

Table V. Bond Orders^a

molecule	C _α -C _X	C _X -X	C _α -CH ₂ ⁺ ; C _α -CH ₃
1	1.04	2.94	
2	1.42	2.52	
3	1.02	2.95	1.00
4	1.27	2.68	1.08
5	1.03	2.96	1.11
6	0.69	2.53	
7	1.00	2.95	1.00
8	1.20	2.75	1.06
9	0.99	2.02	
10	1.15	1.83	
10R	1.00	2.02	
11	0.98	2.02	1.01
12	1.07	1.91	1.11
13b	0.94	2.06	1.12
14	0.97	2.02	1.00
15	1.03	1.95	1.08
16			1.13
17			1.09

^aCalculated in the PRDDO approximation for bond orders as defined in ref 29.

PRDDO wave functions and are given in Table V. As an example, the bond orders for 1 show a C-C bond with slightly more single bond character than a nominal single bond (bond order = 1.0) and slightly less of a C≡N triple bond (bond order = 3.0). In 2, the C-N bond order is reduced by almost 0.5, while the C_α-C bond order is increased by ~0.4. Thus, there is significant double bond character in the C_α-C bond. The C_α-C bond order decreases significantly in 4 as expected from the previous discussion on charges and π-overlap populations while the C-N bond order

(30) Armstrong, D. R.; Perkins, P. G.; Stewart, J. P. *J. Chem. Soc., Dalton Trans.* 1973, 838.

increases. The C_α-C_{H₃} bond order is now greater than 1.0 due to the resonance stabilization of the CH₃ group. The ⁺C-CH₂ bond order is increased in 5 since this is the only resonance stabilization available. Note, however, that it is less than the bond order in CH₃CH₂⁺ (16). The bond orders in 8 follow the general trend of a decrease in the C_α-C_N order and an increase in the C-N order relative to 2. However, even here, there is still an enhanced resonance stabilization of the ⁺C moiety. The bond order C⁺-CH₃ is decreased in 8 as compared to 17 due to the resonance interaction with the CN group. As expected, there is much less resonance stabilization in the CHO substituted ion, 10, as denoted by the bond order. There is less than 0.2 of a bond transferred from the C=O to the C_α⁺-C_O bond on 10 relative to the neutral, as compared to the result found for 2 of ≥0.4 bond transfer. The C_α-C_O bond orders in 12 and 15 decrease, as compared to 10, to the point where in 15 there is only a very small amount of resonance stabilization (~0.06 of a bond) in comparison with the corresponding neutral. The bond orders to the CH₃ groups are comparable to the values found for 17 and are greater than those found in 8. This is expected due to the small resonance interaction of the CHO group in 15.

Conclusion

We have presented results at various theoretical levels on the structures and stabilities of cations substituted by electron-withdrawing CN and CO substituents. These substituents are σ-electron withdrawers but also act as π-electron donors, as revealed by geometries, stabilization energies, charge distributions, and bond orders.

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Registry No. 1, 75-05-8; 2, 34430-18-7; 3, 107-12-0; 4, 74738-52-6; 5, 38607-30-6; 6, 90432-45-4; 7, 78-82-0; 8, 74738-53-7; 9, 75-07-0; 10, 41084-88-2; 11, 123-38-6; 12, 75279-61-7; 13, 62130-89-6; 14, 28-84-2; 15, 75279-62-8; CH₃⁺, 14531-53-4; CH₄, 74-82-8.

Reactions of FeCH₃⁺ and CoCH₃⁺ with Aliphatic Alkanes in the Gas Phase

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Abstract: The gas-phase reactions of FeCH₃⁺ and CoCH₃⁺ with aliphatic alkanes up to C₆H₁₄ were studied. FeCH₃⁺ is completely unreactive with the aliphatic alkanes, while CoCH₃⁺ reacts with all alkanes larger than ethane by initial insertion into a C-H bond resulting in CH₄ loss followed by dehydrogenation or alkane elimination forming Co(allyl)⁺ products. The Co(allyl)⁺ ions react rapidly with the alkanes (except methane) predominantly by dehydrogenation generating allyl-olefin complexes. The results indicate that the cobalt-allyl bond strength, D^o(Co⁺-C₃H₅), is in excess of 72 kcal/mol while D^o(Co⁺-butadiene) appears to be less than 52 kcal/mol. CoCH₃⁺ also abstracts a hydride from alkanes larger than ethane (except for 2,2-dimethylpropane) forming C_nH_{2n+1}⁺ and implying D^o(CoCH₃⁺-H) = 256 ± 10 kcal/mol which together with an earlier reported value of ΔH_f^o(CoCH₃) = 256 ± 4 kcal/mol yields D^o(Co-CH₄) = 49 ± 11 kcal/mol and ΔH_f^o(CoCH₄) = 35 ± 11 kcal/mol. Structures of the major primary product ions were investigated both by collision-induced dissociation (CID) and by specific ion-molecule reactions.

Transition-metal ions have proven to be highly reactive in the gas phase. This has been demonstrated by several recent investigations on the reactions of gas-phase transition-metal ions with a variety of organic species using ion cyclotron resonance (ICR) spectrometry,¹⁻³ Fourier transform mass spectrometry (FTMS),^{4,5}

and ion beam techniques.^{6,7} The group 8 transition-metal ions, Fe⁺, Co⁺ and Ni⁺, have received the most attention which has

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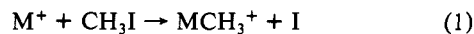
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resulted in a good understanding of their reactions with saturated hydrocarbons.

Reactions with hydrocarbons are fundamentally important since only two types of bonds are available for metal insertion; C-H and C-C bonds. Insertion of the metal ion into a C-H bond produces a hydrido-alkyl intermediate, and insertion into a C-C bond produces a dialkyl intermediate. Beauchamp et al.,⁶⁻⁸ using an ion beam instrument, have recently determined several metal-methyl, metal-hydrogen, and metal-carbene ion bond energies directly. These bond energies have proved very useful in interpreting metal ion reactivity as well as reaction mechanisms. As of yet, however, little is known about the effect of an alkyl or a hydrogen ligand on the bond energy of a second alkyl group or hydrogen atom bound to a metal ion. This information is important since many transition-metal alkyls⁹ and hydrides¹⁰ appear as intermediates in catalytic reactions.

Studying the chemistry of $M-H^+$ and $M-CH_3^+$ species will help to provide a better understanding of the effect hydrogen and methyl ligands have on metal ion reactivity. Recently, we reported the reactions of the group 8 transition-metal hydride ions ($Fe-H^+$, $Co-H^+$, and $Ni-H^+$) with hydrocarbons in the gas phase.¹¹ The reactivity of the metal hydrides differed greatly from that of the bare metal ions. The bare metal ions react with aliphatic alkanes predominantly by C-C bond insertion while the metal hydrides tend to react by C-H bond insertion. Furthermore, the apparent order of reactivity, $NiH^+ > CoH^+ > FeH^+$, is the opposite of the bare metal ion reactivity. Both NiH^+ and CoH^+ appear to be more reactive with alkanes than their respective bare metal ions while FeH^+ appears to be slightly less reactive than Fe^+ .

