

Preliminary communication

A rhodium(I) amide dimer: synthesis, structural characterisation and preliminary reactivity studies

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Received 4 July 1996; revised 30 September 1996

Abstract

A rhodium(I) amide complex was synthesised, isolated and crystallographically characterised: this is the first reported molecular structure of a dimeric rhodium amide complex.

Keywords: Rhodium; Triphenylphosphine; Lithium anilide; Dinuclear amido-bridged complexes

1. Introduction

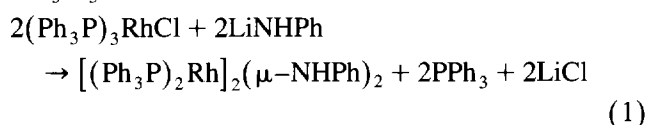
Amido complexes of the late transition metals [1] have been attracting ever increasing attention, primarily because of their potential participation in C–N bond-forming reactions [2]. The inability of electron-rich, late metal centres to accept extensive π -donation from the lone pair of electrons on an amide nitrogen tends to lead to dimeric, bridging amido species [1,3]. Yet, despite this generally accepted tendency, there are very few structurally characterised examples of late transition metal amide dimers containing amide bridges [4–9].

Previously we reported the multinuclear NMR characterization of a series of rhodium amide complexes which had not yet been isolated in the solid state [10], including the *syn*/*anti* isomers of the dimeric complex $[(\text{Ph}_3\text{P})_2\text{Rh}]_2(\mu\text{-NHPH})_2$ **1**. Here we report the isolation and structural characterisation of this dimeric complex, along with a variable temperature NMR study and some preliminary reactivity studies. This represents the first dimeric rhodium amide complex characterised by X-ray diffraction.

2. Results and discussion

2.1. Synthesis of $[(\text{Ph}_3\text{P})_2\text{Rh}]_2(\mu\text{-NHPH})_2$ **1**

Complex **1** is prepared by the addition of slightly more than 1 equiv. of LiNHPH to a THF solution of $(\text{Ph}_3\text{P})_3\text{RhCl}$ [10].



Extraction of the residues of the reaction mixture with toluene and filtration allows the isolation of **1** as red–orange crystals which, upon drying in vacuo, change to an orange powder. The reaction is quantitative, as monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, with isolated yields upwards of 80%. The amide-bridged dimer **1** is extremely air-sensitive both in solution and in the solid state, decomposing to give free triphenylphosphine oxide and unidentified rhodium-containing species. However, the complex is inert towards water and methanol, as has also been reported for a series of dinuclear rhodium complexes containing a single amide bridge [11]. Complex **1** exists in solution as *syn* and *anti* isomers: room temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of this complex always show the two isomers in an approximately 2:1 ratio, regardless of the solvent used or the presence of other rhodium complexes in solution.

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2.2. X-ray crystal structure of **1**

While X-ray quality crystals of **1** were obtained from toluene solutions, the subsequent structural determination was plagued by difficulties with disordered solvent molecules in the unit cell. To obtain crystals from THF solutions, 12-crown-4 (equimolar to the amount of $(\text{Ph}_3\text{P})_3\text{RhCl}$) was added to the initial reaction mixture, causing the precipitation of $(12\text{-crown-4}) \cdot \text{LiCl}$ and allowing the isolation of red crystals of the THF solvate of **1** ($\mathbf{1} \cdot 2\text{THF}$).

An X-ray diffraction analysis of an arbitrarily selected single crystal of the THF solvate of **1** ($\mathbf{1} \cdot 2\text{THF}$) gave the molecular structure of the *anti* isomer, as shown in Fig. 1.

