not give **2b.** At 100 °C **1** and ethylene do react, as reported earlier,[9] to give a new material containing ethyl absorptions in the NMR, but these are very different from those associated with independently prepared[10] **2b.** We have now found that the organic products are volatile and turn out to be a mixture of ethane (36%) and 3-pentanone (15%). To determine whether a molybdenum alkyl is an intermediate in this transformation, we examined the reaction between ethyl complex **2b** and ethylene. In this reaction diethyl ketone is formed in ~10% yield, even in the absence of added hydride **1**. Similarly, methyl complex **2a** reacts with C_2H_4 at 100 °C to give 2-butanone in ~50%



$$\underset{\mathbf{1}}{\mathrm{Cp(CO)_3MoH}} + \mathrm{CH_2{=}CH_2} \xrightarrow{100^\circ} \mathrm{CH_3{-}CH_3} + \mathrm{CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_3} + \mathbf{4} + \mathbf{5}$$

$$\underset{\mathbf{2a},\ \mathbf{2b}}{\mathrm{Cp(CO)_3MoR}} + \mathrm{CH_2{=}CH_2} \xrightarrow{100^\circ} \underset{\mathrm{R\,=\,Me,Et}}{\mathrm{CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}R}} + \mathbf{4}$$

yield.[11]

The chemistry of this molybdenum system mimics that observed in the oxo reaction very closely. The only major difference appears to be the difficulty of converting $[CpMo(CO)_3]_2$ into **1** by reaction with H_2; this prevents closure of the catalytic cycle. Even the formation of ketones from cobalt acyls and olefins has been observed when only small amounts of hydride are present.[12] Concerning the mechanism of the molybdenum reactions reported here, a radical pathway is ruled out, except as a minor component in the benzyl system. An alternative consistent with our data is illustrated in Scheme III. This postulates initial isomerization of **2** to metal acyl **A**, followed by rapid entry of metal hydride into the unsaturated acyl coordination sphere and reductive elimination of aldehyde.[13] The overall similarity of the molybdenum and cobalt systems reinforces the recent conclusions of others[4] that the aldehyde-forming step in the oxo process also involves reaction between a cobalt hydride and cobalt acyl. In the presence of large amounts of ethylene and reduced concentrations of $CpMo(CO)_3H$, alkene traps the initially formed acyl, and the reaction is diverted to form ketone by the alternate route shown in Scheme III. In summary, there now exists good evidence for the accessibility of *three* mechanistic routes in metal hydride-metal alkyl reactions: (a) acyl formation, coordination of metal hydride to unsaturated acyl, and reductive elimination to aldehyde (this work); (b) acyl formation, reaction of acyl with hydride, and reductive elimination to *alkane*;[6] and (c) M-C bond homolysis to give an organic radical, followed by hydrogen atom transfer from metal hydride to the radical.[7]

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(11) We believe the other product of the reaction between methyl complex **2a** and ethylene is methyl vinyl ketone (MVK; formation of this material serves to balance the stoichiometry of the reaction). Formation of this compound by β-elimination in intermediate G (cf. Scheme III) provides hydride **1** which converts some G into saturated ketone. MVK is an extremely sensitive compound and polymerizes readily. That it is not stable to our reaction conditions was demonstrated by adding ~20 mol % MVK to the initial mixture of **2a** and ethylene; the MVK was converted into NMR-unobservable products at a rate somewhat faster than that of 2-butanone formation. For some recent examples of insertion of olefins into metal–acyl bonds in the iron series, see Cooke, M. P., Jr.; Parlman, R. M. *J. Am. Chem. Soc.* **1975,** *97*, 6863; **1977,** *99*, 5222.

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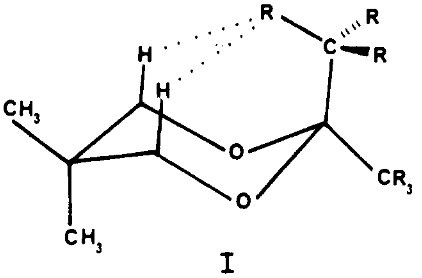
Intrinsic Steric Deuterium Isotope Effects on Proton and Carbon-13 Chemical Shifts

Sir:

Deuterium isotope effects on the NMR chemical shifts of ^1H and ^{13}C in organic molecules are well known.[1] It is useful to distinguish two extreme types of chemical-shift isotope effects: (a) an "equilibrium" chemical-shift isotope effect[2] which involves changes in the populations of two (or more) equilibrating species (double-minimum energy surface), and (b) an "intrinsic" chemical-shift isotope effect which involves a single species (single-minimum energy surface).[3] The intrinsic effects are largest when the deuteron is bonded directly to the observed nucleus, and they generally decrease to virtually zero when the nuclei are separated by more than three bonds.[4] Long-range chemical-shift isotope effects can easily occur in equilibrating systems.[2] In contrast, long-range *intrinsic* isotope effects would be expected only in conjugated (resonance stabilized) anions or cations or in molecules where the deuteron is close in space to the observed nucleus. Although a rough correlation of the intrinsic chemical shift isotope effect with internuclear distance has been noted[5] in two-bond systems for the first-row elements (i.e., in the group XHD vs. XH_2), it is not known whether such a correlation is applicable to compounds where the deuteron and the observed nucleus are separated by several bonds.

We now report the first examples of intrinsic isotope effects on the proton chemical shifts in compounds where the deuteron(s) and the observed proton(s) are separated by five bonds, but where the nuclei are close together in space. The compounds studied are the 1,3-dioxanes, I and I-d_6,[6] and the half-cage acetates, II and II-d.[7] Although I is not a rigid molecule, I and I-d_6 each exist as equal mixtures of two rapidly interconverting chair conformers having exactly the same energies, and isotope effects observed in this system cannot be attributed to population changes. Compound II has a rigid skeleton and is therefore a single species.



I

I ; R:H

I-d_6 ; R:D

The 348-MHz ^1H NMR spectrum of an equal mixture of the 1,3-dioxanes I and I-d_6 exhibits two resolved lines for the methylene protons, which are located about 3.35 ppm from Me_4Si. These signals are separated by 0.90 Hz (2.6 ± 0.07 ppb)[8] (Figure 1), and the splitting is the same at -20 as at $+32$ °C.[9] The low-field signal corresponds to the methylene protons

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