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STUDIES ON MAIN GROUP METAL-TRANSITION-METAL BONDED COMPOUNDS 7. A ^{199}HG NMR STUDY OF SOME GROUP VI TRANSITION-METAL MERCURY COMPOUNDS

M.J. Albright and J.P. Oliver*

Department of Chemistry
Wayne State University
Detroit, Michigan 48202

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SUMMARY

A ^{199}Hg Fourier Transform NMR study has been carried out on $Hg[M(CO)_3C_5H_5]_2$ (M = Cr, Mo, W), $[C_5H_5(CO)_3M]HgCl$, and $[C_5H_5(CO)_3W]HgX$ (X = Cl, Br, I, SCN). The ^{199}Hg chemical shifts are -80, +115, and -348 ppm respectively for the symmetrical compounds, -542, -617, and -997 ppm for the chlorides and -1200, -1529 and -924 ppm for the Br, I, SCN-tungsten derivatives respectively. The ^{199}Hg chemical shifts for several other mercury derivatives are reported for comparison. All chemical shifts are relative to 90% $HgMe_2$/10% internal lock C_6F_6, with positive values indicating decreasing shielding. The $J_{^{199}Hg-^{183}W}$ values are 151, 706, 690, 630 and 684 Hz for the symmetrical compound and the Cl, Br, I and SCN derivatives respectively. The factors which may influence these parameters are discussed briefly.

INTRODUCTION

We have had a continuing interest in the structure, bonding, and spectroscopic properties of compounds which contain main group metal to transition metal bonds and have explored the properties of several of these systems making use of both X-ray diffraction techniques[1-5] and ^{1}H NMR spectroscopy.[1,2,6] With the development of Fourier transform NMR spectroscopy[7], these studies have now been extended to include direct observation of one of the metal atoms involved in the bond, ^{199}Hg.

This nucleus has been studied by FT NMR techniques.[8] Additional information also is available from other studies which include both direct observation and observation indirectly by double resonance techniques,[9,15] thus, providing some base for comparison.

EXPERIMENTAL

The symmetrical transition metal compounds, $[Cp(CO)_3M]_2Hg$, where M = Cr, Mo, W were prepared by the procedure outlined in King and Stone.[10] The unsymmetrical compounds, $Cp(CO)_3MHgX$, where X = SCN, Cl, Br, Cl for M = W,, and X = Cl for M = Cr, Mo, were prepared by a simple exchange process between the symmetrical transition metal complex and the appropriate mercuric halide.[11]

The melting point of the $[Cp(CO)_3W]_2Hg$ was higher than the reported value (this work 240°, reported[11] 215°), but the melting points of the corresponding halides that were prepared from this compound were in good agreement with the report values[11] (chloride 202°(205°), bromide 208°(207°), iodide 156°(156°)). The carbon-hydrogen analysis of the $[Cp(CO)_3W]_2Hg$ was 22.17% C and 1.35% H (theoretical 22.07% C and 1.16% H).[12]

The ^{199}Hg NMR spectra were obtained on a JEOL 4H-100 modified with a PFT-100 pulse Fourier transform package and an EC-100 data system. The ^1H mode used a fixed frequency deuterium lock at 15.287830 MHz and the ^1H frequency was 99.5650 MHz which was varied according to the deuterium solvent used for lock. The ^1H chemical shifts and T_1 values for the protons on the C_5H_5 rings were recorded and are collected in Table I.

The ^{199}Hg frequency was 17.8 MHz with a fixed frequency fluorine lock at 93.653631 MHz. External fluorine lock was used for the transition metal-mercury compounds. A capillary of hexafluorobenzene was held concentrically in the sample tube by a teflon plug with a bore hole. No corrections were made for bulk susceptibility. The ^{199}Hg T_1 was determined for $[C_5H_5(CO)_3W]HgBr$ in DMSO-d_6 to be approximately 0.1 sec. With this information available all subsequent studies on ^{199}Hg were made using an 11 μsec pulse corresponding to

TABLE I

Proton Chemical Shifts and T_1 Relaxation Times for $Cp(CO)_3WHgX$ Derivatives

X	($CDCl_3$)	(DMSO)	T_1 (DMSO)
	ppm[a]		sec[b]
$Cp(CO)_3W$	5.51[c]	5.76	4.1
Cl	5.60	5.83	4.0
Br	5.60	5.83	4.5
I	5.59	5.83	4.7

a) ppm downfield from TMS

b) ±0.2 sec

c) reported as 5.54 ppm, reference 11

a 30° flip angle with a repetition rate of 1 sec. All other experimental conditions are given in Table II. Proton noise decoupling was employed only on the alkyl mercury derivatives.

