

Reactions of Iminophosphanes with Chlorotris(triphenylphosphine)rhodium(I): Generation and NMR Identification of the First Iminophosphanerhodium(I) and Iminophosphanerhodium(III) Complexes

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Iminophosphanes [RO-P=NAr] (R = Me, 2-MeC₆H₄; Ar = 2,4,6-Bu₃C₆H₂) **1a,b** react with RhClL₃ (L = Ph₃P) via ligand exchange to give κP-iminophosphane complexes of rhodium(I) [RhCl(MeOP=NAr)₂L] **2** and [PhCl(2-MeC₆H₄OP=NAr)L₂] **3**. Under analogous conditions, P-halogenoiminophosphanes [X-P=NAr] (X = Cl, Br, I) **3a–c** undergo a facile oxidative addition of the P–X bond, forming five-coordinate iminophosphanerhodium(III) complexes of composition [L₂Cl(X)Rh(σ-P=BAr)] **5**.

Transition metal iminophosphane complexes have attracted considerable interest because of their novel bonding features. Since 1977 a large number of such species have been synthesized and structurally characterized.¹ In these studies, attention has focused on the P-aminoiminophosphanes [R₂N–P=NR].² Compared with the latter, very little is known about the ligating properties of other types of P-functionalized iminophosphanes, especially those containing a reactive X–P single bond.³ We report herein our initial observations which include (a) the generation and NMR characterization of novel P-alkoxy- (or aryloxy-) (2,4,6-tri-*tert*-butylimino)phosphane-κP rhodium(I) complexes, and (b) the discovery of a facile oxidative addition of the halogeno(2,4,6-tri-*tert*-butylimino)phosphanes to rhodium(I) resulting in the formation of five-coordinate iminophosphane-κP rhodium(III) complexes.

Whereas reaction of [RhClL₃] with an equimolar amount of **1a**⁴ in toluene–dichloromethane solution (1:2) at room temperature produced only broad signals in the ³¹P{¹H} NMR spectrum, treatment with an excess of **1a** (3 equiv.) produced an NMR spectrum showing an ABMX pattern (X = Rh) attributable to **2** (Table 1). The AB resonances, which are assigned to two iminophosphane ligands, display rather small coordination shifts with respect to free **1b** which is generally associated with a κP-coordination mode (*cf.*⁵). The symmetry of the spectrum and the *trans*-coupling between P^A and P^M (454 Hz) prove the *cis*-arrangement of the coordinated iminophosphanes.

The reaction of [RhClL₃] with an excess of **1b**⁵ at room temperature in a toluene–dichloromethane mixture (2 h reaction time) gave the monosubstituted iminophosphanerhodium(I) complex **3** as a ca. 4:1 mixture of *trans* and *cis* isomers. The observed AM₂X and AMNX (X = Rh) spectra show chemical shifts and ¹J_{RhP} coupling constants for each type of ligand which are similar to **2**, also suggesting κP-coordination of the iminophosphane. The ¹J_{RhP} values of **2** and **3** are typical for complexes of four-coordinate Rh(I). As compared with Ph₃P, the iminophosphane ligands show a greater magnitude of ¹J_{RhP} due to the formal sp²-hybridisation at phosphorus. This coupling is further increased if the iminophosphane is in a *trans*-position to the chloride, indicating a higher degree of π-backbonding from the ligand in this case.

Solutions of **2** and **3** were stable for many days at room temperature with excess free iminophosphane ligand present.

