neopentyl[bis(dicyclohexylphosphino)ethane]platinum(II) (**1**) produces the reactive intermediate [bis(dicyclohexylphosphino)ethane]platinum(0) (**2**) and that **2** reacts with C–H bonds in saturated and unsaturated hydrocarbons.[8]

Compound **1** was prepared as described in Scheme I.[9] It is unreactive toward water and dioxygen and thermally stable as a crystalline solid. Its structure was established unequivocally by X-ray diffraction (Figure 1).[10] Relevant features of the structure are the cis arrangement of the hydride and alkyl groups and the disposition of the cyclohexyl rings. These rings occupy positions that should minimize intramolecular interactions of their C–H bonds with the platinum center if the solid-state structure persists in solution. We believe that **2** probably has a similarly exposed, unencumbered platinum atom and that the high intermolecular reactivity of **2** reflects, in part, low *intra*molecular reactivity.

Reductive elimination of neopentane from **1** occurs at convenient rates in a variety of solvents at temperatures between 45 and 80 °C (Scheme I); **2**, the inferred intermediate, reacts with C–H bonds in saturated and unsaturated hydrocarbons.[11] Given that very few transition-metal complexes react with saturated hydrocarbons, perhaps the most interesting reactions are those with cyclopentane and 1,1,2,2-tetramethylcyclopropane. Thermolysis of **1** in *n*-hexane or cyclohexane does not yield adducts but instead generates insoluble precipitates.

The decomposition of **1** in benzene is cleanly first order in **1**, with rate constant $k_1 = (2.8 \pm 0.1) \times 10^{-4}\ \mathrm{s}^{-1}$ at 69 °C (determined with the use of ^{31}P NMR spectroscopy). Arrhenius parameters derived from thermolyses at temperatures from 49 to 81 °C are $E_a = 28.0 \pm 0.4$ kcal/mol and $\log A = 14.3 \pm 0.2$. Addition of free bis(dicyclohexylphosphino)ethane has no effect on the rate, but a new product, bis[bis(dicyclohexylphosphino)ethane]platinum(0), forms in competition with **2**. The isotope effect for the reductive elimination of neopentane-d_1 from $L_2Pt(Np)(D)$, $k_H/k_D = 1.5$, is consistent with rate-determining reductive elimination of neopentane,[12] as is the fact that the rate of decomposition is indistinguishable in C_6H_6 and C_6D_6. Increase of the concentration of benzene in mixed benzene/cyclohexane solutions caused a *decrease* in the rate of decomposition and established that benzene was *not* coordinated to **1** before or at the transition state.

We suggest that **2** is a homogeneous model for an "edge" atom in a heterogeneous platinum catalyst. These sites have been shown to be reactive in C–H bond activation in studies with platinum single crystals;[13] **2** is also isolobal[14] with methylene; :CH_2.

Acknowledgment. We thank Professor Roald Hoffmann for encouraging and enlightening discussions.

Supplementary Material Available: Spectral and analytical data for the complexes shown in Scheme I and a table of atomic coordinates and thermal parameters (5 pages). Ordering information is given on any current masthead page.

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(8) Literature precedent suggested that reductive elimination of an alkane from a *cis*-hydridoalkylbis(phosphine)platinum(II) complex would be facile and that the *bent* (bisphosphine)platinum(0) species generated by reductive elimination of neopentane from **1** would be highly reactive. See: Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915–2916. Yoshida, T.; Yamagata, T.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063–2073. Electron-withdrawing groups on the alkyl ligand stabilize the complex with respect to reductive elimination: Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831–1834.

