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The Chemistry of (1—2:5—6-η-Cyclo-octa-1,5-diene)(1—6-η-cyclo-octa-1,3,5-triene)ruthenium(0): Preparation and *X*-Ray Crystal Structure of (1—2:5—6-η-Cyclo-octa-1,5-diene)(1—4-η-cyclo-octa-1,3,5-triene)(trimethyl phosphite)ruthenium(0)†

Paolo Pertici and Giovanni Vitulli *
Centro C.N.R. per le Macromolecole Stereordinate ed Otticamente Attive, Istituto di Chimica Organica, Università di Pisa, 56100 Pisa, Italy
William Porzio and Marcello Zocchi
Istituto di Chimica delle Macromolecole del C.N.R., Via A. Corti 12, 20133 Milan, Italy and Istituto di Chimica Industriale del Politecnico, Sezione di Strutturistica, Piazza Leonardo da Vinci 32, 20133 Milan, Italy
Pier Luigi Barili
Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa, 56100 Pisa, Italy
Giulio Deganello
Istituto di Chimica Generale, Facoltà di Scienze, Via Archirafi 26, Università di Palermo, Italy

The reaction of (1—2:5—6-η-cyclo-octa-1,5-diene)(1—6-η-cyclo-octa-1,3,5-triene)ruthenium with $P(OMe)_3$ yielded the title compound which has been structurally characterized by *X*-ray diffraction studies. The complex crystallizes in the monoclinic space group $P2_1/n$ with unit-cell dimensions a = 13.306(5), b = 9.628(3), c = 16.382(20) Å, β = 111.62(6)°, and Z = 4. The co-ordination geometry around the ruthenium is a distorted square pyramid whose vertices are occupied by the phosphite ligand, the butadiene moiety of cyclo-octatriene, and the two double bonds of cyclo-octadiene.

The complex (1—2:5—6-η-cyclo-octa-1,5-diene)(1—6-η-cyclo-octa-1,3,5-triene)ruthenium(0), $[Ru(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})]$ (1), is a very useful compound in preparative chemistry as well as in catalysis.[1] It appears that η^6 tridentate bonding is tenuous since Ru^0 species containing bidentate $\eta^4\text{-}C_8H_{10}$ are readily formed at room temperature in the presence of carbon monoxide.[2] The tendency for C_8H_{10} to give bidentate co-ordination is of interest and may also play an active role in determining catalytic activity, at least under mild conditions, by allowing the reagent involved to gain access to the metal centre. The isolation of samples of η^4-bonded C_8H_{10} compounds, however, has proved difficult.[3] We have investigated the reaction of (1) with stoicheiometric amounts of phosphorus ligands and we report herein the preparation and the *X*-ray crystal structure of (1—2:5—6-η-cyclo-octa-1,5-diene)(1—4-η-cyclo-octa-1,3,5-triene)(trimethyl phosphite)ruthenium(0), $[Ru(\eta^4\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})\{P(OMe)_3\}]$ (2).

Experimental

All manipulations were carried out under rigorously oxygen-free conditions. Trimethyl phosphite (Merck product, purity 98%) was distilled under vacuum prior to use. The complex $[Ru(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})]$ (1) was prepared as previously reported.[4] Solvents were purified by conventional methods, distilled and stored under nitrogen. Proton n.m.r. spectra were obtained with a CFT-20 Varian spectrometer and mass spectra were performed on a Varian MAT CH7 spectrometer.

Preparation of $[Ru(\eta^4\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})\{P(OMe)_3\}]$ (2).—Trimethyl phosphite (0.2 cm³, 1.53 mmol) was added to a solution of complex (1) (485 mg 1.53 mmol) in n-hexane (40 cm³). The solution was stirred at room temperature for *ca.* 6 h. Evaporation of the solvent to dryness *in vacuo* and recrystallization of the solid residue from n-pentane at −78 °C yielded (2) as light yellow crystals (0.60 g, 90%), m.p. 95 °C (Found: C, 51.2; H, 7.5%; *M*, 440. $C_{19}H_{31}O_3PRu$ requires C, 51.3; H, 7.05%; *M*, 440).

X-Ray Crystal Structure of $[Ru(\eta^4\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})\{P(OMe)_3\}]$ (2).—Light yellow crystals of (2), suitable for *X*-ray studies were obtained by slow recrystallization from n-pentane solutions.

