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Preparation, structure and properties of triphenylphosphine rhodium aryloxides

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In memory of Mark Vol'pin, an enthusiastic scientist, a persistent optimist, and a compassionate, wonderful person

Abstract

The reaction of Wilkinson's catalyst with NaOAr in toluene cleanly affords the corresponding aryloxide complexes Rh(PPh₃)₃OAr (1). In solution, 1 exists in equilibrium with PPh₃ and the corresponding Rh(PPh₃)₂(π -ArO) (2). The addition of HOAr shifts the equilibrium completely toward the corresponding adducts 2 ·2HOAr, due to hydrogen bonding between the oxygen atom of the π -coordinated OAr ligand and two molecules of HOAr. Heating of **1a**-**d** in toluene at 60-80°C leads to the elimination of HOAr with concomitant cyclometallation of a phenyl ring of one PPh₃ ligand, affording mixtures of **1**, 2 ·2HOAr, a cyclometallated Rh complex and PPh₃. At room temperature, a reverse reaction slowly occurs to give equilibrium mixtures of **1**, 2 and PPh₃. Complexes 1 readily react with water, CO and H₂, affording Rh₂(PPh₃)₄(μ -OH)₂, Rh(PPh₃)₅(CC)OAr (3) and HRh(PPh₃)₅, respectively. The latter complex was also obtained when complexes 1 were treated with methanol. The structures of the phenoxide complexes 1 and 2 · 2PhOH and of *p*-nitrophenoxide complex 3 were established by X-ray diffraction. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures: Rhodium complexes; Aryloxide complexes

1. Introduction

The first phosphine rhodium aryloxide was described in 1968 by Keim [1]. The complex was prepared by the treatment of phenol with MeRh(PPh₃)₃ or PhRh(PPh₃)₃ and characterized by elemental analysis as Rh(PPh₃)₃OPh. Later Cole-Hamilton et al. reported [2] that reaction of PhRh(PPh₃)₃ with an excess of phenol led not to the complex described by Keim, but rather to Rh(PPh₃)₂(π -PhO) · 2PhOH, with a π -coordinated phenoxo ligand. The compound was characterized by elemental analysis, 'H NMR and IR spectra. In the following two decades a significant number of late transition metal aryloxides were described [3], including Rh-complexes containing CO [4], cyclooctadiene [5], and Cp* [6] as stabilizing ligands. However, phosphine rhodium aryloxides are still very rare [7,8].

Here we wish to report the preparation and characterization of triphenylphosphinerhodium aryloxo complexes with σ and π -coordinated OAr ligands, their behavior in solution and reactivity toward CO, H₂, water and methanol.

2. Results and discussion

2.J. Synthesis and characterization of (Ph₃P)₃RhOAr (**1a-d**). X-ray structure of **1a**. Dissociation of **1a-d** in a solution

Treatment of Wilkinson's catalyst in toluene with a slight excess of NaOAr for 1 h results in clean formation of complexes **1a-d** (Eq. (1)).

	toluenc, 20°C		
(Ph ₃ P) ₃ RhCl+NaOAr		(Ph ₃ P) ₃ RhOAr	(1)
	- NaCl	1a – d	
		$\mathbf{a}, \mathbf{A}\mathbf{r} = \mathbf{P}\mathbf{h}$	
		b. $Ar = 4 - MeC_6H_4$	
		$c, Ar = 2 - MeC_6H_4$	
		d, $Ar = 4$ -MeOC ₆ H	L

Slow diffusion of pentane vapors into the corresponding filtered and concentrated reaction solution afforded dark red crystals of **1a**. The complex was isolated in 91% yield and characterized by elemental analysis, ³¹P NMR and IR spectroscopy. The complex is moderately air sensitive and should be stored under nitrogen. However, it can be handled in air for a few minutes without significant decomposition. The

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Fig. 1. Perspective drawing for 1a with adopted numbering scheme. Thermal ellipsoids are depicted at 30% probability. Only the *ipso* carbon atoms of PPh₃ are shown. Hydrogen atoms are omitted for clarity.

Table 1 Selected bond distances (\hat{A}) and angles (°) for (Ph,P) ,RhOPh

P(1)-Rh	2.348(1)	C(4)-C(5)	1.381(8)
P(2)-Rh	2.228(1)	C(5)-C(6)	1.413(7)
P(3)-Rh	2.312(1)	P(1)-Rh- $P(2)$	99.07(4)
O-Rh	2.091(3)	P(2)-Rh-P(3)	99.25(4)
0-C(6)	1.315(6)	P(1)-Rh-O	79.24(9)
C(6)-C(1)	1.395(7)	P(3)-Rh-O	88.22(9)
C(1) - C(2)	1.391(8)	P(1) - Rh - P(3)	152.26(4)
C(2)-C(3)	1.378(8)	O-Rh-P(2)	164.8(1)
C(3)-C(4)	1.387(8)	C(6)-O-Rh	123.0(3)

structure of ia was determined by X-ray diffraction. An ORTEP plot of the complex is shown in Fig. 1 and selected bond distances and angles are presented in Table 1. The geometry around the Rh atom is substantially distorted from a square planar arrangement (*trans*-P-Rh-P and *trans*-P-Rh-O angles ~152 and 164°, respectively) with the distortion presumably due to the steric bulk of PPh₃ ligands. The phenyl C-O bond of the phenoxide ligand (1.318 Å) is significantly shorter than that of free pheno! (1.376 Å), and this is typical for late transition metal aryloxides [9].

Complexes **1b-d** could not be isolated in analytically pure form, but were characterized by ³¹P NMR spectra in solution. The data are given in Table 2.

The ³¹P NMR spectra of **1a-d** show a doublet of doublets and doublet of triplets in a 2:1 integral ratio, a pattern char-

Table 2				
^{\$1} P{ ¹ H} I	NMR data	for complexes	(Ph,P),RhOA	r la-d "
		-		

acteristic of square planar rhodium complexes with three phosphine ligands. The spectra also contain a singlet at -5ppm due to free PPh₃ and a doublet, which was assigned to rhodium complexes with π -coordinated aryloxide, **2a**–**d** (see below) in a 1:2 ratio. When triphenylphosphine was added to the solution, the intensity of the doublet decreased with an increase of the intensity of signals of **1a–d**. This observation suggests that complexes **2a–d** are formed by partial dissocation of **1a–d** in solution (Eq. (2)).