Here we report the gas-phase reactions of $FeCH_3^+$ and $CoCH_3^+$ with several aliphatic alkanes. The MCH_3^+ ions were generated by reacting laser desorbed metal ions with methyl iodide¹² with reactions 1 and 2 observed. Only process 2 occurs for Ni^+ , and



thus, $NiCH_3^+$ could not be studied. Structures of major product ions were investigated both by collision-induced dissociation (CID) and by specific ion-molecule reactions. Overall, these metal-methyl ions were found to be less reactive toward alkanes than their corresponding metal hydride ions.

Experimental Section

The theory, instrumentation, and methodology of ion cyclotron resonance (ICR) spectrometry¹³ and Fourier transform mass spectrometry (FTMS)¹⁴ have been discussed elsewhere. All experiments were per-

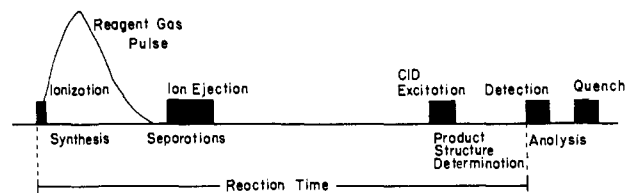


Figure 1. Sequence of events for pulsed valve addition of reagent gas for the FTMS experiments. See Experimental Sections of text for a more detailed explanation.

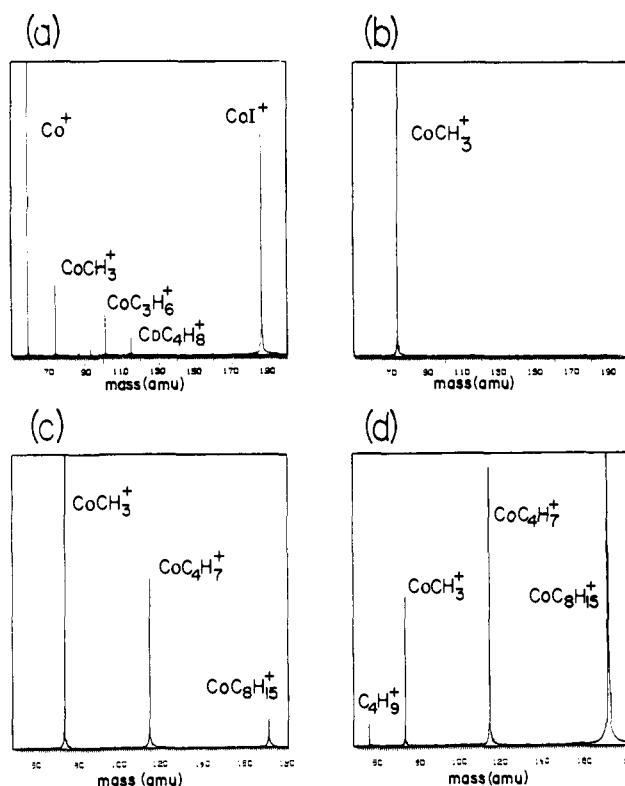


Figure 2. (a) Mass spectrum obtained when Co^+ is allowed to react with CH_3I (pulsed into the vacuum chamber) and isobutane at $\sim 1 \times 10^{-7}$ torr of static pressure for 250 ms. (b) Same as part a except all ions other than $CoCH_3^+$ have been ejected from the cell. (c) Same as part b except a 1-s trap follows isolation. (d) Same as part c except a 3-s trap follows isolation. All spectra are normalized to the most intense peak.

formed by using a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail¹⁵ and equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The cell was constructed in our laboratory and includes a $1/4$ -in.-diameter hole in one of the transmitter plates which permits irradiation with various light sources. High-purity foils of the appropriate metals were attached to the opposite transmitter plate. Metal ions are generated by focusing the beam of a Quanta Ray Nd:YAG laser (frequency doubled to 530 nm) onto a metal foil. Details of the laser ionization technique have been described elsewhere.²

Chemicals were obtained commercially in high purity and used as supplied except for multiple freeze-pump-thaw cycles to remove non-condensable gases. CD_3I was obtained from MSD Isotopes (Merck Chemical Division) containing >99.5 atom % deuterium. Sample pressures were on the order of 1×10^{-7} torr. Argon was used as the collision gas for the collision-induced dissociation (CID) experiments at a total sample pressure of approximately 5×10^{-6} torr. A Bayard-Alpert ion-

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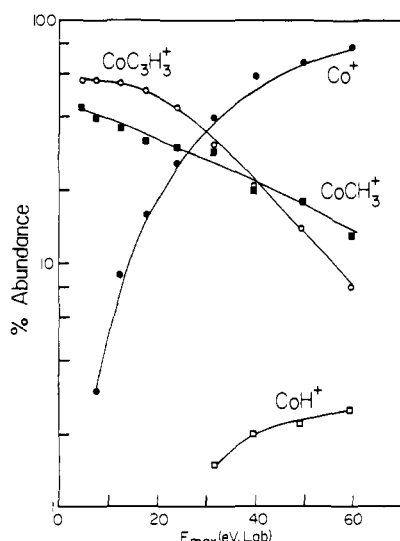
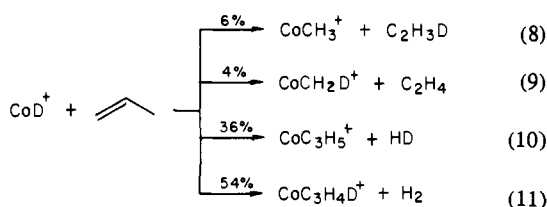


Figure 3. Distribution of CID product intensities vs. kinetic energy for CoC_3H_5^+ ions generated in reaction 6.

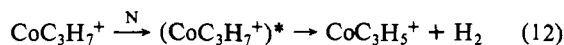
$\text{Co}(\text{alkyl})^+$ intermediates 7 and 8. Two successive β -hydride shifts followed by reductive elimination of hydrogen form $\text{Co}(\text{allyl})^+$ (10). Formation of $\text{Co}(\text{allyl})^+$ in reaction 6 implies $D^\circ(\text{Co}^+-\text{C}_3\text{H}_5) > 72 \text{ kcal/mol}$.^{19,22} Beauchamp et al. have previously assigned $D^\circ(\text{Co}^+-\text{propene}) = 37 \pm 2 \text{ kcal/mol}$ ^{7c} and $D^\circ(\text{Co}^+-\text{CH}_3) = 61 \pm 4 \text{ kcal/mol}$.⁶

CoD^+ reacts with propene¹¹ yielding four products (reactions 8–11). Observation of considerable retention of the label (re-



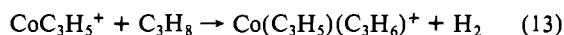
action 11) indicates that the hydrido-propene complex 9 is in equilibrium with the $\text{Co}(\text{alkyl})^+$ products 7 and 8 by reversible β -hydride shifts²³ as shown in Scheme I.