Crystal data. $C_{19}H_{31}O_3PRu$, M = 439.5, Monoclinic, a = 13.306(5), b = 9.628(3), c = 16.382(20) Å, β = 111.62(6)°, U = 1 951.0 Å³, D_c = 1.496 g cm⁻³, Z = 4, space group $P2_1/n$, $F(000)$ = 912, $\mu(\text{Mo-}K_\alpha)$ = 8.8 cm⁻¹, λ = 710 69 Å (graphite monochromator), crystal size 0.15 × 0.20 × 0.24 mm.

Collection of data and structure solution and refinement. Intensity data were collected on a Philips PW1100 computer controlled four-circle diffractometer using the ω—2θ scan mode, scan speed 2.4° min⁻¹, scan width 0.8°, and θ in the range 3—23.25°. Reflections were measured for $k, l \geqslant 0$. Data were corrected for Lorentz and polarization but not for absorption due to the small crystal size and linear absorption coefficient. A total of 2 749 data were collected of which 1 929 with $I > 3\sigma(I)$ were considered ' observed ' and used in the refinement. The structure was solved by Patterson and Fourier methods and was refined by full-matrix least squares with anisotropic thermal parameters to a value of R = 0.098 for the conventional R factor. In a final Fourier-difference map no peak could be clearly attributed to hydrogen atoms.

Results and Discussion

The complex $[Ru(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})]$ (1) readily reacts at room temperature with $P(OMe)_3$ affording $[Ru(\eta^4\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})\{P(OMe)_3\}]$ (2) as a light yellow crystalline compound (Scheme). The complex is very air sensitive in solution and mildly so in the solid state. When pure it may be stored indefinitely at −30 °C under nitrogen. The molecular structure of (2) has been determined by *X*-ray diffraction methods. The structure consists of the packing of discrete units of [Ru(η^4-

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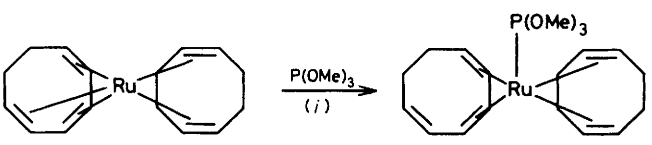
† *Supplementary data available* (No. SUP 23592, 22 pp.): structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



Scheme. (*i*) Room temperature, 6 h, $P(OMe)_3 : Ru = 1 : 1$

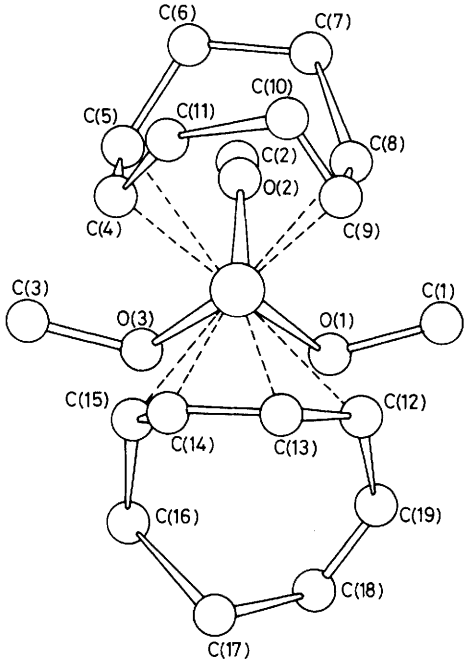


Figure. The molecular structure of $[Ru(\eta^4\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})\{P(OMe)_3\}]$ (2) viewed along the P–Ru bond

$C_8H_{10})(\eta^4\text{-}C_8H_{12})\{P(OMe)_3\}]$, showing only one contact shorter than the commonly accepted van der Waals radii [3.06(3) Å]; that between atoms O(1) and C(3) belonging to two different molecules symmetrically related by the operation $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$. In the molecule, of approximate C_s symmetry (see Figure), the co-ordination geometry around the metal can be described by a distorted square pyramid whose vertices are occupied by the phosphite ligand, the butadiene moiety of cyclo-octatriene, and the double bonds of cyclo-octadiene.

