Methane Oligomerization in the Gas Phase by Third-Row Transition-Metal Ions

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Received November 1, 1990
. *Revised Manuscript Received January 14, 1991*

Alkane dehydrogenation is a common reaction in the gas-phase chemistry of bare transition-metal ions.[1] Reaction with methane, however, is very unusual; exothermic formation of MCH_2^+ requires a metal–carbene bond strength of at least 111 kcal/mol. None of the first-row transition-metal ions meets this requirement,[2] and in the second row, only Zr^+ has so far been found to react with methane.[3] In the third row, however, both Os^+ and Ta^+ dehydrogenate more than one molecule of methane.[4,5] We have investigated the reactions of the third-row ions from Hf^+ through Au^+ and found rapid, sequential reaction with methane to be common (eq 1 and Figure 1). The rapid reactions are often

$$M^+ + nCH_4 \rightarrow \rightarrow MC_nH_{2n}^+ + nH_2 \qquad (1)$$

followed by slower steps that involve extensive ligand coupling. For example, $WC_8H_{16}^+$, which is formed at long reaction times, must contain at least six carbon–carbon bonds (by oxidation-state arguments). We believe that these reactions carry significant implications for fundamental processes in C_1 chemistry. In particular, it is clear that Fischer–Tropsch type methylene coupling does *not* require several metal centers.

Ions are generated in the cell of a Fourier transform ion cyclotron resonance spectrometer by excimer laser (308 nm) ablation of metal targets. Rapid reactions of ions containing the early metals (La,[6] Hf, Ta, W) with oxygen-containing impurities are problematic, especially at high pressures or long reaction times. Mass ambiguities are resolved by using isotopically labeled methane and single, mass-selected metal isotopes. Since the laser ablation process often produces ions that are translationally and electronically excited,[7] one must be careful to distinguish ground-state and excited-state chemistry.

Bonds to third-row transition metals are generally significantly stronger than those to metals of the first and second rows.[2] This may be attributed to the lanthanide contraction and to relativistic effects.[8] Changes in orbital size[8,9] and stability lead to increased overlap and a reduced loss of exchange energy upon bonding. As a result, third-row metals are more reactive than their lighter congeners. The reactivity of the ions La^+ through Au^+ is summarized in Table I. Ground-state La^+, Hf^+, Re^+, and Au^+ (and presumably also Hg^+) are unreactive with methane. Electronically or translationally activated Hf^+ and Re^+ will react, but the back-reactions with added H_2 indicate that both $D(Hf^+–CH_2)$ and $D(Re^+–CH_2)$ are less than 111 kcal/mol.[10]

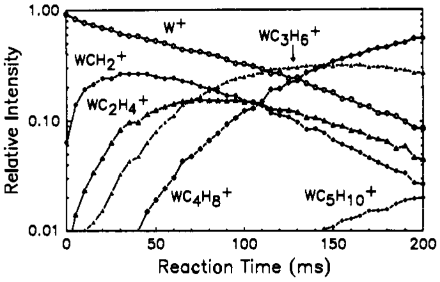

Figure 1. Reaction of labeled $^{186}W^+$ with 3.5×10^{-6} Torr of methane. Successive condensation steps have relative rates of 1:3:3:1:0.05.

Table I. Reactivity of Third-Row M^+ Ions with Methane

M^+	$(k_1/k_c)^a$	facile extent[b]	max. extent[c]
La^+		0[d]	1[e,f]
Hf^+		0	1[f]
Ta^+	0.3	4	4
W^+	0.1	4	8
Re^+		0	4[f,g]
Os^+	0.3	1	4
Ir^+	0.7	2	3
Pt^+	0.4	1	5
Au^+		0[h]	0

[a] Reaction efficiency for first CH_4 molecule. [b] Number of fast, sequential reactions. [c] Maximum number of CH_4 molecules to react. [d] Reference 6. [e] Reference 12. [f] First reaction induced by translational excitation. [g] $ReC_4H_6^+$. [h] See also: Chowdhury, A. K.; Wilkins, C. L. *J. Am. Chem. Soc.* **1987**, *109*, 5336–5343.

