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

NOTE

COMPLEXES OF TRIVALENT PHOSPHORUS DERIVATIVES XII*. AN UNUSUAL CYCLOPENTADIENYLMOLYBDENUM CARBONYL DERIVATIVE OF *trans*-1,2-BIS(DIPHENYLPHOSPHINO)ETHYLENE

R. B. KING** AND PRAMESH N. KAPOOR***
Department of Chemistry, University of Georgia, Athens, Georgia 30601 (U.S.A.)

(Received May 5th, 1969)

Recently a variety of metal complexes of the unsaturated ditertiary phosphine *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ have been prepared[1-5]. In all of these complexes only the phosphorus atoms are bonded to the metal atom leaving the carbon–carbon double bond not bonded to a metal atom. This note describes a novel cyclopentadienylmolybdenum carbonyl complex of the isomeric *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ in which the carbon–carbon double bond as well as the two phosphorus atoms are bonded to metal atoms.

EXPERIMENTAL

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. A nitrogen atmosphere was always provided for the following three operations: (*a*) carrying out reactions, (*b*) handling all filtered solutions of metal complexes, and (*c*) admitting to evacuated vessels. Ultraviolet irradiations were carried out with a water-jacketed Englehard–Hanovia 450 watt mercury lamp immersed into the center of the reaction mixture. The starting materials *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ (tPf=Pf)[6], $[C_5H_5Mo(CO)_3]_2$[7], $CH_3Mo(CO)_3C_5H_5$[8], $C_6H_5CH_2Mo(CO)_3C_5H_5$[9], and (tPf=Pf) $[Mo(CO)_2(COCH_3)(C_5H_5)]_2$[5] were prepared by previously published procedures.

Preparation of (*tPf=Pf*)$Mo_2(CO)_3(C_5H_5)_2$

(*a*). *From* $[C_5H_5Mo(CO)_3]_2$. A mixture of 1.0 g (2.04 mmoles) of $[C_5H_5Mo(CO)_3]_2$, 1.64 g (4.14 mmoles) of *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$, and 300 ml of benzene was exposed to ultraviolet irradiation for 24 h. Solvent was then removed at ~40°/25 mm to give a brown solid. A hexane solution of this solid was chromatographed on a 2 × 50 cm alumina column. A yellow band followed by a red band was

---

[*] For Part XI see ref. 1.

[**] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

[***] Post-doctoral Research Associate.

observed. Both bands were eluted with hexane containing dichloromethane. The eluate from the first (yellow) band contained mainly the unchanged ditertiary phosphine ligand. Evaporation of the eluate from the second (red) band gave 0.4 g (24% yield) of red crystalline (tPf=Pf)$Mo_2(CO)_3(C_5H_5)_2$, m.p. 210° (dec.).

(*b*). *From the alkyls* $RMo(CO)_3C_5H_5$ *(R = methyl or benzyl).* These preparations of (tPf=Pf)$Mo_2(CO)_3(C_5H_5)_2$ were carried out as described above but using the alkyls $RMo(CO)_3C_5H_5$ instead of $[C_5H_5Mo(CO)_3]_2$. From a mixture of 2 g (7.7 mmoles) of $CH_3Mo(CO)_3C_5H_5$ and 1.5 g (3.8 mmoles) of tPf=Pf was obtained 0.6 g (20% yield) of (tPf=Pf)$Mo_2(CO)_3(C_5H_5)_2$. Similarly from a mixture of 0.8 g (2.38 mmoles) of $C_6H_5CH_2Mo(CO)_3C_5H_5$ and 0.94 g (2.37 mmoles) of tPf=Pf was obtained 0.2 g (21% yield) of (tPf=Pf)$Mo_2(CO)_3(C_5H_5)_2$.