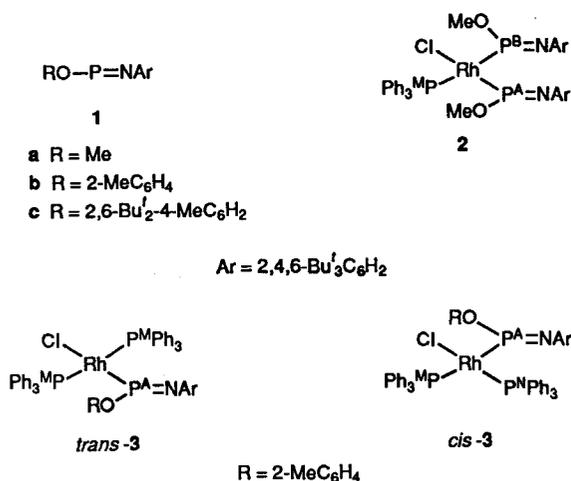
Table 1 ³¹P{¹H} and ¹⁵N NMR data for complexes **2,3** and **5a–e**

Complex	δ ³¹ P ^a	¹ J _{RhP} ^b	² J _{PP} ^b	δ ¹⁵ N ^{a,c}	J _{NP}	J _{NRh} ^b
2	137.9 P ^A	304	67 (AB)			
	120.7 P ^B	195	34 (AM)			
	24.6 P ^M	125	454 (BM)			
<i>trans</i> - 3	123.4 P ^A	334	55 (AM)			
	31.4 P ^M	124				
<i>cis</i> - 3	117.6 P ^A	223	465 (AM)			
	51.8 P ^M	190	55 (AN)			
	30.8 P ^N	121	36 (NM)			
5a	323.9 P ^A	74	4 (AM)	–91	87.1	¹ J _{PN}
	24.8 P ^M	106			3.6	² J _{RhN}
5b	309.2 P ^A	80	7 (AM)		3.1	³ J _{PN}
	26.1 P ^M	101				
5c	272.4 P ^A	102	19 (AM)			
	25.5 P ^M	98				
5d	288.3 P ^A	89	9 (AM)	–114	89.1	¹ J _{PN}
	24.3 P ^M	101			2.7	² J _{RhN}
5e	237.2 P ^A	115	22 (AM)	–147 ^d	2.0	³ J _{PN}
	22.3 P ^M	99			95.2	¹ J _{PN}

^a In ppm (121.5 MHz, C₆D₅CD₃–CH₂Cl₂, ext. H₃PO₄). ^b In Hz. ^c 30.4 MHz, C₆D₅CD₃–CH₂Cl₂, ext. CH₃NO₂. ^d Broad signals.

Attempts to remove the solvent and excess PPh₃ and **1a,b**, however, resulted in decomposition and formation of [RhL₂Cl]₂. In contrast to **1a,b** the sterically crowded **1c** is unreactive towards [RhClL₃] (five-fold excess iminophosphane, 2 weeks at 20°C); obviously in this case the bulky aryloxygroup on phosphorus prevents κP-coordination.

A different type of interaction was observed during the reactions of [RhClL₃] with the halogenoiminophosphanes **4**.⁶ When **4a** (0.5 mmol) in toluene (1.5 ml) was allowed to react with an equimolar quantity of the rhodium complex in dichloromethane (2 ml) at –30°C, a very rapid reaction occurred with liberation of one PPh₃ ligand. The resulting new complex was isolated in 69% yield as a brick-red, air- and moisture-sensitive microcrystalline solid after evaporation of the solvent and crystallization from a cyclohexane–CH₂Cl₂ (1:1) solution at –10°C. Elucidation of the constitution of the product as metal-substituted iminophosphane **5a** was possible on the basis