Electronic structure considerations[11] can explain the inertness of the unreactive third-row ions. La^+ is unique in the third row because it is not subject to the lanthanide contraction. As a result, the 6s orbital is unusually large and diffuse compared with the 5d orbital,[9] reducing the bonding overlap with the CH_2 moiety. In addition, the d^2 ($^3F_2$) ground state requires 4.0 kcal/mol to attain the more favorable d^1s^1 ($^1D_2$) configuration. The only third-row M^+–carbene bond strength known is $D(La^+–CH_2) = 98.2 \pm 1.4$ kcal/mol.[12]

Hf^+ also suffers from an inappropriate electron configuration, this time d^1s^2 ($^2D_{3/2}$), and requires 10.4 kcal/mol to reach d^2s^1 ($^4F_{3/2}$). Ethane is the smallest alkane with which Hf^+ will react (with about 14% efficiency). Likewise, the d^9s^1 configuration ($^3D_3$) of Au^+ lies 43.0 kcal/mol above the ground state d^{10} ($^1S_0$). Hg^+, which was not included in this study, is not expected to react because its $d^{10}s^1$ configuration cannot form a double bond.

Re^+ has the d^5s^1 ground state (^7S) required for bonding and is unreactive for a more subtle reason.[9,13,14] Between every pair of parallel-spin electrons there exists an exchange interaction (the energy behind Hund's rule). The number of such interactions is a maximum for Re^+, which has five s–d interactions (K_{sd}) and 10 d–d interactions (K_{dd}). Bonding results in loss of approximately 58 kcal/mol ($2.5K_{sd} + 2K_{dd}$).[15] This heavy penalty makes Re^+ especially unreactive; propane is the smallest alkane with which it will react, and that reaction proceeds at only 0.3% of the collision rate.[16] $ReCH_2^+$ loses only about 36 kcal/mol ($2.5K_{dd}$) upon bonding to a second carbene fragment, and this reaction is indeed observed (15% efficiency).

The exothermicity of reaction 1 implies very strong binding of the hydrocarbyl ligand to the metal (eq 2).[10] For example,

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[†] Contribution No. 8351.

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$$D(M^+\text{–}C_nH_{2n}) \geq 17.8n + \Delta H_f(C_nH_{2n}) \text{ (kcal/mol)} \quad (2)$$

considering $n = 4$, if the C_4H_8 ligand is 2-butene ($\Delta H_f = -3$ kcal/mol), the metal–olefin bond strength must be at least 68 kcal/mol, For a metallacyclopentane structure, each metal–carbon bond must be at least 69 kcal/mol strong.[17] A bis-ethylene ($\Delta H_f = 25$ kcal/mol) structure requires the metal–olefin bond to exceed an average of 48 kcal/mol. While these metal–ligand bond strengths are all high, they are not sufficiently unreasonable to permit any of these structures to be excluded on thermodynamic grounds. Fragmentation and ligand displacement studies are in progress to elucidate the mechanisms and structures involved in these interesting reactions.

Acknowledgment. This work is supported by the National Science Foundation (Grant CHE 8711567), the Office of Naval Research (Grant N00014-89-J-3198), the Caltech Consortium in Chemistry and Chemical Engineering (founding members: E. I. du Pont de Nemours and Company, Inc.; Eastman Kodak Company; Minnesota Mining and Manufacturing Company; Shell Development Company), and the donors of the Petroleum Research Fund, administered by the American Chemical Society. K.K.I. is grateful to E. H. Fowles for productive conversations and to the Department of Education for fellowship support.

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[17] Estimating $\Delta H_f(1,4\text{-butanediyl}) \approx 2\Delta H_f(n\text{-}C_4H_9^\bullet) - \Delta H_f(n\text{-}C_4H_{10})$.

