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## NOTE

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# Phosphorous containing cobalt carbonyls
## II*. Hexasubstituted triphenylphosphine derivative of dicobalt octacarbonyl

Dicobalt octacarbonyl derivatives containing more than two tertiary phosphine substituents have not previously been described in the literature[1-7].

On treating the homogeneous olefin hydrogenation and isomerization catalyst system composed of cobaltous stearate and Grignard compounds[8] with carbon monoxide and triphenylphosphine at room temperature and atmospheric pressure, the following cobalt complexes were obtained as precipitates: $Co_2(CO)_6(PPh_3)_2$, $CoX_2(PPh_3)_2$, $Co(CO)_2(PPh_3)_2X$ (X = halogen), and a compound showing a composition which corresponded to a Co/CO/$PPh_3$ ratio of 1 : 1 : 3. The first three complexes have been already described in the literature[1-5,9-12] but the last seems to be a hexasubstituted derivative of dicobalt octacarbonyl.

This new compound formed as a yellow crystalline precipitate when a hexane solution of cobaltous stearate was added to a solution of triphenylphosphine in an ethereal Grignard reagent and carbon monoxide was bubbled through the dark brown reaction product. If relatively high concentrations of the reactants (2.5–3 mg-atom Co/100 ml) and Co/Mg/P ratios between 1 : 4 : 4 and 1 : 12 : 12 were used, this compound was the only product in the precipitate. It was formed with either EtMgBr or tert-BuMgCl as Grignard reagents. It was found necessary to start the CO gas inlet after completely charging in the cobaltous stearate.

On the basis of the analytical data this compound could be $Co_2(CO)_2(PPh_3)_6$, (I), or $Co(CO)(PPh_3)_3$, (II), and because of the hydridic nature of the catalyst system[8] the structure $HCo(CO)(PPh_3)_3$, (III), cannot be excluded.

The IR spectrum of the compound shows in the C–O stretching region only a single very strong and sharp band at 1904 $cm^{-1}$. All the three above formulations would be in accord with this spectrum. However, if the dimeric formula (I) applies the appearance of a single carbonyl band shows the axial position of the two CO ligands. The molecule possesses in this latter case a $D_{3d}$ symmetry (the $D_{3h}$ symmetry can be excluded for sterical reasons).

The "free radical" structure (II) of the compound can be excluded because neither in the solid state nor in toluene solution was an ESR signal obtained. This is also in accordance with the result that the compound is diamagnetic ($\chi_g = -3.77 \times 10^{-6}$ $cm^3$ at $T = 296°K$).

Proton NMR measurements (in deuterobenzene, benzene, or cyclohexane solution) showed no hydridic hydrogen, thus excluding the "hydridic" structure (III).

Efforts to determine the molecular weight of (I) remained unsuccessful. With benzene as solvent the values ranged between 300 and 2000, presumably because of rapid decomposition of the complex in benzene solution.

On the basis of the above experimental observations we regard the dimeric structure (I) as the most probable one.

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* For Part I see ref. 7.

The shape of the thermogravimetric (TG) curve is similar to that of the disubstituted $Co_2(CO)_6(PPh_3)_2$ (*cf.* ref. 13). The CO ligands split off from both compounds at about 190°, indicating no significant difference in the Co–C bond strengths. In the second step (340°) the dissociation of the triphenylphosphine ligands can be observed.

The compound is soluble in halogenated hydrocarbons but reacts with them immediately even in the absence of air. A solution in benzene seems to be more stable, but even in this case a precipitate containing $Co_2(CO)_6(PPh_3)_2$ is formed after some time. In solid state the compound is relatively stable in air. It does not react with metallic lithium in tetrahydrofurane solution as it may be expected on the basis of structure (I).

It is worth mentioning that the compound is possibly the same substance which is formed as a byproduct, in addition to $Na[Co(CO)_2(PPh_3)_2]$, from $Co(CO)_2(PPh_3)_2Cl$ and sodium amalgam, as observed by Hieber and Duchatsch[14], who, however, did not succeed in isolating and identifying this product. Furthermore, the reaction between $H_2Co(PPh_3)_3$ (regarded to be a dimer) and CO, as mentioned by Misono and coworkers[16], but not reported in detail, may lead to the same compound.

The liquid part of the reaction products contained in some cases complexes of the type $RCOCo(CO)_3(PPh_3)$[15] wich are readily soluble in the ether/hexane solvent. No attempt was made to isolate them but they were identified by their infrared spectra.

## *Experimental*

*Preparation of* $Co_2(CO)_2(PPh_3)_6$. In a 500 ml reaction vessel 36 mmoles of triphenylphosphine were dissolved in 50 ml of diethyl ether. The ethereal solution (about 20 ml) of 18 mmoles EtMgBr or tert-BuMgCl was added, and then 3 mmoles Co stearate (dissolved in 30 ml hexane) were added during 10 min. After adding the cobaltous stearate, CO gas was led into the reaction mixture through a sintered glas filter; 20–30 min later a yellow crystalline product precipitated which was filtered off and washed with methyl alcohol. The yield was 1.0–2.0 g (3.8–7.6%, calculated on Co-stearate). (Found: C, 74.6; H, 5.38; Co, 6.57. $C_{110}H_{90}Co_2O_2P_6$ calcd.: C, 75.8; H, 5.17; Co, 6.74%.)

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