Crystal Structure and Reactivity of [Ru{$C_6H_4(NH)_2$-1,2}($(PPh_3)_3$] with π-Acid Ligands†

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The structure of the compound [Ru{$C_6H_4(NH)_2$-1,2}$(PPh_3)_3$] **1** has been established from X-ray analysis by direct and Fourier methods and refined by full-matrix least squares to $R = 0.071$ for 3288 observed reflections: monoclinic, space group $P2_1/n$, $a = 18.70(1)$, $b = 13.171(6)$, $c = 23.06(2)$ Å, β 99.86(6)° and $Z = 4$. This complex reacts with an excess of ethylene or styrene and with $P(OMe)_3$ (molar ratio 1 : 1) in hot toluene to yield the complexes [Ru{$C_6H_4(NH)_2$-1,2}L$(PPh_3)_2$] [L = C_2H_4 **3**, CH_2CHPh **4** or $P(OMe)_3$, **5**]. With a slight excess of the diphosphines $(Ph_2P)_2X$ [X = CH_2 (dppm), C_2H_4 (dppe), 1,2-C_6H_4 (dppbz), cis-C_2H_2 (dppen) and C_3H_6 (dppp)], refluxed in toluene, the complexes [Ru{$C_6H_4(NH)_2$-1,2}](PPh_3)(diphosphine)] **6–10** were obtained as dark purple crystalline solids. An excess of PMe_3 in hot toluene solutions of compound **1** afforded brown prismatic crystals of [Ru{$C_6H_4(NH)_2$-1,2}]$(PMe_3)_3$] **11**, whereas with PEt_3 under the same conditions only partial substitution products are obtained, [Ru{$C_6H_4(NH)_2$-1,2}]$(PEt_3)(PPh_3)_2$] **12** and [Ru{$C_6H_4(NH)_2$-1,2}$(PEt_3)_2(PPh_2)$] **13**. When toluene solutions of [Ru{$C_6H_4(NH)_2$-1,2}](CO)$(PPh_3)_2$] **2** were boiled with diphosphines the complexes [Ru{$C_6H_4(NH)_2$-1,2}(CO)(diphosphine)] [dppe **14**, dppbz **15**, dppen **16**, dppp **17** or dppb (X = C_4H_8) **18**] were isolated. The complex [Ru{$C_6H_4(NH)_2$-1,2}]$(CO)_2(PPh_3)$] **19** was also detected as a reaction product of carbonylation of toluene solutions of **1**. All complexes have been characterized by elemental analysis and by IR and NMR spectroscopy.

Stable transition-metal complexes with the ligand $C_6H_4(NH)_2$-1,2^z either with or without other ligands are well known. It is co-ordinated in a chelate[1] ($z = 0, 1-$, or $2-$) or bridging[2] fashion ($z = 2-$); for the latter the bridge enforces a very short M–M distance. One of the previously reported mononuclear complexes is [Ru{$C_6H_4(NH)_2$-1,2}$(PPh_3)_3$] **1** which reacts with CO to give [Ru{$C_6H_4(NH)_2$-1,2}(CO)$(PPh_3)_2$][1d] **2** as the main reaction product. The characterization of **1**, based only on spectroscopic data,[1d] suggested three possible different structures; to elucidate which of them is adopted, the structure has now been solved by X-ray diffraction methods.

There have been few studies of mononuclear *o*-phenylenediamido complexes with π-acid ligands[1d,3,4] in spite of their diversity, not only related to the ligand bonding modes (chelate, bridge), but also concerning the redox properties of the diamide[5-7] which can be included in the group of 'non-innocent ligands'.[1,‡] Other related compounds such as diimino complexes are also formed as the result of a metal centre–diamino ligand redox process[7] and complexes with different diimino ligands are well known.[8]

We now report the reactivity of complex **1** with π-acid ligands to give new complexes where the moiety Ru{$C_6H_4(NH)_2$-1,2} is kept unchanged. Their characterization was carried out by elemental analysis and spectroscopic methods.

Results and Discussion

Crystal Structure of Complex **1**.—The structure of complex **1** is shown in Fig. 1; selected bonds and angles are given in Table 1 and final atomic positional parameters in Table 4. The ruthenium atom is bonded by two nitrogen atoms from the diamido ligand [Ru–N(1) 2.05(1) and Ru–N(2) 2.01(1) Å] and by three phosphorus atoms from triphenylphosphine ligands [Ru–P(1) 2.295(4), Ru–P(2) 2.327(4) and Ru–P(3) 2.333(5) Å] to give an irregular structure close to a square-pyramidal arrangement. Atom P(1) is in an apical position, which as a result of its π interaction with the d_{xz} or d_{yz} metal orbitals [basal angles N(1)–Ru–P(2) 159.1(4) and N(2)–Ru–P(3) 136.3(4)°, significantly different from 180°] leads to a slight

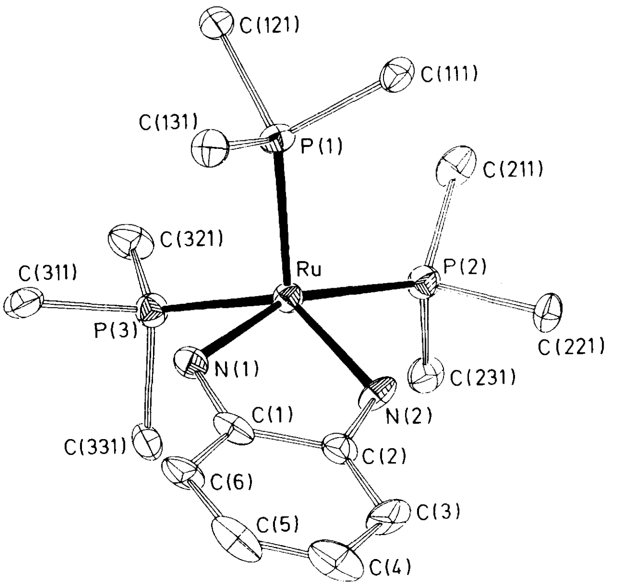

Fig. 1 View of the molecular structure of complex **1** showing the labelling scheme. Only the C-phenyl atoms bonded to the P atoms are given.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, issue 1, pp. xxiii–xxviii.

