IR SPECTRA OF ORGANOPHOSPHINE SUBSTITUTED DERIVATIVES OF (HALOMERCURY)TETRACARBONYLCOBALT

M. VAN RENTERGEM and G. P. VAN DER KELEN*

Laboratory for General and Inorganic Chemistry, University of Gent, Krijgslaan 281, B-9000 Gent (Belgium)

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ABSTRACT

The compounds XHgCo(CO)₃L (X = Cl, Br) form dimeric donor-acceptor complexes of C_{2h} symmetry. The frequencies of the IR-active CO stretching vibrations of a series of compounds {XHgCo(CO)₃L}_n (X = Cl, Br; n = 1, 2) are reported. The tendency towards dimerization decreases in the order L = P(tBu)₃ > P(OMe)₃ > P(OEt)₃ > EtP(OEt)₂ > Et_P(OEt) > Et_P(NEt_2) > PEt_3 > P(nBu)_3 > EtP(NEt_2)_2 > P(NEt_2)_3. The frequency lowering, due to dimerization, increases going from L = P(tBu)₃ to L = P(NEt_2)_3. The force constants of the monomeric compounds XHgCo(CO)₃L (X = Cl, Br) are calculated and compared with those of the dimeric compounds Hg{Co(CO)₃L}₂.

INTRODUCTION

Bis(tetracarbonyl)mercury(II) is known to react with mercury halide HgX_2 (X = Cl, Br), giving the compounds $XHgCo(CO)_4$ in 90% yield [1]. Acetone [1] and ethylacetate [2] are used as solvents. An earlier method [3] uses the reaction of $(CO)_4CoNa$ in THF on an aqueous solution of $HgCl_2$ or $HgBr_2$. Thus far no phosphine-substituted derivatives are known. Moreover, the reported CO stretching frequencies of the parent compounds are not in accordance with each other. Therefore, we transformed our formerly-studied series [4] of compounds $Hg\{Co(CO)_3L\}_2$ into the corresponding series $XHgCo(CO)_3L$ (X = Cl, Br).

Generally, reaction of the phosphine-substituted compounds $Hg\{Co(CO)_{3}L\}_{2}$ with mercury halide HgX_{2} in acetone at room temperature results in a mixture of monomeric and dimeric species $\{XHgCo(CO)_{3}L\}_{n}$ (n = 1, 2). Instead of the two bands expected for the mononuclear compounds $XHgCo(CO)_{3}L$ (Fig. 1A), the lR-spectra of the reaction mixtures showed three separate CO absorption bands (Fig. 1C). The very broad *E*-type band and its highly asymmetric profile led us to suppose that more than one compound was present. Chromatographic separation on an alumina column with acetone resulted in only one species, showing three narrow absorption

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^{*}Author for correspondence.



Fig. 1. IR-spectrum of (A) ClHgCo(CO₃(Et₂N)PEt₂. (B) {ClHgCo(CO)₃(Et₂N)PEt₂}₂, (C) reaction mixture.

bands (Fig. 1B). Molecular weight determinations by the vapor pressure osmometry method pointed to a dimeric structure for this species.

EXPERIMENTAL

Preparation of compounds

Monomeric and dimeric species were found to be in a temperaturedependent equilibrium. At higher temperatures pure monomeric compounds XHgCo(CO)₃L are obtained. Consequently, we improved the method of Conder and Robinson [1] by refluxing the reaction mixture for a few minutes. The compounds XHgCo(CO)₃L (L = CO, PR₃, . .) are very soluble in acetone, fairly soluble in methanol and benzene, but insoluble in n-pentane. Therefore, we have some doubts about the results of Kahn et al. [3], who claimed to have extracted ClHgCo(CO)₄ and BrHgCo(CO)₄ from an aqueous solution with n-hexane. Moreover, the CO stretching frequencies of their compounds, observed in hexadecane solution, differ considerably from those reported by Conder and Robinson [1].

When a saturated solution in acetone is brought upon an alumina column, the phosphine substituted compounds $XHgCo(CO)_3L$ are transformed into

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their dimeric counterparts $\{XHgCo(CO)_3L\}_2$. The dimeric compounds are far less soluble in acetone; spontaneous crystallization from the eluted solution occurred. In some cases the dimers could not be washed through the column with acetone or any other solvent and the dimeric compounds were then obtained by simple recrystallization of the monomeric compounds from methanol/water.

No dimeric compounds $\{XHgCo(CO)_4\}_2$ could be prepared. When a solution of the parent compounds $XHgCo(CO)_4$ was brought upon an alumina column there was spontaneous evolution of CO bubbles. The IR-spectra of the eluted compounds showed only two CO absorption bands instead of the four bands expected for the dimers. Moreover, we failed to transform these new compounds into the starting compounds. Repeated recrystallization of the monomeric compounds $XHgCo(CO)_4$ from methanol/water resulted in the formation of $Hg\{Co(CO)_4\}_3^-$ (absorption bands at 2063, 2041 and 1977 cm⁻¹)¹ rather than $\{XHgCo(CO)_4\}_2$.