Final atomic coordinates with equivalent isotropic displacement parameters are listed in Table 1. Selected bond lengths and angles are given in Table 2. The RhN_2Rh ring is planar, with symmetric anilide bridges, the Rh–Rh distance of 3.376(2) Å and an Rh–N–Rh angle of 102.8(3)° precluding the presence of a rhodium–rhodium bond. Each rhodium is surrounded by a square planar array of ligands; the molecular dimensions are comparable to those of both $[(\text{Ph}_3\text{P})_2\text{Rh}]_2(\mu\text{-OH})_2$ and $[(\text{Ph}_3\text{P})_2\text{Rh}]_2(\mu\text{-Cl})_2$ [12]. An average Rh–N distance of 2.16 Å is typical among the few structurally characterised dinuclear late metal complexes containing bridging amido groups [4–6,8,9,13–15].

2.3. Variable temperature NMR studies of **1**

Previous $^{31}\text{P}\{^1\text{H}\}$ NMR variable temperature studies of **1** generated in situ suggested the presence of an equilibrium between the *syn* and *anti* isomers [10]. Since complex **1** could be isolated pure in the solid state we decided to probe this process more carefully.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of pure **1** in toluene- d_8 at various temperatures (Fig. 2) show that the higher-field signal is not affected as the temperature is lowered to 203 K.

On the contrary, the lower-field signal undergoes a decoalescence as the temperature is lowered to 223 K. Two multiplet signals are seen most clearly at 203 K. The first signal appears as a doublet of doublets ($^1J_{\text{Rh-P}} = 188 \text{ Hz}$, $^2J_{\text{P-P}} = 47 \text{ Hz}$) at 57.8 ppm. The second signal (at approximately 51.5 ppm) overlaps with the doublet due to the second dimeric isomer (so that neither $^1J_{\text{Rh-P}}$ nor $^2J_{\text{P-P}}$ are measurable) and is necessarily ascribed as a doublet of doublets, due to the phosphorus coupling observed in the first signal. These NMR features are tentatively explained as follows: in solution, both *syn* and *anti* isomers exhibit non-planar Rh_2N_2 rings which experience rapid ring inversion. On lowering the temperature to 203 K, this ring inversion is suppressed. For the *syn* isomer, the four phosphorus atoms remain equivalent (higher-field signal) whereas those of the *anti* isomer do not, giving rise to two

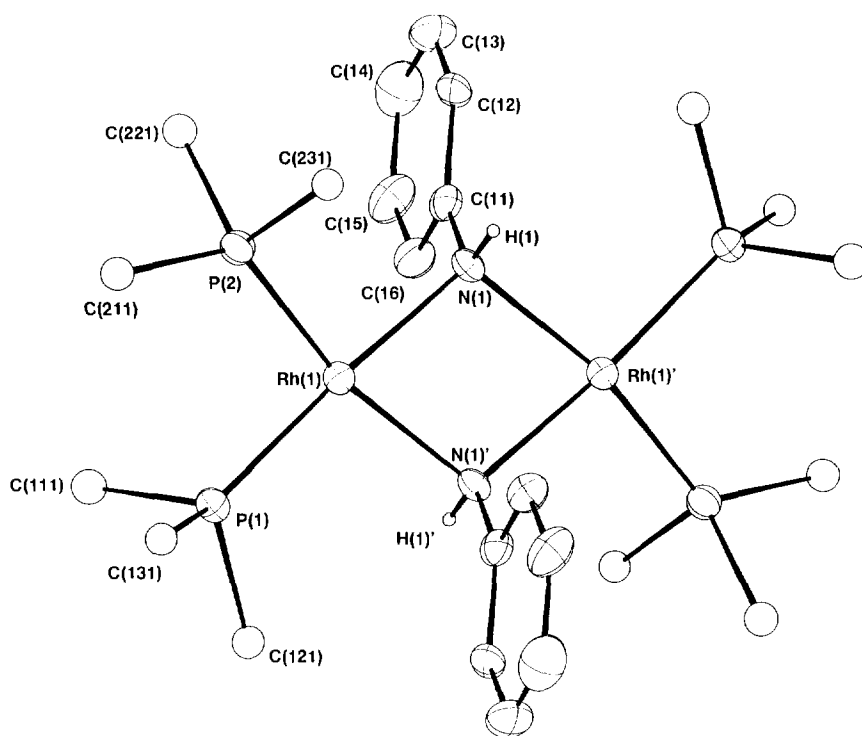


Fig. 1. Molecular structure of *anti* **1** · 2THF showing the atom numbering scheme. For clarity, only one carbon of each phenyl group of PPh_3 is represented and hydrogen atoms, except in NHPH bridges, are omitted.