‡ The existence of free $C_6H_4(NH)_2$-1,2 was postulated in solution.[1c]

Table 1 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for compound **1**

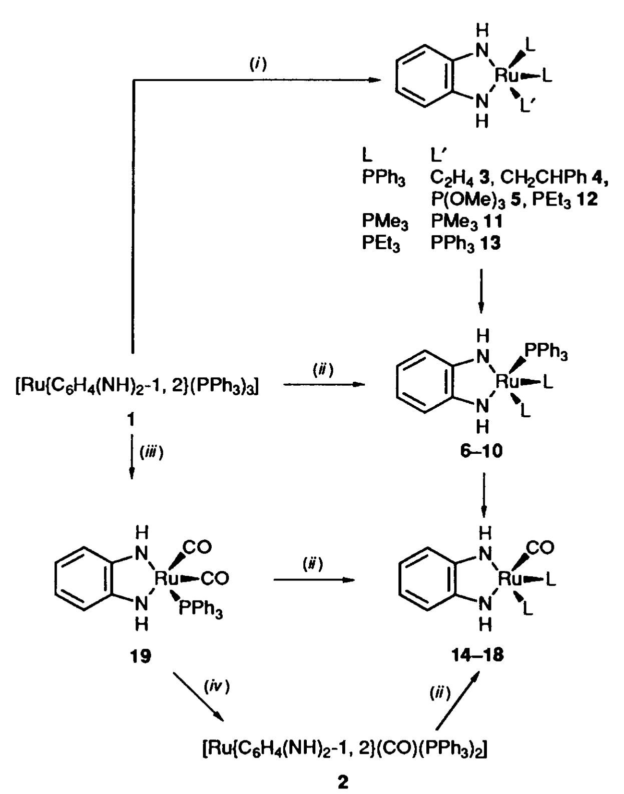
Ru–N(1)	2.05(1)	Ru–P(2)	2.327(4)
Ru–N(2)	2.01(1)	Ru–P(3)	2.333(5)
N(1)–C(1)	1.39(2)	P(1)–C(111)	1.86(2)
N(2)–C(2)	1.38(2)	P(1)–C(121)	1.86(2)
C(1)–C(2)	1.43(2)	P(1)–C(131)	1.87(2)
C(2)–C(3)	1.36(2)	P(1)–C(211)	1.82(2)
C(3)–C(4)	1.38(3)	P(2)–C(221)	1.85(2)
C(4)–C(5)	1.35(3)	P(2)–C(231)	1.86(2)
C(5)–C(6)	1.38(3)	P(3)–C(311)	1.85(2)
C(1)–C(6)	1.39(2)	P(3)–C(321)	1.82(2)
Ru–P(1)	2.295(4)	P(3)–C(331)	1.86(2)
N(1)–Ru–P(1)	95.7(4)	C(1)–C(2)–N(2)	111(2)
N(1)–Ru–P(2)	159.1(4)	C(3)–C(2)–N(2)	129(2)
N(1)–Ru–P(3)	84.5(4)	P(2)–Ru–P(1)	102.1(2)
N(2)–Ru–P(1)	115.2(4)	P(3)–Ru–P(1)	105.3(2)
N(2)–Ru–P(2)	86.1(4)	P(3)–Ru–P(2)	101.1(2)
N(2)–Ru–P(3)	136.3(4)	C(6)–C(1)–C(2)	120(2)
N(2)–Ru–N(1)	76.4(5)	C(3)–C(2)–C(1)	120(2)
C(1)–N(1)–Ru	117(1)	C(4)–C(3)–C(2)	120(2)
C(2)–N(2)–Ru	121(1)	C(5)–C(4)–C(3)	120(2)
C(2)–C(1)–N(1)	115(1)	C(6)–C(5)–C(4)	123(2)
C(6)–C(1)–N(1)	126(2)	C(5)–C(6)–C(1)	118(2)

shortening of the Ru–P(1) distance.[9] The Ru–P(1) line is almost orthogonal to the basal plane N(1)N(2)P(2)P(3) [89.0(0.2)°], the greatest atom deviation from that plane being less than 0.37 Å. The short N–C bonds, with lengths averaging 1.39(2) Å, are consistent with a multiple bond character but not with the expected bond pattern for the C_6 diamide ring, suggesting an important electron delocalization in the ruthenium–diamide system. The N(1)–Ru–N(2) angle, 76.4(5)°, is comparable to equivalent bond angles in compounds where the ligand is likely to be in a dianionic form.[6]

The average Ru–N distance of 2.03(1) Å is short enough to consider some multiple-bond character[4,10] and the N–C distances, 1.38(2) and 1.39(2) Å, also found for $[Ni\{C_6H_4(NH)_2\text{-}1,2\}_2]$ for which a bond order 1.5 is assigned,[11] are shorter than the N–C single bonds in arylamines and related derivatives. The non-innocent character of the $C_6H_4(NH)_2$-1,2 ligand leads us to consider the metal–ligand interaction as the result of the two nitrogen electron pairs donated to the ruthenium (two σ bonds) plus two electrons (for a dianionic ligand) delocalized on the N_2C_2 system, shared with the metal *via* π bonding with the expected shortening of the bond distances among the atoms of the RuN_2C_2 metallacycle.

