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(16) 4-Dodecylpyridinium *tert*-butyl nitrone dodecyl sulfate: mp 51-53 °C from benzene-petroleum ether; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 6 H, CH_3's), 1.23 (s, 40 H, $(CH_2)_{10}$'s), 1.61 (s, 9 H, *tert*-butyl), 4.00 (t, 2 H, CH_2), 4.73 (t, 2 H, CH_2), 8.43 (s, 1 H, "vinyl"), 8.80-9.00 (m, 4 H, aromatic). Calcd: C, 66.62; H, 10.52; N, 4.57. Found: C, 65.84; H, 10.23; N, 4.48.

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(18) 4-Pyridyl *tert*-butyl nitrone: mp 99-101 °C from cyclohexane-petroleum ether; ^{1}H NMR ($CDCl_3$) δ 1.58 (s, 9 H, *tert*-butyl), 7.70 (s, 1 H, "vinyl"), 8.10-8.30 (m, 2 H, aromatic), 8.73-8.90 (m, 2 H, aromatic). Calcd: C, 67.39; H, 7.92; N, 15.72. Found: C, 67.66; H, 7.38; N, 15.65.

(19) Dimethyl 4-methylpyridinium *tert*-butyl nitrone methyl sulfate: mp 150-151 °C; ^{1}H NMR ($CDCl_3$) δ 1.46, 1.56, 1.60, 3.71, 4.51 (s, 3 H, CH_3's), 4.23 (AB q, CH_2 in ring, J_{AB} = 13 Hz), 8.41 (s, 1 H, "vinyl"), 8.83 (m, 4 H, aromatic); ^{13}C NMR (D_2O) 20.67 (2-^{13}C, CH_3), 29.84 (1-^{13}C, CH_3), 50.42 (1-^{13}C, CH_3), 57.79 (1-^{13}C, CH_3), 67.05 (2-^{13}C, CH_2 in ring), 74.69, 102.47 (^{13}C, quaternary in dioxane ring), 128.53 (2-^{13}C, pyridine ring), 135.81 (1-^{13}C, "vinyl"), 146.06 (1-^{13}C, quaternary in pyridine ring), 147.86 (2-^{13}C, pyridine ring). Calcd: C, 47.8; H, 6.4; N, 7.4. Found: C, 46.6; H, 6.1; N, 7.2.

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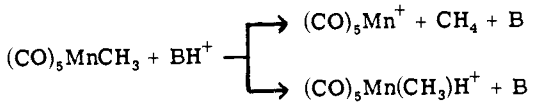
Gas-Phase Organometallic Chemistry. Mechanism and Energetics of Methane Formation Resulting from Protonation of $(CO)_5MnCH_3$

Sir:

Treatment of transition metal alkyl or hydrido complexes with acids in solution often leads to the evolution of alkanes or hydrogen.[1-3] Pentacarbonylmethylmanganese is one compound which shows this reactivity; it decomposes rapidly in acidic media with methane evolution.[1,2] Johnson and Pearson[2] suggest a reaction mechanism involving oxidative addition of the undissociated acid followed by reductive elimination of methane. In many such studies the mechanism of reductive elimination of alkanes remains controversial; in addition there is little quantitative data appropriate for describing the thermochemistry of these processes. This is due in part to the difficulties in characterizing reactive intermediates in solution. Many of the factors contributing to this situation can be eliminated by carrying out related studies in the gas phase, using the techniques of ion cyclotron resonance spectroscopy.[4] A recent gas phase study of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2)^+$, a carbene whose presence could only be inferred in solution, is a case in point.[5] We report here the gas phase reactions of $(CO)_5MnCH_3$ with proton donors, which provide interesting insights into both the mechanism and energetics of methane formation in this system.

