in both ligand moieties. The pH-dependent rate constant, $k_{1,\text{obs}}$, can be expressed by eq 4, where K_L denotes the acidity constant

$$k_{1,\text{obs}} = k_1 \frac{[\text{H}^+]K_L}{([\text{H}^+] + K_a)([\text{H}^+] + K_L)} \tag{4}$$

of the ligand. The employment of least-squares fitting to the pH-dependent rate data gave the values $k_1 = 0.65\ \text{M}^{-1}\ \text{s}^{-1}$ and $K_L = 10^{-6.33}$ M for 7-methylinosine. The latter is comparable to the pK_a value of 6.28 reported for the base moiety in 7-methylinosine 5′-monophosphate at 298.2 K,[10] which lends support to the validity of the kinetic data. The calculated value for the rate constant is compatible with that found earlier for the binding of the $[\text{Pt(dien)(H}_2\text{O)}]^{2+}$ ion to the N1 position of the [Pt(dien)(Ino-*N7*)]$^+$ complex, viz. 0.74 $\text{M}^{-1}\ \text{s}^{-1}$.[3] In other words, a methyl group at N7 affects the coordination ability of the N1 site in the same manner as Pt(II) bound to the N7 position. Similarly, when bound to the N1 ring nitrogen, a methyl group and a Pt(II) ion have comparable influences on the coordination properties of the N7 site, as can be seen from the rate constants of 1-methylinosine and the [Pt(dien)(Ino-*N1*)]$^+$ ion, viz. 0.54 and 0.75 $\text{M}^{-1}\ \text{s}^{-1}$.[3] Accordingly, N1- and N7-methylated 6-oxopurine nucleosides can be employed as model compounds to study the relative binding ability of the N1 and N7 sites of the parent nucleoside.

An analogous treatment of the rate data for 7-methylguanosine gave the values 0.07 $\text{M}^{-1}\ \text{s}^{-1}$ for k_1 and $10^{-6.8}$ M for K_L. The latter is in agreement with the pK_a value 6.7 reported for 7-methylguanosine in the literature.[17] Comparison of the rate constants for 1- and 7-methylguanosines reveals that the former reacts with the $[\text{Pt(dien)(H}_2\text{O)}]^{2+}$ ion 10 times more readily than the latter. By contrast, in the case of inosine derivatives, the reactivity of the 7-methylated compound is slightly higher than that of the N1 isomer. Accordingly, the diminution in the coordination ability of the guanine N1 position must be attributed to sterical retardation of the C2NH_2 group, although this substituent inductively favors complexation (vide supra). The influence of the C2NH_2 group thus parallels the effect of the C6NH_2 group of adenosine, though the latter sterically prevents platination of both N1 and N7.[16]

Registry No. Aquated Pt^{II}(dien), 48102-16-5; 1-MeGuo, 2140-65-0; 7-MeGuo (R = NH_2), 20244-86-4.

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[17] Hendler, S.; Fürer, E.; Srinivasan, P. R. *Biochemistry* **1970**, *9*, 4141-4153.

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Work in Chemistry, University of Waterloo,
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High-Pressure Mass Spectrometric Observation of Metal Carbonyl/Alkyl Adduct Ions of Novel Structure

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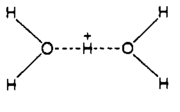
Received September 28, 1990

