Tri- and binuclear ruthenium carbonyl complexes containing bridging ligands derived from *ortho*-substituted anilines. A comparative study of their syntheses using $RuCl_3 \cdot nH_2O$ or $[Ru_3(CO)_{12}]$ as starting materials

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Abstract

The trinuclear carbonyl clusters $[Ru_3(\mu\text{-}H)(\mu,\eta^2\text{-}o\text{-}HNC_6H_2Me_2NH_2)(CO)_9]$ ($o\text{-}H_2NC_6H_2Me_2NH_2$ = 1,2-diamino-4,5-dimethylbenzene) and $[Ru_3(\mu,\eta^2\text{-}o\text{-}OC_6H_4NH_2)_2(CO)_8]$ ($o\text{-}HOC_6H_4NH_2$ = 2-aminophenol) have been prepared by two alternative synthetic routes which involve (a) thermal reaction of $[Ru_3(CO)_{12}]$ with the appropriate ligand or (b) reaction of $RuCl_3 \cdot nH_2O$ with CO in refluxing 2-methoxyethanol, followed by treatment of the resulting solution with the appropriate ligand in the presence of zinc. However, $[Ru_3(\mu\text{-}H)(\mu,\eta^2\text{-}o\text{-}SC_6H_4NH_2)(CO)_9]$ ($o\text{-}HSC_6H_4NH_2$ = 2-aminothiophenol) and $[Ru_3(\mu\text{-}H)(\mu,\eta^2\text{-}o\text{-}OC_6H_4NH_2)(CO)_9]$ can only be prepared by method (a), whereas $[Ru_2(\mu,\eta^2\text{-}o\text{-}SC_6H_4NH)(CO)_6]$ can only be prepared by method (b). The compound $[Ru_3(\mu\text{-}H)(\mu,\eta^2\text{-}o\text{-}SC_6H_4NH_2)(CO)_9]$ has been characterized by X-ray diffraction methods: $C_{15}H_7NO_9Ru_3S$, orthorhombic, space group $Pbca$, a = 11.191(5), b = 16.462(5), c = 21.978(2) Å, V = 4049(2) Å³, Z = 8, T = 293 K, $R(F)$ = 0.043.

Keywords: Ruthenium; Cluster; Carbonyl; Substituted anilines; X-ray structure

1. Introduction

Aniline reacts with $[Ru_3(CO)_{12}]$ under thermal conditions to give $[Ru_3(\mu\text{-}H)(\mu\text{-}NHPh)(CO)_{10}]$ [1]. This amido derivative is probably an intermediate [1,2] in the $[Ru_3(CO)_{12}]$-promoted catalytic hydrogenation of nitrobenzene to aniline [3]. It is curious that this interesting chemistry has prompted very few reactivity studies involving $[Ru_3(CO)_{12}]$ and *ortho*-functionalized anilines [4], in spite of the more varied potential coordination modes of these ligands. To our knowledge, only two reports concerning such reactions have been published; they involve the ligands 1,2-diaminobenzene [5] and 2-diphenylphosphinoaniline [6] and they describe

the trinuclear products $[Ru_3(\mu\text{-}H)(\mu,\eta^2\text{-}o\text{-}HNC_6H_4\text{-}X)(CO)_9]$ (X = NH_2, PPh_2). We now report the reactions of $[Ru_3(CO)_{12}]$ with 2-aminothiophenol and 2-aminophenol, as well as a revision of the reaction of $[Ru_3(CO)_{12}]$ with 1,2-diamino-4,5-dimethylbenzene [5].