By using the correlation method to calculate the oxidation state in chelated $C_6H_4(NH)_2$-1,2 complexes,[12] a value of $\Delta = 2.08$ [$\sigma(\Delta) = 0.18$] resulted and the compound is best assumed to be a ruthenium(II) diamide.

Reactivity of $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(PPh_3)_3]$.—The assumption that this is a five-co-ordinate ruthenium(II) complex would lead one to expect that its reactivity should correspond to that for a sixteen-electron species, namely the addition of a new ligand so as to become co-ordinatively saturated or ligand substitution to give new five-co-ordinate complexes (redox reactions are not considered in the context of this work). Ruthenium(II) complexes, $[RuX_2L_4]$ (X = mono-anionic ligand, L = π-acceptor ligand), for bulky ligands like L = PPh_3 tend to dissociate to $[RuX_2L_3]$ which are able to add new and less bulky ligands.[13] For complexes with phosphines producing a lower steric hindrance the stability towards dissociation is higher,[14] and complexes of the type $[Ru^{II}X_2L_3]$ show a tendency to reach an 18-electron configuration by co-ordinating a sixth ligand. The hypothetical six-co-ordinate $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(PPh_3)_4]$, like other $[RuX_2(PPh_3)_4]$ complexes, must be prone towards dissociation and complex **1** should be the resulting stable species, but, as previously stated, this complex is better regarded as saturated (18e). Thus it did not produce any six-co-ordinate complex with ligands like N_2, CO, PR_3 (R = Me or Et) or $P(OMe)_3$ and only new five-co-ordinate substitution derivatives were detected or collected (see later and Experimental section). The failure to add a new ligand was also observed for the compound $[Mo\{C_6H_4(NH)_2\text{-}1,2\}(CO)_2(PPh_3)_2]$,[15] and for the five-co-ordinate derivatives of **1**, a behaviour not assignable to steric factors as the small or low cone angle ligands would not block the entrance of a new ligand.



Scheme 1 Reagents and conditions: (*i*) L– or L′–toluene, heat; (*ii*) diphosphine L–L (excess)–toluene, heat; (*iii*), CO–toluene; (*iv*) PPh_3–toluene

Analogously, the seven-co-ordinate tungsten(IV) complex $[WCl_2\{C_6H_4(NH)_2\text{-}1,2\}(PMe_3)_3]$[16] can be regarded as having the metal in an eighteen-electron configuration, and the chromium(IV) complex $[CrCl_2\{C_6H_4(NH)_2\text{-}1,2\}(PMe_2Ph)_2]$[17] must be a sixteen-electron species where the smaller size of the metal atom and the higher cone angle of the phosphine compared to those of the tungsten complex would result in no addition of a new ligand. It is also significant that reactions to synthesise the complexes $[M\{C_6H_4(NH)_2\text{-}1,2\}L_m]$ from $C_6H_4(NH)_2$-1,2 and $[MX_2L_n]$ were carried out under basic conditions, using KOH,[15] NR_3[1d,17] or an excess of the phenylenediamine[7,17] in order to deprotonate the ligand. The protonated base was extracted, which suggests the formation of a dianionic ligand, and a M^{n+}–ligand redox process is only expected for the oxidizing M^{n+} unless external oxidants as in the synthesis of $[Ni^{II}\{C_6H_4(NH)_2\text{-}1,2\}_2]$[11] participate in the reaction.

A substitution reaction of complex **1** had been reported[1d] where one CO replaced one PPh_3 to give the monocarbonylic five-co-ordinate complex $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(CO)(PPh_3)_2]$. Other potentially π-acid ligands like alkenes or phosphorus compounds were used to obtain complexes $[Ru\{C_6H_4(NH)_2\text{-}1,2\}L_3]$ (Scheme 1), L being different ligands. Heating **1** with an excess of ethylene or styrene or with trimethyl phosphite in a 1 : 1 molar ratio in toluene produced dark coloured complexes analysing (Table 2) for $[Ru\{C_6H_4(NH)_2\text{-}1,2\}L(PPh_3)_2]$ [L =

Table 2 Colours and analytical data* for ruthenium compounds

Compound	Colour	Analysis (%)		
		C	H	N
3 $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(C_2H_4)(PPh_3)_2]$	Purple	64.7 (65.5)	6.2 (5.9)	3.9 (4.1)
4 $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(CH_2CHPh)(PPh_3)_2]$	Dark brown	72.6 (71.8)	5.5 (5.2)	3.2 (3.3)
5 $[Ru\{C_6H_4(NH)_2\text{-}1,2\}P(OMe)_3\}(PPh_3)_2]$	Purple	62.3 (63.1)	5.2 (5.2)	3.1 (3.2)
6 $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(PPh_3)(dppm)]$	Purple	68.7 (68.9)	5.2 (5.0)	3.1 (3.3)
7 $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(PPh_3)(dppe)]$	Purple	69.2 (69.2)	5.3 (5.2)	2.9 (3.2)
8 $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(PPh_3)(dppbz)]$	Purple	72.2 (70.8)	5.2 (4.9)	2.9 (3.0)
9 $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(PPh_3)(dppen)]$	Purple	69.7 (69.3)	5.3 (4.9)	3.0 (3.2)
10 $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(PPh_3)(dppp)]$	Purple	69.8 (69.4)	5.6 (5.3)	2.9 (3.2)
14 $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(CO)(dppe)]$	Red-purple	61.5 (62.5)	4.7 (4.7)	4.1 (4.4)
15 $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(CO)(dppbz)]$	Dark red	64.9 (65.2)	4.5 (4.4)	4.0 (4.1)
16 $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(CO)(dppen)]$	Purple	62.2 (62.7)	4.6 (4.4)	4.3 (4.4)
17 $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(CO)(dppp)]$	Purple	61.9 (63.5)	5.0 (4.9)	4.5 (4.3)
18 $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(CO)(dppb)]$	Purple	62.8 (63.5)	5.4 (5.1)	4.2 (4.2)
19 $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(CO)_2(PPh_3)]$	Dark red	58.8 (59.4)	4.3 (4.0)	5.1 (5.3)

* Calculated values in parentheses.

