Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

MERCURY(II) DERIVATIVES OF ACETYLACETONE

FLAVIO BONATI AND GIOVANNI MINGHETTI
CNR Laboratory Istituto di Chimica Generale dell' Università, via Venezian 21, 20133 Milan (Italy)

(Received October 21st, 1969)

SUMMARY

The non-existence of mercury(II) acetylacetonate, described in the literature, is reported. Preparations and properties of novel types of acetylacetone derivatives, $(CH_3CO)_2C(HgX)_2$ (X=Cl, Br) and $CH_3CO\text{–}C(HgCl)\text{=}C(OHgCl)\text{–}CH_3$, are described.

INTRODUCTION

Our interest in the acetylacetone derivatives of mercury was aroused by the fact that while C-bonded acetylacetone derivatives of many metals are known[1,2,3] no such derivatives had been described in the case of mercury, an element which gives metal–carbon bonds very easily. Also, mercury(II) acetylacetonate, $(C_5H_7O_2)_2$-Hg, although repeatedly reported by several workers[4-8], had never been analyzed. In addition, related compounds, such as mercury(II) dipivaloylmethanate[6], basic mercury(II) acetylacetonate[9], and an adduct between mercury(II) chloride and acetylacetone[10,11] have been described in the literature, but there is only a passing mention[12] of other very interesting compounds, namely $(CH_3CO_2Hg)_2C(COCH_3)_2$, $HgC(COR)_2$ and $(XHg)_2C(COR)_2$, where X is acetate, propionate, benzoate, or β-diketonate.

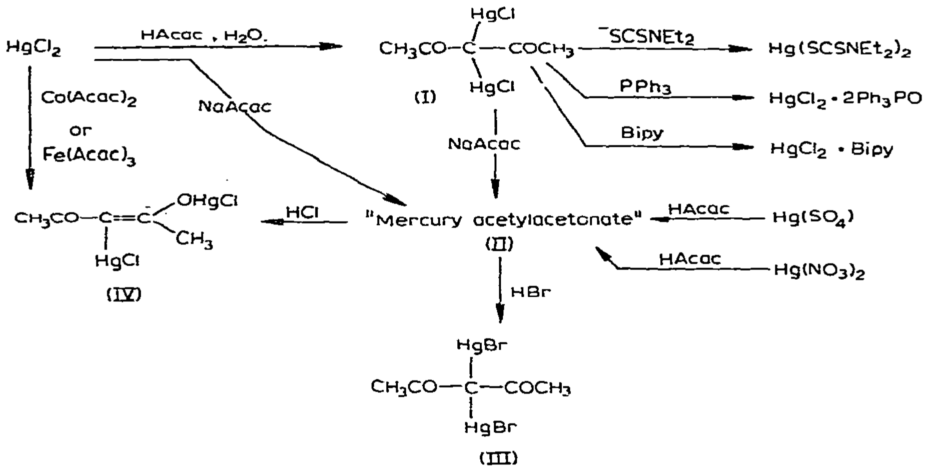
We now describe some unusual derivatives of acetylacetone obtained during our unsuccessful efforts to obtain mercury(II) acetylacetonate.

RESULTS AND DISCUSSION

When the reaction of mercury(II) chloride with acetylacetone was carried out in aqueous solution at room temperature, a white precipitate was immediately obtained and the solution became strongly acidic, in accordance with the following equation:

$$2\,HgCl_2 + (CH_3CO)_2CH_2 \rightarrow \underset{(I)}{(ClHg)_2C(COCH_3)_2} + 2\,HCl$$

The compound, (I), was identified by complete elemental analysis. The infrared spectrum did not show any absorption in the 1500–1600 cm^{-1} region, where all the "normally" coordinated acetylacetonates [*e.g.* cobalt(III), copper(II) or zinc(II)



derivative] absorb[13]; however, a very strong and broad CO stretching frequency was observed at 1685 cm^{-1}, a value which should be compared with 1680 in acetophenone and with 1695 and 1653 in $K[Pt(Acac)_2Cl]$[14], plus bands at 1430 and 1360 typical of a $COCH_3$ group. Carbon–mercury stretching frequencies were found at around 500 cm^{-1}, while there was no evidence supporting the presence of a Hg–O vibration, expected between 400 and 500 cm^{-1} according to Gibson[2]. The value found (343 cm^{-1}) for the Hg–Cl stretching frequency was lower than the value reported for $HgCl_2$ (375 cm^{-1}), but is in the range required for organomercury(II) chlorides (314–350 cm^{-1})[15], and lies on the side of the more electronegative organic groups. The observed value ruled out a structure involving a –Hg–Hg–Cl linkage, since ν(Hg–Cl) is reported at 261 cm^{-1} in the infrared spectrum of Hg_2Cl_2; it also ruled out a structure with four-coordinated mercury, *e.g.* one due to the presence of $>C=O\rightarrow Hg$ bonds: a substantial lowering[16] of both ν(Hg–Cl) and ν(C=O) would be required. According to the requirement of structure (I), no C–H stretching frequency was observed at values higher than 3000 cm^{-1}, and no C–H out-of-plane vibration was observed in the 764–800 cm^{-1} region, thus ruling out any structure with a hydrogen atom in the 3-position of the 2,4-pentanedione moiety.

