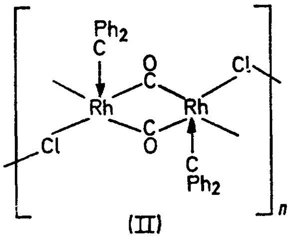
Novel Carbene Complexes of Rhodium

By P. Hong, N. Nishii, K. Sonogashira,* and N. Hagihara

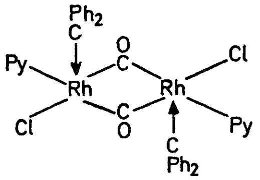
(*The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka* 565, *Japan*)

Summary Stable diphenylcarbene complexes of rhodium (II, III, IV, and V) have been prepared.

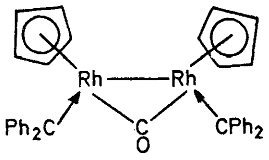
Various transition metal carbene complexes[1-4] in which the carbene ligand is stabilized by an adjacent oxygen or nitrogen atom, have been reported. We now report the preparation of the first diphenylcarbene-rhodium complexes. $[Rh(CO)_2Cl]_2$ (I) (6 mmol), was treated with diphenylketen (18 mmol) in xylene for 4 h under reflux and gave a 75% yield of an insoluble brick red complex (II),† $[Rh(CO)(CPh_2)Cl]_n$, m.p. 290° (decomp.), $\nu_{C=O}$ 1860 cm^{-1}, ν_{Rh-Cl} 275 cm^{-1}. Complex (II) and its diarylcarbene analogues have also been obtained from (I) and diaryldiazomethane in benzene in high yields.



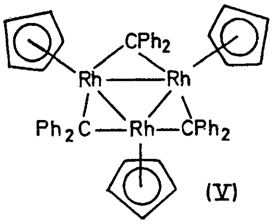
(II)



(III)



(IV)



(V)

Complex (II) is air stable and insoluble in most organic solvents except for bridge-splitting reagents such as pyridine in which it is converted, on recrystallization from CH_2Cl_2–petroleum ether, into red needles of (III) $[Rh(CO)(CPh_2)Cl(C_5H_5N)]_2 \cdot (CH_2Cl_2)_2$. Complex (III) gradually decomposes over 100°, $\nu_{C=O}$ 1836 cm^{-1}, ν_{Rh-Cl} 296 cm^{-1}, mol.wt. (CH_2Cl_2) 822 (calc. 822). Reaction of (II) with cyclopentadienylsodium in THF, after chromatography on an alumina column, gave the air stable, green crystals (IV), $(\pi\text{-}C_5H_5)_2Rh_2(CPh_2)_2(CO)$, 75% yield, m.p. 179—182° (decomp.), $\nu_{C=O}$ 1840 cm^{-1}, M^+ 696.

Complex (IV) slowly lost a bridging carbonyl on heating or if kept at room temperature in benzene, the trinuclear complex (V), $(\pi\text{-}C_5H_5)_3Rh_3(CPh_2)_3$, violet crystals, m.p. 227—228°, M^+ 1002 was obtained.

Complex (II) when treated with triphenylphosphine under reflux in toluene gave $Ph_2C{=}CPh_2$ (VI), $Rh(CO)(PPh_3)_2Cl$ (VII), and $[Rh(PPh_3)_2Cl]_2$ in yields of 77%, 42%, and 33%, respectively. Although our attempt to trap diphenylcarbene in the above reaction using diphenylethylene at 150—160° has been unsuccessful resulting in the formation of (VI) and (VII) in the yields of 56% and 87%, respectively, the formation of (VI) supports the presence of a diphenylcarbene ligand. A similar carbene intermediate has been suggested[5] in the catalytic decarbonylation of diphenylketen with $Co_2(CO)_8$.

On the basis of the above reaction and the i.r. and ^1H n.m.r. spectra of (II), (III), (IV), and (V), we suggest the structures shown.

The structures of (IV) and (V) are related to those of $(\pi\text{-}C_5H_5)_2Rh_2(CO)_3$[6] and $(\pi\text{-}C_5H_5)_3Rh_3(CO)_3$,[7] respectively. Further studies on other carbene complexes and *X*-ray studies of the complexes (III), (IV), and (V) are in progress.

(*Received*, 12*th June* 1972; *Com.* 1021.)

---

† Satisfactory analytical data for all formulated compounds have been obtained.

[1] E. O. Fischer and A. Maasbol, *Angew. Chem.*, 1964, **76**, 645.
[2] F. Bonati, G. Minghetti, T. Boschi, and B. Crociani, *J. Organometallic Chem.*, 1970, **25**, 255.
[3] D. J. Cardin, B. Cetinkaya, M. F. Lappert, Lj. Manojlović-Muir, and K. W. Muir, *Chem. Comm.*, 1971, 400.
[4] M. H. Chisholm and H. C. Clark, *Chem. Comm.*, 1970, 763.
[5] P. Hong, K. Sonogashira, and N. Hagihara, *J. Chem. Soc. Japan*, 1968, **89**, 74.
[6] O. S. Mills and J. P. Nice, *J. Organometallic Chem.*, 1967, **10**, 337.
[7] O. S. Mills and F. Paulus, *Chem. Comm.*, 1966, 815.