Bonding in gas-phase transition-metal species has been studied extensively,[1] because of its importance for catalysis, and novel structures are frequently invoked to explain the chemistry involved. In recent years the concept of noncovalent bonding has been extensively used to describe ionic species observed in mass spectrometric experiments.[2-4] For example, we have obtained unambiguous evidence for the existence of a weakly bound noncovalent $(\text{CO})_5\text{Mn}^+/\text{CH}_4$ complex.[5] Odd-[2] and even-electron[2a,3] hydrogen-bridged cations, $[\text{A}\cdot\cdot\text{H}\cdot\cdot\text{B}]^+$, and odd- and even-electron ion–molecule complexes,[4] $[\text{A}\cdot\cdot\text{B}]^+$, have been proposed both as stable species and as transient intermediates to explain the metastable and collision-induced fragmentation characteristics of (organic) ions. While isotopic labeling experiments and high-level ab initio molecular orbital theory calculations have been performed to support the proposed structures, the evidence for these novel complexes is sometimes inconclusive. In addition, fragmentation mechanisms can sometimes better be explained by "conventional" mechanisms.[6] However, even-electron proton-bound cations have been unequivocally identified as the products of many ion–molecule reactions[3] and some dissociative ionization processes.[7] A great deal of attention has been directed toward those species in which a proton interacts with the lone pairs of the oxygen atoms of two (stable) neutral molecules, e.g. **1**. The latter type of interaction renders the ion unconventional in the sense of a valence bond description, but the bonding can approach covalent bond energies with the stabilization energy relative to the dissociation products, $\text{AH}^+ + \text{B}$ or $\text{A} + \text{BH}^+$, often in the range 120–140 kJ·mol^{-1}.[3c]



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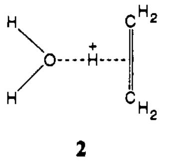

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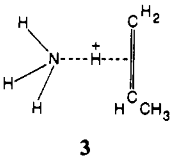

3

Alternatively, a proton can interact with the π system of one (stable) molecule and the lone pairs of an oxygen or nitrogen atom in another (stable) molecule to give novel structures, e.g. **2**[8] and **3**.[9] To date, the latter species have not been unambiguously identified, but both theory[8b,9] and experiment[8-10] lend support to their existence. They have been proposed as intermediates to explain metastable and collision-induced fragmentation pathways of certain ions, and ab initio molecular orbital theory calculations have identified them as stable species on the potential energy surface. In general, the stabilization energy of these species is considerably lower than that of the above mentioned $-\text{O}\cdot\cdot\text{H}\cdot\cdot\text{O}-$

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[1] See e.g.: (a) Russell, D. H., Ed. *Gas Phase Inorganic Chemistry*: Plenum Press: New York, 1989. (b) Marks, T. J., Ed. *Bonding Energetics in Organometallic Compounds*; American Chemical Society: Washington, DC, 1990.

[2] See e.g.: (a) Morton, T. H. *Tetrahedron* **1982**, *38*, 3195. (b) Heinrich, N.; Schmidt, J.; Schwarz, H.; Apeloig, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1317. (c) Burgers, P. C.; Holmes, J. L.; Hop, C. E. C. A.; Postma, R.; Ruttink, P. J. A.; Terlouw, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7315.

[3] See e.g.: (a) Beauchamp, J. L. In *Interactions between Ions and Molecules*; Ausloos, P., Ed.; Plenum Press: New York, 1975; pp 413–444. (b) Larson, J. W.; Clair, R. L.; McMahon, T. B. *Can. J. Chem.* **1982**, *60*, 542. (c) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 6255.

[4] See e.g.: (a) Postma, R. Ph.D. Thesis, University of Utrecht, Utrecht, The Netherlands, 1987. (b) McAdoo, D. J. *Mass Spectrom. Rev.* **1988**, *7*, 363. (c) Hammerum, S. *J. Chem. Soc., Chem. Commun.* **1988**, 858. (d) Hammerum, S.; Audier, H. E. *J. Chem. Soc., Chem. Commun.* **1988**, 860.

[5] Hop, C. E. C. A.; McMahon, T. B. *J. Am. Chem. Soc.* **1991**, *113*, 355.

[6] See e.g.: Bissonnette, M. C.; George, M.; Holmes, J. L. *Int. J. Mass Spectrom. Ion Processes*, in press.

[7] (a) Van Driel, J. H.; Heerma, W.; Terlouw, J. K.; Halim, H.; Schwarz, H. *Org. Mass Spectrom.* **1985**, *20*, 665. (b) Van Baar, B.; Halim, H.; Terlouw, J. K.; Schwarz, H. *J. Chem. Soc., Chem. Commun.* **1986**, 728. (c) Van Baar, B. L. M.; Terlouw, J. K.; Akkök, S.; Zummack, W.; Weiske, T.; Schwarz, H. *Chimia* **1988**, *42*, 226.