Scheme 1

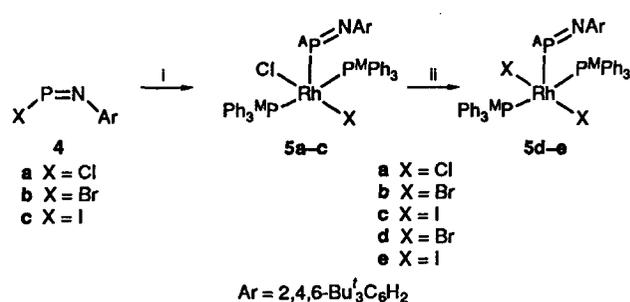
of its ³¹P{¹H} NMR spectrum showing an A₂MX spin system (A, M = ³¹P; X = ¹⁰³Rh). The P^A resonance exhibits a downfield shift of more than 200 ppm relative to uncoordinated **1b** as well as significantly reduced values of both ¹J_{RhP} and ²J_{PP} which are diagnostic for a transition metal-substituted phosphorus ππ-system.^{7†} Further, the ¹J_{RhP^A} coupling constant of the Ph₃P ligands is much smaller than in **2,3**, but is quite comparable with those in the five-coordinate acylrhodium(III) complexes [*trans*-(Ph₃P)₂Cl₂Rh(σ-COR)]¹¹ which form in the reactions of [RhCl₃] with acyl chlorides.[‡] The structural formulation of **5a** is also supported by the similarity of the ³¹P NMR parameters with those of (R₃P₂)XM[σ-P=C(SiMe₃)₂] (M = Ni, Pt; X = Br, I), which were obtained in an analogous reaction by oxidative addition of complexes of Ni⁰ and Pt⁰ with halogenophosphanes.¹⁰ It is essential that like the latter, **5a** is quite inert towards [RhCl(CO)L₂] which is much less reactive in oxidation addition reactions than [RhClL₃].¹⁴ In a similar way as **4a**, the bromo- and iodo-iminophosphanes **4b,c** easily reacted with RhCl₃ to give complexes **5b,c** together with the halogen exchange products **5a** and **5d,e**, respectively. After addition of excess Me₃SiBr or Me₃SiI to the reaction mixtures,¹⁵ followed by concentration of the solutions and re-crystallization of the residue from cyclohexane-dichloromethane (1:1), the complexes **5d,e** were isolated in pure form.§

In conclusion, the synthesis of the iminophosphanerhodium(III) complexes is the first example of direct oxidative addition of *P*-halogenoiminophosphanes to transition metal derivatives. In a broader context, the results presented here suggest that reactions of *P*-functionalized iminophosphanes with low-valent group 6 and 8–10 metal complexes possess a

† Formally, the observed strong deshielding of P^A and the small ¹J_{RhP^A}, ²J_{PP} values may be explained by κN-ligation of **4**.⁸ However, taking into account the pattern of reactivity of halogenoiminophosphanes^{6,9} and the very small magnitude of the ¹J_{Rh¹⁵N} coupling (<4 Hz), this assumption should be dropped.

‡ It seems highly likely that the complexes **5** are of square pyramidal structure similar to the above acylrhodium(III) compounds where the σ-bonded carbon donor is in an apical position.¹² However, there may be considerable distortion from square pyramidal geometry, and a five-coordinate complex having a trigonal bipyramidal structure cannot be excluded. The assumption of a *trans*-diequatorial configuration of Ph₃P is based on data^{11,13} according to which ¹J_{RhP} for a phosphorus *trans* to a halogen is larger than ¹J_{RhP} for two phosphorus atoms *trans* to each other. A phosphorus *trans* to a chloride also resonates at lower field than do mutually *trans* phosphines, e.g. [(Ph₃P)₂Cl₂Rh(COMe)]: δ_P 29.8, ¹J_{RhP} 145 Hz (*cis*): δ_P 23.6, ¹J_{RhP} 108 Hz (*trans*). Our attempts to grow crystals suitable for X-ray diffraction failed.

§ The compounds **5a,d,e** gave ¹H NMR spectra and elemental analyses consistent with the assigned structures.



Scheme 2 Reagents and conditions: i, RhCl(PPh₃)₃ (1 equiv.), toluene-CH₂Cl₂ (1:2), -30°C, 0.5 h; ii, Me₃SiBr or Me₃SiI (excess), benzene, room temp., 3 h

considerable potential in view of the synthesis of new types of metalloiminophosphanes.

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