Inorganica Chimica Acta, *97* (1985) L25–L26

Structure of (η^4-Ph_4C_4CO)(CO)$_3$Ru – a Catalyst Precursor in H-Transfer and Dehydrogenation Reactions of Alcohols

YIGAL BLUM, YOUVAL SHVO*

Department of Chemistry, Tel-Aviv University, 69 978 Tel-Aviv, Israel

and DANIEL F. CHODOSH

Analytical, Physical and Structural Chemistry Department, Smith, Kline and French Laboratories, 1500 Spring Garden Street, Philadelphia, Pa. 19101, U.S.A.

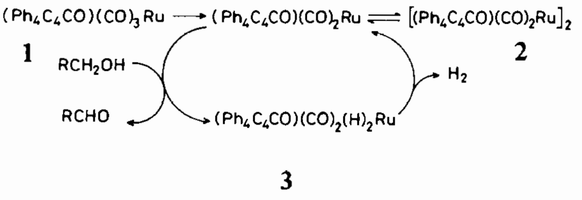
Received September 4, 1984

An X-ray single-crystal study of the title compound confirmed the four-hapto nature of the cyclopentadienone ligand, which shows no bond alternation in the diene system. A twist of 18.7° of the ring carbonyl with respect to the diene plane was observed.

Cyclopentadienone (CPD)–transition metal complexes constitute a group of well-documented organometallic compounds. The most abundant complexes are those with group 8 metals, specifically Fe [1–4], Ru [5], Co [6] and Rh [6]. Our interest in this group stems from our recent discovery that (η^4-Ph_4C_4CO)(CO)$_3$Ru (**1**) functions as a catalyst precursor in hydrogen transfer [7] and dehydrogenation [8] reactions of alcohols to esters (eqn. 1). It has been established [9] that aldehyde is an intermediate in reaction (1). A catalytic cycle (Scheme 1), describing

$$2RCH_2OH \xrightarrow{1} RCO_2CH_2R + H_2\uparrow \qquad (1)$$

the dehydrogenation of alcohols to aldehydes, the first step in reaction (1), has been recently proposed [8]. Complex **2** was isolated and characterized while **3** was observed by IR and NMR.



Scheme 1.

Since complex **1** is the immediate catalyst precursor in the above cycle, the detailed knowledge of its molecular structure is important. Within the iron triad, X-ray structures of CPD–Metal complexes are available only for iron [1–3]. Complex (**1**) was prepared according to a literature procedure [5] and crystals suitable for diffraction analysis were obtained by recrystallization from CH_2Cl_2/petroleum ether. The crystal used for the X-ray work was mounted with epoxy on the end of a thin glass fiber.

Crystal Data

$C_{32}H_{20}Ru_1O_4$, M = 569.58, monoclinic, a = 16.014(2), b = 10.067(2), c = 15.815(2) Å, β = 96.15(1)°, space group $P2_1/n$ (special setting of No. 14), Z = 4, D_c = 1.492 g cm^{-3}, V = 2534.8 Å^3 (at 298 K), μ(Mo Kα) = 6.4 cm^{-1}, λ(Mo-Kα) = 0.71069 Å. Crystal size 0.35 × 0.25 × 0.35 mm. X-ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using an ω-2θ scan technique ($d\omega/d\theta$ = 1.0) with graphite monochromated Mo Kα radiation. A total of 6353 reflections were measured (excluding standards) in the range $2° < 2\theta < 55°$. The data were corrected for Lorentz-polarization effects, isotropic decay (3.5% maximum loss of intensity of standard reflections) and an empirical absorption correction (based on psi scans of nine reflections with $80° < \chi < 90°$) was applied. 3867 unique observations were deemed observed ($I > 3\sigma(I)$) after averaging of equivalent reflections. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares treatment (SDP program library[†]) to converge with R = 0.033 and R' = 0.041 for all reflections. In the final cycle there were 37 atoms (anisotropic), 20 hydrogens (isotropic), 414 variables and 3867 observations[††].

A view of the molecule (CPD phenyl groups omitted for clarity) is shown in Fig. 1. The coordination environment of the Ru is comprised of three terminally coordinated carbonyl ligands and a tetrahapto-tetraphenylcyclopentadienone (CPD) ligand. The CPD–Ru bonding distances (average, 2.220(3) Å) contrast with the non-bonding interaction of the CPD carbonyl carbon (C4) with the metal (2.530(3) Å). C4 and O4 (CPD carbonyl atoms) are displaced 0.33 Å and 0.68 Å respectively from the best least-squares plane calculated for the η^4-CPD carbons (χ^2 = 10) exo with respect to the metal. Intra-ring

---

*Author to whom correspondence should be addressed.

[†] All programs used for structure solution and refinement were from the Enraf-Nonius Structure Determination Package, Enraf-Nonius Service Corporation, Bohemia, N.Y., U.S.A.

[††] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication.