[8] (a) Harrison, A. G. *Org. Mass Spectrom.* **1987**, *22*, 637. (b) Bouchoux, G.; Hoppilliard, Y. Y. *J. Am. Chem. Soc.* **1990**, *112*, 9110.

[9] Reiner, E. J.; Poirier, R. A.; Peterson, M. R.; Csizmadi, I. G.; Harrison, A. G. *Can. J. Chem.* **1986**, *64*, 1652.

[10] (a) Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1977**, *99*, 360. (b) Bowen, R. D.; Williams, D. H. *J. Am. Chem. Soc.* **1978**, *100*, 7454. (c) Bowen, R. D.; Williams, D. H. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *29*, 47. (d) Bowen, R. D.; Williams, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 2752. (e) Meot-Ner, M.; Deakyne, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 469. (f) Meot-Ner, M.; Ross, M. M.; Campana, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 4838. (g) Stamp, J. J.; Siegmund, E. G.; Cairns, T.; Chan, K. K. *Anal. Chem.* **1986**, *58*, 873. (h) Terlouw, J. K.; Weiske, T.; Schwarz, H.; Holmes, J. L. *Org. Mass Spectrom.* **1986**, *21*, 665. (i) Weiss, M.; Crombie, R. A.; Harrison, A. G. *Org. Mass Spectrom.* **1987**, *22*, 216. (j) Wright, A. D.; Bowen, R. D.; Jennings, K. R. *J. Chem. Soc., Perkin Trans. II* **1989**, 1521.

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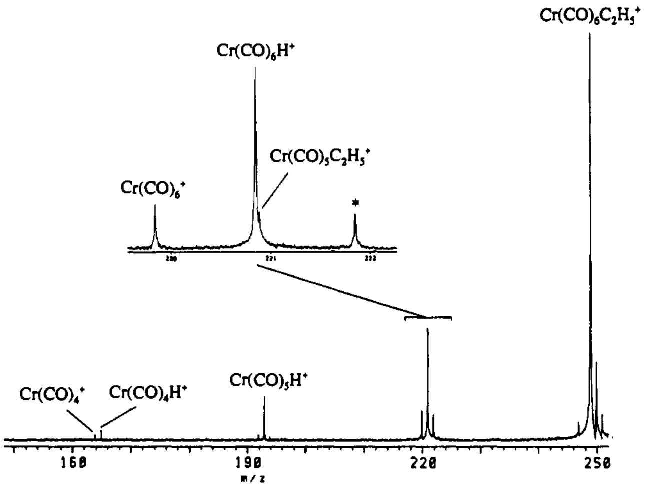

Figure 1. Collision-induced dissociation mass spectrum of isolated [Cr(CO)$_6$]C$_2$H$_5$$^+$ ions, having a center-of-mass energy of 4.0 eV, with Ar as target gas (5 × 10^{-8} mbar) and a 100-ms interaction time. With a shorter interaction time and/or a lower center-of-mass energy [Cr(CO)$_6$]H$^+$ is the only fragment observed. The abundance of C$_2$H$_5$$^+$ (not shown) is stronger than that of *m/z* 165, but weaker than that of *m/z* 193. Some fragmentation of ^{53}Cr or ^{13}C labeled [Cr(CO)$_6$]C$_2$H$_5$$^+$ yielding ^{53}Cr- or ^{13}C-labeled [Cr(CO)$_6$]H$^+$ (asterisk) is observed as well.

bridged species. For example, **2** has been calculated to be bound by only 82 kJ·mol^{-1} relative to H$_3$O$^+$ + C$_2$H$_4$.[8b] In the present manuscript we propose to extend the concept of a proton interacting with two (stable) neutral molecules to more complex transition-metal species.