Instrumental

Infrared spectra of THF solutions were obtained using a Perkin-Elmer 580 spectrophotometer. Laser Raman spectra could not be recorded because of the high photosensitivity of the compounds. The experimental CO stretching frequencies of the compounds $\{XHgCo(CO)_3L\}_n$ (X = Cl, Br; n = 1, 2) are given in Tables 1 to 4.

Molecular weight determinations were performed with a Knauer vapor pressure osmometer, using tetrahydrofuran as solvent.

STRUCTURE OF THE COMPOUNDS {XHgCo(CO),L},

The monomeric compounds $XHgCo(CO)_{3}L$, characterized by a trigonal bipyramidal arrangement around the central cobalt atom and a linear XHgCoL skeleton, belong to the point group C_{3v} . As pointed out by Conder and Robinson [1], the mercury atom in these compounds may be active as a Lewis acid. On the other hand, the halogen atom has some donor properties, so that the formation of halogen-bridged dimers becomes possible. A similar type of dimerization has been observed in both pure and mixed mercury dihalides [5, 6]. The structure proposed consists of a planar rhombus with a metal carbonyl anion attached to each mercury atom. The molecule belongs to the point group C_{2v} or C_{2h} according to either an eclipsed or staggered conformation of the carbonyl groups (Fig. 2).

The vibrational representation is $2A_1$ (IR + R) + A_2 (R) + B_1 (IR + R) + $2B_2$ (IR + R) in the former and $2A_g$ (R) + B_g (R) + A_u (IR) + $2B_u$ (IR) in the latter case. The IR spectra are consistent with a C_{2h} symmetry.

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TABLE 1

Experimental CO stretching frequencies (cm^{-1}) and force constants (mdyn A^{-1}) of the compounds ClHgCo(CO)₃L in THF solution

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L = CO	$\nu_1(A_1)$ 2090_0	ν ₂ (A,) 2065.0	ν _s (E) 1998.0	
	k,(ax) 17.440	k_(eq) 16.567	<i>k_i</i> (eq-eq) 0.437	k _i (eq-ax) 0.121
L =	$\nu(A_1)$	₽(E)	k(eq)	k _i (eq-eq)
PEt,	2022.8	1955.0	15.807	0.363
P(nBu),	2022.0	1955.0	15.803	0.359
P(tBu),	2007.0	1937.6	15.539	0.369
ELP(OEt)	2028.0	1959.0	15.877	0.371
EtP(OEt)	2033.0	1963.5	15.952	0.374
P(OEt),	2037.0	1970.0	16.043	0.362
P(OMe) ₃	2039.0	1971.0	16.065	0.367
ELP(NEL)	2023.0	1954.3	15.8 01	0.368
EtP(NEL).	2020.0	1951.7	15.757	0.365
P(NEL),	2019.2	1951.2	15.747	0.364
(C ₄ H ₅),P	2028.5	1961.5	15.907	0.360
$(C_{H_3})_P(m-FC_{H_3})$	2028.0	1962.0	15.909	0.355
$(C_6H_5)P(m-FC_6H_4)$	2029.5	1962.0	15.917	0.363
$P(m-FC_6H_4)_3$	2029.0	1961.0	15.904	0.365

TABLE 2

Experimental CO stretching frequencies (cm^{-1}) and force constants $(mdyn A^{-1})$ of the compounds BrHgCo(CO), L in THF solution

L = CO	$\nu_{1}(A_{1})$	v ₂ (A ₁)	v ₃ (E)	
	2089.0	2065.0 k;(eq) 16.554	1997.0	
	k ₁ (ax) 17.432		k _i (eq -e q) 0.439	k _i '(eq-ax) 0.116
L =	$\nu(A_1)$	ν(E)	k(eq)	k _i (eq-eq)
PEt,	2023.5	1954.0	15.800	0.372
P(nEu) ₃	2022.0	1954.0	15.792	0.364
P(tBu),	2007.0	1936.7	15.529	0.373
Et_P(OEt)	2027.5	1959.3	15.878	0.366
EtP(OEt)	2031.0	1963.5	15.941	0.363
P(OEt),	2036.7	1968.0	16.020	0.371
P(OMe),	2037.0	1968,5	16.027	0.370
Et_P(NEL)	2022.0	1954.5	15.797	0.361
EtP(NEL)	2018.0	1951.5	15.744	0.356
$P(NEt_2)_3$	2017.5	1951.0	15.736	0.355
(C,H,),P	2026.3	1960.0	15.879	0.356
$(C_{\bullet}H_{\star})_{P}(m-FC_{\bullet}H_{\star})$	2027.0	1961.5	15,898	0.352
(C,H,)P(m-FC,H)	2028.0	1961.5	15.904	0.357
$P(m-FC_6H_4)_3$	2028.5	1961.0	15.901	0.363

