

Journal of Organometallic Chemistry, 377 (1989) 85–88
 Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
 JOM 20201

¹⁹⁹Hg NMR of mercury-bridged transition metal clusters

Sharad Hajela, Edward Rosenberg ^{*},

Department of Chemistry, California State University, Northridge, CA 91330 (U.S.A.)

Roberto Gobetto, Luciano Milone ^{*} and Domenico Osella

*Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica, dei Materiali, Universita di Torino,
 Via Giuria 7-9, I 10125 Torino (Italy)*

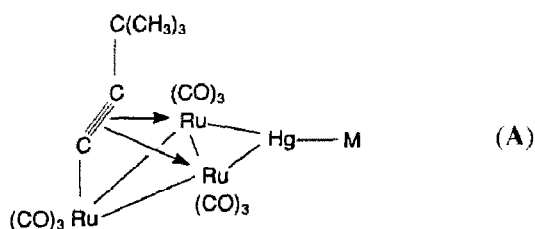
(Received May 23rd, 1989)

Abstract

The ¹⁹⁹Hg NMR data for the series of complexes $(\mu_3\text{-}\eta^2\text{-C}_2\text{tBu})(\text{CO})_9\text{Ru}_3(\mu\text{-Hg})\text{X}$ (X = Cl, Br, I) and $(\mu_3\text{-}\eta^2\text{-C}_2\text{tBu})\text{Ru}(\mu_3\text{-Hg})\text{M}$ (M = MoC₅H₅(CO)₃, Mn(CO)₅, Re(CO)₅, FeC₅H₅(CO)₂, RuC₅H₅(CO)₂, Co(CO)₄) and the phosphine derivative $\text{P}(\text{C}_6\text{H}_5)_3(\text{CO})_8(\mu_3\text{-}\eta^2\text{-C}_2\text{tBu})\text{Ru}_3(\mu_3\text{-Hg})\text{MoC}_5\text{H}_5(\text{CO})_3$ are reported. The ¹⁹⁹Hg chemical shifts vary over a relatively large range for the series (~ 1500 ppm) with some of the mixed transition series showing the largest downfield shifts (relative to Hg(CH₃)₂) reported to date. The data are discussed in light of previously reported ¹⁹⁹Hg shifts for related complexes and although there is no correlation between Hg–M bond lengths in this isostructural series some general correlations of the chemical shifts with the expected polarity of the Hg–M bond based on the reactivity of the complexes and the qualitative theory of ¹⁹⁹Hg chemical shifts can be made. A very large variation in line width is also observed which correlates well with the expected efficiency of quadrupole relaxation mechanisms.

Introduction

We have been studying the chemistry of complexes containing the electron deficient three center two electron mercury-transition metal bond [1–6]. In particular, we have focused our studies on the readily synthesized series $(\mu_3\text{-}\eta^2\text{-C}_2\text{tBu})(\text{CO})_9\text{Ru}_3(\mu\text{-Hg})\text{X}$ (X = Cl, Br, I) [1,6] and $(\mu_3\text{-}\eta^2\text{-C}_2\text{tBu})(\text{CO})_9\text{Ru}_3(\mu_3\text{Hg})\text{M}$ (M = Mo(C₅H₅)(CO)₃ [2,6], Mn(CO)₅ [6], Re(CO)₅ [6], FeC₅H₅(CO)₂ [6], Ru(C₅H₅)(CO)₂ [6], Co(CO)₄ [6], see structure A). The halide derivative (X = Br) contains a four coordinate mercury atom in the solid state resulting from dimerization via halogen bridges but is monomeric and three coordinate in solution [1]. In



the mixed transition metal mercury clusters of the series Ru_3HgM , the mercury atom is three coordinate in the solid state and in solution [2]. In light of the recent reports of the ^{199}Hg chemical shifts on the two coordinate mercury transition metal complexes $[(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\text{M}]_2\text{Hg}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and $(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\text{MHgX}$ ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{Cl}, \text{Br}, \text{I}$) [7,8] we thought it would be useful to obtain ^{199}Hg NMR data on the three coordinate series referred to above for comparison. In addition, the series Ru_3HgM contains a wider range of Hg–M bonds than has previously been studied and provides a possible means of evaluating changes in ^{199}Hg chemical shifts as function of the type of transition metal moiety bound to mercury (via normal two center-two electron bonds) in an isostructural series of compounds. We report here the chemical shift and line width data for the compounds represented by structure **A** along with a discussion of the observed trends and a comparison with previously published data.