Experimental Section

The experiments were performed with a Bruker Spectrospin CMS 47 Fourier transform ion cyclotron resonance (ICR) mass spectrometer[11a] equipped with a high-pressure external ion source.[11b] Cr(CO)$_6$ and Mn$_2$(CO)$_{10}$ were used as precursors and CH$_4$ was the chemical ionization agent. Chemical ionization pressures up to 4 mbar and 2 keV electrons were used for ionization. Gas-flow restrictions and differential pumping provided a high-pressure gradient from the ion source to the ICR cell; for a pressure inside the ion source of 4 mbar, the pressure in the ICR cell was a 4 × 10^{-9} mbar. The product ions were transferred from the high-pressure ion source to the ICR cell and trapped, followed by a 2-s delay to thermalize the ions by collision with argon present in the ICR cell (5.0 × 10^{-8} mbar). By the ejection of all other ions from the ICR cell, the ion of interest was isolated. An rf pulse at the exact cyclotron frequency was then used to increase the translational energy of this ion to a known value. The length of the rf pulse determined the translational energy of the ion.[12] In the subsequent delay collision-induced dissociation (CID) took place with Ar as target gas. The fragment ions were detected in broad-band mode (full mass spectrum) and narrow-band mode (single ion detection). Each experiment was repeated 16 times to obtain a good signal-to-noise ratio. To determine the threshold energy for relevant collision-induced dissociations from the center-of-mass energy, E_{cm}, dependence of the fragment ion intensity, the latter curve was analyzed with an empirical model (eq 1),[13] where E_t is the threshold

$$\sigma(E_{cm}) = \sigma_0(E_{cm} - E_t)^n/E_{cm}^m \qquad (1)$$

energy for the endothermic reaction, σ_0 is an energy-independent scaling factor, and n and m are variables. Armentrout et al.[13,14] have found that the form with $m = 1$ is one of the most useful in deriving accurate thermochemistry. In addition, this form has been predicted theoretically for translationally driven reactions.[15] The other parameters, σ_0, E_t, and n, were optimized by using a nonlinear least-squares analysis to give the best fit to the experimental data.

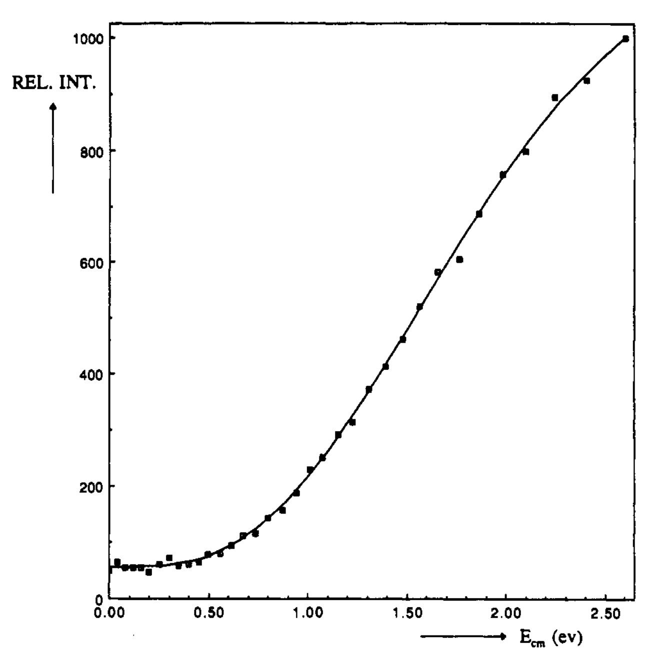

Figure 2. Energy dependence for the collision-induced loss of C$_2$H$_4$ from isolated [Cr(CO)$_6$]C$_2$H$_5$$^+$ with Ar as target (5 × 10^{-8} mbar) and a 10-ms interaction time (single collision conditions). The *y* axis represents the ratio of the intensities of the fragment and parent ions normalized to 1000 for the ratio at a center-of-mass energy of 2.6 eV.