In contrast, it is well known that carbonylation of $RuCl_3 \cdot nH_2O$ in refluxing 2-methoxyethanol gives a yellow solution which, upon reaction with zinc, affords $[Ru_3(CO)_{12}]$ [7]. This solution has also been used to make the carbonyl derivatives $[Ru_2(\mu\text{-}pz)_2(CO)_6]$ (Hpz = pyrazole) and $[Ru_3(\mu\text{-}PPh_2)_3(CO)_9]Cl$ by treating it with the appropriate ligand in the presence of zinc [8,9]. We report here that the products obtained from the reactions of $[Ru_3(CO)_{12}]$ with 1,2-diamino-4,5-dimethylbenzene and 2-aminophenol can also be prepared by the synthetic method noted above, starting from the cheaper and more readily available $RuCl_3 \cdot nH_2O$; however, this is not the case for 2-aminothiophenol.
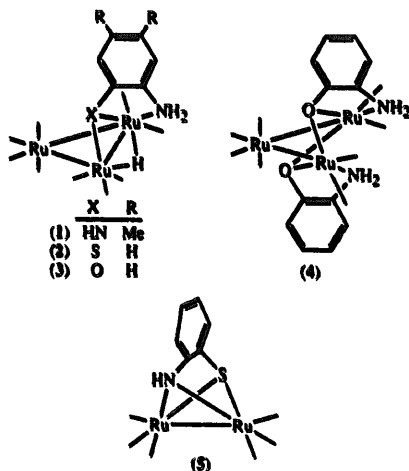
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2. Results and discussion

2.1. [Ru₃(CO)₁₂] as starting material

The reactions of [Ru$_3$(CO)$_{12}$] with 1,2-diamino-4,5-dimethylbenzene and 2-aminothiophenol in THF at reflux temperature, under nitrogen, gave the trinuclear derivatives [Ru$_3$(μ-H)(μ,η^2-o-HNC$_6$H$_2$Me$_2$NH$_2$)-(CO)$_9$] (1) and [Ru$_3$(μ-H)(μ,η^2-o-SC$_6$H$_4$NH$_2$)(CO)$_9$] (2) respectively (Scheme 1). In a previous report, it was stated that the synthesis of complex 1 required a carbon monoxide atmosphere in order to minimize the formation of the polymeric derivative [{Ru$_2$(μ,η^2-HNC$_6$H$_2$Me$_2$NH)(CO)$_4$}(μ,η^2-H$_2$NC$_6$H$_2$Me$_2$NH$_2$)]$_n$ [5]. We have now observed that a carbon monoxide atmosphere is unnecessary for ligand to [Ru$_3$(CO)$_{12}$] ratios smaller than 1.5, since these small ratios prevent the formation of polymeric materials without affecting the yield of compound 1, and the reaction time is reduced from 6–8 h to 2 h.

An X-ray diffraction study of complex 1 revealed an asymmetric trinuclear structure in which an Ru–Ru edge is spanned by a hydride ligand and by the amido fragment of the monodeprotonated ligand o-HNC$_6$H$_2$-Me$_2$NH$_2$, which also has the NH$_2$ group coordinated to one of the metal atoms of the same edge, as shown in Scheme 1 [5]. The ^{1}H NMR spectrum of compound 2 suggested a structure similar to that of 1, since it showed the presence of a hydride ligand as well as the aminothiophenolate ligand o-SC$_6$H$_4$NH$_2$. This structure has been confirmed by an X-ray diffraction study (Tables 1–3). Fig. 1 shows that the S atom of the o-SC$_6$H$_4$NH$_2$ ligand bridges the Ru(1)–Ru(2) edge, which is also spanned by the hydride ligand, and that the NH$_2$ group binds the Ru(2) atom in a position approximately *trans* to the Ru(2)–Ru(3) edge. The cluster shell is completed by nine CO ligands, four are attached to Ru(3), three to Ru(2), and two to Ru(1). An

analogous asymmetric structure has been reported for the complex [Ru$_3$(μ-H)(μ,η^2-o-HNC$_6$H$_4$PPh$_2$)(CO)$_9$] [6]. It is interesting to note that *ortho*-functionalized anilines prefer to form asymmetric trinuclear carbonyl clusters while the related clusters [Ru$_3$(μ-H)(μ,η^2-XC$_5$H$_4$N)(CO)$_9$] (X = NH, S), derived from 2-aminopyridine [10,11] and 2-mercaptopyridine [11,12], are symmetric (the NH or S groups span an Ru–Ru edge and the pyridine nitrogen binds the unique Ru atom).