(*c*). *From (tPf=Pf)*$[Mo(CO)_2(COCH_3)(C_5H_5)]_2$. A suspension of 0.9 g (0.98 mmoles) of (tPf=Pf)$[Mo(CO)_2(COCH_3)(C_5H_5)]_2$ in 400 ml of benzene was exposed to ultraviolet light for 24 h to give a brown solution. Solvent was removed from this solution at ~40°/30 mm. A solution of the brown residue in dichloromethane was chromatographed on a 2 × 50 cm alumina column. The red band was eluted with hexane containing dichloromethane. Evaporation of the eluate at ~25°/40 mm gave 0.15 g (19% yield) of red crystalline (tPf=Pf)$Mo_2(CO)_3(C_5H_5)_2$, m.p. 204° (dec.).

Properties of (tPf=Pf)$Mo_2(CO)_3(C_5H_5)_2$

Analyses. Calcd. for (tPf=Pf)$Mo_2(CO)_4(C_5H_5)_2$ (*i.e.*, $C_{40}H_{32}O_4P_2Mo_2$): C, 57.8; H, 3.9; O, 7.7; P, 7.5; Mo, 23.1%; mol. wt., 830. Calcd. for (tPf=Pf)$Mo_2(CO)_3(C_5H_5)_2$ (*i.e.*, $C_{39}H_{32}O_3P_2Mo_2$): C, 58.3; H, 4.0; O, 6.0; P, 7.7; Mo, 23.9%; mol. wt., 802. Product from $[C_5H_5Mo(CO)_3]_2$ and tPf=Pf, found: C, 59.0; H, 4.2; O, 6.4; P, 7.5%. Product from $CH_3Mo(CO)_3C_5H_5$ and tPf=Pf, found: C, 58.1; H, 4.1; O, 6.7; P, 7.0%; mol. wt., 939 (osmometer in benzene by Schwarzkopf Microanalytical Laboratory, Woodside, New York).

*Infrared spectrum**. The positions of the ν(CO) frequencies exhibited a marked dependence on the medium as follows:

KBr pellet: 1908 (s), 1862 (s), and 1797 (s) cm^{-1}
Nujol mull: 1911 (s), 1901 (m), 1867 (s), and 1806 (s) cm^{-1}
Cyclohexane solution: 1916 (s), 1875 (m), and 1836 (m) cm^{-1}
Dichloromethane solution: 1984 (s) and 1906 (m) cm^{-1}

The infrared spectrum in the 1700–650 cm^{-1} region (KBr pellet) exhibited the following bands: 1477 (w), 1432 (m), 1417 (vw), 1300 (vw), 1256 (vvw), 1176 (vw), 1149 (vw), 1118 (vw), 1098 (w), 1086 (w), 1061 (vw), 1053 (vvw, sh), 1018 (vw), 1005 (vvw), 993 (vw), 844 (vvw), 808 (w), 792 (m), 779 (vw), 738 (w), 731 (w), 703 (w), 688 (m), and 677 (w) cm^{-1}.

Proton NMR spectrum. Resonances at τ 2.3–2.8 (broad and complex, peaks at τ 2.6 and 2.78), τ 5.40 (singlet), and τ 5.57 (doublet, $J = 2$ Hz) of approximate relative intensities 22/5/5 arising from the 22 aromatic and olefinic protons, the five protons of the one of the non-equivalent π-cyclopentadienyl rings, and the five protons of the other π-cyclopentadienyl ring, respectively.

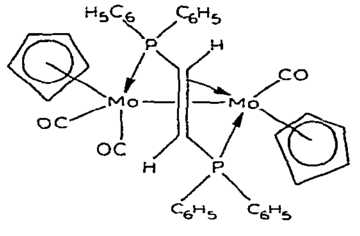
---

* These spectra were run on a Perkin-Elmer Model 621 spectrometer with grating optics.