(9) Spectral and analytical data for **1**: ^{1}H NMR (C_6D_6) δ 2.52 ("t" with Pt satellites, $J_{P\text{-}H} = 7$, $J_{Pt\text{-}H} = 78$ Hz, 2 H), 2.25–1.95 (m, 6 H), 1.95–1.0 (m, 51 H), –0.15 (d of d with Pt satellites, $J_{P\text{-}H} = 18$, $J_{P'\text{-}H} = 194$, $J_{Pt\text{-}H} = 1175$ Hz, 1 H); ^{31}P NMR (C_6D_6) δ 75.9 (s with Pt satellites, $J_{Pt\text{-}P} = 1664$ Hz), 62.9 (s with Pt satellites, $J_{Pt\text{-}P} = 1798$ Hz); IR (neat) 2010 cm^{-1}; mp (capillary sealed under Ar) 120–130 °C dec. Anal. Calcd for $C_{31}H_{60}P_2Pt$: C, 53.97; H, 8.77; P, 8.98. Found: C, 54.11; 53.94; H, 8.69, 8.74; P, 8.92, 8.96.

(10) Crystal structure information: $C_{31}H_{60}P_2Pt$, FW = 689.86. Monoclinic, space group $C_{2h}{}^5\text{-}P2_1/n$. At –150 °C, $a = 11.517$ (8) Å, $b = 15.730$ (11) Å, $c = 17.364$ (13) Å, $\beta = 90.32$ (3)°, $V = 3146$ Å^3 with 4 formula units per cell; $D_{calcd} = 1.456$ g cm^{-3} (–150 °C); $D_{obsd} = 1.36$ g cm^{-3} (20 °C); $\mu = 46.22$ cm^{-1}. Data were collected on a CAD4 diffractometer at –150 °C (Mo Kα radiation out to $\theta = 31°$). A total of 10182 unique $F_o{}^2$ values were used in the final refinement of 311 variables. Included in the final model were anisotropic motion of the non-hydrogen atoms and isotropic motion of the hydride ligand. Other H atoms were located on an earlier Fourier map and their positions were idealized in the final refinement. This refinement converged to a value of 0.069 for $R(F^2)$ and for the 7056 F^2 values having $F_o{}^2 > 3\ (F_o{}^2)$ to a value of $R(F)$ of 0.044.

(11) Except for *cis*-hydridophenyl[bis(dicyclohexylphosphino)ethane]platinum(II) and (3,3-dimethyl-1-butene)[bis(dicyclohexyl)phosphino)ethane]platinum(0), the platinum-containing reaction products were identified by comparison with independently synthesized, fully characterized complexes. In all cases, the reaction products were indistinguishable by ^{1}H and ^{31}P NMR spectroscopy from the independently synthesized complexes. *cis*-Hydridophenyl[bis(dicyclohexylphosphino)ethane]platinum(II) and (3,3-dimethyl-1-butene)[bis(dicyclohexylphosphino)ethane]platinum(0) were isolated from preparative-scale thermolyses of **1** in benzene and in a cyclohexane solution of 3,3-dimethyl-1-butene, respectively. Spectral and analytical data for all of the complexes shown in Scheme I are available as supplementary material; complete details of the syntheses will be published later. The sole organic product was neopentane, identified by its GC retention time and GC/MS.

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(14) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711–724. Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006–2026.

Reaction of Group 4 Metal η^2-Acyls with Pyridine: Formation of α,α-Disubstituted-2,6-pyridinedimethoxide Ligands

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Received July 28, 1986

Over the last 10 years the early-transition-metal, lanthanide, and actinide η^2-acyl functional group has received considerable study by both synthetic and theoretical chemists.[2-4] This has been prompted by the unique reactivity of these groups compared to their more well-studied, later-transition-metal analogues. We wish to report here the observed insertion of group 4 metal η^2-acyls into the ortho-CH bonds of pyridine ligands. This result not only demonstrates a novel reactivity for the functionality but also represents a high-yield synthetic route to α,α-disubstituted-2,6-pyridinedimethoxide ligands; ligands that have received recent attention by a number of research groups.[5]

Hydrocarbon solution of the compounds $M(OAr')_2(CH_3)_2$ (M = Zr, Hf; OAr′ = 2,6-di-*tert*-butylphenoxide)[7b] react with carbon

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(1) (a) Camille and Henry Dreyfus Teacher-Scholar, 1985–1990. (b) Fellow of the Alfred P. Sloan Foundation, 1986–1988.

