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Supplementary Material Available: Tables of atomic coordinates, temperature factors, crystal data and data collection parameters, and bond distances and angles (13 pages); structure factor tables (12 pages). Ordering information is given on any current masthead page.

Kinetics of Intermolecular Oxidative Addition of Primary, Secondary, and Tertiary CH Bonds to $(\mathrm{OC})_3\mathrm{Mn}^-$

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Intermolecular oxidative addition of alkane CH bonds to coordinatively unsaturated transition-metal complexes continues as an intriguing area of research in organometallic chemistry[1] since the first reports by Janowicz and Bergman[2] and Hoyano and Graham[3] in 1982. While oxidative addition of primary and secondary alkane CH bonds to several metal complexes are well established, we are not aware of success in oxidatively adding alkane tertiary CH bonds to metal complexes.[4] We wish to report kinetic evidence that $(\mathrm{OC})_3\mathrm{Mn}^-$ oxidatively adds isobutane by competitive insertion of the metal into the primary and tertiary CH bonds and that the relative rates for the oxidative addition of CH bonds to $(\mathrm{OC})_3\mathrm{Mn}^-$ are primary (1°) < secondary (2°) < tertiary (3°).

Our studies are carried out in a previously described flowing afterglow apparatus.[5] A mixture of $(\mathrm{OC})_5\mathrm{Mn}^-$ (m/z 195), $(\mathrm{OC})_4\mathrm{Mn}^-$ (m/z 167), and $(\mathrm{OC})_3\mathrm{Mn}^-$ (m/z 139) is produced by dissociative attachment of energetic electrons with $\mathrm{Mn_2(CO)_{10}}$ in a fast flow of helium buffer gas ($P_{\mathrm{He}} = 0.7$ torr, $\bar{v} = 58$ m/s) at 298 K.[6] Neither $(\mathrm{OC})_5\mathrm{Mn}^-$ or $(\mathrm{OC})_4\mathrm{Mn}^-$ react with the alkanes under these conditions ($k < 10^{-13}$ cm^3 molecule^{-1} s^{-1}).

Addition of $\mathrm{C_2H_6}$ to the flow containing the 14-electron $(\mathrm{OC})_3\mathrm{Mn}^-$ gave attenuation of the signal for m/z 139 and concomitant formation of the signal for the product ion at m/z 167 with the suggested mechanism in eq 1.[7] The structure of the m/z 167

$$\underset{m/z\ 139}{(\mathrm{OC})_3\mathrm{Mn}^-} + \mathrm{C_2H_6} \rightleftarrows [(\mathrm{OC})_3\mathrm{Mn(H)(C_2H_5)}^- \rightleftarrows (\mathrm{OC})_3\mathrm{Mn(H)_2(C_2H_4)}^-] \rightarrow \underset{m/z\ 167}{(\mathrm{OC})_3\mathrm{Mn(C_2H_4)}^-} + \mathrm{H_2} \quad (1)$$

ion was characterized as the 16-electron η^2-$\mathrm{C_2H_4}$ complex from its further ion–molecule reactions with $\mathrm{D_2}$ where up to four H/D exchanges were observed (m/z 168–171) and with $\mathrm{H_2S}$ and $(\mathrm{CH_3})_3\mathrm{SiH}$ which yield the corresponding adducts of H–S[6] and H–Si bond oxidative addition.[8,9] Statistical correction of the rate constant for reaction 1 yields (k/1° CH bond) (Table I).

Table I. Kinetic Data for the Reactions of $(\mathrm{OC})_3\mathrm{Mn}^-$ with Alkanes in This Study

alkane	k_{total},[a] cm^3 molecule^{-1} s^{-1}	statistically corrected k/CH bond,[b] cm^3 molecule^{-1} s^{-1}	k_{rel}(CH)[b]
$\mathrm{C_2H_6}$	$(8.0 \pm 0.1) \times 10^{-12}$	1.3×10^{-12} (1°)	1
$\mathrm{c\text{-}C_5H_{10}}$	$(9.5 \pm 0.5) \times 10^{-11}$	9.5×10^{-12} (2°)	7
$(\mathrm{CH_3})_3\mathrm{CH}$	$(3.4 \pm 0.4) \times 10^{-11}$	1.5×10^{-12} (1°)	
		2.0×10^{-11} (3°)	13
$(\mathrm{CH_3})_2\mathrm{CH_2}$	$(2.2 \pm 0.2) \times 10^{-11}$		

[a] The errors are the maximum deviations from the average rate constants determined in at least three kinetic runs for each alkane. [b] The average k_{total} is used to calculate the (k/CH bond) values (see text).