The ^1H NMR spectrum showed only one, sharp signal at τ 7.71 ppm, *cf.* τ 7.75 ppm observed for the methyl groups of the two C-bonded acetylacetone ligands in $K[Pt(Acac)_2Cl]$ and the value of *ca.* τ 8.0 for the "normal" acetylacetonates[1,17]. While in the platinum derivative a coupling constant, $J(^{195}Pt–CH_3)$ 10 Hz, was observed, no satellite bands due to ^{199}Hg (relative abundance 16.86%, spin $\frac{1}{2}$) were observed, thereby excluding the presence of a $-CH_2HgCl$ group.

On the basis of the preceding data, structure (I) is proposed. The compound is rather unstable, especially in solution. It reacts with neutral or charged ligands such as triphenylphosphine, 2,2′-bipyridine, or sodium diethyldithiocarbamate to yield $HgCl_2\cdot 2Ph_3PO$, $HgCl_2\cdot$Bipy or $Hg(SCSNEt_2)_2$ respectively; exchange reactions were not successful, *e.g.* silver acetate yielded silver chloride as the only isolable product.

Similar reactions were attempted with mercury(II) bromide, cyanide, or acetate, and with mercury(I) chloride without success.

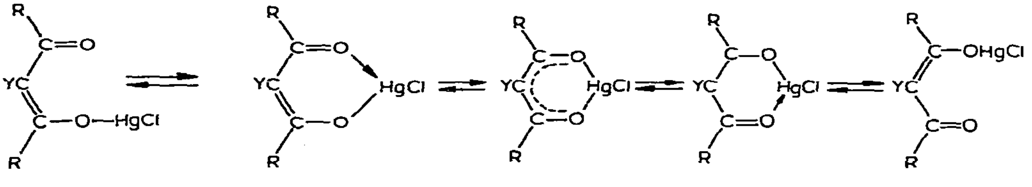
The preparation[4,5,8] of mercury(II) acetylacetonate was attempted using saturated aqueous mercury chloride along with aqueous sodium acetylacetonate, or either an aqueous suspension of mercury(II) sulphate or an aqueous solution of mercury(II) nitrate along with acetylacetone. In all cases an amorphous white powder, (II), was obtained, which decomposed gradually on heating. The infrared spectrum of all the products was the same in all cases, including that of the reaction product from $(ClHg)_2C(COCH_3)_2$, (I), and aqueous sodium acetylacetonate. However, the analytical data were not reproducible even for preparations carried out in apparently the same experimental conditions, and in no case did the complete analysis indicate a composition such as $Hg(C_5H_7O_2)_2$ or as $Hg_2(C_5H_7O_2)_2(C_5H_6O_2)$. The infrared spectrum showed multiple bands in the 1600–1700 cm^{-1} region and in the low frequency region. It is therefore likely that what has generally been considered as mercury(II) acetylacetonate is either a mixture of variable proportions of insoluble C- and O-bonded complex acetylacetone derivatives, or an oligomeric molecule in which C- and O-bonded, mono- and bi-valent acetylacetone residues are linked by mercury atoms.

In an effort to clarify the nature of the so-called mercury(II) acetylacetonate, (II), some of its reactions were studied. Aqueous hydrobromic acid gave $(BrHg)_2C(COCH_3)_2$, (III), hydrochloric acid gave an isomer of (I), $CH_3COC(HgCl)=C(OHgCl)CH_3$, (IV), hydroiodic acid gave a mixture of products which were not separated, and the non-complexing perchloric acid did not react. The rather different reaction products obtained by decomposition with HCl and HBr showed that the conclusions about the structure of (II) reached solely on the basis of chemical reactions should be regarded with suspicion. Other evidence could not be assembled because of the marked insolubility of compound (II).

Infrared, NMR and other data on compound (III) pointed to its similarity with compound (I); in particular, the IR spectrum was the same as for compound (I), except that the metal halide vibration at 343, ν(Hg–Cl), was shifted to 245 cm^{-1}, ν(Hg–Br).