Reaction of a variety of proton donors BH^+ with $(CO)_5MnCH_3$[6] yields two products, as indicated by eq 1 and 2.[7] At



$$(CO)_5MnCH_3 + BH^+ \longrightarrow (CO)_5Mn^+ + CH_4 + B \quad (1)$$

$$(CO)_5MnCH_3 + BH^+ \longrightarrow (CO)_5Mn(CH_3)H^+ + B \quad (2)$$

first glance the product of reaction 1 appears to involve loss of CH_4 from the conjugate acid formed in reaction 2. The usual situation in proton transfer reactions, generalized in eq 3, is for proton transfer from B_1 to B_2 to occur when $PA(B_2) \geqslant PA(B_1)$, where PA(B) is the proton affinity of B.[4] When the reaction is sufficiently exothermic, excess energy retained by B_2H^+ results in its decomposition. With this expected behavior, the present results are particularly surprising in that *the conjugate acid $(CO)_5Mn(CH_3)H^+$ is observed only with bases whose proton affinity is substantially below those which yield the product $(CO)_5Mn^+$ as an abundant ion.*

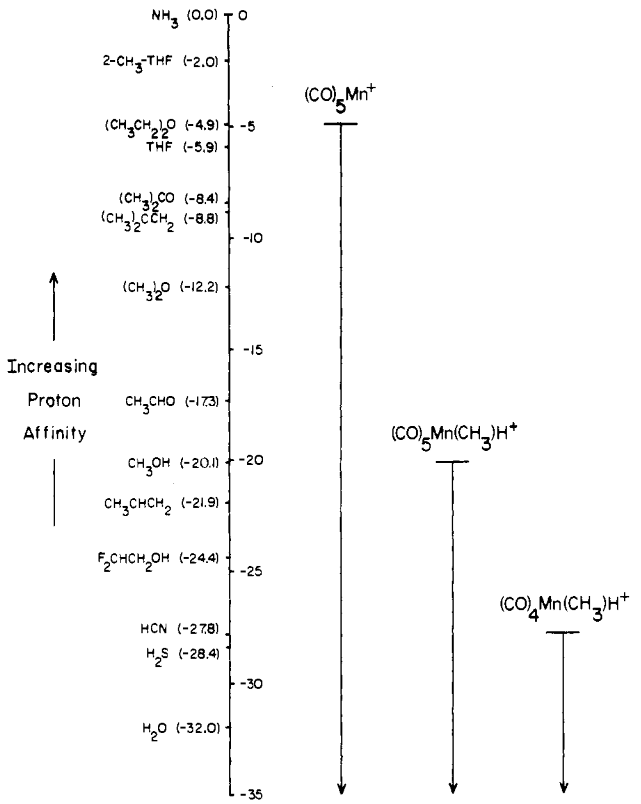


Figure 1. Range of proton donors for which the products $(CO)_5Mn^+$ (reaction 1), $(CO)_5Mn(CH_3)H^+$ (reaction 2), and $(CO)_4Mn(CH_3)H^+$ (reaction 4) are observed. The proton affinity (kilocalories/mole) of each base examined, $PA(B) - PA(NH_3)$, is given in parentheses.[8]

$$B_1H^+ + B_2 \rightleftharpoons B_2H^+ + B_1 \quad (3)$$

The important features of the observed reactions, as illustrated in Figure 1, are as follows. Methane elimination takes place with proton donors for which $PA(B) \leqslant 203 \pm 3$ kcal/mol.[8] If it is assumed that, for $PA(B) > 203 \pm 3$ kcal/mol, reaction 1 is not observed because it is endothermic, the heat of formation of $(CO)_5Mn^+$ is calculated to be 8 ± 4 kcal/mol.[9,10] Onset of reaction 2 establishes a proton affinity of $(CO)_5MnCH_3$ as 188 ± 3 kcal/mol.[8] The homolytic metal hydride bond dissociation energy, $D[(CO)_5MnCH_3{}^+ - H]$, is calculated from this to be 67 ± 3 kcal/mol.[11] If the proton transfer reaction is sufficiently exothermic, internal excitation of the product of reaction 2 may be sufficient for dissociation to occur (eq 4), in which CO is lost in preference to CH_4.[12] Decomposition according to reaction 4 is observed with donors less basic than HCN. This result indicates $D[(CO)_4Mn(CH_3)(H)^+ - CO] \sim 7 \pm 2$ kcal/mol.[8]