(2) (a) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (b) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. (c) Fachinetti, G.; Fochi, G.; Floriani, C.; Stoeckli-Evans, H. *J. Chem. Soc., Dalton Trans.* **1977**, 2297. (e) Curtis, M. D.; Shiu, K. B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550 and references therein. (f) Marsella, J.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596. (g) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218. (h) Gell, K. I.; Posin, G.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846.

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(4) (a) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440. Tatsumi, K.; Nakamura, A.; Hoffmann, R., *Organometallics* **1985**, *4*, 404.

(5) (a) Hawkins, J. M.; Dewan, J. C.; Sharpless, K. B., *Inorg. Chem.* **1986**, *25*, 1501. (b) Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 1768.

(6) Anal. Calcd for $ZrO_4N_2C_{42}H_{58}$ (**1**): C, 67.61; H, 7.84; N, 3.75. Found: C, 67.62; H, 8.21; N, 3.75%. $HfO_4N_2C_{42}H_{58}$ (**2**): C, 60.53; H, 7.01; N, 3.36. Found: C, 60.10; H, 7.18; N, 2.95%.

0002-7863/86/1508-8095$01.50/0

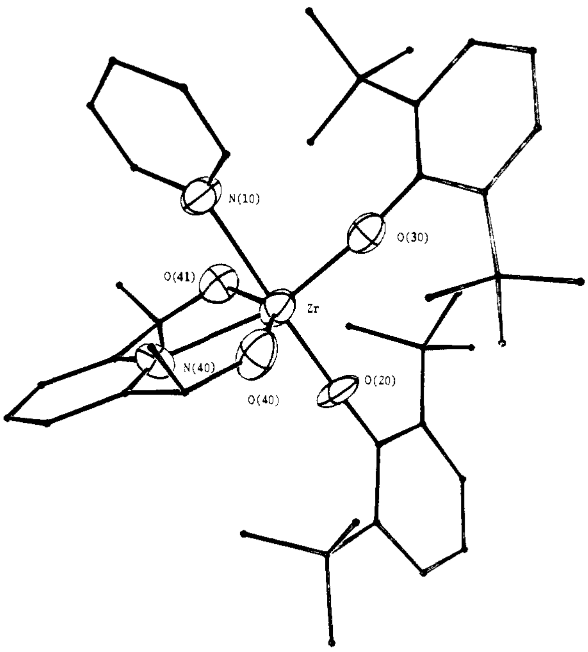
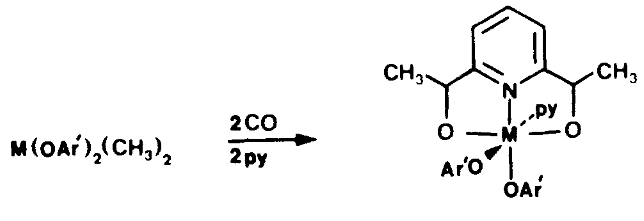


Figure 1. ORTEP view of **1** emphasising the central coordination sphere. Selected bond distances (Å) and angles (deg): Zr–O(20) = 2.015 (6); Zr–O(30) = 2.006 (5); Zr–O(40) = 1.988 (5); Zr–O(41) = 2.034 (5); Zr–N(10) = 2.473 (7); Zr–N(40) = 2.295 (6); O(20)–Zr–O(30) = 98.4 (2); –O(40) = 102.5 (2); –O(41) = 93.1 (2); –N(10) = 175.8 (2); –N(40) = 102.6 (3); O(30)–Zr–O(40) = 101.2 (2); –O(41) = 115.0 (2); –N(10) = 80.3 (2); –N(40) = 158 (3); O(40)–Zr–O(41) = 137.9 (2); –N(10) = 81.7 (2); –N(40) = 69.9 (2); O(41)–Zr–N(10) = 83.9 (2); –N(40) = 68.7 (2); N(10)–Zr–N(40) = 79.1 (3).

