A New Cobalt Complex Containing η^3- and η^2-Bonded Diallyl Ether: Synthesis and *X*-Ray Crystal Structure of $[Co(CH_2CHCH_2OCHCHCH_2)(PPh_3)_2]$

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The reaction of $CoH(N_2)(PPh_3)_3$ with diallyl ether in toluene yields $[Co(CH_2CHCH_2OCHCHCH_2)(PPh_3)_2]$, which has been shown by a single crystal *X*-ray study to contain the $CH_2CHCH_2OCHCHCH_2$ group as a bidentate ligand linked to the cobalt atom *via* η^3- and η^2-bonds.

Recently we have reported that various low-valent transition metal complexes such as Ni^0L_n and RuH_2L_4 react with esters and ethers with selective cleavage of the C–O bond.[1] We now report the selective cleavage of the C–O bond of diallyl ether by $CoH(N_2)(PPh_3)_3$, (**1**), followed by a further reaction involving C–H bond scission of another diallyl ether to give the title compound (**2**).

Diallyl ether was added to (**1**) in toluene to give complex (**2**) with liberation of equimolar amounts of nitrogen, propene, and allyl alcohol per mole of Co. The air-sensitive complex (**2**) was recrystallized from a mixture of tetrahydrofuran and diethyl ether, yield 74%, m.p. 140 °C (decomp.) (satisfactory analytical data were obtained). The i.r. spectrum of (**2**) shows a ν(C–O) band at 1080 cm^{-1}. The $^{31}P\{^1H\}$ n.m.r. spectrum of (**2**) in $[^2H_8]$toluene at −78 °C shows two doublets at 56.6 and 62.9 p.p.m. (downfield from external PPh_3) with a coupling constant of 24.4 Hz, indicating the non-equivalence of the two PPh_3 ligands. Nine different broad resonances due to the diallyl ether moiety were observed in the ^1H n.m.r. spectrum of (**2**) in $[^2H_8]$toluene at −40 °C (1H each at δ 4.76, 4.48, 4.35, 4.19, 3.02, 2.30, 1.42, 1.21, and 0.86). A yellowish brown crystal of approximate dimensions 0.4 × 0.4 × 0.6 mm^3 was mounted in a glass capillary under an argon atmosphere.

$CoH(N_2)(PPh_3)_3$
(**1**)

$[Co(CH_2CHCH_2OCHCHCH_2)(PPh_3)_2]$
(**2**)

Crystal data: $C_{42}H_{39}CoOP_2$, $M = 680.7$, monoclinic, space group $P2_1/n$, $a = 13.339(2)$, $b = 18.038(2)$, $c = 14.599(2)$ Å, $\beta = 93.91(2)°$, $Z = 4$, $D_c = 1.29$ g cm^{-3}, Mo-K_α radiation. 4290 Structure factors with $F_o > 3\sigma(F_o)$ were derived from 5511 intensities collected using a SYNTEX-R3 diffractometer. The structure was solved by the heavy atom method and refined by block-diagonal least-squares to an *R* value of 0.046 ($R_w = 0.067$), with Co, P, O, and C anisotropic and H atoms in calculated positions.†

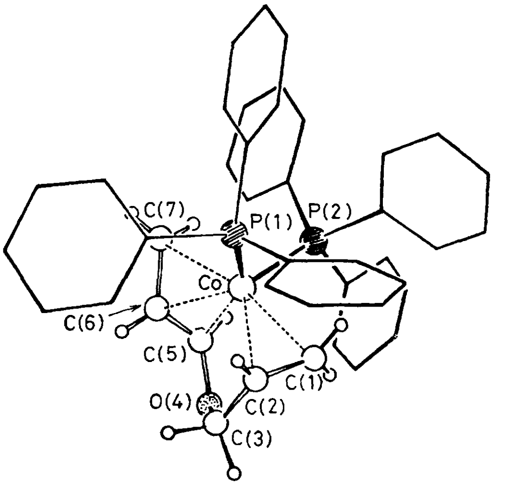
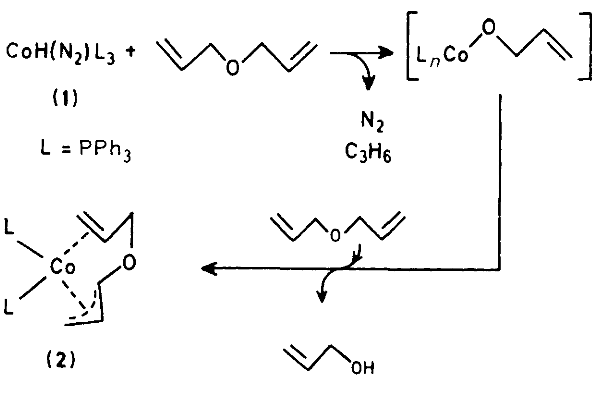


Figure 1. A perspective drawing of complex (**2**) $[Co(CH_2CHCH_2$-$OCHCHCH_2)(PPh_3)_2]$. Important bond lengths (Å) and angles (°) are: Co–P(1) 2.213(1), Co–P(2) 2.222(1), P(1)–Co–P(2) 109.2(2), Co–C(1) 2.059(5), Co–C(2) 2.050(5), Co–C(3) 2.919(5), Co–O(4) 2.888(4), Co–C(5) 2.026(5), Co–C(6) 1.981(5), Co–C(7) 2.088(5). Bond lengths and angles in the ligand are: C(1)–C(2) 1.384(6), C(2)–C(3) 1.511(7), C(3)–O(4) 1.437(6), O(4)–C(5) 1.395(6), C(5)–C(6) 1.411(6), C(6)–C(7) 1.397(7), C(1)–C(2)–C(3) 120.5(4), C(2)–C(3)–O(4) 111.0(3), C(3)–O(4)–C(5) 111.1(3), O(4)–C(5)–C(6) 120.8(4), C(5)–C(6)–C(7) 116.3(4).



Scheme 1. Proposed reaction scheme.

The structure of the complex is shown in Figure 1. The cobalt atom is co-ordinated by the two phosphorus atoms of

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† 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. Any request should be accompanied by the full literature citation for this communication.

All computations were carried out using the UNICS programs of The Crystallographic Society of Japan with a slight modification on a HITAC-M-180 computer at the Hiroshima University Information Processing Centre.

the phosphine ligands and by the five carbon atoms of the 1-2-η:5-7-η-4-oxahepta-1,5-dien-5-yl ligand in a distorted tetrahedral environment. The co-ordination geometry of the $C_3H_5OC_3H_4$ ligand resembles that of the C_8H_{13} ligand in $Co(C_8H_{13})(C_4H_6)$ which acts as a 1-2-η:5-7-η type bidentate ligand.[2] However, the geometry in the present system is quite different from the reported structure of (but-2-enyl 1-methylallyl ether)pentane-2,4-dionatorhodium(I) in which the diallyl ether moiety co-ordinates to the Rh^I by the four carbon atoms on either side of the two double bonds and makes a square planar configuration with the two oxygen atoms of the pentane-2,4-dionato group.[3]

From the chemical evidence and the molecular structure obtained, a reasonable mechanistic scheme for this reaction has been deduced and is given in Scheme 1. The proposed stepwise mechanism has been further supported by the facile formation of an aryloxo complex, $Co(OPh)L_3$, with liberation of propene on the interaction of (**1**) with allyl phenyl ether.[4]

Received, 20th April 1983; Com. 489

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