The CoC_3H_7^+ ions generated in reaction 7 undergo a subsequent reaction to produce CoC_3H_5^+ . Surprisingly, this reaction occurs not only in the presence of propane but with Ar as the neutral gas as well. In both cases, CoC_3H_7^+ reacts in a first-order fashion at roughly the Langevin collision rate. These unusual results are consistent with collision-induced dissociation of CoC_3H_7^+ to form CoC_3H_5^+ at thermal energy (reaction 12). The maximum energy



transfer for a thermal collision for CoC_3H_7^+ is less than 1 kcal/mol implying a very low activation barrier for β -hydride abstraction for Co^+ .²⁴

The collision-induced decomposition of CoC_3H_5^+ , produced in reaction 6, was studied, and a plot of CID fragment ion abundances vs. kinetic energy for CoC_3H_5^+ is shown in Figure 3. Elimination of H_2 , C_2H_2 , C_3H_4 , and C_3H_5 is observed, in contrast to $\text{Co}(\text{ethene})^+$, $\text{Co}(\text{propene})^+$, $\text{Co}(\text{isobutene})^+$ and $\text{Co}(\text{butadiene})^+$ species where only direct cleavage of the olefin ligand is seen.⁵ The product of reactions 6 and 12, CoC_3H_5^+ , reacts rapidly with propane resulting in elimination of hydrogen (reaction 13).



This reaction is considerably faster than the initial reaction of CoCH_3^+ with propane. Benzene displaces C_3H_6 exclusively from

(23) Reversible β -hydride transfers have been observed in gas-phase metal ion chemistry. See, for example, ref 1b, 4b, 6, 7a, and 17.

(24) β -Hydride shifts appear to be more facile for Co^+ than for either Fe^+ or Ni^+ ; see, for example, ref 5b.

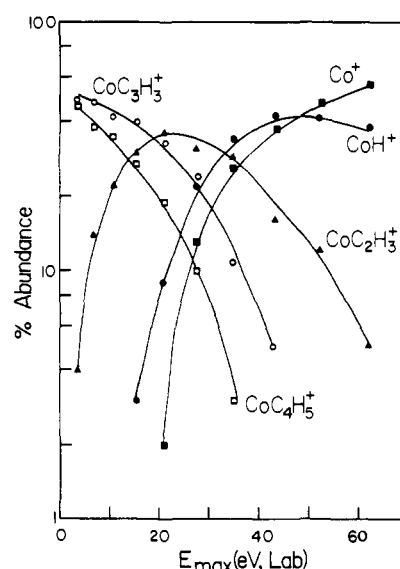
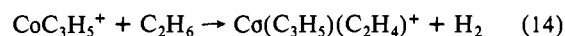


Figure 4. Distribution of CID product intensities vs. kinetic energy for CoC_4H_7^+ formed from reaction of CoCH_3^+ with *n*-butane.

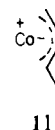
the product of reaction 13; however, CoC_3H_5^+ is unreactive with benzene. CID of the product of reaction 13 yields predominantly C_3H_6 loss at low kinetic energy. At higher energies, C_3H_6 loss followed by loss of H_2 , C_2H_2 , or C_3H_5 (the allyl CID products) is also observed. These results are consistent with formation of an allyl-propene complex in reaction 13. In addition, CoC_3H_5^+ also reacts rapidly with ethane (process 14). No reaction,



however, is observed with CH_4 . The product of reaction 14 yields CID spectra very similar to that for the product of reaction 13 with loss of C_2H_4 dominating at low energy. The products of reactions 6, 7, 13, and 14 are all unreactive with D_2 .

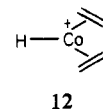
Reactions with Butane, Pentane, and Hexane. The neutral losses for the primary reactions of CoCH_3^+ with butane, pentane, and hexane are listed in Table I. In general, the primary reactions can be adequately described by processes similar to those presented in Scheme I.

CoCH_3^+ reacts with butane generating only one product, CoC_4H_7^+ , in contrast to reaction with propane where two products are observed. Presumably, CoC_4H_9^+ is generated by initial loss of CH_4 followed by dehydrogenation producing a (methallyl) Co^+ complex (11) as predicted by Scheme I. Complete absence of



CoC_4H_9^+ formation indicates that it retains sufficient internal energy for dehydrogenation to occur. Formation of 11 implies that $D^\circ(\text{Co}^+-\text{methallyl}) > 68 \text{ kcal/mol}$.^{19,22}

A plot of CID fragment ion abundances vs. kinetic energy for CoC_4H_7^+ (complex 11) is illustrated in Figure 4. Elimination of H_2 , CH_4 , C_2H_4 , C_4H_6 , and C_4H_7 is observed. Loss of C_4H_6 probably proceeds through a hydrido-butadiene intermediate (12).



Complete absence of H^\cdot loss generating CoC_4H_6^+ implies $D^\circ(\text{Co}^+-\text{butadiene}) < D^\circ(\text{Co}^+-\text{H}) = 52 \pm 4 \text{ kcal/mol}$.⁶ This lower limit is consistent with the fact that butadiene does not displace H^\cdot from CoH^+ ,²⁵ whereas, for example, benzene does.¹¹

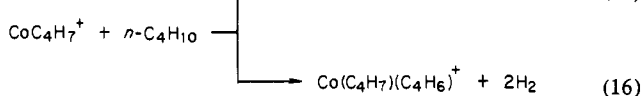
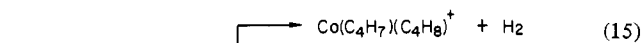
(25) Jacobson, D. B.; Freiser, B. S., unpublished results.

Table I. Distribution of Neutral(s) Lost for the Primary and Secondary Reactions of $CoCH_3^+$ with Aliphatic Alkanes^a