X	R
(1) HN	Me
(2) S	H
(3) O	H

(4)

(5)

Scheme 1.

Table 1
Selected bond lengths and angles in compound 2

Bond lengths (Å)

Ru(1)–Ru(2)	2.862(1)	Ru(1)–Ru(3)	2.816(1)
Ru(2)–Ru(3)	2.793(1)	Ru(1)–S(1)	2.415(2)
Ru(2)–S(1)	2.388(2)	Ru(2)–N(1)	2.208(5)
Ru(1)–C(1)	1.894(8)	Ru(1)–C(2)	1.918(8)
Ru(1)–C(3)	1.98(1)	Ru(2)–C(4)	1.885(9)
Ru(2)–C(5)	1.92(1)	Ru(3)–C(6)	1.94(1)
Ru(3)–C(7)	1.935(8)	Ru(3)–C(8)	2.01(1)
Ru(3)–C(9)	1.99(1)		

Bond angles (°)

Ru(1)–Ru(2)–Ru(3)	59.72(2)	Ru(1)–Ru(3)–Ru(2)	61.35(2)
Ru(2)–Ru(1)–Ru(3)	58.93(3)	Ru(1)–S(1)–Ru(2)	73.15(5)
N(1)–Ru(2)–S(1)	81.5(2)	Ru(1)–Ru(2)–N(1)	105.6(2)

Table 2
Crystallographic and refinement data for compound 2

Formula	C$_{15}$H$_7$NO$_9$Ru$_3$S
Formula weight	680.49
Crystal system	Orthorhombic
Space group	*Pbca*
a, b, c (Å)	11.191(5), 16.462(5), 21.978(2)
Volume (Å^3)	4049(2)
Z	8
F(000)	2592
D$_{calc}$ (g cm^{-3})	2.233
μ (mm^{-1})	2.359
Crystal size (mm^3)	0.23×0.17×0.10
Radiation (λ(Å))	Mo Kα (0.71073)
Diffractometer	Enraf-Nonius CAD4
Monochromator	Graphite
Temperature (K)	293(2)
Scan method	ω–2θ
θ limits (°)	1.85–24.97
h, k, l ranges	0–13, 0–19, 0–26
Reflections collected	4017
Independent reflections	3559
$R_{int} = \Sigma(I - \langle I \rangle)/\Sigma I$	0.074
Reflections with $I > 2\sigma(I)$	2747
Restraints, parameters	0, 271
$R(F)_{I > 2\sigma(I)}$ [a]	0.0429
$R_w(F^2)_{all\ data}$ [b]	0.1348
GOF [c]	1.070
Δ/σ	0.001
Max, min $\Delta\rho$ (eÅ^{-3})	1.082, −0.990

[a] $R(F) = \sigma \|F_o| - |F_c\|/\Sigma|F_o|$. [b] $R_w(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [c] Goodness of fit (GOF) = $[\Sigma w(F_o^2 - F_c^2)^2/(N - P)]^{1/2}$.

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^3$) for the non-H atoms of compound 2