$$(Ph_3P)_3RhOAr \rightleftharpoons (Ph_3P)_2Rh(\pi-ArO) + PPh_3$$
(2)
2a-d

2.2. Synthesis and characterization of $(Ph_3P)_2Rh(\pi-ArO)$ (2a-d)

The formulation of **2a–d** as complexes with two PPh₃ per rhodium atom and π -coordinated OAr-ligands was established by their preparation from [Rh(PPh₃)₂Cl₂]₂ and the corresponding NaOAr (Eq. (3)).

$$[(Ph_{3}P)_{2}Rh(\mu-Cl)]_{2} + 2NaOAr$$

$$(3)$$

$$\overset{CH_{2}Cl_{2}, 2VC}{\rightarrow} (Ph_{3}P)_{2}Rh(\pi-ArO)$$

$$\overset{-2NaCl}{2a-d}$$

The ³¹P NMR spectra of the reaction mixtures showed doublets with P–Rh coupling constants and chemical shifts identical to those of the doublets observed in the ³¹P NMR spectra of the corresponding **1a–d**. The complexes were isolated as very air sensitive amorphous light brown solids and characterized by ³¹P and ¹H NMR spectra. The ³¹P NMR data are given in Table 3. The ¹H NMR spectra unequivocally confirm that **2a–d** contain a phenyl ring π -bonded to rhodium. The proton resonances of the OAr ligands appeared in the region of 4.4–5.6 pprn, i.e. they are significantly shifted to higher field as compared to the resonances of the corresponding phenols or O-bonded OAr ligands. This is commonly observed when there is π -coordination of a phenyl ring to a metal [10].

The addition of PPh₃ to solutions of **2a-d** in toluene or in methylene chloride gave rise to the appearance of signals of the corresponding **1a-d** in the ³¹P NMR spectra. These data confirm that dissociation of **1a-d** in a solution is indeed an equilibrium process. The equilibrium constant did not depend

Ar (compound) Doublet δ (ppm)	Doublet of doublets		J(P-P) (Hz)	Doublet of triplets	
	δ (ppm)	J(P-Rh) (Hz)		δ (ppm)	J(P-Rh) (Hz)
Ph (1a)	30	156	39.5	-48	173
4-MeC ₆ H ₄ (1b)	29	157.5	40	49.5	172.5
2-MeC,H, (1c)	31	156.5	40	50	171
2-MeOC ₆ H ₄ (1d)	29	158	.36	-49.5	172

* Recorded at 121.4 MHz in toluene at 293 K; chemical shifts are relative to external 85% H₃PO₄.

Ar(compound)	δ (ppm)	J(P-Rh) (Hz)	Ar(compound)	δ (ppm)	J(PRh) (Hz)
Ph (2a) 4-MeC _o H ₄ (2b)	48 47.5	212 210	2-MeC ₆ H ₄ (2c) 4-MeOC ₆ H ₄ (2d)	49 46.5	216 214

Table 3		
³¹ Pf ¹ H3 NMR data for complexes	$(Ph,P),Rh(\pi,OAr)$ (2a-	h

* Recorded at 121.4 MHz in CH2Cl2 at 293 K; chemical shifts are relative to external 85% H2PO4.

on the type of OAr (in the range of accuracy of the measurements), but was sensitive to the nature of the solvent (e.g. the equilibrium constant was estimated as 1×10^{-4} mol 1^{-1} in toluene and 2×10^{-2} mol 1^{-1} in methylene chloride).

2.3. Reaction of **1a-d** with phenols. Synthesis and characterization of Rh(PPh₃)₂(π-ArO) 2HOAr (**2a-d** 2HOAr). X-ray structure of **2a** 2PhOH

Strong hydrogen bonding between phenols and aryloxy ligands is a well established feature of transition metal aryloxides [8,11]. It was of interest to investigate the effect of such bonding with phenols on the equilibrium of dissociation of 1a-d. Gradual addition of the corresponding phenols to 1a-d in toluene increased the intensity of signals of PPh3 and 2a-d with the simultaneous decrease in the intensity of the signals of 1a-d in the ³¹P NMR spectra. The characteristic pattern of 1a-d completely disappeared from the spectra after the addition of 2 equiv. of HOAr. Only a singlet of PPh3 and a doublet with the same chemical shift and P-Rh coupling constant as those of 2a-d were observed in the spectra at this point. The ratio of the doublet to PPh₃ was 2:1. No changes occurred on further addition of HOAr. It is conceivable from these data, that hydrogen bonding of phenols with 2a-d is much stronger than with la-d. The formation of strong hydrogen bonds of phenols with π -coordinated OAr ligands of 2a-d drives the equilibrium of dissociation of 1a-d (Eq. (2)) to the right and the net process can be represented by Eq. (4).

$$(Ph_3P)_3RhOAr + 2HOAr$$
 (4)

$$\rightarrow (Ph_3P)_2Rh(\pi-ArO) \cdot 2HOAr + PPh_3$$

2a - d \cdot 2HOAr

Slow diffusion of pentane vapors in concentrated toluene solutions of **1a–d**, containing 2 equiv. of their respective phenols, afforded red crystals of the corresponding **2a–d**·2HOAr. Two complexes, **2a**·2PhOH and **2b**·2(4-MeC₆H₄OH) were isolated in high yield and characterized by elemental analysis, ³¹P, ¹H, ¹³C NMR and IR spectroscopy. The structure of **2a**·2PhOH was determined by X-ray diffraction. An ORTEP plot of the complex is shown in Fig. 2, selected bond distances and angles are presented in Table 4. The structural arrangement of the complex consists of a (Ph₃P)₋Rh fragment attached to the arene ring of the phenoxy ligand, which in turn is connected via two hydrogen bonds to a pair of phenol molecules. Being oriented toward the Rh



Fig. 2. Perspective drawing for 2a · 2PhOH with adopted numbering scheme. Thermal ellipsoids are depicted at 30% probability. Only the *ipso* carbon atoms of PPh, are shown. Hydrogen atoms (except for O-H) are omitted for clarity.