alkane	primary reactions $CoCH_3^+ + \text{alkane} \rightarrow$ $CoA^+ + \text{neutral(s)}$			secondary reactions $CoA^+ + \text{alkane} \rightarrow$ $CoB^+ + \text{neutral(s)}$		
	neutral(s)	A ⁺	rel %	neutral(s)	B ⁺	rel %
methane		no reaction				
ethane		no reaction				
propane	CH ₄ , H ₂	$CoC_3H_5^+$	70	H ₂	$CoC_6H_{11}^+$	100
	CH ₄ ($CoCH_4$)	$CoC_3H_7^{+b}$ $C_3H_7^+$	29 1			
butane	CH ₄ , H ₂	$CoC_4H_7^+$	97	H ₂	$CoC_8H_{15}^+$	78
				2H ₂	$CoC_8H_{13}^+$	22
pentane	CH ₄ , C ₂ H ₆	$CoC_3H_5^+$	16	2H ₂	$CoC_8H_{13}^+$	22
				C ₂ H ₆	$CoC_6H_{11}^+$	28
				2H ₂	$CoC_8H_{13}^+$	43
				H ₂	$CoC_8H_{15}^+$	29
hexane	2CH ₄	$CoC_4H_7^{+c}$	2	C ₂ H ₆	$CoC_8H_9^+$	10
	CH ₄ , H ₂	$CoC_5H_9^+$	74	2H ₂	$CoC_{10}H_{17}^+$	58
				H ₂	$CoC_{10}H_{19}^+$	32
	($CoCH_4$)	$C_5H_{11}^+$	8	C ₂ H ₆	$CoC_8H_{15}^+$	13
	CH ₄ , C ₂ H ₆	$CoC_4H_7^+$	6	2H ₂ , H [•]	$CoC_{10}H_{16}^+$	38
				2H ₂	$CoC_{10}H_{17}^+$	49
	2CH ₄ , H ₂	$CoC_5H_7^+$	15	C_3H_8	$CoC_8H_{13}^+$	8
				C ₃ H ₆	$CoC_8H_{15}^+$	7
				C ₂ H ₆	$CoC_9H_{15}^+$	8
				C ₂ H ₄	$CoC_9H_{17}^+$	6
2-methylpropane	2CH ₄	$CoC_5H_9^+$	13	H ₂	$CoC_{11}H_{19}^+$	71
				C ₃ H ₈	$CoC_8H_{15}^+$	11
				C ₂ H ₆	$CoC_9H_{17}^+$	8
				C ₂ H ₆	$CoC_9H_{17}^+$	8
	CH ₄ , H ₂	$CoC_6H_{11}^{+d}$	53	2H ₂	$CoC_{12}H_{21}^+$	70
				H ₂	$CoC_{12}H_{23}^+$	30
	($CoCH_4$)	$C_6H_{13}^+$	13			
	CH ₄ , H ₂	$CoC_4H_7^+$	96	H ₂	$CoC_8H_{15}^+$	100
	($CoCH_4$)	$C_4H_9^+$	4			
	2,2-dimethylpropane	2CH ₄	$CoC_4H_7^+$	74	CH ₄	$CoC_8H_{15}^+$
			2H ₂	$CoC_9H_{15}^+$	10	
			H ₂	$CoC_9H_{17}^+$	30	
2-methylbutane	CH ₄	$CoC_5H_{11}^{+b}$	26	2H ₂ , H [•]	$CoC_9H_{14}^+$	58
	2CH ₄	$CoC_4H_7^+$	5	2H ₂	$CoC_9H_{15}^+$	42
2,3-dimethylbutane	CH ₄ , H ₂	$CoC_5H_9^+$	86	2H ₂	$CoC_{10}H_{17}^+$	40
				H ₂	$CoC_{10}H_{19}^+$	60
	($CoCH_4$)	$C_5H_{11}^+$	9	CH ₄ , H ₂	$CoC_{10}H_{17}^+$	45
	2CH ₄	$CoC_5H_9^+$	3	2H ₂	$CoC_{11}H_{19}^+$	55
2,2-dimethylbutane	CH ₄ , H ₂	$CoC_6H_{11}^+$	70	CH ₄ , H ₂	$CoC_{11}H_{19}^+$	13
				2H ₂	$CoC_{12}H_{21}^+$	38
				H ₂	$CoC_{12}H_{23}^+$	49
	($CoCH_4$)	$C_6H_{13}^+$	27	C ₂ H ₆	$CoC_8H_{15}^+$	15
	CH ₄ , C ₂ H ₆	$CoC_4H_7^+$	15	CH ₄ , H ₂	$CoC_9H_{15}^+$	24
				2H ₂	$CoC_{10}H_{17}^+$	27
				H ₂	$CoC_{10}H_{19}^+$	34
	2CH ₄	$CoC_5H_9^+$	61	C ₂ H ₆	$CoC_9H_{17}^+$	4
				CH ₄ , H ₂	$CoC_{10}H_{17}^+$	27
				2H ₂	$CoC_{11}H_{19}^+$	37
			H ₂	$CoC_{11}H_{21}^+$	32	
	CH ₄ , H ₂ ($CoCH_4$)	$CoC_6H_{11}^{+e}$ $C_6H_{13}^+$	15 9			

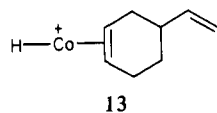
^a Product distributions are reproducible to $\pm 10\%$. ^b These products decompose to yield the allyl species; see text for explanation. ^c Product intensity was too low for its secondary reactions to be studied. ^d Of this ion 70% remains unreactive. ^e No secondary reactions were observed.

The $CoC_4H_7^+$ ions react rapidly with butane by dehydrogenation (reactions 15 and 16). CID of the product of reaction

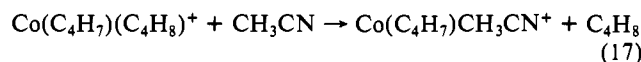


15 yields several fragmentations including elimination of H₂, 2H₂,

3H₂, C₂H₄ + 2H₂, C₂H₄ + 2H₂ + H[•], C₃H₄ + 3H₂, C₄H₈ as well as C₄H₈ followed by H₂, CH₄, C₂H₄, and C₄H₇ losses (the methallyl elimination products). Several of these elimination products may proceed through a coupling of the two ligands prior to elimination. For example, elimination of C₂H₄ + 2H₂ may proceed by initial loss of H₂ followed by a Diels–Alder cycloaddition of the hydrido-bis(butadiene) species producing complex 13. Elimination of C₂H₄ and H₂ results in formation of a hydrido-benzene complex²⁶ which, if formed with sufficient internal

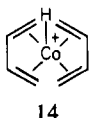


energy, can eliminate a hydrogen atom.²⁷ Although the CID results are suggestive, in this case they yield little concrete structural information. Acetonitrile, however, reacts with the product of reaction 15 by simply displacing C_4H_8 (reaction 17).

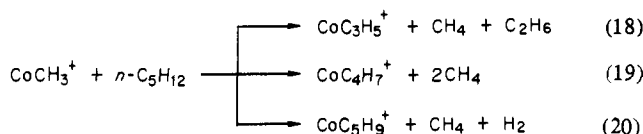


$Co(\text{methallyl})^+$ is unreactive with acetonitrile. This suggests that the product of reaction 15 does indeed consist of the given formulation.

The product of reaction 16 yields similar CID product ions to that for CID of the product of reaction 15. In this case, loss of $C_3H_4 + 2H_2$ ($CoC_3H_5^+$ formation) is the dominant process. Surprisingly, no reaction is seen with acetonitrile, even though it can displace butadiene in $CoC_4H_6^+$. This may indicate that the ligands have coupled. Alternatively, formation of a hydrido-bis(butadiene) complex **14**, formally a 17-electron species, could prevent acetonitrile from displacing butadiene due to steric constraints.



Three primary reaction products are observed for $CoCH_3^+$ with pentane (reactions 18–20). Formation of $CoC_3H_5^+$ may result



from initial CH_4 elimination followed by either loss of ethane or loss of ethene and hydrogen. Loss of C_2H_4 and H_2 implies $D^0(Co^+-C_3H_5) > 95$ kcal/mol while loss of ethane yields $D^0(Co^+-C_3H_5) > 62$ kcal/mol.^{19,22} A value of 95 kcal/mol for $D^0(Co^+-C_3H_5)$ seems unreasonably high and, therefore, the neutral products listed in reaction 18 appear to be responsible for $CoC_3H_5^+$ formation.