C_2H_4 **3**, CH_2CHPh **4**, or $P(OMe)_3$ **5**], and with an excess of the diphosphines $(Ph_2P)_2X$ in boiling toluene gave purple crystalline complexes having the formula $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(PPh_3)(L\text{–}L)]$ [X = CH_2 (dppm) **6**, C_2H_4 (dppe) **7**, 1,2-C_6H_4 (dppbz) **8**, *cis*-C_2H_2 (dppen) **9**, or C_3H_6 (dppp) **10**]. Their ^{31}P NMR spectra support the five-co-ordinte structure (see Experimental section) with equivalency between both diphosphine phosphorus atoms, consisting of one doublet (L–L) and one triplet (PPh_3) with low-field chemical shifts for the five membered diphosphine rings, δ *ca.* 84 and at higher fields for the four- and six-membered chelates, δ 17.98 for dppm and 43.22 for dppp, the chemical shift for PPh_3 being little affected by the kind of diphosphine ligand (between δ 54.91 and 62.45). The reaction of **1** with 1,4-bis(diphenylphosphino)butane (dppb) was tried under boiling in toluene, xylenes or mesitylene but only after more than 4 h the original dark green colour of **1** changed slightly to a purple shade, indicating the low tendency of dppb to form chelates. When a large excess of trimethylphosphine was boiled in toluene with **1**, after adding hexane and cooling (−20 °C), large brown needles were obtained from a purple solution which on contact with air suddenly ignited. Thus the samples could not be used for elemental analysis, but spectroscopic information was obtained and is in accordance with the formula $[Ru\{C_6H_4(NH)_2\text{-}1,2\}](PMe_3)_3]$ **11**.

The reaction of complex **1** with PEt_3 either in boiling toluene or dioxane for more than 3 h led to a purple solution containing a mixture of the complexes $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(PEt_3)(PPh_3)_2]$ **12**, $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(PEt_3)_2(PPh_3)]$ **13** and other unidentified products. Thus, the reactivity of **1** towards PEt_3 is lower than that observed for PMe_3, which can be explained in terms of the larger cone angle for the former (between those for PMe_3 and PPh_3) as electronic considerations cannot solely account for the observed differences.

When the compound **2** reacted in boiling toluene with an excess of a ditertiary phosphine (L–L) the reddish purple complexes $[Ru\{C_6H_4(NH)_2\text{-}1,2\}(CO)(L\text{–}L)]$ (L–L = dppe **14**, dppbz **15**, dppen **16**, dppp **17**, or dppb **18**) were obtained, the ^{31}P NMR spectra of which show a unique singlet at the expected chemical shift for chelating diphosphines in accord with the metallocycle size[18] as observed for the earlier diphosphine complexes. Their IR spectra in the CO region (toluene solutions) consisted of only one ν(CO) absorption between 1935 and 1909 cm^{-1}, with higher values for the better chelating diphosphines. In an analogous reaction of **2** with dppm the expected substitution derivative was not detected and only a mixture of decomposition products (^{31}P NMR evidence) was obtained after boiling in xylenes or mesitylene. These carbonyl complexes were also detected as products of carbonylation of complexes **6**–**10** and from reaction of **19** with diphosphines.

The carbonylation of **1** in toluene gives, after 3–4 h, a solution in which only the dicarbonyl complex **19** is detected by infrared spectroscopy, being the more stable species, but attempts to crystallize or precipitate it by addition of hexane gave the less-soluble compound **2** (in solution there is also an excess of PPh_3 released from **1**), and the solid obtained is usually a mixture of **2** and **19** or only **2** if crystallization is allowed to occur for several hours. The use of **2** as starting compound to obtain **19** by bubbling CO through its solutions led to a few crystals of a pure sample; most of the solid obtained after hexane additions was also a mixture of the mono- and the di-carbonyl complexes.

In all the infrared spectra the $C_6H_4(NH)_2\text{-}1,2$ ligand was detected by its ν(NH) between 3360 and 3295 cm^{-1} as weak absorptions, and the bands of medium intensity observed between 1400 and 1300 cm^{-1} can be assigned to ν(CN). The ^1H NMR spectra, when recorded, only unequivocally showed resonances from phenyl phosphine groups, and only for compound **19** a clear singlet at δ 8.83 could be assigned to equivalent amido protons; the resonances from the diphosphine $(CH_x)_n$ groups appeared as poorly resolved multiplets. From the ^{31}P NMR spectra for the complexes $[Ru\{C_6H_4(NH)_2\text{-}$

1,2}LL'$_2$] (L = phosphine, L' = phosphine or L'$_2$ = diphosphine), where two signals were observed at room temperature, it is possible to exclude, under the experimental conditions, a Berry mechanism.

Experimental

All reactions were carried out under nitrogen using Schlenk techniques. Toluene and hexane were freshly distilled under nitrogen after drying by refluxing over sodium. Xylenes, dioxane and mesitylene (S. C. R. grade) were used without purification.

Microanalytical data (C, H and N) were obtained from a Perkin Elmer 240-B elemental analyser. Infrared spectra were recorded as Nujol mulls (KBr discs) or solutions (CaF_2 discs) with a Perkin Elmer 1720-XFT spectrometer, ^1H and ^{31}P NMR spectra on a Bruker AC-300 spectrometer (data relative to $SiMe_4$ and 85% external H_3PO_4).