0020-1693/85/$3.30

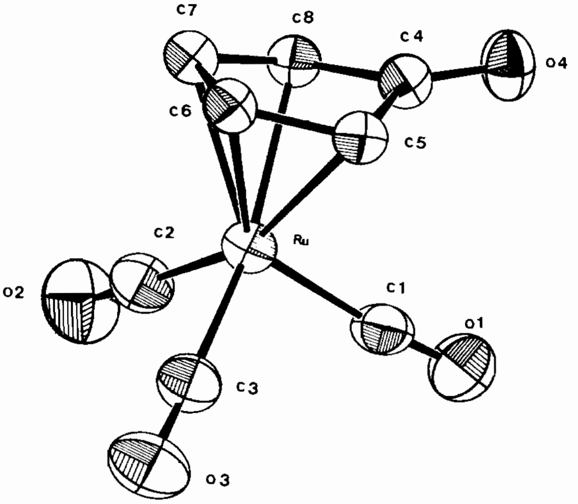


Fig. 1. An ORTEP diagram of **1**; phenyl groups omitted for clarity. Bond lengths are: Ru–C1 = 1.953(4), Ru–C2 = 1.926(4), Ru–C3 = 1.911(3), Ru–C5 = 2.240(3), Ru–C6 = 2.209(3), Ru–C7 = 2.216(3), Ru–C8 = 2.216(3), O1–C1 = 1.119(4), O2–C2 = 1.132(4), O3–C3 = 1.138(4), O4–C4 = 1.224(4), C4–C5 = 1.491(4), C4–C8 = 1.485(4), C5–C6 = 1.438(4), C6–C7 = 1.437(4), C7–C8 = 1.455(4).

distances involving phenyl-substituted metal bonded carbons range from 1.437(4) Å to 1.455(4) Å, in contrast with intra-ring distances involving C4 (1.491(4) Å, 1.485(4) Å).

The structural data clearly indicate no bond alternation in the diene system of the CPD ring of **1**. The lack of such bond's alternation is indicative of back donation from the occupied metal d-orbitals to the LUMO of the diene. A variable degree of bond alternation was encounted in CPD–Fe crystal structures [1–3].

Examination of the C≡O infra red stretching region of **1** (2081, 2026, 2005 cm^{-1}) and of (η^4-$Ph_4C_4CO)(CO)_3Fe$ (2060, 2015, 1988 cm^{-1}) reveals a shift to higher frequencies in passing from the Fe to the Ru complex. Such a shift also supports a higher degree of back donation Metal → CPD in **1** relative to the analogous Fe complex. Substitution of Fe by Ru in a CPD complex should augment back donation as the d-electrons in the latter are less stable than those in the former. For a similar reason Ru has a greater tendency than Fe to be oxidized from the d^8 configuration (in **1**) to the d^6 configuration (in **3**) (Scheme 1). This was shown experimentally as (η^4-$Ph_4C_4CO)(CO)_3Fe$ is much less reactive than **1** in reaction (1).

It was also noted that the ring carbonyl (C4–O4) is twisted (18.7°) from the 1,4-diene plane. Similar deviations, 19.9° and 20.1°, were observed in the crystal structures of (η^4-$C_4H_4CO)(CO)_3Fe$ [1] and (η^4-$(CF_3)_4C_4CO)(CO)_3Fe$ [3] respectively. Such a lack of coplanarity was predicated from HMO consideration which shows no interaction between the ring carbonyl and the d_{xz}-orbital of the metal.

Finally, we noted that the CPD carbonyl approximately eclipses one of the terminally coordinated carbonyl ligands, as evidenced by the 7.0° dihedral angle formed between the best least-squares planes calculated for Ru–C4–O4 and Ru–C1–O1. The steric effects introduced by this conformation are evidenced by the lengthening of the Ru–C1 bond (1.952(4) Å) with concomitant shortening of the C1–O1 bond (1.119(4) Å). This eclipsing carbonyl should therefore be more susceptible to thermal as well as photochemical dissociation, a step required for the initiation of the catalytic cycle (Scheme 1), provided of course that the solid state geometry is retained in solution.

Acknowledgements

The authors thank the Basic Research Fund of Tel-Aviv University for partial financial support and Johnson Matthey Chemicals Ltd. for a loan of ruthenium trichloride.

References

1 K. Hoffmann and E. Weiss, *J. Organomet. Chem., 128,* 237 (1977).
2 G. C. Cash and R. C. Pettersen, *Inorg. Chem., 17,* 650 (1978).
3 N. A. Bailey and R. Mason, *Acta Crystallogr., 21,* 652 (1966).
4 E. Weiss, R. Merenyi and W. Hubel, *Chem. Ber., 95,* 1170 (1962).
5 M. I. Bruce and J. R. Knight, *J. Organomet. Chem., 12,* 411 (1968) and refs. therein.
6 A. P. Corrigan and R. S. Dickson, *Aust. J. Chem., 34,* 1401 (1981) and refs. therein.
7 Y. Blum and Y. Shvo, *Isr. J. Chem., 24,* 144 (1984).
8 Y. Blum and Y. Shvo, submitted for publication.
9 Y. Blum and Y. Shvo, *J. Organomet. Chem., 263,* 93 (1984).