Table 1

Fractional atomic coordinates and equivalent isotropic thermal parameters U_{eq} or isotropic thermal parameters U_{iso} for **1**·2THF. E.s.d.s in parentheses refers to the last digit

Atom	x	y	z	U_{eq}^a	U_{iso}
Rh(1)	0.24689(3)	0.15197(5)	0.52259(3)	0.0331	
P(1)	0.2362(1)	0.0912(2)	0.6090(1)	0.0381	
P(2)	0.2394(1)	0.0369(2)	0.4663(1)	0.0386	
N(1)	0.2694(3)	0.2248(5)	0.4498(3)	0.0322	
C(11)	0.3336(4)	0.2172(5)	0.4492(4)	0.0398	
C(12)	0.3556(5)	0.2002(6)	0.3966(5)	0.0452	
C(13)	0.4171(6)	0.1941(7)	0.3972(5)	0.0637	
C(14)	0.4611(5)	0.2041(8)	0.4533(7)	0.0692	
C(15)	0.4419(5)	0.2220(7)	0.5058(5)	0.0659	
C(16)	0.3787(4)	0.2294(6)	0.5048(4)	0.0483	
C(111)	0.2993(4)	0.0227(6)	0.6493(4)		0.047(3)
C(112)	0.3462(5)	0.0030(7)	0.6216(5)		0.063(3)
C(113)	0.3963(7)	-0.0521(9)	0.6525(6)		0.098(4)
C(114)	0.3945(7)	-0.079(9)	0.7110(7)		0.099(4)
C(115)	0.3511(6)	-0.0588(8)	0.7385(6)		0.086(4)
C(116)	0.3005(5)	-0.0080(7)	0.7082(5)		0.062(3)
C(121)	0.2354(4)	0.1562(6)	0.6764(4)		0.039(2)
C(122)	0.2856(5)	0.2086(7)	0.6963(5)		0.053(3)
C(123)	0.2895(5)	0.2583(7)	0.7478(5)		0.069(3)
C(124)	0.2441(6)	0.2567(8)	0.7791(6)		0.077(4)
C(125)	0.1942(6)	0.2052(8)	0.7614(5)		0.073(3)
C(126)	0.1903(4)	0.1565(7)	0.7089(4)		0.055(3)
C(131)	0.1641(4)	0.0329(6)	0.6033(4)		0.038(2)
C(132)	0.1596(4)	-0.0460(6)	0.6234(4)		0.049(3)
C(133)	0.1023(5)	-0.0849(7)	0.6155(5)		0.059(3)
C(134)	0.0489(5)	-0.0437(8)	0.5909(5)		0.074(3)
C(135)	0.0509(5)	0.0353(7)	0.5701(5)		0.062(3)
C(136)	0.1087(5)	0.0738(6)	0.5760(4)		0.050(3)
C(211)	0.2026(4)	-0.0585(6)	0.4845(4)		0.041(2)
C(212)	0.1403(5)	-0.0773(7)	0.4605(5)		0.057(3)
C(213)	0.1149(5)	-0.1536(8)	0.4735(5)		0.069(3)
C(214)	0.1521(6)	-0.2078(8)	0.5108(5)		0.074(3)
C(215)	0.2125(5)	-0.1900(7)	0.5361(5)		0.065(3)
C(216)	0.2397(5)	-0.1164(6)	0.5238(5)		0.056(3)
C(221)	0.3066(4)	-0.0104(6)	0.4437(4)		0.044(3)
C(222)	0.3003(5)	-0.0805(7)	0.4074(5)		0.056(3)
C(223)	0.3505(6)	-0.1148(8)	0.3891(5)		0.075(3)
C(224)	0.4081(6)	-0.0797(8)	0.4092(5)		0.077(4)
C(225)	0.4170(5)	-0.0125(8)	0.4457(5)		0.071(3)
C(226)	0.3654(5)	0.0217(6)	0.4629(5)		0.054(3)
C(231)	0.1844(4)	0.0608(6)	0.3914(4)		0.038(2)
C(232)	0.1314(5)	0.1051(6)	0.3945(4)		0.049(3)
C(233)	0.0851(5)	0.1229(7)	0.3409(5)		0.063(3)
C(234)	0.0925(5)	0.0935(7)	0.2857(5)		0.061(3)
C(235)	0.1441(5)	0.0531(7)	0.2805(5)		0.068(3)
C(236)	0.1920(5)	0.0358(7)	0.3342(5)		0.055(3)
O(1)	0.5000	0.262(1)	0.2500		0.199(8)
C(1)	0.508(1)	0.394(1)	0.2852(9)		0.194(9)
C(2)	0.513(1)	0.309(1)	0.306(1)		0.180(8)
O(2)	0.013(1)	0.302(2)	0.190(1)		0.146(9)
C(21)	0.045(1)	0.326(2)	0.241(2)		0.22(1)
C(31)	-0.025(4)	0.386(4)	0.211(3)		0.26(1)
C(32)	-0.031(4)	0.335(5)	0.191(3)		0.26(1)

