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Formation of Mixed-Metal Binuclear Carbonyl Ions $[MCr(CO)_n]^+$ in the Gas Phase by the Laser Ablation–Molecular Beam Method

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In the laser ablation–molecular beam (LAMB) method, laser ablation of metal substrates in vacuum is utilized for the formation of novel organometallic and metal complex compounds containing monopositive metal ions. Mixed-metal binuclear carbonyl ions $[MCr(CO)_n]^+$, $n=0$–6, are prepared in the gas phase by the reaction of laser-ablated metal ions (M^+) and $Cr(CO)_6$ in the molecular beam injected nearby. The relative abundance of these ions, for M = transition metals, can essentially be explained by the M^+–Cr bond dissociation energies. Results of density functional calculation show that this is essentially valid © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

Laser ablation of solid metals in vacuum in conjunction with a molecular beam injected nearby is a rich source of novel organometallic and metal complex chemistry. In the laser ablation–molecular beam (LAMB) method developed in our group,[1–14] laser ablation of a metal substrate in vacuum is utilized for the preparation of a variety of monopositive metal ions (M^+) in the gas phase. The key aspect here is that every metal is prepared in a state of monopositive atomic ions by this method. A molecular beam of molecules or clusters is injected nearby. Ion–molecule reactions of the monopositive metal ions with the molecules or clusters in the beam occur, and the product ions are probed by mass spectroscopy. Novel organometallic ions are prepared when organic or organometallic molecules or clusters are used in the beam; metal complexes of new types are formed when inorganic molecules or clusters are used. Thus, the LAMB method serves as a simple and versatile way of opening up a broad new field of novel organometallic or metal complex chemistry of monopositive metal ions hitherto unexplored. Reactions with benzene clusters produce a variety of novel metallocenes.[5, 6] Ammine-type complexes of monopositive metal ions in the gas phase are given on using ammonia clusters in the beam.[8] Only a limited number (such as two or three) of ligands is allowed in the first coordination (solvation) sphere, in contrast to the familiar hexacoordinated Werner-type complexes in aqueous solutions. In addition, reactions with binary clusters (ammonia–water,[11, 12] ammonia–methanol,[10, 12] methanol–water,[12, 13] ammonia–acetone[14]) reveal metal-dependent characteristics of competitive coordination (solvation).

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Three types of competitive coordination (solvation), i.e. selective, non-selective and magic-number-like, are observed.

In the reactions of M^+ with metal carbonyls, such as $Cr(CO)_6$ and $Mn_2(CO)_{10}$,[3,7] a variety of mixed-metal binuclear and trinuclear carbonyls, e.g. $[MCr(CO)_n]^+$ ($n=0$–6) and $[Mn_2(CO)_n]^+$ ($n=0$–10), are prepared. Most of them are coordinatively unsaturated. Some of those containing transition metals may have some relevance to catalysis chemistry. In the present paper, results on the reactions with $Cr(CO)_6$, briefly reported previously,[7] are detailed in some depth.

EXPERIMENTAL

The experimental procedure of the LAMB method has been reported previously.[7] The essential part of the apparatus is shown schematically in Fig. 1. Briefly, laser light (the second harmonic of a Quanta-Ray DCR-2 Nd^{3+} : YAG laser at 532 nm, *ca* 7 ns, 10 Hz) was focused using a quartz lens onto the surface of a metal substrate (*ca* 1×1 cm^2) located in a vacuum chamber evacuated to a base pressure of 5×10^{-6} Torr. The laser light was shot onto the metal substrate through a pair of holes cut in an axial-type 'ionizer' in front of an Extrel (the former Extra-Nuclear) 164–2 quadrupole (inner diameter 0.95 cm). Metal ions (M^+) ejected from the surface of the metal substrate entered the ionizer through the hole. At this time laser light was no longer present, since it was a 7 ns pulsed light. A molecular beam of $Cr(CO)_6$ was injected through another pair of holes of the ionizer cut perpendicular to the first pair. An ion–molecule reaction in the crossing region gave the product ions $[MCr(CO)_n]^+$ ($n=0$–6). These product ions were extracted by the ion optics into the quadrupole, together with the metal ion and fragment ions of $Cr(CO)_6$. They were mass-selected and detected by a channeltron (Galileo 4816). The mass-dependent sensitivity of the mass spectrometer was calibrated using the known spectrum of perfluorokerosine. Ammonia clusters were used as a secondary standard.