Table 4			
Selected bond	distances (Å)	for (Ph ₃ P)	Rh(n-OPh)

P(1)-Rh	2.2462(9)	C(1)-C(2)	1.416(6)
O(1)-C(1)	1.277(5)	C(2) - C(3)	1.384(7)
O(2)-C(81)	1.355(6)	C(3) - C(4)	1.405(8)
O(3)-C(76)	1.365(6)	C(4) - C(5)	1.372(8)
O(1)-O(2)	2.668(1)	C(5)-C(6)	1.409(6)
0(1)-0(3)	2.608(1)	C(1) - C(6)	1.420(6)
RhC(1)	2.542(4)	C(71)-C(72)	1.374(8)
Rh-C(2)	2.474(4)	C(72)-C(73)	1.381(9)
RhC(3)	2.327(4)	C(73)-C(74)	1.365(8)
RhC(4)	2.252(4)	C(74)-C(75)	1.381(8)
Rh-C(5)	2.295(4)	C(75)-C(76)	1.381(7)
RhC(6)	2.298(4)	C(76)-C(71)	1.367(7)

atom their planes assume an angle of 98° and are almost perpendicular to the plane of the π -coordinated phenoxide. With the exception of the PPh₃ ligands, this arrangement is very similar to that found in Cp*Ru(π -PhO) · 2PhOH [12]. The line bisecting the P1RhP2 triangle is almost perpendicular to the plane of the OPh ligand, which is pivoted around this axis in such a way that the oxygen atom is much closer to P2 (4.075 Å) than to P1 (5.656 Å). When π -coordinated, the OPh anion is usually referred to as an η^5 -oxocyclohexadienyl ligand [6,7,12] (structure (c), Fig. 3). This type of coordination results in a substantial elongation of the Rh*ipso* C distance, loss of planarity of the ring and shortening



Fig. 3. Mesomeric structures for π -complexing of phenoxo-group: (a) as η^4 -cyclohexadienonyl, (b) as η^4 -phenoxide, (c) as η^5 -cyclohexadienonyl.

of the C-O bond. The distances of Rh to both the ipso carbon (2.538 Å) and to the ortho carbon C2 (2.474 Å) are clearly longer than the distances to the other carbon atoms of the OPh ligand (2.251-2.327 Å) in 2a 2PhOH. The C₆ ring is essentially planar (torsion angles lie in the range 0.4-10.6°) and the oxygen atom is only slightly displaced from its mean plane (0.142 Å). The C1-O1 bond (1.277 Å) is shorter than the C-O bond in NaOPh 3H₂O (1.309-1.336 Å) [13], but is substantially longer than the corresponding bond in [Cp*Rh(η⁵-estradienonyl)]BF₄ (1.20 Å) [6]. These data indicate the large contribution from mesomer (a) (Fig. 3) to the structure of 2a · 2PhOH and the complex can therefore be best described as $(Ph_3P)_2Rh(\eta^4-PhO) \cdot 2PhOH$. The anomalously long Rh-ortho carbon distance (2.65 Å) was also found in the closely related (Ph₃P)₂Rh(π-2,6-t-Bu₂-4-MeC₆H₂O) complex [7]. It should be noted that only the η^4 mode of coordination gives the most common 16 e configuration of Rh(I), whereas the η^{5} and η^{6} - types both imply an 18 e count. Another argument in favor of the η^4 mode of coordination of the OPh ligand in 2a · 2PhOH is the orientation of the (Ph₃P)₂Rh fragment around the axis connecting the metal and the middle of the C6 ring so as to maximize the interaction of the Rh with the C3-C4 and C6-C5 bonds of the ring (Fig. 4). However the Rh--C1 and Rh-C2 distances in 2a · 2PhOH are probably not long enough to exclude any bonding interaction, so we prefer not to assign a



Fig. 4. Top view of $2a \cdot 2PhOH$. Only the P atoms of PPh_x are shown. Hydrogen atoms are omitted for clarity. Two molecules of hydrogen bonded PhOH are not shown.

definite hapticity to the OPh ligand and to refer to complexes of type 2 as $(Ph_3P)_2Rh(\pi-ArO)$.

The presence of a broad band at 2600-2700 cm⁻¹ in the IR and a broadened signal at ~ 11 ppm in the 'H NMR spectra of 2a,b.2HOAr is indicative of a strong hydrogen bonding [14] in the complexes. The proton resonances of π -coordinated OAr ligands appear at higher field as compared with the resonances of hydrogen bonded phenols, which in turn appear in the aromatic region of the spectra. The presence of the two sets of resonances clearly shows that exchange between the π -coordinated aryloxide and hydrogen bonded HOAr either does not occur at all or is slow on the NMR time scale. However addition of PhOH to a solution of 2b-2(4-MeC₆H₄OH) resulted in appearance of the doublet for 2a 2PhOH in the ³¹P NMR spectrum which increased in intensity during ~40 min and remained constant after that period of time. These data indicate that π -OAr/HOAr exchange does occur, although rather slowly. Exchange between hydrogen bonded and free HOAr is rapid as indicated by the observation of a single averaged resonance of the phenolic protons in the 'H NMR spectra of the solution.

2.4. Formation of the orthometallated complex Rh(C₀H₄PPh₂)(PPh₃)₂ (4) from **la-d**

Heating of solutions of **1a-d** in toluene to $60-80^{\circ}$ C for 5 min led to dramatic changes in the ³¹P NMR spectra. The signals of **1a-d** decreased in intensity, the doublet of **2a-d** and singlet of PPh₃ increased, and a new pattern consisting of three multiplets centered at -54, 40.8 and 45.8 ppm, appeared in the spectra. Each multiplet of the new pattern contained eight lines and was interpreted as a doublet of doublets of doublets ¹. The new pattern is assigned to *ortho*metallated square planar Rh complex, **4**. The fact that the same pattern was observed in the ³¹P NMR spectra after heating of various **1a-d**, and the absence of high field resonances in the ¹H NMR spectra, suggest that **4** contains neither OAr nor hydride ligands. The proposed structure and schematic representation of the ³¹P NMR spectrum of the complex are shown on Fig. 5.

Cyclometallation reactions on metallocomplexes are well known [16] and representative *ortho*-metallated compounds are well characterized [17,18]. The complex 4 was described

¹Similar characteristic pattern was observed in ¹¹P NMR of $HRu(C_0H_1PPh_2)(PPh_3)_2(C_3H_4)$, see Ref. [15].



Fig. 5. ³¹P NMR data for complex 4. Measured in C, D, at 20°C. Chemical shifts are relative to 85% H₁PO₄ as external standard.



in 1968 by Keim [1] and later successively used in catalysis [19] and organometallic synthesis [20]. Although neither X-ray nor ³¹P NMR data were published, there are no doubts about the structure and composition of the complex. The published synthesis of 4 involves thermal decomposition of MeRh(PPh₃)₃ or PhRh(PPh₃)₃ in solution and proceeded via reductive elimination of methane or benzene from an intermediate hexa-coordinated Rh hydride [1]. It seems likely, that formation of 4 from **1a-d** occurs in a similar way and also involves a Rh(III) hydride as an intermediate, which undergoes reductive elimination of phenol (Scheme 1).