^a U_{eq} is defined as the cube root of the product of the principal axes.

doublets of doublets in the ³¹P{¹H} NMR spectrum at 203 K (Fig. 3).

An approximate ΔG^\ddagger of 9.9(±0.2) kcal mol⁻¹ for

this process has been calculated, based on a coalescence temperature of 228 K. $\{\Delta G^\ddagger$ was calculated using the value for the rate constant k_c (where $k_c = \pi\Delta\nu_c/(2)^{1/2}$) in the Eyring equation $\Delta G^\ddagger = -RT_c \ln[(k_c h)/(k_B T_c)]$; where R is the gas constant, T_c is the temperature of coalescence, $\Delta\nu_c$ is the peak separation at the low T limit, h is Planck's constant and k_B is the Boltzmann constant [16]. Here, $T_c = 228$ K and $\Delta\nu_c = 638$ Hz. The coalescence temperature was estimated visually from the spectra and has an error of approximately ±5 K.} Such a fluxional behaviour has already been observed for Rh₂S₂ rings with a free activation energy of 9.0–10.5 kcal mol⁻¹ [17]. In order to definitely discard the hypothesis of an equilibrium between the two isomers of **1**, it has been shown that no change occurs in the ³¹P{¹H} NMR spectrum of **1** when the toluene-*d*₈ solution is heated from 293 to 343 K.

2.4. Reactivity studies

Reactivity studies of **1** have been initiated. The complex undergoes reversible ligand exchange with P(OMe)₃ to give the analogous *syn/anti* isomer pair [(MeO)₃P]₂Rh(μ-NHPh)₂ **2**, as determined by ³¹P{¹H} NMR.

Complex **1** reacts reversibly with CO in THF, the initially orange solution changing to bright yellow under an atmosphere of CO and reverting to orange when the gas is removed under vacuum. When the reaction is repeated using a suspension of **1** in pentane, a yellow solid is isolated ($\nu_{\text{CO}} = 1981, 1968$ cm⁻¹ (KBr pellet));

Table 2

Selected interatomic distances (Å) and bond angles (deg) with e.s.d.s in parentheses for **1**·2THF^a