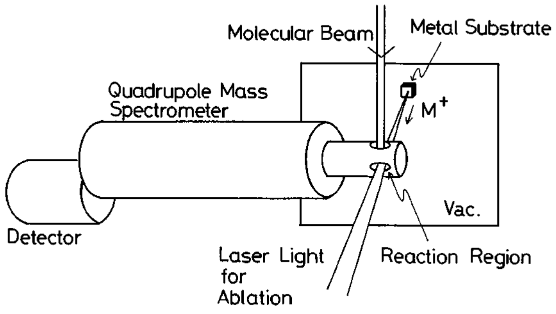

Figure 1 Schematic view of the experimental apparatus.

Focusing was crucial for the production of metal ions; only neutral metal atoms were produced when laser light was not focused. Typical values of fluence on the metal surface were 100–200 mJ cm^{-2} pulse^{-1}. The ionizer was equipped with a filament for electron impact. However, the filament was not used in the present experiment because ions were produced by laser light, and the products were also ions. The ionizer here simply worked as a small reaction chamber.

RESULTS AND DISCUSSION

As already reported briefly,[7] the observed relative abundance of $[MCr(CO)_n]^+$ ($n=0$–6) for the first- and second-series transition metals (titanium to nickel, and zirconium to palladium) manifested an interesting trend, as shown in Fig. 2. In the first series, the numbers of CO eliminated in the reaction represented by Eqn [1],

$$M^+ + Cr(CO)_6 \rightarrow MCr(CO)_n^+ + (6-n)CO, \quad [1]$$

i.e. $(6-n)$, is a minimum for M=Mn and increases when one goes to the left, or to the right, in the Periodic Table.

The most inert nature of Mn among these metals was found in our study of reactions with ethylamine, diethylamine and triethylamine.[4] A similar trend was reported by Tonkyn and Weishaar[15] for the reactions of M^+ and C_2H_6. The trend mentioned above is in parallel with that reported by Kappes and Staley[16] for the reactions of Ti^+ to Ni^+ with $Cr(CO)_6$ by a different experimental technique (ion cyclotron resonance). Therefore, the trend is not due to experimental details, but reflects the characteristics inherent for each transition metal. However, such a trend was not repeated for the transition metals in the second series: all of these metals showed elimination of more than two, and

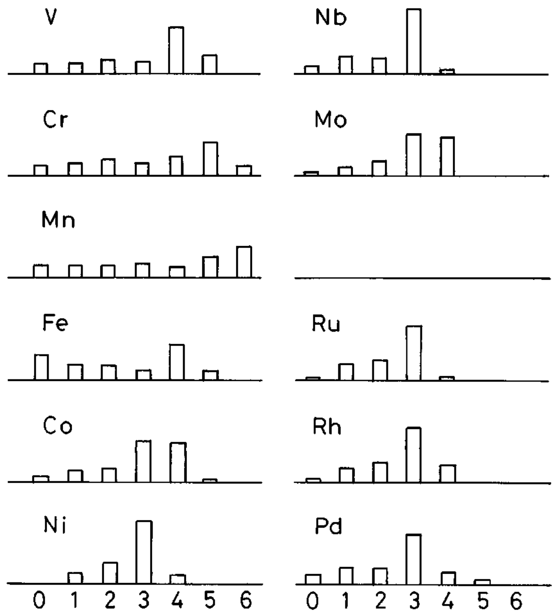

Figure 2 Relative abundance of product ions $[MCr(CO)_n]^+$, $n = 0$–6.

mostly three, CO groups.

