Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

SOME NEW COBALT AND PLATINUM COMPLEXES OF DIPHENYLCYCLOPROPENONE

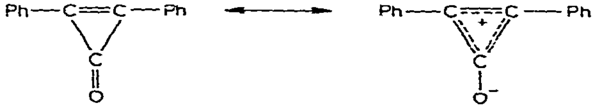
W. L. FICHTEMAN, P. SCHMIDT AND M. ORCHIN
Department of Chemistry, University of Cincinnati, Cincinnati, Ohio (U.S.A.)

(Received October 5th, 1967)

In connection with some work in progress on the stereochemistry of the oxo reaction, we were led to investigate the reaction of diphenylcyclopropenone (DPCP) with dicobaltoctacarbonyl. DPCP reacts in a typical Lewis base fashion[1] with the liberation of carbon monoxide and the formation of the cobalt(II) salt:

$$3\,Co_2(CO)_8 + 12\,DPCP \rightarrow 2\,Co(DPCP)_6[Co(CO)_4]_2 + 8\,CO$$

This reaction indicates that the cyclic ketone behaves as though it possesses the dipolar structure:



In the dipolar form, DPCP may be compared to pyridine *N*-oxide as a ligand, and in view of our extensive work on the Pt(II) complexes of pyridine *N*-oxides[2], we extended our studies on such complexes to DPCP. The appearance of a recent report[3] describing the preparation and structure of a variety of DPCP complexes of other metals prompts us to describe our efforts at this time.

We wish to report the preparation of square planar complexes, *trans*-$PtCl_2$(DPCP)(L), where L is ethylene, *cis*-2-butene, carbon monoxide, and tri-n-butylphosphine. The infrared absorption bands of these complexes are shown in Table 1.

The assignment of the 1830 and 1620 cm^{-1} bands of free diphenylcyclopropenone has been of considerable interest. Although these bands are involved with both C=C and C=O stretching vibrations[4,5], the C=O vibration is now thought to predominate in the 1620 band. The data of Table 1 clearly indicate that the oxygen and not the olefinic linkage of DPCP is bonded to the metal, since the 1620 cm^{-1} band is lowered in each of the complexes. This conclusion is in agreement with the recent work[3b].

The infrared spectra of deuterochloroform and of benzene solutions of the platinum complexes showed the 1620 cm^{-1} band characteristic of free diphenylcyclopropenone as well as the bands in the 1520–1560 cm^{-1} region characteristic of the complexes. Thus the ethylene complex in $CDCl_3$ showed bands at 1852, 1621, 1593, 1581, 1559, 1547 and 1528 cm^{-1}. Apparently, both benzene and chloroform cause partial dissociation of the cyclopropenone from platinum.

It is interesting to note that the carbon monoxide stretching frequency of (DPCP)(CO)$PtCl_2$ in halocarbon mull found at 2110 cm^{-1} is essentially the same as found for the corresponding pyridine *N*-oxide complex[6].

The ultraviolet spectrum of free diphenylcyclopropenone shows a low intensity band at 359 mμ tentatively assigned to an intramolecular charge transfer[4]. This band was greatly broadened and reduced in intensity in the ultraviolet spectra of the ethylene and carbonyl platinum complexes in cyclohexane. This effect is similar to that reported for the addition of methanol to a cyclohexane solution of diphenylcyclopropenone[4] and again indicates M←O bonding. Incidentally, the ready solubility of our complexes in contrast to those reported earlier permits solution spectra and hence more detailed structural information.

TABLE 1

INFRARED SPECTRAL DATA IN THE 1800–1500 cm^{-1} REGION[a]

DPCP	1830, 1616, 1580(sh)
(DPCP)(C_2H_4)$PtCl_2$	1838, 1593, 1572, 1543, 1517
(DPCP)(*cis*-C_4H_8)$PtCl_2$	1851, 1593, 1572, 1546, 1520
(DPCP)(CO)$PtCl_2$	1845, 1590, 1574, 1540, 1521
(DPCP)(Bu_3P)$PtCl_2$	1869, 1845, 1809, 1593, 1576, 1562
Co$(DPCP)_6[Co(CO)_4]_2$	1868, 1597, 1580, 1566

[a] KBr disk; halocarbon mull spectra showed no significant differences in these bands. All bands are strong except the 1572 ones which are medium.

EXPERIMENTAL

Infrared spectra were determined with a Perkin–Elmer Model 337 Spectrophotometer and spectra were all calibrated with polystyrene film. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. The ultraviolet spectra were obtained with a Cary Model 11 recording spectrophotometer.

The cobalt complex with diphenylcyclopropenone

A solution of DPCP (0.848 g, 4.12 mmoles) in benzene (15 ml) was placed in a serum-stoppered flask connected to a gas burette. The system was flushed with carbon monoxide and a solution of dicobaltoctacarbonyl (0.409 g, 1.20 mmoles) in benzene (15 ml) was added. Gas evolution began immediately and a yellow precipitate appeared after 10 min. The reaction mixture was stirred for 18 h and the yellow precipitate was filtered, washed with pentane, and dried in a stream of carbon monoxide. The complex (m.p. 96–98° dec.) was stored under an atmosphere of carbon monoxide because its decomposition occurs upon exposure to air*. Upon addition of a mineral acid, dense fumes of hydrocobalttetracarbonyl were evolved. An intense band at about 560 cm^{-1} which was not present in the free cyclopropenone was assigned to the Co–C–O bending vibrations of the cobalt tetracarbonyl anion[7]. (Found: C, 71.62; H, 3.53. $C_{98}H_{60}Co_3O_{14}$ calcd.: C, 71.83; H, 3.69%.)

