Short Communication

Synthesis and structure of the coordinatively unsaturated σ-aryl rhodium(III) complex $Rh(C_6H_5)Cl_2(PPh_3)_2$

J. Fawcett, J. H. Holloway and
G. C. Saunders*

Department of Chemistry, University of Leicester, Leicester LE1 7RH (UK)

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Abstract

The reaction between $RhHCl_2(PPh_3)_3$ and $Hg(C_6H_5)_2$ yields the five-coordinate, 16-electron rhodium(III) complex $Rh(C_6H_5)Cl_2(PPh_3)_2$. The molecular structure was determined by single-crystal X-ray diffraction (triclinic, $P\bar{1}$, $a=9.532(28)$, $b=9.523(24)$, $c=21.800(19)$ Å, $\alpha=112.9(1)$, $\beta=85.9(1)$, $\gamma=94.0(1)°$, $Z=2$). $Rh(C_6H_5)Cl_2(PPh_3)_2$ exhibits square pyramidal geometry with close approach of two of the *ortho* hydrogen atoms of the triphenylphosphine ligands to the rhodium atom.

Introduction

The syntheses of five-coordinate σ-aryl complexes of the Group VIII metals ruthenium, osmium and iridium by the reaction between hydride complexes and diaryl mercury reagents, have recently been reported [1, 2]. The ruthenium and osmium hydride complexes $MHCl(CO)(PPh_3)_3$ react with diaryl mercury reagents to form the complexes $MRCl(CO)(PPh_3)_2$ in high yield (eqn. (1)). The molecular structures of Ru(*p*-tolyl)Cl(CO)$(PPh_3)_2$ and Ru(*o*-tolyl)Cl(CO)$(PPh_3)_2$ were determined by X-ray crystallography. The former displays square pyramidal geometry whilst the latter has trigonal bipyramidal geometry [1]. The osmium analogues are presumed to possess analogous geometries.

$$MHCl(CO)(PPh_3)_3 + HgR_2 \longrightarrow MRCl(CO)(PPh_3)_2 + Hg + RH + PPh_3 \qquad (1)$$

M = Ru, Os; R = phenyl, *p*-tolyl, *o*-tolyl

Similarly, the reactions between the iridium hydride complex $IrHCl_2(PPh_3)_3$ and HgR_2 (R = phenyl, *p*-tolyl) yield the five-coordinate σ-aryl iridium complexes $IrRCl_2(PPh_3)_2$ in *c.* 50% yield (eqn. (2)) [3]. These complexes are presumed to possess square pyramidal geometry by analogy to Ru(*p*-tolyl)Cl(CO)$(PPh_3)_2$.

$$IrHCl_2(PPh_3)_3 + HgR_2 \longrightarrow IrRCl_2(PPh_3)_2 + Hg + RH + PPh_3 \qquad (2)$$

R = phenyl, *p*-tolyl

The reaction between $IrHCl_2(PPh_3)_3$ and Hg(*o*-tolyl)$_2$ yields the anomalous product Ir(*o*-tolyl){Hg(*o*-tolyl)}Cl$(PPh_3)_2$ in *c.* 20% yield [2]. For steric reasons, this complex is presumed to exhibit trigonal bipyramidal geometry.

The scope of the reaction between metal hydrides and diaryl mercury reagents has now been extended to include a route to σ-aryl complexes of rhodium(III). In the present communication we report the reactions between the rhodium(III) hydride complex $RhHCl_2(PPh_3)_3$ and HgR_2 (R = phenyl, *o*-tolyl), and the molecular structure of $Rh(C_6H_5)Cl_2(PPh_3)_2$.

