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THE CRYSTAL STRUCTURE OF BIS(TRIPHENYLPHOSPHINE)-(η-CYCLOHEXA-1,3-DIENE)RHENIUM TRIHYDRIDE

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Summary

Bis(triphenylphosphine)(η-cyclohexa-1,3-diene)rhenium trihydride, $(Ph_3P)_2(\eta$-$C_6H_8)ReH_3$ (I) crystallises in the space group $C2/c$ with cell dimensions a 22.76(2), b 10.14(1) c 29.813(6) Å, β 97.69(8)°. The final refinement of 126 variables using 1580 non-zero reflections resulted in a final R value of 0.064. In spite of uncertainties in some of the atomic positions, the structure of I is compatible with a trihydrido diene compound with a distorted pentagonal bipyramidal configuration, rather than with a dihydrido cyclohexenyl compound having an "agostic" CH$\rightharpoonup$Re interaction. The factors which govern the structure of the complexes $(Ph_3P)_2(\eta$-1,3-diene)ReH_3 are discussed.

Introduction

Transition metal complexes with both hydride and conjugated diene ligands are rare [1–4], and only the monohydrido butadiene compounds $(Ph_2MeP)_3(\eta$-$C_4H_6)RuH$ and $(i\text{-}Pr_3P)_2(\eta$-$C_4H_6)IrH$ have been characterized crystallographically [1,2]. It was thus of interest to determine the crystal structure of one of the compounds prepared from the reaction of$(Ph_3P)_2ReH_7$ with dienes and formulated as trihydridodiene complexes $(Ph_3P)_2(\eta$-1,3-diene)ReH_3 [5]. From their slow limit NMR spectra, it was deduced that the most stable configuration of these complexes is a pentagonal bipyramid (see the structure of the cyclohexa-1,3-diene derivative IA in Fig. 1).

Recently, Brookhart and Green suggested that certain compounds described as hydrido-η-diene complexes could be better formulated as "agostic" η-allyl complexes with a 3-centre 2-electron bond [6]. The NMR data for compound I published in our earlier paper [5] are in fact, also consistent with a rapidly equilibrating mixture of "agostic" species IB (Fig. 1). In order to decide whether the most stable structure of

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compound I is the trihydrido diene species IA or the "agostic" species IB, we carried out further NMR studies on this complex in solution, (the results are presented in an accompanying paper [16]) and also determined its crystal structure, which is described and discussed in this paper.

Experimental

Compound I was prepared as described in ref. 5; small crystals were obtained by recrystallisation from CH_2Cl_2-acetone.

Crystal data

$C_{42}H_{41}P_2Re$, $M = 794$, a 22.76(2), b 10.14(1), c 29.813(6) Å, β 97.69(8)°, U 6819 Å^3; space group $C2/c$ from structure analysis, $Z = 8$, D_c 1.55 g cm^{-3}, $\mu(\text{Mo-}K_\alpha) =$ 37.01.

Data collection

Mo-K_α radiation ($\lambda = 0.71069$ Å graphite monochromator), $\theta/2\theta$ scan mode. $3.0 < 2\theta < 44.0$.

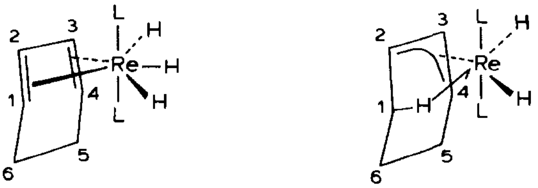
After a photographic study by precession, a crystal with a parallelepiped shape (0.1 × 0.1 × 0.3 mm) was set up on a laboratory made automatic three circle diffractometer. The lattice constants and orientation matrix were obtained by a least squares analysis from nine reflections. The intensities of two standard reflections (0 2 0) and (3 1 6) were measured every 100 reflections; no significant fluctuations were observed. Lorentz and polarisation corrections were applied. ψ scan curves were roughly linear so that no absorption correction was made, indeed the crystal was small. To each structure factor was assigned a standard deviation $\sigma = \Delta I/2F$ where ΔI was the error on the integrated intensity. Of the 3342 independent reflections recorded at room temperature, 1762 with $F < 3\sigma(F)$ were not included in subsequent calculations.

Determination and refinement of the structure

Computations were performed using standard programs [7]. All refinements were carried out using SHELX 76 programs. Scattering factors were taken from International Tables [8] including $\Delta f'$ and $\Delta f''$ for rhenium and phosphorus. Agreement factors were defined as

$$R = \Sigma(|F_{\text{obs}} - F_{\text{calc}}|)/\Sigma|F_{\text{obs}}|$$

$$R_w = \Sigma\left[(|F_{\text{obs}} - F_{\text{calc}}|)\cdot w^{1/2}\right]/\Sigma(|F_{\text{obs}}|\cdot w^{1/2})$$



(IA) (IB)

Fig. 1. Possible structures of complex I (L = Ph_3P). IA, trihydridodiene structure, IB "agostic" structure.

