

[Hg₃{HC(PPh₂)₃}(OAc)_n](O₃SCF₃)_m, n + m = 6: COMPLEXES CONTAINING AN ACIDIC CARBON

MARIA LUSSE and PAUL PERINGER*

*Institut für Anorganische und Analytische Chemie der Universität Innsbruck, Innrain 52a,
 A-6020 Innsbruck (Austria)*

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Summary

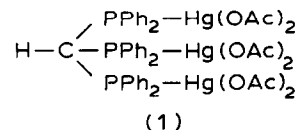
The reaction of the ligand HC(PPh₂)₃ (tripod) with Hg(OAc)₂ and [Hg(Me₂SO)₆](O₃SCF₃)₂ in various stoichiometries but with a tripod/Hg ratio of 1/3 gives complexes which are carbon acids. The acidity of the methine group is attributed to the cumulative electron-withdrawing effect of the [PPh₂Hg^{II}] groups. The new complexes were characterized by ³¹P and ¹⁹⁹Hg NMR spectroscopy. The ¹⁹⁹Hg, ¹⁹⁹Hg couplings have values between 1050 and 1710 Hz.

Introduction

The ligand HC(PPh₂)₃ (tripod) has been shown to stabilize triangular arrays of metal atoms. Because of the close proximity of the metal centers the complexes formed are of interest with respect to their potential catalytic activity and the analogy they offer to reactions on metal surfaces [1–9].

Results and discussion

The reaction of tripod with 3 equiv. of Hg(OAc)₂ in methanol results in the coordination of one mercury atom to each PPh₂ group (1).



This is evidenced by the size of the one bond mercury–phosphorus coupling constant [10] (Table 1) as well as by the multiplicity of the ¹⁹⁹Hg{¹H} NMR pattern of the isotopomer containing one ¹⁹⁹Hg atom (abundance 34.9%).

Remarkably, no coupling ³J(¹⁹⁹Hg, ¹H) could be detected in contrast to the

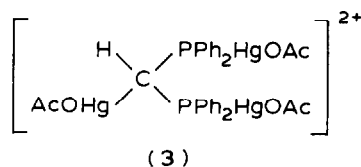
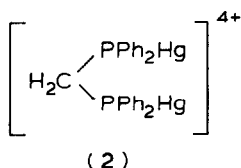
TABLE 1

NMR PARAMETERS FOR $[\text{Hg}_3(\text{tripod})(\text{OAc})_n(\text{O}_3\text{SCF}_3)_m]^a$

<i>n</i>	<i>m</i>	$\delta(^{31}\text{P})$	$\delta(^{199}\text{Hg})$	$^1J(^{199}\text{Hg}, ^{31}\text{P})$	$^2J(^{31}\text{P}, ^{31}\text{P})$	$^3J(^{199}\text{Hg}, ^{31}\text{P})$	$J(^{199}\text{Hg}, ^{199}\text{Hg})$	<i>T</i> (K)
6	0	33.6	979	8759	31	215	1050	273
4	2	34.0		8361	36	242	1200	
3	3	37.1	919	8838	37	241	1710	

^a 0.1 mmol/ml MeOH, 300 K unless otherwise stated, chemical shifts in ppm to high frequency of 85% H_3PO_4 or aqueous $\text{Hg}(\text{ClO}_4)_2$ solution (2 mmol HgO/cm^3 60% HClO_4), coupling constants in Hz.

related compounds **2** and **3** exhibiting couplings of 156 and 300 Hz [11,12], respectively.



The absence of this coupling seems to be caused by fast intermolecular proton exchange of the methine group on the NMR time scale or by dissociation of the methine proton, and indicates that the methine group is acidic. The acidity is thought to be due to the cumulative electron-withdrawing effect of the 3 $[\text{Hg}(\text{PPh}_2)(\text{OAc})_2]$ groups. The electron-withdrawing effect of $[\text{PPh}_2\text{Hg}^{\text{II}}]$ groups has recently been revealed by the observation of facile mercuration of the methylene group of dppm ($\text{CH}_2(\text{PPh}_2)_2$) upon treatment with 3 equiv. of Hg^{II} [12].

No mercuration of the methine group of **1** is observed, even upon addition of a fourth equivalent of $\text{Hg}(\text{OAc})_2$.

