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NOTE

COMPLEXES CONTAINING METAL–TIN BONDS

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Compounds possessing bonds between tin and transition metals have been known for some time, but their general properties are still being investigated. In particular some analogies can be found between organotin halides and compounds such as R_MSnX_3 or $(R_M)_2SnX_2$, where X is a halogen and R_M an organometallic radical, such as π-$C_5H_5Fe(CO)_2$, π-$C_5H_5Mo(CO)_3$, or Co(ligand)$(CO)_3$ (see also refs. 1–4).

We tried to carry out with these R_M–Sn compounds some other reactions known for organotin halides, namely the formation of complexes with chelating ligands, such as bipyridine, 8-hydroxyquinolinate, dithiocarbamate, and β-diketonate. Stable and isolable compounds were obtained only with the first and the second ligand mentioned above. These compounds had the general formula $R_MSnClOx_2$ or π-$C_5H_5Fe(CO)_2SnCl_3 \cdot$ 2,2′-bipyridine. Owing to the bulky ligands, clathrated benzene molecules were found in one case. While the bipyridine adduct was easily obtained pure, the other compounds were accompanied by oils, by degradation products of the starting material, such as dichlorotin(IV) bis(hydroxyquinolinate), and by 8-

TABLE 1

INFRARED SPECTRAL DATA RELATING TO ν(CO)

Compound[a]	Bands[b]	Condition	Ref.
$CpFe(CO)_2SnClOx_2$	2010, 1990; 1900	Nujol	[c]
$CpFe(CO)_2SnCl_3$	2047; 2007	CH_2Cl_2	6
$CpFe(CO)_2SnEt_3$	1978; 1924	CH_2Cl_2	6
$CpFe(CO)_2SnCl_3 \cdot Bipy$	2025, 2011; 1978, 1966	Nujol	[c]
$CpMo(CO)_3SnCl_3$	2049; 1988; 1964	CH_2Cl_2	6
$CpMo(CO)_3SnMe_3$	1997; 1922; 1895	CCl_4	6
$CpMo(CO)_3SnClOx_2$	2000; 1940, 1912	Nujol	[c]
$(CO)_3LCoSnClOx_2 \cdot C_6H_6$	2035 w; 1880 (br)	Nujol	[c]
$(CO)_3LCoSnClOx_2$	2045 w; 1885 (br)	Nujol	[c]
$(CO)_3LCoSnCl_3$	2060 w; 2000 (br), 1960	Nujol	3

[a] Cp is π–C_5H_5, Ox is 8-hydroxyquinolinate, Bipy is 2,2′-bipyridine, L is tri-n-butylphosphine. [b] All bands are strong unless stated otherwise. Bands are separated by a semicolon; a comma indicates only splitting or shoulder. [c] This work.

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hydroxyquinoline hydrochloride. For this reason the products, which are sparingly soluble, and rather unstable in solution, could be purified only with severe losses.

Infrared spectra were recorded in nujol mull. In all cases a remarkable lowering (*ca.* 100 cm^{-1}) of the carbonyl stretching frequencies was observed on passing from the corresponding R_MSnCl_3 compound to the oxine derivative. This change is bigger than that observed on passing from R_MSnCl_3 to R_MSnEt_3 compounds (see Table 1). Back-donation from the transition metal towards the carbonyl group cannot be increased further by substituting two of the three chlorine atoms with two OR ($R = C_9H_6N$) groups more than by substituting all the three chlorine atoms with alkyl groups. Therefore it can safely be assumed that at least one 8-hydroxyquinolinato group is acting as a bidentate ligand and that hexacoordinate tin(IV) is present in these compounds; consequently it should be possible to have steric isomers. Although π-$C_5H_5Fe(CO)_2SnClOx_2$ gave a labile red and a stable green species, it was possible to isolate only the green one; the preparation of the red species could not be reproduced, while that of the green species was reproduced successfully.

Infrared spectrum of the bipyridine adduct showed the bands of this ligand in typical complexes[5].

EXPERIMENTAL

(π-*Cyclopentadienyldicarbonyliron*)*trichloro*(2,2′-*bipyridine*)*tin*(*IV*)

To a benzene solution (25 ml) of $C_5H_5Fe(CO)_2SnCl_3$ (0.485 g) bipyridine (0.283 g) in benzene (8 ml) was added. After a few minutes, the red-orange precipitate was filtered off, washed with benzene and dried (0.43 g); m.p. 136–138°; insoluble in organic solvents. (Found: C, 37.37; H, 2.38; Cl, 18.90; N, 4.99. $C_{17}H_{13}Cl_3FeN_2O_2Sn$ calcd.: C, 36.55; H, 2.33; Cl, 19.08; N, 5.01%.)

