

Chemistry of Electron Deficient Organometallic Anions: Gas Phase Reactions of $[\text{Cr}(\text{CO})_3]^-$ with Amines

I. K. GREGOR

School of Chemistry, The University of New South Wales, Kensington, N.S.W., 2033, Australia

(Received March 5, 1987)

Fourier transform ion cyclotron resonance (FTICR) spectroscopy has recently emerged as a significant technique for the investigation of ion/molecule reactions in the gas phase where bimolecular encounters between ions and neutral molecules can be studied in the absence of solvation phenomena [1–4]. With a trapped ion cell ionic products of ion/molecule reactions can be detected and identified under high mass resolution conditions for reaction times varying from a few milliseconds to seconds in contrast with the much shorter reaction times, and low mass resolution, allowed by flowing afterglow (FA) or drift cell ion cyclotron resonance (ICR) techniques. Many potentially reactive electron deficient anions hitherto have been identified as fragmentation products in electron and chemical ionization negative ion mass spectra of organometallic compounds [5–13]. The species $[\text{Cr}(\text{CO})_x]^-$ with $x = 3–5$ are well known products of dissociative electron capture by $\text{Cr}(\text{CO})_6$ in the gas phase [8–10] with the 13-electron radical anion $[\text{Cr}(\text{CO})_3]^-$ having recently been shown to exhibit reactivity with a variety of organic substrates [6, 14, 15]. Results are now presented which focus principally on new reactions of this nucleophile with a series of primary, secondary and tertiary amines, respectively I–IX.

Experimental

A Spectrospin CMS-47 FTICR spectrometer incorporating a 6 cm diameter X 6 cm cylindrical trapped ion cell, 15 cm bore 4.7 Tesla superconducting magnet and Bruker Aspect 3000 computer was used in this study [16, 17]. $[\text{Cr}(\text{CO})_3]^-$ ions (10% relative abundance) were formed by electron ionization of $\text{Cr}(\text{CO})_6$ at a pressure of 5×10^{-8} mbar with 5.0 eV electrons together with $[\text{Cr}(\text{CO})_5]^-$ (100%) and $[\text{Cr}(\text{CO})_4]^-$ (10%). The latter two ions were ejected from the cell immediately prior to the reaction delay when the reactions of $[\text{Cr}(\text{CO})_3]^-$ were being examined. In separate experiments the reactivity of both mass selected $[\text{Cr}(\text{CO})_5]^-$ and $[\text{Cr}(\text{CO})_4]^-$ ions with amines was also assessed. Neutral amine reactants were admitted to the FTICR cell at ambient temperature, c. 30 °C, in the pressure ratio 5:1 to the neutral metal carbonyl. Reaction delays of 1 s were used to establish ionic product distributions for the ion/molecule reactions listed in Tables I and II. The empirical formulae of all ionic reaction products were established by accurate mass measurements from high resolution spectra [17], whilst ion/molecule reaction channels were deduced by selective ion ejections or plots of the temporal variations of fractional ion abundances. Chromium hexacarbonyl was obtained from Strem Chemicals Inc. and the organic amines were high purity commercial samples from Matheson Gases, Aldrich, Fluka and B.D.H. which were used after undergoing multiple freeze–pump–thaw cycles to remove non-condensables. D-labelled compounds used were ND_3 , 99 atom%D; and CD_3CN , 99.7 atom%D both from MSD isotopes; CD_3NH_2 and $(\text{CD}_3)_2\text{NH}$ from their respective Aldrich 98 atom%D-hydrochlorides. Where appropriate, compound purities were checked from broad band positive ion mass spectra run on the CMS-47 instrument.

TABLE I. Ionic Product Distributions for Reactions of $[\text{Cr}(\text{CO})_3]^-$ with Amines $\text{R}^1\text{R}^2\text{R}^3\cdot\text{N}$ a, b

