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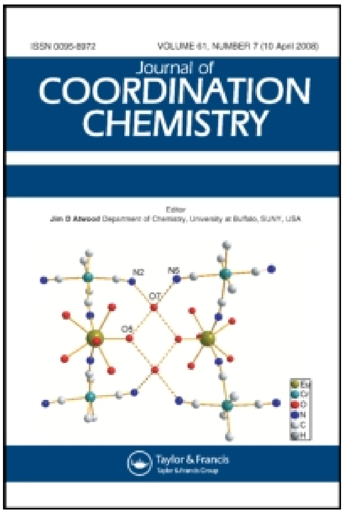

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X-RAY CRYSTAL STRUCTURE OF SOLVENT-FREE HYDRIDOTRIS(TRIPHENYLPHOSPHINE) RHODIUM, $HRh(PPh_3)_3$

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Hydridotris(triphenylphosphine)rhodium $HRh(PPh_3)_3$, I, crystallizes out of a toluene/hexane mixture free from solvent in the space group $P2_1/a$ with $a=23.289(8)$, $b=19.985(6)$, $c=9.810(2)$Å, $\beta=97.83(2)°$, $V=4523(2)$Å^3 and $D_{calcd}=1.308$ g cm^{-3} for $Z=4$. Molecules of I exhibit a distorted square planar geometry in which the angle subtended by the phosphines adjacent to the hydride ligand is 147.28(4)°. A difference Fourier map based on low-angle diffraction data provided evidence for the hydride ligand with a Rh-H distance of 1.63Å. In contrast to the known structure of $HRh(PPh_3)_3 \cdot HN(CH_3)_2 \cdot THF$, II, which contains solvent of crystallization, and has no ortho hydrogen rhodium separations less than 3.01Å, a phenyl ring in I has rotated so as to place a hydrogen within 2.87Å of the rhodium center.

Keywords: x-ray, rhodium, hydride, complexes, phosphines

INTRODUCTION

Hydridorhodium phosphine complexes play a central role in numerous homogeneous catalytic reaction systems and continue to be the subject of intensive investigation.[2] We have recently examined the chemistry of $HRh(PPh_3)_3$, I,[3-6] as part of a general investigation of the synthesis of heterometallic lanthanide and yttrium polyhydride complexes containing transition metals.[7] During our studies of the reactivity of I, we encountered some previously unreported properties of this complex which prompted further investigation. We report here on the effect of the presence or absence of coordinating solvents on the appearance of the hydride ^1H NMR resonance and we describe a number of distinctive differences between the published crystal structure of $HRh(PPh_3)_3 \cdot HN(CH_3)_2 \cdot THF$,[5] II, which contains solvent of crystallization, and the structure of solvent-free I. These differences involve the structural expression of phenyl ortho-hydrogen metal interactions, a long-recognized type of incipient C-H bond activation,[8] and suggest some limits on the crystallographic observability of this important interaction.

EXPERIMENTAL

All procedures were conducted using standard inert atmosphere techniques in a nitrogen-filled glovebox.[9] Solvents were distilled under nitrogen from sodium or potassium benzophenone ketyl.

Preparation of $HRh(PPh_3)_3$, I

Unsolvated $HRh(PPh_3)_3$ was prepared according to the method of Dewhirst, *et al.*,[4] using the commercially-available Al $(i-Bu)_3$ (Texas Alkyls) in place of Al $(i-Pr)_3$.

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TABLE II
Fractional atomic coordinates for $HRh(PPh_3)_3$.