Scheme I



M = Zr (**1**); Hf (**2**).

monoxide (1000 psi; Zr, 4 h; Hf, 24 h) in the presence of pyridine (py, >2 equiv) to give high yields (typically 80–95%) of complexes of stoichiometry $[M(OAr')_2(CH_3)_2(py)_2(CO)_2]$, M = Zr (**1**), Hf (**2**).[6] Our initial thoughts were that these compounds contained ene-diolate ligands formed by an intramolecular coupling reaction in a bis-η^2-acyl intermediate.[7] However, the spectroscopic properties of **1** and **2** were inconsistent with this idea. The product was identified by an X-ray diffraction study of crystals of **1** obtained from hexane solution (Figure 1).[8] It can be seen that the carbonylation has led to the formation of an α,α-dimethyl-2,6-pyridinedimethoxide ligand bound to the metal through two oxygens and one nitrogen atom (Scheme I). The two aryloxide ligands and an unchanged molecule of pyridine complete the approximate octahedral environment about the metal. Spectroscopic studies (^{1}H and ^{13}C NMR) are consistent with this formulation.[9] In particular the α-C*HMe*O resonances as a quartet and doublet in the ^{1}H NMR are particularly characteristic. The use of pyridine-d_5 results in the total loss of the other pyridine derived signals in the resulting products. Furthermore the presence of the two chiral centers in the 2,6-pyridinedimethoxide ligand should result in two diastereomers (meso and threo).[5] The solid-state structure of **1** indicated a disorder of the methyl group on one of the α-carbons, indicating that complexes containing the two diastereomers cocrystallize.[10] Also the ^{13}C NMR of either the recrystallized material or crude reaction product show both the meso and threo ligand isomers present in equal amounts.[9] The threo ligand results in only one type of aryloxide group while the meso form makes the two OAr′ groups nonequivalent. Hence three C*Me*$_3$ groups in the ratio of 2:1:1 are observed in the ^{13}C NMR spectrum. This interpretation assumes that rapid dissociation and recoordination of the py ligand is taking place. This is confirmed by the observation of only one set of C_5H_5N resonances in the ^{13}C NMR spectrum so that exchange between the threo and meso isomers is taking place. In the solid state, the four Zr–O distances are all comparable and typical for this bond found in other Zr(IV) alkoxides and aryloxides. However, the Zr–N(40) distance to the tridentate pyridinedimethoxide group is 0.18 Å shorter than the corresponding distance to the pyridine ligand. Presumably this shortening is a consequence of the strong Zr–O bonds pulling the central nitrogen atom of the chelate into the metal.

Mechanistically one can envisage a number of pathways for the carbonylation reaction.[11] However, carrying out the reaction in the presence of equiumolar amounts of C_5H_5N and C_5D_5N (both in large excess) led to the formation of **1**, containing 50/50 deuterio and nondeuterio 2,6-pyridine dimethoxide ligands as judged by ^{1}H NMR. Hence there appears to be little if any primary kinetic isotope effect associated with the reaction. The use of the dibenzyl complexes $M(OAr')_2(CH_2Ph)_2$ (M = Zr, Hf) results in the formation of α,α-dibenzyl-2,6-pyridinedimethoxide ligands under identical conditions. However, a difference here is the ready loss of pyridine from the product to form the sparingly soluble compounds [M(OAr′)$_2$(OCHbz(py)bzCHO)] (M = Zr, Hf).[7a] We presently believe these reactions involve sequential nucleophilic attack on the ortho position of a coordinated pyridine ligand by η^2-acyl groups formed by the migratory insertion of CO into the initial M–CH$_3$ bonds.[12] However, the bis(iminoacyl) Zr(OAr′)$_2$(η^2-PhNCMe)$_2$ fails to react with pyridine over days. Further synthetic and mechanistic studies of this reactivity are planned.[13]

Acknowledgment. We thank the Department of Energy (Grant DE-FG22-85PC80909) for support of this research. I.P.R gratefully acknowledges the Camille and Henry Dreyfus Foundation for the award of a Teacher–Scholar Grant as well as the

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(7) We have previously documented the intramolecular coupling of η^2-acyl and η^2-iminoacyl ligands at related group 4 metal aryloxide centers to produce enamidolate and enediamide ligands; see: (a) McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1072. (b) Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 1896.

