Inorganica Chimica Acta, *101* (1985) 147–150

Molybdenum-95 NMR Chemical Shifts of some Molybdenum Carbonylate Anions[≠]

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Received August 17, 1984

Abstract

Molybdenum-95 NMR chemical shifts are reported for a range of molybdenum(0) carbonylate anions of the type $[Mo(CO)_5X]^-$ formed by warming dimethylsulfoxide solutions of molybdenum hexacarbonyl and alkali metal hydroxide, halide and pseudohalides. The chemical shift values extend over a thousand ppm and reflect the importance of ligand field strength, polarizability and electronegativity factors in determining the Mo-95 chemical shifts; the 'normal halogen dependence' is confirmed for these d^6 species. The decreasing shielding effects of the coordinated anions in the $[Mo(CO)_5X]^-$ complexes is in the order $H^- > CN^- > I^- > \mathit{N}CO^- > \mathit{N}CS^- > \mathit{N}CSe^- > Br^- > N_3^- > \mathit{N}O_2^- > Cl^- > \mathit{O}_2CH^- > \mathit{O}_2N^- > \mathit{O}CH_3^- > F^-$.

Introduction

Since the pioneering work of Hieber and coworkers over twenty-five years ago [2] numerous methods for the generation of carbonylate anions have been developed [3]. Metal carbonyls will, for example, undergo thermal or photochemical substitution of one or more carbonyl groups with the anions of simple salts (halides and pseudohalides) to form the corresponding carbonylate anions in polar solvents. The existence of more than one product [4], unexpected products [5], and ambidentate pseudohalogen bonding modes [6] have been noted, for example, with group 6B metal hexacarbonyls. Considerable attention has been paid the known variety of carbonylate anions in their role as versatile synthetic reagents [3, 7]. Recent interest in the reaction of group 6B metal hexacarbonyls with alkali metal hydroxides in protic solvents, originally studied by Hieber *et al.* [8], stems from involvement of the carbonylate anion products in the homogeneous catalysis of the water-gas shift reaction (WGSR) [9–11].

Several studies in recent years have established Mo-95 spectroscopy as a sensitive probe of electronic effects in diamagnetic molybdenum compounds; for instance, chemical shifts range from −445 to −2200 ppm for Mo(0) complexes[†]. Our recent identification [13] in DMSO solution of unstable complexes of the type $[Mo(CO)_5L]^-$ and $[Mo(CO)_4(L–L)]^-$ (L = Cl, Br, dithiocarbamato; L–L = dithiocarbamato, xanthato and phosphorodithioato) led us to investigate by Mo-95 NMR spectroscopy the present more extensive series of carbonylate anions. The chemical shift data for the products of the reaction of alkali metal salts with $Mo(CO)_6$ in DMSO solution demonstrates the sensitivity and usefulness of Mo-95 NMR spectroscopy in identifying unstable species in reaction mixtures.

Experimental

Mo-95 spectra were recorded by using the pulsed FT NMR technique with a Bruker WH-400 NMR spectrometer on naturally abundant (15.7 atom%) samples. The spectra were obtained at ambient temperature with a probe specifically tuned for Mo-95 at 26.08 MHz using a field strength of 9.3956 T. The external standard was 2 M K_2MoO_4 at pH 11. The resolution was typically 3 Hz (0.12 ppm) per data point. Samples were prepared *in situ* from dinitrogen saturated DMSO at 60–65 °C and syringed into septum-sealed NMR tubes. The concentration as well as the reaction time (1/2 hr to 5 hrs) varied from sample to sample. Usually a 1:1 molar ratio of alkali metal salt and $Mo(CO)_6$ were mixed in DMSO and warmed at 60–65 °C until a change in colour and/or IR spectra indicated appreciable conversion of $Mo(CO)_6$ to the metallate anion.

Solution IR spectra were obtained on diluted samples subsequent to NMR analyses using matched KBr or NaCl sealed cells on a Perkin-Elmer 180 grating IR spectrophotometer.

[≠] Presented in part at the 67th Canadian Chemical Conference, Chemical Institute of Canada, Montreal, Que., June 3-6, 1984.

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[†] For recent publications concerning Mo-95 NMR studies on Mo(0) compounds see ref. 12.

0020-1693/85/$3.30

TABLE I. Mo-95 NMR Chemical Shifts for some Molybdenum Carbonylate Anions[a].