Ionic Products	Amine					
	$\text{R}^1=\text{R}^2=\text{R}^3=\text{H}$ I	$\text{R}^1=\text{CH}_3$ $\text{R}^2=\text{R}^3=\text{H}$ II	$\text{R}^1=\text{R}^2=\text{CH}_3$ $\text{R}^3=\text{H}$ III	$\text{R}^1=\text{C}_2\text{H}_5$ $\text{R}^2=\text{R}^3=\text{H}$ IV	$\text{R}^1=\text{R}^2=\text{C}_2\text{H}_5$ $\text{R}^3=\text{H}$ V	$\text{R}^1=\text{R}^2=\text{R}^3=\text{CH}_3$ VI
$[\text{R}^1\text{R}^2\text{N}\cdot\text{Cr}(\text{CO})_3]^-$	0.33					N.R.
$[(\text{R}^1-\text{H})\text{R}^2\text{N}\cdot\text{Cr}(\text{CO})_3]^-$		0.31	0.57	0.11	0.57	
$[(\text{R}^1-2\text{H})(\text{R}^2-\text{H})\text{N}\cdot\text{Cr}(\text{CO})_3]^-$			0.10			
$[\text{R}^1-2\text{H})\text{N}\cdot\text{Cr}(\text{CO})_3]^-$		0.32		0.50		
$[\text{R}^1\text{R}^2\text{R}^3\text{N}\cdot\text{Cr}(\text{CO})_2]^-$	0.67	0.34	0.27	0.33	0.08	
$[(\text{R}^1-\text{H})\text{R}^2\text{N}\cdot\text{Cr}(\text{CO})_2]^-$				0.04	0.36	
$[(\text{R}^1-2\text{H})\text{N}\cdot\text{Cr}(\text{CO})_2]^-$		0.02		0.01		
$[\text{CN}\cdot\text{Cr}(\text{CO})_3]^-$			0.06	0.02		

aBased on ^{52}Cr isotopes.

bReaction times of 1 s.

TABLE II. Ionic Product Distributions for Reactions of $[\text{Cr}(\text{CO})_3]^-$ with Cyclic Amines^{a, b}

Ionic Products	Amine		
	Pyrrrolidine $\text{C}_4\text{H}_9\text{N}$ VII	Piperidine $\text{C}_5\text{H}_{11}\text{N}$ VIII	Pyridine $\text{C}_5\text{H}_5\text{N}$ IX
$[\text{C}_5\text{H}_9\text{N}\cdot\text{Cr}(\text{CO})_3]^-$		0.18	
$[\text{C}_5\text{H}_7\text{N}\cdot\text{Cr}(\text{CO})_3]^-$		0.07	
$[\text{C}_5\text{H}_{11}\text{N}\cdot\text{Cr}(\text{CO})_2]^-$		0.75	
$[\text{C}_5\text{H}_5\text{N}\cdot\text{Cr}(\text{CO})_2]^-$			1.0
$[\text{C}_4\text{H}_7\text{N}\cdot\text{Cr}(\text{CO})_3]^-$	0.39		
$[\text{C}_4\text{H}_9\text{N}\cdot\text{Cr}(\text{CO})_2]^-$	0.14		
$[\text{C}_4\text{H}_5\text{N}\cdot\text{Cr}(\text{CO})_2]^-$	0.46		

^aBased on ^{52}Cr isotopes.^bReaction times of 1 s.

Results and Discussion

Table I lists the ionic product distributions for the reactions of $[\text{Cr}(\text{CO})_3]^-$ with the amines I–VI. The empirical formulae of the productions were established not only from accurate mass measurements, but also from parallel reactions carried out between $[\text{Cr}(\text{CO})_3]^-$ and the deuterated analogues of I–III, viz. ND_3 , CD_3NH_2 , $(\text{CD}_3)_2\text{NH}$. The one reaction channel common to I–V and also VII–IX, Table II, involved decarbonylation to give product ions of the type $[\text{amine}\cdot\text{Cr}(\text{CO})_2]^-$ which appeared as the principal ionic product in the reactions of I and VIII. A similar reaction has been identified recently with $[\text{Cr}(\text{CO})_3]^-$ /alkene or/polyene systems [6].

Whereas interaction of NH_3 with $[\text{Cr}(\text{CO})_3]^-$ yielded an ion of highest m/z corresponding to $[\text{H}_2\text{N}\cdot\text{Cr}(\text{CO})_3]^-$ by H^+ elimination, the primary amines II and IV gave reaction products where both one and two molecules of H_2 were eliminated. Moreover, the reaction of CD_3NH_2 with $[\text{Cr}(\text{CO})_3]^-$ yielded products identified as $[\text{CD}_2\text{NH}\cdot\text{Cr}(\text{CO})_3]^-$ and $[\text{DCN}\cdot\text{Cr}(\text{CO})_3]^-$ by HD and 2HD eliminations. Ion abundance/time plots for these latter two species, Fig. 1, indicated that they were formed by competing reaction channels possibly from a common precursor intermediate formed in an initial fast reaction. The implication here is that the reactions occur as a result of the $[\text{Cr}(\text{CO})_3]^-$ metal centre insertion into N–H bonds with the second H_2 or HD elimination resulting in the formation of a $\text{C}\equiv\text{N}$ bond in the respective products $[\text{HCN}\cdot\text{Cr}(\text{CO})_3]^-$ for II or $[\text{DCN}\cdot\text{Cr}(\text{CO})_3]^-$ for its D-labelled analogue. Support for this proposal comes from the reactions of the secondary amines III, V, VII, VIII with $[\text{Cr}(\text{CO})_3]^-$. In all cases product ions indicative of only H_2 elimination were identified. From the D-labelled analogue of III, viz. $(\text{CD}_3)_2\text{NH}$, this was shown to involve HD elimination, consistent with a metal carbonylate ion