Alternatively, ion activation can be omitted in the above described procedure and the reactivity of the isolated ions with certain substrates (CH$_3$OH and C$_2$H$_5$OH) can be examined by varying the delay between isolation of the ion of interest and detection.

All compounds were of commercial origin and showed no detectable impurities.

Results and Discussion

The high-pressure mass spectrum of Cr(CO)$_6$ + CH$_4$ was dominated by *m/z* 221, [Cr(CO)$_6$]H$^+$, but an appreciable amount of the *m/z* 249 [Cr,C$_8$,O$_6$,H$_5$]$^+$ ion, generated via reactions 2–5,

$$CH_4 + e^- \rightarrow CH_4^{\bullet+} + 2e^- \qquad (2)$$

$$CH_4^{\bullet+} \rightarrow CH_3^+ + H^\bullet \qquad (3)$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \qquad (4)$$

$$C_2H_5^+ + Cr(CO)_6 \rightarrow [Cr(CO)_6]C_2H_5^+ \qquad (5)$$

was also observed (ca. 50% of *m/z* 221[16]). The CID mass spectrum of the latter ion was dominated by *m/z* 221 (see Figure 1). From the high mass resolution attainable with the FT-ICR mass spectrometer, it was determined that *m/z* 221 corresponded to [Cr(CO)$_6$]H$^+$. The threshold for collision-induced C$_2$H$_4$ loss was found to be rather low, 60 ± 5 kJ·mol^{-1} (see Figure 2). CO loss from *m/z* 249 was only observed at much higher energies. For example, at a center-of-mass energy of 3.0 eV C$_2$H$_4$ loss was ca. 9.0 times as intense as CO loss. Since Cr(CO)$_6$ is a *hexacoordinate* species, the structure of the *m/z* 249 ion is of some interest.

To date it had been assumed that protonation of Cr(CO)$_6$ occurs at the metal position with the proton affinity (PA) being 756 kJ·mol^{-1}.[17] With use of pulsed ionization high-pressure mass spectrometry,[18] proton transfer between protonated Cr(CO)$_6$ and

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(11) (a) Allemann, M.; Kellerhals, H.-P.; Wanczek, K. P. *Int. J. Mass Spectrom. Ion Processes* **1983**, *46*, 139. (b) Kofel, P.; McMachon, T. B. *Int. J. Mass Spectrom. Ion Processes* **1990**, *98*, 1.

(12) Hop, C. E. C. A.; McMahon, T. B.; Willett, G. D. *Int. J. Spectrom. Ion Processes* **1990**, *101*, 191.

(13) Sunderlin, L.; Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 78 and references therein.

(14) (a) Boo, B. H.; Armentrout, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 3549. (b) Aristov, N.; Armentrout, P. B. *J. Chem. Phys.* **1987**, *91*, 6178. (c) Sunderlin, L. S.; Armentrout, P. B. *J. Am. Chem. Soc.* **1989**, *111*, 3845. (d) Boo, B. H.; Elkind, J. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1990**, *112*, 2083.

(15) Chesnavich, W. J.; Bowers, M. T. *J. Phys. Chem.* **1979**, *83*, 900.

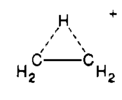
(16) The relative abundance of these ions was dependent on the ion source pressure (2.5 Torr) and temperature (298 K).

(17) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629.

(18) See, e.g.: Kebarle, P. In *Techniques for the Study of Ion-Molecules Reaction*; Farrar, J. W., Saunders, W. H., Jr., Eds.; Wiley: New York, 1988; pp 221–286.