Rh(1)–Rh(1) [†]	3.376(2)		
Rh(1)–P(1)	2.221(2)	P(1)–C(131)	1.826(9)
Rh(1)–P(2)	2.244(3)	P(2)–C(211)	1.85(1)
Rh(1)–N(1)	2.156(7)	P(2)–C(221)	1.84(1)
Rh(1)–N(1) [†]	2.164(8)	P(2)–C(231)	1.849(9)
P(1)–C(111)	1.84(1)	N(1)–C(11)	1.42(1)
P(1)–C(121)	1.837(9)	N(1)–H(1)	0.84(8)
P(1)–Rh(1)–P(2)	95.41(9)	Rh(1)–P(2)–C(221)	123.2(3)
P(1)–Rh(1)–N(1)	169.6(2)	C(221)–P(2)–C(221)	97.0(4)
P(2)–Rh(1)–N(1)	92.7(2)	Rh(1)–P(2)–C(231)	105.6(3)
P(1)–Rh(1)–N(1) [†]	96.6(2)	C(221)–P(2)–C(231)	98.6(4)
P(2)–Rh(1)–N(1) [†]	161.0(2)	Rh(1)–N(1)–Rh(1) [†]	103.8(4)
N(1)–Rh(1)–N(1) [†]	77.2(3)	Rh(1)–N(1)–Rh(1) [†]	102.8(3)
Rh(1)–P(1)–C(111)	118.1(3)	Rh(1)–N(1)–C(11)	111.2(5)
Rh(1)–P(1)–C(121)	117.7(3)	Rh(1)–N(1)–C(11)	108.4(5)
C(111)–P(1)–C(121)	96.3(4)	Rh(1)–N(1)–H(1)	116.2(54)
Rh(1)–P(1)–C(131)	116.1(3)	Rh(1) [†] –N(1)–H(1)	100.7(55)
C(111)–P(1)–C(131)	104.8(4)	C(11)–N(1)–H(1)	115.8(54)
C(121)–P(1)–C(131)	100.7(4)	N(1)–C(11)–C(12)	124.4(9)
Rh(1)–P(2)–C(221)	124.6(3)	N(1)–C(11)–C(16)	118.4(8)

[†] Denotes the symmetry operation 1/2 – x, 1/2 – y, 1 – z.