(8) Crystal data for $ZrO_4N_2C_{42}H_{58}$ (**2**) at 22 °C: space group $P2_1$, a = 10.559 (5) Å, b = 18.153 (5) Å, c = 11.155 (4) Å, β = 105.73 (4)°, Z = 2, d_{calcd} = 1.199 g cm^{-3}. Of the 4034 unique reflections collected using Mo Kα radiation, $4° \leq 2\theta \leq 45°$, the 2841 with $F > 3\sigma(F)$ were used in the refinement. Final residuals are R = 0.043, R_w = 0.058.

(9) Selected spectroscopic data: ^{1}H NMR (C_6D_6, 30 °C) (**1**) δ 1.27 (d), 1.31 (d, α-CH*Me*O of meso and threo ligands, 8.0-Hz coupling), 5.75 (q, α-C*H*MeO of meso and threo, 8.0-Hz coupling), 6.43 (3-H of pyridinedimethoxide ring of both diastereomers), 1.35 (s), 1.36 (s, OAr′-*t*-*Bu* protons of the threo and meso isomers overlapping), 8.53 (m, py-2*H*), 6.69 (m, py-3*H*), 6.8–7.4 (m, other aromatics). The ^{1}H NMR of **2** is almost identical with that of **1** except for the position of the α-C*H*MeO quartet at δ 5.84. ^{13}C NMR (C_6D_6, 30 °C) (**1**) δ 24.4, 24.5 (α-CH*Me*O of meso and threo ligands), 81.5, 82.1 (α-*C*HMeO), 31.7 (OAr–C*Me*$_3$ of complex containing threo ligand), 31.4, 32.1 (OAr–C*Me*$_3$ of complex containing meso ligand); (**2**) δ 24.9, 25.0 (α-CH*Me*O), 80.6, 81.2 (α-*C*HMeO), 31.8 (OAr–C*Me*$_3$ of threo), 31.4, 32.2 (OAr–C*Me*$_3$ of meso).

(10) The crystal used in this study contained a 50/50 mixture of the (*S*,*R*) and (*S*,*S*) diastereomers. Presumably other crystals in the sample would contain the other (*R*,*S*) and (*R*,*R*) pair. The lack of disorder of one of the α-CHMeO groups (*S* in this case) appears to be needed in order to accommodate one of the *t*-Bu groups of aryloxide ligand, O(20).

(11) The intramolecular insertion of a samarium η^2-acyl into the CH bond of an aryl group has recently been proposed; see: Evans, W. J.; Hughes, L. A.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 1722.

(12) The formation of adducts between tantalum η^2-acyls and pyridine was recently reported; see: Arnold, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1986**, *108*, 5355.

(13) Since the submission of this communication we have learned of a related reactivity between pyridine and η^2-sila-acyl compounds: Tilley, T. D., personal communication.

Alfred P. Sloan Foundation for the award of a Fellowship.

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 $(OC)_3Mn^-$

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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 $(OC)_3Mn^-$ 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 $(OC)_3Mn^-$ are primary (1°) < secondary (2°) < tertiary (3°).

Our studies are carried out in a previously described flowing afterglow apparatus.[5] A mixture of $(OC)_5Mn^-$ (m/z 195), $(OC)_4Mn^-$ (m/z 167), and $(OC)_3Mn^-$ (m/z 139) is produced by dissociative attachment of energetic electrons with $Mn_2(CO)_{10}$ in a fast flow of helium buffer gas (P_{He} = 0.7 torr, $\bar{v}$ = 58 m/s) at 298 K.[6] Neither $(OC)_5Mn^-$ or $(OC)_4Mn^-$ react with the alkanes under these conditions ($k < 10^{-13}$ cm^3 molecule^{-1} s^{-1}).