Atom	x	y	z	U_{eq} [a]
Ru(1)	799(1)	856(1)	1285(1)	37(1)
Ru(2)	274(1)	2368(1)	1868(1)	35(1)
Ru(3)	631(1)	2307(1)	612(1)	41(1)
C(1)	−354(7)	486(5)	718(3)	45(2)
O(1)	−1059(5)	244(4)	393(2)	65(2)
C(2)	2121(7)	500(6)	798(4)	59(2)
O(2)	2921(6)	323(5)	518(3)	97(3)
C(3)	668(8)	−139(6)	1790(4)	62(2)
O(3	575(7)	−720(4)	2028(3)	48(2)
C(4)	−1281(8)	2802(4)	1813(3)	46(2)
O(4)	−2221(5)	3042(4)	1813(3)	67(2)
C(5)	958(7)	3439(6)	1890(3)	101(3)
O(5)	1360(8)	4066(4)	1873(3)	87(2)
C(6)	−1082(8)	2116(5)	636(3)	51(2)
O(6)	−2075(5)	2000(5)	613(3)	70(2)
C(7)	842(7)	1878(5)	−201(4)	72(2)
O(7)	941(6)	1641(5)	−682(3)	82(2)
C(8)	2382(10)	2446(6)	790(3)	66(3)
O(8)	3321(6)	2560(6)	853(3)	57(2)
C(9)	380(9)	3463(7)	380(4)	71(3)
O(9)	225(9)	4075(4)	211(4)	59(2)
S(1)	2078(2)	1606(1)	1968(1)	40(1)
N(1)	152(5)	2089(4)	2849(2)	59(1)
C(10)	1804(6)	1138(4)	2693(3)	81(2)
C(11)	863(6)	1409(4)	3054(3)	40(2)
C(12)	631(7)	1017(6)	3588(4)	58(2)
C(13)	1290(10)	348(6)	3758(4)	69(3)
C(14)	2233(9)	92(5)	3405(4)	62(2)
C(15)	2480(7)	483(5)	2882(3)	51(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

2.2. $RuCl_3 \cdot nH_2O$ as starting material

It is known that $[Ru_3(CO)_{12}]$ [7] and many chlorocarbonylruthenium(II) complexes [16] can be prepared from the yellow solution obtained by bubbling CO through a solution of $RuCl_3 \cdot nH_2O$ in 2-methoxy- or 2-ethoxyethanol at reflux temperature for 2–3 h. The exact composition of this solution is as yet uncertain, although it gives the colourless $[Ru_2Cl_2(\mu\text{-Cl})_2(CO)_6]$ upon prolonged reaction (8–10 h) with carbon monoxide [16d]. In order to check whether compounds 1–4 could also be prepared from $RuCl_3 \cdot nH_2O$, the reactions of the yellow solution with the appropriate ortho-functionalized aniline ligands, in the presence of zinc as reducing agent, were studied.

Effectively, compounds 1 and 4 could be prepared in moderate yields by treating the yellow solution with 1,2-diamino-4,5-dimethylbenzene or 2-aminophenol, in the presence of zinc, at reflux temperature. No evidence for the formation of complex 3 was obtained in the reaction with 2-aminophenol, even using small ligand to $RuCl_3 \cdot nH_2O$ ratios. However, analogous reactions with 2-aminothiophenol afforded mixtures of compounds from which the binuclear ruthenium(I) derivative $[Ru_2(\mu,\eta^2\text{-}o\text{-SC}_6H_4NH)(CO)_6]$ (5) could be separated and characterized by analytical and spectroscopic methods. Its ^1H NMR spectrum shows the resonances of one NH (singlet) and four aromatic protons, while its IR spectrum contains the carbonyl pattern characteristic of binuclear ligand-bridged ruthenium(I) hexacarbonyl