A mechanism for formation of the products in reactions 18–20 is outlined in Scheme II. Initially, $CoCH_3^+$ oxidatively inserts into a C–H bond resulting in reductive elimination of methane. β -Hydride shifts result in formation of the hydrido-pentene complexes **15** and **16**, which may interconvert by reversible β -hydride shifts.²³ The 1-pentene complex **15** may decompose either by dehydrogenation or insertion into an allylic C–C bond generating **17** followed by reductive elimination of ethane. Co^+ reacts with 1-pentene generating predominantly $CoC_3H_6^+$ and $CoC_2H_4^+$, presumably through insertion into an allylic C–C bond.^{5,7b} The 2-pentene complex **16** predominantly eliminates hydrogen with some insertion into the terminal C–C bond resulting in methane loss.

The variation of fragment ion intensities vs. kinetic energy for CID of $CoC_3H_5^+$, formed in reaction 20, is shown in Figure 5. At low energy elimination of H_2 dominates while at higher energies loss of $2H_2$ dominates with some C_2H_4 , C_2H_6 , and C_4H_6 elimination also observed. The dehydrogenation processes are very efficient over the entire energy range studied. Presumably, the $CoC_3H_5^+$ species consists of pentenyl bound to Co^+ . Dehydro-

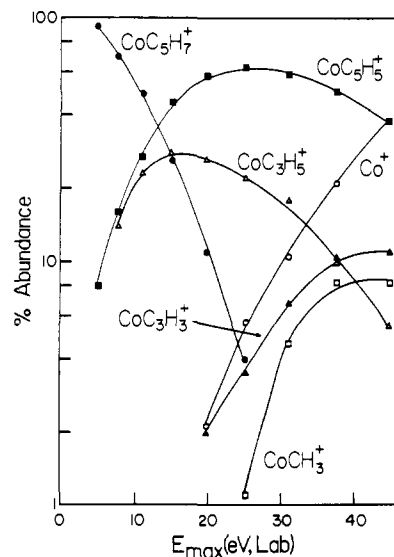
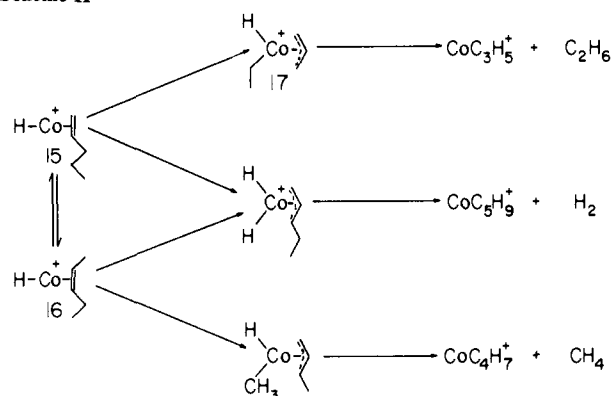
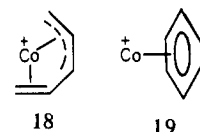


Figure 5. Distribution of CID product intensities vs. kinetic energy for $CoC_3H_5^+$ generated in reaction 19.

Scheme II

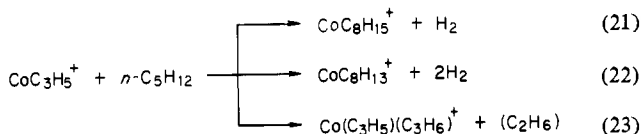


genation apparently produces $Co(\text{pentadienyl})^+$ (**18**) which can undergo dehydrocyclization forming $Co(\text{cyclopentadienyl})^+$ (**19**).



Evidence for structure **19** is that the CID process observed for $CoC_3H_5^+$ generated from $CoC_5H_9^+$ is identical with that of "authentic" $Co-c-C_3H_5^{+4c}$ where direct loss of C_3H_5 in low efficiency is the only cleavage observed. At high energy, elimination of C_2H_4 from $CoC_3H_5^+$ may generate a $Co(\text{allyl})^+$ species which can decompose further by elimination of H_2 and C_2H_2 . This then accounts for the C_2H_6 and C_4H_6 losses.

$CoC_3H_5^+$, generated in reaction 18, reacts with pentane producing both C–C bond cleavage and dehydrogenation products (reactions 21–23). The products of reactions 21 and 22 may be

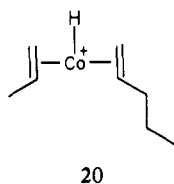


formed by initial C–H bond insertion followed by β -hydride shifts resulting in elimination of hydrogen. The neutral product(s) in reaction 23 may be either $H_2 + C_2H_4$ or C_2H_6 . Loss of $H_2 + C_2H_4$ would require $D^0(C_3H_5Co^+-C_3H_6) > 51$ kcal/mol while C_2H_6 elimination would require $D^0(C_3H_5Co^+-C_3H_6) > 19$ kcal/mol.^{19,22} Since $D^0(Co^+-C_3H_6) = 37 \pm 2$ kcal/mol,^{7c} loss of $H_2 + C_2H_4$

(26) Bis(butadiene) Fe^+ decomposes by this process in the gas phase resulting in formation of $Fe(C_6H_6)^+$; see ref 4b.

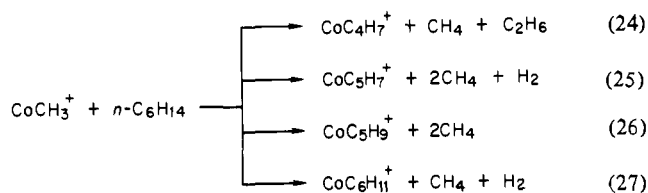
(27) $Co-c-C_6H_7^+$ loses predominantly $H\cdot$ upon low-energy collisional activation. See: Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.*, following paper in this issue.

appears to be energetically inaccessible. The allyl ligand, however, may enhance the bond strength of propene to Co^+ sufficiently for this multiple loss to become exothermic. Initial dehydrogenation would generate an allyl-pentene complex which could eliminate C_2H_4 by insertion into the allylic C-C bond of 1-pentene. The alternative loss of C_2H_6 , however, could proceed by initial insertion into a C-H bond followed by β -hydride shifts resulting in formation of complex **20**. Insertion into the allylic C-C bond of



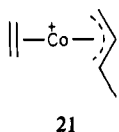
the 1-pentene ligand would permit reductive elimination of ethane to generate the (allyl)(propene) Co^+ species. The reactions of CoC_3H_5^+ , formed in reaction 20, with pentane are similar to the CoC_3H_5^+ reactions (Table I) providing supporting evidence for an allylic structure.