Results and discussion

The ^{199}Hg chemical shifts measured at 48.2 MHz in saturated CDCl_3 along with the $\Delta\nu_{\frac{1}{2}}$ data and values from previous studies of related compounds are shown in Table 1. The most obvious trend in the data is that the chemical shifts for the three coordinate mercury atoms bound to transition metals (compounds **14–20**) span a range significantly to lower field (+50 to +748 ppm) compared with the two coordinate mercury transition metal complexes **1–3** whose shifts range from –348 to +329 ppm [7,8]. It has been proposed by several authors [7,8,9] that increasing downfield shifts for mercury reflect increasing covalent character in the bond between mercury and the directly bound atoms. This apparently arises from a decreased average excitation energy on mercury increasing the contribution by the paramagnetic term of the screening tensor. One would expect that the more delocalized 3-center-2-electron bonds would be more covalent in nature than the 2-center-2-electron analogs. The chemical shifts reported for **14–17** are the most downfield reported to date by 100–200 ppm [9].

This overall trend is also observed to a lesser degree when comparing the halide complexes **4–9** where the chemical shift range of –1529 to –574 ppm is to higher field when compared to the three coordinate halide complexes **11–13** with a chemical shift range of –736 to –203 ppm. This proposed increase in covalent bond character for the three center-two-electron mercury-transition metal bond is entirely consistent with their chemical properties. These compounds show a higher thermal stability towards dissociation and much slower redistribution reactions (i.e., $2\text{M}_3\text{HgX} \rightleftharpoons \text{Hg}(\text{M}_3)_2 + \text{HgX}_2$) and in general have lower equilibrium constants for this reaction [3–5]. The observed chemical shift for the two-coordinate mercury cobalt complex **10** (+329 ppm) is in the middle of the range observed for the three

Table 1

¹⁹⁹Hg NMR data for transition metal mercury derivatives ^a

No.	Compound	Shift (ppm)	$\Delta\nu_{\frac{1}{2}}$ (Hz)
1	[C ₅ H ₅ (CO) ₃ Cr] ₂ Hg	-80 ^c	
2	[C ₅ H ₅ (CO) ₃ Mo] ₂ Hg	+236 ^b (+115°)	50 ^b
3	[C ₅ H ₅ (CO) ₃ W] ₂ Hg	-348 ^c	
4	C ₅ H ₅ (CO) ₃ MoHgCl	-574 ^b	50 ^b
5	C ₅ H ₅ (CO) ₃ MoHgBr	-759 ^b	45 ^b
6	C ₅ H ₅ (CO) ₃ MoHgI	-1107 ^b	35 ^b
7	C ₅ H ₅ (CO) ₃ WHgCl	-997 ^c	
8	C ₅ H ₅ (CO) ₃ WHgBr	-1200 ^c	
9	C ₅ H ₅ (CO) ₃ WHgI	-1529 ^c	
10	[(CO) ₄ Co] ₂ Hg	+329	79
11	(μ_3 - η^2 -C ₂ ¹ Bu)(CO) ₉ Ru ₃ (μ -Hg)Cl	-203.2	82
12	(μ_3 - η^2 -C ₂ ¹ Bu)(CO) ₉ Ru ₃ (μ -Hg)Br	-371.5	92
13	(μ_3 - η^2 -C ₂ ¹ Bu)(CO) ₉ Ru ₃ (μ -Hg)I	-736	227
14	(μ_3 - η^2 -C ₂ ¹ Bu)(CO) ₉ Ru ₃ (μ_3 -Hg)Mo(CO) ₃ C ₅ H ₅	+748	62
15	P(C ₆ H ₅) ₃ (μ_3 - η^2 -C ₂ ¹ Bu)(CO) ₈ Ru ₃ (μ_3 -Hg)Mo(CO) ₃ C ₅ H ₅	+700.1 (<i>J</i> ^{31P-¹⁹⁹Hg}) 66 Hz)	119
16	(μ_3 - η^2 -C ₂ ¹ Bu)(CO) ₉ Ru ₃ (μ_3 -Hg)Mn(CO) ₅	+662.9	96
17	(μ_3 - η^2 -C ₂ ¹ Bu)(CO) ₉ Ru ₃ (μ_3 -Hg)Re(CO) ₅	+676.1	345
18	(μ_3 - η^2 -C ₂ ¹ Bu)(CO) ₉ Ru ₃ (μ_3 -Hg)FeC ₅ H ₅ (CO) ₂	+60.6	36
19	(μ_3 - η^2 -C ₂ ¹ Bu)(CO) ₉ Ru ₃ (μ_3 -Hg)RuC ₅ H ₅ (CO) ₂	+329.9	90
20	(μ_3 - η^2 -C ₂ ¹ Bu)(CO) ₉ Ru ₃ (μ_3 -Hg)Co(CO) ₄	+50.2	200

