for the reaction of hydroxide ions with norbornadiene, yielding benzyl and cycloheptatrienyl anions as products.[22] In the flowing afterflow apparatus, structural isomers are distinguished by successive proton-exchange reactions with CH_3OD or D_2O.[23]

Multiphoton electron detachment represents a convenient general method for obtaining infrared spectra of negative ions because most photodetachment thresholds lie well below thresholds for photodissociation. In addition, stable negative ions may be formed by proton transfer from an enormous number of molecules with labile protons. With the development of moderately intense (>1 W/cm^2) lasers in other regions of the infrared, more extensive spectra will be obtained, yielding detailed information about structure and bonding in molecular ions. With sufficient laser intensities it is anticipated that recording infrared spectra may become a routine application of mass spectrometry.

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Periodic Trends in Transition Metal-Hydrogen, Metal-Carbon, and Metal-Oxygen Bond Dissociation Energies. Correlation with Reactivity and Electronic Structure

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The strengths of bonds formed between transition metals and various substituent groups are of fundamental importance in the areas of surface chemistry, organometallic chemistry, and catalysis. The scarcity of such thermodynamic information has led us to develop new experimental methods for the determination of the thermochemical properties of organometallic species.[2-8] Most important are ion beam experiments in which an examination of the translational energy dependence of endothermic reactions yields bond energies of product species.[5-8] Studies of the general process 1, where M^+ is an atomic metal ion and R_2 = H_2, C_2H_6, C_2H_4,

$$M^+ + R_2 \rightarrow MR^+ + R \qquad (1)$$

and O_2, provide the bond energies of metal hydrides, methyls, carbenes, and oxides summarized in Table I.[9] Experimental techniques and methods of analysis have been detailed in previous work.[5-7] The results presented in Table I represent the first such data base involving transition-metal species. A close examination of these data reveals a correlation of metal-ligand σ bond energies with the electronic configuration of the metal ion and permits some interesting comparisons of metal ion thermochemistry and reactivity.

Table I. Summary of Metal-Ligand Bond Dissociation Energies[a,b]

	Cr^+-R	Mn^+-R	Fe^+-R	Co^+-R	Ni^+-R	Zn^+-R
R = H	35 ± 4	53 ± 3[c]	58 ± 5	52 ± 4	43 ± 2	60[d]
R = CH_3	37 ± 7	71 ± 7[c]	68 ± 4	61 ± 4	48 ± 5	67 ± 1[e]
R = CH_2	65 ± 7	94 ± 7	96 ± 5	85 ± 7	86 ± 6	
R = O	77 ± 5	57 ± 3	68 ± 3	65 ± 3	45 ± 4	
promotion energy[f]	34.2	0	0	9	24.0	0

[a] All data in kcal/mol at 298 K. [b] All values from this study or ref 5-8 unless otherwise indicated. [c] These values are somewhat uncertain due to difficulties in interpretation of the data; the results for MnH^+ agree within experimental error with those reported in ref 4. [d] Reference 12. [e] Reference 14. [f] Promotion energy from lowest state derived from the $3d^n$ configuration to the lowest state derived from the $3d^{n-1}4s^1$ configuration. Values from reference 10.

Figure 1 shows the correlation of M^+-R bond energies for R = H and CH_3 with the difference in energies between the metal ion ground state and the lowest state derived from the $3d^{n-1}4s^1$ configuration.[10] For Mn^+, Fe^+, and Zn^+, the $3d^{n-1}4s^1$ configuration gives rise to the ground state, while Cr^+, Co^+ and Ni^+ have a ground state derived from the $3d^n$ configuration. The correlation suggests that formation of the first metal-ligand σ bond involves mainly the 4s orbital on the metal. A similar conclusion was reached by Scott and Richards[11] in a survey of experimental and theoretical results for the neutral metal hydrides, ScH through FeH. They suggest that the $3d^{n-1}4s^1$ configuration of the metal gives rise to the ground state of the hydride and that the d electrons are largely nonbonding.