The structure of compound (IV) must be quite different from that of compound (I). The infrared spectrum showed absorption typical of ν(Hg–Cl), ν(Hg–C), and strong bands at 1596 and 1669 cm^{-1}. The latter absorption is in the region typical of unsaturated ketones, and the former may be assigned to ν(C=C) lowered by conjugation. Also the low frequency region showed more bands here than in compound (I), suggesting a less symmetric structure: ν(Hg–Cl) could be observed at 331, and, perhaps, at 309, while a medium intensity band was found at 497 cm^{-1}.

The NMR spectrum at 33° showed only one signal and no evidence for satellite bands. The spectrum is compatible with structure (IV), required by the infrared spectrum, only if fast exchange is present:



(IV) : $R = CH_3$, $Y = HgCl$ (V) : $R = (CH_3)_3C$, $Y = H$

where mercury could be three- or, more likely, four-coordinate if dimerization or solvation takes place. Our NMR spectrum should be compared with that reported[6] for mercury(II) dipivaloylmethanate, (V), for which the infrared spectrum showed bands at 1680 and 1630 cm^{-1}: only one CH_3 and one CH signal were detected.

It is noteworthy that compound (IV) could be obtained independently from $M(Acac)_n$, where M = Co or Cu and $n = 2$, or M = Fe and $n = 3$, in aqueous suspension at room temperature. The failure of the reaction when the kinetically stable $Cr(Acac)_3$ or $Co(Acac)_3$ were employed suggests that the reaction goes through an intermediate stage where the acetylacetonate ring is not chelated to the metal.

EXPERIMENTAL

Decomposition ranges were determined on a Leitz Heiztischmikroskop and are uncorrected. Molecular weights were measured on a Mechrolab Osmometer in acetone at 37°, and are likely to be unreliable because the compounds attack metals. Infrared spectra were recorded on Perkin–Elmer 137 and 621 instruments. ^1H NMR data were recorded on a Perkin–Elmer R-10 machine operating at 60.0 Mc. and 33°, using tetramethylsilane as internal standard. C, H and N analyses were carried out in our Microanalytical Laboratory, O analyses at that of the University of Padua, while Hg and halogen content were determined as HgS and silver halide, respectively, in our laboratory.

3,3-*Bis(chloromercury)*-2,4-*pentadione*, (*I*)[18]

To a solution of mercury(II) chloride (6.9 g, 0.0254 mole) in water (100 ml) acetylacetone was added dropwise (5.08 g, 5.2 ml, 0.0508 mole). The addition was carried out under stirring during 30 min at room temperature. The initially neutral solution became soon acid (pH 2). The resulting white precipitate was filtered off, washed with the minimum amount of cold water, and dried under reduced pressure (2.138 g), m.p. 152–154° (dec.). The compound was recrystallized unchanged (IR and m.p.) from acetone, methyl ethyl ketone, ethyl acetate, methanol; it could be extracted unchanged with cold chloroform, wherein it is sparingly soluble. (Found: C, 10.35; H, 1.24; Cl, 13.22; Hg, 69.70; O, 5.99; Mol.wt., 282, 295. $C_5H_6Cl_2Hg_2O_2$ calcd.: C, 10.50; H, 1.05; Cl, 12.47; Hg, 70.30; O, 5.60%; mol.wt., 570.) The compound is not an electrolyte in acetone or acetonitrile; the resistance of an aqueous solution is (concentration in 10^4 mole/liter): 0.163 (9.04), 0.148 (8.5), 0.139 (6.8), 0.172 (3.4), 0.285 (1.7) 10^5 ohm, and, by extrapolation, $\Lambda_0 = 235$ ohm$^{-1}\cdot$cm$^2\cdot$mole^{-1}. NMR spectrum: only one signal at τ 7.71 ppm (C_3D_6O). Infrared spectrum (nujol and C_4Cl_6 mull): 302w, 343s, 364vw, 458w, 521vs, 566s, 636w, 667s, 714w, 842s, 968s, 1007w, 1021s, 1044s, 1148s, br, 1187s, 1254vw, 1350sh, 1360s, br, 1397s, 1410s, 1425s, 1450s, 1640sh, 1685s, br, 1765w, 2830w, 2895s, 2930s, 2980w, 3240vw, 3340vw cm^{-1}.