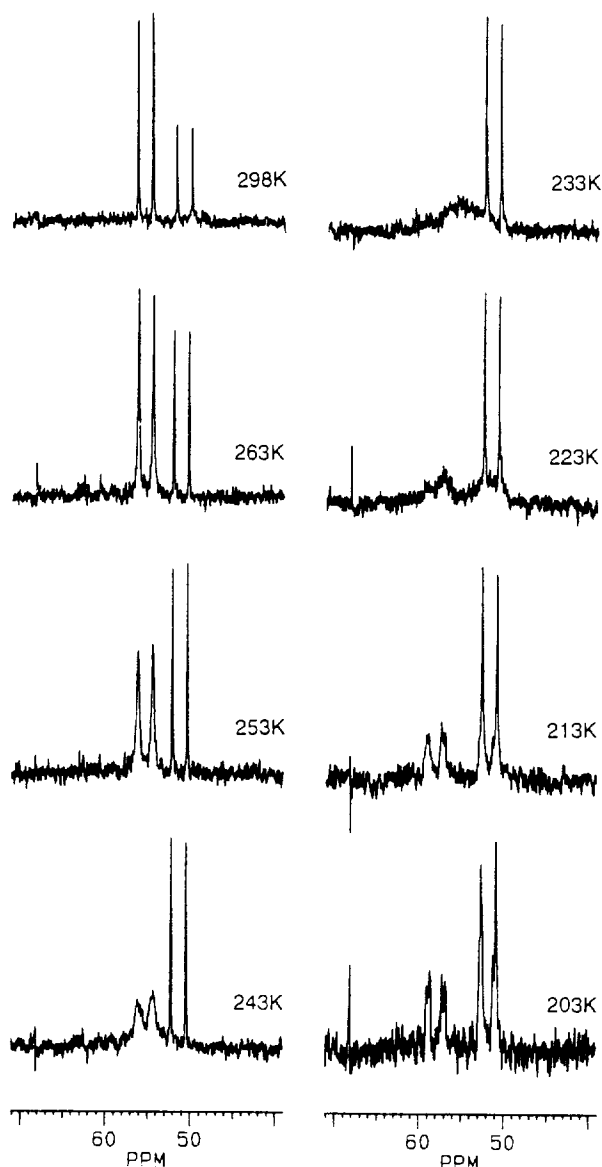


Fig. 2. Variable temperature 81.0 MHz $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[(\text{Ph}_3\text{P})_2\text{Rh}]_2(\mu\text{-NHPh})_2$, in C_7D_8 .

so far, no single product has been purified from this reaction.

Cleavage of the dimer was not effected by the addition of pyridine. We are currently attempting to isolate and purify the products of the above reactions. Further studies anticipated include the use of $^t\text{BuLi}$ to prepare

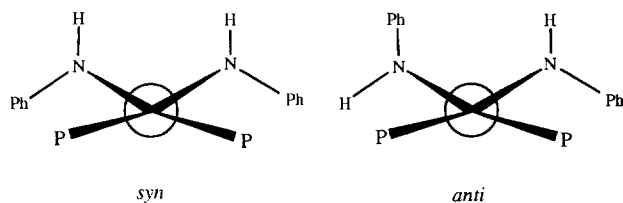


Fig. 3. View along the Rh–Rh axis of the *syn* and *anti* isomers of the Rh_2N_2 ring in a static envelope conformation.

anionic rhodium(I) imido complexes [18] and the addition of heterocumulenes such as isocyanates to **1**.

3. Experimental section

3.1. General procedure and reagent syntheses

All manipulations were performed under argon using standard Schlenk tube and vacuum line techniques or in a Vacuum Atmospheres HE-553-2 workstation equipped with an MO-40-2H purification system.

THF was dried and deoxygenated by distillation from sodium–benzophenone ketyl under argon. Toluene was dried and deoxygenated by distillation from molten sodium under argon. Pentane and hexane were dried and deoxygenated by distillation from P_2O_5 under nitrogen. Deuterated benzene (C_6D_6 , 99.6 at.% D) and deuterated toluene (C_7D_8 , 99.6 at.% D) were purchased from S.d.S. and dried over 4 Å molecular sieves. The dried, deuterated solvents were then degassed using three ‘freeze–pump–thaw’ cycles. Carbon monoxide N20 was purchased from L’Air Liquide.

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from Johnson Matthey, and $(\text{Ph}_3\text{P})_3\text{RhCl}$ was prepared by the standard literature method [19]. Aniline was purchased from Janssen, dried by refluxing over calcium hydride overnight and distilled under partial vacuum. *n*-Butyllithium (1.6 M in hexane) was purchased from Janssen and used after titration [20]. 12-crown-4 was purchased from Aldrich and used without further purification.

Elemental analyses were carried out by the Laboratory In-house Service.

^1H NMR spectra were recorded on Bruker AC-200 or Bruker AMX-400 spectrometer. With benzene- d_6 as solvent the spectra were referenced to $\text{C}_6\text{D}_3\text{H}$ at 7.15 ppm and with toluene- d_8 as solvent the spectra were referenced to the CD_2H residual proton at 2.09 ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 81.015 MHz on the Bruker AC-200 or at 161.98 on the Bruker AMX 400 and were referenced to external $\text{P}(\text{OMe})_3$ at +141.0 ppm relative to 85% H_3PO_4 .