Experimental

$Rh(C_6H_5)Cl_2(PPh_3)_2$

A slurry of $RhHCl_2(PPh_3)_3$ [4] (1.198 g, 1.2 mmol) and $Hg(C_6H_5)_2$ (0.524 g, 1.5 mmol) in benzene (150 cm^3) was heated at reflux under nitrogen for 30 min. The dark red solution was filtered through a celite pad to remove elemental mercury and concentrated to 80 cm^3 by rotary evaporation. Ethanol (100 cm^3) was added and the solution further concentrated to yield a red microcrystalline powder, which was filtered, washed with ethanol (2×50 cm^3) and dried *in vacuo*. Yield 0.673 g (58%).

Anal. Calc. for $C_{42}H_{35}Cl_2P_2Rh$: C, 65.05; H, 4.55; Cl, 9.1. Found: C, 65.6; H, 4.5; Cl, 8.6%. IR spectrum (cm^{-1}) (Nujol mull): 1555m, 1190w, 1093s, 1047w, 1016m, 991w, 750m, 730m, 706sh, 692s. ^{1}H NMR ($CDCl_3$): 7.44 (m, 12H, PPh_3), 7.31 (t, $J=8.2$ Hz, 12H, PPh_3), 6.81 (t, $J=7.2$ Hz, 1H, H_{para}), 6.67 (d, $J=8.2$ Hz, 2H, H_{ortho}), 6.50 (vt, $J=7.7$ Hz, 2H, H_{meta}). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 21.78 (d, ^1J(P–Rh) = 105.8 Hz). ^{13}C NMR ($CDCl_3$): 138.34 [dm, ^1J(C–H) = 166.6 Hz, C_6H_5], 135.12 [dtm, ^1J(C–H) = 163.4 Hz, J(C–P) = 4.5 Hz, PPh_3 *meta* or *ortho*], 130.41 [dtm, ^1J(C–H) = 161.2 Hz, ^2J(C–H) = 7.1 Hz, PPh_3 *para*], 129.12 [tm, J(C–P) = 23.7 Hz, PPh_3 *ipso*], 127.98 [dtm, ^1J(C–H) = 158.0 Hz, J(C–P) = 4.8 Hz, PPh_3 *ortho* or *meta*], 126.61 [dd,

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*Author to whom correspondence should be addressed.

^1J(C–H) = 158.0 Hz, ^2J(C–Rh or C–H) = 7.8 Hz, C_6H_5], 123.94 [dm, ^1J(C–H) = 157.1 Hz, C_6H_5].

X-ray diffraction study

A crystal suitable for X-ray crystallography was grown from dichloromethane–ethanol. The crystal data, data collection and refinement parameters of the structure are given in Table 1. Data were corrected for Lorentz and polarization factors. The positions of rhodium, chlorine and phosphorus atoms were located by direct methods [5]. The carbon atoms were located from successive difference Fourier maps and initially refined as rigid groups with constrained D_{6h} symmetry [6]. Initially, all hydrogen atoms were included in calculated positions. The constraints on the carbon and hydrogen atoms of the two phenyl rings C(11)–C(16) and C(41)–C(46) were then removed. All non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms H(2), H(6), H(12) and H(42) were refined with individual isotropic parameters. Blocked matrix (2 blocks) least-squares refinement on 405 parameters converged to yield the final indices $R = 0.054$ and $R_w = 0.057$. Selected interatomic distances and bond angles are given in Table 2. See also 'Supplementary material'.

TABLE 1. Summary of crystallographic data

Formula	$C_{42}H_{35}Cl_2P_2Rh$
Molecular weight	775.50
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	9.532(28)
b (Å)	9.523(24)
c (Å)	21.800(19)
α (°)	112.9(1)
β (°)	85.9(1)
γ (°)	94.0(1)
V (Å^3)	1817
Z	2
ρ (calc.) (g cm^{-3})	1.418
F(000)	792
Diffractometer	Stoe STADI-2
Radiation	Mo Kα ($\lambda = 0.7107$ Å)
μ (Mo Kα) (cm^{-1})	6.55
Scan type	omega
Scan range	variable
θ limits (°)	7 to 54
Octants collected	$\pm h$, $\pm k$, $+l$
No. data collected	7304
No. unique reflections	7266
No. reflections used	6103
Criteria	$I > 3\sigma(I)$
R (%)	5.41
R_w (%)	5.67
No. parameters	405
Weighting parameter (g)[a]	0.0006
Residual electron density (eÅ^{-3})	−2.5 to 0.98 (1.0 Å from Rh)

[a] Weighting $w = 1/[\sigma^2(F) + g(F)^2]$.