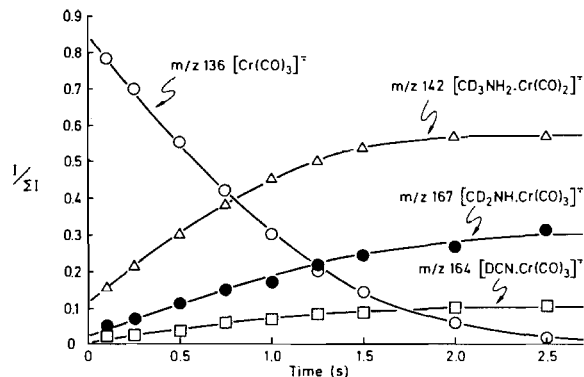


Fig. 1. Temporal variations of ion abundances for the reactions of $[\text{Cr}(\text{CO})_3]^-$ with CD_3NH_2 . ^{52}Cr isotopes considered. Corrected to account for side reactions between $[\text{Cr}(\text{CO})_3]^-$ and $\text{Cr}(\text{CO})_6$ to give $[\text{Cr}_2(\text{CO})_x]^-$ with $x = 5-8$ at long trapping times [7, 18]. $I/\Sigma I$ = Ion abundance/sum of product-ion abundances.

insertion into the N–H rather than the polar C–N bond with the production of an imine metal anionic complex via an hydrido-metal intermediate [6]. It is of significance that in separate experiments $[\text{Cr}(\text{CO})_3]^-$ was shown to react with CH_3CN and CD_3CN to give the products $[\text{CN}\cdot\text{Cr}(\text{CO})_3]^-$ as well as $[\text{CH}_3\text{CN}\cdot\text{Cr}(\text{CO})_2]^-$ and $[\text{CD}_3\text{CN}\cdot\text{Cr}(\text{CO})_2]^-$, with CH_3 elimination and decarbonylation, rather than insertion into the polar $\text{C}\equiv\text{N}$ bond, proceeding at comparable rates for the $\text{CH}_3\text{CN}/[\text{Cr}(\text{CO})_3]^-$ reaction. Also, whereas the secondary amines V and VII only react with $[\text{Cr}(\text{CO})_3]^-$ to eliminate H_2 , diethylether gives as its principal ionic reaction product with $[\text{Cr}(\text{CO})_3]^-$ an apparent alkoxy-metal bonded species $[\text{C}_2\text{H}_5\text{O}\cdot\text{Cr}(\text{CO})_3]^-$ [18].

It is significant too that no reaction was detected between $[\text{Cr}(\text{CO})_3]^-$ and trimethylamine VI. This is consistent with the mechanism proposed for H_2 elimination from these secondary and primary amines requiring the presence of at least one N–H bond for the insertion reaction to proceed via a hydrido-metal intermediate. At this juncture it is thought that steric constraints preclude the formation of a decarbonylated product of the type $[\text{amine}\cdot\text{Cr}(\text{CO})_2]^-$ for VI whereas for the reaction of $[\text{Cr}(\text{CO})_3]^-$ with IX the single reaction product detected was $[\text{C}_5\text{H}_5\text{N}\cdot\text{Cr}(\text{CO})_2]^-$. The reaction of $[\text{Cr}(\text{CO})_3]^-$ with triethylamine gave low abundances of product ions identified as $[(\text{C}_2\text{H}_5)_3\text{N}\cdot\text{Cr}(\text{CO})_3 - \text{H}_2]^-$ and $[(\text{C}_2\text{H}_5)_3\text{N}\cdot\text{Cr}(\text{CO})_3 - \text{H}_2 - \text{C}_2\text{H}_5]^-$ which suggests initial insertion of $[\text{Cr}(\text{CO})_3]^-$ into a C–N bond leading to these products via a tertiary amide intermediate. It is of interest also to note some similarities in $[\text{Cr}(\text{CO})_3]^-$ /amine reactions with those previously observed between Co^+ and amines [19].