The compound reacted with aqueous silver acetate yielding silver chloride in nearly quantitative yield. It reacted with aqueous sodium diethyldithiocarbamate (4 equivs.) yielding yellow mercury(II) diethyldithiocarbamate in 73% yield, identified by comparison with a known sample. The compound (0.9902 g) and 2,2′-bipyridine (0.272 g) in acetone (50 ml) gave a white precipitate, isolated by filtration and washed with acetone (0.6794 g), $HgCl_2\cdot$Bipy. (Found: C, 28.13; H, 1.79; N, 6.51. $C_{10}H_8Cl_2HgN_2$ calcd.: C, 28.10; H, 1.87; N, 6.55%). An acetone solution of (I) (1.191 g in 50 ml) was treated with an acetone (50 ml) solution of triphenylphosphine (1.098 g) The white precipitate was filtered and extracted with boiling methanol in a Soxhlet apparatus; on cooling the extract gave crystals of bis(triphenylphosphine oxide)dichloromercury, identified by analysis (Found: C, 52.54; H, 3.70. $C_{36}H_{30}Cl_2HgO_2P_2$ calcd.: C, 52.25; H, 3.63%.) and by comparison with the reaction product from $HgCl_2$ and Ph_3P in boiling ethanol[19].

"*Mercury acetylacetonate*", (*II*)

(1). *From* $HgCl_2$. To a saturated aqueous solution of mercury(II) chloride (13.8 g in 200 ml) acetylacetone (10.4 ml), previously neutralized with dilute NaOH, was added. The solution was allowed to stand for *ca.* 1 h, then the white precipitate was collected, washed with water, and acetone, and dried *in vacuo* (14.62 g), m.p. (dec.) >220°. Although the infrared spectrum of the powder was the same in all the preparations carried out, the analytical data were not constant. (Found: C, 26.75, 25.1, 24.93, 25.73; H, 3.05, 2.79, 2.75, 3.19; O, not determined, 8.87, 9.98, 14.41. $C_{10}H_{14}HgO_4$ calcd.: C, 30.1; H, 3.51; O, 16.05. $C_{15}H_{20}Hg_2O_6$ calcd.: C, 25.80; H, 2.86; O, 13.77%.) The compound is insoluble in organic solvents. Infrared spectrum: 291 m, 367m, 397m, 436w, 513s, 525s, 562vw, 627w, 671w, 704w, 718w, 795vw, 845s, 915s, 967w, 1010s, 1030m, 1150s, 1170sh, 1240s,br, 1340s, 1375s,br, 1460s,br, 1630s,br, 1680s,br, 1730sh cm^{-1}.

(2). *From* $HgSO_4$. Acetylacetone (2.0 ml) was added to a suspension of mercury(II) sulphate (2.016 g) in water (5.0 ml). The yellow basic sulphate dissolved and a white product precipitated slowly. The white precipitate was filtered off, washed with water and acetone, and dried under vacuum (1.230 g). (Found: C, 29.18; H, 3.39; O, 15.33%.) The infrared spectrum was the same as that of the samples obtained in (1).

(3). *From* $Hg(NO_3)_2$. The reaction product was obtained similarly and had the same infrared spectrum of the powder obtained in (1). (Found: C, 26.46; H, 3.02; N, 0.0%.)

(4). *From* (*I*). Reaction of (I) with stoichiometric amounts of aqueous sodium acetylacetonate under stirring gave after 3 h, a white precipitate which was filtered and washed several times with acetone. After drying *in vacuo* it was identified as (II) through its infrared spectrum. (Found: C, 25.64; H, 2.78; Hg, 59.0%.) A product with the same infrared spectrum was obtained from (I) and excess pyridine after 1 month.

3,3-*Bis*(*bromomercury*)-2,4-*pentadione*, (*III*)

Product (II), obtained as in (1), (2.334 g) was suspended in water (10 ml), treated with hydrobromic acid (35 ml, 0.2 *N*) overnight under stirring. The white product was filtered off, washed with the minimum amount of cold water and crystallized from acetone to yield the compound, m.p. 125–135° (1.31 g), purified by crystallization from acetone three times. (Found: C, 8.81; H, 0.93; Br, 23.65; mol.wt., 348. $C_5H_6Br_2Hg_2O_2$ calcd.: C, 9.11; H, 0.91; Br, 24.25%; mol.wt., 659.) The compound is soluble in acetone, alcohol, ethyl acetate, tetrahydrofuran, slightly soluble in water and chloroform, insoluble in benzene, ether, and hydrocarbons. At 20° the conductivity of a 10^{-3} *M* solution in acetone was found to be 3.39 $ohm^{-1} \cdot cm^2 \cdot mole^{-1}$. The NMR spectrum showed only one signal at τ 7.72 ppm (hexadeuteroacetone solution). The NMR spectrum is a good test for the homogeneity of the sample: sometimes a second and less intense signal is found at τ 6.7 ppm, while there is no remarkable difference in the infrared spectrum.