TABLE 2. Selected interatomic distances (Å) and bond angles (°) for $Rh(C_6H_5)Cl_2(PPh_3)_2$

Rh–P(1)	2.368(1)	C(44)–C(45)	1.383(10)
Rh–P(2)	2.371(1)	C(45)–C(46)	1.404(8)
Rh–Cl(1)	2.360(1)	C(46)–C(41)	1.394(7)
Rh–Cl(2)	2.359(1)	C(12)–H(12)	1.00(8)
Rh–C(1)	2.016(3)	C(13)–H(13)	0.94(5)
P(1)–C(11)	1.834(6)	C(14)–H(14)	0.89(7)
P(1)–C(21)	1.858(2)	C(15)–H(15)	0.92(7)
P(1)–C(31)	1.844(3)	C(16)–H(16)	1.06(3)
P(2)–C(41)	1.841(5)	C(42)–H(42)	1.00(6)
P(2)–C(51)	1.842(3)	C(43)–H(43)	0.98(9)
P(2)–C(61)	1.849(3)	C(44)–H(44)	0.99(7)
C(11)–C(12)	1.402(6)	C(45)–H(45)	1.12(7)
C(12)–C(13)	1.404(9)	C(46)–H(46)	1.02(7)
C(13)–C(14)	1.366(10)		
C(14)–C(15)	1.384(8)		
C(15)–C(16)	1.398(10)	Rh...H(2)	3.020
C(16)–C(11)	1.395(8)	Rh...H(6)	3.025
C(41)–C(42)	1.388(8)	Rh...H(12)	2.865
C(42)–C(43)	1.405(8)	Rh...H(42)	2.842
C(43)–C(44)	1.383(8)		
P(1)–Rh–P(2)	173.9(0)	C(41)–P(2)–Rh	109.0(2)
Cl(1)–Rh–P(1)	94.7(0)	C(51)–P(2)–Rh	118.0(1)
Cl(1)–Rh–P(2)	84.6(0)	C(61)–P(2)–Rh	114.9(1)
Cl(2)–Rh–P(1)	84.8(0)	C(2)–C(1)–Rh	119.9(2)
Cl(2)–Rh–P(2)	94.7(0)	C(6)–C(1)–Rh	120.1(2)
Cl(1)–Rh–Cl(2)	168.8(0)	C(12)–C(11)–P(1)	120.5(4)
C(1)–Rh–P(1)	92.8(1)	C(42)–C(41)–P(2)	120.3(3)
C(1)–Rh–P(2)	93.3(1)	H(12)–C(12)–C(11)	119(4)
C(1)–Rh–Cl(1)	95.5(1)	H(42)–C(42)–C(41)	118(4)
C(1)–Rh–Cl(2)	95.7(1)		
C(11)–P(1)–Rh	108.4(2)		
C(21)–P(1)–Rh	115.0(1)		
C(31)–P(1)–Rh	118.1(1)		

e.s.d.s in parentheses.