The only metal carbonylate ion/amine reaction detected between the 17- and 15-electron species

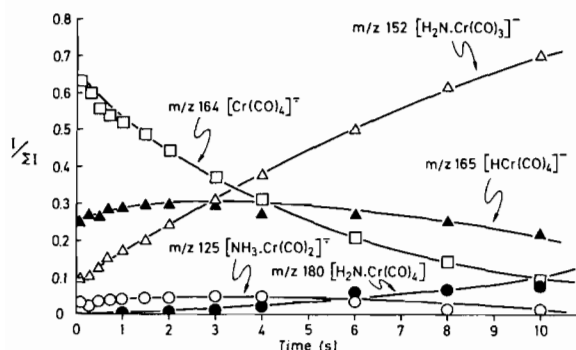


Fig. 2. Temporal variations of ion abundances for the reactions of $[\text{Cr}(\text{CO})_4]^-$ with NH_3 . ^{52}Cr isotopes considered. $I/\Sigma I$ = Ion abundance/sum of product-ion abundances.

$[\text{Cr}(\text{CO})_5]^-$, $[\text{Cr}(\text{CO})_4]^-$ and **I–IX** was that given by NH_3 and $[\text{Cr}(\text{CO})_4]^-$ which yielded the products indicated in the time plot, Fig. 2. Amongst these the species $[\text{HCr}(\text{CO})_4]^-$ is of particular interest and its identification supportive of the proposed implication of Cr–H bonding in mechanisms involving metal insertion into N–H bonds in a reaction channel leading to H_2 elimination.

Acknowledgements

Partial support of this work by the Australian Research Grants Scheme is acknowledged and Dr. J. H. J. Dawson is thanked for helpful discussion.

References

- 1 C. L. Johlman, R. L. White and C. L. Wilkins, *Mass Spectrom. Rev.*, **2**, 389 (1983).
- 2 D. A. Laude, C. L. Johlman, R. S. Brown, D. A. Weil and C. L. Wilkins, *Mass Spectrom. Rev.*, **5**, 107 (1986).
- 3 A. G. Marshall, *Acc. Chem. Res.*, **18**, 316 (1985).
- 4 N. M. M. Nibbering, 'Specialist Periodical Reports, Mass Spectrometry', Vol. 8, (Senior Reporter, M. E. Rose), Royal Society of Chemistry, London, 1985, p. 141.
- 5 I. K. Gregor and M. Guilhaus, *Mass Spectrom. Rev.*, **3**, 39 (1984).
- 6 I. K. Gregor, *J. Organomet. Chem.*, **329**, 201 (1987).
- 7 R. C. Dunbar, J. F. Ennever and J. P. Fackler, *Inorg. Chem.*, **12**, 2734 (1973).
- 8 S. Pignataro, *Chim. Ind. (Milan)*, **57**, 25 (1975).
- 9 R. E. Winters and R. W. Kiser, *J. Chem. Phys.*, **44**, 1964 (1966).
- 10 R. N. Compton and J. A. D. Stockdale, *Int. J. Mass Spectrom. Ion Phys.*, **22**, 47 (1976).
- 11 M. R. Blake, J. L. Garnett, I. K. Gregor and S. B. Wild, *J. Organomet. Chem.*, **178**, C37 (1979).
- 12 M. R. Blake, J. L. Garnett, I. K. Gregor and S. B. Wild, *Org. Mass Spectrom.*, **13**, 20 (1978).
- 13 M. R. Blake, J. L. Garnett, I. K. Gregor and S. B. Wild, *Org. Mass Spectrom.*, **15**, 369 (1980).
- 14 S. W. McElvany and J. Allison, *Organometallics*, **5**, 416 (1986).
- 15 S. W. McElvany and J. Allison, *Organometallics*, **5**, 1219 (1986).
- 16 M. Allemann, H.-P. Kellerhals and K.-P. Wanczek, *Int. J. Mass Spectrom. Ion Proc.*, **46**, 139 (1983).
- 17 G. Klass, M. Allemann, P. Bischofburger and H.-P. Kellerhals, 'Application Note II', Spectrospin AG, Fallanden, Switzerland, November, 1983.
- 18 I. K. Gregor, unpublished results.
- 19 B. D. Radccki and J. Allison, *J. Am. Chem. Soc.*, **106**, 946 (1984).