All of the $[MCr(CO)_n]^+$ ions ($n = 0$–6) observed are coordinatively unsaturated. The 18-Electron Rule or EAN rule for metal carbonyls dictates that completion of an electronic shell requires formulas such as $VCr(CO)_{12}^+$, $MnCr(CO)_{11}^+$ and $CoCr(CO)_{10}^+$. Incidentally, all of these must contain one bridging CO. The cases M = Cr, Fe and Ni require dimerization of the ion to fulfil the EAN rule. However, no ions with $n > 6$ were observed in our experiment. Therefore, the experimentally observed trend is not due to stable closed-shell formation.

We must consider whether a direct M–Cr bond is formed or not in these product ions. Formation of the M–O–C–Cr type of linkage dominates for metal ions with a strong Lewis acid nature, e.g. alkali-metal ions, Mg^{2+}, Al^{3+}, or Ti^{3+}, V^{3+} and Zr^{3+} ions.[17] For monopositive ions of most transition elements, however, direct M–Cr bond formation can safely be assumed. Since no structural data are at present available on these binuclear carbonyls, we proceed empirically: a simple conjecture leads to the idea that the energy gain for the simple association reaction (Eqn [2])

$$M^+ + Cr(CO)_6 \rightarrow MCr(CO)_6^+ \qquad [2]$$

is essentially due to formation of an M^+–Cr bond. Naturally, some redistribution of CO between M^+ and Cr must accompany the reaction. In this simplified picture it is tacitly assumed that all the bond energies of M^+–CO, Cr–CO and M^+–(CO)–Cr (a bridge bond) are the same. While this is an oversimplification, this way of thinking can provide a reasonably plausible model for the observed trend, as shown below.

Firstly, we wish to compare the numbers of released CO molecules with the M^+–Cr bond energy. However, values of the M^+–Cr bond energy necessary in such a consideration are not available. There has been some progress on the studies of metal–dimer (homogeneous and heterogeneous) bond energies.[18–20] Howver, these data are still very limited, and those on Cr-containing heterodimer are absent, except for only one case of CuCr.[21] We have to make calculations of $M^+ - Cr$ bond energy values using some assumptions. In principle these values can be calculated using a cycle (Scheme 1) and Eqn [3].

$$\begin{tikzcd}
M^+ + Cr & M + Cr \arrow[l, "IP(M)"'] \\
M^+–Cr \arrow[u, "D(M^+–Cr)"] \arrow[r, "-IP(MCr)"'] & M–Cr \arrow[u, "D(M–Cr)"']
\end{tikzcd}$$

Scheme 1

$$D(M^+–Cr) = -IP(MCr) + D(M–Cr) + IP(M) \qquad [3]$$

In this cycle, $D(M^+–Cr)$ and $D(M–Cr)$ are bond dissociation energies. IP(M) and IP(MCr) are ionization energies. All the necessary values on the right-hand side of Eqn [3] are lacking, however, except for those of IP(M) and $D(Cu - Cr)$. Because the values of IP(MCr) are lacking, IP(MFe) values obtained experimentally by Hettich and Freiser[22] are used as substitutes, as in the previous report.[7] Vaues of D(M–Cr) are estimated, as in Ref. 20, by Eqn [4].

$$D(M–Cr) = \tfrac{1}{2}\{D(M-M) + D(Cr–Cr)\} + 96(\chi_M - \chi_{Cr})^2 \qquad [4]$$

In this equation, χ_M and χ_{Cr} are Pauling's electronegativities for M and Cr, respectively.[23] D values are in kJ mol^{-1}. The calculation is shown in Table 1, which shows the accuracy of the numerals obtained. These are the optimal results at present. More reliable values of D(M–Cr) and IP(MCr) should become available to place the calculations on a more reliable basis. However, we can obtain a reasonably good set of $D(M^+–Cr)$ values by proceding along these