The fact that the formation of 4 is accompanied by an increase of the intensity of the signals of 2a-d and PPh₃ in the ³¹P NMR spectra, suggests that HOAr is not released into solution, but reacts with still present 1a-d (cf. Eq. (4)), giving corresponding 2a-d · 2HOAr and PPh₃. Therefore formation of 4 from 1a-d proceeds in accordance with Eq. (5).

$$3(Ph_3P)_3RhOAr \rightleftharpoons 2(PPh_3)_2Rh(C_6H_4PPh_2)$$

$$4$$

$$(5)$$

$$+2a - d \cdot 2HOAr + 2PPh_3$$

Prolonged (up to 1 h) heating of 1a-d at $80^{\circ}C$ in solution did not lead to full conversion into 4. The relative intensity

of the signals of 4 in the ³¹P NMR spectra was the same as in spectra obtained after 5 min of heating, so that ~ 30% of the initial amount of **1a-d** was still present in the solution. The characteristic pattern of 4 slowly vanished and finally disappeared from the spectra, when the solution was kept at room temperature for 2 days. The initial spectrum of **1a-d** was completely restored after that period of time, but repeated heating of the solution again gave rise to aforementioned changes. It is concaivable from these data, that the formation of 4 is an equilibrium process. At elevated temperatures the equilibrium is quick³y established and shifted toward the formation of the ortho-metallated complex. At room temperature the formation of 4 is thermodynamically unfavorable, but the equilibrium is established slowly, so that the reverse reaction requires a fong time for completion.

2.5. Reaction of $(PPh_{sh}Rh(\mu-OH)_2$ with p-nitrophenol in the presence of PPh_* Preparation and characterization of $(PPh_{s})_{s}RhOC_{s}H_{s}NO_{2}$ (1e)

Recently we reported that the binuclear hydroxo rhodium complex [(PPh₃)₂Rh(μ -OH)]₂ can be 'neutralized' by various carboxylic and even relatively weak C–H and M–H acids to give water and the corresponding complexes with Rh–O, Rh-C and Rh-M bonds [21]. Since phenols are stronger O-H acids ($pK_a \approx 10$) than water, it seemed reasonable to expect that the reactions with [(PPh₃)₂Rh(μ -OH)]₂ will lead to the corresponding rhodium aryloxides. Surprisingly, no reaction was observed when the complex was treated with various HOAr in toluene or methylene chloride. Even *p*-nitrophenol which is quite acidic ($pK_a = 7.14$) did not give any products. However, when 2 molar equivalents of PPh₃ were added to the solution, fast and clean transformation occurred in accordance with Eq. (6), giving (PPh₃)₃RhOC₆H₄NO₂ (1e) as the sole metalloorganic product. In contrast, phenol, anisole, *o*- and *p*-cresol were not reactive even in the presence of PPh₃.

$$\{(Ph_{3}P)_{2}Ru(\mu-OH)\}_{2} + 2HOC_{6}H_{4}NO_{2} + 2PPh_{3}$$

$$\rightarrow 2(Ph_{3}P)_{3}RhOC_{6}H_{4}NO_{2}$$

$$^{-2H_{2}O} Ie$$
(6)

Complex 1e was isolated as a 1:2 benzene solvate and characterized by elemental analysis, IR and NMR spectroscopy. The orange crystals of 1e 2C6H6 slowly darkened when kept in air, however the complex can be handled in air for several minutes without any decomposition. The analytical and spectral data (see Section 4) are in agreement with the structure of 1e as a square planar Rh complex with three triphenylphosphine ligands and the OC₆H₄NO₂ moiety coordinated to the metal via the phenolic oxygen. The 'H NMR spectrum of 1e in C6D6 at 20°C shows two sharp doublets for the o- and m-protons of the OC₆H₄NO₂ ligand at 6.4 and 7.9 ppm, respectively. The signals became very broad when the spectrum was recorded at 60°C, indicating some dynamic exchange process. Sharp doublets centered at 6.1 and 7.3 ppm were observed in the spectrum of le in CD₂Cl₂ at -20° C, but the signals became very broad at room temperature. Signals of PPh₃ ligands appeared as sharp lines in the ³¹P NMR spectrum of 1e in CD₂Cl₂ at 20°C. The lines did not become broader when triphenylphosphine was added to the solution, indicating that exchange between free and coordinated PPh₃ is slow on the NMR time scale under these conditions and line broadening in the 'H NMR is not caused by cis/trans exchange of PPh3 ligands. These data suggest that the dynamic process which occurs in a solution of le, probably involves a reversible dissociation of p-nitrophenoxy anion from the complex. The degree of dissociation is low, and no new signals appear in the ¹H and ³¹P NMR spectra. Line broadening in the 'H NMR spectra occurs probably due to shortening of the spin-spin relaxation time.

When 2 molar equivalents of *p*-nitrophenol were added to a solution of 1e in $C_6 D_6$, the ¹H NMR spectrum showed a broad signal at 10.6 ppm, which was assigned to the phenolic protons of hydrogen bonded *p*-nitrophenol. The aromatic protons of the $OC_6 H_4 NO_2$ ligand were indistinguishable from the corresponding protons of *p*-nitrophenol and appeared as very broad resonances at 6.3 and 7.7 ppm. Further addition of *p*-nitrophenol led to a gradual shift of the signal of phenolic protons to lower frequency. These data indicate that *p*-nitrophenol forms strong hydrogen bonds with the $OC_6H_4NO_2$ ligand of Ie, and that *p*-nitrophenoxy ligand undergoes fast exchange with free and hydrogen bonded *p*-nitrophenol in solution.

Although 1e and 1a-d have the same molecular arrangement, their behavior in solution is very different. According to ³¹P NMR spectra, 1e shows no tendency to eliminate PPh₃ with concomitant formation of a complex with π -coordinated OC₆H₄NO₂ ligand (cf. Eqs. (2), (4) for 1a-d). Moreover, 1e does not give any *ortho*-metallated species in observable concentrations even under prolonged heating in solution. Such behavior may be attributable to the electron withdrawing effect of the NO₂ group, which makes the aromatic ring of the ligand electron poor and unlikely to coordinate the Rh in a π -fashion.

2.6. Reactivity of **la-e** and **2a-d** towards H₂O, MeOH, H₂ and CO. Preparation of (Ph₃P)₂Rh(CO)(OAr) (**3a-e**). X-ray structure of **3e**

Since transition metal alkoxides (aryloxides) are regarded as important intermediates in various metal catalyzed organic reactions [22,23], it was of interest to investigate and compare the reactivity of Rh aryloxides **1a-e** and **2a-d** toward CO, H₂, water and alcohols.