The compounds [Ru{$C_6H_4(NH)_2$-1,2}$(PPh_3)_3$] **1** and [Ru{$C_6H_4(NH)_2$-1,2}(CO)$(PPh_3)_2$] **2** were prepared by published methods.[1c] All other products were used as supplied.

[Ru{$C_6H_4(NH)_2$-1,2}$(C_2H_4)(PPh_3)_2$] **3**.—Ethylene was bubbled through a solution of complex **1** (0.20 g, 0.20 mmol) in toluene (10 cm^3) for 3 h while heating at 100 °C. Hexane (20 cm^3) was added to the red solution which was left at room temperature for 2 d. The purple crystalline solid obtained was washed with hexane and dried *in vacuo*. Yield *ca*. 70%. IR: 3330vw, 3295vw, 3045w, 1580w, 1570w, 1480s, 1430s, 1355m, 1210m, 1180m, 1090s, 740vs and 695 vs cm^{-1} (Nujol mull). ^{31}P-{^1H} NMR (C_6D_6): δ 63.40 (s, 2 P, PPh_3).

[Ru{$C_6H_4(NH)_2$-1,2}$(CH_2CHPh)(PPh_3)_2$] **4**.—Complex **1** (0.43 g, 0.43 mmol) and a large excess of $PhCHCH_2$ (1.5 cm^3, 13.12 mmol) were refluxed with toluene (2.5 cm^3) for 10 h. Hexane (5 cm^3) was added and the solution kept at −20 °C for 2 d. The dark brown crystalline solid was collected, washed with hexane and dried *in vacuo*. Yield *ca*. 70%. IR: 3320w, 3050m, 1600w, 1525w, 1490m, 1475m, 1430s, 1180w, 1150w, 1085m, 745s and 695vs cm^{-1} (Nujol mull) ^{31}P-{^1H} NMR (C_6D_6): δ 55.40 (s, 2 P, PPh_3).

[Ru{$C_6H_4(NH)_2$-1,2}{$P(OMe)_3$}$(PPh_3)_2$] **5**.—Complex **1** (0.25 g, 0.25 mmol) and $P(OMe)_3$ (0.03 g, 0.25 mmol) were boiled in toluene (5 cm^3) for 1 h. Hexane (5 cm^3) was added to the purple solution which was left at −20 °C for 2 d. The purple crystalline solid was collected, washed with hexane and dried *in vacuo*. Yield *ca*. 60%. IR: 3350vw, 3322w, 3050m, 1570w, 1480s, 1435s, 1315s, 1095m, 1088m, 1048vs, 1028vs, 752s, 742s, 730s, 718s, 695vs, 680m and 650w cm^{-1} (Nujol mull). ^{31}P-{^1H} NMR (C_6D_6): δ 59.03 (d, 2 P, PPh_3) and 160.45 [t, *J*(PP) 56.0 Hz, 1 P, $P(OMe)_3$].

[Ru{$C_6H_4(NH)_2$-1,2}(PPh_3)(dppm)] **6**.—Complex **1** (0.35 g, 0.35 mmol) and $(Ph_2P)_2CH_2$ (0.33 g, 0.86 mmol) were refluxed in toluene (6 cm^3) for 2 h. Hexane (15 cm^3) was added and the purple solution filtered and left at −20 °C for 1 d. The purple crystals were collected, washed with hexane and dried *in vacuo*. Yield *ca*. 70%. IR: 3350vw, 3310vw, 3040m, 1580w, 1568w, 1478m, 1430vs, 1310m, 1095m, 770m, 742s, 738s, 728s, 695vs, 530m, 507s, 495s and 465m cm^{-1} (Nujol mull). ^{31}P-{^1H} NMR (C_6D_6): δ 62.45 (t, 1 P, PPh_3) and 17.98 [d, *J*(PP) 29.3 Hz, 2 P, dppm].

[Ru{$C_6H_4(NH)_2$-1,2}(PPh_3)(dppe)] **7**.—Complex **1** (0.40 g, 0.40 mmol) and $(Ph_2P)_2(CH_2)_2$ (0.35 g, 0.88 mmol) were refluxed in toluene (7 cm^3) for 1 h. Hexane (15 cm^3) was added to the purple solution, which was filtered and left at −20 °C for 1 d. The purple crystals were collected, washed with hexane and dried *in vacuo*. Yield *ca*. 80%. IR: 3350vw, 3325vw, 3045m, 1580w, 1475m, 1430s, 1360m, 1325m, 1090m, 747m, 738s, 730s, 695vs, 658m, 560m, 520s, 507m and 410m, cm^{-1} (Nujol mull). ^{31}P-{^1H} NMR (C_6D_6): δ 84.19 (d, 2 P, dppe) and 58.39 [t, *J*(PP) 24.4 Hz, 1 P, PPh_3].

Table 3 Crystal data for complex **1**

Formula	$C_{60}H_{51}N_2P_3Ru$
M	994.07
Crystal system	Monoclinic
Space group	$P2_1/n$
Crystal colour	Dark green
Crystal size/mm	0.23 × 0.17 × 0.13
a/Å	18.70(1)
b/Å	13.171(6)
c/Å	23.06(2)
β/°	99.86(6)
U/Å^3	5597(6)
Z	4
D_c/Mg m^{-3}	1.18
μ(Mo-Kα)/cm^{-1}	3.93
F(000)	2056
Drift correction range	0.97–1.01
h, *k*, *l* range	−22, 0, 0 to 21, 15, 27
Number of measured reflections	9767
Number of unique reflections	9767
R_{int} (for some duplicate measurements)	0.067
Observed reflections	3288 [$I > 3\sigma(I)$]
Number of refined parameters	596
R, *R'*	0.071, 0.073
g value	0.0036
Maximum shift/e.s.d.	0.036
Final peaks in Fourier difference synthesis/e Å^{-3}	
Maximum	1.14
Minimum	−0.45