$$[(CO)_5Mn(CH_3)H^+]^* \rightarrow (CO)_4Mn(CH_3)H^+ + CO \quad (4)$$

These data are consistent with two available reactive sites on $(CO)_5MnCH_3$; reactions 1 and 2 are *not* competitive in the sense of having common or readily interconverted intermediates. We propose that protonation of the manganese-methyl bond leads to formation of methane with little or no activation barrier. Protonation at a second site, accessible with stronger proton donors, forms a kinetically stable protonated complex.[13] Solution data on protonation of similar species[1-3] lead us to believe the $(CO)_5Mn(CH_3)H^+$ ion is a hydridomethyl species with the proton on the metal center.[14] The manganese-hydride bond dissociation energy of 67 ± 3 kcal/mol is comparable with those of other first-row transition metal hydrides.[15-17] The elimination of methane from $[(CO)_5Mn(CH_3)H^+]$ is not competitive with loss of CO. The above data indicate an activation energy for reductive elimination in excess of 7 ± 2

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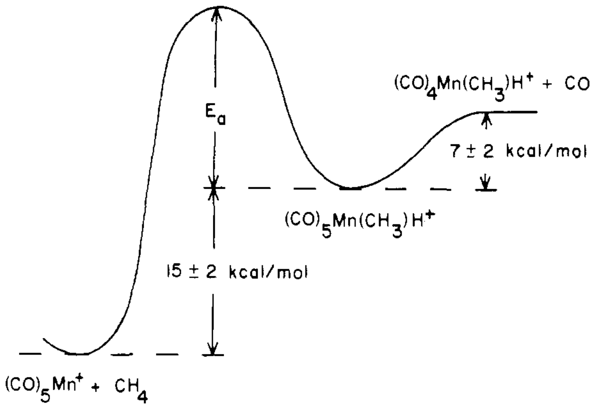

Figure 2. Energetic relationships between species resulting from reductive elimination of CH_4 or loss of CO from protonated $(CO)_5MnCH_3$.

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 $PA(B) \leq 206 \pm 2$ kcal/mol and formation of $(CO)_5Re(CH_3)H^+$ observed for $PA(B) \leq 191 \pm 2$ 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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(9) The heat of formation of $(CO)_5Mn^+$ for this work is calculated using the following auxilliary data. $\Delta H_f°[(CO)_5MnCH_3, g] = -174.6 \pm 2$ kcal/mol: D. L. S. Brown, J. A. Connor, and H. A. Skinner, *J. Organomet. Chem.*, **81**, 403 (1974). $\Delta H_f°(H^+) = 367.2$ kcal/mol and $\Delta H_f°(CH_4) = -17.9$ kcal/mol: D. R. Stull and H. Prophet, Ed., "JANAF Thermochemical Tables", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, 37 (1971). These and all subsequent data are at 298 K.
(10) This value of 8 ± 4 kcal/mol for $\Delta H_f°[(CO)_5Mn^+]$ is in reasonable agreement with the previously reported value of 16 ± 3 kcal/mol, calculated using the following data. $\Delta H_f°[Mn_2(CO)_{10}] = -381.8 \pm 1.1$ kcal/mol: D. L. S. Brown, J. A. Connor, and H. A. Skinner, *J. Organomet. Chem.*, **81**, 403 (1974). $\Delta H° = 24.9 \pm 2$ kcal/mol for the reaction $Mn_2(CO)_{10} \rightleftharpoons 2Mn(CO)_5$ and $IP[Mn(CO)_5] = 8.44 \pm 0.1$ eV: D. R. Bidinosti and N. S. McIntyre, *Can. J. Chem.*, **48**, 593 (1970).
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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 (π-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 (π-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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