2.6.1. Reaction with H₂O

Complexes **1a-d** are very moisture sensitive. In solution they react immediately with water to give $[(PPh_3)_2Rh(\mu-OH)]_2$, which was identified by ³¹P NMR, PPh₃ and corresponding phenols. Hydrolysis of **2a-d**-2HOAr occurs similarly, but requires ~ 30 min for completion. The *p*-nitrophenoxo Rh complex **1e** did not give any products, detectable by ³¹P NMR when it was stirred with water in benzene or dissolved in wet THF.

2.6.2. Reaction with MeOH

The addition of MeOH to a toluene solution of **1a–d** results in formation of HRh(PPh₃)₃, which was isolated in high yield and identified by comparison of ³¹P and ¹H NMR spectra with published data [19]. The reaction probably involves β-elimination of hydrogen from an intermediate Rh methoxy complex with the formation of formaldehyde and the rhodium hydride. According to ³¹P NMR spectra, complex 1e, as well as **2a–d**, do not give any products when treated with methanol in toluene solution.

2.6.3. Reaction with H₂

Complexes **1a-d** readily react with hydrogen in toluene, affording HRh(PPh₃)₃, which was identified by ³¹P NMR. The reaction takes several minutes of bubbling H₂ into the solution. Under the same conditions complexes **2a-d** were unreactive. Passing H₂ through a solution of **1e** in toluene produced a mixture of unidentified products, but no HRh(PPh₃)₃ was detected by ³¹P NMR.



Fig. 6. Perspective drawing for 3e with adopted numbering scheme. Thermal ellipsoids are depicted at 30% probability. Only the *ipso* carbon atoms of PPh, are shown. Hydrogen atoms are omitted for clarity.

2.6.4. Reaction with CO

Bubbling CO into a toluene or benzene solution of 1a-e or $2a-d \cdot 2HOAr$ for several minutes cleanly affords the corresponding $(Ph_3P)_2Rh(CO)(OAr)$ (3a-e) (Eqs. (7) and (8)).

$$(Ph_{3}P)_{3}RhOAr + CO \rightarrow (Ph_{3}P)_{2}Rh(CO)OAr + PPh_{3}$$

$$1a - e \qquad 3a - e \qquad (7)$$

$$(Ph_3P)_2Rh(\pi-ArO) \cdot 2HOAr + CO$$

$$2a - d \cdot 2HOAr \qquad (8)$$

$$\rightarrow (Ph_3P)_2Rh(CO)OAr + 2HOAr$$

$$3a - d$$

In general, one can expect insertion of CO into Rh-OAr bond with the formation of corresponding (aryloxy)carbonyls, as observed for [Pt(triphos)(OAr)][PF₆] [3a] and [(ArO)Ir(CO)(PPh₃)₂] [24]. However, this reaction did not occur in the case of 1a-e or 2a-d · 2HOAr and reactions (7) and (8) were quantitative according to ³¹P NMR spectra. Complex 3e was isolated in high yield as air stable yellow crystals and characterized by elemental analysis, IR and NMR spectroscopy and an X-ray diffraction study. The structures of 3a-d were confirmed by alternative synthesis from RhCl(CO)(PPh₃)₂ and the corresponding NaOAr. The complexes were isolated as air stable yellow crystals and characterized by elemental analysis and spectroscopy² (see Section 4). An ORTEP plot of 3e and selected bond lengths and angles are presented in Fig. 6 and Table 5, respectively. The central Rh atom in 3e has an essentially square planar geometry, with the trans angles being 173.5 and 176.8° for P1-Rh-P2 and O1-Rh-C43, respectively. The p-nitrophenoxy fragment is trans to the CO ligand and bonded to the metal via phenolic oxygen. The values of the C-C, C-O, C-N and O-N bond lengths for the OC6H4NO2 ligand

Table 5 Selected bond distances (Å) and angles (°) for (Ph₁P)₂Rh(CO)OC₆H₄NO₂

P(1)-Rh	2.3346(8)	P(1)-Rh-O(1)	94.66(5)
P(2)-Rh	2.3403(8)	P(1)-Rh-C(7)	88.16(8)
C(7)-Rh	1.814(3)	C(7)-Rh-P(2)	90.79(8)
C(7)-O(7)	1.156(3)	O(1)-Rh-P(2)	86.55(5)
O(1)-Rh	2.069(2)	O(7)-C(7)-Rh	178.2(2)
C(1)-O(1)	1.307(3)	Rh-O(1)-C(1)	130.2(2)

Table 6 Bond distances (Å) in $4 \cdot NO_2C_nH_2O$ units of *p*-nitrophenol, 3e and $4 \cdot NO_2C_nH_2OK \cdot H_3O$

Bond distance	p-nitrophenol	3e	4-NO ₂ C ₆ H ₄ OK · H ₂ O
CI-C2	1.393(6)	1.417(3)	1.424(2)
C2-C3	1,380(6)	1.374(3)	1.373(2)
C3-C4	1.383(6)	1.398(3)	1.400(2)
C4-C5	1.388(6)	1.390(3)	1.400(2)
C5-C6	1.377(6)	1.374(3)	1.373(2)
C1-C6	1.387(6)	1.422(3)	1.428(2)
C1-01	1.351(6)	1.306(3)	1.292(2)
C4N	1.442(6)	1.446(3)	1.418(2)
N-02	1.232(6)	1.235(3)	1.241(2)
N-03	1.236(6)	1.248(3)	1.247(2)

(Table 6) lie within the range of values reported for *p*-nitrophenol [25] and its potassium salt [26].

3. Conclusions

The present study shows that the properties of rhodium aryloxo complexes of general formula $(Ph_3P)_3Rh(OC_8H_4R)$ are quite sensitive to the nature of the substituents in the aromatic ring of the aryloxo ligand. Complexes **1a-d**, containing electron donor substituents, are very labile, and readily react with H_3O , MeOH, H_2 and CO. In solution they exist as equilibrium mixtures with PPh₃ and the corresponding

² Complex 3a was characterized previously by IR in solution, see Ref. [4].

(PPh₃)₂Rh(π -ArO). In the presence of phenols the equilibrium is completely shifted toward complexes with π -coordinated OAr, due to the formation of strong hydrogen bonds between the oxygen atom of the ligand and two molecules of HOAr. Upon heating in solution **1a–d** readily eliminate the corresponding phenol with *ortho*-metallation of the aromatic ring of a triphenylphosphine ligand.

Unlike 1a-d, complex 1e, which contains an electron withdrawing NO₂ group, is relatively inert. In solution it shows no tendency to dissociate to PPh₃ and the corresponding complex with a π -coordinated OAr ligand. The complex does not give any *ortho*-metallated species even under prolonged heating in solution. Although 1e reacts with CO in the same way as complexes 1a-d do, it is inert towards water and methanol.