Table 1 Calculation of dissociation energies of M^+–Cr bonds

Metal	D(M–M)[a] (eV)	$\frac{1}{2}$[D(M–M)+D(Cr–Cr)] (kJ mol^{-1})	$\chi_M-\chi_{Cr}$[b]	$96(\chi_M-\chi_{Cr})^2$ (kJ mol^{-1})	D(M–Cr) (kJ mol^{-1})	IP(M) − IP(MCr)[c] (kJ mol^{-1})	D(M^+–Cr)[d] (kJ mol^{-1})
Ti	1.23±0.17	145	−0.1	0.96	146	79	225±16
V	2.49±0.13	206	0	0	206	129	335±13
Cr	1.78±0.35	172	0	0	172	74	246±34
Mn	0.23[e]	86	−0.1	0.96	87	—	—
Fe	0.90±0.10	129	0.2	3.84	133	180	313±10
Co	1.69[e]	157	0.2	3.84	161	131	292
Ni	2.07±0.01	186	0.2	3.84	190	100	290±10
Cu	—	—	—	—	154±14[f]	99	253±14
Nb	5.0±0.2[g]	327	0	0	327	37	364±19
Ta	5.1[h]±1.0	331	−0.1	0.96	332	47	379±98

[a] From Morse (Ref. 20), unless otherwise indicated.
[b] From Pauling (Ref. 23).
[c] The IP(MFe) value of Hettich and Freiser (Ref. 22) is used as a substitute for IP(MCr).
[d] Estimated by Eqn [3].
[e] In eV, from Huber and Herzberg (Ref. 29).
[f] The only existing literature value (Kant *et al.*, Ref. 21), compiled in Morse's review (Ref. 20).
[g] From Weltner and Zee (Ref. 19).
[h] Krasnov's (Ref. 30) central value, compiled in Table 5 of Gingerich's review (Ref. 18).

lines. In Fig. 3 we plot the average values the number of CO groups released $(6-\bar{n})$ against the $D(M^+-Cr)$ values obtained from Eqn [3]. It can be discerned from the figure that more CO groups are eliminated for those metals forming stronger M^+–Cr bonds. The straight line in the figure corresponds to the case that energy gain according to Eqn [5],

$$\Delta E = D(M^+\text{–Cr}) - (6-n)D(M'\text{–CO}) \qquad [5]$$

is zero, i.e. the reaction to which Eqn [5] applies is thermoneutral. Here it is tacitly assumed that all of the M–CO, Cr–CO or M–(CO)–Cr (bridge) bond energies in $MCr(CO)_n^+$, represented simply by D(M′–CO), are the same as that of a Cr–CO bond, which is taken to be 110 kJ mol^{-1}.[24] It is to be noted that the experimental points are found close to this straight line.

We can assume that such a result is reasonable for gas-phase reactions. When the reaction occurs in the gas phase and the excess energy released as the result of the reaction is not removed, this energy gain must remain as internal energy of the product ion. Then the total energy of the reaction system $M^+ + Cr(CO)_6$ remains above the dissociation limit (Fig. 4). In

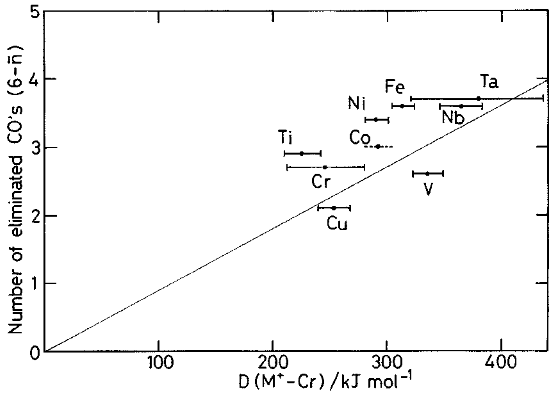

Figure 3 Relationship of average number of eliminated CO groups and M^+–Cr dissociation energies. Straight line: see text.