[Ru{$C_6H_4(NH)_2$-1,2}(PPh_3)(dppbz)] **8**.—Complex **1** (0.20 g, 0.20 mmol) and 1,2-$(Ph_2P)_2C_6H_4$ (0.15 g, 0.32 mmol) were refluxed during 45 min in toluene (3 cm^3) to give a purple solution. Hexane (5 cm^3) was added and after 1 d at −20 °C a purple crystalline solid was collected, washed with hexane (3 × 2 cm^3) and dried *in vacuo*. Yield *ca*. 70%. IR: 3345m, 3048m, 1584w, 1433s, 1310m, 1106m, 1089s, 737s, 697vs, 671m, 554s and 526vs cm^{-1} (Nujol mull). ^{31}P-{^1H} NMR (C_6D_6): δ 84.84 (d, 2 P, dppbz) and 61.04 [t, *J*(PP) 30.5 Hz, 1 P, PPh_3].

[Ru{$C_6H_4(NH)_2$-1,2}(PPh_3)(dppen)] **9**.—Complex **1** (0.28 g, 0.28 mmol) and *cis*-$Ph_2PCHCHPPh_2$ (0.35 g, 0.88 mmol) were boiled in toluene (6 cm^3) for 1.5 h. The purple solution was left at −20 °C for 3 d. The purple crystals were collected, washed with hexane and dried *in vacuo*. Yield *ca*. 70%. IR: 3330vw, 3040w, 1580vw, 1475m, 1430s, 1360m, 1085m, 730s and 690vs cm^{-1} (Nujol mull). ^{31}P-{^1H} NMR (C_6D_6): δ 84.35 (d, 2 P, dppen) and 56.50 [t, *J*(PP) 30.0 Hz, 1 P, PPh_3].

[Ru{$C_6H_4(NH)_2$-1,2}(PPh_3)(dppp)] **10**.—Complex **1** (0.10 g, 0.10 mmol) and $(Ph_2P)_2(CH_2)_3$ (0.10 g, 0.24 mmol) were refluxed in toluene (3 cm^3) for 30 min. Hexane (5 cm^3) was added to the purple solution which was left at room temperature for 2 d. The purple crystals were collected, washed with hexane and dried *in vacuo*. Yield *ca*. 70%. IR: 3310vw, 3040m, 1580w, 1475m, 1435s, 1307m, 1090m, 1080m, 735s, 690vs and 660m cm^{-1} (Nujol mull). ^{31}P-{^1H} NMR (C_6D_6): δ 54.91 (t, 1 P, PPh_3) and 43.22 [d, *J*(PP) 29.8 Hz, 2 P, dppp].

[Ru{$C_6H_4(NH)_2$-1,2}$(PMe_3)_3$] **11**.—An excess of PMe_3 (1 cm^3, 10.5 mmol) was added to a solution of complex **1** (0.50 g, 0.50 mmol) in toluene (5 cm^3), and the mixture refluxed for 1 h. Hexane (6 cm^3) was added to the cold solution and kept at −20 °C for 1 d. The needle-shaped brown crystals, pyrophoric in air, were collected, washed with hexane and dried *in vacuo*. Yield *ca*. 50%. IR: 3335vw, 3330vw, 1558w, 1475m, 1425s,

Table 4 Fractional positional parameters for complex **1** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Ru	0.003 51(7)	0.235 45(9)	0.165 80(6)
P(1)	−0.019 1(2)	0.405 4(3)	0.175 1(2)
P(2)	−0.107 7(2)	0.175 9(3)	0.116 8(2)
P(3)	0.005 6(2)	0.167 1(3)	0.259 4(2)
N(1)	0.113 9(6)	0.246(1)	0.191 4(6)
N(2)	0.042 8(7)	0.196 6(9)	0.093 2(6)
C(1)	0.156 0(8)	0.231(1)	0.147 9(8)
C(2)	0.116 4(9)	0.200(1)	0.092 2(8)
C(3)	0.153(1)	0.177(1)	0.047 4(8)
C(4)	0.227(1)	0.190(2)	0.055(1)
C(5)	0.264(1)	0.222(1)	0.107(1)
C(6)	0.230 5(8)	0.243(1)	0.154 7(8)
C(111)	−0.069(1)	0.475(1)	0.110 2(8)
C(112)	−0.039(1)	0.530(1)	0.069 3(9)
C(113)	−0.078(1)	0.582(2)	0.022 7(9)
C(114)	−0.153(1)	0.575(1)	0.012 3(9)
C(115)	−0.187(1)	0.521(1)	0.052 5(9)
C(116)	−0.145(1)	0.471(1)	0.101 5(9)
C(121)	−0.064 6(9)	0.472(1)	0.229 8(8)
C(122)	−0.079 2(9)	0.575(1)	0.225 9(9)
C(123)	−0.110(1)	0.625(2)	0.267(1)
C(124)	−0.127(1)	0.577(2)	0.313(1)
C(125)	−0.112(1)	0.471(2)	0.319 8(9)
C(126)	−0.080(1)	0.421(1)	0.276 4(9)
C(131)	0.069 8(9)	0.473(1)	0.185 8(9)
C(132)	0.116 8(9)	0.460(1)	0.144 5(9)
C(133)	0.185(1)	0.504(2)	0.152(1)
C(134)	0.208(1)	0.559(2)	0.202(1)
C(135)	0.165(1)	0.571(1)	0.244(1)
C(136)	0.095(1)	0.530(1)	0.236 7(9)
C(211)	−0.195 1(9)	0.230(1)	0.124 4(8)
C(212)	−0.200 3(9)	0.273(1)	0.180 0(9)
C(213)	−0.268(1)	0.323(1)	0.188(1)
C(214)	−0.324(1)	0.329(2)	0.139(1)
C(215)	−0.317(1)	0.287(2)	0.087(1)
C(216)	−0.253 8(9)	0.237(2)	0.077 6(8)
C(221)	−0.114 5(8)	0.179(1)	0.035 8(7)
C(222)	−0.122(1)	0.093(1)	0.000 9(9)
C(223)	−0.124(1)	0.102(2)	−0.062 3(9)
C(224)	−0.115(1)	0.195(2)	−0.085 6(9)
C(225)	−0.110(1)	0.279(2)	−0.053(1)
C(226)	−0.107 9(9)	0.274(1)	0.009 9(8)
C(231)	−0.125(1)	0.039(1)	0.126 6(8)
C(232)	−0.191 0(9)	−0.001(1)	0.129(1)
C(233)	−0.201(1)	−0.104(2)	0.132(1)
C(234)	−0.139(1)	−0.170(2)	0.132(1)
C(235)	−0.074(1)	−0.132(1)	0.130 7(8)
C(236)	−0.067(1)	−0.026(1)	0.126 4(8)
C(311)	0.079 0(9)	0.213(1)	0.317 3(9)
C(312)	0.118(1)	0.148(2)	0.357(1)
C(313)	0.174(2)	0.186(2)	0.400(1)
C(314)	0.189(1)	0.286(2)	0.401(1)
C(315)	0.151(1)	0.353(2)	0.362 1(9)
C(316)	0.098(1)	0.312(2)	0.318 8(9)
C(321)	−0.069(1)	0.157(1)	0.300 5(9)
C(322)	−0.066(1)	0.201(2)	0.356(1)
C(323)	−0.128(2)	0.196(2)	0.385(1)
C(324)	−0.191(1)	0.144(2)	0.357(2)
C(325)	−0.193(1)	0.098(2)	0.300(1)
C(326)	−0.132(1)	0.105(1)	0.274(1)
C(331)	0.033 5(9)	0.032(1)	0.257 4(8)
C(332)	0.094(1)	0.010(1)	0.230(1)
C(333)	0.120(1)	−0.089(2)	0.230(1)
C(334)	0.082(1)	−0.166(1)	0.259(1)
C(335)	0.024(1)	−0.144(2)	0.286(1)
C(336)	0.003(1)	−0.049(1)	0.2859(9)