A weighting scheme based on counting statistics $w = 0.82/[\sigma(F)]^2$ was used in the last cycles of refinement.

The space group $C2/c$ was chosen on the ground of statistical tests. The rhenium position was unambiguously revealed by a Patterson map. Subsequent rephased Fourier synthesis showed four large peaks around rhenium where only two were

TABLE 1

ATOMIC COORDINATES

Atom	x/a	y/b	z/c
Re	0.19549(5)	−0.0063(3)	0.35732(4)
P(1)	0.1226(3)	−0.0939(8)	0.4009(3)
P(2)	0.2907(3)	0.0945(8)	0.3646(3)
C(1)	0.134(2)	0.107(4)	0.302(1)
C(2)	0.187(2)	0.066(5)	0.292(2)
C(3)	0.202(1)	−0.060(3)	0.284(1)
C(4)	0.164(2)	−0.150(4)	0.298(1)
C(5)	0.099(1)	−0.129(3)	0.281(1)
C(6)	0.080(1)	0.018(3)	0.2837(8)
C(111)	0.0566(7)	0.002(2)	0.4094(6)
C(112)	0.0479(7)	0.132(2)	0.3942(6)
C(113)	−0.0011(7)	0.203(2)	0.4042(6)
C(114)	−0.0415(7)	0.145(2)	0.4294(6)
C(115)	−0.0329(7)	0.015(2)	0.4446(6)
C(116)	0.0161(7)	−0.056(2)	0.4346(6)
C(121)	0.1519(9)	−0.119(2)	0.4610(7)
C(122)	0.1595(9)	−0.243(2)	0.4816(7)
C(123)	0.1827(9)	−0.252(2)	0.5272(7)
C(124)	0.1982(9)	−0.138(2)	0.5522(7)
C(125)	0.1906(9)	−0.015(2)	0.5316(7)
C(126)	0.1675(9)	−0.005(2)	0.4860(7)
C(131)	0.0933(7)	−0.258(2)	0.3838(7)
C(132)	0.0339(7)	−0.273(2)	0.3658(7)
C(133)	0.0132(7)	−0.395(2)	0.3490(7)
C(134)	0.0518(7)	−0.502(2)	0.3503(7)
C(135)	0.1112(7)	−0.487(2)	0.3684(7)
C(136)	0.1320(7)	−0.365(2)	0.3851(7)
C(211)	0.3404(8)	0.021(2)	0.3286(6)
C(212)	0.3514(8)	0.088(2)	0.2896(6)
C(213)	0.3853(8)	0.028(2)	0.2597(6)
C(214)	0.4082(8)	−0.099(2)	0.2687(6)
C(215)	0.3972(8)	−0.165(2)	0.3077(6)
C(216)	0.3633(8)	−0.105(2)	0.3377(6)
C(221)	0.3360(9)	0.095(2)	0.4207(6)
C(222)	0.3970(9)	0.073(2)	0.4257(6)
C(223)	0.4303(9)	0.080(2)	0.4685(6)
C(224)	0.4025(9)	0.109(2)	0.5063(6)
C(225)	0.3415(9)	0.131(2)	0.5013(6)
C(226)	0.3082(9)	0.124(2)	0.4585(6)
C(231)	0.2978(6)	0.273(2)	0.3535(7)
C(232)	0.2468(6)	0.347(2)	0.3403(7)
C(233)	0.2517(6)	0.480(2)	0.3289(7)
C(234)	0.3075(6)	0.538(2)	0.3307(7)
C(235)	0.3584(6)	0.464(2)	0.3438(7)
C(236)	0.3536(6)	0.331(2)	0.3552(7)

expected. The position of rhenium nearly in the plane $x\,0\,z$ induced a pseudosymmetry. Of the four peaks observed the two highest presented a more realistic geometry and proved to be the correct solution in subsequent computations. Fourier synthesis based upon the phases calculated in this refinement revealed all non-hydrogen atoms without any ambiguity and any extra peaks. The six phenyl rings were constrained to D_{6h} symmetry and refined as rigid groups. Only rhenium and phosphorus were refined anisotropically. The refinement of the cyclohexadiene carbon atoms led to unrealistic bond lengths for the saturated part of the ring; thus the CH_2–CH_2 distance was constrained to 1.54 Å with a standard deviation of 0.04 Å. This resulted in a final value of 1.56 Å with a reasonable geometry of the ring. For the last refinement cycles hydrogen atoms were introduced in idealized positions but allowed to move with their parent carbon atoms and assigned a refineable overall isotropic thermal parameter.