various bases, B, was examined by measuring the relative intensities of $[Cr(CO)_6]H^+$ and BH^+ as a function of the ion source residence time.[19] At elevated temperature (>100 °C) the PA of $Cr(CO)_6$ was determined to be within experimental error equal to the literature value, 756 kJ·mol^{-1}.[17] However, below 40 °C protonated $Cr(CO)_6$ was in equilibrium with bases with a considerably lower PA, which indicated a PA for $Cr(CO)_6$ between 690 and 710 kJ·mol^{-1}. In support of this, $[Cr(CO)_6]H^+$ was observed to undergo slow proton transfer to H_2S ($PA(H_2S) = 712$ kJ·mol^{-1} [20]) in the ICR cell. On the basis of the linear relationship between the oxygen 1S binding energy (determined via X-ray photoelectron spectroscopy[21]) and the PA of oxygen bases,[22] the oxygen PA of $Cr(CO)_6$ was estimated to be 703 kJ·mol^{-1}. Thus, at low temperature protonation occurs at the oxygen atom of one of the carbonyl groups, whereas higher temperatures result in metal protonation. An energy barrier between the two forms apparently prevents isomerization of the two structures at low temperature. These results are supported by recent infrared spectroscopic data,[23] where it was observed that molecules like $(CF_3)_3COH$ and HCl form a hydrogen bridge with the carbonyl oxygen atom of transition-metal carbonyl complexes in a liquid-xenon matrix; the binding energy of such adducts was determined to be ca. 25 kJ·mol^{-1}. It was also concluded that protonation at the metal center proceeded with the participation of these H-bonded complexes as intermediates.

The facile loss of C_2H_4 from $[Cr(CO)_6]C_2H_5^+$ suggests a *loosely bound* complex. By analogy with protonated $Cr(CO)_6$, the ethyl cation can be expected to interact initially with one of the carbonyl oxygen atoms in $Cr(CO)_6$, which might be followed by ethyl cation transfer to the metal center. However, it can reasonably be assumed that, if rearrangement is possible, the barrier separating the two structures will be considerably higher than that in protonated $Cr(CO)_6$. The highest level ab initio calculations performed to date have shown that the bridged structure of $C_2H_5^+$ (4) is the only minimum found on the $C_2H_5^+$ potential energy surface.[24] Therefore we suggest that the bridging hydrogen atom of a nonclassical $C_2H_5^+$ ion interacts with a lone pair of one of the carbonyl oxygen atoms, generating structure 5, which is rapidly thermalized in the high-pressure environment of the ion source. The energy required for C_2H_4 loss from 5 is in good agreement with stabilization energies obtained for similarly bridged systems. For example, it was calculated that alkene losses from **2**[8b] and **3**[9] require 82 and 42 kJ·mol,$^{-1}$ respectively, and benzene was found to be bound to $(CH_3)_3NH^+$ by 67 kJ·mol^{-1}.[10e]



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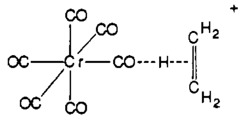

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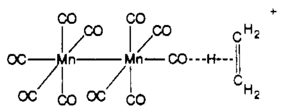
Since $Cr(CO)_6$ is a hexacoordinate species formation of a covalent $Cr-C_2H_5$ bond is for steric reasons unlikely. If $C_2H_5^+$ had been covalently bound to the $Cr(CO)_6$ moiety at one of the carbonyl groups, a much higher stabilization energy might have been expected; e.g., at least 160 kJ·mol^{-1} is required for C_2H_4 loss in ions containing a $-C(O)C_2H_5$ group.[20] In addition, for $C_2H_5^+$ bound to the carbon atom of one of the carbonyl groups a significant signal at *m/z* 57, $C_2H_5CO^+$, could be expected, since its generation is energetically more favorable than most other fragmentation routes.[25] However, no signal at *m/z* 57 was observed.

Reactivity studies showed that the $C_2H_5^+$ group can easily be transferred from $[Cr(CO)_6]C_2H_5^+$ to CH_3OH and C_2H_5OH, generating protonated methyl ethyl ether and dimethyl ether (or an isomer), respectively. The facile transfer of an intact ethyl group would seem to preclude a structure in which the proton is bound to the metal center and ethylene is held primarily by weak electrostatic interaction.

Thus, we propose that the $[Cr(CO)_6]C_2H_5^+$ ions have structure 5, although additional generation of isomeric species cannot be ruled out. On the basis of the above conclusion, it comes as no surprise that all attempts to methylate $Cr(CO)_6$ with dimethyl halonium ions failed.