RESULTS AND DISCUSSION

The ^{199}Hg chemical shifts and coupling constants, $^1J_{^{199}Hg-^{183}W}$, for the compounds investigated are collected in Table II. The chemical shift values are referenced to 90% $HgMe_2$/10% C_6F_6 which makes them reasonably compatible with the literature data. The precision of measurement is better than 1 ppm, however the known variation in δ as a function of concentration, temperature, and solvent makes any small variations meaningless. The total observed range for the chemical shifts of the transition metal-mercury derivatives studied is ~1600 ppm which is divided into two groups. The first group is represented by the symmetrical compounds which range from +115 to -348 ppm with the shielding increasing in the order Mo < Cr < W. These observations, along with those cited elsewhere,[8,9]

(continued on p. 104)

TABLE II

^{199}Hg Spectral Parameters, Experimental Conditions, and Related Information for Transition Metal-Mercury Derivatives and Selected Organomercury Species

Compound	δ ppm^a	$^1J_{^{199}Hg-X}$ (Hz)	$^1K^b$ $(10^{20}cm^{-3})$	Solvent	Conc [M]	Temp °C	λ_{max} (nm)^c	$\nu_{C=O}$ cm^{-1}
$HgMe_2$	0^e	692^d	1280	10% C_6F_6	---	26°	---	---
$HgEt_2$	-294^e	648	1200	80% C_6D_6/ 20% C_4F_6	2.49	---	---	---
MeHgCl	-848^f	1665^g	---	---	---	---	---	---
MeHgBr	-911^f	1625^g	---	---	---	---	---	---
MeHgI	-1143^f	1543^g	---	---	---	---	---	---
$MeHgNO_3$	-2532^h	1800^i	3340	70% HNO_3	4M	25°	---	---
$Hg[Mo(CO)_3(C_5H_5)]_2$	+115	---	---	DMSO	0.0324	40°	364	2001 (1906)
$Hg[Cr(CO)_3(C_5H_5)]_2$	-80	---	---	DMSO	saturated	40°	---	---
$Hg[W(CO)_3(C_5H_5)]_2$	-348	151	1790	DMSO	saturated	40°	353.5	1997 (1883)
$[Cr(CO)_3(C_5H_5)]HgCl$	-542	---	---	DMSO	0.418	30°	---	---
$[Mo(CO)_3(C_5H_5)]HgCl$	-617	---	---	DMSO	0.336	30°	262	2024 (1936)
$[W(CO)_3(C_5H_5)]HgCl$	-997	706	7980	DMSO	0.213	40°	261	2020 (1926)
$[W(CO)_3(C_5H_5)]HgBr$	-1200	690	7800	DMSO	0.296	30°	271	2016 (1922)
$[W(CO)_3(C_5H_5)]HgSCN$	-924	684	7740	DMSO	0.301	30°	283.5	2017 (1924)
$[W(CO)_3(C_5H_5)]HgI$	-1529	630	7120	DMSO	0.274	30°	292.5	2012 (1918)

[a] ppm reported from $HgMe_2$; positive values indicate downfield shift.

[b] $^{1}K = \frac{2\pi}{h}\frac{J_{AB}}{\gamma_A \gamma_B}\ 10^{20}\mathrm{cm}^{-3}$, see "Nuclear Magnetic Resonance, 1, viii (1972), Chemical Society, Burlington House, London for a discussion of the reduced coupling constant and references therein.

[c] See reference 11.

[d] F.J. Weigert and J.P. Roberts, Inorg. Chem. 1973, 12, 313.

[e] This work.

[f] See reference 9e.

[g] See reference 8c.

[h] See reference 8a; The UV and IR data are representative of those reported for a number of mercury derivatives reported. The first IR frequence reported is the highest energy carbonyl band while the frequency in ( ) is the lowest energy carbonyl band.

[i] F.A.L. Anet and J.L. Sudmeier, J. Magn. Resonance 1969, 1, 124.

indicated that mercury salts which are more polar or which undergo dissociation are more shielded (more negative δ values) while the symmetrical covalently bound systems are deshielded (more positive δ values). The values observed for this series of compounds lie downfield in a very narrow region giving rise to the suggestion that they all are relatively covalent, nonpolar systems, despite the significant changes in the central metal atoms bound to Hg. The second series of compounds is that of the unsymmetrically substituted derivatives.