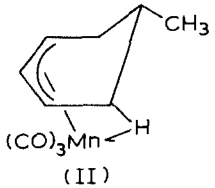
The final refinement of 126 variables using 1580 observations resulted in $R = 0.064$ and $R_w = 0.056$.

Final atomic coordinates for all non-hydrogen atoms are listed in Table 1 and bond distances and angles in Table 2. A list of observed and calculated structure factors is available from the authors (Y. Dromzee and Y. Jeannin).

Description of the structure and discussion

A perspective drawing of the crystal structure of I is shown in Fig. 2. Points of note are that the two triphenylphosphine ligands show the P(1)–Re–P(2) angle of 142.5° and the six membered ring ligand is not symmetrically oriented with respect to the P(1)–Re–P(2) plane: the distances from this plane to C(1) and C(6), 1.537 and 1.211 Å, are larger than the distances to C(4) and C(5), which are 1.115 and 0.322 Å, respectively. The three hydride ligands were not located in the difference map but it is reasonable to assume that they lie between the two phosphine ligands, on the opposite side from the hydrocarbon ligand, in the bisecting plane of P(1) Re P(2).

The structure of I, assuming that the hydrocarbon ligand is a cyclohexa-1,3-diene molecule, may be regarded as an approximate pentagonal bipyramid IA with the two phosphine ligands apical. The important distortions from ideal geometry can be explained in terms of steric hindrance. The closing of the P(1)–Re–P(2) angle is obviously due to the mutual repulsion of the phosphine and the hydrocarbon ligands. The twisting of the ring may be caused by both intramolecular effects (the two triphenylphosphine ligands are not symmetrical because of the staggered conformation of the phenyl groups) and intermolecular repulsions. For instance, the distance between one hydrogen on C(5) of the cyclohexadiene ring and the hydrogen atom on C(213) of the triphenylphosphine ligand of an adjacent molecule, found to be 2.754 Å, would be 1.944 Å in an imaginary structure with the ring symmetrically oriented with respect to the P(1)–Re–P(2) plane.



(II)

This configuration of a distorted pentagonal bipyramid is consistent with the NMR data for I [5]. However, we envisaged the possibility of compound I having the structure IB with a 3-centre 2-electron bond. The cyclic ligand of I can be compared with either the known η-cyclohexa-1,3-diene ligands [9] or the "agostic" cyclohexenyl ligand of complex II [10]. In η-cyclohexa-1,3-diene complexes, the C(1), C(2), C(3) and C(4) atoms are coplanar, as are the C(4), C(5), C(6) and C(1) atoms, whereas large deviations of these carbon atoms from their mean planes were observed in the case of complex II.

Unfortunately, uncertainties in some of the atomic positions prevent a thorough discussion of some bond lengths and angles (Table 2). As no disorder of the cyclohexadiene ring was observed on the difference map based upon $Re[P(C_6H_5)_3]_2$, these uncertainties are attributed to the small size of the crystal, which resulted in only 1580 non zero reflections being obtained from the 3342 measured reflections. In particular, the C(2)–Re bond is much shorter than is usual in rhenium π-complexes [11,12] and the angle C(1)–C(2)–C(3) is obviously incorrect. However, the atomic positions of the C(4), C(5), C(6) and C(1) atoms seem reasonable, and may be used with more confidence. The deviations of these atoms from their mean plane do not exceed 0.018 Å, and correspond to a torsion angle of only 3.3°. These deviations are similar to those observed in other cyclohexa-1,3-diene transition metal complexes [9] and are much smaller than those found in the "agostic" complex I [10], in which the corresponding torsion angle is 29.3°. In spite of the aforementioned uncertainties, the planarity of the C(4), C(5), C(6) and C(1) atoms favours the trihydrido-1,3-diene structure IA over the "agostic" structure IB.