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TABLE 3

Ligand	ν(B _u),	$\nu(B_{\underline{u}})_2$	$\nu(A_{u})$
	2012.0	1981.0	1938.0
P(nBu),	2012.5	1980.5	1937.5
P(tBu),	2003.0	1973.0	1928.5
ELP(OEt)	2019.0	1986.6	1944.7
EtP(OEt),	2023.0	1992.0	1950.5
P(OEt),	2030.5	1998.6	1957.0
P(OMe),	2032.0	2001.0	1958,0
Et_P(NEt_)	2012.5	1982.6	1939.0
EtP(NEt,)	2009.0	1978.0	1934.5
P(NEt_),	2008.3	1977.0	1934.5
(C,H,),P	INSOLUBLE IN THF		
(C, H,), P(m-FC, H)	n.o.	1994.0	1951.0
$(C,H,)P(m-FC,H_{\star})$	2023.5	1996.0	1952.0
$P(m-FC_6H_4)_3$	2023.0	1997.0	1953.0

Experimental CO stretching frequencies (cm⁻¹) of the compounds ${ClHgCo(CO)_{3}L}_{2}$ in THF solution

TABLE 4

Experimental CO stretching frequencies (cm^{-1}) of the compounds $\{BrHgCo(CO),L\}_{-}$ in THF solution

Ligand	v(B _u),	$\nu(B_{\rm u})_{\rm c}$	v(A _u)
 РЕĻ	2011.0	1981.5	1938.0
P(nBu),	2012.5	1981.0	1937.5
P(tBu),	2002.0	1972.5	1927.5
Et_P(OEt)	2014.0	1986,5	1944.5
EtP(OEt)	2023.5	1992.0	1950.2
P(OEt),	2030.0	1998.5	1956.5
P(OMe),	2033.0	2000.5	1957.8
ELP(NEL)	2014.0	1983.0	1940.0
ELP(NEL)	2010,6	1979.0	1936.1
P(NEL),	2008.0	1977.4	1934.5
(C,H,),P	INSOLUBLE IN THF		
(C, H,) P(m - FC, H)	n.o.	1992.0	1950.5
(C,H,)P(m-FC,H,)	2023.0	1996.0	1951.5
$P(m - FC_6 H_4)_3$	2023.0	1997.0	1952.5

FORCE CONSTANT CALCULATIONS

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Once the frequencies of the A_1 and E vibrations are known, the energy factored force field of the compounds XHgCo(CO)₃L is fully determined. The force constants are given by the equations

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Fig. 2. Possible geometries of $\{XHgCo(CO), L\}$, molecules.

$$k = \frac{1}{3} \{ y(A_1) + 2y(E) \} \text{ and } k_i = \frac{1}{3} \{ y(A_1) - y(E) \}$$

with $y = 0.40407 \times 10^{-5} \nu_{CO}^2$.

The force field of the parent compounds $XHgCo(CO)_4$ is undetermined. Assuming a maximal interaction between axial and equatorial CO-groups [7, 8], the force constants are given by the equations

$$k_{1}(ax) = \frac{1}{2} \{y_{1}(A_{1}) + y_{2}(A_{1})\}$$

$$k_{2}(eq) = \frac{1}{6} \{y_{1}(A_{1}) + y_{2}(A_{1}) + 4y_{3}(E)\}$$

$$k_{i}(eq-eq) = \frac{1}{6} \{y_{1}(A_{1}) + y_{2}(A_{1}) - 2y_{3}(E)\}$$

$$k_{i} \cdot (eq-ax) = \frac{1}{2\sqrt{3}} \{y_{1}(A_{1}) - y_{2}(A_{1})\}$$

As only three of the six absorption frequencies are known, the force constants of the dimeric compounds $\{XHgCo(CO)_3L\}_2$ cannot be obtained.

The force constants of the compounds $XHgCo(CO)_3L$ (X = Cl, Br) are given in Table 1 and 2.

RESULTS AND DISCUSSION

In Fig. 3, the CO stretching frequencies of the monomeric and dimeric compounds $\{XHgCo(CO)_{3}L\}_{n}$ (n = 1, 2; X = Cl and Br) are plotted against



Fig. 3. CO stretching frequencies (cm^{-1}) of the compounds $\{XHgCo(CO)_3L\}_n$ (n = 1 and 2; X = Cl and Br) versus increasing ligand donor properties $(k_{eq} \text{ for } LFe(CO)_4)$.