Atom	*x/a*	*y/b*	*z/c*
Rh	0.13217(1)	0.30734(2)	0.15917(3)
P(1)	0.15741(4)	0.4024(1)	0.0536(1)
P(2)	0.06041(5)	0.2423(1)	0.2156(1)
P(3)	0.21989(5)	0.2583(1)	0.2307(1)
C(11)	0.1360(2)	0.3992(2)	−0.1347(4)
C(12)	0.1006(2)	0.3470(2)	−0.1893(4)
C(13)	0.0851(2)	0.3412(3)	−0.3304(5)
C(14)	0.1045(2)	0.3876(3)	−0.4172(5)
C(15)	0.1390(2)	0.4397(3)	−0.3637(5)
C(16)	0.1554(2)	0.4459(2)	−0.2223(4)
C(21)	0.1149(2)	0.4724(2)	0.1115(4)
C(22)	0.1136(3)	0.4767(3)	0.2521(5)
C(23)	0.0810(3)	0.5251(3)	0.3052(6)
C(24)	0.0481(2)	0.5693(3)	0.2201(6)
C(25)	0.0492(2)	0.5648(3)	0.0824(6)
C(26)	0.0827(2)	0.5162(2)	0.0274(5)
C(31)	0.2299(2)	0.4413(2)	0.0619(4)
C(32)	0.2724(2)	0.4101(3)	−0.0021(6)
C(33)	0.3273(2)	0.4375(3)	0.0016(7)
C(34)	0.3402(3)	0.4972(4)	0.0685(7)
C(35)	0.2989(3)	0.5284(4)	0.1289(9)
C(36)	0.2444(2)	0.5008(3)	0.1257(7)
C(41)	0.0034(2)	0.2861(2)	0.2974(4)
C(42)	−0.0310(2)	0.2528(3)	0.3797(5)
C(43)	−0.0728(2)	0.2870(3)	0.4392(6)
C(44)	−0.0808(2)	0.3542(3)	0.4176(6)
C(45)	−0.0469(2)	0.3880(3)	0.3376(6)
C(46)	−0.0046(2)	0.3551(3)	0.2774(5)
C(51)	0.0211(2)	0.2073(2)	0.0564(4)
C(52)	−0.0371(2)	0.2152(3)	0.0156(6)
C(53)	−0.0631(3)	0.1927(4)	−0.1123(7)
C(54)	−0.0310(3)	0.1606(4)	−0.1981(7)
C(55)	0.0265(3)	0.1509(4)	−0.1581(7)
C(56)	0.0529(2)	0.1746(3)	−0.0318(6)
C(61)	0.0705(2)	0.1682(2)	0.3279(5)
C(62)	0.1048(2)	0.1772(2)	0.4555(5)
C(63)	0.1116(2)	0.1253(3)	0.5490(5)
C(64)	0.0858(3)	0.0647(3)	0.5194(8)
C(65)	0.0516(3)	0.0549(3)	0.3962(8)
C(66)	0.0435(2)	0.1066(3)	0.2974(6)
C(71)	0.2584(2)	0.2326(2)	0.0876(4)
C(72)	0.3119(2)	0.2004(2)	0.1099(5)
C(73)	0.3383(2)	0.1791(3)	0.0009(7)
C(74)	0.3114(3)	0.1891(3)	−0.1325(7)
C(75)	0.2579(3)	0.2192(3)	−0.1567(5)
C(76)	0.2317(2)	0.2409(2)	−0.0461(5)
C(81)	0.2290(2)	0.1783(2)	0.3271(4)
C(82)	0.2046(2)	0.1219(2)	0.2618(4)
C(83)	0.2104(2)	0.0598(2)	0.3247(5)
C(84)	0.2411(2)	0.0534(2)	0.4557(5)
C(85)	0.2651(2)	0.1087(2)	0.5204(5)
C(86)	0.2600(2)	0.1715(2)	0.4576(4)
C(91)	0.2698(2)	0.3129(2)	0.3410(4)
C(92)	0.2508(2)	0.3353(2)	0.4610(5)
C(93)	0.2855(3)	0.3753(3)	0.5533(5)
C(94)	0.3384(3)	0.3964(3)	0.5239(6)
C(95)	0.3569(2)	0.3774(3)	0.4032(7)
C(96)	0.3233(2)	0.3353(2)	0.3120(5)
H(1)	0.0694	0.3354	0.0901

signal. These observations are consistent with, but do not prove the existence of, an exchange process involving an ortho metallation of a phenyl hydrogen, since such C-H addition processes are known to be inhibited by the presence of coordinating solvents.[6,12] In any event, it is clear that the effects of solvent interactions on the appearance of NMR spectra need to be given consideration during spectral analysis of hydridorhodium systems.

Structure of $HRh(PPh_3)_3$, I.

As was found for **II**,[5] solvent-free **I** crystallizes in monomeric units containing rhodium coordinated only by three phosphines and a hydride ligand.[13] A view of the molecule indicating the coordination geometry and numbering scheme is presented in Figure 1. Final fractional coordinates are given in Table II. Selected interatomic bond distances and angles are listed in Table III.

TABLE III
Selected bond lengths and angles in $HRh(PPh_3)_3$.

Bond distances (Å)

Rh	– P(1)	2.279(1)
Rh	– P(2)	2.245(1)
Rh	– P(3)	2.288(1)
Rh	– H(1)	1.63
P(1)	– C(11)	1.847(4)
P(1)	– C(21)	1.846(4)
P(1)	– C(31)	1.852(4)
P(2)	– C(41)	1.861(4)
P(2)	– C(51)	1.837(4)
P(2)	– C(61)	1.842(5)
P(3)	– C(71)	1.838(4)
P(3)	– C(81)	1.853(4)
P(3)	– C(91)	1.837(4)

Bond angles (deg)

P(1)	– Rh	– P(2)	147.28(4)
P(2)	– Rh	– P(3)	109.87(5)
P(1)	– Rh	– P(3)	102.81(5)
P(1)	– Rh	– H(1)	78.3
P(2)	– Rh	– H(1)	69.2
C(11)	– P(1)	– Rh	111.96(14)
C(21)	– P(1)	– Rh	108.04(13)
C(31)	– P(1)	– Rh	128.34(14)
C(21)	– P(1)	– C(11)	104.54(18)
C(21)	– P(1)	– C(31)	101.10(19)
C(11)	– P(1)	– C(31)	100.29(19)
C(41)	– P(2)	– Rh	115.66(15)
C(51)	– P(2)	– Rh	108.21(14)
C(61)	– P(2)	– Rh	125.09(15)
C(51)	– P(2)	– C(41)	104.05(19)
C(51)	– P(2)	– C(61)	102.11(21)
C(61)	– P(2)	– C(41)	99.24(19)
C(71)	– P(3)	– Rh	113.13(15)
C(81)	– P(3)	– Rh	124.10(13)
C(91)	– P(3)	– Rh	113.15(13)
C(71)	– P(3)	– C(81)	96.64(18)
C(91)	– P(3)	– C(71)	106.27(19)
C(91)	– P(3)	– C(81)	101.14(18)