Four products are generated in the reaction of hexane with CoCH_3^+ (reactions 24-27). Formation of these products can be



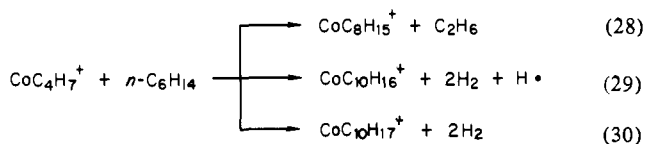
envisioned as proceeding through processes similar to those outlined for pentane in Scheme II. The product of reaction 24 probably consists of $\text{Co}(\text{methallyl})^+$ (structure **11**). CoC_5H_7^+ , produced in reaction 25, is probably pentadienyl bound to Co^+ (structure **18**), implying $D^\circ(\text{Co}^+-\text{pentadienyl}) > 92$ kcal/mol.^{19,22}

The product of reaction 27, $\text{CoC}_6\text{H}_{11}^+$, reacts with hexane producing the dehydrogenation products $\text{CoC}_{12}\text{H}_{23}^+$ (30%) and $\text{CoC}_{12}\text{H}_{21}^+$ (70%). Interestingly, only 30% of the $\text{CoC}_6\text{H}_{11}^+$ formed in reaction 27 is reactive, suggesting that it is composed of at least two structures. The reactive species is believed to be an intact allyl species, 3-hexenyl, bound to Co^+ . CID of $\text{CoC}_6\text{H}_{11}^+$ yields nearly exclusively loss of C_2H_4 at low energy. At high energy, significant amounts of CoC_4H_5^+ , CoC_3H_3^+ , CoC_2H_3^+ , and CoH^+ are observed. These are the major CID products for $\text{Co}(\text{methallyl})^+$ (Figure 4) and are probably generated by initial loss of C_2H_4 forming an activated $\text{Co}(\text{methallyl})^+$ complex which decomposes further. This suggests that the $\text{CoC}_6\text{H}_{11}^+$ initially formed in reaction 27 may retain sufficient internal energy for 70% of it to rearrange to structure **21**, presumably the unreactive form of $\text{CoC}_6\text{H}_{11}^+$. In analogy to the $\text{Co}(1\text{-hexene})^+$ complex



which decomposes predominantly by insertion into the allylic C-C bond producing a bis(propene) Co^+ complex,^{5,7b} $\text{Co}(3\text{-hexenyl})^+$ can decompose by insertion into the C-C bond adjacent to the terminal C-C bond with β -hydride shifts resulting in formation of complex **21** prior to decomposition.

The product of reaction 24 reacts with hexane producing three products (reactions 28-30). CoC_5H_7^+ and CoC_5H_9^+ , produced



in reactions 25 and 26, react with hexane generating predominantly

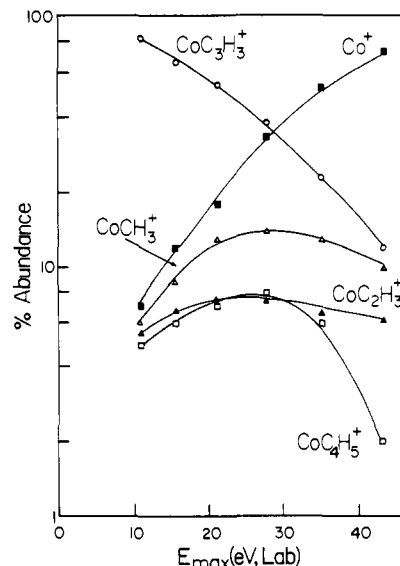
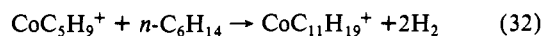
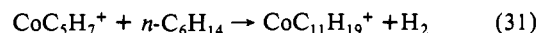
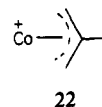


Figure 6. Distribution of CID product intensities vs. kinetic energy for CoC_4H_7^+ formed from reaction of CoCH_3^+ with isobutane.

one product (reactions 31 and 32); however, several other minor products were also observed (Table I).

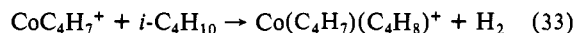


Reactions with 2-Methylpropane and 2,2-Dimethylpropane. CoCH_3^+ reacts with 2-methylpropane generating only one product, CoC_4H_7^+ (see Table I), which presumably consists of 2-methallyl bound to Co^+ (structure **22**). A plot of fragment ion abundance

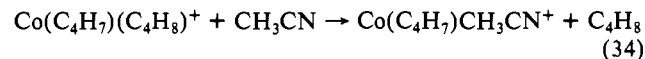


vs. kinetic energy for CID of this CoC_4H_7^+ ion is shown in Figure 6. Loss of CH_4 dominates with elimination of H_2 , C_2H_4 , C_3H_4 , and C_4H_7 also observed. As can be seen by a comparison of Figures 4 and 6, CID can distinguish between $\text{Co}(\text{methallyl})^+$ and $\text{Co}(2\text{-methallyl})^+$. Formation of complex **22** from 2-methylpropane implies $D^\circ(\text{Co}^+-\text{C}_4\text{H}_7) > 69$ kcal/mol.^{19,22} No reaction is observed between complex **22** and acetonitrile, whereas acetonitrile readily displaces butadiene from CoC_4H_6^+ . This clearly indicates that allyl species are more strongly bound to Co^+ than butadiene, as suggested earlier for CID of $\text{Co}(\text{methallyl})^+$ (Figure 4).

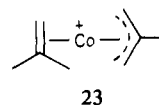
The CoC_4H_7^+ ion (complex **22**) reacts with 2-methylpropane losing H_2 exclusively (reaction 33). Acetonitrile displaces ex-



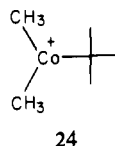
clusively C_4H_8 from the product of reaction 33 yielding $\text{Co}(\text{C}_4\text{H}_7)(\text{CH}_3\text{CN})^+$ (reaction 34). No further reaction is seen with



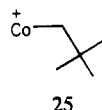
acetonitrile. CID of the product of reaction 33 is considerably different than that for $\text{Co}(\text{C}_4\text{H}_7)(\text{C}_4\text{H}_8)^+$ produced in reaction 15 with loss of C_4H_8 dominating along with some H_2 elimination at low energy. At high energies, loss of C_4H_8 generating an activated $\text{Co}(2\text{-methallyl})^+$ complex followed by CH_4 elimination dominates. The above results are consistent with formation of complex **23** in reaction 33.



CoCH_3^+ reacts with 2,2-dimethylpropane yielding two products, CoC_4H_7^+ and $\text{CoC}_5\text{H}_{11}^+$. CoC_4H_7^+ may be formed by either loss of 2CH_4 or C_2H_6 followed by dehydrogenation. Elimination of ethane would require initial insertion into a C-C bond forming **24**. This intermediate should be able to eliminate either ethane



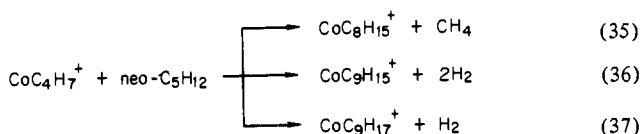
forming CoC_4H_9^+ or 2,2-dimethylpropane regenerating the reactant CoCH_3^+ . If intermediate **24** is involved in CoC_4H_7^+ formation, then some CoCH_3^+ should be formed in the reaction with CoCD_3^+ . No CoCH_3^+ is observed, however, suggesting that CoC_4H_7^+ is not formed by initial insertion into a C-C bond but rather by initial insertion into a C-H bond. Methane loss then results in formation of a $\text{Co}(\text{alkyl})^+$ species containing no β -hydrogens (complex **25**). Loss of methane in **25** proceeds by a



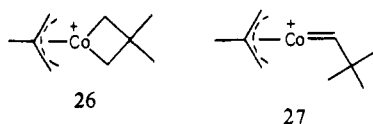
β -methyl shift²⁸ followed by a β -hydride shift resulting in formation of a $\text{Co}(\text{2-methylallyl})^+$ species (structure **22**). The CID spectra of this CoC_4H_7^+ complex are identical (same peaks, intensities, and energy dependence within experimental error) with that for CoC_4H_7^+ produced from 2-methylpropane.