4. Experimental

All manipulations were carried out under inert atmosphere using standard Schlenk techniques. The solvents were dried and distilled prior to use. The rhodium complexes $(Ph_3P)_3RhC1 [27], [(Ph_3P)_2RhC1]_2 [27], (Ph_3P)_3Rh_2(\mu OH)_2 [21] and (Ph_3P)_3Rh(CO)C1 [27] were prepared as$ described elsewhere. The NaOAr reagents were preparedfrom the corresponding phenols and a three-fold excess ofNaNH₂ in THF. The stirred mixture was heated to reflux,cooled, unreacted NaNH₂ was filtered, and the filtrates wereused as stock solutions. The other chemicals were purchasedfrom Aldrich and were used as received. The following instruments were used: Varian Gemini-200 (¹H NMR), VarianXL-300 (¹³C and ³¹P NMR), Bomem MB-100 (FT-IR) andPerkin-Elmer 2400 Series II (combustion microanalysis).

4.1. Synthesis of (Ph,P),RhOPh (1a)

A mixture of (Ph₃P) ₃RhCl (410 mg, 0.443 mmol), toluene (8 ml) and NaOPh (0.9 M solution in THF, 0.5 mmol) was stirred for 1 h at room temperature. The resulting brown solution was filtered, and reduced in volume to ~3 ml. Pentane vapors were allowed to diffuse into the solution overnight. The precipitated dark red crystals were separated, washed with toluen (2×2 ml), pentane (2×6 ml) and vacuum dried to give 398 mg (91%) of analytically pure 1a. ³¹P NMR: see Table 2. IR (KBr) (selected bands): 1586m, 1482s, 1433s, 1295s, 1090m cm⁻¹, Anal. Calc. for C₆₀H₅₀OP₃Rh: C, 73.3; H, 5.1. Found: C, 73.2; H, 5.2%.

4.2. Synthesis of (Ph₃P)₃RhOC₀H₄NO₂ (1e)

(Ph₃P)₃RhCl (205 mg, 0.221 mmol) was added to a mixture of KOH (2 g), water (3 ml) and benzene (10 ml), and the reaction mixture was refluxed with stirring for 2 h. The orange organic layer was filtered through cotton wool, the aqueous phase was washed with benzene (3×2 ml), the washings were filtered, and *p*-nitrophenol (31 mg, 0.223 mmol) was added to the combined filtrates. The resulting red solution was stirred for 30 min, diluted with heptane (6 ml), reduced in volume under vacuum to ~ 8 ml and left overnight. The precipitated orange crystals were rinsed with benzene, washed with plenty of pentane and vacuum dried. The yield of spectroscopically pure le · 2C₆H₆ was 210 mg (92%). ³¹P NMR $(C_6 D_6)$: δ 31.3 (dd, J(P-Rh) = 151 Hz, J(P-P) = 40Hz), 51.1 (dt, J(P-Rh) = 176 Hz, J(P-P) = 40 Hz). ¹H NMR (C_6D_6): $\delta 6.5$ (d, J = 8.8 Hz, 2H), 6.8 (m, 27H), 7.6 (m, 18H), 7.95 (d, J = 8.8 Hz, 2H). ¹³C{¹H} NMR (C₆D₆): δ 120.5 (s, OC₆H₄NO₂), 125 (s, OC₆H₄NO₂), 127.35 (d, J = 10 Hz, trans-PC₆H₅), 127.6 (virtual t, J = 9.5 Hz, cis-PC6H5), 129.15 (s, trans-PC6H5), 129.2 (s, cis-PC6H5), 134.1 (virtual t, J=39.5 Hz, $cis-PC_6H_5$), 134.7 (s, $OC_6H_4NO_2$, 134.9 (d, J = 11 Hz, trans- PC_6H_5), 135.1 (virtual t, J = 12 Hz, cis-PC₆H₅), 137 (d, J = 44.5 Hz, trans-PC₆H₅), 177.3 (s, OC₆H₄NO₂). IR (KBr) (selected bands): 1577s, 1485m, 1433m, 1288vs, 1106m, 1090m cm⁻⁺. The compound was recrystallised from toluene for elemental analysis. Anal. Calc. for C24H65NO3P3Rh (le·2MeC6H5): C, 73.3; H, 5.4; N, 1.2. Found: C, 73.4; H, 5.2; N, 1.1%.

4.3. Synthesis of (Ph,P)2Rh(π-ArO)·2ArOH(2a,b·2ArOH)

4.3.1. 2a · 2PhOH

A mixture of (Ph₃P)₃RhCl (113 mg, 0.122 mmol), toluene (6 ml) and NaOPh (0.9 M solution in THF, 0.25 mmol) was stirred for 1 h at room temperature and filtered. Solid PhOH (30 mg, 0.32 mmol) was added to the filtrate, and the resulting solution was reduced in volume to ~3 ml. Pentane vapors were allowed to diffuse into the solution for 2 days. The precipitated dark red crystals were separated, washed with toluene (2×2 ml), pentane (2×6 ml) and vacuum dried to give 92 mg (83%) of 2a · 2PhOH. The compound was recrystallized from benzene. ³¹P{¹H} NMR (C_6D_6): δ 47.5 (d, J = 213 Hz). ¹H NMR (C₆D₆): δ 4.4 (t, J = 5.9 Hz, 1H), 5.15 (m, 2H), 5.6 (d, J = 7 Hz, 2H), 6.8 (m, 2H), 6.9 (m, 18H), 7.2 (m, 8H), 7.5 (m, 12H), 10.7 (broad s, 2H). ¹³C{¹H} NMR (C₆D₆): δ 84.3 (s, π -C₆H₅O), 97.3 (s, π - C_6H_5O), 104.9 (s, π - C_6H_5O), 116.3 (s, PhOH), 119.1 (s, PhOH), 127.8 (virtual t, J = 10 Hz, PC_6H_5), 129.5 (s, PC_6H_5), 129.7 (s, PhOH), 134.3 (virtual t, J = 12 Hz, $PC_{o}H_{5}$, 136.4 (virtual t, J=46 Hz, $PC_{0}H_{5}$), 158.7 (s, PhOH), 164.6 (s, π-OC₆H₅). IR (KBr) (selected bands): 2700v broad, 1602w, 1589m, 1541s, 1478vs. 1468vs, 1434s, 1271m, 1247s, 1093s cm⁻¹. Anal. Calc. for C₅₄H₄₇O₃P₂Rh: C. 71.4; H. 5.2, Found: C. 71.8; H. 5.2%.