1415m, 1305vs, 1298vs, 1290vs, 1278s, 1273s, 1210m, 1018m, 960s, 940vs, 852m, 848m, 717vs, 663vs, 635m, 620m, 605m, 452m and 410m cm^{-1} (Nujol mull). ^{31}P-{^{1}H} NMR (C_6D_6): δ −7.12 (s, 3 P, PMe_3).

Reaction of Complex **1** *with* PEt_3.—Complex **1** (0.25 mg, 0.25 mmol) and PEt_3 (0.25 cm^3, 20.3 mmol) were boiled in toluene (3 cm^3) or dioxane for 3 h. Hexane (5 cm^3) was added to the purple solution and after standing at room temperature for 1 d the dark solid was collected, washed with hexane and dried *in vacuo*. Yield 0.11 g. ^{31}P-{^{1}H} NMR (C_6D_6): δ 60.3 (d, 2 P, PPh_3) and 41.1 [t, *J*(PP) 26.7, 1 P, PEt_3], for **12**; 60.9 (t, 1 P, PPh_3) and 41.8 [d, *J*(PP) 23.2 Hz, 2 P, PEt_3] for **13**.

[Ru{$C_6H_4(NH)_2$-1,2}(CO)(dppe)][17] **14**.—Complex **2** (0.10 g, 0.13 mmol) and $(Ph_2P)_2(CH_2)_2$ (0.11 g, 0.28 mmol) were refluxed for 1.5 h in toluene (4 cm^3). Hexane (16 cm^3) was added to the red-purple solution which was left at room temperature for 4 d. The reddish crystals were collected, washed with hexane and dried *in vacuo*. Yield *ca.* 70%. IR: 3355vw, 3329w, 3054w, 1920vs, 1878w, 1479m, 1435s, 1417m, 1355m, 1314m, 1102s, 809m, 736s, 703s, 690s, 653m, 583w, 568m, 560m, 543w, 524s, 507m, 497m, 477w, 464w and 435w (Nujol mull); ν(CO) 1925vs cm^{-1} (toluene). ^{31}P-{^{1}H} NMR (C_6D_6): δ 82.38 (s, 2 P, dppe).

[Ru{$C_6H_4(NH)_2$-1,2}(CO)(dppbz)] **15**.—Complex **2** (0.12 g, 0.16 mmol) and 1,2-$(Ph_2P)_2C_6H_4$ (0.14 g, 0.31 mmol) were refluxed for 1.5 h in toluene (5 cm^3). Hexane (10 cm^3) was added and the purple solution was left at room temperature for 3 d. The dark red crystalline solid was collected, washed with hexane and dried *in vacuo*. Yield *ca.* 50%. IR: 3345w, 3335w, 3045w, 1914s, 1903s, 1580m, 1564m, 1475m, 1441s, 1430s, 1365m, 1355m, 1307m, 1202m, 1182m, 1140m, 1105m, 1090s, 1022m, 1012m, 997m, 770m, 740s, 724s, 692s, 670s, 648m, 615m, 584m, 550m, 525s, 515s, 490m, 463m (Nujol mull); ν(CO) 1918vs cm^{-1} (toluene). ^{31}P-{^{1}H} NMR (C_6D_6): δ 79.61 (s, 2 P, dppbz).