If the noted correlation holds across the periodic table, bond energies of other transition metals can be predicted. Indeed, Sc^+, Ti^+, and V^+ should all have strong hydride and methyl bonds since they have promotion energies of 0, 0, and 7.4 kcal/mol, respectively.[10] Copper ions are predicted to have weak bonds (~15 kcal/mol) since the promotion energy is 63 kcal/mol.[10] Concerning other rows of the periodic table, the only available bond energies are for the group 2B metals Zn, Cd, and Hg.[12-14] Metal ion hydride bond energies for Cd^+ and Hg^+ are 48 and 70 kcal/mol,[13] respectively, while the methyl bond energies are 54 and 68 kcal/mol,[14] respectively. Since Cd^+ and Hg^+ both have $d^{10}s^1$ ground states, these values clearly do not fit the correlation of Figure 1. The group 8 metal ions Rh^+ and Pd^+ have promotion energies of 73 and 72 kcal/mol,[10] respectively, from their ground states (derived from $3d^n$ configurations) to the lowest states derived from the $3d^{n-1}4s^1$ configuration. Metal hydrogen bond energies of these species would be very small if the above correlation were to hold. However, ICR studies of the reactions of Rh^+ suggest a reasonably strong Rh^+-H bond,[15] which may imply that the

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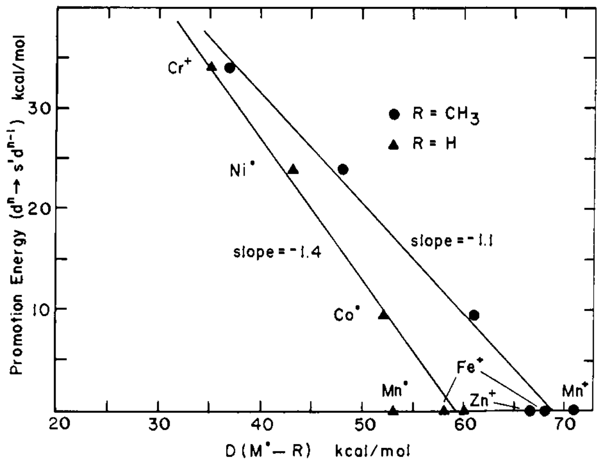

Figure 1. Promotion energy vs. metal ion hydride bond energies (triangles) and metal ion methyl bond energies (circles) for Cr^+, Mn^+, Fe^+, Co^+, Ni^+ and Zn^+. The promotion energy is between the lowest states derived from the $3d^n$ and the $3d^{n-1}4s^1$ configurations.

metal 4d orbitals are used in σ bonding for the second-row transition-metal series. This conclusion is in agreement with the considerations of Scott and Richards[11] relating to bonding in the second-row neutral metal hydrides.

No simple correlation such as Figure 1 could be found for the metal carbene or metal oxide bond energies.[16] Since these bonds probably include substantial π character, it is not surprising that no single metal electronic configuration is appropriate in all cases. It should also be noted that the metal carbene and oxide bond energies do not correlate with one another as do the hydride and methyl bond energies. This may indicate that metal carbene and metal oxide bonding are not as similar as might first be imagined.

The reactivity of the five transition-metal ions with alkanes may be understood in terms of the thermochemistry in Table I. Fe^+, Co^+, and Ni^+ have been observed to cleave and dehydrogenate alkanes containing three or more carbons in facile exothermic reactions.[6,17-19] If the second metal hydride and methyl bond energies for these three metals are comparable to the first, then insertion of the metal ions into C–H or C–C bonds, the first step in reaction with alkanes, is substantially exothermic. Fe^+ is indiscriminate in inserting into C–C and C–H bonds, Ni^+ is more selective in comparison, and the behavior of Co^+ is intermediate.[17] For example, Fe^+ inserts more readily into the stronger terminal C–C bonds of hydrocarbons than either Co^+ or Ni^+.[17,18] These observations are in accordance with the bond energies summarized in Table I. Mn^+ and Cr^+, however, are not observed to react at all with alkanes.[8,18,19] For Cr^+, this appears to be due to the weakness of the chromium hydride and methyl bonds. Manganese ions present an interesting dilemma. We believe the failure of Mn^+ to react with alkanes is due to a weak *second* metal–ligand bond which must form with participation of the half-filled d shell. In bonding to what is probably a high-spin configuration, the loss of considerable electron-exchange energy weakens the resultant bond. Indeed, this is precisely why $Cr^+(^6S, 3d^5)$ has such a weak *first* bond.