The three phosphorus atoms surrounding the rhodium atom in **I** are even more nearly coplanar with the metal than in the solvated case: in **I**, the rhodium lies only 0.022 Å from the plane defined by the phosphorus atoms, as compared to 0.164 Å for the analogous distance in **II**. The stereochemical influence of the hydride ligand in **I** is less marked than in **II**: the P_1Rh-P_2 angle has closed from 151.7(2)° in **II** to 147.28(4)° in **I**, a change toward the limiting angle of 120° for an idealized trigonal planar geometry. In addition, the *trans* influence of the hydride on the Rh-P bonds lengths is unmistakable in **II**, as the Rh-P_3 distance is 0.048Å longer than the average of the Rh-P_1 and Rh-P_2 separations. In the structure of **I**, the presence of the hydride ligand does not affect the lengths as greatly: the RH-P_3 distance (2.288(1)Å) is indeed 0.043Å greater than that of Rh-P_2 (2.245(1)Å), but is only marginally longer (0.009Å) than Rh-P_1 (2.279(1)Å). Variations of such magnitude, however, are not unusual in transition metal hydride complexes.[14]

The high quality of the diffraction data made an attempt to locate the hydride ligand feasible. Calculation of a difference map using data refined with the constraint $\sin\theta/\lambda \leqslant 0.40$ yielded a peak of height 0.85 $eÅ^{-3}$ at a distance of 1.63Å from the rhodium. The peak position itself was not refined, but it very probably represents the location of the hydride ligand, as it stands significantly above the background noise (the next largest peak was of height 0.22 $eÅ^{-3}$) and it lies in a stereochemically reasonable position. The distance of 1.63Å from rhodium is within the range found for similar second-row systems (*cf* 1.70(15)Å in $HRuCl(PPh_3)_3$,[15] 1.60(12)Å in $HRh(CO)(PPh_3)_3$,[16] and 1.58(7)Å in $HRh(TolNCHNTol)(CO)(PPh_3)_2$[17]). In addition, the peak lies only 0.18Å from the P_1-P_2-P_3 plane, and the P_1-Rh-H(1) and P_2-Rh-H(1) angles are 78.3° and 69.2°, respectively (see Figure 1). The hydride ligand was not located in the structure of **II**.

Perhaps the most intriguing difference between the geometry of **I** and **II** lies in the orientation of the phenyl rings on the phosphines. The closest calculated approach of an ortho hydrogen to the rhodium in **II** is 3.01Å (based on C-H=0.95Å), and the authors justifiably state that there is no observable ortho hydrogen rhodium interaction in the molecule. In **I**, by contrast, there are two calculated ortho hydrogen separations less than 3.0Å, specifically Rh-H(76) (2.90Å), and Rh-H(12) (2.87Å), (see Figure 1). Although both distances are long for hydrogen interactions,[18] the resulting weak influence is presumably associated with the orientation of the phenyl rings in **I** with respect to that found in the structure of **II**.

The dihedral angle ψ between the plane defined by the rhodium atom, the adjacent phosphorus, and the directly-bonded carbon (Rh-P-C_α) and the least-squares plane of the associated phenyl ring probably affords the most concise indication of phosphine orientation in the molecules. In **I**, ψ for the rings bearing the two close ortho hydrogens (rings 7 and 1) is 3.1° and 10.2°, respectively. The angle is correspondingly small in other complexes containing postulated agostic hydrogen interactions:[8] *e.g.*, 12.0° in $Pd[PPh(t\text{-}Bu)_2]_2$,[20] 11.5° in $Pt[PPh(t\text{-}Bu)_2]_2$,[20] and 15.7° in $RuHCl(PPh_3)_3$.[16] In **II**, the ring with the closest ortho hydrogen metal contact (C-(25-30)) has $\psi = 24.7°$, indicating a minimal degree of interaction.[21]

Concern has been expressed in the literature over the extent to which ortho hydrogen metal interactions observed in solid state structures persist in solution.[23] In the structures of **I** and **II**, we have an unusual situation in which such interaction does not persist even in the solid state, *i.e.*, the solvation and the resulting crystal packing forces in **II** suppress the manifestation of secondary Rh-H(phenyl) interactions evident in **I**. The calculated rhodium ortho hydrogen distance of *ca* 2.9Å in **I** (based on a C-H distance of 0.95Å) may thus represent a threshold value for observable ortho hydrogen interactions in such rhodium systems. Any interactions at longer distances might well be obscured by crystal packing effects.

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SUPPLEMENTARY MATERIAL AVAILABLE

Tables of thermal parameters and structure factor amplitudes have been deposited with the editor and are available on request.

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