[Ru{$C_6H_4(NH)_2$-1,2}(CO)(dppen)] **16**.—Complex **2** (0.05 g, 0.066 mmol) and *cis*-$Ph_2PCHCHPPh_2$ (0.04 g, 0.10 mmol) were refluxed in toluene (3 cm^3) for 30 min. Hexane (5 cm^3) was added to the solution, which was filtered and kept at room temperature for 3 d. A purple crystalline solid was collected, washed with hexane and dried *in vacuo*. Yield *ca.* 80%. IR: 3345w, 3054m, 1953s, 1589m, 1436s, 1187m, 1120m, 1100m, 773m, 743s, 724m, 696vs, 555m, 541s, and 520m (Nujol mull); ν(CO) 1935vs cm^{-1} (toluene). ^{31}P-{^{1}H} NMR (C_6D_6): δ 89.20 (s, 2 P, dppen).

[Ru{$C_6H_4(NH)_2$-1,2}(CO)(dppp)] **17**.—Complex **2** (0.10 g, 0.13 mmol) and $(Ph_2P)_2(CH_2)_3$ (0.07 g, 0.17 mmol) were refluxed in toluene (5 cm^3) for 1 h. A purple crystalline solid and a purple solution were obtained. After 6 h at room temperature, solution was filtered and the solid collected, washed with hexane and dried *in vacuo*. Yield *ca.* 75%. IR: 3332w, 3053w, 1881vs, 1434s, 1299m, 1099s, 741s, 693vs, 664s, 560m, 516vs (Nujol mull); ν(CO) 1911vs cm^{-1} (toluene). ^{31}P-{^{1}H} NMR (C_6D_6): δ 42.78 (s, 2 P, dppp).

[Ru{$C_6H_4(NH)_2$-1,2}(CO)(dppb)] **18**.—Complex **2** (0.05 g, 0.066 mmol) and $(Ph_2P)_2(CH_2)_4$ (0.05 g, 0.12 mmol) were refluxed in toluene (3 cm^3) for 1 h. Hexane (5 cm^3) was added to the purple solution which, after filtering, was left at room temperature for 3 d. The solid was collected, washed with hexane and dried *in vacuo*. Yield *ca.* 80%. IR: 3339w (br), 3053w, 1904vs, 1596w, 1495m, 1436s, 1313m, 1184m, 1098m, 806w, 742s, 697vs, 669w, 547m, and 513s (Nujol mull); ν(CO)

1909vs cm^{-1} (toluene). ^{31}P-{^{1}H} NMR (C_6D_6): δ 52.59 (s, 2 P, dppb).

[Ru{$C_6H_4(NH)_2$-1,2}$(CO)_2(PPh_3)$] **19**.—When CO was bubbled through a solution of complex **1** (0.20 g, 0.20 mmol) in toluene (5 cm^3) for 3 h at room temperature a purple solution was obtained [ν(CO) 1998vs and 1938vs cm^{-1}] which yielded a purple-brown precipitate by addition of a large excess of hexane and cooling at −20 °C for 5 h. The solid was filtered off, washed with hexane and dried *in vacuo*. Its IR spectrum showed a mixture of the known complex **2** [ν(NH) 3373vw and 3335w, ν(CO) 1896vs cm^{-1} (Nujol mull)] and **19** [ν(NH) 3355vw and 3324w, ν(CO) 1991vs and 1928vs (Nujol mull), 2003vs and 1946s cm^{-1} (toluene)]. NMR (C_6D_6): ^{1}H, δ 8.38 (s, 2 H, NH); ^{31}P-{^{1}H}, δ 59.92 (s, 1 P, PPh_3). A few crystals of **19** were obtained pure to allow elemental analysis and spectroscopic characterization.

Crystallographic Data Collection, Resolution and Refinement of the Structure of Complex **1**.—Experimental data for the structure determination of complex **1** are collected in Table 3. They were collected at 293 K on an Enraf-Nonius-CAD4 single-crystal diffractometer using Mo-Kα radiation (λ = 0.710 73 Å) and a graphite-crystal monochromator. Unit-cell dimensions were determined from the angular settings of 25 reflections, $0 < \theta < 25°$. The space group was determined from systematic absences. The ω–2θ scan technique was used, with a variable scan rate and a maximum scan time of 60 s per reflection. The intensity of the primary beam was checked by monitoring three standard reflections every 60 min. A drift correction was applied. Profile analysis[19] was performed on all reflections. A semiempirical absorption correction was applied, using Ψ scans[20] (correction factors range from 0.69 to 1.00). Lorentz and polarization corrections were applied and the data were reduced to $|F_o|$ values. The structure was solved by the Patterson method using SHELX 86[21] and Fourier synthesis. Isotropic least-squares refinement was performed using SHELX 76.[22] The refinement converged to R = 0.11 and at this stage further absorption corrections were applied using DIFABS[23] resulting in a further decrease in R to 0.09; maximum and minimum absorption corrections 1.34 and 0.62. Further anisotropic refinements followed by a Fourier difference synthesis allowed the location of all of the non-hydrogen atoms. During the final stages of the refinement the positional parameters and the anisotropic thermal parameters of the non-hydrogen atoms were refined. Hydrogen atoms were geometrically placed and their overall isotropic thermal parameters fixed at 0.09(1) Å^2. The function $\Sigma w(F_o - F_c)^2$ was minimized, where $w = 1/[\sigma^2(F_o) + gF_o^2]$ and $\sigma(F_o)$ was obtained from counting statistics (g is given in Table 3). The highest residual electron density was due to the presence of some solvent molecules, likely toluene (NMR evidence), which could not be located nor refined. The atomic scattering factors were taken from ref. 24. The structures were drawn with the EUCLID[25] program and the geometrical calculations were made with PARST.[26] All calculations were made on a DEC MicroVax 3400 computer of the Scientific Computer Centre of the Universidad de Oviedo. Final atomic coordinates are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters and remaining bond lengths and angles.

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