The $\text{CoC}_5\text{H}_{11}^+$ ions generated from 2,2-dimethylpropane are observed to eliminate CH_4 when trapped in the presence of either 2,2-dimethylpropane or argon. Similar to the CoC_3H_7^+ ions produced in reaction 7, these $\text{CoC}_5\text{H}_{11}^+$ ions appear to decompose in a first-order fashion at roughly the Langevin collision rate.

Three products are observed in the reactions of CoC_4H_7^+ produced from 2,2-dimethylpropane with 2,2-dimethylpropane (reactions 35-37). These reactions are considerably slower than



any of the other $\text{Co}(\text{allyl})^+$ reactions and may be attributed to the lack of β -hydrogens available for transfer after initial insertion into a C-H bond. The product of reaction 35 may be formed by initial oxidative addition of a C-H bond to CoC_4H_7^+ , β -methyl abstraction, and reductive elimination of methane forming complex **23**. Loss of H_2 (reaction 37) may proceed through initial insertion into a C-H bond followed by a γ -hydride abstraction generating **26** or an α -hydride abstraction forming **27**. Alternatively, con-



siderable rearrangement of the carbon skeleton of 2,2-dimethylpropane may occur prior to dehydrogenation, or the two ligands may have coupled.

Reactions with 2-Methylbutane, 2,2-Dimethylbutane, and 2,3-Dimethylbutane. The distributions of neutral losses for the primary reactions of CoCH_3^+ with the methylbutanes are listed in Table I. Loss of CH_4 followed by dehydrogenation dominates for both 2-methylbutane and 2,3-dimethylbutane and probably proceeds by processes similar to those outlined in Scheme I for propane. CID of CoC_5H_9^+ produced from 2-methylbutane is similar to that

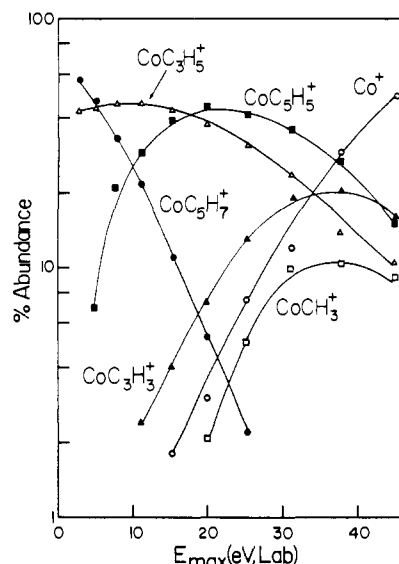
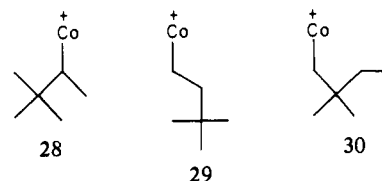


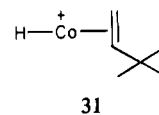
Figure 7. Distribution of CID product intensities vs. kinetic energy for CoC_5H_9^+ produced by reaction of CoCH_3^+ with 2-methylbutane.

for CoC_5H_9^+ produced from pentane; however, more CoC_3H_5^+ is generated in the former (Figure 7). Dehydrogenation to form CoC_5H_5^+ in Figure 7 may proceed through initial rearrangement to a linear CoC_5H_9^+ species. $\text{CoC}_6\text{H}_{11}^+$ generated from 2,3-dimethylbutane predominantly eliminates C_3H_6 forming CoC_3H_5^+ upon collisional activation.

Loss of 2CH_4 is the dominant process for reaction of CoCH_3^+ with 2,2-dimethylbutane. Here, initial loss of CH_4 can generate $\text{Co}(\text{alkyl})^+$ species **28-30** which do not have two β -hydrogens directly available for H_2 elimination. For complexes **28** and **29**,



β -hydride abstraction produces **31**. β -Methyl migration followed

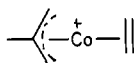


by reductive elimination of methane results in formation of CoC_5H_9^+ . Complex **30** has no β -hydrogens available for abstraction. Either a β -methyl shift resulting in elimination of methane or a β -ethyl shift resulting in ethane loss may occur. The CoC_4H_7^+ ions formed in this way would be expected to consist of 2-methylallyl bound to Co^+ (structure **22**), and the CID spectra of this complex are in fact identical (same peaks, intensities, and energy dependence within experimental error) with that for CoC_4H_7^+ produced from 2-methylpropane (see Figure 6). The variation in fragment ion intensities vs. kinetic energy for CID of the CoC_5H_9^+ ions is identical (within experimental error) with that for CoC_3H_7^+ produced above from 2-methylbutane. Assuming that the probability for CoCH_3^+ insertion is similar for all the C-H bonds and that β -methyl and β -ethyl migrations are equally likely, then the $\text{CoC}_5\text{H}_9^+/\text{CoC}_4\text{H}_7^+$ ratio should be 11/3. As can be seen in Table I, the $\text{CoC}_5\text{H}_9^+/\text{CoC}_4\text{H}_7^+$ ratio of 67/17 is roughly a 11/3 ratio.

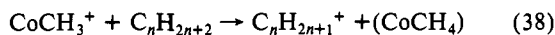
Surprisingly, $\text{CoC}_6\text{H}_{11}^+$ formed from 2,2-dimethylbutane is completely unreactive. This suggests that a simple $\text{Co}(\text{allyl})^+$ species is not generated but rather a complex consisting of an allyl-alkene structure in analogy to structure **21** is generated. Elimination of C_2H_4 is the only CID fragmentation observed at low kinetic energy while loss of C_2H_4 followed by CH_4 elimination dominates at higher energies. This is consistent with formation

(28) β -Methyl transfers have been observed in solution-phase chemistry. See, for example: Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471.

of structure **32** where C_2H_4 elimination generates a $\text{Co}(2\text{-methyl})^+$ species which can subsequently eliminate CH_4 .