$[Ru_3(CO)_{12}]$ reacted with 2-aminophenol (1 : 1 ratio) in refluxing THF to give a mixture of $[Ru_3(\mu\text{-H})(\mu,\eta^2\text{-}o\text{-OC}_6H_4NH_2)(CO)_9]$ (3), $[Ru_3(\mu,\eta^2\text{-}o\text{-OC}_6H_4NH_2)_2(CO)_8]$ (4), and $[Ru_4(\mu\text{-H})_4(CO)_{12}]$. A chromatographic workup allowed the separation of the two latter compounds, but complex 3 was always contaminated with some of complex 4. The use of 2-aminophenol to $[Ru_3(CO)_{12}]$ ratios greater than 2 resulted in the formation of complex 4 only. The structure proposed for complex 3 in Scheme 1 is based on the similarity of its IR and ^1H NMR spectra with those of complex 2. The ^1H NMR spectrum of compound 4 indicates the absence of hydride ligands and the presence of the aminophenolate ligand $o\text{-OC}_6H_4NH_2$ (the NH_2 group is observed as two doublets, as expected for diasterotopic hydrogens). The formulation of complex 4 as an open 50-electron symmetric trinuclear cluster (Scheme 1) is also supported by its elemental analysis and by the X-ray structures of the 50-electron compounds $[Ru_3(\mu,\eta^2\text{-}o\text{-OC}_6H_4X)_2(CO)_8]$ (X = OMe [13], Cl [14], CH=N-p-tol [15]), which also contain ortho-functionalized phenolate ligands.
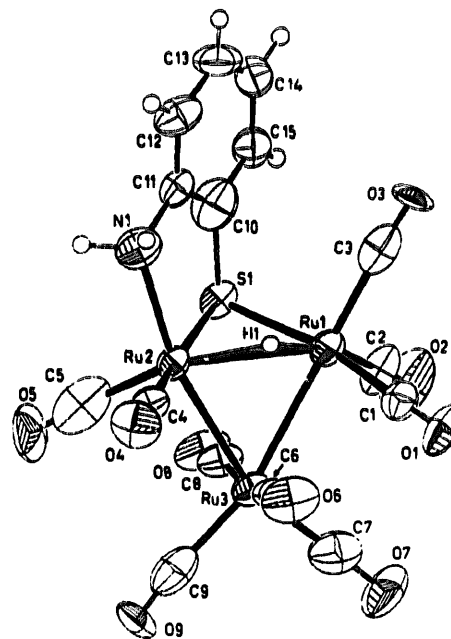

Fig. 1. A view of the molecular structure of compound 2. Thermal ellipsoids are drawn at the 50% probability level.

derivatives [17]. These data strongly support the structure proposed for compound 5 in Scheme 1.

3. Concluding remarks

This work has revealed that, in trinuclear ruthenium carbonyl clusters derived from anilines containing ortho-NH_2, -SH, and -OH groups, the bridging ligands behave as five-electron donors, being coordinated in their monodeprotonated form to two of the three metal atoms. While the incorporation of only one ligand is preferred in the case of diamino and aminomercapto derivatives, two ligands are preferably incorporated in the case of 2-aminophenol.

Although [$Ru_3(CO)_{12}$] is the customary starting material for the synthesis of bi- and trinuclear ruthenium carbonyl compounds [16a,17], this work adds new examples to the very few [8,9,18] in which $RuCl_3 \cdot nH_2O$ has been used as a starting material for the preparation of such compounds.

4. Experimental section

4.1. General data

Solvents were dried and distilled under nitrogen prior to use. Unless otherwise stated, the reactions were carried out under nitrogen using Schlenk-vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region). $RuCl_3 \cdot nH_2O$ (42.39% Ru) was obtained from Johnson Matthey. All other starting materials were purchased from Aldrich. Infrared spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1 mm CaF_2 cells. NMR spectra were run at 23°C with Bruker AC-200 and AC-300 instruments, using $SiMe_4$ as internal standard ($\delta = 0$ ppm). Microanalyses were obtained from the University of Oviedo Analytical Service.

4.2. Reactions of [$Ru_3(CO)_{12}$] with ortho-substituted anilines

4.2.1. With 1,2-diamino-4,5-dimethylbenzene

A solution of [$Ru_3(CO)_{12}$] (200 mg, 0.313 mmol) and 1,2-diamino-4,5-dimethylbenzene (55 mg, 0.404 mmol) in THF (20 ml) was stirred at reflux temperature for 2 h. The solvent was removed under reduced pressure and the residue chromatographed on neutral alumina (activity IV). Hexane eluted a trace amount of [$Ru_3(CO)_{12}$]. Dichloromethane eluted complex 1, which was obtained as an orange solid (162 mg, 75%). The use of a larger excess of 1,2-diamino-4,5-dimethylbenzene resulted in lower yields of complex 1. Anal. Found: C, 29.37; H, 1.88; N, 3.92. $C_{17}H_{12}N_2O_9Ru_3$.