(π-*Cyclopentadienyldicarbonyliron*)*bis*(8-*hydroxyquinolinato*)*chlorotin*(*IV*)

To a methanol solution of 8-hydroxyquinoline (1.135 g) a saturated methanol solution of $[C_5H_5Fe(CO)_2]_2SnCl_2$ (1.06 g) was added. On concentrating and cooling the green solution afforded a green solid (0.581 g), which was purified by extraction with benzene in a Soxhlet apparatus, decompn. *ca.* 200°. (Found: C, 48.50, 48.29; H, 2.91, 2.75; N, 4.52, 4.37; O, 10.10. $C_{25}H_{17}ClFeN_2O_4Sn$ calcd.: C, 48.4; H, 2.75; N, 4.52; O, 10.33%.)

A similar preparation afforded a mixture of green and red solid; the mixture was converted to the green compound on standing under methanol while stirring for *ca.* 1 h.

[*Tricarbonyl*(*tri-n-butylphosphine*)*cobalt*]*bis*(8-*hydroxyquinolinato*)*chlorotin*(*IV*)

A tetrahydrofuran solution (50 ml) of $(CO)_3(n\text{-}Bu_3P)CoSnCl_3$ (0.8669 g) was added to a solution (50 ml) of 8-oxyquinoline (1.340 g) in the same solvent. After *ca.* 30 min a whitish precipitate was filtered (124 mg) and the solution concentrated to 1/3 of its original volume. The IR spectrum of the whitish precipitate was similar to that of pure 8-hydroxyquinoline hydrochloride. The yellow precipitate obtained on concentration was washed repeatedly with benzene, diethyl ether, and acetone; comparison of the IR spectrum with that of an authentic sample and analysis showed that it was bis(8-hydroxyquinolinato)dichlorotin(IV). (Found: C, 45.7; H, 2.90; N, 5.85.

$C_{18}H_{14}Cl_2N_2O_2Sn$ calcd.: C, 45.2; H, 2.5; N, 5.85%.) The mother liquor was evaporated to dryness, and the residue was then extracted with benzene; on addition of hexane and concentration yellow crystals separated. The analytical sample was crystallized twice from benzene/hexane, m.p. 75°. [Found: C, 53.63; H, 4.96; Cl, 4.12; N, 3.14; O, 10.20; mol.wt. (osmometry, benzene, 37°, 1.12% w/w), 906. $C_{39}H_{45}$-$ClCoN_2O_5PSn$ calcd.: C, 54.0; H, 5.19; Cl, 4.10; N, 3.23; O, 9.25%; mol.wt., 865.2.]

Alternative preparation. The reagents (1.2288 and 1.87) were mixed in benzene solution (100 ml); after 1 h the first precipitate was discarded, heptane added to the solution, which was then concentrated to small volume. The yellow crystals (1.020 g) were filtered and crystallized twice from benzene/hexane, to give the product described above (m.p., mixed m.p., superimposable IR spectrum). The benzene-free compound, m.p. 100–104°, was obtained on heating at 60°/0.1 mm till constant weight. [Found: C, 50.3; H, 4.96; N, 3.56; mol. wt. (benzene, osmometry at 37°), 813. $C_{33}H_{39}ClCoN_2O_5PSn$ calcd.: C, 49.88; H, 4.97; N, 3.38%; mol.wt., 787.2.]

(π-Cyclopentadienyltricarbonylmolybdenum)bis(8-hydroxyquinolinato)chlorotin(IV)

A benzene solution (100 ml) of π-$C_5H_5Mo(CO)_3SnCl_3$ (1.092 g) was added slowly to a benzene solution (150 ml) of 8-hydroxyquinoline (2.020 g). A yellowish precipitate was filtered off, it had an IR spectrum similar to that of 8-hydroxyquinoline hydrochloride. Heptane was added to the solution, which was concentrated to afford a yellow precipitate (0.437 g), which was crystallized from toluene and from acetone, to give a solid (decompn. *ca.* 130°). (Found: C, 44.50; H, 2.65; N, 3.81. $C_{26}H_{17}ClMo$-N_2O_5Sn calcd.: C, 45.4; H, 2.47; N, 4.07%.)

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REFERENCES

1 F. Bonati and G. Wilkinson, *J. Chem. Soc.*, (1964) 179.
2 F. Bonati, S. Cenini, D. Morelli and R. Ugo, *Inorg. Nucl. Chem. Lett.*, 1 (1965) 107.
3 F. Bonati, S. Cenini and R. Ugo, *J. Chem. Soc.*, *A*, (1967) 932.
4 F. Bonati, S. Cenini, D. Morelli and R. Ugo, *J. Chem. Soc.*, *A*, (1966) 1052.
5 V. Carassiti, A. Seminara and A. Seminara-Musumeci, *Ann. Chim. (Rome)*, 54 (1964) 1025.
6 R. Ugo, S. Cenini and F. Bonati, *Inorg. Chim. Acta*, 1 (1967) 451.