The atomic fractional co-ordinates are given in Table 1. The carbon atoms have unusually high thermal parameters, suggesting, especially in the case of the C_8H_{10} ligand, important librations and explaining the rather high *R* value (see Experimental section). Some selected bond distances, angles, and torsion angles are reported in Table 2. In cyclo-octatriene the non-co-ordinated double bond appears to be statistically distributed between C(17)–C(18) and C(18)–C(19). However, considering the already cited librations of this ligand in the complex, one may attribute this effect to a thermal motion artefact rather than to a 1,3,6-isomerization of the starting cyclo-octatriene. This type of isomerization would have no precedents, whereas isomerization of co-ordinated 1,3,6- to 1,3,5-cyclo-octatrienes has been reported to occur at 65 °C,[5] see equation (i). The ^1H n.m.r. spectrum of

$$\left.\begin{array}{l}[Fe_2(CO)_7(C_8H_{10}\text{-}1,3,6)]\\ [Fe_2(CO)_8(C_8H_{10}\text{-}1,3,6)]\end{array}\right\rangle \xrightarrow{65\ ^\circ C} [Fe_2(CO)_6(C_8H_{10}\text{-}1,3,5)] \quad (i)$$

Table 1. Atomic fractional co-ordinates (× 10^5 for Ru and P, × 10^4 for C) for complex (2) with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru	48 944(10)	14 813(14)	20 344(10)
P	32 803(35)	3 143(45)	15 727(36)
O(1)	3 251(9)	−1 333(12)	1 382(9)
O(2)	2 399(9)	904(14)	709(10)
O(3)	2 635(14)	125(14)	2 217(13)
C(1)	3 576(20)	−1 850(22)	689(17)
C(2)	1 298(15)	307(29)	339(21)
C(3)	2 344(20)	1 342(23)	2 608(19)
C(4)	4 894(16)	3 763(18)	2 197(17)
C(5)	3 837(14)	3 443(18)	1 586(15)
C(6)	3 446(16)	3 639(22)	594(16)
C(7)	3 817(18)	2 589(24)	69(15)
C(8)	4 676(10)	1 615(17)	668(14)
C(9)	5 765(15)	2 129(25)	1 201(18)
C(10)	5 981(19)	3 678(26)	1 161(20)
C(11)	5 740(17)	4 468(22)	1 842(18)
C(12)	5 989(14)	−353(22)	2 315(14)
C(13)	6 510(16)	835(22)	2 887(15)
C(14)	6 030(20)	1 655(27)	3 368(14)
C(15)	5 107(14)	1 307(22)	3 329(14)
C(16)	4 900(28)	5(37)	3 835(18)
C(17)	5 843(25)	−1 220(36)	4 105(21)
C(18)	5 786(22)	−1 951(30)	3 414(24)
C(19)	5 743(17)	−1 683(28)	2 632(19)

(2), moreover, correlates with that of the known complex $[Fe(CO)_3(1\text{—}4\text{-}\eta\text{-}C_8H_{10}\text{-}1,3,5)]$.[6]

The Ru–C distances increase from C(15) to C(12) (2.04, 2.16, 2.18, and 2.23 Å respectively) indicating a decreasing bond strength. The Ru–C(15) bond length is very significantly shorter than the other metal–C(diene) distances. To the best of our knowledge this is the shortest Ru–C(diene) distance ever observed in similar structures,[7] showing an asymmetric bond between the metal and the diene C(12)—C(15) moiety. The cyclo-octadiene ligand shows the normal tub conformation, with the two double bonds co-ordinated to the metal. The P–O and C–O distances in the phosphite ligand are comparable with those found in other phosphites[8] [mean values 1.59(1) and 1.46(2) Å respectively]. As expected on the basis of the *X*-ray structure, the i.r. spectrum of complex (2) (Nujol mull) contains a band at 1 640 cm^{-1} which is consistent with C_8H_{10} bonded as a bidentate ligand. The ^1H n.m.r. spectrum ([$^2H_8$]toluene solution) is complex showing resonances at δ 5.67 (m, 2 H), 4.75 (m, 4 H), 3.22 (d, 9 H), and 2.4—1.5 p.p.m. (m, 16 H) assigned by double resonance to unco-ordinated C_8H_{10} olefinic protons, co-ordinated C_8H_{10} olefinic protons, phosphite ligand methyl groups, and olefinic and aliphatic C_8H_{12} and aliphatic C_8H_{10} protons, respectively. The spectrum shows no line broadening up to *ca.* 60 °C, when decomposition of (2) begins. This fact does not rule out fluxional behaviour of (2), since usually higher temperatures are required for detection of a net metal 1,3-shift[9] in the similar η^4-polyolefin complexes where cyclic conjugation of the polyene system is interrupted by $-(CH_2)_n-$ groups [$\Delta G^\ddagger$ = 20—24 kcal mol^{-1} (83.7—100.4 kJ mol^{-1})]. The use of the Forsen–Hoffman technique of spin-saturation transfer has demonstrated fluxional behaviour, for instance, in the tricarbonyl(η^4-cycloheptatriene)iron complex,[10,11] while direct observation of the phenomenon by variable-temperature n.m.r. spectra was frustrated by decomposition of the complex.[9]