Calc.: C, 29.53; H, 1.75; N, 4.05. The IR and ^1H NMR spectra, as well as the X-ray diffraction structure, of this complex have been reported previously [5].

4.2.2. With 2-aminothiophenol

A solution of [$Ru_3(CO)_{12}$] (500 mg, 0.782 mmol) and 2-aminothiophenol (110 mg, 0.879 mmol) in THF (30 ml) was stirred at reflux temperature for 1 h. The solvent was removed under reduced pressure and the residue chromatographed on neutral alumina (activity IV). Dichloromethane eluted complex 2, which was obtained as an orange solid (330 mg, 62%). The use of a larger excess of 2-aminothiophenol resulted in lower yields of complex 2. Anal. Found: C, 26.77; H, 0.97; N, 2.01. $C_{15}H_7NO_9Ru_3S$. Calc.: C, 26.48; H, 1.04; N, 2.06. IR ν(CO) (THF): 2087 (m), 2048 (s), 2008 (vs), 2000 (s), 1938 (w) cm^{-1}. ^1H NMR (CDCl$_3$): 7.75 (d, $J = 8$ Hz, 1 H), 7.21 (m, 3 H), 5.07 (d, $J = 12$ Hz, NH), 4.70 (d, $J = 12$ Hz, NH), -14.31 (s, μ-H) ppm.

4.2.3. With 2-aminophenol

A solution of [$Ru_3(CO)_{12}$] (300 mg, 0.469 mmol) and 2-aminophenol (128 mg, 1.173 mmol) in THF (30 ml) was stirred at reflux temperature for 3 h. The solvent was removed under reduced pressure and the residue was chromatographed on neutral alumina (activity IV). Dichloromethane eluted complex 4, which was obtained as a yellow solid (155 mg, 44%). Anal. Found: C, 32.63; H, 1.69; N, 3.61. $C_{20}H_{12}N_2O_{10}Ru_3$. Calc.: C, 32.31; H, 1.63; N, 3.77. IR ν(CO) (THF): 2076 (m), 2002 (s), 1927 (m) cm^{-1}. ^1H NMR (CDCl$_3$): 7.11 (td, $J = 7.6$ and 1.1 Hz, 1 H), 6.90 (dd, $J = 7.6$ and 1.1 Hz, 1 H), 6.70 (dd, $J = 7.6$ and 1.3 Hz, 1 H), 6.54 (td, $J = 7.6$ and 1.3 Hz, 1 H), 4.69 (d, $J = 12$ Hz, NH), 3.70 (d, $J = 12$ Hz, NH) ppm. The use of ligand to Ru_3 ratios smaller than 2 resulted in mixtures of the complexes 3, 4, and [$Ru_4(\mu-H)_4(CO)_{12}$]. A chromatographic workup allowed the separation of complexes 4 and [$Ru_4(\mu-H)_4(CO)_{12}$] as pure products, but complex 3 was always contaminated with some complex 4. Spectroscopic data for 3 ν(CO) (CH$_2$Cl$_2$): 2096 (w), 2059 (vs), 2011 (s), 1978 (m), 1938 (w) cm^{-1}. ^1H NMR (CDCl$_3$): 7.12 (m, 3 H), 6.80 (td, $J = 6.7$ and 1.1 Hz, 1 H), 4.79 (d, $J = 12$ Hz, NH), 4.53 (d, $J = 12$ Hz, NH), -10.99 (s, μ-H) ppm.

4.3. Reactions starting from $RuCl_3 \cdot nH_2O$

Carbon monoxide was bubbled through a solution of $RuCl_3 \cdot nH_2O$ (500 mg, ca. 2.054 mmol) in 2-methoxyethanol (30 ml) at reflux temperature until the colour turned pale yellow (ca. 3 h). The appropriate ligand was then added, followed by addition of granular zinc (ca. 1 g). The mixture was stirred at reflux temperature under CO for t min. After cooling down to room

temperature, the solids were filtered off, the solvent was removed (rotary evaporator), and the residue was chromatographed on neutral alumina (activity IV). The results for each ligand were as follows.