The reaction of $(\mathrm{OC})_3\mathrm{Mn}^-$ with cyclopentane also gave the product ion of dehydrogenation, m/z 207 (eq 2). However, the

$$\underset{m/z\ 139}{(\mathrm{OC})_3\mathrm{Mn}^-} + \mathrm{c\text{-}C_5H_{10}} \xrightarrow{-\mathrm{H_2}} [(\mathrm{OC})_3\mathrm{Mn}(\eta^2\text{-}c\text{-}\mathrm{C_5H_8})^-] \rightarrow \underset{m/z\ 207}{(\mathrm{OC})_3\mathrm{Mn(H)}(\eta^3\text{-}c\text{-}\mathrm{C_5H_7})^-} \quad (2)$$

absence of reaction of the m/z 207 ion with the above neutrals[8,9] used with the m/z 167 ion suggests that the m/z 207 ion is an 18-electron complex negative ion formed by oxidative addition of an allylic CH bond to Mn in the intermediate olefin complex. The rate constant and (k/2° CH bond) are give in Table I.

The reaction of $(\mathrm{OC})_3\mathrm{Mn}^-$ with $(\mathrm{CH_3})_3\mathrm{CH}$ similarly gave the m/z 195 product ion (eq 3). The product ion of m/z 195 was

$$(\mathrm{OC})_3\mathrm{Mn}^- + (\mathrm{CH_3})_3\mathrm{CH} \xrightarrow{-\mathrm{H_2}} [(\mathrm{OC})_3\mathrm{Mn}^-\text{–}(>\!=)] \rightarrow \underset{m/z\ 195}{(\mathrm{OC})_3\mathrm{Mn(H)}[\eta^3\text{-}(2\text{-}\mathrm{CH_3})\mathrm{C_3H_4}]^-} \quad (3)$$

also characterized as the 18-electron hydrido–π-allyl structure in eq 3 based on its lack of reaction with $\mathrm{D_2}$, $\mathrm{H_2S}$, and $(\mathrm{CH_3})_3\mathrm{SiH}$.[8,9] $(\mathrm{CH_3})_3\mathrm{CH}$ contains nine 1° CH bonds vs. one 3° CH bond for potential intermolecular oxidative addition to $(\mathrm{OC})_3\mathrm{Mn}^-$. If we assume that ($k$/1° CH bond) obtained from the reaction of $(\mathrm{OC})_3\mathrm{Mn}^-$ with $\mathrm{C_2H_6}$ applies to the reaction with $(\mathrm{CH_3})_3\mathrm{CH}$ and correct it for the 14% increase in the number of collisions between $(\mathrm{OC})_3\mathrm{Mn}^-$ and $(\mathrm{CH_3})_3\mathrm{CH}$ vs. $\mathrm{C_2H_6}$ due to the larger polarizability and dipole moment of $(\mathrm{CH_3})_3\mathrm{CH}$, ($k$/1° CH bond) = 1.5×10^{-12} cm^3 molecule^{-1} s^{-1} in $(\mathrm{CH_3})_3\mathrm{CH}$. Therefore, the kinetic contribution of reaction by the nine 1° CH bonds of $(\mathrm{CH_3})_3\mathrm{CH}$ is 1.4×10^{-11} cm^3 molecule^{-1} s^{-1} which is 41% of k_{total} for this reaction (Table I). The remaining 59% of k_{total}, 2.0×10^{-11} cm^3 molecule^{-1} s^{-1}, is due to oxidative addition of the 3° CH bond in $(\mathrm{CH_3})_3\mathrm{CH}$ based on the above assumption. This analysis is qualitatively supported by the determination of a smaller kinetic deuterium isotope effect for the 1° CH bonds in $(\mathrm{CH_3})_3\mathrm{CH}$ ($k_{(\mathrm{CH_3})_3\mathrm{CH}}/k_{(\mathrm{CD_3})_3\mathrm{CH}} = 1.3$) compared to $\mathrm{C_2H_6}$ ($k_{\mathrm{C_2H_6}}/k_{\mathrm{C_2D_6}} = 2.2$). Assuming that other factors are equal, this result shows a significantly lower contribution of oxidative addition of the 1° CH bonds to k_{total} for the reaction of $(\mathrm{OC})_3\mathrm{Mn}^-$ with $(\mathrm{CH_3})_3\mathrm{CH}$ than with $\mathrm{C_2H_6}$.

Since these overall reactions of dehydrogenation of the alkane by $(\mathrm{OC})_3\mathrm{Mn}^-$ involve the two steps of initial intermolecular oxidative addition followed by intramolecular migration of a hydrogen from an alkyl β-carbon to Mn, it was essential to eliminate the contribution of the intramolecular second step to the observed k_{total}'s for these reactions. We believe that the results of the reactions of $(\mathrm{OC})_3\mathrm{Mn}^-$ with $(\mathrm{CH_3})_2\mathrm{CH_2}$ and $(\mathrm{CH_3})_2\mathrm{CD_2}$ accomplish this end. The reaction of $(\mathrm{OC})_3\mathrm{Mn}^-$ with $(\mathrm{CH_3})_2\mathrm{CH_2}$ yields the product ion of m/z 181 characterized as the 18-electron hydride–π-allyl complex in eq 4 by failure of the m/z 181 ion to react with $\mathrm{H_2S}$ and $(\mathrm{CH_3})_3\mathrm{SiH}$.[8,9]

$$(\mathrm{OC})_3\mathrm{Mn}^- + (\mathrm{CH_3})_2\mathrm{CH_2} \rightarrow \underset{m/z\ 181}{(\mathrm{OC})_3\mathrm{Mn(H)}(\eta^3\text{-}\mathrm{C_3H_5})^-} + \mathrm{H_2} \quad (4)$$