The chemical shifts for these derivatives are given in Table II and range from -542 ppm to -1529 ppm. The chloride derivatives for the Cr, Mo and W compounds show shielding increasing in the order Cr < Mo < W which is the order of increasing atomic number of the metal atom. The trend for the symmetrical species has Cr and Mo reversed. One possible explanation for this is that the symmetrical Cr compound is less covalent because of unfavorable overlap of the orbitals of the small Cr atom with the large orbitals associated with the Hg atom. This slight polarization would shield the Hg and may be sufficient to move this symmetrical Cr compound upfield of the analogous Mo compound. One experimental indication that the Cr-Hg bond is different than those involving the heavier metals is that decomposition of this derivative occurs much more rapidly for the Cr compound than for the other two symmetrical compounds. Furthermore, for the series of unsymmetrical derivatives, $[Cp(CO)_3W]HgX$ (X = SCN, Cl, Br, I), the mercury becomes more shielded in proceeding from the SCN to I derivative. This trend is parallel to that observed in the methylmercuric halides and the inorganic mercury halides.

Although it is clear that one cannot account for the chemical shift variations on a theoretical basis, it is of interest to determine if they may be correlated with other observable parameters such as IR frequencies or UV transitions. As noted in Table II, there is a rough correlation between the UV transitions and the chemical shifts for the unsymmetrical compounds but it is not of sufficient quality to be useful for predicting chemical shift values.

The variations of the coupling between the directly bonded nuclei, Hg and W, also parallels that observed in other systems. The value observed in the symmetrical species, $^{1}J_{^{199}Hg-^{183}W}$ = 151 Hz, is about one fourth of the values observed in the unsymmetrical derivatives which decrease in the order Cl> Br> SCN >I with the corresponding values of 706, 690, 684 and 630 Hz. This parallels the values observed for the alkyl mercuric halides with decreasing absolute values of the coupling constants with decreasing electronegativity of the substituent. For both the $(R_3P)_2HgX_2$[13] and the $(X_3P)W(CO)_5$[14] systems the respective one bond couplings, $^1J_{^{199}Hg-^{31}P}$ and $^1J_{^{183}W-^{31}P}$, decrease in the same order with decreasing electronegativity.

It has been suggested that the Fermi contact interaction dominates the coupling in this type system,[15] however, it is quite clear that simple change in s orbital contributions cannot account for the magnitude of the changes observed. In the related organomercury systems, Henneike[16] has attempted to calculate J_{Hg-H} in a variety of compounds using the extended Huckel approach. His observations are that the magnitude of the coupling constant is very sensitive to the charge separation in the molecule and that the major portion of the change going from the symmetric to unsymmetric compounds can be accounted for in this way and that the Fermi contact term does indeed predominate even though other factors may enter in. Coupling also has been discussed by Brown, et al[17] who concluded that $^1J_{C-Hg}$ is dependent on both the C-Hg bond strength and on the s orbital contribution to the C-Hg bond. This is essentially the same observation as that of Henneike. Similar trends also have been observed for other nuclei. For example Mitchell, et al[18] have reported roughly the same trends for ^{207}Pb NMR parameters and have attributed much of the variation to the charge separation. Again one may attempt to correlate changes in ^1J values with bond strength as reflected in carbonyl stretching frequencies or with UV transitions which are assumed to represent the ΔE values in the Fermi contact interaction. Examination of Table II shows only a rough correlation with ν_{CO} occuring for the unsymmetrical species while the symmetrical derivative falls completely out of line. Comparison with the UV transitions, however, shows a surprisingly good correlation with the Hg-W coupling constant suggesting that the reported UV transitions are a fair representation for the ΔE_{av}. Further one may note that there is little difference among the various unsymmetrical derivatives--the major difference is between these species and the symmetrical compounds. Also, both the symmetrical and unsymmetrical species have been proven to be monomeric by molecular weight studies in dichloromethane and nonconductive in nitro benzene even though they are related by an exchange mechanism.[11] The major difference, therefore, must arise as a result of the changes in the mercury-halide bond and the subsequent effects on the Hg-W bond.

The conclusion, ultimately reached, is that the Fermi contact mechanism predominates, that increasing charge on Hg causes an increase in coupling because of orbital contraction, and that the sign of the one bond coupling constants are the same for C, P and W since these behave in a parallel manner.

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