3.2. Synthesis of di(μ -anilido)tetrakis(triphenylphosphine)dirhodium $[(\text{Ph}_3\text{P})_2\text{Rh}]_2(\mu\text{-NHPh})_2$ **1**

A THF solution of lithium anilide (prepared in situ from $^n\text{BuLi}$ and aniline, 0.51 mmol in 4 ml) was added to a solution of $(\text{Ph}_3\text{P})_3\text{RhCl}$ (0.257 g, 0.28 mmol) in THF (5 ml), cooled to -5°C in an ice/ethanol bath. The dark red solution gradually lightened in colour with warming to room temperature, the final solution being a bright cherry red. The solution was stirred at room temperature for 30 min, then the THF was removed under vacuum. The resulting residues were extracted with toluene (5 ml, 2×2 ml) and the combined extracts

were filtered through a Celite pad. Red–orange crystals, obtained from a minimum volume of toluene, became an orange powder after drying under vacuum. Yield 81% (0.179 g).

To prepare X-ray quality crystals the reaction was repeated in THF and 12-crown-4 (equimolar to the amount of $(\text{Ph}_3\text{P})_3\text{RhCl}$ used) was added, causing the precipitation of $(12\text{-crown-4}) \cdot \text{LiCl}$. The solution was filtered through a Celite pad and concentrated slightly, eventually yielding red needles. Anal. Found: C, 69.65; H, 5.57; N, 1.72. $\text{C}_{84}\text{H}_{72}\text{N}_2\text{P}_4\text{Rh}_2 \cdot 2\text{C}_4\text{H}_8\text{O}$ Calc.: C, 69.79; H, 5.60; N, 1.77%. ^1H NMR of the *syn/anti* mixture (200.1 MHz, room temperature, δ (ppm), C_6D_6): 7.83–7.58 (mult, H *ortho* (PPh_3)), 7.58–7.31 (mult, H *ortho* (PPh_3 , NPh)), 6.92–6.74 (mult, H *meta*, H *para* (PPh_3), H *meta* (NPh)), 6.72–6.56 (mult, H *para* (PPh_3 , NPh)), 6.38–6.31 (mult, H *ortho* (NPh)), 1.81 (s, N–H (major isomer)), 0.59 (s, N–H (minor isomer)). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, room temperature, δ (ppm), C_6D_6): 56.0 (d, $^1J_{\text{P-Rh}} = 176$ Hz), 51.6 (d, $^1J_{\text{P-Rh}} = 179$ Hz).

3.3. X-ray crystal structure determination of 1

Crystal data, data collection parameters, structure solution and refinement parameters are listed in Table 3. A crystal of *anti* $1 \cdot 2\text{THF}$ was mounted in a Lindemann capillary in a glove box under an inert atmosphere, and the sealed capillary transferred to the goniometer head. Data collection was performed at room temperature ($T = 293$ K) on an Enraf–Nonius CAD₄ diffractometer using graphite-monochromated Mo K α radiation ($\omega/2\theta$ scan mode used). The structure was solved by direct methods (SHELXS 86 [21]) and refined by full direct-matrix least-squares techniques in the anisotropic approximation. The weighting scheme used in the last refinement cycles was $\{w = w'[1 - (\Delta F)/6\sigma(F_o)^2]\}^2$ where $w' = 1/\sum_i A_i T_i(x)$ with n coefficients A_i for the Chebyshev polynomial $A_i T_i(x)$ where x was $F_c/F_c(\text{max})$ [22]. To minimize the number of variable parameters, phenyl groups and THF solvent molecules were isotropically refined, whereas the remaining atoms were anisotropically refined. Of the two THF solvent molecules, one was found to be disordered with a statistical distribution of O and C atoms around a two-fold axis. All hydrogen atoms with the exception of the THF solvent molecules were located from difference Fourier synthesis. The H atom attached to N(1) was isotropically refined. Crystallographic calculations were carried out using the CRYSTALS program [23] adapted on a PC. Anisotropic thermal parameters for non-hydrogen atoms, atomic coordinates for H atoms and a full list of interatomic distances and angles have been deposited at the Cambridge Crystallographic Data Centre.