**32**

Hydride Abstraction by CoCH_3^+ . In addition to the reactions described above, CoCH_3^+ also undergoes hydride abstraction (process 38) with aliphatic alkanes larger than ethane, with the exception of 2,2-dimethylpropane. This reaction ranged from



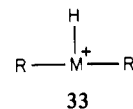
a low of 1% for propane to a high of 27% for 2,3-dimethylbutane (Table I). The neutral products in reaction 38 may consist of three possibilities: CoCH_4 , $\text{Co} + \text{CH}_4$, and $\text{CoCH}_2 + \text{H}_2$. Formation of $i\text{-C}_3\text{H}_7^+$ from propane in reaction 38 is 43 kcal/mol endothermic for $\text{Co} + \text{CH}_4$ and 70 kcal/mol endothermic for $\text{CoCH}_2 + \text{H}_2$.^{19,22,29} This indicates that CoCH_4 must be formed in reaction 38 for it to be energetically feasible. Reaction 38 will occur only when the hydride affinity of CoCH_3^+ , $D^\circ(\text{CoCH}_3^+-\text{H}^-)$, is greater than that for the neutral alkane. Observation of reaction 38 for propane implies $D^\circ(\text{CoCH}_3^+-\text{H}^-) > 250$ kcal/mol (abstraction of a secondary hydride from propane), $D^\circ(\text{Co}-\text{CH}_4) > 43$ kcal/mol, and $\Delta H_f^\circ(\text{CoCH}_4) < 41$ kcal/mol.³⁰ While other explanations may exist, the fact that 2,2-dimethylpropane does not exhibit reaction 38 implies that hydride abstraction cannot occur from a primary carbon. Absence of hydride abstraction from 2,2-dimethylpropane suggests $D^\circ(\text{CoCH}_3^+-\text{H}^-) < 262$ kcal/mol, $D^\circ(\text{Co}-\text{CH}_4) < 55$ kcal/mol, and $\Delta H_f^\circ(\text{CoCH}_4) > 29$ kcal/mol.^{19,22,30,31}

The above results suggest that $\Delta H_f^\circ(\text{CoCH}_4) = 35 \pm 11$ kcal/mol. Beauchamp et al.⁶ have recently assigned $D^\circ(\text{Co}-\text{H}) = 39 \pm 6$ kcal/mol and $D^\circ(\text{Co}-\text{CH}_3) = 41 \pm 10$ kcal/mol. The use of these values leads to $D^\circ(\text{CoCH}_3-\text{H}) \sim 112$ kcal/mol and $D^\circ(\text{CoH}-\text{CH}_3) \sim 114$ kcal/mol. These values are in the range of $D^\circ(\text{CH}_3-\text{H}) = 104$ kcal/mol²² and considerably greater than $D^\circ(\text{Co}-\text{H})$ and $D^\circ(\text{Co}-\text{CH}_3) \sim 40$ kcal/mol, implying formation of a cobalt-methane complex in reaction 38 as opposed to a hydrido-methyl complex. In a related study FeH^+ was observed to abstract a hydride from aldehydes and ethers, and formation of a stable neutral iron dihydride is proposed.³²

Conclusions

The first row group 8 transition-metal ions (Fe^+ , Co^+ , and Ni^+) react with aliphatic alkanes predominantly by initial insertion across C-C bonds.⁵⁻⁷ In stark contrast to this behavior, FeH^+ , CoH^+ , and NiH^+ were found to react nearly exclusively by initial

insertion into C-H bonds.^{11,32} CoCH_3^+ is found to parallel the CoH^+ behavior by predominantly inserting into C-H bonds resulting in initial elimination of methane. This implies that CoCH_3^+ initially forms a dialkyl-hydride complex **33**. Elimination of

**33**

methane followed by dehydrogenation or alkane elimination results in formation of a $\text{Co}(\text{allyl})^+$ species. The inert behavior of FeCH_3^+ implies that formation of intermediate **33** may be energetically unfavorable for Fe^+ , even though both $D^\circ(\text{M}^+-\text{CH}_3)$ and $D^\circ(\text{M}^+-\text{H})$ are greater for Fe^+ than for Co^+ .¹⁹ Whereas both NiH^+ and CoH^+ are more reactive than the bare metal ions toward aliphatic alkanes, FeH^+ was found to be less reactive than Fe^+ .¹¹ CoCH_3^+ is slightly less reactive than Co^+ while FeCH_3^+ is considerably less reactive than Fe^+ toward aliphatic alkanes. These observations suggest that the decreased reactivity of MCH_3^+ relative to MH^+ is a result of the methyl group causing C-H insertion to be less energetically favorable than when a hydride ligand is present.

Several different isomeric structures were distinguished in this study using collision-induced dissociation (CID) and specific ion-molecule reactions. For example, CID of $\text{Co}(\text{methallyl})^+$ and $\text{Co}(2\text{-methallyl})^+$ yields several fragmentations which allow these two species to be distinguished. The $\text{Co}(\text{allyl})^+$ species react rapidly with all alkanes (except CH_4) predominantly by dehydrogenation generating allyl-olefin complexes. Both CID and ion-molecule reactions were able to distinguish several of these isomeric species. Allyl ligands are strongly bound to Co^+ with $D^\circ(\text{Co}^+-\text{C}_3\text{H}_5) > 74$ kcal/mol. This is considerably greater than $D^\circ(\text{Co}^+-\text{butadiene})$ which appears to be less than 52 kcal/mol.

Two Co-alkyl⁺ species are generated, CoC_3H_7^+ and $\text{CoC}_5\text{H}_{11}^+$, which decompose yielding CoC_3H_5^+ and CoC_4H_7^+ , respectively. These decompositions are pseudo first order and occur at approximately the Langevin collision rate. These unusual results are consistent with thermal collisional activation of long-lived metastable intermediate ions. The maximum internal energy transfer for a thermal collision is less than 1 kcal/mol implying a very low activation barrier for decomposition.

CoCH_3^+ abstracts a hydride from alkanes larger than ethane (with the exception of 2,2-dimethylpropane). It appears that a neutral CoCH_4 species is generated and that CH_4 is bound to the metal as methane. The hydride affinity of CoCH_3^+ , $D^\circ(\text{CoCH}_3^+-\text{H}^-)$, is 256 ± 10 kcal/mol implying $D^\circ(\text{Co}-\text{CH}_4) = 49 \pm 11$ kcal/mol and $\Delta H_f^\circ(\text{CoCH}_4) = 35 \pm 11$ kcal/mol.

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Registry No. 1 (M = Fe), 90143-29-6; 1 (M = Co), 76792-06-8; CH_4 , 74-82-8; C_2H_6 , 74-84-0; C_3H_8 , 74-98-6; $n\text{-C}_4\text{H}_{10}$, 106-97-8; $n\text{-C}_5\text{H}_{12}$, 109-66-0; $n\text{-C}_6\text{H}_{14}$, 110-54-3; 2-methylpropane, 75-28-5; 2,2-dimethylpropane, 463-82-1; 2-methylbutane, 78-78-4; 2,3-dimethylbutane, 79-29-8; 2,2-dimethylbutane, 75-83-2.

(29) The proton affinity of CoCH_2 is determined to be 222 kcal/mol from which $\Delta H_f^\circ(\text{CoCH}_2) = 112$ kcal/mol can be derived. Jacobson, D. B.; Freiser, B. S., unpublished results.

(30) This is calculated by using a value for the electron affinity of H. $\text{EA}(\text{H}) = 0.754$ eV from: Wagman, D. D.; Evans, W. H.; Parker, V. B.; Harlow, I.; Bailey, S. M.; Schumm, R. H. *Natl. Bur. Stand. (U.S.), Tech. Note* **1968**, 270-3.

(31) $\Delta H_f^\circ(\text{neo-C}_5\text{H}_{11}^+) = 188$ kcal/mol from: Lossing, F. P.; Maccoll A. *Org. Mass Spectrom.* **1982**, 17, 1.

(32) Halle, L. F.; Klein, F. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, 106, 2543.