

### Preliminary communication

## A NEW RHODIUM COMPLEX WITH CARBON DIOXIDE

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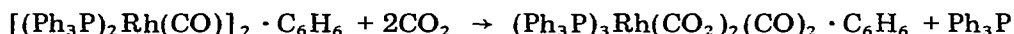
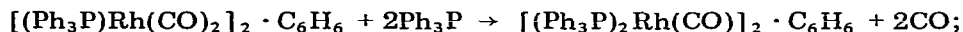
### Summary

The complex  $(\text{Ph}_3\text{P})_3\text{Rh}_2(\text{CO})_2(\text{CO}_2)_2 \cdot \text{C}_6\text{H}_6$  was prepared by action of carbon dioxide on complexes of zerovalent rhodium.

Study of complexes of carbon dioxide with transition metals is a new and promising field in organometallic chemistry. Three rhodium complexes with  $\text{CO}_2$  are known at the present time: two of them,  $(\text{Ph}_3\text{P})_5\text{Rh}_2(\text{CO}_2)\text{Cl}_2$  [1] and  $(\text{Ph}_3\text{P})_6\text{Rh}_2\text{H}_2(\text{CO}_2)$  [2] have been prepared directly by reaction of carbon dioxide with a rhodium compound, and one indirectly by oxidation of CO ligand with molecular oxygen [3].

We found that the action of carbon dioxide on a benzene solution of  $[(\text{Ph}_3\text{P})\text{Rh}(\text{CO})_2]_2 \cdot \text{C}_6\text{H}_6$  [4] in the presence of triphenylphosphine at room temperature and normal pressure gives a lemon-yellow complex which according to chemical analysis has composition of  $(\text{Ph}_3\text{P})_3\text{Rh}_2(\text{CO}_2)_2(\text{CO})_2 \cdot \text{C}_6\text{H}_6$  (I) m.p. 140–146° (dec.). It is insoluble in alcohol, acetone, ether, hexane, moderately soluble in chloroform and benzene, and well soluble in THF;

The complex was synthesized under conditions of formation of  $[(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})]_2 \cdot \text{C}_6\text{H}_6$  which probably is an intermediate in synthesis of (I). The reaction scheme may be the following:



The IR spectrum of the compound shows the carbonyl group absorption [ $\nu(\text{Rh}-\text{CO})$  1970  $\text{cm}^{-1}$ ], frequencies of triphenylphosphine ligands and also two intensive bands at 1600 and 1355  $\text{cm}^{-1}$  and a line of average intensity at 825  $\text{cm}^{-1}$ .

In the IR spectrum of complex (I) prepared from  $^{13}\text{CO}_2$  these lines are shifted to 1580, 1340 and 800  $\text{cm}^{-1}$  (Fig. 1).

These results enable us to conclude that the frequencies 1600, 1355 and 825  $\text{cm}^{-1}$  are the modes of coordinated  $\text{CO}_2$  ligands.

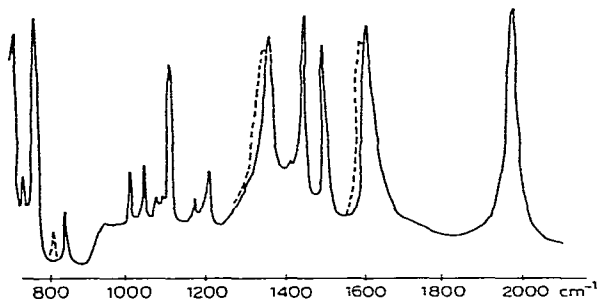


Fig. 1. IR spectra of  $(\text{PPh}_3)_3\text{Rh}_2(\text{CO})_2(\text{CO}_2)_2 \cdot \text{C}_6\text{H}_6$ . Solid line shows spectrum of  $^{12}\text{CO}_2$  complex, dashed line shows  $^{13}\text{CO}_2$  complex.

Solid complex (I) is stable in air. One mole of carbon dioxide per rhodium atom evolves upon acidification with sulfuric acid and also in the thermal decomposition of the complex (gas evolution starts at  $90^\circ$  and ceases at  $150^\circ$ ). Solvated benzene was revealed by means of chromatographic analysis of the pyrolysis products ( $150^\circ$ ).

Treatment of a benzene solution of complex (I) with carbon monoxide gave starting complex  $[(\text{Ph}_3\text{P})\text{Rh}(\text{CO})_2]_2 \cdot \text{C}_6\text{H}_6$  and 2 moles of carbon dioxide. It is noteworthy that passing air through the benzene solution of complex (I) leads to  $(\text{Ph}_3\text{P})_3\text{Rh}_2(\text{CO}_2)(\text{CO})_2 \cdot \text{C}_6\text{H}_6$  obtained earlier by an independent method by Iwashita and Hayata [3]. This compound contains one  $\text{CO}_2$  molecule per two rhodium atoms. The IR spectrum of this complex has also three frequencies of the coordinated  $\text{CO}_2$  molecule: 1498, 1368 and  $813\text{ cm}^{-1}$ .

## References

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