In the analogous carbonyl complex $[Ru(CO)(\eta^4\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{12})]$ (3), detected as an intermediate in the reaction of (1) with CO to give $[Ru(CO)_3(\eta^4\text{-}C_8H_{12})]$, a 1—2:5—6-η co-

Table 2. Selected interatomic distances (Å), angles (°), and torsion angles (°), for complex (2) with e.s.d.s in parentheses

Ru–P	2.291(5)	C(4)–C(5)	1.43(3)
Ru–C(4)	2.213(17)	C(4)–C(11)	1.60(4)
Ru–C(5)	2.307(17)	C(5)–C(6)	1.53(3)
Ru–C(8)	2.152(23)	C(6)–C(7)	1.52(4)
Ru–C(9)	2.181(29)	C(7)–C(8)	1.53(3)
Ru–C(12)	2.227(20)	C(8)–C(9)	1.47(2)
Ru–C(13)	2.179(19)	C(9)–C(10)	1.53(4)
Ru–C(14)	2.157(19)	C(10)–C(11)	1.48(4)
Ru–C(15)	2.042(19)	C(12)–C(13)	1.48(3)
P–O(1)	1.61(1)	C(12)–C(19)	1.46(4)
P–O(2)	1.57(1)	C(13)–C(14)	1.42(4)
P–O(3)	1.60(2)	C(14)–C(15)	1.26(3)
O(1)–C(1)	1.44(3)	C(15)–C(16)	1.58(4)
O(2)–C(2)	1.48(2)	C(16)–C(17)	1.66(5)
O(3)–C(3)	1.46(3)	C(17)–C(18)	1.31(5)
		C(18)–C(19)	1.29(5)

C(5)–C(4)–C(11)	118.8(16)	C(19)–C(12)–C(13)	124.5(14)
C(4)–C(5)–C(6)	125.5(13)	C(12)–C(13)–C(14)	125.3(14)
C(5)–C(6)–C(7)	117.8(14)	C(13)–C(14)–C(15)	117.2(17)
C(6)–C(7)–C(8)	111.5(16)	C(14)–C(15)–C(16)	122.5(14)
C(7)–C(8)–C(9)	121.0(13)	C(15)–C(16)–C(17)	116.6(20)
C(8)–C(9)–C(10)	117.6(16)	C(16)–C(17)–C(18)	110.7(22)
C(9)–C(10)–C(11)	111.9(19)	C(12)–C(18)–C(19)	126.5(17)
C(10)–C(11)–C(4)	115.7(16)	C(18)–C(19)–C(12)	136.0(15)

Ru–P–O(1)–C(1)	64	C(19)–C(12)–C(13)–C(14)	69
Ru–P–O(2)–C(2)	178	C(15)–C(16)–C(17)–C(18)	75
Ru–P–O(3)–C(3)	−56	C(16)–C(17)–C(18)–C(19)	−50
C(12)–C(13)–C(14)–C(15)	−3	C(17)–C(18)–C(19)–C(12)	−15
C(13)–C(14)–C(15)–C(16)	−75	C(18)–C(19)–C(12)–C(13)	−11
C(14)–C(15)–C(16)–C(17)	23		

ordination of the C_8H_{10} ligand was suggested on the basis of n.m.r. data.[2] The *X*-ray analysis of complex (2), however, could also suggest a C_8H_{10} 1—4-η bonding mode in complex (3), the n.m.r. spectra of such complexes being too complicated for unambiguous structural assignments.

Preliminary results suggest that the bidentate η^4-C_8H_{10} is reasonably labile and that complex (2) may therefore serve as preparative material for new Ru^0 complexes.

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