From NMR spectra of the isotopomer of **1** containing two ^{199}Hg atoms (abundance 7.1%) the coupling constant between the ^{199}Hg nuclei can be determined. Figures 1a and b show the experimental and computer simulated $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1**, involving a value of $J(^{199}\text{Hg}, ^{199}\text{Hg})$ of 1050 Hz. Very few data are available on Hg–Hg couplings [13–16]. A value of 1061 Hz was reported [14] for $[\text{Hg}_2(\mu\text{-dppm})_2](\text{O}_3\text{SCF}_3)_2$, the most closely related compound for which data are available. The coupling increases markedly as the OAc groups in **1** are sequentially replaced by O_3SCF_3 i.e. with increasing *m* complexes of the stoichiometry $[\text{Hg}_3(\text{tripod})(\text{OAc})_n](\text{O}_3\text{SCF}_3)_m$, $n + m = 6$ (Table 1). The presence of the non-coordinating anion O_3SCF_3 is assumed to increase the electron-withdrawing effect of the $[\text{PPh}_2\text{Hg}^{\text{II}}]$ group, giving rise to an increase in the acidity of the methine carbon–hydrogen linkage and in the carbanionoid character of the complexes.

Compound **1** slowly decomposes in solution with formation of $(\text{HgOAc})_2$. Cooling of methanolic solutions of **1** gave a white solid, but microanalytical results were unsatisfactory presumably because of contamination by $(\text{HgOAc})_2$. The rate of decomposition of the compounds $[\text{Hg}_3(\text{tripod})(\text{OAc})_n](\text{O}_3\text{SCF}_3)_m$ increases with *m*. No NMR parameters could be obtained, for $[\text{Hg}_3(\text{tripod})](\text{O}_3\text{SCF}_3)_6$ (**2**), even at low temperature.

The decomposition of **2** involves the fission of a P–C bond of tripod. In Me_2SO as solvent, $[\text{Hg}_2(\mu\text{-dppm})_2](\text{O}_3\text{SCF}_3)_4$ [14] and $[\text{Hg}(\eta^1\text{-dppm})_2](\text{O}_3\text{SCF}_3)_2$ [17] were

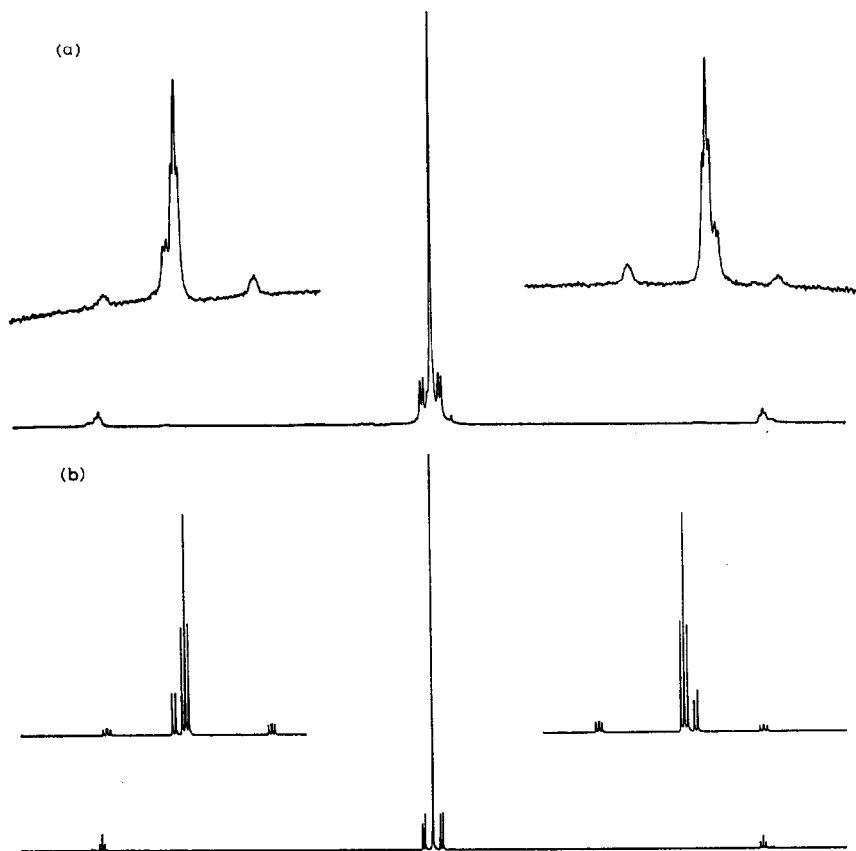


Fig. 1. (a) Experimental $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1**. (b) Weighted superposition of the computer simulated $^{31}\text{P}\{^1\text{H}\}$ spectra of the isotomers of **1** containing 0, 1 or 2 ^{199}Hg atoms.

identified as decomposition products. In MeOH as solvent $[\text{Hg}(\text{PPh}_2\text{OMe})]^{2+}$ was identified, indicating the fate of the PPh_2 group cleaved off.

Experimental

NMR spectra were recorded on a Bruker WP-80 spectrometer operating in the FT mode. The program PANIC (Bruker) was used, on a Bruker Aspect 2000 computer, for the simulation of the spectra and for the refinement of the parameters by iteration. The compound $[\text{Hg}(\text{Me}_2\text{SO})_6](\text{O}_3\text{SCF}_3)_2$ was obtained as previously described [18]. The other reagents were commercially available.

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