Binding of 2,2′-Bipyridine to the Dirhodium(II) Tetraacetate Core: Unusual Structural Features and Biological Relevance of the Product $Rh_2(OAc)_4(bpy)$

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Received September 24, 1990

Dirhodium tetracarboxylate complexes have attracted considerable interest due to their catalytic[2] and antitumor activity.[2,3] We have long been intrigued by the latter, the ability of $Rh_2(O_2CR)_4$ complexes to prolong the survival times of tumorous mice.[3] The mechanism of action is unknown, but it has been suggested to be inhibition of DNA replication, involving $Rh_2(O_2CR)_4$ binding directly to DNA bases.[4,5] For the better understood antitumor agent *cis*-$(NH_3)_2PtCl_2$, the primary DNA-binding mode is loss of the two Cl^- ions and intrastrand Pt attachment to the N7 atoms of two adjacent guanine bases.[6] The same is considered possible for the Cp_2MX_2 (M = Ti, V, Nb, Mo; X = halide) complexes and certain other metal-based antitumor agents.[7] The d(pGpG) unit thus acts as a bidentate chelate group. Conventional wisdom would suggest that $Rh_2(OAc)_4$ could not bind in a similar fashion, since the two labile (axial) sites are at opposite ends of the molecule. It might, therefore, be concluded that $Rh_2(OAc)_4$ binds to a single base or is akin to *trans*-$(NH_3)_2PtCl_2$, which binds to two nonadjacent DNA bases having one or more intervening nucleotides. We wondered whether such a conclusion is necessarily sound and whether $Rh_2(OAc)_4$ could indeed bind in a similar fashion to *cis*-$(NH_3)_2PtCl_2$.[8] A search of the Rh literature failed to unearth a $Rh_2(O_2CR)_4$ unit bound to a single bidentate nitrogen chelate.[9] We have therefore sought such a species using a bidentate group (2,2′-bipyridine; bpy) to mimic the "chelating" ligation of adjacent guanine bases. We herein describe the results of this study.

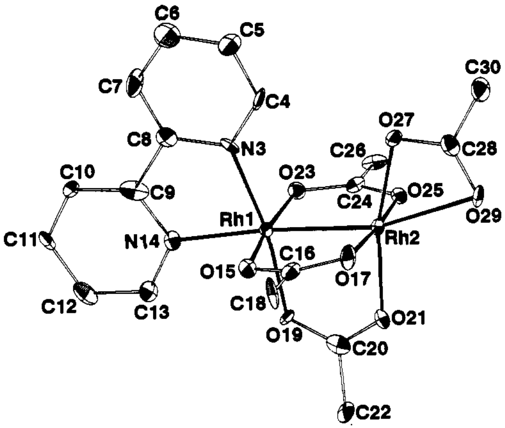

Figure 1. ORTEP representation of complex **1**. Selected bond lengths (Å) and angles (deg): Rh1–Rh2, 2.475 (2); Rh1–O15, 2.050 (8); Rh1–O19, 2.033 (7); Rh1–N3, 2.039 (9); Rh1–N14, 2.120 (10); Rh2–O17, 2.038 (8); Rh2–O21, 2.034 (8); Rh2–O25, 2.043 (8); Rh2–O27, 2.051 (8); Rh2–O29, 2.466 (8); Rh1–Rh2–O29, 163.5 (2); Rh2–Rh1–N14, 175.1 (3); C28–O27–Rh2, 99.9 (7); O27–Rh2–Rh1, 106.9 (2); O27–Rh2–O29, 57.1 (3); N3–Rh1–N14, 80.0 (4).

A wine-red solution of $Rh_2(OAc)_4 \cdot 2MeOH$ in MeCN was treated with 1 equiv of bpy. Following overnight storage at ambient temperature, green crystals of $Rh_2(OAc)_4(bpy)$ (**1**) were collected in 35–42% yield.[10a] A similar reaction with 2 equiv of bpy also gave green crystals of **1**, as did warming of the latter reaction solution to ~40 °C for a few hours. The unusual

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