Results and discussion

On heating $RhHCl_2(PPh_3)_3$ and $Hg(C_6H_5)_2$ in benzene at reflux for *c.* 30 min a dark red solution develops and elemental mercury is deposited. The red, five-coordinate rhodium(III) complex $Rh(C_6H_5)Cl_2(PPh_3)_2$ was isolated from the solution in *c.* 50% yield. Analytical and spectroscopic data were consistent with this formulation. In particular, the $^{31}P\{^1H\}$ NMR spectrum exhibits a doublet at δ 21.78 ppm with a coupling constant, ^1J(P–Rh), of 105.8 Hz consistent with a five-coordinate rhodium(III) complex with either square pyramidal or trigonal bipyramidal geometry [7]. The structure of $Rh(C_6H_5)Cl_2(PPh_3)_2$ was determined by X-ray crystallography. The crystal data and selected interatomic distances and bond angles are presented in Tables 1 and 2, respectively. $Rh(C_6H_5)Cl_2(PPh_3)_2$ exhibits square pyramidal geometry with apical phenyl and basal, mutually *trans* phosphine ligands (Fig. 1). The C(1)–Rh–P and C(1)–Rh–Cl angles lie between 91 and 97°. The coordination about the rhodium atom

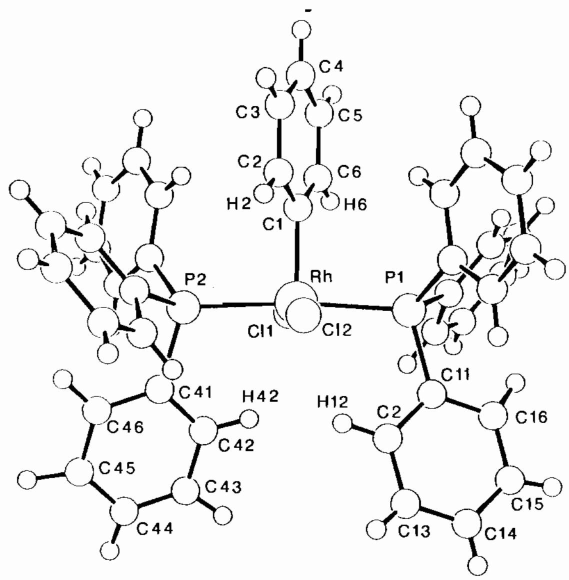

Fig. 1. Molecular structure of $Rh(C_6H_5)Cl_2(PPh_3)_2$.

may also be considered to be distorted octahedral with one site occupied by one of the *ortho* hydrogen atoms of each triphenylphosphine ligand. Both these hydrogen atoms show a close approach to the rhodium atom suggestive of an agostic interaction [8]. The non-bonded distances of 2.842 and 2.865 Å are close to the sum of the van der Waals radii [9] and comparable to those in similar complexes [10–19]. The Rh–P–C bond angles for the phenyl rings with the agostic hydrogen atoms are at least 5° less than the other Rh–P–C angles, which is also suggestive of attractive Rh...H–C interactions. Interestingly, the *ortho* hydrogen atoms of the metal-bound phenyl ring, which are not involved in agostic interactions, are only *c.* 0.17 Å more distant from the rhodium atom. The geometry is similar to the recently reported rhodium(III) complex $RhHCl_2(P\text{-}i\text{-}Pr_3)_2$, which, however, appears to have no agostic hydrogen atoms at the sixth coordination site and adopts square pyramidal geometry rather than trigonal bipyramidal geometry due to the poorer σ-donor character of the chloride ligands than that of the hydride ligand [20].

On heating $RhHCl_2(PPh_3)_3$ and Hg(*o*-tolyl)$_2$ in benzene at reflux for *c.* 1 h, a red solution developed. However, no elemental mercury was deposited. Hg(*o*-tolyl)$_2$ was recovered and no tractable rhodium-containing compound was obtained. Thus it appears that neither of the expected products, Rh(*o*-tolyl)$Cl_2(PPh_3)_2$ and Rh(*o*-tolyl){Hg(*o*-tolyl)}$Cl(PPh_3)_2$, are formed by this reaction and decomposition of the rhodium hydride species occurs under the reaction conditions.

Supplementary material

Full tables of bond lengths and angles, fractional atomic coordinates, thermal parameters and structure factors can be obtained on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

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