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Synthesis of 11α,9α-Epoxymethanothromboxane A_2: A Stable, Optically Active TxA_2 Agonist

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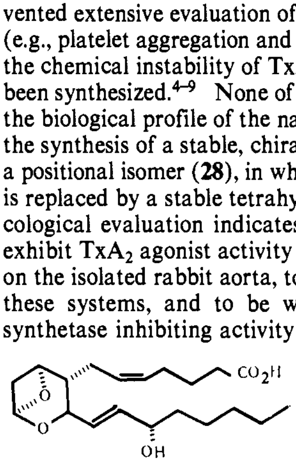
The structural elucidation of rabbit aorta contracting substance, subsequently renamed thromboxane A_2 (**1**, TxA_2), by Samuelsson and co-workers constitutes a noteworthy achievement in the chemistry of eicosanoids.[1,2] The ephemeral nature of **1** ($t_{1/2}$ of ca. 32 s at 37 °C in pH 7 aqueous solution), however, has prevented extensive evaluation of its potent pharmacological effects (e.g., platelet aggregation and vasoconstriction).[3] To circumvent the chemical instability of TxA_2, several carbon congeners have been synthesized.[4-9] None of these analogues, however, displays the biological profile of the natural material. We wish to report the synthesis of a stable, chiral analogue of TxA_2 (**2**), as well as a positional isomer (**28**), in which the labile oxetane ring of TxA_2 is replaced by a stable tetrahydrofuran moiety. Initial pharmacological evaluation indicates that **2** is the *first compound* to exhibit TxA_2 agonist activity in rabbit platelet rich plasma and on the isolated rabbit aorta, to be devoid of antagonist effects in these systems, and to be without appreciable thromboxane synthetase inhibiting activity.



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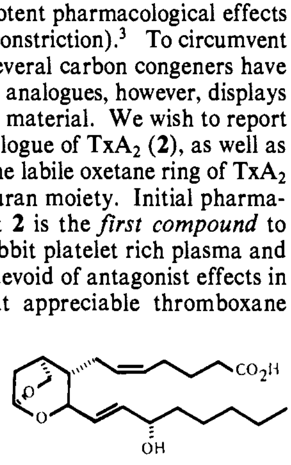

2

The key synthetic transformation leading to the construction of the bridged tetrahydrofuran ring of **2** was envisioned as being the stereoselective insertion of a methylene unit into the lactone moiety of chiral **3**.[10] This construct began with the alkylation of lactone **3** (Scheme I) with benzyl bromide (5 equiv) and NaH (2 equiv) in hexamethylphosphoramide for 3 h to give, after silica gel chromatography, **4**[11,12] (65%). Reaction of lactone **4** with dimethylamine (10 equiv) in THF for 24 h (**5**:[11] mp 133–135 °C) followed by oxidation with Jones reagent (1.5 equiv) at −10 °C provided, after silica gel chromatography, **6**[11] (79% from **4**), mp 126–128 °C. Treatment of ketone **6** with the lithium salt of *N,S*-dimethyl-*S*-phenylsulfoximine[13] (3 equiv) in THF at −78 °C for 2 h (vide infra) followed by reductive elimination of the β-hydroxysulfoximine intermediate with aluminum amalgam (15

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