Fig. 4. Force constants of the compounds ClHgCo(CO), L and Hg{Co(CO), L}, versus increasing ligand donor properties (k_{eq} for LFe(CO),).

the net electron donor properties of the ligands L, for which we chose as a measure the equatorial CO stretching force constants of the corresponding compounds $LFe(CO)_4$ [9]. In Fig. 4, the force constants of the compounds $ClHgCo(CO)_3L$ are compared with those of the compounds $Hg\{Co(CO)_3L\}_2$. Except for the monomeric compounds $XHgCo(CO)_3P(tBu)_3$, a linear decrease of the CO stretching frequencies and/or force constants with increasing ligand donor properties is observed for all series of compounds.

The particularly low CO stretching frequencies and force constants of the compounds XHgCo(CO)₃P(tBu)₃ can be explained by steric effects. Structural data of LFe(CO)₄ compounds [10, 11] indicate that the L-M-(CO)_{eq} bond angles increase with ca. 5° going from L = MMe₃ (M = As, Sb) to the very bulky P(tBu)₃ group. Such a drastic increase of the declination angle should cause a repulsion of the mercury atom, resulting in a diminished electron transfer from the cobalt to the mercury atom. Whether the Co \rightarrow Hg σ bond strength or the ($d_{\pi} \rightarrow p_{\pi}$) overlap [12] is weakened, the CO stretching frequencies and force constants of the P(tBu)₃ derivatives are lower than expected from the linear relation of Fig. 3 and 4. In consequence of this, the mercury atom in these compounds remains a quite strong Lewis acid.

Contrary to those of the monomeric compounds $XHgCo(CO)_3P(tBu)_3$, the CO stretching frequencies of the dimeric compounds $\{XHgCo(CO)_3P(tBu)_3\}_2$ do show a linear relation between the frequencies and the ligand donor properties. The absence of steric effects in the dimeric compounds can be explained by an increased Hg—Co bond distance resulting from the donor—acceptor interaction of both monomers [13]. However, structural data of analogous compounds are not available.

Apart from L = P(tBu)₃, the frequency lowering due to dimerization, $\{\nu(A_1) - \nu(B_{u_1})\}$ and $\{\nu(E) - \nu(A_u)\}$, increases with increasing ligand donor properties. For the lower-frequency bands at least, a linear relationship is found. The tendency towards dimerization seems to decrease in the same order. At room temperature, reaction of Hg{Co(CO)₃P(tBu)₃}₂ with HgX₂ (X = Cl, Br) in acetone solution resulted in the formation of the $\frac{1}{2}$ -ure dimeric compounds {XHgCo(CO)₃P(tBu)₃}₂. With L = P(OMe)₃ and P(OEt)₃, the reaction mixtures consisted mainly of the dimeric compounds, while the monomeric compounds were the main products in the reaction of the compounds Hg{Co(CO)₃L}₂ with L = PEt₃ and P(nBu)₃.

From these experimental features, we conclude that the Lewis acidity of the mercury atom [1] in the compounds $XHgCo(CO)_3L$ decreases in the order $L = P(tBu)_3 > P(OMe)_3 > P(OEt)_3 > EtP(OEt)_2 > Et_2P(OEt) >$ $Et_2P(NEt_2) > PEt_3 > P(nBu)_3 > EtP(NEt_2)_2 > P(NEt_2)_3$.

In Fig. 4 the CO stretching force constants of the dinuclear compounds $Hg{Co(CO)_3L}_2$ are included [4]. The compounds $XHgCo(CO)_3L$ (X = Cl, Br) have higher force constants than the compounds $Hg{Co(CO)_3L}_2$ This can be explained by the weaker base strength [1] of Cl⁻ and Br⁻ compared with $Co(CO)_3L^-$, resulting in an enhanced drift of electrons from the cobalt to the mercury atom. As the basicity of the cobalt carbonyl anion increases

with increasing donor properties of the ligand L [14], when a better σ donating and/or poorer π back-bonding ligand is substituted for CO, the difference between the force constants of both series of compounds increases. The force constants of the bromo mercury compounds are slightly lower than those of the chloro mercury compounds, corresponding to the small difference in Pauling electronegativity of both halides.

The Hg—Co bond distance in the compounds $XHgCo(CO)_4$ seems to increase with increasing basicity of X. Going from $(OC)_4Co-HgCo(CO)_4$ [15] to $(\pi C_5H_5)Fe(CO)_2$ —HgCo(CO)_4 [16] the Hg—Co distance increases from 2.50 to 2.56 Å. In view of the lower basicity of Cl⁻ and Br⁻ as compared with Co(CO)_4, we expect a shorter Hg—Co distance in the compounds $XHgCo(CO)_4$ with X = Cl and Br. However, molecular structure determinations [17] show no significant difference between the Hg—Co bond lengths in Hg[Co(CO)_4]_2 (2.499 Å) and BrHgCo(CO)_4 (2.482 Å).

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