The Disruption of Furan by Bis(triphenylphosphine)rhenium Heptahydride: Synthesis and Crystal Structure of the 1-Oxapentadienyl Complex Re(η^5-C_4H_5O)(PPh_3)$_2$(CO)

Denise Baudry,*[a] Jean-Claude Daran,[b] Yves Dromzee,[b] Michel Ephritikhine,*[a] Hugh Felkin,[a] Yves Jeannin,*[b] and Janusz Zakrzewski[a]

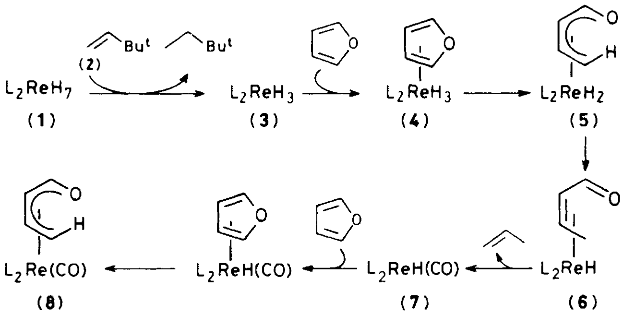
[a] *Institut de Chimie des Substances Naturelles, C.N.R.S., 91190 Gif-sur-Yvette, France*

[b] *Laboratoire de Chimie des Métaux de Transition, Université de Paris VI, 4 Place Jussieu, 75230 Paris Cedex, France*

Reaction of furan with $(Ph_3P)_2ReH_7$ and 3,3-dimethylbutene yields the 1-oxapentadienyl complex Re(η^5-C_4H_5O) $(PPh_3)_2(CO)$, the *X*-ray crystal structure of which has been determined.

The rhenium heptahydride (**1**) reacts with a variety of organic molecules. With dienes, it leads to the formation of trihydrido-diene complexes,[1] and, in the presence of the olefin (**2**) as a hydrogen acceptor, it reacts with benzene derivatives to give dihydrido-cyclohexadienyl products.[2] Moreover, the same system (**1**) + (**2**) also activates saturated hydrocarbons.[3]

We thought that it would be interesting to look at the reaction of (**1**) and (**2**) with furan, especially because, to our knowledge, no π-organotransition-metal complex arising from this molecule has yet been described.[4] We have found that this reaction unexpectedly gives the 1-oxapentadienyl (4-oxobut-2-enyl) complex (**8**). 1-Oxapentadienyl complexes are rare, and none has been characterised by *X*-ray analysis. The few examples so far reported have been obtained from the reactions of manganese or iridium complexes[5] with α,β-unsaturated ketones, or from the rearrangement of acyl-substituted η^3-allyl manganese complexes.[6] Here we describe the preparation and the *X*-ray crystal structure of compound (**8**).



Scheme 1. Postulated route for the formation of the oxapentadienyl complex (**8**). L = Ph_3P.

The heptahydride (**1**) (300 mg) and the olefin (**2**) (0.54 ml) were refluxed with furan (0.31 ml) in cyclohexane or, better,

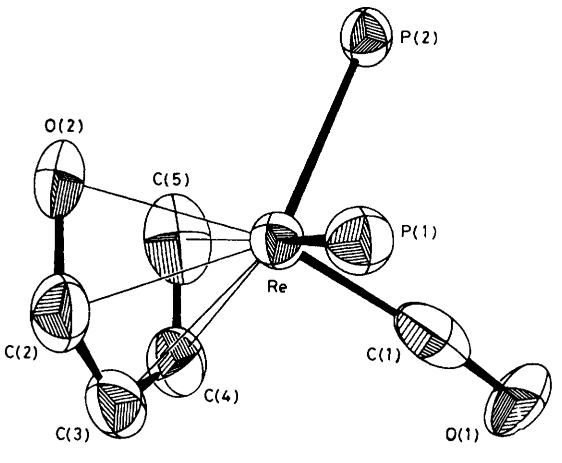


Figure 1. The *X*-ray crystal structure of (**8**). The phenyl groups bonded to P(1) and P(2) have been omitted for clarity. Some important geometrical parameters: Re–P(1) 2.398(3), Re–P(2) 2.388(3), Re–C(1) 1.89(2), Re–O(2) 2.23(1), Re–C(3) 2.29(1), Re–C(4) 2.21(1), Re–C(5) 2.22(1), O(2)–C(2) 1.30(1), C(2)–C(3) = C(3)–C(4) = C(4)–C(5) = 1.40(2) Å; ∠O(2)–C(2)–C(3) 121(1), C(2)–C(3)–C(4) 124(1), C(3)–C(4)–C(5) 122(1), P(2)–Re–P(1) 100.2(1), P(1)–Re–C(1) 88.2(4), P(2)–Re–C(1) 93.5(4), P(2)–Re–C(5) 85.7(4), P(1)–Re–O(2) 93.7(2)°. The distance between the Re atom and the 1-oxapentadienyl ligand plane is 1.70 Å.

tetrahydrofuran (5 ml) for 10 min. The 1-oxapentadienyl complex (**8**) was purified by chromatography (Al_2O_3) and recrystallisation (acetone–dichloromethane), and isolated in 55% yield as air-stable yellow crystals. 2,2-Dimethylbutane, propene, and propane were also formed in the reaction. The n.m.r. spectra of (**8**) showed five inequivalent hydrogen atoms linked to the four different carbon atoms of the oxapentadienyl ligand.†

Crystals of (**8**) suitable for *X*-ray structural analysis were obtained from layered hexane–dichloromethane and the structure is shown in Figure 1.‡ The configuration of the molecule is of the 'piano stool' type; the 1-oxapentadienyl ligand is planar and the C–C bond lengths are all equal (1.40 Å).