Compound Reacted[b] with $Mo(CO)_6$	$\delta(^{95}Mo)$ (ppm)	Compound Reacted[b] with $Mo(CO)_6$	$\delta(^{95}Mo)$ (ppm)
NaOH	−1980 (−1940, −943)[c]	NaN_3	−1523 (−1604)[c]
KOH	−1980 (−1544, −1495)[c]	$NaNO_2$	−1514 (−1435)[c]
$NaBH_4$	−1940		
NaCN	−1887	$[Et_4N]Cl$ NaO_2CH	−1513 −1495
$[Bu_4N]I$	−1660[d]		(−1941, −1847)[c]
KCNO	−1604	KCNSe	−1438 (−1887, −1867, −1735, −1603, −1590, −1452, −1360)[c]
KCNS	−1596	$NaOCH_3$[e]	−1435 (−1784, −1859)[c]
	(−1370)[c]	$NaBF_4$	−947
$[Et_4N]Br$	−1540[d]	KF	−943

[a] Spectra obtained at 26.08 MHz (9.3956T), referenced to aqueous 2 M K_2MoO_4 at pH 11. Typical parameters: 1000 transients, 90° pulse, 95 μsec pulse width, spectral width of 10 kHz. [b] DMSO solutions of *ca.* 0.1 mol dm^{-3} prepared *in situ* under dinitrogen; IR spectra in carbonyl region also obtained for these reaction mixtures. [c] Minor peaks are given in parenthesis. [d] Previously obtained, see refs. [13] and [16]. [e] In THF.

Results and Discussion

Molybdenum(0) carbonylate anions of the type $[Mo(CO)_5X]^-$ are formed by warming (60–65 °C) DMSO solutions of molybdenum hexacarbonyl and alkali metal hydroxide, halide and pseudohalides. Since most of the products were previously isolated from other solvents, their generation *in situ* for observation by Mo-95 NMR spectroscopy was simply followed by the observation of characteristic IR bands in the carbonyl region. As found previously for $[Mo(CO)_5L]^-$ complexes [13], a three band pattern with a strong band near 1920 cm^{-1} in virtually all of the spectra seemed diagnostic of the presence of a pentacarbonyl species. The presence of more complex spectra (three peaks are expected for pentacarbonyl complexes) indicated the existence of either a tetracarbonyl species and/or at least one other pentacarbonyl compound. In those cases it is clear that the Mo-95 NMR spectrum is more characteristic and helpful in identifying those species that are present in the reaction mixtures.

Table I lists the Mo-95 NMR chemical shifts and their tentative assignments for the carbonylate anions formed in this study. For ambidentate ligands, the assigned mode of coordination is indicated in the text by italizing the donor atom. The reactions of $Mo(CO)_6$ with BH_4^-, CN^-, NCO^-, BF_4^- and the halide ions led to only one peak in the respective Mo-95 NMR spectrum, so the assignments to the one species present are reasonably unambiguous. Our formulation of $[Mo_2(CO)_{10}H]^-$ (with BH_4^-) [14], $[Mo(CO)_5\mathit{C}N]^-$ [4, 15] and $[Mo(CO)_5\mathit{N}CO]^-$ [5] as products is consistent with earlier IR spectral studies that characterized these anions. The $\delta(^{95}Mo)$ value for $[Mo(CO)_5F]^-$ at −943 ppm extends the known halide series [13, 16] and confirms the 'normal halogen dependence' [17] for these d^6 species. In contrast, an inverse correlation is observed for some d^0 Mo(VI) complexes such as the MoE_4^{2-} anions (E = O, S, Se) [18] and for some series of Ti(IV) [19] and V(V) [20] halides. The reaction of $Mo(CO)_6$ with $NaBF_4$ most likely leads to the formation of $[Mo(CO)_5F]^-$ since the chemical shift value is very similar to that obtained for the single species observed for the KF case.

Several of the reactions of alkali metal salts with $Mo(CO)_6$ gave rise to Mo-95 NMR spectra with two or more peaks. With assistance from previous synthetic and IR spectral studies of these systems we have tentatively assigned structures to the species present in solution. For instance, the two peaks observed for the NaN_3 reaction with $Mo(CO)_6$ can be assigned (Fig. 1) to $[Mo(CO)_5N_3]^-$ (major peak at −1523 ppm) and to $[Mo(CO)_5\mathit{N}CO]^-$ (minor peak at −1604 ppm, as found for the KNCO reaction itself).

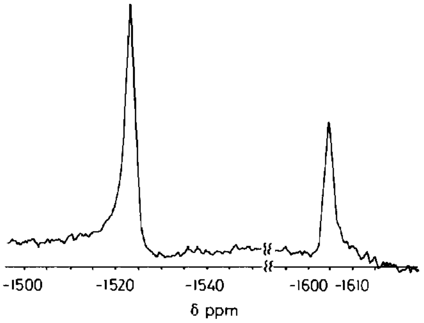

Fig. 1. Mo-95 NMR spectrum of a DMSO solution of products formed in the reaction of NaN_3 with $Mo(CO)_6$. Chemical shifts, $\delta(^{95}Mo)$, are relative to 2 M K_2MoO_4 as external standard. Parameters were as follows: 90° pulse, 95 μsec pulse width, 4386 Hz sweep width, resolution of 0.535 Hz per point, line broadening of 10.0 Hz, 647 transients. The scale is 10 ppm per division.

IR spectroscopy had previously been used to establish that the isocyanate group is formed by attack of the azide ion on a carbonyl group [5].