^a All shifts reported downfield positive with respect to neat (CH₃)₂Hg in a concentric 4 mm tube on saturated CDCl₃ solutions at +30°C. ^b From reference 7 in DMSO-*d*₁. ^c From reference 8 in CDCl₃.

coordinate complexes **14–22**. This is a relatively low field chemical shift compared with the two coordinate-mercury molybdenum complex **2** (+236 ppm, in the same solvent) and is thought to reflect the Hg-transition metal bond length, 2.50 Å [10], distinctly shorter than the two center two electron bonds between mercury and molybdenum which lie in range of 2.6–2.7 Å [8].

It is interesting to note that the differences in chemical shift between analogous Cl, Br and I complexes in the three series **4–6**, **7–9** and **11–13** are remarkably similar with Δ ppm Br–Cl being 185, 203 and 168 ppm, respectively, and Δ ppm I–Br being 348, 329 and 365, respectively.

The effect of phosphine substitution on the ¹⁹⁹Hg chemical shift in **15** relative to **14** is in the same direction and of similar magnitude to that observed in the series L(CO)₂(C₅H₅)MoHgX [8] (L = CO, phosphine, X = halide); a small three bond ¹⁹⁹Hg–³¹P coupling constant is observed (Table 1).

There is a considerable variation in the linewidth of the ¹⁹⁹Hg resonances reported here (35–45 Hz) compared with those previously reported (35–50 Hz) for complexes **2** and **4–6**. Linewidths for mercury resonances should be strongly dependent on scalar coupling relaxation to directly bound quadrupolar nuclei [9]. These contributions to *T*₂ would in turn depend directly on the magnitude of the quadrupolar coupling constant with mercury and inversely with the difference in the Larmor frequency between mercury and the coupled quadrupolar nucleus [9]. Indeed, there is a crude correlation of the linewidth with the resonance frequency in the results reported here with **13**, **17** and **20** showing the broadest lines while **18**

shows the narrowest. Naturally any quantitative correlation would require knowledge of the quadrupolar coupling constants.

Experimental

The complexes shown in Table 1 were all synthesized by published literature procedures [1–6]. The purity of the compounds was checked by ^1H NMR and infrared spectroscopy before measuring the ^{199}Hg NMR shifts.

Spectra were measured on a Jeol GX270/89 spectrometer at 48.2 MHz using a pulse repetition rate of 0.7 sec and a 90° pulse (10 μsec). Solutions were all in the concentration range of 0.07 to 0.1 M in CDCl_3 . A 4 mm concentric capillary containing neat dimethyl mercury in the 10 mm tubes was used as an external standard for all chemical shifts measured at 28°C .

Acknowledgements

We gratefully acknowledge the National Science Foundation (CHE8711549E.R.), the NATO Science Program (R.G. 0705/87; E.R. and L.M.) and Consiglio Nazionale delle Ricerche (L.M.) for support of this research.

References

- 1 E. Rosenberg, K. King, R. Fahmy, A. Tiripicchio and M. Camellini-Tiripicchio, *J. Am. Chem. Soc.*, 102 (1980) 3626.
- 2 E. Rosenberg, K.I. Hardcastle, S.E. Ermer, K. King and A. Tiripicchio, *Inorg. Chem.*, 22 (1983) 1339.
- 3 E. Rosenberg, D. Ryckman, R.W. Gellert and I. Hsu, *Inorg. Chem.*, 25 (1986) 194.
- 4 E. Rosenberg, J. Wang and R.W. Gellert, *Organometallics*, 7 (1988) 1093.
- 5 E. Rosenberg, B. Novak and S. Hajela, *Organometallics*, 8 (1989) 468.
- 6 (a) E. Rosenberg, R. Gobetto, S. Hajela, M. Day, R. Muftikian and K.I. Hardcastle, manuscript in preparation; (b) E. Rosenberg and B. Novak, *Inorg. Synth.*, 26 (1989) in press.
- 7 M.J. Albright and J.P. Oliver, *J. Organomet. Chem.*, 172 (1979) 99.
- 8 M.M. Kubicki, R. Kergoat, J. LeGall, J.E. Guerschuis, J. Douglade and R. Mercier, *Aus. J. Chem.*, 35 (1982) 1543.
- 9 J.L. Dechter, In, 1985, Ed. S.J. Lippard (Ed.), *Prog. Inorg. Chem.*, Wiley, New York, 1985, p. 393.
- 10 G.M. Sheldrick and R.N.F. Simpson, *J. Chem. Soc. A.* (1968) 1005.