Two furan rings are opened during the formation of (**8**); one is transformed into propene and the carbonyl ligand in (**8**), and the other is found as the oxapentadienyl ligand. The reaction is stereospecific; experiments with [2-^{2}H]furan indicate that the 'extra' hydrogen atom in the product (**8**) is in the *anti* position, as shown. These facts can be accounted for by the reaction sequence illustrated in Scheme 1, in which the 14e species (**3**) [which we also assume to be the active intermediate in the reactions of (**1**) with other organic molecules[1–3]] combines with furan to form the complex (**4**). Stereospecific intramolecular hydrogen transfer and ring opening then lead to the oxapentadienyl dihydride (**5**). A second hydrogen migration gives the complex of crotonaldehyde (**6**) which is decarbonylated to give propene and the hydrido carbonyl intermediate (**7**).§ The reaction of (**7**) with a second molecule of furan, by the same sequence as (**3**) → (**5**), gives the product (**8**).

The rhenium complex (**8**) is, to our knowledge, the first organotransition-metal compound isolated from a reaction with furan¶ and the first example of a complex containing an unsubstituted 1-oxapentadienyl ligand.

Received, 25th April 1983; Com. 512

References

1 D. Baudry, M. Ephritikhine, and H. Felkin, *J. Organomet. Chem.*, 1982, **224**, 363.

2 D. Baudry, M. Ephritikhine, H. Felkin, Y. Jeannin, and F. Robert, *J. Organomet. Chem.*, 1981, **220**, C7.

3 D. Baudry, M. Ephritikhine, H. Felkin, and J. Zakrzewski, *J. Chem. Soc., Chem. Commun.*, 1982, 1235, and references cited therein.

4 F. M. Dean, *Adv. Heterocycl. Chem.*, 1982, **30**, 167; K. H. Pannell, B. L. Kalsotra, and C. Párkányi, *J. Heterocycl. Chem.*, 1978, **15**, 1057.

5 R. L. Bennett and M. I. Bruce, *Aust. J. Chem.*, 1975, **28**, 1141; C. White, S. J. Thompson, and P. M. Maitlis, *J. Organomet. Chem.*, 1977, **134**, 319.

6 W. D. Bannister, M. Green, and R. N. Haszeldine, *J. Chem. Soc (A)*, 1966, 194; M. Green and R. I. Hancock, *ibid.*, 1968, 109.

---

† Satisfactory elemental analyses have been obtained for complex (**8**) (C, H, P). Selected spectral data: i.r.(Nujol) ν(CO): 1820 cm^{-1}; ^{1}H n.m.r. at 400 MHz δ(C_6D_6): 6.32 [s, H(2)], 5.09 [m, H(4)], 4.99 [d, *J*{H(3)H(4)} 6 Hz, H(3)], 3.12 [m, *J*{H(5*syn*)H(4)} 8 Hz, H(5*syn*)], and 2.18 [dt, *J*{H(5*anti*)H(4)} 12 Hz, *J*{H(5*anti*)P} 2 Hz, H(5*anti*)]; ^{13}C n.m.r. δ(CD_2Cl_2): 200.9 [C(1)], 138.2 [C(2)], 86.5 and 83.7 [C(3) and C(4)], and 56.6 p.p.m. [C(5)]. Numbering of atoms is as in Figure 1.

‡ *Crystal data for* (**8**): $C_{41}H_{35}P_2O_2Re$, monoclinic, space group $P2_1/c$, $a = 9.669(6)$, $b = 15.61(2)$, $c = 22.89(2)$ Å, $\beta = 102.39(4)°$, $U = 3375(5)$ Å^3, $Z = 4$, $D_c = 1.59$ g cm^{-3}, $I > 3\sigma(I)$, $\mu = 37.42$ cm^{-1}, $3 < 2\theta < 46°$. Final R 0.0546 and R_w 0.0514 for 3686 reflections (Mo-K_α radiation). The atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ As propane is also found in the reaction mixture, propene seems to be in competition with (**2**) for the dehydrogenation of (**1**).

¶ Recently, complexes containing 2-pyrone and vinylcarbene ligands have been prepared from 2-alkoxyfurans (T. Mitsudo, Y. Ogino, Y. Komiya, H. Watanabe, and Y. Watanabe, *J. Chem. Soc., Chem. Commun.*, 1982, 962).