In the reaction of $(\mathrm{OC})_3\mathrm{Mn}^-$ with $(\mathrm{CH_3})_2\mathrm{CD_2}$, complex **1** will be produced as the intermediate irrespective of initial 1° CH or

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(8) Generally, 15- and 16-electron metal complex negative ions oxidatively add $\mathrm{H_2S}$ and $(\mathrm{CH_3})_3\mathrm{SiH}$ forming termolecular adducts with apparent bimolecular rate constants of 10^{-10} to 10^{-11} cm^3 molecule^{-1} s^{-1}. If the coordinatively unsaturated complex contains a hydride ligand, $\mathrm{H_2}$ is usually reductively eliminated in the bimolecular reaction.

(9) The fast bimolecular reactions of the product ions of m/z 167, 207, 195, and 181 with $\mathrm{SO_2}$ yield $(\mathrm{OC})_3\mathrm{Mn(SO_2)}^-$ with loss of $\mathrm{C_2H_4}$, $\mathrm{c\text{-}C_5H_8}$, $\mathrm{C_4H_8}$, and $\mathrm{C_3H_6}$, respectively.

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$$\underset{\mathbf{1}}{(OC)_3Mn(H)(D)(\eta^2\text{-}C_3H_5D)^-}$$

2° CD bond oxidative addition followed by β-D or β-H migration, respectively. If the intramolecular β-migrations and their microscopic reverse rearrangements are slow compared to the fast unimolecular fragmentation of **1**, the sole product will be the *m/z* 182 ion formed by reductive elimination of HD from **1**. The results of the reaction with $(CH_3)_2CD_2$ in eq 5 with formation of about

$$(CO)_3Mn^- + (CH_3)_2CD_2 \begin{cases} \xrightarrow{0.56} \underset{m/z\ 182}{(OC)_3Mn(C_3H_5D)^- + HD} \\ \xrightarrow{0.44} \underset{m/z\ 183}{(OC)_3Mn(C_3H_4D_2)^- + H_2} \end{cases} \tag{5}$$

equal amounts of the *m/z* 182 and 183 ions clearly show that H/D scrambling in **1** is extensive, but not statistical, during the brief lifetime of the excited ion. This result means that intramolecular rearrangements of H and D between Mn and the β-carbons are fast and reversible and will not contribute significantly to the observed kinetics.

These kinetic results establish the reactivity order for oxidative addition of aliphatic CH bonds to $(OC)_3Mn^-$ as 1° < 2° < 3°, although the quantitative values given may be in error. The absence of observed oxidative addition of 3° CH bonds in the condensed phase[4] is probably due to the steric bulk of the transition-metal complex used rather than a significant difference in the intrinsic reactivities of 1°, 2°, and 3° CH bonds in the two phases.

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Chirality Transmission via a 6-Endo Free-Radical-Mediated Cyclization Process. Regio- and Stereocontrolled Synthesis of the 22-Hydroxylated Steroid Side Chains

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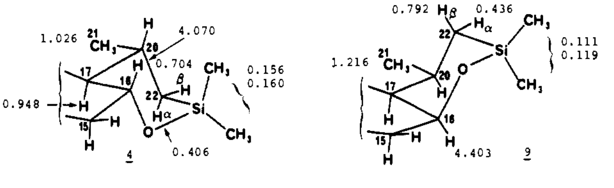
Primarily through the extensive efforts of Stork,[1] Hart,[2] and Curran,[3] C–C bond formation via free-radical-mediated cyclization reactions now has a firmly established role in synthetic organic chemistry as a highly versatile and often indispensable method of skeleton construction.[4] The large volume of data delineating radical reactivity compiled over the past several decades un-



coupling constants (Hz)

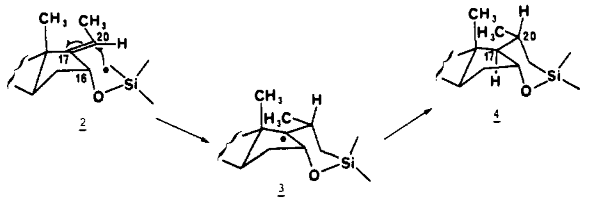
$J_{15,16}$ = 3.5 $J_{15',16}$ = 9.3
$J_{16,17}$ = 9.3 $J_{17,20}$ = 10.5
$J_{20,21}$ = 6.4 $J_{20,22\alpha}$ = 14.5
$J_{20,22\beta}$ = 4.0 $J_{22\alpha,22\beta}$ = 14.4

coupling constants (Hz)

$J_{15,16}$ = 3.7 $J_{15',16}$ = 7.7
$J_{16,17}$ = 6.4 $J_{20,21}$ = 7.1
$J_{20,22\alpha}$ = 3.8 $J_{20,22\beta}$ = 14.7
$J_{22\alpha,22\beta}$ = 14.5

Figure 1. NMR data in $CDCl_3$ (360 MHz); chemical shifts in δ (ppm).

Scheme I



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