---

* *Note added in proof.* After our article was accepted. C. W. Bird, E. M. Biggs and J. Hudec (*J. Chem. Soc.*, (1967) 1862) reported the preparation of the identical compound having similar properties but less analytical purity.

*trans-Dichloro-DPCP-ethyleneplatinum(II)**

A solution of DPCP (0.103 g, 0.5 mmole) in chloroform (2 ml) was added to a stirred solution of ethylene platinous chloride $[Pt_2Cl_4(C_2H_4)_2]$ (0.144 g, 0.25 mmole) in chloroform (5 ml). An immediate color change from orange to yellow occurred. After being stirred for several min, the product was precipitated by the addition of pentane (100 ml) to give 0.195 g (79%) of product, m.p. 104–106°. (Found: C, 41.10; H, 2.87. $C_{17}H_{14}Cl_2OPt$ calcd.: C, 40.80; H, 2.82%.)

trans-Dichloro-DPCP-(cis-2-butene)platinum(II)

Ethylene platinous chloride was converted to the *cis*-2-butene analogue as described elsewhere[8,9]. The synthesis then proceeded exactly as for the ethylene complex except that the chloroform solution was maintained at 0° during the very slow pentane addition (100 ml) to avoid the formation of oils. No further purification of the complex (m.p. 75–85°) was required. (Found: C, 43.31; H, 3.58. $C_{19}H_{18}Cl_2OPt$ calcd.: C, 43.19; H, 3.43%.)

trans-Dichloro-DPCP-carbonylplatinum(II)[10]

Carbon monoxide was bubbled slowly through a solution of $(DPCP)(C_2H_4)PtCl_2$ (0.250 g) in chloroform (5 ml) dried over molecular sieves (Linde 4A) until a color change from yellow-orange to pale yellow occurred (about 1 min). Pentane (100 ml) was added immediately to induce precipitation of the product. Excessive exposure to carbon monoxide or any delay in the addition of pentane causes a coloration change with rapid formation of metallic platinum. Traces of water cause rapid decomposition. The complex (m.p. 136–137° dec.) is purified by reprecipitation from chloroform by pentane and exhibited a $\nu(C{\equiv}O)$ at 2110 cm^{-1}. (Found: C, 38.19; H, 2.21. $C_{16}H_{10}Cl_2O_2Pt$ calcd.: C, 38.41; H, 2.02%.)

trans-Dichloro-DPCP-tri-n-butylphosphineplatinum(II)

A solution of DPCP (0.165 g, 0.80 mmole) in chloroform (1 ml) was added to a stirred solution of $(n\text{-}Bu_3P)_2PtCl_4$ (0.235 g, 0.40 mmole) in chloroform (4 ml). No abrupt change in color could be detected, so stirring was continued for 10 min. Pentane (100 ml) was added, but no precipitate formed. The solvent was partially removed under reduced pressure and yellow crystals formed. Repeated pentane addition together with chilling yielded yellow crystals of the complex, m.p. 88–90°. (Found: C, 48.85; H, 5.56. $C_{27}H_{37}Cl_2OPPt$ calcd.: C, 50.39; H, 5.80%.)

ACKNOWLEDGEMENT

We wish to thank Engelhard Industries, Inc. for a generous supply of platinum, the National Science Foundation for a fellowship to P. S. and the donors to the Petroleum Research Foundation of the American Chemical Society for partial support of this research.

---

* These complexes are tentatively assigned a *trans* configuration because of the high *trans* directing ability of the olefin and phosphine.

REFERENCES

1 I. Wender, H. W. Sternberg and M. Orchin, *J. Amer. Chem. Soc.*, 74 (1952) 1216.
2 L. Garcia, S. I. Shupack and M. Orchin, *Inorg. Chem.*, 1 (1962) 893 and later articles.
3 (a) C. W. Bird and E. M. Hollins, *Chem. Ind. (London)*, (1964) 1362;
(b) C. W. Bird and E. M. Briggs, *J. Chem. Soc., A*, (1967) 1004.
4 E. Osawa, K. Kitamura and Z. Yoshida, *J. Amer. Chem. Soc.*, 89 (1967) 3814.
5 A. Krebs and B. Schrader, *Z. Naturforsch*, 21b (1966) 194.
6 M. Rycheck, *Ph.D. thesis*, Cincinnati, 1966.
7 I. Wender, H. W. Sternberg, R. A. Freidel, S. J. Metlin and R. E. Markby, *Bulletin 600, Bureau of Mines*, 1962.
8 H. B. Jonassen and W. B. Kirsch, *J. Amer. Chem. Soc.*, 79 (1957) 1279.
9 P. Schmidt and M. Orchin, *Inorg. Chem.*, 6 (1967) 1260.
10 W. H. Clement and M. Orchin, *J. Organometal Chem.*, 3 (1965) 98.