Table 3
Crystal and collection data for $1 \cdot 2\text{THF}$

Crystal parameters	
Formula	$\text{C}_{84}\text{H}_{72}\text{N}_2\text{P}_4\text{Rh}_2 \cdot 2\text{C}_4\text{H}_8\text{O}$
Formula weight (g)	1583.4
Shape	parallelepiped
Size (mm^3)	$0.5 \times 0.4 \times 0.3$
Crystal system	monoclinic
Space group	$C2/c$
a (\AA)	21.931(6)
b (\AA)	16.381(3)
c (\AA)	22.162(6)
β (deg)	103.62(2)
V (\AA^3)	7738(3)
Z	4
$F(000)$	3192
$d(\text{calc})$ (g cm^{-3})	1.359
$\mu(\text{Mo K}\alpha)$ (cm^{-1})	5.49
Data collection	
Diffractometer	Enraf–Nonius CAD4F
Monochromator	graphite
Radiation	Mo K α ($\lambda = 0.71073$)
Scan type	$\omega/2\theta$
Scan range θ (deg)	$0.8 + 0.345 \text{tg } \theta$
2θ range (deg)	$3 < 2\theta < 40$
Reflections collected	3902 ($\pm h, k, l$)
Reflections merged (R_m)	3604 (0.0274)
Reflections used ($I > 3\sigma(I)$)	1970
Refinement	
R	0.0429
R_w	0.0479
Weighting scheme	$\{w = w'[1 - (\Delta F)/6\sigma(F_o)^2]\}^2$
Coefficient A_r	2.81, -0.929, 1.68
Goodness of fit	1.28
l.s. Parameters	264

3.4. Reactivity studies of 1

Reaction of 1 with trimethyl phosphite: $\text{P}(\text{OMe})_3$ (0.013 ml, 0.11 mmol) was added to a solution of **1** (45 mg, 0.028 mmol) in THF (10 ml). Over 15 min the solution colour changed from dark to light orange. The solvent was removed under vacuum and benzene- d_6 added to the residues to prepare an NMR sample. The resulting orange solution was shown to contain only **1** and traces of $\text{P}(\text{OMe})_3$ by $^{31}\text{P}\{^1\text{H}\}$ NMR. The reaction was repeated in an NMR tube by addition of $\text{P}(\text{OMe})_3$ (0.006 ml, 0.051 mmol) to a solution of **1** (10 mg, 0.006 mmol) in toluene- d_8 (0.8 ml). $^{31}\text{P}\{^1\text{H}\}$ NMR spectra collected over several hours at low temperatures (243–298 K) showed a slow conversion of **1** to a mixture of *syn* and *anti* $[\{(\text{MeO})_3\text{P}\}_2\text{Rh}]_2(\mu\text{-NHP})_2$ **2**. $^{31}\text{P}\{^1\text{H}\}$ NMR (δ (ppm), C_7D_8): 146.2 (d, $^1J_{\text{Rh-P}} = 263$ Hz), 143.9 (d, $^1J_{\text{Rh-P}} = 266$ Hz), isomers observed in a 1:2 ratio.

Reaction of 1 with carbon monoxide: A suspension of **1** (45 mg, 0.028 mmol) in pentane (10 ml) was stirred under CO (1 atm). The orange precipitate changed in colour to yellow over several minutes. The mixture was

stirred for an hour, then the pentane was removed by canula, leaving a yellow solid (IR: $\nu_{\text{CO}} = 1981, 1968 \text{ cm}^{-1}$ (KBr pellet)); attempts to purify a single product from this reaction have so far failed. When the reaction is carried out using THF, in which the dimer **1** is soluble, the yellow solution generated by the addition of CO returns to an orange colour when the CO atmosphere is removed under vacuum. $^{31}\text{P}\{^1\text{H}\}$ NMR analysis of the residues of this reaction mixture shows only the starting dimer **1**.

Acknowledgements

The authors wish to thank the CNRS and the Région Midi-Pyrénées for financial support. L.R. thanks the Ministère Français des Affaires Etrangères for a post-doctoral fellowship.

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