4.3.2. 2b · 2(4-MeC,H,OH)

The complex was prepared in the similar way and recrystallized from toluene. The yield was 89%. ³¹P{¹H} NMR (C₆D₆): δ 46 (d, J = 209 Hz). ¹H NMR (C₆D₆): δ 1.55 (s, 3H), 2.15 (s, 6H), 4.5 (d, J = 7.2 Hz, 2H), 5.5 (d, J = 7.2 Hz, 2H), 5.9 (m, 18H), 6.98 (d, J = 8.5 Hz, 4H), 7.33 (d, J = 8.5 Hz, 4H), 7.5 (m, 12H), 11.4 (s, 2H). ¹³C{¹H} NMR (C₆D₆): δ 18.7 (s, π -CH₃C₆H₄O), 20.7 (s, HOC₆H₄CH₃), 92.8 (s, π -CH₃C₆H₄O), 102.6 (s, π -CH₄C₆H₄O), 105.2 (s,

HOC₆H₄CH₃), 117.4 (s. HOC₆H₄CH₃), 127.2 (s. π -CH₃C₆H₄O), 127.8 (virtual t, J = 10 Hz, PC₆H₅), 129.5 (s. PC₆H₅), 130.2 (s. HOC₆H₄CH₃), 134.3 (virtual t, J = 12 Hz, PC₆H₅), 136.4 (virtual t, J = 46.5 Hz, PC₆H₅), 157.2 (s. HOC₆H₄CH₃), 163.4 (s. π -CH₃C₆H₄O). IR (KBr) (selected bands): 2660v broad, 1610m, 1591w, 1545s, 1513s, 1497vs, 1485s, 1433s, 1267s, 1247s, 1091s cm⁻¹. Anal. Calc. for C₅₇H₅₃O₃P₂Rh: C, 72.0; H, 5.6. Found: C, 71.7; H, 5.5%.

4.4. Synthesis of (Ph₃P)₂Rh(CO)OAr (3a-d)

A mixture of $(Ph_3P)_2Rh(CO)Cl$ (104 mg, 0.150 mmol), NaOAr (THF solution, 0.2 mmol) and benzene (6 ml) was stirred for 1 h at room temperature and filtered. The filtrate was diluted with heptane (8 ml), reduced in volume to ~8 ml and left for 2 h. The precipitated yellow crystals were washed with benzene (2×2 ml), pentane (2×6 ml) and dried to give **3a-d**. The complexes were found to be analytically and spectroscopically pure without recrystallization.

4.4.1. Complex 3a

Yield: 95%. ³¹P{¹H} NMR (CDCl₃): δ 28 (d, *J* = 139.5 Hz). ¹H NMR (CDCl₃): δ 6.1 (t, *J* = 7.2 Hz, 1H), 6.2 (d, *J* = 7.9 Hz, 2H), 6.5 (m, 2H), 7.1 (m, 18H), 7.6 (m, 12H). ¹³C{¹H} NMR (CDCl₃): δ 112 (s, OPh), 120.6 (s, OPh), 127.5 (s, OPh), 128.2 (virtual t, *J* = 10 Hz, PC₆H₅), 130 (s, PC₆H₅), 132.4 (virtual t, *J* = 44 Hz, PC₆H₅), 134.5 (virtual t, *J* = 13.5 Hz, PC₆H₅), 167 (s, OPh), 189.4 (dt, *J*(C-Rh) = 67 Hz, *J*(C-P) = 17.5 Hz, CO). IR (KBr) (selected bands): 1953vs, 1587m, 1483m, 1433m, 1290m, 1093m cm ⁻¹. Anal. Calc. for C₄₃H₃₅O₂P₂Rh: C, 69.0; H, 4.7%.

4.4.2. Complex 3b

Yield: 97%. ³¹P{¹H} NMR (C_6D_6): δ 27 (d, J = 140 Hz). ¹H NMR (C_6D_6): δ 2.1 (s, 3H), 6.6 (m, 4H), 7.0 (m, 18H), 7.9 (m, 12H). ¹³C{¹H} NMR (C_6D_6): δ 20.8 (s, OC₆H₄CH₃), 120.7 (s, OC₆H₄CH₃), 121 (s, OC₆H₄CH₃), 128.4 (virtual t, J = 10 Hz, PC₆H₅), 128.8 (s, OC₆H₄CH₃), 130.1 (s, PC₆H₅), 133.3 (virtual t, J = 43.5 Hz, PC₆H₅), 134.9 (virtual t, J = 13 Hz, PC₆H₅), 166 (s, OC₆H₄CH₃), 191 (dt, J(C-Rh) = 66 Hz, J(C-P) = 17 Hz, CO). IR (KBr) (selected bands): 1954vs, 1601m, 1497s, 1478m, 1433s, 1278s, 1096m cm⁻¹. Anal. Calc. for C₄₄H₃₇O₂P₂Rh: C, 69.3; H, 4.9. Found: C, 69.7, H, 5.1%.

4.4.3. Complex 3c

Yield: 88%. ³¹P{¹H} NMR (C_6D_6): δ 29.5 (d, J = 140.5 Hz). ¹H NMR (C_6D_6): δ 1.9 (s, 3H), 6.4 (dt, ¹J = 7.2 Hz, ²J = 1.2 Hz, 1H), 6.7 (dt, ¹J = 7.2 Hz, ²J = 1.8 Hz, 1H), 6.85 (m, 2H), 7.0 (m, 18H), 7.9 (m, 12H). ¹³C{¹H} NMR (C_6D_6): δ 18.1 (s, $OC_6H_4CH_3$), 113 (s, $OC_6H_4CH_3$), 120.8 (s, $OC_6H_4CH_3$), 126 (s, $OC_6H_4CH_3$), 123.3 (virtual t, J = 9.5 Hz, PC_6H_5), 129 (s, $OC_6H_4CH_3$), 132.5 (s, PC_6H_5), 133.2 (virtual t, J = 12.5 Hz, PC_6H_5), 166 (s, $OC_6H_4CH_3$), 191 (dt, J(C-1)

Rh) = 66 Hz, J(C-P) = 17 Hz, CO). IR (KBr) (selected bands): 1953vs, 1588m, 1477s, 1433s, 1284s, 1095m cm⁻¹. Anal. Calc. for $C_{44}H_{37}O_2P_2Rh$: C, 69.3; H, 4.9. Found: C, 69.7; H, 4.8%.