Chloromercury(*II*) 3-(*chloromercury*)-4-*oxo*-2-*penten*-2-*olate*, (*IV*)

(1). Product (II), obtained as in (1), (2.083 g) was suspended in water (10 ml) and treated with hydrochloric acid (60 ml, 0.1 *N*). The acid suspension was stirred overnight, the white product was filtered off, washed with a minimum amount of cold water and crystallized from acetone to yield the compound, m.p. (dec.) 200–210°. (Found: C, 10.46; H, 1.09; O, 5.28; mol.wt., 455. $C_5H_6Cl_2Hg_2O_2$ calcd.: C, 10.50; H, 1.05; O, 5.60%.) The compound is soluble in acetone and alcohol, very slightly soluble in water and chloroform, insoluble in benzene, ether and hydrocarbons. It is not an electrolyte in acetone. The NMR spectrum in C_3D_6O showed only one signal at τ 7.64 ppm; sometimes, additional small signals are found at τ 6.75, 6.67 ppm and are assigned to inhomogeneity of the sample. Infrared spectrum: 272vw, 309m, 331s, 367m, 498m, 566m, 612m, 670w, 800w, 856w, 990m, 1015m, 1183s, 1213s, 1258w, 1357s, 1375m, 1450s,br, 1596s,br, 1652sh, 1669s cm^{-1}.

(2). Cobalt(II) acetylacetonate (0.087 g, 0.00338 mole) was added to an aqueous solution of mercury(II) chloride (3.67 g; 50 ml), and the mixture was stirred overnight The slightly acidic suspension (pH 4–5) was filtered and a pale-pink precipitate (2.02 g) was collected, and crystallized from acetone to yield the product, white, m.p. (dec.) 200–210° (Found: C, 10.64; H, 1.08; O, 6.50%.) with the same infrared spectrum as that of the sample above described.

While $Co(Acac)_3$ and $Cr(Acac)_3$ do not react under the above conditions, the same product can be obtained, although with more difficulty, from $Cu(Acac)_2$, and $Fe(Acac)_3$.

ACKNOWLEDGEMENT

Financial support by the Consiglio Nazionale delle Ricerche is gratefully acknowledged.

REFERENCES

1 F. Bonati, *Organometal. Chem. Rev.*, 1 (1966) 379.
2 D. Gibson, *Coord. Chem. Rev.*, 4 (1969) 225.
3 J. P. Fackler, Jr., *Progr. Inorg. Chem.*, 7 (1966) 388.
4 G. T. Morgan and H. W. Moss, *J. Chem. Soc.*, 105 (1914) 195.
5 S. Tanatar and E. Kurowsky, *J. Russ. Phys.-Chem. Ges.*, 40 (1908) 580; *Chem. Zentr.*, II (1908) 1096.
6 G. S. Hammond, D. C. Nonhebel and C. S. Wu, *Inorg. Chem.*, 2 (1963) 73.
7 D. C. Nonhebel, *J. Chem. Soc.*, (1963) 738.
8 A. N. Nesmeyanov, A. Z. Rubezhov, L. A. Leites and S. P. Gubin, *J. Organometal. Chem.*, 12 (1968) 187.
9 F. Gach, *Monatsh. Chem.*, (1900) 98.
10 G. B. Marini-Bettolo and L. Paoloni, *Gazz. Chim. Ital.*, 75 (1945) 78.
11 L. Paoloni, *Gazz. Chim. Ital.*, 89 (1959) 2171.
12 T. Keating, M.Sc. Thesis, mentioned in ref. 2.
13 K. Nakamoto, *Infrared Spectra of inorganic and coordination Compounds*, Wiley, London, 1963, p. 216.
14 J. Lewis, R. F. Long and C. Oldham, *J. Chem. Soc.*, (1965) 6740.
15 G. E. Coates and D. Ridley, *J. Chem. Soc.*, (1964) 166.
16 G. B. Deacon and A. J. Canty, *Inorg. Nucl. Chem. Lett.*, 4 (1968) 135.
17 F. Bonati and R. Ugo, *J. Organometal. Chem.*, 11 (1968) 341.
18 F. Bonati and G. Minghetti, *Angew. Chem.*, 80 (1968) 664.
19 R. C. Evans, F. G. Mann, H. S. Peiser and D. Purdie, *J. Chem. Soc.*, (1940) 1219.