The above result is not an isolated case. Similar species have also been seen in the high-pressure mass spectrum of $Mn_2(CO)_{10}$ + CH_4. In this case, both an intense *m/z* 391 signal, $[Mn_2(CO)_{10}]H^+$, as well as signals at *m/z* 419, $[Mn_2,C_{12},O_{10},H_5]^+$, and *m/z* 433, $[Mn_2,C_{13},O_{10},H_7]^+$, were present (ca. 16% and 8% of *m/z* 391[16]). Although the *m/z* 419 and 433 signals were too weak to determine threshold energies, it could be established unambiguously that alkene losses (C_2H_4 and C_3H_6, respectively) were the least energy demanding fragmentation pathways with threshold energies below 100 kJ·mol^{-1}. The threshold energy for CO loss from $[Mn_2(CO)_{10}]H^+$ was established as 80 ± 7 kJ·mol^{-1}. Thus, the threshold energy for alkene loss from *m/z* 419 and 433 can reasonably expected to be less than 80 kJ·mol^{-1}. Because these ions are coordinately saturated as well, we propose that these ions must result from addition of $C_2H_5^+$ and $C_3H_7^+$, generated via CH_4 chemical ionization, to $Mn_2(CO)_{10}$. Again, the results are most compatible with hydrogen-bridged species 6 and 7.



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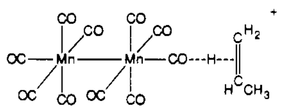

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In summary, we have shown that threshold collision-induced dissociation experiments can be used advantageously to identify organometallic ions of novel structure as well as to obtain a quantitative measure of selected bond energies. Future contributions from this laboratory will give more examples.

Acknowledgment. T.B.M. thanks the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Petroleum Research Fund, administered by the American Chemical Society, for financial support. We are grateful to G. K. Koyanagi for the pulsed ionization high-pressure mass spectrometry experiments.

Registry No. $Cr(CO)_6$, 13007-92-6; $Mn_2(CO)_{10}$, 10170-69-1; CH_4, 74-82-8.

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(19) Koyanagi, G. K.; Hop, C. E. C. A.; McMahon, T. B. To be published.

(20) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(21) Baaker, A. A.; Chen, H.-W.; Jolly, W. L. *Electron. Spectrosc. Relat. Phenom.* **1980**, *20*, 333.

(22) McMahon, T. B.; Kebarle, P. *J. Chem. Phys.* **1985**, *83*, 3919.

(23) (a) Lokshin, B. V.; Kazaryan, S. G.; Ginzberg, A. G. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1986**, *35*, 2390. (b) Lokshin, B. V.; Kazarian, S. G.; Ginzberg, A. G. *J. Mol. Struct.* **1988**, *174*, 29.

(24) Wong, M. W.; Baker, J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1987**, *109*, 2245.

(25) $\sum\Delta H_f([Cr(CO)_6]H^+ + C_2H_4) = -26$ kJ·mol^{-1}; $\sum\Delta H_f(Cr(CO)_6^{\bullet+} + C_2H_5^{\bullet}) = -4$ kJ·mol^{-1}; $\sum\Delta H_f(C_2H_5CO^+ + Cr(CO)_5) = -52$ kJ·mol^{-1}; $\sum\Delta H_f(C_2H_5^+ + Cr(CO)_6) = -6$ kJ·mol^{-1}. All heats of formation are from ref 20 except those of $[Cr(CO)_6]H^+$ and $Cr(CO)_5$, −78 and −643 kJ·mol^{-1}, respectively. The former was obtained by using the PA of $Cr(CO)_6$, 700 kJ·mol^{-1} (see text). The Cr–CO bond dissociation energy in $Cr(CO)_6$, 154 kJ·mol^{-1},[26] gave $\Delta H_f(Cr(CO)_5)$.

(26) Smith, G. P. *Polyhedron* **1988**, *7*, 1605.