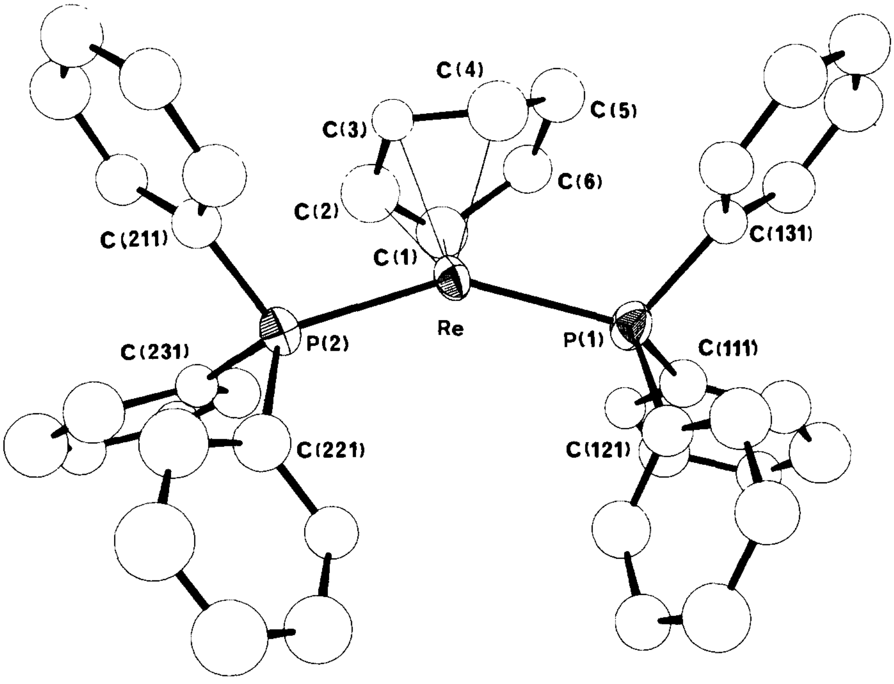


Fig. 2. Perspective view of the crystal structure of I.

TABLE 2

BOND LENGTHS (Å) AND ANGLES (°)

(a) Coordination around Re

Re-P(1)	2410(8)	Re-P(2)	2.381(7)		
Re-C(1)	2.33(3)	Re-C(2)	2.07(5)	Re-C(6)	2.27(3)
Re-C(4)	2.32(4)	Re-C(5)	3.21(3)	Re-C(6)	3.19(2)

108P(1)-Re-P(2)	142.5(3)

(b) The triphenylphosphine ligands

P(1)-C(111)	1.84(2)	P(1)-C(121)	1.84(2)	P(1)-C(131)	1.84(2)
P(2)-C(211)	1.82(2)	P(2)-C(221)	1.84(2)	P(2)-C(231)	1.85(2)

C-C constrained to be 1.395
C-H constrained to be 1.08

C(111)-P(1)-C(121)	97.9(9)	C(211)-P(2)-C(221)	102.7(9)
C(121)-P(1)-C(131)	102.5(9)	C(221)-P(2)-C(231)	96.3(10)
C(131)-P(1)-C(111)	104.1(9)	C(231)-P(2)-C(211)	102.7(8)

(c) The cyclohexadiene ring

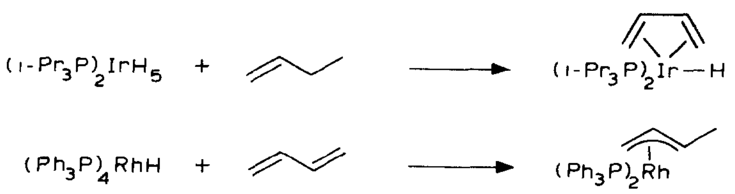
C(5)-C(6) constrained to be 1.54(4)

C(1)-C(2)	1.35(6)	C(2)-C(3)	1.35(6)	C(3)-C(4)	1.36(5)
C(4)-C(5)	1.52(5)	C(5)-C(6)	1.56(4)	C(6)-C(1)	1.55(4)

C(1)-C(2)-C(3)	126(4)	C(2)-C(3)-C(4)	113(4)
C(3)-C(4)-C(5)	116(3)	C(4)-C(5)-C(6)	112(3)
C(5)-C(6)-C(1)	112(20	C(6)-C(1)-C(2)	115(3)

Thus, neither in the solid state nor in solution (see the accompanying paper [16]) could we find any evidence for an "agostic" structure of the complexes $(Ph_3P)_2(\eta$-1,3-diene)ReH_3. Apart from a cationic iridium compound [13], the only "agostic" allyl complexes reported are those of first row transition metals [6]. This tendency could be a reflection of the greater stability of η-allyl complexes of first row metals compared to those of heavier metals; for example (Scheme 1), the reaction of butadiene with $(Ph_3P)_4RhH$ gives a 16e allyl compound [14] whereas the reaction of but-1-ene with $(i\text{-}Pr_3P)IrH_5$ gives a monohydrido butadiene complex [2], which was unambiguously characterized by its crystal structure. Furthermore, transition metal hydride complexes are more stable and more numerous for the heavier metals [15]. These observations combined suggest that "agostic" structures may be relatively less favoured in the case of the third row metals. The paucity of examples at present available prevents us, however, from drawing any firm conclusions.

SCHEME 1



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