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Preliminary communication

Carbon dioxide complex formation with arylsilver compounds

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Certain tetraorgano-tin and -lead compounds react with silver salts to give organosilver–silver salt coordination compounds $RAg{\cdot}nAgX$[1,2]. Recently we described the synthesis of uncomplexed phenylsilver via this reaction under special conditions[3]. We now have found that arylsilver–silver nitrate coordination compounds can react with carbon dioxide with formation of stable carbon dioxide complexes.

Addition of solid or gaseous carbon dioxide to a saturated yellow solution of phenylsilver–silver nitrate[3] in ethanol (about 0.05% by weight), cooled below 0°, gave during a period of a few hours to some days a white precipitate having the analytical composition $C_7H_5O_2Ag_2$ (I). The residual colourless ethanol solution still contained all the silver nitrate originally present in the dissolved phenylsilver–silver nitrate, as well as benzene in an amount corresponding to the equation:

$$2\,C_6H_5Ag{\cdot}nAgNO_3 \xrightarrow[EtOH]{CO_2} C_7H_5O_2Ag_2 + C_6H_6 + 2nAgNO_3$$

Under similar conditions no reaction takes place between carbon dioxide and uncomplexed phenylsilver[3], which because of its polymeric structure is extremely insoluble in non-coordinating solvents.

Compound I has a relatively high stability, comparable with that of phenylsilver: at room temperature it remains unchanged in dry air during one day, but at 74° an explosive decomposition occurs (rate of heating 5°/min). I is extremely insoluble in all common solvents, in contrast with phenylsilver which dissolves moderately in coordinating solvents such as pyridine and *N,N*-dimethylformamide. The IR spectrum of I mainly resembles strongly the spectrum of phenylsilver but shows additional, very strong absorptions at 1496, 1326 and 828 cm^{-1} and moderate absorptions at 325, 290 and 280 cm^{-1}. The complex $Rh_2(CO)_2(CO_2)(PPh_3)_3(C_6H_6)$ has been reported[4] to show strong IR absorptions at 1498, 1368 and 813 cm^{-1} which were ascribed to the presence of coordinated carbon dioxide, probably in a bent form. Thermal decomposition of compound I gives carbon dioxide, biphenyl and silver(0) as the only products. The same products are formed along with benzene on treatment with HCl, HNO_3 or CH_3COOH. Benzoic acid and phenyl formate are absent from the degradation products, indicating that no insertion of carbon dioxide into the silver—carbon bond has occurred.

From our results we conclude that compound I is a coordination polymer consisting of phenylsilver, silver(0), and coordinated carbon dioxide: $[C_6H_5Ag\cdot CO_2\cdot Ag]_n$.

We have prepared similar complexes, $[RAg\cdot CO_2\cdot Ag]_n$, from *p*-substituted arylsilver compounds, such as *p*-allylphenylsilver and *p*-methoxyphenylsilver. Their IR spectra show absorptions of the parent compound RAg as well as the characteristic absorptions of coordinated carbon dioxide mentioned above.

The reaction described is, as far as we know, the first example of a reaction between an organometallic compound containing an M—C σ-bond and carbon dioxide leading to a stable coordination product, without subsequent carbon dioxide insertion into the M—C bond. Further studies of the molecular structure and chemical properties of these complexes are in progress.

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