4.3.1. 1,2-Diamino-4,5-dimethylbenzene

Starting amount 130 mg (0.956 mmol), reaction time 90 min, chromatographic eluant dichloromethane, product 1 (206 mg, 47%).

4.3.2. 2-Aminothiophenol

Starting amount 141.4 mg (1.130 mmol), reaction time 45 min, chromatographic eluant hexane–dichloromethane (1:1), product 5 (yellow solid, 84 mg, 15%). Anal. Found: C, 29.48; H, 1.13; N, 2.67. $C_{12}H_5NO_6$-Ru_2S. Calc.: C, 29.21; H, 1.02; N, 2.84. IR $\nu(CO)$ (CH_2Cl_2): 2086 (m), 2058 (vs), 2005 (s), 1927 (vw) cm^{-1}. ^1H NMR $(CDCl_3)$: 7.05 (dd, $J = 7.6$ and 1.1 Hz, 1 H), 6.53 (dd, $J = 7.6$ and 1.1 Hz, 1 H), 6.37 (m, 2 H), 3.30 (s, NH) ppm. A second band (orange) was eluted with dichloromethane; it contained a mixture of complex 2 (major product) and some other unidentified products (^1H NMR).

4.3.3. 2-Aminophenol

Starting amount 156.9 mg (1.438 mmol), reaction time 75 min, chromatographic eluant dichloromethane, product 4 (120 mg, 24%).

4.4. Crystal structure of compound 2

An orange crystal, obtained by layering pentane on a solution of the complex in dichloromethane at −20°C, was used for the X-ray diffraction study. A selection of crystal and refinement data is given in Table 2.

The cell dimensions were determined by least-squares refinement of 25 reflections with $15 < \theta < 20°$. Space group Pbca from systematic absences. Intensities were measured with a variable scan rate and a maximum scan time of 60 s per reflection.

Three standard reflections were monitored every 60 min, revealing no intensity fluctuations. Final drift correction factors were between 0.97 and 1.01. Profile analysis was performed on all reflections [19]. A semi-empirical absorption correction based on Ψ-scans was applied [20], $\mu(Mo\ K\alpha) = 23.59\ cm^{-1}$ (min, max correction factors 0.823, 0.999). Lorentz and polarization corrections were applied and data were reduced to $|F_o|$ values.

The structure was solved by Patterson interpretation using DIRDIF92 [21]. Isotropic least-squares refinement, using a local version [22] of SHELX [23], was followed by an empirical absorption correction [24] (min, max correction factors 0.74, 1.16). Full-matrix anisotropic least-squares refinement over F^2, using the program SHELX93 [25], followed by a difference Fourier synthesis

allowed the location of all the hydrogen atoms. After refinement of the positional and anisotropic thermal parameters of the non-hydrogen atoms, the hydrogen atoms were refined isotropically. The hydride H atom was refined with free coordinates and free temperature factor, while the remaining H atoms were refined constraining bond angles but with free distances to their parent atoms, with a common thermal parameter for both amino H atoms and another common thermal parameter for the aryl H atoms. Function minimized $\sum w(F_o^2 - F_c^2)^2$, $w = 1/[\sigma^2(F_o^2) + (0.0951P)^2]$, with $\sigma(F_o)$ from counting statistics and $P = (F_o^2 + 2F_c^2)/3$. Atomic scattering factors were taken from Ref. [26]. Geometrical calculations were made with PARST [27]. The structure plot was drawn with the EUCLID package [28]. Final atomic coordinates are given in Table 3. All calculations were carried out on an Alpha AXP3000 workstation at the Scientific Computer Centre of the University of Oviedo.

Acknowledgment

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