DISCUSSION

The complex (tPf=Pf)$Mo_2(CO)_3(C_5H_5)_2$ is a red crystalline air-stable solid. Direct oxygen analyses on samples prepared by two different methods support the presence of only three carbonyl groups for two molybdenum atoms rather than four carbonyl groups for two molybdenum atoms. The infrared spectrum of this complex exhibits three ν(CO) frequencies in cyclohexane, a Nujol mull*, or a potassium bromide pellet as expected for a tricarbonyl derivative with no particular symmetry. None of these ν(CO) frequencies is in the region expected for bridging carbonyl groups. The proton NMR spectrum of this complex besides indicating diamagnetism exhibits two π-cyclopentadienyl resonances indicating the environments of the two molybdenum atoms to be different as would necessarily be the case with a dimolybdenum tricarbonyl derivative without bridging carbonyl groups. The NMR resonance for the twenty phenyl protons in (tPf=Pf)$Mo_2(CO)_3(C_5H_5)_2$ is also observed but the resonance due to the two olefinic protons in this complex could not be observed either due to insufficient signal-to-noise ratio or to being lost in the phenyl resonance.

The available data on (tPf=Pf)$Mo_2(CO)_3(C_5H_5)_2$ suggest structure (I) for this complex. In this structure the carbon–carbon double bond of the unsaturated ditertiary phosphine is bonded to one of the metal atoms. This unusual structural feature is necessary in order to give both metal atoms the rare gas configuration**. In most cases carbon–carbon double bonds of unsaturated phosphines do not bond to metal atoms. However, a precedent for bonding between a carbon–carbon double bond of an unsaturated tertiary phosphine and a metal atom exists in the complex $(C_8H_8P\text{-}C_6H_5)_2Mo(CO)_3$[11], which, like in (tPf=Pf)$Mo_2(CO)_3(C_5H_5)_2$, has the carbon–carbon double bond especially well positioned for bonding to the metal atom.



(I)

Ultraviolet irradiation of *cis*-$(C_6H_6)_2PCH{=}CHP(C_6H_5)_2$(cPf=Pf) with the benzyl derivative $C_6H_5CH_2Mo(CO)_3C_5H_5$ in benzene solution did not give (I) but instead gave a 5% yield of *cis*-(cPf=Pf)$_2$Mo(CO)$_2$ identical to material prepared by previously[5] reported methods. This supports the assumption above that *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ did not isomerize to the *cis* isomer in its photochemical reaction with cyclopentadienylmolybdenum carbonyl derivatives to give (tPf=Pf)-

---

* The splitting of the highest ν(CO) frequency in the Nujol mull spectrum probably arises from a solid state effect.

** It is not possible to draw structures with molybdenum–molybdenum double or triple bonds (*i.e.* $[(CH_3)_5C_5Mo(CO)_2]_2$[10] and give both metal atoms the favored rare gas configuration without having bridging carbonyl groups which would be in disagreement with the infrared data.

$Mo_2(CO)_3(C_5H_5)_2$ and that therefore the unsaturated phosphine ligand in (I) is still the *trans*-isomer.

ACKNOWLEDGEMENT

We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-68-1435. We are also indebted to the Alfred P. Sloan Foundation for the support of one of us (P.N.K.) during the period of this project.

REFERENCES

1 R. B. King and A. Efraty, *Inorg. Chem.*, in press.
2 H. N. Ramaswamy, H. B. Jonassen and A. M. Aguiar, *Inorg. Chim. Acta*, 1 (1967) 141.
3 R. B. King and C. A. Eggers, *Inorg. Chim. Acta*, 2 (1968) 33.
4 R. B. King, L. W. Houk and K. H. Pannell, *Inorg. Chem.*, 8 (1969) 1042.
5 R. B. King, L. W. Houk and P. N. Kapoor, *Inorg. Chem.*, 8 (1969) in press.
6 A. M. Aguiar and D. Daigle, *J. Amer. Chem. Soc.*, 86 (1964) 2299.
7 R. G. Hayter, *Inorg. Chem.*, 2 (1963) 1031; R. B. King, *Organometal. Syn.*, 1 (1965) 109.
8 T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3 (1956) 104.
9 R. B. King and A. Fronzaglia, *J. Amer. Chem. Soc.*, 88 (1966) 709.
10 R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, 8 (1967) 287.
11 R. B. King and K. H. Pannell, *Inorg. Chem.*, 7 (1968) 273.