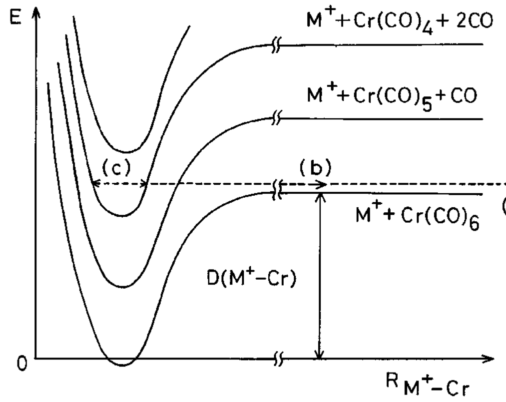

Figure 4 Model potential-energy curves (schematic). M^+ approaches (a), leaves again in excess energy is not taken out (b) or remains in the complex when some CO groups are eliminated (c).

Table 2 M^+–Cr bond energies by the density functional calculation[a, b, c]

	Ti	V	Cr	Mn	Fe
$E(MCr^+)$/(au)	−1893.5878	−1988.1247	−2088.6293	−2195.1097	−2307.8803
(Multiplicity)	(4)	(3)	(2)	(3)	(4)
$E(M^+)$/(au)	−849.0676	−943.6545	−1044.1499	−1150.6657	−1263.3533
(Multiplicity)	(4)	(5)	(6)	(7)	(6)
Bond energy (au)	0.0965	0.0465	0.0557	0.0203	0.1033
(kJ mol^{-1})	253.4	122.1	146.2	53.3	271.2

[a] Bond energy is estimated by the following energy difference: $E(M^+)+E(Cr)-E(MCr^+)$.

[b] 1 atomic unit (au) = 27.212 eV = 2625.5 kJ mol^{-1}.

[c] E(Cr, septet) = −1044.4237 au.

this case the product ion must dissociate, releasing M^+ ion again, resulting in no net reaction. However, if some CO are eliminated in the reaction (Eqn [6]),

$$M^+Cr(CO)_6 \rightarrow MCr(CO)_n^+ + (6-n)CO \quad [6]$$

some part of the excess energy is consumed in the scission of CO, and the net reaction proceeds. When all the excess energy is consumed, the energy gain for the reaction is zero ($\Delta E \sim 0$), i.e. the reaction is thermoneutral. Then the maximum of the distribution of $MCr(CO)_n^+$ must occur around the n which satisfies such a condition.

We have recently performed density functional calculations, using the deMon program developed by St Amant and Salahub[25] and modified by Kobayashi.[26]. Calculated M^+–Cr bonding energy values are shown in Table 2.[27] All values in the table are for the lowest-energy multiplicity. The multiplicities of M^+ are in accordance with reported spectroscopic data.[28] The calculated M^+–Cr bonding energy is the least for M = Mn and it increases when one goes to the left or right in the Periodic Table, supporting the explanation given above.

Of course the concept in the present paper is oversimplified. However, we believe that such an initial study is useful to shed new light onto hetero-binuclear metal carbonyl chemistry, in that it can clarify the important role of direct M–Cr bond energies in the relative stabilities of a series of coordinatively unsaturated mixed-metal binuclear carbonyls. A similar idea may be applicable to trinuclear carbonyls etc. Naturally, a more detailed discussion should follow as our basic understanding of this field is improved. Many data should become available, such as M–Cr and M^+–Cr bond energies, distribution of CO between M and Cr atoms [some of the CO groups may form bridge(s)], and bond energies of individual M–CO and Cr–CO and M–(CO)–Cr (bridge) bonds, before we can reach further conclusions. Structural studies of product ions by matrix isolation/FTIR measurements are under way.

CONCLUSIONS

A variety of novel coordinatively unsaturated mixed-metal binuclear carbonyl ions $[MCr(CO)_n]^+$, $n = 0$–6, have been detected by the laser ablation–molecular beam (LAMB) technique, in which laser-ablated monopositive metal ions are allowed to react with $Cr(CO)_6$ in a molecular beam injected nearby and the product ions are detected by mass spectroscopy. The observed relative abundance of the ions for the first- and second-series transition metals manifested an interesting trend, and the trend has been interpreted by an empirical rule, that more CO molecules are eliminated for the metal (M) which forms a stronger M^+–Cr bond. Results of density functional calculaton show that this explanation is essentially valid.

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