Previous IR studies [6] indicated that the thiocyanate ion reacts with $Mo(CO)_6$ to form N-bonded mononuclear and NCS-bridged binuclear species. The major peak at −1596 ppm in the Mo-95 NMR spectrum in this case may therefore be assigned to the $[Mo(CO)_5NCS]^-$ ion. The minor peak at −1370 ppm may be assigned to either the NCS^- bridged binuclear species $[Mo_2(CO)_{10}(NCS)]^-$ or to the *S*CN-bonded mononuclear isomer.

The Mo-95 NMR spectrum of the DMSO reaction mixture of KSeCN and $Mo(CO)_6$ shows a large number of peaks, indicating extensive decomposition. The peak at −1887 ppm is undoubtedly due to the formation of $[Mo(CO)_5CN]^-$. The peaks at −1590, −1438 and −1360 are tentatively assigned to *N*CSe, *Se*CN, and μ-NCSe species, respectively.

The Mo-95 NMR spectrum of the THF solution obtained by warming NaOMe with $Mo(CO)_6$ showed two strong peaks at −1859 and −1435 ppm. The former is undoubtedly unreacted $Mo(CO)_6$ [12(c)], whilst the latter is assigned to the $[Mo(CO)_5OMe]^-$ ion. A weak broad peak at −1784 ppm is unassigned.

The IR spectrum of the reaction mixture of $NaNO_2$ with $Mo(CO)_6$ is complex, and suggestive of the presence of both penta- and tetracarbonyl species (Peaks occur at 2050(w), 1970(s), 1925(vs, b) and 1850(s) in the carbonyl region). The equal intensity peaks in the Mo-95 NMR spectrum are tentatively assigned to $[Mo(CO)_5NO_2]^-$ (−1514 ppm is in the range observed for other N-bonded anions) and to $[Mo(CO)_4O_2N]^-$ (a downfield shift to −1435 ppm is consistent with a bidentate nitrito group). Although a nitrosylation reaction occurs with $Fe(CO)_5$ [21], it seems unlikely under our reaction conditions [22]. Consideration of the π-acceptor character of NO and the resonance positions for molybdenum species containing NO groups [12a] appears to rule out the assignment of the −1435 ppm peak to a nitrosylation product.

Earlier workers [12(b)] reported a value of −1937 ppm for the Mo-95 chemical shift of $[Mo_2(CO)_{10}H]^-$ in THF solution. We find that the reaction of $NaBH_4$ with $Mo(CO)_6$ in warm DMSO solution leads (with vigorous evolution of a gas) to the formation of one product; *i.e.*, the single peak at −1940 ppm in the Mo-95 NMR spectrum is assigned to the H-bridged binuclear species. The $[Mo_2(CO)_{10}H]^-$ complex is also identified in the reaction mixtures of hydroxyl and formate ions with $Mo(CO)_6$. In the latter case, the major peak at −1495 ppm in the Mo-95 NMR spectrum of the DMSO solution can be attributed to the formato complex $[Mo(CO)_5O_2CH]^-$ [9–11]. A minor peak at −1847 ppm in that case is attributable to $Mo(CO)_6$. It is interesting to note that the mononuclear hydrido species $[HMo(CO)_5]^-$ (*vide infra*) is not formed with the formate ion under our reaction conditions. Recent work [9–11] suggested that the $[HMo(CO)_5]^-$ ion was the primary product of the decarboxylation of the $[Mo(CO)_5O_2CH]^-$ ion. The reaction of OH^- with $Mo(CO)_6$ in warm DMSO solution leads to a number of products that can be identified by Mo-95 NMR spectroscopy. The assignment of a major peak at −1980 ppm is consistent with earlier reports [9–11] that $[HMo(CO)_5]^-$ is a dominant product. Peaks due to $[Mo_2(CO)_{10}H]^-$ (minor peak at −1940 ppm) and $[Mo(CO)_5O_2CH]^-$ (minor peak at −1495 ppm) are also observed, as are other minor peaks. Further Mo-95 NMR investigation of the reactions of $Mo(CO)_6$ with OH^- and O_2CH^- are underway because of the implication of the reaction products in the WGSR [9–11].

In conclusion, this work shows the utility of Mo-95 NMR spectroscopy in identifying reactive species in solution. The chemical shifts observed for a range of carbonylate anions reflect the importance of ligand field strength, polarizability and electronegativity factors in determining the Mo-95 chemical shifts. The decreasing shielding effect of the coordinated anions in the $[Mo(CO)_5X]^-$ complexes is in the order $H^- > CN^- > I^- > NCO^- > NCS^- > NCSe^- > Br^- > N_3^- > NO_2^- > Cl^- > O_2CH^- > O_2N^- > OCH_3^- > F^-$.

Acknowledgements

The authors thank N.S.E.R.C. of Canada for an operating grant (E.C.A.) and Imperial Oil (Canada) for a University Research Grant (J.M.). The Mo-95 NMR Spectra were obtained at the Southwestern Ontario NMR Centre funded by a Major Installation Grant from N.S.E.R.C. of Canada.

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