4.4.4. Complex 3d

Yield: 95%. ³¹P{¹H} NMR (C_6D_6): δ 27.5 (d, J = 139.5 Hz). ¹H NMR (C_6D_6): δ 3.4 (s, 3H), 6.4 (m, 4H), 7.0 (m, 18H), 7.9 (m, 12H). ¹³C{¹H} NMR (C_6D_6): δ 55 (s, $OC_6H_4OCH_3$), 113.6 (s, $OC_6H_4OCH_3$), 120.2 (s, $OC_6H_4OCH_3$), 127.8 (virtual t, J = 9 Hz, PC_6H_5), 131.5 (s, PC_6H_5), 132.7 (virtual t, J = 43 Hz, PC_6H_5), 134.3 (virtual t, J = 12 Hz, PC_6H_5), 148.6 (s, $OC_6H_4OCH_3$), 161.8 (s) $CC_6H_4OCH_3$), 190.5 (dt, J(C-Rh) = 66 Hz, J(C-P) = 17.5 Hz, CO). IR (KBr) (selected bands): 1965vs, 1491s, 1433m, 1224m, 1096m cm⁻¹. Anal. Calc. for $C_{44}H_{37}O_3P_2$ Rh: C, 67.9; H, 4.8. Found: C, 68.1; H, 4.6%.

4.5. Synthesis of $(Ph_3P)_2Rh(CO)OC_0H_4NO_2$ (3e)

Carbon monoxide was bubbled through a solution of $(Ph_3P)_3RhOC_6H_4NO_3 \cdot 2CH_3Ph$ (48 mg, 0.040 mmol) in benzene (6 ml) for 5 min. The resulting pale yellow solution was diluted with heptane (6 ml), reduced in volume to ~ 6 ml under vacuum and left overnight. The precipitated yellow crystals were washed with benzene $(2 \times 2 \text{ ml})$, pentane (2×6 ml) and vacuum dried to give 28 mg (0.036 mmol, 91%) of 3e. ³¹P{¹H} NMR (CDCl₃): δ 29.5 (d, J=134.5 Hz). ¹H NMR (CDCl₃): 86.1 (m, 2H), 6.9 (m, 18H), 7.65 (m, 12H), 7.75 (m, 2H). ${}^{13}C{}^{1}H} NMR (CDCl_3): \delta 119.6$ $(s, OC_6H_4NO_2)$, 125.2 $(s, OC_6H_4NO_2)$, 128.4 (virtual t, $J = 8.5 \text{ Hz}, \text{PC}_{6}\text{H}_{5}), 130.5 (s, \text{PC}_{6}\text{H}_{5}), 131.5 (virtual t, J = 45)$ Hz, PC_6H_5), 134 (s, $OC_6H_4NO_2$), 134.3 (virtual t, J = 13 $H_{z}, PC_{6}H_{5}$, 175 (s, $OC_{6}H_{4}NO_{5}$), 189.7 (dt, J(C-Rh) = 70Hz, J(C-P) = 17 Hz, CO). IR (KBr) (selected bands): 1980s, 1580s, 1489m, 1467m, 1433m, 1289vs, 1097s cm⁻¹. Anal. Calc. for C43H34NO4P2Rh: C, 66.4; H, 4.4; N, 1.8. Found: C, 66.5; H, 4.6; N, 1.8%.

4.6. Single-crystal X-ray diffraction study of (Ph₃P)₃RhOPh (1a), (Ph₃P)₂RhOPh · 2PhOH (2a · 2PhOH) and (Ph₃P)₂Rh(CO)OC₆H₄NO₂ (3e)

Crystal data and refinement parameters are summarized in Table 7. The crystals suitable for X-ray analysis were obtained by crystallization from concentrated toluene solutions. The crystals were mounted on glass fibers. All measurements were made at -110° C on a Siemens Smart CCD diffractometer with Mo K α_1 radiation. Systematic absences in the diffraction data and unit-cell parameters are uniquely consistent with the reported space groups for 1a and 3e. No symmetry higher than triclinic was observed for 2a · 2PhOH. Solution in the centric space group option yielded chemically reasonable and computationally stable results. During the data collection standards were measured after every 150 reflections. No crystal decay was noticed. Each structure was

Table 7
Summary of crystallographic data for 1a, 2a 2PhOH and 3e

Complex	la	2a·2PhOH	3e
Formula	C _{so} H _{so} OP,Rh	C ₄ H ₄₇ O ₃ P ₂ Rh	C ₁ ,H ₁ ,NO ₁ P.Rh
Formula weight	982.82	908.77	793.56
Crystal dimensions (mm)	0.2×0.1×0.08	0.2×0.2×0.2	$0.2 \times 0.2 \times 0.2$
Crystal system	orthorombic	triclinic	monoclinic
Lattice parameters			
a (Å)	12.3095(3)	10.5639(1)	15.7469(3)
b (Å)	20.7943(6)	12.4749(1)	14.6046(2)
c (Å)	37.7345(9)	18.3573(2)	17.4164(1)
α (°)		70.821(1)	
β(°)		85.859(1)	112.862(1)
γ(°)		81.396(1)	
Space group	Pbca	P-1	P2,/n
Ζ	8	2	4
V (Å')	9658.8(4)	2258.53(1)	3690.73(9)
D_{cale} (g cm ⁻¹)	1.352	1.333	1.428
Т(К)	163	163	163
Radiation (Mo K α_1) λ (Å)	0.71073	0.71073 Å	0.71073
μ (Mo K α) (cm ⁻¹)	4.95	4.92	5.93
Transmission (max./min.)	1.287	1.503	1.303
R(F) (%)	5.79	4.22	2.29
$R(wF^2)$ (%)	11.34	10.72	5.32
N_{ν}/N_{ν}	11.8	11.6	10.4
GOF	1.18	1.10	1.04

Quantity minimized = $R(wF^2) = \sum \left[\left(w(F_w^2 - F_y^2)^2 \right) / \sum \left(wF_w^2 \right)^{1/2} : R = \sum \Delta / \sum (F_w), \Delta = \left[(F_w - F_y) \right] \right]$

solved by direct methods, completed by Fourier synthesis and refined by full-matrix least squares procedures based on F^2 . The data were corrected for absorption by using redundant data at different effective azimuthal angles. Two symmetrically unique but chemically equivalent, co-crystallysed phenol molecules were located in the asymmetric unit of **2a** · 2PhOH. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The phenolic hydrogen atoms of **2a** · 2PhOH were initially located from the difference map but were treated as rigid groups with idealized geometry in subsequent refinement. All other hydrogen atoms were treated as idealized contributions. All software and sources of atomic scattering factors are contained in the SHEXTL(5.03) program library [28].

5. Supplementary material

Listing of crystallographic details, atomic parameters, bond distances and angles, isotropic and anisotropic thermal parameters and ORTEP drawings for 1a, $2a \cdot 2PhOH$ and 3e(89 pages) are available from the authors upon request.

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