Addition of C_2H_6 to the flow containing the 14-electron $(OC)_3Mn^-$ 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

$$\underset{m/z\ 139}{(OC)_3Mn^-} + C_2H_6 \rightleftarrows [(OC)_3Mn(H)(C_2H_5)^-] \rightleftarrows$$

$$(OC)_3Mn(H)_2(C_2H_4)^-] \rightarrow \underset{m/z\ 167}{(OC)_3Mn(C_2H_4)^-} + H_2 \quad (1)$$

ion was characterized as the 16-electron η^2-C_2H_4 complex from its further ion–molecule reactions with D_2 where up to four H/D exchanges were observed (m/z 168–171) and with H_2S and $(CH_3)_3SiH$ 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 $(OC)_3Mn^-$ 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]
C_2H_6	$(8.0 \pm 0.1) \times 10^{-12}$	1.3×10^{-12} (1°)	1
c-C_5H_{10}	$(9.5 \pm 0.5) \times 10^{-11}$	9.5×10^{-12} (2°)	7
$(CH_3)_3CH$	$(3.4 \pm 0.4) \times 10^{-11}$	1.5×10^{-12} (1°)	
		2.0×10^{-11} (3°)	13
$(CH_3)_2CH_2$	$(2.2 \pm 0.2) \times 10^{-11}$		

[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 $(OC)_3Mn^-$ with cyclopentane also gave the product ion of dehydrogenation, m/z 207 (eq 2). However, the

$$\underset{m/z\ 139}{(OC)_3Mn^-} + c\text{-}C_5H_{10} \xrightarrow{-H_2} [(OC)_3Mn(\eta^2\text{-}c\text{-}C_5H_8)^-] \rightarrow$$

$$\underset{m/z\ 207}{(OC)_3Mn(H)(\eta^3\text{-}c\text{-}C_5H_7)^-} \quad (2)$$

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 $(OC)_3Mn^-$ with $(CH_3)_3CH$ similarly gave the m/z 195 product ion (eq 3). The product ion of m/z 195 was

$$(OC)_3Mn^- + (CH_3)_3CH \xrightarrow{-H_2} [(OC)_3Mn^-\text{–}(>\!=)] \rightarrow$$

$$\underset{m/z\ 195}{(OC)_3Mn(H)[\eta^3\text{-}(2\text{-}CH_3)C_3H_4]^-} \quad (3)$$

also characterized as the 18-electron hydrido–π-allyl structure in eq 3 based on its lack of reaction with D_2, H_2S, and $(CH_3)_3SiH$.[8,9] $(CH_3)_3CH$ contains nine 1° CH bonds vs. one 3° CH bond for potential intermolecular oxidative addition to $(OC)_3Mn^-$. If we assume that (k/1° CH bond) obtained from the reaction of $(OC)_3Mn^-$ with C_2H_6 applies to the reaction with $(CH_3)_3CH$ and correct it for the 14% increase in the number of collisions between $(OC)_3Mn^-$ and $(CH_3)_3CH$ vs. C_2H_6 due to the larger polarizability and dipole moment of $(CH_3)_3CH$, (k/1° CH bond) = 1.5×10^{-12} cm^3 molecule^{-1} s^{-1} in $(CH_3)_3CH$. Therefore, the kinetic contribution of reaction by the nine 1° CH bonds of $(CH_3)_3CH$ 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 $(CH_3)_3CH$ 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 $(CH_3)_3CH$ ($k_{(CH_3)_3CH}/k_{(CD_3)_3CH}$ = 1.3) compared to C_2H_6 ($k_{C_2H_6}/k_{C_2D_6}$ = 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 $(OC)_3Mn^-$ with $(CH_3)_3CH$ than with C_2H_6.

Since these overall reactions of dehydrogenation of the alkane by $(OC)_3Mn^-$ 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 $(OC)_3Mn^-$ with $(CH_3)_2CH_2$ and $(CH_3)_2CD_2$ accomplish this end. The reaction of $(OC)_3Mn^-$ with $(CH_3)_2CH_2$ 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 H_2S and $(CH_3)_3SiH$.[8,9]

$$(OC)_3Mn^- + (CH_3)_2CH_2 \rightarrow \underset{m/z\ 181}{(OC)_3Mn(H)(\eta^3\text{-}C_3H_5)^-} + H_2 \quad (4)$$

In the reaction of $(OC)_3Mn^-$ with $(CH_3)_2CD_2$, 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 H_2S and $(CH_3)_3SiH$ 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, 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 SO_2 yield $(OC)_3Mn(SO_2)^-$ with loss of C_2H_4, c-C_5H_8, C_4H_8, and C_3H_6, respectively.

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